

Analytic Approach to Electron Correlation in Atoms

RONALD J. WHITE AND FRANK H. STILLINGER, JR.

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

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A novel perturbative treatment of electron correlation in N -electron atoms is devised. The unperturbed starting point is a central-force "hydrogenic" problem in the full dN -dimensional configuration space (d =dimensionality). The central potential in this solvable "hydrogenic" problem is obtained by averaging the actual electron-electron and electron-nucleus potentials over all $dN-1$ hyperspherical polar angles in the configuration space. The relevant projected Green's functions are computed for the ground states of the model one-dimensional two-electron atom (with delta function interactions), as well as for the real three-dimensional helium isoelectronic sequence. The corresponding first-order wavefunctions exhibit weakly singular logarithmic behavior (at three-particle confluence) of the type first advocated by Fock. Second-order energies are evaluated for both of these two-electron problems. The basic ingredients of our hyperspherical coordinate method for three-electron atoms are displayed, in preparation for later application. Explicit suggestions are made for inclusion of singular terms in high-accuracy atomic and molecular variational wavefunctions.

I. INTRODUCTION

Quantum theory has been applied to the study of the spectra and properties of atoms and molecules for over 40 years. In this time theorists have achieved quite reasonable success considering the fact that the Schrödinger equation has been solved exactly only for one-electron systems. Because of the relative ease of treating one-electron systems the theory of atomic structure was originally based on an independent particle model with self-consistent atomic orbitals.¹

In recent years it has become increasingly evident that electron correlation must be understood and accounted for if a quantitative *ab initio* approach to atomic and molecular structure is to become a reality.² We present in the following a novel approach to correlation in atomic theory.

If the Hamiltonian for an N -electron atom is written in terms of spherical coordinates in $3N$ dimensions (hyperspherical coordinates), the potential energy is homogeneous of degree minus one in the radial variable $\rho = (r_1^2 + \dots + r_N^2)^{1/2}$, while the kinetic energy is the sum of a radial operator and an angular operator. We approach the solution of the eigenvalue problem by perturbation theory and find it natural to choose the zeroth-order potential energy to be the average of the true potential energy over the $3N-1$ angular variables. This corresponds to a model which may be thought of as a generalized hydrogen atom in $3N$ dimensions.³ For this model it is relatively simple to construct explicitly the reduced Green's function necessary for the solution of the perturbation equations.

Section II discusses the hyperspherical coordinates themselves and gives the form of the Laplacian in these coordinates. In Sec. III the technique mentioned in the last paragraph is applied to a delta-function model of the two-electron atom in order to establish the ability of the method to predict the correct form of the known wavefunction. Section IV concerns the ground state of the real two-electron atom. It is shown that three-body effects of a form proposed by Fock⁴ enter the wavefunction naturally in first order.

In Sec. V we consider briefly the extension of the hyperspherical coordinate method to three electron atoms (and ions). It is pointed out that electron spin *per se* does not enter the problem, and that one again is concerned only with finding spatial eigenfunctions of the spin-free Hamiltonian H . However, one must be careful to satisfy certain accessory conditions on the spatial functions which, for the zeroth-order Hamiltonian with a hyperspherically averaged potential, require selection of a special excited state. In principal, similar but more complicated considerations apply to any nonrelativistic atom or ion with more than three electrons, so in principle our method is a general technique for the study of electron correlation.

The final section (Sec. VI) proposes inclusion of special logarithmic functions that are suggested by our analysis in accurate variational trial wavefunctions for molecules such as H_2 .

II. HYPERSPHERICAL COORDINATES

Consider an atomic system with N electrons ($N > 1$). The number of coordinates necessary to specify the position of these electrons relative to a fixed point (the nucleus) is, in general, $3N$. If the Laplacian operator is written in terms of the three-dimensional spherical coordinates for each electron (r_i, θ_i, ϕ_i) it has the well-known form

$$\nabla_{3N}^2 = \sum_{i=1}^N \left(\frac{1}{r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} - \frac{L^2(\theta_i, \phi_i)}{r_i^2} \right), \quad (1)$$

where $L^2(\theta_i, \phi_i)$ is Laplace's operator on a sphere in three dimensions,

$$-L^2(\theta_i, \phi_i) = (\sin\theta_i)^{-1} (\partial/\partial\theta_i) \sin\theta_i (\partial/\partial\theta_i) + (\sin^2\theta_i)^{-1} (\partial/\partial\phi_i)^2. \quad (2)$$

In spaces of dimensionality exceeding 3, a variety of choices for "spherical" coordinates is available depending on how one defines the angles. For N -electron atoms, one can choose to form an orthogonal hyperspherical coordinate system in the following way. Let

$2N$ of the angular variables be the θ_i, ϕ_i mentioned above. From the N r_i define a single radial coordinate ρ and $N-1$ angular coordinates χ_n by the relationships

$$r_1 = \rho \cos \chi_1 \quad (\pi/2 \geq \chi_i \geq 0),$$

$$r_2 = \rho \sin \chi_1 \cos \chi_2,$$

...

$$r_N = \rho \sin \chi_1 \sin \chi_2 \cdots \sin \chi_{N-1},$$

$$\partial(r_1, r_2, \dots, r_N) / \partial(\rho, \chi_1, \dots, \chi_{N-1}) = \rho^{N-1} (\sin \chi_1)^{N-2} (\sin \chi_2)^{N-3} \cdots \sin \chi_{N-2}. \quad (3)$$

Then it may be shown that⁵

$$\nabla_{3N}^2 = \frac{1}{\rho^{3N-1}} \frac{\partial}{\partial \rho} \rho^{3N-1} \frac{\partial}{\partial \rho} - \frac{1}{\rho^2} \Lambda_{3N}^2(\chi_1, \dots, \chi_{N-1}, \theta_1, \dots, \theta_N, \phi_1, \dots, \phi_N), \quad (4)$$

where the generalized angular-momentum operator $-\Lambda_{3N}^2$ is given by

$$-\Lambda_{3N}^2 = (\sin^{3N-4} \chi_1 \cos^2 \chi_1)^{-1} \frac{\partial}{\partial \chi_1} \sin^{3N-4} \chi_1 \cos^2 \chi_1 \frac{\partial}{\partial \chi_1} - \frac{L^2(\theta_1, \phi_1)}{\cos^2 \chi_1} - \frac{\Lambda_{3N-3}^2(\chi_2, \dots, \chi_{N-1}, \theta_2, \dots, \theta_N, \phi_2, \dots, \phi_N)}{\sin^2 \chi_1}. \quad (5)$$

Note that $L^2(\theta, \phi)$ is to be identified with $\Lambda_3^2(\theta, \phi)$.

The eigenvalues and eigenfunctions of the generalized angular momentum operator are known^{5,6} and the case $N=2$ has been explored in detail.^{7,8} Since we do not require the detailed properties of Λ_{3N}^2 for $N > 2$ in what follows we shall omit further study of these operators.

III. THE DELTA-FUNCTION MODEL OF THE TWO-ELECTRON ATOM

We will first consider the problem of two one-dimensional "particles" which interact with a fixed center and with each other by short-range Dirac delta function potentials.⁹ The displacements of the particles from the fixed center will be denoted by x and y , respectively. The Hamiltonian for this model system will be taken to be

$$H = -\frac{1}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) - \delta(x) - \delta(y) + \lambda \delta(x-y), \quad -\infty \leq x, y \leq \infty \quad (6)$$

in suitable units. The particles are thus attracted to the fixed center and repelled by each other. The parameter λ governs the strength of the mutual interaction of the

particles relative to their interaction with the fixed center.

We are interested in the ground-state eigenfunction of this Hamiltonian. When $\lambda=0$, this state is particularly simple with eigenfunction $\exp(-|x| - |y|)$ and eigenvalue -1.0 in the units chosen. For small λ it is natural to apply standard Rayleigh-Schrödinger perturbation theory¹⁰ to this eigenvalue problem with λ itself serving as an obvious perturbation parameter. This analysis has been carried out¹¹ through first order in λ , but since the results are not generally available we present one method of obtaining them in Appendix A. The result for the eigenfunction is

$$\begin{aligned} \Psi(x, y) &= \exp(-|x| - |y|) \left(1 - \frac{3}{2}\lambda + \frac{1}{4}\lambda |x+y| + \frac{1}{4}\lambda |x-y| \right) \\ &+ \frac{\lambda}{2\pi} \int_0^\infty \frac{dk}{(1+k^2)^{3/2}} \left\{ \exp[-|x+y|(1+k^2)^{1/2}] \right. \\ &\quad \times \cos(|x-y|k) - \exp[-|x-y|(1+k^2)^{1/2}] \\ &\quad \left. \times \cos(|x+y|k) \right\} + O(\lambda^2), \quad (7) \end{aligned}$$

and the corresponding expansion for the eigenvalue is¹¹

$$\begin{aligned} E(\lambda) &= -1.0 + 0.5\lambda - \left[\frac{3}{8} - (2/3\pi) \right] \lambda^2 + \left[(6\pi)^{-1} - \frac{5}{128} \right] \lambda^3 + O(\lambda^4) \\ &= -1.0 + 0.5\lambda - 0.16279\lambda^2 + 0.013989\lambda^3 + O(\lambda^4). \quad (8) \end{aligned}$$

We will now approach this problem quite differently. In terms of the polar coordinates

$$\begin{aligned} \rho^2 &= x^2 + y^2, & 0 \leq \rho < \infty, \\ \theta &= \tan^{-1}(y/x) - \frac{1}{4}\pi, & -\pi \leq \theta \leq \pi \end{aligned} \quad (9)$$

(which are the direct but simple analogs of the hyperspherical coordinates introduced in the preceding section), where θ is measured counterclockwise from the line $x=y$, $x, y > 0$, the potential energy for the model,

$$\begin{aligned} U(\rho, \theta) &= -\delta(x) - \delta(y) + \lambda \delta(x-y) \\ &= -\rho^{-1} \left[\delta(\theta + \frac{1}{4}\pi) + \delta(\theta - \frac{1}{4}\pi) + \delta(\theta + \frac{3}{4}\pi) + \delta(\theta - \frac{3}{4}\pi) \right] + (\lambda/2^{1/2}\rho) [\delta(\theta) + \delta(\theta - \pi)], \quad (10) \end{aligned}$$

is homogeneous of degree minus one in ρ . If we average this potential over the angle θ we obtain

$$U_0(\rho) = (2\pi)^{-1} \int_{-\pi}^{\pi} U(\rho, \theta) d\theta = -Z_0/\rho, \tag{11}$$

where $Z_0 = (4 - 2^{1/2}\lambda)/2\pi$. In spite of the fact that U_0 is quite different from U itself due to the short-range character of the latter, we will perform a perturbation calculation using U_0 as the zeroth-order potential. This should be a nontrivial test of the technique of angular averaging of a potential and the results should yield qualitative conclusions about the reliability of the general technique.

