

between the two calibration methods used by Holzapfel and Franck,<sup>18,19</sup> suggests that the earlier melting curve is close to correct up to  $\sim 70$  kbar, but that the pressures above this were overestimated by 10%–20%. A correction such as this is necessarily quite uncertain,<sup>19</sup> but it seems to us to be at least in the right direction. The corrected, but approximate, melting curve is shown in Fig. 4. The points can be fitted by the Simon equation in the form

$$P - 22 = 6.429[(T/354.8)^{4.543} - 1],$$

with a standard deviation of 5.7°C.

There has been some controversy about the reality and explanation of an inflexion in the shock Hugoniot of water at 115 kbar, found by Al'tshuler *et al.*<sup>20</sup> but

<sup>19</sup> E. U. Franck (private communication).

<sup>20</sup> L. V. Al'tshuler, K. K. Krupnikov, B. N. Lebedev, V. I. Zhuchikhin, and M. I. Brazhnik, *Zh. Eksp. Teor. Fiz.* **34**, 874 (1958) [*Sov. Phys.—JETP* **7**, 606 (1958)].

not by Walsh and Rice<sup>21</sup> or Zel'dovich.<sup>22</sup> A comparison<sup>23</sup> of the melting curve of ice VII<sup>5</sup> with the pressure-temperature curve for shock waves moving into water showed that the two curves meet only in the narrow range between 30 and 45 kbar. The present correction of the melting curve of ice VII does not affect this conclusion.

#### ACKNOWLEDGMENTS

The authors would like to thank Mrs. Martha C. Pistorius for writing the computer program used in fitting the data. J. Erasmus and his staff and G. O'Grady and his staff kept the equipment in good repair, and were responsible for the manufacture of the furnace parts. Calculations were carried out on the IBM System 360 of the National Research Institute for Mathematical Sciences.

<sup>21</sup> J. M. Walsh and M. H. Rice, *J. Chem. Phys.* **26**, 815 (1957).

<sup>22</sup> Y. B. Zel'dovich, S. B. Korner, M. V. Sinitsyn, and K. B. Yushko, *Dokl. Akad. Nauk SSSR* **138**, 1333 (1961) [*Sov. Phys.—Dokl.* **6**, 494 (1961)].

<sup>23</sup> S. D. Hamann, *Advan. High Pressure Res.* **1**, 85 (1966).

## Numerical Solution of Quantum-Mechanical Pair Equations\*

VINCENT MCKOY AND N. W. WINTER

*Gates and Crellin Laboratories of Chemistry, † California Institute of Technology, Pasadena, California*

(Received 26 January 1968)

We discuss and illustrate the numerical solution of the differential equation satisfied by the first-order pair functions of Sinanoğlu. An expansion of the pair function in spherical harmonics and the use of finite difference methods convert the differential equation into a set of simultaneous equations. Large systems of such equations can be solved economically. The method is simple and straightforward, and we have applied it to the first-order pair function for helium with  $1/r_{12}$  as the perturbation. The results are accurate and encouraging, and since the method is numerical they are indicative of its potential for obtaining atomic-pair functions in general.

### INTRODUCTION

In the Hartree-Fock approximation each electron moves in a potential averaged over the motions of all others. This is an excellent starting point, and a great deal of chemical knowledge can be obtained this way. Many properties require more accurate wavefunctions for their prediction and understanding. The difference between the Hartree-Fock and exact wavefunction is referred to as the correlation wavefunction. It is important to have methods of finding the correlation wavefunction and its effect on physical observables.

Sinanoğlu<sup>1</sup> has developed a many-electron theory of atoms and molecules. This theory can provide the wave-

\* Supported in part by a grant from the NSF (GP 6965).

† Contribution No. 3642.

<sup>1</sup> Some early references are O. Sinanoğlu in *J. Chem. Phys.* **33**, 1212 (1960); *Phys. Rev.* **122**, 493 (1961); *Proc. Roy. Soc. (London)* **A260**, 379 (1961); *Proc. Natl. Acad. Sci. U.S.A.* **47**, 1217 (1961). For a review of the theory and an extensive list of references see O. Sinanoğlu, *Advan. Chem. Phys.* **6**, 315 (1964).

function and energy of an atom or molecule to chemical accuracy, and it does so in such a way that it does not become rapidly difficult or uneconomical as the number of electrons increases. In one of his early papers<sup>1</sup> the first-order correction to the single-particle wavefunction was expressed in terms of pair functions which describe the correlation between pairs of electrons.<sup>2</sup> These first-order pair functions are solutions of nonhomogeneous partial differential equations. The equations are just like those for an actual two-electron system, except that each electron moves in the Hartree-Fock (HF) field of the entire medium. This has not been fully appreciated, especially from a computational standpoint. Each pair energy has a variational principle, and attempts to solve the pair equations have been mainly

<sup>2</sup> In later papers the pair theory was made accurate to all orders, i.e., beyond first order. We refer the reader to the review article in Ref. 1. The complete form of the many-electron theory is not a perturbation theory.

by this method. The variational method reduces the calculation to the evaluation of a large number of integrals. The presence of a nonlocal potential in the HF operator does lead to some difficult integrals, which can become more difficult if higher powers of the inter-electronic coordinate are included. A large effort has gone into evaluating such atomic integrals.

In this paper we discuss and illustrate the numerical solution of the differential equation satisfied by a pair function. An expansion of the pair function in spherical harmonics and the use of finite-difference methods convert the differential equation into a set of simultaneous equations. Large systems of such equations can be solved quite economically, e.g., about 2000 equations in two minutes. The method has many attractive features, and we have applied it to the equation of the first-order pair function for the helium atom. The results are accurate and encouraging, and since the method is numerical, these results are truly indicative of its potential in solving for atomic pair functions in general.

**THEORY**

**A. Sinanoğlu's Pair Equations**

The total Hamiltonian,  $H$ , and the zeroth-order Hamiltonian,  $H_0$ , for an  $N$ -electron atom are

$$H = \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j}^N \frac{1}{r_{ij}} \tag{1}$$

and

$$H_0 = \sum_{i=1}^N (h_i^0 + V_i), \tag{2a}$$

respectively. In Eq. (2a)  $V_i$  is the Hartree-Fock potential, which is the same for all electrons. For closed-shell atoms  $V_i$  is uniquely defined.<sup>3</sup> Also in Eq. (2a),

$$h_i^0 = -\frac{1}{2} \nabla_i^2 - (Z/r_i). \tag{2b}$$

The zeroth-order function  $\psi^{(0)}$  satisfies

$$H_0 \psi^{(0)} = E_0 \psi^{(0)}, \tag{3}$$

where

$$E_0 = \sum_i \epsilon_i$$

and each HF orbital satisfies the equation

$$(h_i^0 + V_i) \phi_i = \epsilon_i \phi_i. \tag{4}$$

The zeroth-order wavefunction  $\psi^{(0)}$  is just the antisymmetrized product of HF orbitals,

$$\psi^{(0)} = A(\phi_1(1) \phi_2(2) \cdots \phi_N(N)) \tag{5}$$

The first-order correction to  $\psi^{(0)}$ ,  $\psi^{(1)}$ , satisfies the

equation

$$(H_0 - E_0) \psi^{(1)} = (E_1 - H_1) \psi^{(0)}, \tag{6}$$

where the perturbation  $H_1$  is

$$H_1 = \sum_{i<j}^N \frac{1}{r_{ij}} - \sum_{i=1}^N V_i. \tag{7}$$

Equation (6) is an inhomogeneous partial differential equation in  $3N$  spatial variables. It has solutions if the corresponding homogeneous equation are orthogonal to the inhomogeneity,  $(E_1 - H_1) \psi^{(0)}$ . The general solution of Eq. (6) is

$$\psi^{(1)} = \psi_p^{(1)} + c \psi^{(0)}, \tag{8}$$

i.e., a sum of a particular solution,  $\psi_p^{(1)}$ , plus a contribution from the homogeneous solution. The constant,  $c$ , is chosen so that  $\langle \psi^{(0)}, \psi^{(1)} \rangle = 0$ .

From Sinanoğlu's analysis<sup>1</sup> the first-order wavefunction can be written as

$$\psi^{(1)} = \sum_{i<j}^N \frac{A}{\sqrt{2}} (\phi_1(1) \phi_2(2) \cdots \phi_{i-1} \hat{u}_{ij}^{(1)} \phi_{j+1} \cdots \phi_N), \tag{9}$$

where  $\hat{u}_{ij}^{(1)}(\mathbf{x}_i, \mathbf{x}_j)$ , a first-order pair function, satisfies the nonhomogeneous differential equation

$$(e_i + e_j) \hat{u}_{ij}^{(1)} = -Q(1/r_{12}) B(\phi_i(1) \phi_j(2)). \tag{10}$$

The operator,  $Q$ , makes a two-electron function orthogonal to all occupied H-F orbitals; i.e.,

$$Q = 1 - \sum_{i=1}^N (|\phi_i(1)\rangle \langle \phi_i(1)| + |\phi_i(2)\rangle \langle \phi_i(2)|) + \sum_{i<j}^N |B(\phi_i(1) \phi_j(2))\rangle \langle B(\phi_i(1) \phi_j(2))|, \tag{11}$$

and  $e_i$  is just the HF operator minus an orbital energy,  $\epsilon_i$ ,

$$e_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \sum_{j=1}^N S_j(\mathbf{x}_i) - \sum_{j=1}^N R_j(\mathbf{x}_i) - \epsilon_i, \tag{12}$$

with

$$B(\phi_i(1) \phi_j(2)) = (1/\sqrt{2}) (\phi_i(1) \phi_j(2) - \phi_i(2) \phi_j(1)), \tag{13a}$$

$$S_j(\mathbf{x}_i) \phi_k(\mathbf{x}_i) = \left( \int \phi_j(\mathbf{x}_j) r_{ij}^{-1} \phi_j(\mathbf{x}_j) d\mathbf{x}_j \right) \phi_k(\mathbf{x}_i), \tag{13b}$$

and

$$R_j(\mathbf{x}_i) \phi_k(\mathbf{x}_i) = \left( \int \phi_j(\mathbf{x}_j) r_{ij}^{-1} \phi_k(\mathbf{x}_j) d\mathbf{x}_j \right) \phi_j(\mathbf{x}_i). \tag{13c}$$

We also define

$$V_c(\mathbf{x}_i) = \sum_{j=1}^N S_j(\mathbf{x}_i) \tag{14a}$$

<sup>3</sup> For a discussion of the many-electron theory for open-shell systems see H. J. Silverstone and O. Sinanoğlu, J. Chem. Phys. **44**, 1899, 3608 (1966).

and

$$V_s(\mathbf{x}_i) = \sum_{j=1}^N R_j(\mathbf{x}_i). \quad (14b)$$

The pair functions are also rigorously orthogonal to all occupied HF orbitals, i.e.,

$$\int \hat{u}_{ij}^{(1)}(\mathbf{x}_1, \mathbf{x}_2) \phi_k(\mathbf{x}_1) d\mathbf{x}_1 = 0.$$

The second-order energy,  $E_2$ , is

$$E_2 = \sum_{i < j}^N \langle B(\phi_i(1)\phi_j(2)), r_{12}^{-1} \hat{u}_{ij}^{(1)}(\mathbf{x}_1, \mathbf{x}_2) \rangle. \quad (15)$$

The pair function,  $\hat{u}_{ij}^{(1)}$ , is the solution of the first-order part of the Schrödinger equation for two electrons in the HF "sea." The effect of the medium enters through the HF potentials in the operators  $e_i$  and  $Q$ .

One can write the solution of Eq. (10) as follows:

$$\hat{u}_{ij}^{(1)} = Q u_{ij}, \quad (16)$$

where  $Q$  is defined in Eq. (11) and  $u_{ij}$  satisfies the equation

$$(e_i + e_j) u_{ij} = [J_{ij} - K_{ij} - (1/r_{12})] B(\phi_i(1)\phi_j(2)), \quad (17)$$

with  $J_{ij}$  and  $K_{ij}$  the Coulomb and exchange integrals for orbitals  $\phi_i$  and  $\phi_j$ . This approach has some advantages if one needs to expand  $u_{ij}$  in a series of spherical harmonics. The general solution to Eq. (17) is obtained by orthogonalizing a particular solution to  $B(\phi_i\phi_j)$ . If  $B(\phi_i(1)\phi_j(2))$  belongs to a two-electron irreducible representation, then Eq. (17) has a unique solution, e.g.,  $1s^2$  pair of electrons. However, when  $B(\phi_i(1)\phi_j(2))$  is not a pure two-electron symmetry state, then Eq. (16) does not have a solution,<sup>1</sup> and one must write

$$B(\phi_i\phi_j) = \sum_{s=1}^m a_s \phi_{ij}^s, \quad (18)$$

where  $\phi_{ij}^s$  are unperturbed pure symmetry states. Then,

$$u_{ij} = \sum_{s=1}^m a_s u_{ij}^s \quad (19)$$

$$(e_i + e_j) u_{ij}^s = [\langle \phi_{ij}^s | (1/r_{12}) | \phi_{ij}^s \rangle - (1/r_{12})] \phi_{ij}^s. \quad (20)$$

The solution of Eq. (10) does not require any vector coupling schemes such as Eqs. (18) and (20), but the obvious symmetry properties of  $u_{ij}^s$  are convenient if  $u_{ij}$  is expanded in spherical harmonics. We have given Eqs. (17) and (20) because the use of symmetry pairs leads to simplifications in the numerical treatment of these equations. Equation (17) is also very similar to the equation one obtains starting from a bare nuclei Hamiltonian, i.e., a hydrogenic  $\psi^{(0)}$ . In that case, the first-order wavefunction is again written like Eq. (9) but with  $\hat{u}_{ij}^{(1)}$  replaced by  $u_{ij}$ , which satisfies an equation very similar to Eq. (17), i.e.,

$$\begin{aligned} [-\frac{1}{2}\nabla_1^2 - \nabla_2^2 - (Z/r_1) - (Z/r_2) - \epsilon_i - \epsilon_j] u_{ij} \\ = [J_{ij} - K_{ij} - (1/r_{12})] B(\phi_i(1)\phi_j(2)). \quad (21) \end{aligned}$$

The comparison between Eqs. (17) and (21) is obvious.

In the perturbation study of helium, starting from an unscreened hydrogenic  $\psi^{(0)}$ , one usually writes

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - (Z/r_1) - (Z/r_2), \quad (22)$$

$$H_1 = 1/r_{12}, \quad (23)$$

and  $\psi^{(1)}$  satisfies Eq. (6). Comparison of Eqs. (6), (21), (22), and (23) shows that  $\psi^{(1)}$  is just an example of a pair function. This is the example we use to illustrate our method of solution of pair equations. Numerical details of the method demonstrate that these results are indicative of its usefulness for obtaining atomic pair functions in general.