We thus partition the Hamiltonian (6) into two parts,

$$H = H_0 + \xi H_1 \tag{12}$$

(ultimately $\xi = 1$, of course), with

$$H_0 = -\frac{1}{2}\nabla^2 + U_0$$

and

$$H_1 = U - U_0,$$

and assume that the wavefunction and eigenvalue are expandable as

$$\Psi = \psi_0 + \xi\psi_1 + \dots, \tag{13}$$

$$E = E_0 + \xi E_1 + \xi^2 E_2 + \xi^3 E_3 + \dots. \tag{14}$$

The first two equations in the perturbation hierarchy are

$$(H_0 - E_0)\psi_0 = 0 \tag{15}$$

and

$$(H_0 - E_0)\psi_1 = (E_1 - H_1)\psi_0. \tag{16}$$

The requisite solution of the former of these equations is

$$\psi_0 = (8/\pi)^{1/2} Z_0 \exp(-2Z_0\rho),$$

$$E_0 = -2Z_0^2 = -0.81057 + 0.57316\lambda - 0.10132\lambda^2, \tag{17}$$

while

$$E_1 = \langle \psi_0 | H_1 | \psi_0 \rangle = 0.$$

We will use a Green's function technique to solve (16). The required Green's function is defined by the equation

$$[H_0(1) - E_0]G_0(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2) = \delta(\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2) - \psi_0(\rho_1)\psi_0(\rho_2) \tag{18}$$

together with suitable regularity conditions at the origin and at infinity. To uniquely determine G_0 we require it to be orthogonal to the homogeneous solution ψ_0 , and we note that the relevant part of G_0 will have the same symmetry as Ψ itself.

To begin, we use the completeness relation of the Fourier series to represent the delta function in (18),

$$\delta(\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2) = \frac{\delta(\rho_1 - \rho_2)}{2\pi\rho_1} \sum_{n=-\infty}^{\infty} \exp[in(\theta_1 - \theta_2)], \tag{19}$$

and then we expand $G_0(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2)$ in a corresponding Fourier series. The part of G_0 that has the correct symmetry is thus written as

$$G_0(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2) = g_0(\rho_1, \rho_2) + 2 \sum_{n=1}^{\infty} g_n(\rho_1, \rho_2) \cos[n(\theta_1 - \theta_2)], \tag{20}$$

where the g_n satisfy the equation

$$\left[-\frac{1}{2} \left(\frac{d^2}{d\rho_1^2} + \rho_1^{-1} \frac{d}{d\rho_1} - \frac{n^2}{\rho_1^2} \right) - \frac{Z_0}{\rho_1} + 2Z_0^2 \right] g_n(\rho_1, \rho_2) = \frac{\delta(\rho_1 - \rho_2)}{2\pi\rho_1} - \psi_0(\rho_1)\psi_0(\rho_2)\delta_{n,0}, \tag{21}$$

with $\delta_{n,0}$ being the Kronecker delta. We now scale ρ_1 and ρ_2 as

$$R_1 = 4Z_0\rho_1, \quad R_2 = 4Z_0\rho_2$$

and rewrite (21) as

$$\left(\frac{d^2}{dR_1^2} + R_1^{-1} \frac{d}{dR_1} - \frac{n^2}{R_1^2} + (2R_1)^{-1} - \frac{1}{4} \right) g_n(R_1, R_2) = \frac{1}{8Z_0^2} \psi_0(R_1)\psi_0(R_2)\delta_{n,0} - \pi^{-1} \frac{\delta(R_1 - R_2)}{R_1}. \tag{22}$$

The solution of (22) is relatively simple by standard techniques, and after applying the boundary conditions and the condition of orthogonality we obtain

$$g_0(R_1, R_2) = \pi^{-1} \exp[-(R_1 + R_2)] \times \left(1 - \gamma - R_1 - R_2 + \int_0^{R_<} \frac{e^t - 1}{t} dt - \log R_> \right) \tag{23}$$

and

$$g_n(R_1, R_2) = \pi^{-1} \frac{\Gamma(n)}{\Gamma(2n+1)} (R_1 R_2)^n \exp[-\frac{1}{2}(R_1 + R_2)] \times \Phi(n, 2n+1, R_<)\Psi(n, 2n+1, R_>), \quad n > 0, \tag{24}$$

where γ is the Euler-Mascheroni constant, $R_>$ and $R_<$ are the greater and lesser of R_1 and R_2 , and Φ and Ψ are confluent hypergeometric functions¹² defined as

$$\Phi(a, b, z) = \frac{\Gamma(b)}{\Gamma(b-a)\Gamma(a)} \int_0^1 \exp(zt) t^{a-1} \times (1-t)^{b-a-1} dt \tag{25}$$

and

$$\Psi(a, b, z) = [\Gamma(a)]^{-1} \int_0^{\infty} \exp(-zt) t^{a-1} \times (1+t)^{b-a-1} dt. \tag{26}$$

We now desire to sum the Fourier series (20) and obtain a more useful integral representation of G_0 . The

key formula necessary to sum the series is¹³

$$(xy)^{\frac{1}{2}(b-1)}y^{b-1} \exp[-\frac{1}{2}(x+y)t] \Phi(a, b, xt) \Psi(a, b, yt) = \frac{\Gamma(b)}{\Gamma(a)} \int_0^\infty ds (\cosh \frac{1}{2}s)^{b-2a} \exp[-\frac{1}{2}(x+y)t \cosh s] \times I_{b-1}[t(xy)^{1/2} \sinh s],$$

$$y > x > 0, \quad \text{Re}(t) > 0, \quad |\text{arc}(t)| < \pi, \quad \text{Re}(a) > 0, \quad (27)$$

where I_n is the usual imaginary-argument Bessel function, and for our use the parameters in (27) assume the values $a = n, b = 2n + 1, t = 1, x = R_<, y = R_>$. Inserting the g_n obtained by using (27) and (24) into (20) and interchanging the order of summation and integration, we find

$$G_0(\varrho_1, \varrho_2) = g_0(R_1, R_2) + \frac{2}{\pi} \int_0^\infty ds (\cosh \frac{1}{2}s) \exp[-\frac{1}{2}(R_1+R_2) \cosh s] \sum_{n=1}^\infty I_{2n}[(R_1R_2)^{1/2} \sinh s] \cos(n\theta_{12}), \quad (28)$$

where $\theta_{12} = \theta_1 - \theta_2$. The sum in (28) may now be performed by using the expansion¹⁴

$$\exp(z \cos \phi) = I_0(z) + 2 \sum_{n=1}^\infty I_n(z) \cos(n\phi), \quad (29)$$

with the result that

$$G_0(\varrho_1, \varrho_2) = g_0(R_1, R_2) + \pi^{-1} \int_0^\infty ds (\cosh \frac{1}{2}s) \exp[-\frac{1}{2}(R_1+R_2) \cosh s] \times \{ \cosh[(R_1R_2)^{1/2} \cos(\frac{1}{2}\theta_{12}) \sinh s] - I_0[(R_1R_2)^{1/2} \sinh s] \}. \quad (30)$$

We now wish to use this representation of the reduced Green's function to find the solution of (16) for ψ_1 . To solve (16) multiply both sides of that equation by G_0 and integrate over the variables with subscript 1. Use the Hermitian property of $H_0 - E_0$ in conjunction with (18) to obtain

$$\psi_1(\rho, \theta) = - \int_0^\infty \rho_1 d\rho_1 \int_{-\pi}^\pi d\theta_1 \psi_0(\rho_1) H_1(\rho_1, \theta_1) G_0(\varrho, \varrho_1). \quad (31)$$

Note that ψ_1 is orthogonal to ψ_0 since G_0 has that property. Inserting (30) into (31), interchanging the order of integration, and performing the angular integration leads to ($R_1 \equiv t$)

$$\psi_1(R, \theta) = - \frac{1}{2^{1/2}\pi^{3/2}} \int_0^\infty ds (\cosh \frac{1}{2}s) \exp(-\frac{1}{2}R \cosh s) \int_0^\infty dt \exp[-\frac{1}{2}(1+\cosh s)t] \times \{ 2\pi Z_0 I_0(R^{1/2}t^{1/2} \sinh s) - \sum_{k=1}^6 a_k \cosh[R^{1/2}t^{1/2} \cos \frac{1}{2}(\theta - \theta_k) \sinh s] \}, \quad (32)$$

where

$$a_1 = a_2 = a_3 = a_4 = 1, \\ a_5 = a_6 = -\lambda/\sqrt{2}, \\ \theta_1 = \frac{1}{4}\pi, \quad \theta_2 = -\frac{1}{4}\pi, \quad \theta_3 = \frac{3}{4}\pi, \quad \theta_4 = -\frac{3}{4}\pi, \quad \theta_5 = 0, \quad \theta_6 = \pi.$$

The integration over the variable t may be carried out by utilizing the facts that

$$\int_0^\infty \exp(-y) I_0(xy^{1/2}) dy = \exp(x^2/4) \quad (33a)$$

and

$$\int_0^\infty \exp(-y) \cosh(xy^{1/2}) dy = 1 + \frac{1}{2}\pi^{1/2}x \exp(\frac{1}{4}x^2) \text{erf}(\frac{1}{2}x), \quad (33b)$$

where the error function is defined as

$$\text{erf}(x) = \frac{2}{\pi^{1/2}} \int_0^x \exp(-t^2) dt.$$

The result is ($u = \sinh \frac{1}{2} s$)

$$\psi_1(R, \theta) = \psi_0(R) \int_0^\infty \frac{du}{u(1+u^2)} [\exp(-Ru^2) - 1] + \frac{\psi_0(R)}{2\pi^{1/2}Z_0} R^{1/2} \times \sum_{k=1}^6 a_k \cos \frac{1}{2}(\theta - \theta_k) \int_0^\infty \frac{du}{1+u^2} \exp[-Ru^2 \sin^2 \frac{1}{2}(\theta - \theta_k)] \operatorname{erf}[R^{1/2}u \cos \frac{1}{2}(\theta - \theta_k)]. \quad (34)$$