## B. Reduction of Pair Equations

For quantitative results one must solve Eqs. (10), (17), or (21). Most attempts so far have used a variational approach. Equation (15) can be written

$$E^{(2)} = \sum_{i < j} \epsilon_{ij}^{(2)}, \quad (24)$$

and one has a minimum principle<sup>1</sup> for each  $\epsilon_{ij}^{(2)}$ , i.e.,

$$\begin{aligned} \epsilon_{ij}^{(2)} \approx \epsilon_{ij}^{t(2)} = 2 \langle B(\phi_i\phi_j), m_{ij} \hat{u}_{ij}^{t(1)} \rangle \\ + \langle \hat{u}_{ij}^{t(1)}, (e_i + e_j) \hat{u}_{ij}^{t(1)} \rangle, \quad (25) \end{aligned}$$

with

$$\begin{aligned} m_{ij}(1, 2) = (1/r_{12}) - \bar{S}_i(1) - \bar{S}_i(2) - \bar{S}_j(2) \\ - \bar{S}_j(1) + J_{ij} - K_{ij}, \quad (26a) \end{aligned}$$

$$\bar{S}_i(1) = S_i(1) - R_i(1), \quad (26b)$$

and  $\hat{u}_{ij}^{t(1)}$  is varied to minimize  $\epsilon_{ij}^{t(2)}$ . With a variational form for  $\hat{u}_{ij}^{t(1)}$ , one evaluates all the integrals in Eq. (25) and determines  $\hat{u}_{ij}^{(1)}$ . For different types of pairs one has a choice of  $\hat{u}_{ij}^{(1)}$ , e.g., a configuration-interaction (CI), open-shell, and a  $r_{12}$ -type  $\hat{u}_{ij}^{(1)}$ . We will comment later on their relative merits in comparison with the numerical method. We now show that these pair functions can be obtained accurately by solving the partial differential equation by numerical methods. The method is direct, with simple programming requirements.

The pair function,  $\hat{u}_{ij}^{(1)}$ , is expanded in a series of surface harmonics, the coefficients in the expansion being functions of the radii of the two electrons,<sup>4</sup>

$$\begin{aligned} \hat{u}_{ij}^{(1)} = \sum_{lm:l'm'} (r_1 r_2)^{-1} \hat{u}_{lm:l'm'}(r_1, r_2) \\ \times S_{lm}(\theta_1, \phi_1) S_{l'm'}(\theta_2, \phi_2). \quad (27) \end{aligned}$$

For a spherically symmetric pair function the spatial part of  $\hat{u}_{ij}^{(1)}$  depends only on  $r_1$ ,  $r_2$ , and  $\theta_{12}$ . However, for states of arbitrary symmetry one has to expand in

<sup>4</sup> For a suggestion along these lines see J. Musher in *Modern Quantum Chemistry—Istanbul Lectures, Part II, Interaction*, O. Sinanoğlu, Ed. (Academic Press Inc., New York, 1965).

terms of angular symmetries with respect to the two electrons separately. The  $1/r_{12}$  term on the right-hand side of Eq. (10) can be written

$$r_{12}^{-1} = \sum_{l=0}^{\infty} U_l(r_1, r_2) \sum_{m=-l}^l S_{lm}(\theta_1, \phi_1) S_{l-m}(\theta_2, \phi_2), \quad (28)$$

where  $U_l(r_1, r_2)$  stands for

$$\begin{pmatrix} r_{<}^l \\ r_{>}^{l+1} \end{pmatrix}$$

and  $S_{lm}$  is a surface harmonic. Substitution of the expansion Eq. (27) into Eq. (17) or Eq. (10) gives

$$\begin{aligned} & (e_i + e_j) \hat{u}_{ij}^{(1)}(r_1, r_2) \\ &= \sum_{lm, l'm'} \left[ -\frac{1}{2r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial}{\partial r_1} \right) - \frac{1}{2r_2^2} \frac{\partial}{\partial r_2} \left( r_2^2 \frac{\partial}{\partial r_2} \right) + \frac{l(l+1)}{2r_1^2} + \frac{l'(l'+1)}{2r_2^2} + V(r_1) + V(r_2) - \epsilon_i - \epsilon_j \right] \\ & \quad \times (r_1 r_2)^{-1} \hat{u}_{lm:l'm'}(r_1, r_2) S_{lm}(\theta_1, \phi_1) S_{l'm'}(\theta_2, \phi_2). \quad (29) \end{aligned}$$

For closed-shell systems the Hartree-Fock potential,  $V(r_1)$ , is spherically symmetric. For open-shell systems one still requires the potential to be spherically symmetric and the orbitals, symmetry orbitals.<sup>3</sup> With the expansion, Eq. (28), the right-hand side of Eq. (10) or Eq. (17) becomes a sum of terms,

$$\sum_{ll'mm'} G_{lm:l'm'}(r_1, r_2) S_{lm}(1) S_{l'm'}(2).$$

The  $G_{lm:l'm'}$  are combinations of terms  $U_l(r_1, r_2)$  and the radial factors of the H-F orbitals. One now obtains a set of uncoupled equations, one for each term in Eq. (27),

$$\left( -\frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{1}{2} \frac{\partial^2}{\partial r_2^2} + \frac{l(l+1)}{2r_1^2} + \frac{l'(l'+1)}{2r_2^2} + V(r_1) + V(r_2) - \epsilon_i - \epsilon_j \right) \hat{u}_{lm:l'm'}^{(1)} = r_1 r_2 G_{lm:l'm'}(r_1, r_2). \quad (30)$$

In deriving Eq. (30) we have used relationships such as

$$S_{ij}(\theta, \phi) S_{kl}(\theta, \phi) = \sum_{\alpha\beta} a_{ijk\alpha\beta} S_{\alpha\beta}(\theta, \phi), \quad (31)$$

where  $a_{ijk\alpha\beta}$  are numerical coefficients. Equation (30) is our basic equation. It is a second-order elliptic partial differential equation in two variables, and no closed-form solution exists.

### C. Analysis

Of the numerical methods for solving partial differential equations, those employing finite differences are most frequently used. Finite-difference methods are approximate in the sense that derivatives at a point are approximated by difference quotients over a small interval; i.e.,  $\partial\phi/\partial x$  is replaced by  $\delta\phi/\delta x$  where  $\delta x$  is small, but the solutions are not approximate in the sense of being crude estimates. In these methods the area of integration is divided into a set of square meshes, and an approximate solution to the differential equation is found at these mesh points. This solution is obtained by approximating the partial differential equation by  $n$  algebraic equations. The values at the mesh points form a vector which is the solution of the set of simultaneous linear equations. A numerical solution contains no arbitrary constants, so that we always obtain particular integrals rather than complete primitives of the differential equation.

In operator notation Taylor's series can be written<sup>5</sup>

$$\begin{aligned} y(x+h) &= y(x) + h(dy/dx) + \frac{1}{2}h^2(d^2y/dx^2) + \dots \\ &= \exp(hD)y(x). \quad (32a) \end{aligned}$$

Define a central difference operator  $\delta$ ,

$$\delta y(x + \frac{1}{2}h) = y(x+h) - y(x), \quad (32b)$$

and one has the operator equation

$$\begin{aligned} \delta &= \exp(\frac{1}{2}hD) - \exp(-\frac{1}{2}hD) \\ &= 2 \sinh(\frac{1}{2}hD), \quad (32c) \end{aligned}$$

and hence

$$\begin{aligned} h^2 D^2 &= (2 \sinh^{-1} \frac{1}{2} \delta)^2 \\ &= \delta^2 - \frac{1}{12} \delta^4 + \frac{1}{96} \delta^6 - \dots \quad (33) \end{aligned}$$

The second derivative of a function at the  $i$ th point is

$$h^2 (d^2y/dx^2)_i = \delta^2 y_i - \frac{1}{12} \delta^4 y_i + \frac{1}{96} \delta^6 y_i. \quad (34)$$

The operators  $\delta^2$  and  $\delta^4$ , etc., are defined by the equations

$$\delta^2 y(x) = y(x+h) + y(x-h) - 2y(x), \quad (35)$$

$$\begin{aligned} \delta^4 y(x) &= y(x+2h) - 4y(x+h) + 6y(x) \\ & \quad - 4y(x-h) + y(x-2h). \quad (36) \end{aligned}$$

<sup>5</sup> See, for example, L. Fox, *The Numerical Solution of Two-Point Boundary Problems in Ordinary Differential Equations* (Oxford University Press, New York, 1957).

Here,  $h$  is the spacing between neighboring mesh points, and the partial derivatives of Eq. (30) become

$$h^2[(\partial^2/\partial x^2) + (\partial^2/\partial y^2)]u(x, y) = (\delta_x^2 + \delta_y^2)u(x, y) - \frac{1}{12}(\delta_x^4 + \delta_y^4)u(x, y) + O(\delta^6). \quad (37)$$

At a point  $u(x, y)$  one has

$$[(\partial^2/\partial x^2) + (\partial^2/\partial y^2)]u(x, y) = (1/h^2)[u(x+h, y) + u(x-h, y) + u(x, y+h) + u(x, y-h) - 4u(x, y)] + Cu(x, y), \quad (38)$$

with

$$C = -(1/12h^2)(\delta_x^4 + \delta_y^4) + (1/90h^2)(\delta_x^6 + \delta_y^6) - \dots \quad (39)$$

As a first approximation we neglect  $Cu$  in Eq. (38) and therefore replace the differential operator by the first term on the right-hand side. This leads to a truncation error in the expansion of the differential operator. The form of this truncation error is important, as it allows us to predict the convergence of the numerical solution as one approaches the exact solution (see Appendix A). From Eqs. (33)–(39) it is obvious that the local truncation error in the second-difference approximation is  $O(h^2)$ . The term  $Cu$  in Eq. (39) contains higher difference operators, which can be included by an iterative technique (see Appendix B).

One must now specify the boundary conditions for Eq. (30). We treat the problem as a boundary-value one, specifying the value of the solution on a boundary enclosing the area of integration (Dirichlet boundary conditions). The functions  $\hat{u}_{im:vn}^{(1)}$  vanish along the boundaries  $r_1=0, r_2=0$ . These functions also vanish as  $r_1$  or  $r_2 \rightarrow \infty$ . This boundary condition must be modified so as to handle the equation on a finite numerical grid. There are two alternatives, and both are based on the condition that the solutions approach zero exponentially and essentially do so at some finite value of the independent variable. One can choose a value of  $r_1=R_1$  and make the solution vanish on this boundary, i.e.,  $u(R_1, r_2) = u(r_1, R_1) = 0$ . One then moves this boundary out to  $r_1=R_2, R_3$ , etc., until at least two adjacent values at the boundary are zero to the required number of significant figures. The boundary condition is then accurately satisfied. The other alternative is based on the asymptotic form of the solution of Eq. (30). We can use this as a boundary condition. For large values of  $r_1$  and  $r_2$  the solution behaves like  $g(r_1, r_2) \exp[-\alpha(r_1+r_2)]$ , where  $g(r_1, r_2)$  varies slowly. This behavior becomes a boundary condition,

$$u(r_1, r_2) = e^{\alpha h} u(r_1+h, r_2). \quad (40)$$

The boundary condition is satisfied when Eq. (40) holds between neighboring points. Both alternatives work

well and bring all atoms of interest within reach of the method.

With Eq. (38) the differential equation is obviously replaced by a set of algebraic equations. In matrix form these equations are

$$\mathbf{A}\mathbf{u} = \mathbf{b}, \quad (41)$$

where  $u$  is a column vector, the components of which are approximate solutions to the differential equation at a set of internal points. Were it not for the nonlocal exchange potentials of Eq. (30) [see Eqs. (13b) and (14b)], the matrix  $\mathbf{A}$ , Eq. (41), would have a very simple structure; e.g., for  $M$  divisions along each dimension the only nonzero elements lie on the diagonal, the super-, and sub-diagonal, and on lines parallel to the diagonal but  $M$  strips above and below the diagonal. This is a banded matrix of half-bandwidth equal to  $M$ . We now show that (a) large systems of such equations can be solved rapidly and accurately, and (b) once such solutions have been obtained, the nonlocal operators can be taken into account with a small increase in computing time. We put more emphasis on (a), but (b) is shown quite convincingly.

For  $B$  internal points in each dimension we have  $N$  equations with  $N=B^2$ . The matrix  $A$  then has dimensions  $B^2 \times B^2$ ; e.g., with  $B$  about 40 one has a  $1600 \times 1600$  matrix. We use the method of triangular resolution to solve the matrix equation, Eq. (41). The method has been efficiently programmed,<sup>6</sup> and very large systems of equations can be solved economically. We give a very brief outline of the method. If the leading minors of the matrix  $A$  are nonzero, there is a unique lower triangular matrix  $\mathbf{L}$  and a unique upper triangular matrix  $\mathbf{U}$  so that  $\mathbf{A} = \mathbf{L}\mathbf{U}$ . An upper triangular matrix is one which has zeros above the diagonal. The solution proceeds by eliminating the lower triangular elements, taking pivots successively along the principal diagonal, and the only recorded quantities are the multipliers needed for the triangular resolution ( $\mathbf{L}$ ) and the triangularized array ( $\mathbf{U}$ ). The band structure is preserved in the  $\mathbf{L}$  and  $\mathbf{U}$  factors.<sup>7</sup> Solution of the linear equations is straightforward; i.e., for  $\mathbf{A}\mathbf{x} = \mathbf{b}$  one solves  $\mathbf{L}\mathbf{y} = \mathbf{b}$  and  $\mathbf{U}\mathbf{x} = \mathbf{y}$  by forward and backward substitution. The  $\mathbf{L}$  and  $\mathbf{U}$  matrices can be used to operate on any number of right-hand vectors,<sup>8</sup> i.e.,  $\mathbf{b}$  of Eq. (42).

<sup>6</sup> It can be shown that there is no limit on the number of rows of equations that can be handled and that the upper limit on the bandwidth is set by the requirement of having  $\frac{1}{2}M^2$  terms in memory at any one time. For an IBM 7094 an upper limit to the  $M$  is about 200. This corresponds to a large number of equations. For details of the program see C. W. McCormick and K. J. Hebet, "Solution of Linear Equations with Digital Computers," Tech. Rept., Engineering Division, California Institute of Technology, 1965 (unpublished).

<sup>7</sup> L. Fox, *Numerical Solution of Ordinary and Partial Differential Equations* (Pergamon Press, Inc., London, 1962).

<sup>8</sup> Most of the computing time is required to obtain the  $L$  and  $U$  factors and the time to forward- and back-substitute is much less. This feature enables us to include, by an iterative scheme, both nonlocal potentials and higher-order differences. See Appendix B for details.

For a method to be practical the computing-time requirements must be realistic. The real advantage of triangular resolution for band matrices is that the running time for inversion of an  $N \times N$  matrix is proportional to  $N^3$  rather than  $M^2N$  for triangular resolution.  $M$  is the half-bandwidth. For this differential equation  $N \approx M^2$ , and the ratio of running times for matrix inversion to triangular resolution is  $M^2$ . Matrix inversion does not preserve band structure, and the time to determine a new set of roots, i.e., solve Eq. (40) with a new vector  $\mathbf{b}$ , is proportional to  $N^2$ . The time savings involved here are significant, e.g., a factor of 1600 for  $M \approx 40$ . In the next section we give an example which shows that the method is numerically and economically feasible.