The first integral in (34) may be represented by an exponential integral as

$$\int_0^\infty \frac{du}{u(1+u^2)} [\exp(-Ru^2) - 1] = -\frac{1}{2}[\gamma + \log R + \exp(R) E_1(R)], \quad (35)$$

where as before γ is the Euler-Mascheroni constant and

$$E_1(R) = \int_R^\infty \exp(-t) \frac{dt}{t} = -\gamma - \log R - \sum_{n=1}^\infty \frac{(-1)^n R^n}{nn!}.$$

The final form of the first-order wavefunction is thus

$$\psi_1(R, \theta) = -\frac{1}{2}\psi_0(R) [\gamma + \log R + \exp(R) E_1(R)] + \frac{R^{1/2}\psi_0(R)}{2\pi^{1/2}Z_0} \times \sum_{k=1}^6 a_k \cos \frac{1}{2}(\theta - \theta_k) \int_0^\infty \frac{du}{1+u^2} \exp[-Ru^2 \sin^2 \frac{1}{2}(\theta - \theta_k)] \operatorname{erf}[R^{1/2}u \cos \frac{1}{2}(\theta - \theta_k)], \quad (36)$$

where the a_k and θ_k are defined following (32). Although the last integral in (36) may be represented in a variety of ways we have not been able to reduce it to a standard function.

We have utilized ψ_1 [(36)] in a second-order energy calculation, and we obtain

$$E_2 = \langle \psi_0 | H_1 | \psi_1 \rangle = -\left[1 - \frac{2}{\pi} - \frac{2}{\pi^2} + \lambda \left(1 - \frac{5}{2^{3/2}} + \frac{4}{\pi} - \frac{2^{1/2}}{\pi} \right) + \lambda^2 \left(\frac{1}{8} - \frac{1}{2\pi^2} \right) \right]. \quad (37)$$

If this is combined with E_0 [(17)], the result is

$$E_0 + E_2 = -0.97131 + 0.51784\lambda - 0.17566\lambda^2. \quad (38)$$

Our purpose in deriving (36) in detail has not been primarily to obtain a better eigenfunction that has been obtained previously, Eq. (7). We are also not interested in doing a highly accurate eigenvalue calculation; variational techniques are better suited to this task. We are however interested in the analytical form of the wavefunction predicted by this technique.

It is a simple matter to show that the ground-state eigenfunction of H given by Eq. (6) is not analytic in the variable ρ near $\rho=0$. In other words, the eigenfunction may not be expanded as

$$\sum_{n=0}^\infty \rho^n f_n(\theta)$$

in the vicinity of $\rho=0$. The correct behavior [to $O(\lambda^2)$] for small ρ may be obtained from (7). It is not difficult to demonstrate (see Appendix A) that the

leading order nonanalytic term in ψ for small ρ is

$$-(\lambda/\pi) xy \log(x^2 + y^2). \quad (39)$$

Through first order in λ no higher powers of the logarithm itself occur, although it is probable that weaker singularities at $\rho=0$ with new powers of the logarithm occur with each new power of λ . This type of term, an intrinsic three-body effect, is extremely difficult to discover by any technique other than a potentially exact analytic approach.

Investigation of the first-order wavefunction obtained in (36) shows that it is likewise nonanalytic in ρ with a small- ρ leading-order nonanalytic term of the same form as (39) (though multiplied by a slightly different factor). Thus the wavefunction obtained by correcting a crude zeroth-order "hydrogenic" approximation to first order displays already the apparent nonanalytic form of the true wavefunction near the origin.

In the case of the delta function model we have discovered nothing by the present technique beyond that already given by other methods. It is where other techniques cannot be applied so easily, as in the actual two-electron atom, that the present procedure has its primary significance.

IV. THE GROUND STATE OF THE TWO-ELECTRON ATOM

The general technique of employing perturbation theory to correct a model hyperspherically averaged potential will now be applied to the simplest nontrivial real atomic system, the ground state of the two-electron atom. The nonrelativistic Hamiltonian for this system

has the well-known form

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - r_1^{-1} - r_2^{-1} + (\lambda/r_{12}), \quad \lambda = Z^{-1}, \quad (40)$$

in Z -reduced atomic units, Z being the nuclear charge. Since we are interested in the ground state of this system, there is no need to introduce the full set of hyperspherical coordinates given in Sec. II. Only three coordinates are relevant for this state (as for any S state), and we take these to be⁴

$$\begin{aligned} \rho^2 &= r_1^2 + r_2^2, & \infty \geq \rho \geq 0, \\ \tan(\frac{1}{2}\alpha) &= r_2/r_1, & \pi \geq \alpha \geq 0, \\ \cos\theta &= (r_1^2 + r_2^2 - r_{12}^2)/2r_1r_2, & \pi \geq \theta \geq 0. \end{aligned} \quad (41)$$

The Laplacian then has the form

$$\nabla_1^2 + \nabla_2^2 = \frac{\partial^2}{\partial \rho^2} + \frac{5}{\rho} \frac{\partial}{\partial \rho} - \frac{4}{\rho^2} \Lambda^2(\alpha, \theta), \quad (42)$$

where the angular operator Λ^2 is

$$\Lambda^2 = -(\sin^2\alpha)^{-1} \left(\frac{\partial}{\partial \alpha} \sin^2\alpha \frac{\partial}{\partial \alpha} + (\sin\theta)^{-1} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} \right). \quad (43)$$

The scalar product is

$$\langle \psi, \phi \rangle = \pi^2 \int_0^\infty d\rho \int_0^\pi d\alpha \int_0^\pi d\theta \rho^5 \sin^2\alpha \sin\theta \psi^* \phi, \quad (44)$$

and an angular integration will be denoted by $\langle \psi, \phi \rangle_\Omega$, where

$$\langle \psi, \phi \rangle_\Omega = \pi^2 \int_0^\pi d\alpha \int_0^\pi d\theta \sin^2\alpha \sin\theta \psi^* \phi. \quad (45)$$

The finite, continuous, square-integrable eigenfunctions of Λ^2 are the set

$$\begin{aligned} \Phi_{n,l}(\alpha, \theta) &= N_{n,l} (\sin\alpha)^l C_{n-l}^{(l+1)}(\cos\alpha) P_l(\cos\theta), \\ n &= 0, 1, 2, \dots, l = 0, 1, \dots, n, \end{aligned} \quad (46)$$

where the P_l are Legendre polynomials defined by the generating function

$$(1+x^2-2x\cos\theta)^{-1/2} = \sum_{l=0}^{\infty} P_l(\cos\theta) x^l \quad (47)$$

and the $C_n^{(l)}$ are Gegenbauer polynomials defined by the generating function

$$(1+x^2-2x\cos\alpha)^{-l} = \sum_{n=0}^{\infty} C_n^{(l)}(\cos\alpha) x^n, \quad l \neq 0. \quad (48)$$

The normalization constant $N_{n,l}$ has the value

$$N_{n,l} = 2^l l! [(2l+1)(n+1)(n-l)!/\pi^3(n+l+1)!]^{1/2} \quad (49)$$

if the $\Phi_{n,l}$ are normalized by the requirement that

$$\langle \Phi_{n,l}, \Phi_{m,k} \rangle_\Omega = \delta_{n,m} \delta_{l,k}.$$

The eigenvalues of Λ^2 are

$$\Lambda^2 \Phi_{n,l} = n(n+2) \Phi_{n,l} \quad (50)$$

with degeneracy $n+1$.

In terms of these variables, the potential energy for the two-electron atom,

$$U(\rho, \alpha, \theta) = -\frac{\sec(\alpha/2)}{\rho} - \frac{\csc(\alpha/2)}{\rho} + \frac{\lambda}{\rho(1-\sin\alpha\cos\theta)^{1/2}}, \quad (51)$$

is homogeneous of degree minus one in ρ . We average this potential over the angles α and θ to obtain our model potential

$$U_0(\rho) = (1/\pi^3) \langle 1, U \rangle_\Omega = -Z_0/\rho, \quad (52)$$

where

$$Z_0 = (8/3\pi)(4-2^{1/2}\lambda).$$

By adding and subtracting U_0 we thus decompose the Hamiltonian into H_0 and H_1 ,

$$H = H_0 + \xi H_1, \quad (53)$$

with

$$H_0 = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + U_0,$$

$$H_1 = U - U_0,$$

and $\xi = 1$. The eigenvalue problem

$$(H - E)\Psi = 0 \quad (54)$$

is approached by expanding the eigenfunction and eigenvalue in a power series in the (artificial) parameter ξ ,

$$\Psi = \psi_0 + \xi \psi_1 + \dots,$$

$$E = E_0 + \xi E_1 + \xi^2 E_2 + \xi^3 E_3 + \dots, \quad (55)$$

and solving the resulting hierarchy of equations.

The first of these equations is the eigenvalue problem

$$(H_0 - E_0)\psi_0 = 0, \quad (56)$$

with the simple solution

$$\psi_0 = [(\frac{4}{3}Z_0)^6/5! \pi^3]^{1/2} \exp(-\frac{2}{3}Z_0\rho),$$

$$E_0 = -\frac{2}{3}Z_0^2$$

$$= -0.922250 + 0.652129\lambda - 0.115281\lambda^2. \quad (57)$$

The choice of Z_0 , Eq. (52), makes $E_1 = 0$, and the next equation to be solved is

$$(H_0 - E_0)\psi_1 = -H_1\psi_0. \quad (58)$$

We solve this equation by a Green's function technique very similar to that employed in the preceding section on the delta-function model. The requisite Green's function is the solution of the differential equation

$$[H_0(1) - E_0]G_0(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2) - \psi_0(\rho_1)\psi_0(\rho_2) \quad (59)$$

together with the usual boundary conditions at the origin and at infinity. G_0 is also required to be orthogonal to ψ_0 .