RESULTS

When the differential equation is converted into a set of simultaneous linear equations the term  $V_c(\mathbf{r}_1)$  [see Eq. (14a)] is just an algebraic operator evaluated at every mesh point on the grid. For H-F orbitals one would evaluate integrals such as  $S_i(\mathbf{r}_2)$ , Eq. (13a), analytically and tabulate them at the necessary points.

For a numerical method it makes no difference to the analysis whether the potential term,  $V_c(\mathbf{r}_1)$ , in Eq. (30) is given by HF orbitals or is just the electron-nucleus attraction, i.e., hydrogenic zeroth-order Hamiltonian. They both give rise to numerical arrays, which are evaluated even before the numerical analysis really begins. Hence, to demonstrate our method we pick the simplest pair equation, that for the helium atom starting from a hydrogenic  $H_0$ . The important issue here is the practicality of solving the number of simultaneous equations which must be solved so as to obtain an accurate value of a pair energy. Also, for helium we have a series of previous results on the energy contribution of each partial wave to the second-order energy.

Consider Eqs. (21) and (27). For a  $u_{ij}$  of  $S$  symmetry only those  $u_{lm:l'm'}$  with  $l=l'$  are nonzero, and  $u_{lm:l'-m}$  is independent of  $m$ . This gives the partial wave expansion,

$$u(1s^2) = \sum_{l=0}^{\infty} \frac{u_l(\mathbf{r}_1, \mathbf{r}_2)}{r_1 r_2} P_l(\cos\theta_{12}). \tag{42}$$

Recall that  $u(1s^2)$  must be made so that  $\langle u(1s^2), B(1s\alpha 1s\beta) \rangle = 0$ . The differential equations are

$$\left( -\frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{1}{2} \frac{\partial^2}{\partial r_2^2} - \frac{Z}{r_1} - \frac{Z}{r_2} - 2\epsilon_{1s} \right) u_0(\mathbf{r}_1, \mathbf{r}_2) = P_{1s}(\mathbf{r}_1) P_{1s}(\mathbf{r}_2) (J_{1s1s} - r_{>}^{-1}), \tag{43}$$

$$\left( -\frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{1}{2} \frac{\partial^2}{\partial r_2^2} + \frac{l(l+1)}{2r_1^2} + \frac{l'(l'+1)}{2r_2^2} - \frac{Z}{r_1} - \frac{Z}{r_2} - 2\epsilon_{1s} \right) u_l(\mathbf{r}_1, \mathbf{r}_2) = -\frac{r_{<}^l}{r_{>}^{l+1}} P_{1s}(\mathbf{r}_1) P_{1s}(\mathbf{r}_2) \tag{44}$$

for  $l=0$  and  $l \geq 1$ , respectively, and

$$P_{1s}(\mathbf{r}) = r R_{1s}(r). \tag{45}$$

In Eqs. (43) and (44) we have  $\epsilon_{1s} = -2.0$ ,  $E_1 = 1.25$ , and  $R_{1s} = 4\sqrt{2}e^{-2r}$ . Tables I and II give the results for the first three partial waves. Here the second-order energy

decouples into a sum over the partial wave contributions,  $E_2(l)$ . All integrations are done by the trapezoidal rule, and

$$E_2(l=0) = \langle u_0(\mathbf{r}_1, \mathbf{r}_2), (1/r_{12}) B(1s(1) 1s(2)) \rangle - E_1 \langle u_0, B(1s(1) 1s(2)) \rangle, \tag{46a}$$

$$E_2(l \geq 1) = \langle u_l(\mathbf{r}_1, \mathbf{r}_2), (1/r_{12}) B(1s(1) 1s(2)) \rangle. \tag{46b}$$

In Tables I and II we have given the computing times necessary to solve the equations at each mesh size. We feel it is important to communicate the computing needs of a given method. Computing times for this method are quite low. For  $l=0$  we require  $u(\mathbf{r}_1, \mathbf{r}_2)$  to vanish at  $R=5$  and obtained the solutions at seven different mesh sizes:  $h = \frac{1}{4}, \frac{1}{5}, \frac{1}{6}, \frac{1}{7}, \frac{1}{8}, \frac{1}{9}, \frac{1}{10}$ . To test the boundary condition we allowed  $u(\mathbf{r}_1, \mathbf{r}_2)$  to vanish at  $R=6$  and, at a mesh size of  $\frac{1}{4}$ , found  $E_2(l=0) = -0.12607$ , compared to  $-0.12605$  for the same condition at  $R=5$ . With the exponential behavior of the function as a boundary condition at  $R=5$  we obtained  $E_2(l=0) = -0.12607$ , while at  $R=4$  one finds  $E_2(l=0) = -0.1261$ . The boundary condition poses no difficulty. For  $h = \frac{1}{4}$  there are 361 equations, and the entire problem can be loaded into the random access memory of an IBM 7094 and

TABLE I. Results for the  $l=0$  partial wave of the helium pair function.<sup>a</sup>

Mesh size <sup>b</sup>	Number of equations <sup>c</sup>	$E_2(l=0)$	Execution time (seconds on IBM 7094)
$\frac{1}{4}$	361	-0.12605	3 <sup>d</sup>
$\frac{1}{5}$	576	-0.12678	16 <sup>e</sup>
$\frac{1}{6}$	841	-0.12664	27
$\frac{1}{7}$	1156	-0.12640	52
$\frac{1}{8}$	1521	-0.12619	82
$\frac{1}{9}$	1936	-0.12603	115
$\frac{1}{10}$	2401	-0.12591	169

<sup>a</sup> See Eq. (43). The perturbation is  $1/r_{12}$ .  
<sup>b</sup> Spacing between grid points.  
<sup>c</sup> Number of points at which an approximate solution to the differential equation is obtained.  
<sup>d</sup> This size problem fits completely in random access memory.  
<sup>e</sup> This size problem requires auxiliary disk storage.

TABLE II. Results for the  $l=1$  and 2 partial waves of the helium pair function.

Mesh size	$E_2(l=1)$	$E_2(l=2)$	Execution time <sup>b</sup>
$\frac{1}{4}$	-0.033051 <sup>a</sup>	-0.0056616	2 <sup>o</sup>
$\frac{1}{5}$	-0.030387	-0.0049862	3 <sup>e</sup>
$\frac{1}{6}$	-0.029073	-0.0046351	12 <sup>d</sup>
$\frac{1}{7}$	-0.028333	-0.0044302	23
$\frac{1}{8}$	-0.027874	-0.0043007	37
$\frac{1}{9}$	-0.027569	-0.0042137	50
$\frac{1}{10}$	-0.027356	-0.0041525	82

<sup>a</sup> All integrals evaluated by the trapezoidal rule.  
<sup>b</sup> Execution time in seconds on an IBM 7094.  
<sup>c</sup> This size problem fits entirely in core.  
<sup>d</sup> This size problem requires auxiliary storage.

solved within 3 sec. At  $h=\frac{1}{5}$  one requires disk storage to handle the 576 equations, and the execution time is 16 sec. Table II gives the results for  $l=1$  and  $l=2$  partial waves. The execution times are lower than those for the  $l=0$  case, since the exponential boundary condition could be imposed at  $R=4$  for these higher partial waves. One can expect this behavior for the higher  $l$  components of pair functions. Requiring the function to vanish at  $R=6$  affected the seventh significant figure in the energy.

Tables III-V give the results of extrapolating the values at varying mesh sizes (Tables I and II). In Appendix A we derive the convergence of the solution of the corresponding finite difference equations,  $u(h)$ , towards the solution of the differential equation itself,  $u$ . We show that

$$u - u(h) = a_2 h^2 + a_4 h^4 + \dots, \quad (47)$$

TABLE III. Extrapolants from finest meshes.<sup>a</sup>

$l$	Mesh size	Results from direct quadrature	$h^2$ extrapolants <sup>c</sup>	$h^4$ extrapolants <sup>d</sup>
$l=0$	$\frac{1}{6}$	-0.126194 <sup>b</sup>	-0.12541	-0.12531
	$\frac{1}{8}$	-0.126030	-0.12537	
	$\frac{1}{10}$	-0.125905		
$l=1$	$\frac{1}{8}$	-0.027874	-0.026422	-0.026498
	$\frac{1}{9}$	-0.027569	-0.026449	
	$\frac{1}{10}$	-0.027356		
$l=2$	$\frac{1}{8}$	-0.0043007	-0.0038862	-0.003902
	$\frac{1}{9}$	-0.0042137	-0.0038919	
	$\frac{1}{10}$	-0.0041525		

<sup>a</sup> See Eq. (48) of text.  
<sup>b</sup> Results from direct quadrature on numerical solutions (Tables I and II).  
<sup>c</sup> Extrapolants from pairs of successive values in the preceding column assuming an  $h^2$  convergence.  
<sup>d</sup> Extrapolants from the three values in the first column assuming an  $h^2$  and  $h^4$  convergence.

TABLE IV. Extrapolants from intermediate meshes.<sup>a</sup>

$l$	Mesh size	Results from direct quadrature	$h^2$ extrapolants <sup>c</sup>	$h^4$ extrapolants <sup>d</sup>
$l=0$	$\frac{1}{6}$	-0.126642 <sup>b</sup>	-0.12562	-0.12526
	$\frac{1}{8}$	-0.126194	-0.12539	
	$\frac{1}{10}$	-0.125905		
$l=1$	$\frac{1}{6}$	-0.029073	-0.026332	-0.026495
	$\frac{1}{8}$	-0.027874	-0.026436	
	$\frac{1}{10}$	-0.027356		
$l=2$	$\frac{1}{6}$	-0.0046351	-0.0038707	-0.0038996
	$\frac{1}{8}$	-0.0043007	-0.0038892	
	$\frac{1}{10}$	-0.0041525		

<sup>a</sup> See Eq. (48) of text.  
<sup>b</sup> Results from direct quadrature on numerical solutions (Tables I and II).  
<sup>c</sup> Extrapolants from pairs of successive values in the preceding column assuming an  $h^2$  convergence.  
<sup>d</sup> Extrapolants from the three values in the first column assuming an  $h^2$  and  $h^4$  convergence.

where  $u, u(h), a_2$ , and  $a_4$  are functions of the independent variables and  $h$  is the mesh size. We therefore know exactly how an approximate solution approaches the exact one. This convergence property forms the basis of an extrapolation technique which allows us to obtain a high degree of accuracy for the pair energies. We checked the use of Eq. (47) by comparing an actual solution with an extrapolated one. The agreement is excellent.

The integrals for  $E_2$  are evaluated by the trapezoidal rule. The error term for quadrature by the trapezoidal rule can be expressed as a power series in the interval size,  $h$ . In Appendix A we show that the second-order energy, evaluated by the trapezoidal rule and with the finite difference solution, converges to the exact value

TABLE V. Extrapolants from values at various meshes.

$l$	Values used in extrapolation	Extrapolants
$l=0$	$(\frac{1}{6}, \frac{1}{7})^a$	-0.12574
	$(\frac{1}{5}, \frac{1}{6}, \frac{1}{7})$	-0.12512
	$(\frac{1}{6}, \frac{1}{7}, \frac{1}{8})$	-0.12521
$l=1$	$(\frac{1}{4}, \frac{1}{5})$	-0.02564
	$(\frac{1}{5}, \frac{1}{6})$	-0.02609
	$(\frac{1}{6}, \frac{1}{7}, \frac{1}{8})$	-0.02645
$l=2$	$(\frac{1}{5}, \frac{1}{6}, \frac{1}{7})$	-0.02649
	$(\frac{1}{4}, \frac{1}{5})$	-0.003786
	$(\frac{1}{5}, \frac{1}{6})$	-0.003837
$l=2$	$(\frac{1}{4}, \frac{1}{5}, \frac{1}{6})$	-0.003878
	$(\frac{1}{4}, \frac{1}{5}, \frac{1}{6}, \frac{1}{7})$	-0.003896
	$(\frac{1}{4}, \frac{1}{5}, \dots, \frac{1}{10})$	-0.003905

<sup>a</sup> The values at these mesh sizes were used in the extrapolation.

as follows:

$$E_2 = E_2(h) + b_2 h^2 + b_4 h^4 + \dots, \quad (48)$$

where  $E_2(h)$  is the energy obtained at each mesh size. With Eq. (48) we can derive very accurate extrapolants. To obtain the best results one obviously extrapolates the results from the finer meshes. If one simply wants a good estimate of a pair energy, extrapolation from coarser meshes may be sufficient. Tables III and IV give the extrapolants based on results from the finest meshes, i.e.,  $h = \frac{1}{8}, \frac{1}{9}, \frac{1}{10}$  and those derived from the results at  $h = \frac{1}{6}, \frac{1}{8}, \frac{1}{10}$ , respectively. The various columns of Tables III and IV correspond to an extrapolation from a successively higher-order polynomial, i.e., an  $h^2$  and  $h^4$  extrapolation. The successive columns of both Tables indicate that the extrapolation is stable and yields excellent results. Table V lists extrapolants derived from the results at various mesh sizes. We do this primarily to show the kind of extrapolants one can obtain from results at cruder meshes. These compare well with the best results of Table III. This approach can yield useful estimates of pair correlation energies. For the  $l=1$  partial wave extrapolation from mesh sizes  $\frac{1}{4}, \frac{1}{5}, \frac{1}{6}$  give  $-0.02645$ . These solutions were obtained with a total computing time of 17 sec. Table V also lists some extrapolants based on very high-order polynomials; e.g., use of the results at all seven mesh sizes implies an  $h^{10}$  extrapolation and for  $l=2$  gives  $E_2(l=2) = -0.003905$ . Other extrapolants indicate a similar stability.

For comparison we use the most recent results on the helium-atom pair function. Byron and Joachain<sup>9</sup> solved the pair equation variationally and also gave the contributions of the various partial waves to  $E_2$ . They used two different types of trial functions. For  $u_l(r_1, r_2)$  of Eq. (42) they chose (a) a "configuration-interaction" type expansion,

$$u_l(r_1, r_2) = \sum_{m,n} c_{lmn} (r_1^m r_2^n + r_1^n r_2^m) \times r_1 r_2 \exp[-2(r_1 + r_2)], \quad (49a)$$

and (b) a function of the form

$$u_l(r_1, r_2) \sum_{m,n} c_{lmn} r_1^m r_2^n \exp[-2(r_1 + r_2)]. \quad (49b)$$

TABLE VI. Comparison of numerical results with variational calculations.

$E_2(l)$	Variational			Numerical <sup>d</sup>
	Case I <sup>a</sup>	Case II <sup>b</sup>	Case III <sup>c</sup>	
$l=0$	-0.12533	-0.12532	-0.12501	-0.12531
$l=1$	-0.026495	-0.026475	-0.025903	-0.026498
$l=2$	-0.003906	-0.003893	-0.003531	-0.003902

<sup>a</sup> See Eq. (49b) (30 variational parameters).