Let us utilize the completeness relation of the $\Phi_{n,l}$ to represent the delta function in (59)

$$\delta(\varrho_1, \varrho_2) = \frac{\delta(\rho_1 - \rho_2)}{\rho_1^5} \sum_{n=0}^{\infty} \sum_{l=0}^n \Phi_{n,l}(\alpha_1, \theta_1) \Phi_{n,l}(\alpha_2, \theta_2) \tag{60}$$

and expand the reduced Green's function similarly,

$$G_0(\rho_1, \rho_2) = \sum_{n=0}^{\infty} \sum_{l=0}^n g_n(\rho_1, \rho_2) \Phi_{n,l}(\alpha_1, \theta_1) \Phi_{n,l}(\alpha_2, \theta_2). \tag{61}$$

The equation which determines the g_n is

$$\left[-\frac{1}{2} \left(\frac{\partial^2}{\partial \rho_1^2} + \frac{5}{\rho_1} \frac{\partial}{\partial \rho_1} - \frac{4n(n+2)}{\rho_1^2} \right) - \frac{Z_0}{\rho_1} - E_0 \right] g_n(\rho_1, \rho_2) = \frac{\delta(\rho_1 - \rho_2)}{\rho_1^5} - \pi^3 \psi_0(\rho_1) \psi_0(\rho_2) \delta_{n,0}. \tag{62}$$

The solution of (62) which satisfies the boundary conditions and the condition of orthogonality is

$$g_0(R_1, R_2) = (2/5!) (\frac{4}{5} Z_0)^4 \exp[-\frac{1}{2}(R_1 + R_2)] \times \left[11 - 5\gamma - R_1 - R_2 - 5 \log R_> + 5! \sum_{k=0}^3 \frac{R_>^{k-4}}{k!(4-k)} + 5! \int_0^{R_<} \frac{dt}{t^5} \left(\exp(t) \sum_{k=0}^4 \frac{t^k}{k!} \right) \right] \tag{63}$$

and

$$g_n(R_1, R_2) = \frac{2(2n-1)!}{(4n+4)!} (\frac{4}{5} Z_0)^4 (R_1 R_2)^{2n} \times \exp[-\frac{1}{2}(R_1 + R_2)] \Phi(2n, 4n+5, R_<) \times \Psi(2n, 4n+5, R_>), \quad n > 0, \tag{64}$$

where $R_i = \frac{4}{5} Z_0 \rho_i$, $R_>$ and $R_<$ are the greater and lesser of R_1 and R_2 , Φ and Ψ are the confluent hypergeometric functions defined by (25) and (26), and γ is the Euler-Mascheroni constant. There is a strong similarity between (63), (64) and (23), (24), and one may obtain an integral representation of G_0 in the same way that Eq. (30) was obtained in the two-dimensional case. However, this representation is not so useful in the present circumstance, and we prefer to proceed somewhat differently.

The first-order wavefunction is obtained as

$$\psi_1(\varrho_2) = -\langle \psi_0(\rho_1), H_1(\varrho_1) G_0(\varrho_1, \varrho_2) \rangle_1 \tag{65}$$

once G_0 is known. The subscript on the bracket means integration is carried out over the variables labeled 1. Expanding $H_1(\varrho_1)$ in the complete set $\Phi_{n,l}$,

$$H_1(\varrho_1) = \rho_1^{-1} \sum_{n=0}^{\infty} \sum_{l=0}^n H_{n,l}^{(1)} \Phi_{n,l}(\alpha_1, \theta_1), \tag{66}$$

and employing the corresponding form for G_0 , Eq. (61), leads to the expanded form for ψ_1 ,

$$\psi_1(\varrho) = \sum_{n=0}^{\infty} \sum_{l=0}^n \psi_{n,l}^{(1)}(\rho) \Phi_{n,l}(\alpha, \theta), \tag{67}$$

where

$$\psi_{n,l}^{(1)}(\rho) = -H_{n,l}^{(1)} \int_0^{\infty} \rho_1^4 \psi_0(\rho_1) g_n(\rho_1, \rho) d\rho_1. \tag{68}$$

In Appendix B it is shown that

$$H_{n,l}^{(1)} = 0, \quad n=0=l \text{ or } n-l \text{ odd} \\ = \frac{2\pi^{1/2}}{(n+1/2)(n+3/2)} [-4(n+1) + (-1)^{n/2} 2^{1/2} \lambda], \quad l=0, n \text{ even} \\ = \lambda 2^{n+5/2} \Gamma(l+3/2) \left(\frac{\pi(n-l)!(n+1)}{(2l+1)(n+l+1)!} \right)^{1/2} \sum_{k=0}^{(n-l)/2} \frac{(-1)^k (n-k)!}{2^{2k} k! \Gamma(n-2k+5/2)}, \quad l > 0, n-l \text{ even.} \tag{69}$$

By using Eq. (27) to represent the product in (64) the $\psi_{n,l}^{(1)}$ may be written as ($R = \frac{4}{5} Z_0 \rho$)

$$\psi_{n,l}^{(1)}(R) = \frac{-2H_{n,l}^{(1)}}{(\frac{4}{5} Z_0) R^2} \psi_0(R) \int_0^{\infty} dR_1 \int_0^{\infty} ds R_1^2 [\coth(s/2)]^5 \times \exp[-\frac{1}{2} R (\cosh s - 1)] \exp[-\frac{1}{2} R_1 (\cosh s + 1)] I_{4n+4}(R^{1/2} R_1^{1/2} \sinh s), \quad n > 0. \tag{70}$$

Interchanging the order of integration and making the substitution $t = R_1 \cosh^2(s/2)$ for R_1 gives

$$\psi_{n,l}^{(1)} = \frac{-2H_{n,l}^{(1)} \psi_0(R)}{(\frac{4}{5} Z_0) R^2} \int_0^{\infty} \frac{ds \exp[-R \sinh^2(\frac{1}{2}s)]}{\cosh(s/2) [\sinh(\frac{1}{2}s)]^5} \int_0^{\infty} dt t^2 \exp(-t) I_{4n+4}[2R^{1/2} t^{1/2} \sinh(\frac{1}{2}s)], \tag{71}$$

and using the fact that¹⁵

$$\Phi(a, b, x) = \frac{\Gamma(b)}{\Gamma(a)} x^{(1-b)/2} \int_0^{\infty} dt \exp(-t) t^{1/2(2a-1-b)} I_{b-1}(2x^{1/2} t^{1/2}), \tag{72}$$

we obtain our final form for $\psi_{n,l}^{(1)}[u = \sinh^2(s/2)]$,

$$\psi_{n,l}^{(1)} = \frac{-2H_{n,l}^{(1)}(2n+4)!}{(\frac{4}{5}Z_0)(4n+4)!} R^{2n}\psi_0(R) \int_0^\infty \frac{du}{1+u} u^{2n-1} \exp(-Ru) \Phi(2n+5, 4n+5, Ru). \quad (73)$$

The first-order correction to the wavefunction is easily shown to be nonanalytic in the variable $\rho [= (r_1^2 + r_2^2)^{1/2}]$. In fact, up to order ρ^2 , the form of $\psi_0 + \psi_1$ implied by Eq. (73) is

$$\psi_0 + \psi_1 \propto 1 - r_1 - r_2 + \frac{1}{2}\lambda r_{12} - [2^{11/2}Z_0\lambda / (7 \times 5^2 \times 3\pi)] r_1 r_2 \cos\theta \log(r_1^2 + r_2^2) + O(\rho^2). \quad (74)$$

The logarithmic term appearing here is the direct analog of the one shown in Eq. (39) for the delta-function atom. Furthermore, only singularities of the type $\rho^n \log\rho$, $n \geq 2$, appear in ψ_1 . It is probable, however, that weaker singularities at $\rho = 0$ with higher powers of the logarithm occur in the higher-order corrections to the wavefunction (ψ_2 , ψ_3 , etc.). Thus, the expansion of the wavefunction in the variable ρ for the two-electron atom is very likely that predicted by Fock.⁴ Since we do not discuss the convergence properties of our perturbation approach or investigate the higher-order corrections to the wavefunction, we have no proof that the resulting form obtained for the wavefunction is correct. But since we are led to the same form for the wavefunction as that obtained by Fock by an analysis quite different from the present one, with different sources of weakness, we feel that this form is almost certainly correct.

We have used the $\psi_{n,l}^{(1)}$, Eq. (73), to calculate various components of the second-order energy. Since

$$E_2 = \langle \psi_0, H_1 \psi_1 \rangle = \sum_{n=0}^{\infty} \sum_{l=0}^n E_{n,l}^{(2)}, \quad (75)$$

where

$$E_{n,l}^{(2)} = \frac{H_{n,l}^{(1)}}{(\frac{4}{5}Z_0)^5} \int_0^\infty R^4 \psi_0(R) \psi_{n,l}^{(1)}(R) dR,$$

we have

$$E_{n,l}^{(2)} = \frac{-2(H_{n,l}^{(1)})^2(2n+4)!}{5!\pi^3(4n+4)!} \times \int_0^\infty dR \int_0^\infty \frac{du R^{2n+4}}{1+u} u^{2n-1} \exp[-R(u+1)] \times \Phi(2n+5, 4n+5, Ru). \quad (76)$$

Changing variables to s and t defined as $s = u/(1+u)$, $t = R(1+u)$ gives

$$E_{n,l}^{(2)} = \frac{-2(H_{n,l}^{(1)})^2(2n+4)!}{5!\pi^3(4n+4)!} \times \int_0^1 ds s^{2n-1} (1-s)^5 \int_0^\infty dt t^{2n+4} \exp(-t) \times \Phi(2n+5, 4n+5, st), \quad (77)$$

and performing the t integration¹⁶ leads to the result

$$E_{n,l}^{(2)} = \frac{-2(H_{n,l}^{(1)})^2[(2n+4)!]^2}{5!\pi^3(4n+4)!} \times \int_0^1 ds s^{2n-1} (1-s)^5 {}_2F_1(2n+5, 2n+5; 4n+5; s), \quad (78)$$

where ${}_2F_1$ is the ordinary hypergeometric series

$${}_2F_1(a, b; c; x) = \frac{\Gamma(c)}{\Gamma(a)\Gamma(b)} \sum_{n=0}^{\infty} \frac{\Gamma(n+a)\Gamma(n+b)}{\Gamma(n+c)} \frac{x^n}{n!}.$$