<sup>b</sup> See Eq. (49b). Only positive powers of  $r$  with 36 variational parameters.

<sup>c</sup> Equation (49a) with 20 parameters.

<sup>d</sup> Numerical integration of the partial differential equations.

<sup>9</sup> F. W. Byron and C. J. Joachain, Phys. Rev. **157**, 1 (1967).

TABLE VII. Upper bounds derived from numerical solution.<sup>a</sup>

Mesh size	$M^b$	$E_2(l=0)$	$M$	$E_2(l=1)$	$M$	$E_2(l=2)$
$\frac{1}{4}$	7	-0.1239	8	-0.02554	7	-0.003222
$\frac{1}{5}$	7	-0.1246	7	-0.02605	8	-0.003630
$\frac{1}{6}$	7	-0.1251	8	-0.02625	9	-0.003753
$\frac{1}{7}$	7	-0.1252	7	-0.02634	9	-0.003802
$\frac{1}{8}$	9	-0.1252	8	-0.02641	9	-0.003839

<sup>a</sup> See Eq. (50b).

<sup>b</sup>  $M-1$  is the order of a polynomial covering a triangular region.

Functions of type (a) are standard, and those of type (b) are correlated in their radial part, and they avoid some difficult integrals due to nonlocal potentials that appear when interelectronic coordinates are used. Such functions may seem inadmissible as trial functions, since they have a finite discontinuity in the first derivative at  $r_1=r_2$ . The variational principle nevertheless is still valid giving an upper bound. Table VI gives their values<sup>9</sup> listed as Cases I-III and our best extrapolants. For Case I a function of type (b) is used but each partial wave contains 30 terms with  $-1 \leq m+n \leq 4$ . In Case II functions of type (b) are again used, but with 36 terms and  $m+n \leq 7$  (no negative powers of  $r_1 r_2$ ). For Case III they<sup>9</sup> used a function of type (a) with 20 variational parameters. The results of Table VI clearly show that the numerical method of finite differences, coupled with extrapolation based on the convergence properties of the finite difference solution, can give results as accurate as the variational method.

It is easy to derive a convenient analytical fit to the numerical solution by simply projecting various functional forms on to it. To demonstrate this we use functions of the type in Eq. (49b). These analytical fits can obviously provide upper bounds to  $E_2$ . Since the solutions of Eqs. (43) and (44) are symmetric about the line  $r_1=r_2$ , consider the region  $r_1 > r_2$  and let  $x=r_1$  and  $y=r_2$  there. The numerical solution should have the form<sup>10</sup>

$$u(x, y) = \exp[-\alpha(x+y)]\pi(x, y), \quad (50a)$$

where  $\pi(x, y)$  is a polynomial in the triangular area  $r_1 > r_2$ ,

$$\pi(x, y) = \sum_{m=1}^M \sum_{n=1}^m c_{mn} x^{m-n} y^{n-1}. \quad (50b)$$

In principle  $\alpha$  can be varied, but here it is clearly equal to two. One just takes the solution vector, multiplies it by  $\exp[\alpha(x+y)]$ , and puts a polynomial,  $\pi(x, y)$ , through a selected number of points of the resulting vector. Equation (25) then gives an upper bound. The equation determining the  $c_{mn}$ 's can be solved in a matter of seconds. Table VII gives some of these results. At crude meshes one can obtain estimates that compare

<sup>10</sup> See comments below Eq. (49b) on the use of such functions in the variational expression. One must handle the integrals containing the kinetic energy operator properly.

well with the configuration-interaction results of Table VI; e.g., at a mesh size of  $\frac{1}{5}$  for the  $l=1$  and 2 partial waves  $E_2(l) = -0.02605$  and  $-0.00363$ , respectively, versus  $-0.025903$  and  $-0.003531$  of Table VI. An interesting observation is that the numerical result always lies below the best available estimate of the energy of each partial wave, so that the true value is apparently bracketed by the numerical and variational results; e.g., at a mesh size of  $\frac{1}{10}$   $E_2(l)$  for  $l=0, 1$ , and 2 is  $-0.1259$ ,  $-0.02736$ , and  $-0.00415$ , respectively, by numerical integration and  $-0.1252$ ,  $-0.02641$ , and  $-0.003839$  variationally. These bracket the accurate results of  $-0.12533$ ,  $-0.026495$ , and  $-0.003906$ . This bracketing occurs at all mesh sizes, and the limits become smaller as the mesh is refined.

### NONLOCAL POTENTIALS

Our results demonstrate that the pair equations can be solved by the finite-difference method if the exchange potentials in Eq. (30) were absent. In that case the differential equation is replaced by a matrix equation in which the matrix is banded. Such a system of equations can be solved quite efficiently by triangular decomposition; i.e.,  $\mathbf{A}$  [Eq. (41)] is decomposed into its  $L$  and  $U$  factors. With the matrix  $A$  in triangular form the system  $\mathbf{Ax} = \mathbf{b}$  is solved by a forward and backward substitution. The lower and upper triangular matrices,  $L$  and  $U$ , are stored and are always available. This allows one to include nonlocal potentials and higher difference corrections (Appendix B) by an iterative technique, with a small increase in computing time.

There are two starting points. One can drop the exchange operator  $V_e(\mathbf{r})$  completely [see Eqs. (13b) and (14b)] and solve the resulting equations

$$\mathbf{A}\mathbf{u}_0 = \mathbf{b}. \quad (51)$$

The term  $-[V_e(\mathbf{r}_1) + V_e(\mathbf{r}_2)]u(\mathbf{r}_1, \mathbf{r}_2)$  has been neglected for the first iteration. Write  $u \approx u_0 + \Delta u_0$ , and the correction  $\Delta u_0$  is approximately given by the equation

$$\mathbf{A}(\Delta \mathbf{u}_0) = [V_e(\mathbf{r}_1) + V_e(\mathbf{r}_2)]\mathbf{u}_0, \quad (52)$$

which can be solved by a forward and backward substitution since the  $L$  and  $U$  factors are available. One would really like to replace the nonlocal operator by a local operator. Various effective local potentials can approximate the exchange potential quite well, e.g., those of Slater<sup>11</sup> and Kohn and Sham.<sup>12</sup> Slater suggests that the exchange potential be represented by

$$V_e^s(\mathbf{r}) = (3/2\pi)[3\pi^2 n(\mathbf{r})]^{1/3}, \quad (53)$$

where

$$n(\mathbf{r}) = \sum_{i=1}^N \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}),$$

and  $\psi_i(\mathbf{r})$  satisfies an equation like the HF equations, but with  $V_e$  of Eq. (53). The advantage is that this  $V_e^s(\mathbf{r})$  is an algebraic operator, and one now has an equation like Eq. (51) with a different band matrix,  $A_s$ :

$$A_s u_0 = b. \quad (54)$$

The operator  $(V_e^s - V_e)$  is neglected for the first iteration. As in Eq. (52), one solves for the correction  $\Delta u^0$ .

Since the facility of including exchange potentials is important, we give some estimates of the additional computing requirements. If the problem fits in random access memory, a solution of the matrix equation requires about  $\frac{1}{2}M^4 + 2M^3$  operations. But with the  $L$  and  $U$  matrices available only  $2M^3$  operations are required to solve for a new root. Thus, the additional time per iteration to include the nonlocal potentials will be about  $4/(4+M)$  of the initial time, which for  $M=20$  is about 16%. With auxiliary storage and bandwidths that are not too large, one can prove that this percentage will be less than 25% and will decrease the larger the number of equations becomes.