Finally, we obtain¹⁷

$$E_{n,l}^{(2)} = \frac{-2(H_{n,l}^{(1)})^2}{\pi^3(2n+5)^2} \times {}_3F_2(6, 2n+5, 1; 2n+6, 2n+6; 1), \quad (79)$$

where ${}_3F_2$ is a generalized hypergeometric series

$${}_3F_2(a, b, c; d, e; x) = \frac{\Gamma(d)\Gamma(e)}{\Gamma(a)\Gamma(b)\Gamma(c)} \times \sum_{n=0}^{\infty} \frac{\Gamma(n+a)\Gamma(n+b)\Gamma(n+c)}{\Gamma(n+d)\Gamma(n+e)} \frac{x^n}{n!}.$$

We evaluated the $E_{n,l}^{(2)}$ to $n=l=10$, and we present these results in Table I. It must be pointed out that this computation is very easy, and it would be a simple matter to extend the second-order energy calculation to virtually any desired accuracy, but the present results are sufficient for our purposes. Performing the summation over n and l and adding the result to E_0 , Eq. (17), we obtain

$$E_0 + \sum_{n=0}^{10} \sum_{l=0}^n E_{n,l}^{(2)} = -0.97623 + 0.64185\lambda - 0.16052\lambda^2. \quad (80)$$

To this order in λ , the exact energy is^{18,19}

$$E(\lambda) = -1.0 + 0.625\lambda - 0.15767\lambda^2 + O(\lambda^3), \quad (81)$$

and (80) is seen to compare favorably with the exact result considering the crudeness of the zeroth-order model.

V. THREE-ELECTRON ATOMS

A three-electron generalization of the delta-function model considered in Sec. III would stem from the

TABLE I. Components of the second-order energy in Z -reduced atomic units.

l	n	$E_{n,l}^{(2)}$		
		Coefficient of λ^0	Coefficient of λ^1	Coefficient of λ^2
0	2	-0.046404	-0.010938	-0.000645
0	4	-0.005460	+0.000772	-0.000027
0	6	-0.001386	-0.000140	-0.000004
0	8	-0.000502	+0.000039	-0.000001
0	10	-0.000224	-0.000014	-0.000000
1	1	0	0	-0.036312
1	3	0	0	-0.000343
1	5	0	0	-0.000028
1	7	0	0	-0.000005
1	9	0	0	-0.000001
2	2	0	0	-0.005156
2	4	0	0	-0.000156
2	6	0	0	-0.000019
2	8	0	0	-0.000004
2	10	0	0	-0.000001
3	3	0	0	-0.001373
3	5	0	0	-0.000077
3	7	0	0	-0.000012
3	9	0	0	-0.000003
4	4	0	0	-0.000499
4	6	0	0	-0.000041
4	8	0	0	-0.000008
4	10	0	0	-0.000002
5	5	0	0	-0.000219
5	7	0	0	-0.000024
5	9	0	0	-0.000005
6	6	0	0	-0.000110
6	8	0	0	-0.000014
6	10	0	0	-0.000004
7	7	0	0	-0.000060
7	9	0	0	-0.000009
8	8	0	0	-0.000036
8	10	0	0	-0.000006
9	9	0	0	-0.000022
10	10	0	0	-0.000014

Hamiltonian:

$$H = -\frac{1}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \delta(x) - \delta(y) - \delta(z) + \lambda [\delta(x-y) + \delta(x-z) + \delta(y-z)]. \quad (82)$$

When $\lambda \geq 0$, this one-dimensional "lithium atom" may well fail to bind all three electrons, but for sufficiently negative λ we tentatively assume that a bound state exists. It is therefore of some interest to see how our preceding considerations can be adapted to this relatively simple quantum-mechanical four-body problem. We shall see that the results are instructive concerning the way that our hyperspherical technique can be applied to the sequence of real three-dimensional three-electron atoms and ions.

The ground state should be a degenerate spin doublet, and one of them will fall within the spin space

of the three spin functions:

$$\alpha(1)\alpha(2)\beta(3), \quad \alpha(1)\beta(2)\alpha(3), \quad \beta(1)\alpha(2)\alpha(3). \quad (83)$$

In Appendix C it is shown that any such doublet wavefunction for three-electron systems must have the following form:

$$\psi(123) = F(123)\alpha(1)\alpha(2)\beta(3) + F(312)\alpha(1)\beta(2)\alpha(3) + F(231)\beta(1)\alpha(2)\alpha(3), \quad (84)$$

where F is a function only of spatial coordinates, and must obey the conditions

$$F(123) = -F(213) \quad (85)$$

and

$$F(123) + F(312) + F(231) = 0. \quad (86)$$

For the type of one-dimensional problem that H in Eq. (82) typifies, a convenient representation of the desired class of functions $F(x, y, z)$ is easy to construct. Note first that the points (x, y, z) , (z, x, y) , and (y, z, x) lie in a plane

$$x + y + z = \text{const} \quad (87)$$

at the vertices of an equilateral triangle, whose centroid is pierced by the normal vector from the origin to plane (87) (see Fig. 1). This suggests the following coordinate rotation:

$$\begin{aligned} u &= (1/\sqrt{3})(x+y+z), \\ v &= -6^{-1/2}(x+y) + (\sqrt{2}/\sqrt{3})z, \\ w &= (1/\sqrt{2})(x-y), \end{aligned} \quad (88)$$

for which Fig. 1 displays unit vectors. Then after setting

$$F(x, y, z) \equiv \mathfrak{F}(u, v, w), \quad (89)$$

we note that restraint (85) merely requires \mathfrak{F} to be an odd function of w .

Next define

$$\begin{aligned} r &= (v^2 + w^2)^{1/2}, \\ \phi &= \arctan(w/v); \end{aligned} \quad (90)$$

these are polar coordinates in the $u = \text{const}$ plane, with ϕ measured counterclockwise from the v axis (see Fig. 1). The oddness of \mathfrak{F} in w implies the relevance of a Fourier sine series:

$$\mathfrak{F}(u, v, w) = \sum_{n=1}^{\infty} \mathfrak{F}_n(u, r) \sin(n\phi), \quad (91)$$

and then condition (86) requires

$$\begin{aligned} 0 &= \sum_{n=1}^{\infty} \mathfrak{F}_n(u, r) [\sin(n\phi) + \sin(n\phi + \frac{2}{3}n\pi) + \sin(n\phi - \frac{2}{3}n\pi)] \\ &= \sum_{n=1}^{\infty} \mathfrak{F}_n(u, r) [1 + 2 \cos(\frac{2}{3}n\pi)] \sin(n\phi). \end{aligned} \quad (92)$$

Since the $\sin(n\phi)$ are orthogonal, their multipliers in this last expression must separately vanish. When integer n is a multiple of 3,

$$1 + 2 \cos\left(\frac{2}{3}n\pi\right) = 3, \quad (93)$$

so the \mathcal{F}_n must vanish. However, when n is not divisible by three,

$$1 + 2 \cos\left(\frac{2}{3}n\pi\right) = 0, \quad (94)$$

and so the corresponding \mathcal{F}_n need not vanish. Hence the general representation is

$$F(x, y, z) = \sum'_{n=1}^{\infty} \mathcal{F}_n(u, r) \sin(n\phi), \quad (95)$$

where the prime excludes n 's divisible by three.

Following the procedure established in Secs. III and IV, we write H in (82) as $H_0 + \xi H_1$, where H_0 involves a spherical average of the six delta-function interactions:

$$H_0 = -\frac{1}{2} \left(\frac{1}{\rho^2} \frac{\partial}{\partial \rho} \rho^2 \frac{\partial}{\partial \rho} - \frac{L^2(\theta, \phi)}{\rho^2} \right) - \frac{Z_0(\lambda)}{\rho},$$

$$Z_0(\lambda) = \frac{3}{2} [1 - (\lambda/\sqrt{2})], \quad (96)$$

and where H_1 puts back the asphericity of the original interactions:

$$H_1 = -\delta(x) - \delta(y) - \delta(z) + \lambda [\delta(x-y) + \delta(x-z) + \delta(y-z)] + Z_0(\lambda) / (x^2 + y^2 + z^2)^{1/2}. \quad (97)$$

The wavefunction ψ_0 for the unperturbed Hamiltonian H_0 must also conform to representation (95), of course. H_0 is precisely the hydrogen atom Hamiltonian in suitable units, and it is significant to observe that

$$F_0(x, y, z) \propto (\sin\phi) r \exp(-\frac{1}{2}Z_0 r) = (1/\sqrt{2}) (2p_x - 2p_y), \quad (98)$$

a $2p$ eigenfunction of H_0 with energy

$$E_0 = -\frac{1}{8} [Z_0(\lambda)]^2, \quad (99)$$

has form (95). Therefore the lowest-energy p state (rather than the lowest s state for two-electron atoms) serves as the unperturbed spatial eigenfunction in our hyperspherical coordinate method.²⁰ The first-order wavefunction would then require the reduced Green's function for the hydrogen atom (modified to exclude the above $2p$ state), which could be constructed by Hostler's method of projection from the known full Green's function for hydrogen (see Ref. 21).

The more realistic three-electron atom in three dimensions can in principle be handled by a straightforward extension of the strategy for the one-dimensional model. Now the Hamiltonian is

$$H = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - r_1^{-1} - r_2^{-1} - r_3^{-1} + \lambda (r_{12}^{-1} + r_{13}^{-1} + r_{23}^{-1}). \quad (100)$$

As in the preceding cases we propose averaging the potential function over angles in the full configuration

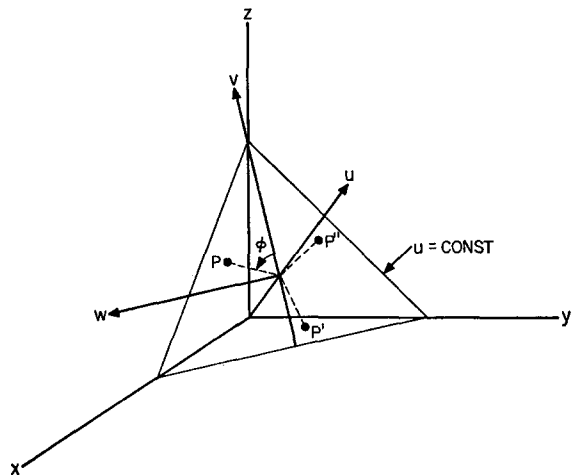


FIG. 1. Configuration space for the one-dimensional three-electron atom. The points P , P' , and P'' differ by cyclic permutation of coordinates, and they lie at vertices of an equilateral triangle, equidistant from the threefold u axis.

space (now of nine dimensions) at fixed radius:

$$\rho = (x_1^2 + y_1^2 + \dots + z_3^2)^{1/2}. \quad (101)$$

The resulting central-force Hamiltonian is then found to be

$$H_0 = -\frac{1}{2} \left(\frac{1}{\rho^8} \frac{\partial}{\partial \rho} \rho^8 \frac{\partial}{\partial \rho} - \frac{\Lambda_3^2}{\rho^2} \right) - \frac{Z_0(\lambda)}{\rho},$$

$$Z_0(\lambda) = (105/16) (1 - 2^{-1/2}\lambda), \quad (102)$$

which defines the unperturbed problem. By analogy with the one-dimensional three-electron problem, one anticipates that one of the nine lowest-lying p states for H_0 provides the correct unperturbed spatial function $F_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, and in order to satisfy conditions (85) and (86) the nodal hyperplane for this p function must be

$$0 = x_1 - x_2 + y_1 - y_2 + z_1 - z_2. \quad (103)$$

This starting point then in principle permits one to analyze correlation in the lithium isoelectronic sequence by the same type of Green's function technique that we have carried out in detail for the helium isoelectronic sequence.²⁰

VI. DISCUSSION

One of the most significant features of the analysis presented here is the natural occurrence of certain logarithmic terms predicted by Fock.⁴ It would seem to us that these weakly singular terms, which represent a true three-body effect, would occur quite generally in many electron systems²² (atoms and molecules). Thus whenever two electrons with opposing spins are in the vicinity of the same nucleus, we would expect the wavefunction to have the same general type of logarithmic structure.

It is clear that the inclusion of these logarithmic terms greatly improves the convergence of accurate

variational calculations for the $1^1S^{23,24}$ and $2^3S^{25,26}$ states of helium. It would be interesting to see the effect that inclusion of these terms would have on the accurate variational calculations recently carried out for the hydrogen molecule.²⁷ In particular, the addition of expressions of the form

$$\{1 \pm \xi_1 \eta_1 \pm \xi_2 \eta_2 + \xi_1 \xi_2 \eta_1 \eta_2 + [(\xi_1^2 - 1)(\xi_2^2 - 1) \times (1 - \eta_1^2)(1 - \eta_2^2)]^{1/2} \cos(\phi_1 - \phi_2)\} \\ \times \log[(\xi_1 \pm \eta_1)^2 + (\xi_2 \pm \eta_2)^2]$$

in elliptic coordinates [$\xi_i = (r_{ai} + r_{bi})/R$, $\eta_i = (r_{ai} - r_{bi})/R$, $\phi_i =$ rotation about z_i axis] should be considered since these are the direct transcription of the helium-atom contributions.

Although perturbation-variation calculations of high order have been carried out for the ground state of the two-electron atom,^{18,19} these calculations have not included the weakly singular terms mentioned here. It would be valuable to ascertain the effect of the inclusion of these terms on the systematic error introduced by using a finite basis set in this type of calculation.

The success of the technique developed in this paper is due to the fact that the zeroth-order problem, a "hydrogen" atom in $3N$ dimensions ($N =$ number of electrons), is separable in hyperspherical coordinates, thereby permitting a simple construction of the relevant reduced Green's function. A superior zeroth-order model for atoms would be one with noninteracting electrons (appropriate for Z^{-1} perturbation theory²⁸). However, efforts to construct the required Green's function for this latter model have thus far had only formal success,²⁹ and we feel that the model presented here introduces mathematical simplicity (at the expense of some physical insight).

The extension of the perturbation technique presented here to higher order, and to larger numbers of electrons is certainly feasible, although difficult. In fact, the extension to the three-electron atom (outlined in Sec. V) may be very interesting since singular four-body effects, which would not necessarily be just a sum of three-body effects, may appear as all electrons are brought into the nucleus.

APPENDIX A

We outline here the conventional perturbation theory of the ground state of the delta-function atom, for which the unperturbed state excludes interaction between the two electrons. It is convenient to rewrite the Hamiltonian (6) thus:

$$H = -\frac{1}{2}[(\partial^2/\partial x^2) + (\partial^2/\partial y^2)] - \delta(x) - \delta(y) \\ + \lambda_+ V_+ + \lambda_- V_-, \quad (A1)$$

where

$$V_+(x, y) = \frac{1}{2}[\delta(x-y) + \delta(x+y)], \\ V_-(x, y) = \frac{1}{2}[\delta(x-y) - \delta(x+y)] \quad (A2)$$

are even and odd components of the electron interaction (ultimately $\lambda_+ = \lambda_- = \lambda$). Since sign reversal of λ_- is merely equivalent to a rotation by angle $\pi/2$ in the x, y plane, the ground-state energy $\epsilon(\lambda_+, \lambda_-)$ must be an even function of its second variable.

The cusp conditions that must be satisfied by a continuous wavefunction $\psi(x, y)$ along the singular lines of the potential energy ($x=0$, $y=0$, $x=y$, $x=-y$) are readily obtainable from (A1),

$$\frac{1}{2}\{\partial\psi(0+, y)/\partial x\} - \{\partial\psi(0-, y)/\partial x\} = -\psi(0, y), \\ \frac{1}{2}\{\partial\psi(x, 0+)/\partial y\} - \{\partial\psi(x, 0-)/\partial y\} = -\psi(x, 0), \\ \frac{1}{2}\{\partial\psi(x, x+)/\partial y\} - \{\partial\psi(x, x-)/\partial y\} \\ = -\frac{1}{4}(\lambda_+ + \lambda_-)\psi(x, x), \\ \frac{1}{2}\{\partial\psi(-x, x+)/\partial y\} - \{\partial\psi(-x, x-)/\partial y\} \\ = -\frac{1}{4}(\lambda_+ - \lambda_-)\psi(-x, x). \quad (A3)$$

One can easily verify that the function

$$\psi(x, y) = \exp[-|x| - |y| + \frac{1}{4}\lambda_+(|x-y| + |x+y|)] \quad (A4)$$

exactly satisfies Eqs. (A1) and (A3) for all λ_+ when $\lambda_- = 0$. The corresponding energy is

$$\epsilon(\lambda_+, 0) = -1 + \frac{1}{2}\lambda_+ - \frac{1}{8}\lambda_+^2. \quad (A5)$$

The complete double series for ϵ consequently starts out as follows:

$$\epsilon(\lambda_+, \lambda_-) = -1 + \frac{1}{2}\lambda_+ - \frac{1}{8}\lambda_+^2 + \epsilon_{02}\lambda_-^2 + \epsilon_{12}\lambda_+\lambda_-^2 \\ + \epsilon_{22}\lambda_+^2\lambda_-^2 + \epsilon_{04}\lambda_-^4 + \epsilon_{32}\lambda_+^3\lambda_-^2 + \epsilon_{14}\lambda_+\lambda_-^4 + \dots \quad (A6)$$

Succeeding terms would contain at least six λ 's with an even number of λ_- 's equal to or exceeding 2. The first-order wavefunction induced by the V_+ perturbation is obvious from (A4):

$$\psi_+^{(1)}(x, y) = \frac{1}{4}(|x-y| + |x+y|) \exp(-|x| - |y|); \quad (A7)$$

the corresponding first-order $\psi_-^{(1)}$ induced by V_- must be calculated by the perturbation formalism. We will use the familiar technique of expansion in unperturbed eigenfunctions.¹⁰

The single-particle states in the unperturbed problem are of three types. There is a single bound state (with energy $-\frac{1}{2}$)

$$\phi_b(x) = \exp(-|x|), \quad (A8)$$

and the unbound states are either odd in x ,

$$\phi_s(x) = (2/L)^{1/2} \sin(kx), \quad (A9)$$

and vanish at the nucleus, or even in x and suffer a phase shift there,

$$\phi_e(x) = (2/L)^{1/2} \cos\{k[|x| + \Delta(k)]\}. \quad (A10)$$

Here L is an arbitrarily large quantization interval

symmetrically chosen along the x axis with respect to the nucleus. The energies of continuum states ϕ_s and ϕ_c are $\frac{1}{2}k^2$, and the requisite cusp condition at $x=0$ requires the phase shift $\Delta(k)$ to satisfy the condition

$$\tan[k\Delta(k)] = k^{-1}. \quad (\text{A11})$$

The first-order contribution to the wavefunction resulting from V_- has the following structure:

$$\psi_-^{(1)} = - \sum_{n>0} [\langle n | V_- | 0 \rangle / (E_n + 1)] \psi_n^{(0)}, \quad (\text{A12})$$

where running index n covers excited states $\psi_n^{(0)}$ of the unperturbed two-electron atom with energies E_n . In detail these excited states are

$$\begin{aligned} \psi_{bs}^{(0)} &= L^{-1/2} [\exp(-|x|) \sin(ky) \\ &\quad + \sin(kx) \exp(-|y|)], \\ \psi_{bc}^{(0)} &= L^{-1/2} [\exp(-|x|) \cos(k|y| + k\Delta) \\ &\quad + \cos(k|x| + k\Delta) \exp(-|y|)], \\ \psi_{ss}^{(0)} &= 2^{1/2} L^{-1} [\sin(k_1x) \sin(k_2y) + \sin(k_2x) \sin(k_1y)], \\ \psi_{cc}^{(0)} &= 2^{1/2} L^{-1} [\cos(k_1|x| + k_1\Delta_1) \cos(k_2|y| + k_2\Delta_2) \\ &\quad + \cos(k_2|x| + k_2\Delta_2) \cos(k_1|y| + k_1\Delta_1)], \\ \psi_{sc}^{(0)} &= 2^{1/2} L^{-1} [\sin(k_1x) \cos(k_2|y| + k_2\Delta_2) \\ &\quad + \cos(k_2|x| + k_2\Delta_2) \sin(k_1y)]. \quad (\text{A13}) \end{aligned}$$