### CONCLUSIONS

We have shown that the first-order pair equations proposed by Sinanoğlu can be solved both economically and conveniently by numerical integration. One of the advantages of the method is its simplicity, and its success depends on the ability to solve a large number of simultaneous linear equations efficiently. One can obtain an approximate solution at around 2000 mesh points in just under 2 min on an IBM 7094. Such solutions would be sufficient for many purposes. With this number of equations one must use auxiliary disk storage, and a fair bit of time is spent transmitting information between computing units. On a machine with a larger random access storage but, hypothetically, with the same basic cycle time, such a calculation would take about 40 sec. The programming is simple, and the few integrations necessary are done by the trapezoidal rule. Nonlocal potentials can be treated with a small increase by the same iterative technique.

We also prove how the finite difference solution must converge toward the exact solution as the mesh size goes to zero. This convergence forms the basis of a stable extrapolation procedure which gives an accurate value for the pair energy. On the other hand, very little is known about the convergence properties of variational methods. The expansion in spherical harmonics has some conceptual advantage, and the solutions for the radial functions converge nicely for all  $l$  values. The boundary condition poses no difficulty.

We chose the first-order pair function as the example in this paper, but there are other pairs that are more accurate than these first-order pairs.<sup>2</sup> In many cases one expects  $\mathcal{A}_{ij}^{(0)}$  to suffice, but if one wants to go to more accurate pairs, numerical methods are also applicable.

<sup>11</sup> J. C. Slater, Phys. Rev. **81**, 385 (1951).

<sup>12</sup> W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965). For comments on this choice of exchange potential see J. C. Slater, Massachusetts Institute of Technology, Solid State and Molecular Theory, Quarterly Progress Report No. 58, 1965 (unpublished).

For example, consider the pair equation which satisfies the equation<sup>2</sup>

$$(e_i + e_j + Qm_{ij})\hat{\psi}_{ij} = 0. \tag{55}$$

$Q$  is defined in Eq. (11), and

$$\hat{\psi}_{ij} = B(\phi_i(1)\phi_j(2)) + \hat{u}_{ij}. \tag{56}$$

The corresponding pair energy provides a lower bound to the exact pair energy.<sup>13</sup> One can write

$$(e_i + e_j)\hat{u}_{ij} = -Q(1/r_{12})B(\phi_i(1)\phi_j(2)) - Qm_{ij}\hat{u}_{ij}. \tag{57}$$

Neglecting the second term on the right-hand side, Eq. (57) becomes identical with Eq. (10) for  $\hat{u}_{ij}^{(1)}$ . An obvious approach to the solution of Eq. (57) would be iterative; i.e., take  $\hat{u}_{ij}^{(1)}$  and use the  $L$  and  $U$  matrices to solve for  $\Delta u_{ij}$  due to the term  $Qm_{ij}\hat{u}_{ij}$  [see discussion below Eq. (52)]. The algebra on the spherical harmonics may be more involved, but comparison between  $\hat{u}_{ij}^{(1)}$  and  $\hat{u}_{ij}$ , Eq. (57), will be informative.

**APPENDIX A**

An advantage of the numerical method is that one can derive the convergence of the numerical solution,  $u(x, y, h)$ , towards the exact solution,  $u(x, y)$ . One expands  $u(x, y)$ ,

$$u(x, y) = u(x, y, h) + Ah + Bh^2 + Ch^3 + \dots, \tag{A1}$$

where  $A, B, C, \dots$ , are functions of  $x$  and  $y$ . The differential equation, Eq. (30), has the form

$$f(D)u = g(x, y), \tag{A2}$$

where

$$f(D) = -\frac{1}{2}(\partial^2/\partial x^2) - \frac{1}{2}(\partial^2/\partial y^2) + p(x, y), \tag{A3}$$

and the numerical solution,  $u(h)$ , satisfies

$$Lu(h) = g(x, y). \tag{A4}$$

The difference between Eq. (A2) and Eq. (A4) is the local truncation error, Eq. (39). This error contains only even powers of  $h$ , with zero constant term, so

$$Lu(h) = [f(D) + (ch^2 + dh^4 + \dots)]u(h). \tag{A5}$$

Substituting for  $u(h)$  and equating powers of  $h$ ,

$$f(D)u = g(x, y), \tag{A6}$$

$$f(D)A = 0, \tag{A7}$$

$$f(D)B - cu = 0, \tag{A8}$$

$$f(D)C + cA = 0. \tag{A9}$$

Note that Eq. (A5) has its form due to the use of central differences. From Eqs. (A7) and (A9)  $A$  and  $C$  are zero. Thus, Eq. (A1) becomes

$$u - u(h) = Bh^2 + Dh^4 + \dots. \tag{A10}$$

<sup>13</sup> O. Sinanoğlu (private communication).

The basic integrals are of the type

$$I = \int_0^a dx \int_0^z f(x, y) dy. \tag{A11}$$

Here  $f(x, y)$  contains the numerical solution, and this is known approximately at fixed intervals. In evaluating  $I$  there are two sources of error: (i) that of Eq. (A10), and (ii) the quadrature by the trapezoidal rule. With a known function  $f(x, y)$ , the form of  $I$  would be

$$I = T(h) + ah^4 + O(h^6), \tag{A12}$$

where  $T(h)$  is the value of the integral evaluated by the trapezoidal rule. Use of the numerical solution, instead of the exact solution, to evaluate  $T(h)$  introduces terms proportional to  $h^2, h^4$ , etc., into Eq. (A12). The final form is

$$I = T_0(h) + a_2h^2 + a_4h^4 + \dots. \tag{A13}$$

**APPENDIX B**

In Eq. (38) we neglected the term  $Cu$  and retained just the second difference operator. Instead of going to very fine meshes one may include fourth differences, e.g., Eq. (36), and this may give an accurate solution at coarser meshes.<sup>7</sup> Consider the first term of Eq. (39),

$$C = -(1/12h^2)(\delta_x^4 + \delta_y^4), \tag{B1}$$

and write the new matrix equation

$$(A + C)y = b. \tag{B2}$$

The matrix  $A$  dominates, and for a first approximation,  $y^{(1)}$ , one has

$$Ay^{(1)} = b. \tag{B3}$$

The first correction  $z$  to  $y^{(1)}$  is approximately

$$Az = -Cy^{(1)}. \tag{B4}$$

With the  $L$  and  $U$  matrices available, Eq. (B4) is easily solved. At points next to the boundary the term  $Cy^{(1)}$  requires values of the function beyond the boundaries [see Eq. (36)]. One often extrapolates across the boundary, but there is an apparent indeterminacy at the boundary [see Eq. (43)]. One can derive a relation between the point next to the boundary and the first external one through a cusplike condition. In the region  $r_1 > r_2$  let  $x = r_1, y = r_2$ , and  $y \rightarrow 0$ ; we have

$$-\frac{1}{2} \left( \frac{\partial^2 u}{\partial x^2} \right)_{x_i} - \frac{1}{2} \left( \frac{\partial^2 u}{\partial y^2} \right)_{y \rightarrow 0} + \left[ \left( \frac{l(l+1)}{2y^2} - \frac{Z}{y} \right) u \right]_{y \rightarrow 0} = 0. \tag{B5}$$

Substitution from Eq. (35) into Eq. (B5), and with

$$(\partial u / \partial y)_{y_i} = \{ [u(x, y_2 + h) - u(x, y_2 - h)] / 2h \} + O(h^2), \tag{B6}$$

one obtains the necessary relationship. The limits  $(u/y)_{y \rightarrow 0}$  and  $(u/y^2)_{y \rightarrow 0}$  are evaluated using L'Hopital's rule for indeterminate forms.