Only the third of these, $\psi_{ss}^{(0)}$, will give nonvanishing matrix elements of V_- with the unperturbed ground state:

$$\psi_{bb}^{(0)} = \exp(-|x| - |y|), \quad (\text{A14})$$

and one readily computes these matrix elements to be

$$\begin{aligned} \langle \psi_{ss}^{(0)} | V_- | \psi_{bb}^{(0)} \rangle &= \frac{4(2^{1/2})}{L} \\ &\times \{ [4 + (k_1 - k_2)^2]^{-1} - [4 + (k_1 + k_2)^2]^{-1} \}. \quad (\text{A15}) \end{aligned}$$

In the $L \rightarrow \infty$ limit, the excited state sum in expression (A12) passes into a double integral over the momenta k_1 and k_2 . Upon utilizing (A15) for the matrix elements, this integral is found to be

$$\begin{aligned} \psi_-^{(0)}(x, y) &= - \frac{4}{\pi^2} \int_0^\infty dk_1 \int_0^\infty dk_2 \{ [4 + (k_1 - k_2)^2]^{-1} \\ &\quad - [4 + (k_1 + k_2)^2]^{-1} \} \frac{\sin(k_1x) \sin(k_2y)}{2 + k_1^2 + k_2^2}. \\ &= \frac{2}{\pi^2} \int_{-\infty}^{+\infty} dk_1 \int_{-\infty}^{+\infty} dk_2 \{ [4 + (k_1 - k_2)^2]^{-1} \\ &\quad - [4 + (k_1 + k_2)^2]^{-1} \} \frac{\exp[i(k_1x + k_2y)]}{4 + (k_1 - k_2)^2 + (k_1 + k_2)^2}. \quad (\text{A16}) \end{aligned}$$

Introduce the following change of variables:

$$u = \frac{1}{2}(k_1 - k_2), \quad v = \frac{1}{2}(k_1 + k_2). \quad (\text{A17})$$

Then we find that

$$\psi_-^{(1)}(x, y) = F(x - y, x + y) - F(x + y, x - y), \quad (\text{A18})$$

where

$$F(s, t) = \frac{1}{4\pi^2} \int_{-\infty}^{+\infty} du \int_{-\infty}^{+\infty} dv \frac{\exp[i(su + tv)]}{(1 + u^2)(1 + u^2 + v^2)}. \quad (\text{A19})$$

The v integral in this last expression may be carried out by the calculus of residues to give

$$F(s, t) = (4\pi)^{-1} \int_{-\infty}^{+\infty} du (1 + u^2)^{-3/2} \times \exp[i|s| |u - |t|| (1 + u^2)^{1/2}]. \quad (\text{A20})$$

Consequently,

$$\begin{aligned} \psi_-^{(1)}(x, y) &= (4\pi)^{-1} \int_{-\infty}^{+\infty} du (1 + u^2)^{-3/2} \\ &\times \{ \exp[i|x - y| |u - |x + y|| (1 + u^2)^{1/2}] \\ &\quad - \exp[i|x + y| |u - |x - y|| (1 + u^2)^{1/2}] \}; \quad (\text{A21}) \end{aligned}$$

this result in combination with $\psi_+^{(1)}$ in (A7) constitutes the required first-order wavefunction which appears in Eq. (7) of the main text in slightly modified form.

If $\rho = (x^2 + y^2)^{1/2}$ is very small (so that both x and y are of comparably small magnitude), the arguments shown in Eq. (A21) for the two exponential functions will remain very small until $|u|$ equals or exceeds ρ^{-1} (roughly). By rewriting Eq. (A21) thus:

$$\begin{aligned} \psi_-^{(1)}(x, y) &= \frac{1}{4} [|x - y| - |x + y|] + (4\pi)^{-1} \\ &\times \int_{-\infty}^{+\infty} du (1 + u^2)^{-3/2} \{ [\exp(i|x - y| |u - |x + y|| (1 + u^2)^{1/2}) \\ &\quad - [\exp(i|x + y| |u - |x - y|| (1 + u^2)^{1/2}) \\ &\quad - i|x + y| |u + |x - y|| (1 + u^2)^{1/2}] \}, \quad (\text{A22}) \end{aligned}$$

we facilitate extraction of the small- ρ character of $\psi_-^{(1)}$. When $|u| < \rho^{-1}$, it suffices to expand the exponentials in (A22) through second order, to reckon the integrand to be

$$2xy(1 + 2u^2)/(1 + u^2)^{3/2} \quad (|u| \lesssim \rho^{-1}), \quad (\text{A23})$$

but when $|u|$ exceeds ρ^{-1} , the integrand is essentially $u^{-2}(|x + y| - |x - y|)(1 - i \operatorname{sgn} u)$ ($|u| \gtrsim \rho^{-1}$).

$$(\text{A24})$$

The first of these differs insignificantly from

$$4xy/|u|$$

over virtually the entire large range $-\rho^{-1} \leq u \leq \rho^{-1}$, and thus contributes

$$(2xy/\pi) \ln(\rho^{-1}) = -(xy/\pi) \ln(x^2 + y^2) \quad (\text{A25})$$

to $\psi_-^{(1)}$. The remaining contributions from $|u| \geq \rho^{-1}$,

for which estimate (A24) is appropriate, are $O(\rho^2)$ and are hence dominated at small ρ by the $\rho^2 \ln \rho$ type of term exhibited in (A25). In the same vein, note that only $O(\rho^2)$ terms would reflect variation in choice of transition points [chosen to be $\pm \rho^{-1}$ in passing from form (A23) to (A24)] to the extent of multiplication by order-unity factors (i.e., $\pm c\rho^{-1}$).

APPENDIX B

For two-electron atoms, the hyperspherical averaging procedure leads to the consideration of [see Eqs. (51)–(53)]

$$H_1 = (Z_0/\rho) - r_1^{-1} - r_2^{-1} + (\lambda/r_{12}) \quad (\text{B1})$$

as a perturbation. We wish to expand this function in the complete set of angular functions $\Phi_{n,l}(\alpha, \theta)$ [defined by Eq. (46)]. The homogeneity of H_1 in ρ permits it to be written as

$$H_1 = \rho^{-1} \sum_{n=0}^{\infty} \sum_{l=0}^n H_{n,l}^{(1)} \Phi_{n,l}(\alpha, \theta). \quad (\text{B2})$$

The $H_{n,l}^{(1)}$ are thus obtained as

$$H_{n,l}^{(1)} = \pi^2 \int_0^\pi d\alpha \int_0^\pi d\theta \sin^2 \alpha \sin \theta \Phi_{n,l}(\alpha, \theta) \times [Z_0 - \sec \frac{1}{2} \alpha - \csc \frac{1}{2} \alpha + \lambda / (1 - \sin \alpha \cos \theta)^{1/2}]. \quad (\text{B3})$$

The definition of Z_0 , Eq. (52), makes $H_{0,0}^{(1)}$ vanish. The parity of the $\Phi_{n,l}$ with respect to interchange of the electrons 1 and 2 ($\alpha \rightarrow \pi - \alpha$) requires $H_{n,l}^{(1)}$ to vanish when $n-l$ is odd. Using the well-known expansion

$$(1 - \sin \alpha \cos \theta)^{-1/2} = \sum_{l=0}^{\infty} P_l(\cos \theta) \times \begin{cases} \sec(\alpha/2) (\tan(\alpha/2))^l, & \pi/2 \geq \alpha \geq 0 \\ \csc(\alpha/2) (\cot(\alpha/2))^l, & \pi \geq \alpha \geq \pi/2, \end{cases} \quad (\text{B4})$$

and the fact that³⁰

$$C_n^{(1)}(\cos \alpha) = [\sin(n+1)\alpha / \sin \alpha], \quad (\text{B5})$$

we obtain the $l=0$, n even result,

$$H_{n,0}^{(1)} = [2\pi^{1/2} / (n + \frac{1}{2})(n + \frac{3}{2})] \times [-4(n+1) + (-1)^{n/2} 2^{1/2} \lambda]. \quad (\text{B6})$$

The $l>0$, $n-l$ even result is obtained by utilizing the expansion³¹

$$C_{n-l}^{(l+1)}(\cos \alpha) = \sum_{k=0}^{(n-l)/2} \frac{(-1)^k (n-k)! (2 \cos \alpha)^{n-l-2k}}{l! k! (n-l-2k)!}. \quad (\text{B7})$$

One finally obtains

$$H_{n,l}^{(1)} = \lambda 2^{n+5/2} \Gamma(l + \frac{3}{2}) \left(\frac{\pi(n-l)!(n+1)}{(2l+1)(n+l+1)!} \right)^{1/2} \times \sum_{k=0}^{(n-l)/2} \frac{(-1)^k (n-k)!}{2^{2k} k! \Gamma(n-2k + \frac{5}{2})}, \quad l > 0, n-l \text{ even}. \quad (\text{B8})$$

APPENDIX C

Although the general structure of the lithium atom ground-state wavefunctions must surely be well known,³² a simple and cogent statement of that structure seems not to be available in standard references. Therefore we offer here an elementary derivation that is useful in connection with Sec. V above.

As usual, let $\alpha(i)$ and $\beta(i)$ be spin functions for electron i with z components $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively. Quartet wavefunctions for lithium, with all spins parallel, involve only symmetric combinations of spin functions for the three electrons. One such quartet function would be

$$\psi(123) = f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \alpha(1) \alpha(2) \alpha(3), \quad (\text{C1})$$

and the over-all antisymmetry of ψ requires that the spatial function f change sign if any two of its argument vectors $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$ are interchanged.

The lithium ground-state wavefunction is not a quartet however, but a doublet function. If we restrict attention to total spin z component equal to $+\frac{1}{2}$, we need be concerned only within spin functions $\alpha(1)\alpha(2)\beta(1)$, $\alpha(1)\beta(2)\alpha(3)$, and $\beta(1)\alpha(2)\alpha(3)$, so that the wavefunction may be expanded in terms of them thus:

$$\begin{aligned} \psi(123) = & F(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \alpha(1) \alpha(2) \beta(3) \\ & + F_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \alpha(1) \beta(2) \alpha(3) \\ & + F_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \beta(1) \alpha(2) \alpha(3). \end{aligned} \quad (\text{C2})$$

We must see now what restraints apply to the spatial functions F , F_2 , and F_3 so that ψ in (C2) obeys the Pauli principle.

Antisymmetry with respect to interchange of space and spin variables of electrons 1 and 2 requires the following:

$$\begin{aligned} \psi(123) = & -\psi(213) \\ = & -F(213) \alpha(1) \alpha(2) \beta(3) \\ & -F_2(213) \beta(1) \alpha(2) \alpha(3) - F_3(213) \alpha(1) \beta(2) \alpha(3). \end{aligned} \quad (\text{C3})$$

Since the three spin functions are orthogonal, their separate coefficients in (C2) and (C3) must be equal:

$$\begin{aligned} F(123) = & -F(213), \\ F_2(123) = & -F_3(213), \\ F_3(123) = & -F_2(213). \end{aligned} \quad (\text{C4})$$

The first of these conditions specifies spatial antisymmetry for $F(123)$ with respect to its first two variables; the latter two are equivalent to one another and permit elimination of F_3 from ψ :

$$\begin{aligned} \psi(123) = & F(123) \alpha(1) \alpha(2) \beta(3) \\ & + F_2(123) \alpha(1) \beta(2) \alpha(3) \\ & - F_2(213) \beta(1) \alpha(2) \alpha(3). \end{aligned} \quad (\text{C5})$$

Next apply the (1, 3) antisymmetry condition on ψ to expression (C5):

$$\begin{aligned}\psi(123) &= -\psi(321) \\ &= -F(321)\beta(1)\alpha(2)\alpha(3) \\ &\quad -F_2(321)\alpha(1)\beta(2)\alpha(3) \\ &\quad +F_2(231)\alpha(1)\alpha(2)\beta(3). \quad (C6)\end{aligned}$$

Comparison of this last result with (C5) leads to three conditions again:

$$\begin{aligned}F(123) &= F_2(231), \\ F_2(123) &= -F_2(321), \\ F_2(213) &= F(321). \quad (C7)\end{aligned}$$

The first and third of these are equivalent, and may be used to eliminate F_2 from ψ :

$$\begin{aligned}\psi(123) &= F(123)\alpha(1)\alpha(2)\beta(3) \\ &\quad +F(312)\alpha(1)\beta(2)\alpha(3) \\ &\quad +F(231)\beta(1)\alpha(2)\alpha(3). \quad (C8)\end{aligned}$$

The second of Eqs. (C7), when expressed in terms of F , simply reaffirms the first of Eqs. (C4) demanding oddness under exchange of this latter function's first two variables.

The same procedure may be followed with respect to ψ antisymmetry under 2, 3 interchange. However no new conditions on F arise.

The functional representation (C8) is necessary but not sufficient. The three spin functions $\alpha\alpha\beta$, $\alpha\beta\alpha$, and $\beta\alpha\alpha$ each contain both quartet ($S^2=15/4$) and doublet ($S^2=3/4$) components. They may in fact be linearly combined to produce a pure quartet function,

$$q = (1/\sqrt{3})[\alpha(1)\alpha(2)\beta(3) + \alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3)], \quad (C9)$$

and two doublet functions,

$$\begin{aligned}d_1 &= 6^{-1/2}[2\alpha(1)\alpha(2)\beta(3) - \alpha(1)\beta(2)\alpha(3) \\ &\quad - \beta(1)\alpha(2)\alpha(3)], \\ d_2 &= (1/\sqrt{2})[\alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3)]. \quad (C10)\end{aligned}$$

By inverting (C9) and (C10) we find

$$\begin{aligned}\alpha(1)\alpha(2)\beta(3) &= (1/\sqrt{3})q + (\sqrt{2}/\sqrt{3})d_1, \\ \alpha(1)\beta(2)\alpha(3) &= (1/\sqrt{3})q - 6^{-1/2}d_1 + (1/\sqrt{2})d_2, \\ \beta(1)\alpha(2)\alpha(3) &= (1/\sqrt{3})q - 6^{-1/2}d_1 - (1/\sqrt{2})d_2. \quad (C11)\end{aligned}$$

This permits ψ in Eq. (C8) to be rewritten in terms of q , d_1 , and d_2 components:

$$\begin{aligned}\psi(123) &= (1/\sqrt{3})[F(123) + F(312) + F(231)]q \\ &\quad + 6^{-1/2}[2F(123) - F(312) - F(231)]d_1 \\ &\quad + (1/\sqrt{2})[F(312) - F(231)]d_2. \quad (C12)\end{aligned}$$

At first sight it might seem that three distinct states are possible, by putting extra conditions on F to make any pair of the square-bracketed quantities in (C12) vanish. In fact only two such independent states can be so constructed. If we demand that the d_2 component of (C12) vanish:

$$F(312) = F(231), \quad (C13)$$

the implied invariance of F to cyclic permutation of its arguments automatically makes the d_1 component vanish as well, so a pure quartet state results. Similarly, the requirement that the d_1 component be zero makes the d_2 component zero [condition (C13) is again obtained], and the same quartet state results. This quartet state is essentially the same one shown in Eq. (C1) except for rotation applied to the spins.

Quartet character is eliminated from ψ by requiring

$$F(123) + F(312) + F(231) = 0, \quad (C14)$$

and neither doublet component may subsequently be annihilated without having ψ degenerate identically to zero. The resulting single doublet function therefore is

$$\begin{aligned}\psi(123) &= F(123)\alpha(1)\alpha(2)\beta(3) + F(312)\alpha(1)\beta(2)\alpha(3) \\ &\quad + F(231)\beta(1)\alpha(2)\alpha(3). \quad (C15)\end{aligned}$$

This is the required canonical form, and the accessory conditions that must be imposed on F [the first of Eqs. (C4), and (C14)] appear in Eqs. (85) and (86) of the main text.

Since the Hamiltonian operators for the class of problems considered in this paper are spin independent, the function F must be an eigenfunction of H with the same eigenenergy E as the complete wavefunction ψ itself:

$$HF = EF. \quad (C16)$$

Of course F is also subject to the conventional and universal conditions of boundedness and square integrability.

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Chlorine NMR in CsCoCl₃ and CsMnCl₃ and ESR in CsMg(Co)Cl₃*

H. RINNEBERG† AND H. HARTMANN

Institut für physikalische Chemie der Universität, Frankfurt am Main, Germany

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Analysis of the ³⁵Cl NMR in single crystals of CsMgCl₃, CsMnCl₃ at 300°K and of CsCoCl₃ at different temperatures yielded the chlorine quadrupole coupling and for the latter two compounds the paramagnetic shift tensors. We found at 300°K: for CsMgCl₃, $\nu_Q = 4.465$ Mc/sec, $\eta = 0.235$; for CsMnCl₃, $\nu_Q = 5.2645$ Mc/sec, $\eta = 0.2683$ (bent bridge), $\nu_Q = 9.1835$ Mc/sec, $\eta = 0.0234$ (linear bridge); for CsCoCl₃, $\nu_Q = 6.87925$ Mc/sec, $\eta = 0.4293$. From the ESR spectrum of CsMg(Co)Cl₃, the g and hyperfine tensors were determined ($g_{||} = 7.37$, $g_{\perp} = 2.51$, $A_{||}(\text{Co}) = 339 \times 10^{-4}$ cm⁻¹, $A_{\perp}(\text{Co}) = 21 \times 10^{-4}$ cm⁻¹). Using these data and $Dq = 660$ cm⁻¹, $E_P = 12\,000$ cm⁻¹ inferred from the optical spectrum, the spin expectation values $\langle S_{||} \rangle$ and $\langle S_{\perp} \rangle$ were calculated for CsCoCl₃. The following superhyperfine constants parallel ($A_{||}$) and perpendicular (A_{\perp}) to the Me-Cl bond are computed from the measured paramagnetic shifts: $A_{||} = 1.59$, $A_{\perp} = 1.40$ (CsMnCl₃, Cl_I, linear bridge), $A_{||} = 1.68$, $A_{\perp} = 1.70$ (CsMnCl₃, Cl_{II}, bent bridge), $A_{||} = 4.74$, $A_{\perp} = 1.65$ (CsCoCl₃), all in units 10⁻⁴ cm⁻¹. No transition to the ordered magnetic state has been observed for CsMnCl₃ for temperatures down to 20°K, contrary to ESR data in the literature.

INTRODUCTION

Previous analysis of the ³⁵Cl NMR in CsCuCl₃ and CsNiCl₃¹ yielded the quadrupole and superhyperfine (SHF) coupling constants showing a decrease in covalency when going from the copper to the nickel complex. Here we report the transferred hyperfine interaction in CsCoCl₃ and CsMnCl₃ together with the ³⁵Cl NMR in the isomorphous CsMgCl₃. In the latter compound no chemical shift could be observed within the experimental accuracy. Finally we include a note on the optical and ESR spectrum of CsCoCl₃ and CsMg(Co)Cl₃, respectively, which have been recorded to obtain information about the splitting of the Co²⁺ ground state needed to discuss the NMR data.

EXPERIMENTAL

Single Crystals and Apparatus

All single crystals have been grown in quartz ampoules by vertical Bridgman technique using CsMnCl₃ (dehydration of CsMnCl₃·2H₂O at 150°C in a dry stream of HCl) CsMgCl₃ (obtained according to the

method of Richards and Parker² starting from an equimolar mixture of CsCl and MgCl₂·NH₄Cl·6H₂O) and a stoichiometric mixture of CsCl and anhydrous CoCl₂ (dehydration of CoCl₂·6H₂O at 400°C in dry HCl) as starting materials.

All NMR spectra were observed with a Varian V 4200B wide-line spectrometer operating between 2 and 16 Mc/sec. The magnetic field strength was measured using a proton magnetometer. Sample temperatures between 84 and 300°K were obtained by cooling with dry nitrogen gas.

In order to reduce the effect of demagnetizing fields the samples were ground to cylindrical or ellipsoidal shape, taking care to optimize the filling factor. Their orientation in the magnetic field was achieved using a two-circle goniometer,³ and for rotation patterns a one-circle goniometer¹ of high accuracy.

The EPR spectra were recorded with a Varian V 4502 spectrometer operated at 9.2 kMc/sec. The sample temperature (25°K) was obtained by evaporating liquid hydrogen in a specially designed Dewar described elsewhere.⁴ All temperatures were measured using copper-constantan thermocouples.