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Electron Correlation in Three-Electron Atoms and Ions

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Electron correlation in three-electron atoms and ions is studied in two important regions of configuration space: the vicinity of the nucleus, and the vicinity of three-electron coalescence away from the nucleus. In both cases, weakly singular logarithmic behavior of the wave function obtains. A study is made of the nodal characteristics of the wave function near the nucleus. Model systems are introduced which reflect some of the salient features present in the actual atomic system. Suggestions are made as to the utility of the present type of analysis with special attention to the recent transcorrelated approach to the Schrödinger equation.

I. INTRODUCTION

Two-electron atomic systems have been studied extensively by both numerical (variational)[1,2] and analytical[3,4] techniques. The analytical approaches have sought to determine the structure of the wave function itself in certain singular regions of configuration space and in so doing to serve as an aid to those engaged in performing extremely accurate variational calculations.

Three-electron atomic systems have not yet been subjected to so thorough an analysis. These systems have been approached almost exclusively by variational[5-7] techniques, and the results obtained are not yet comparable in accuracy to those obtained for the two-electron systems.

It is the purpose of this paper to present a nonvariational study of three-electron atoms and ions in order to guide possible future work on small atomic systems. We use model atomic systems to lead us to the salient features of the actual atomic systems, and then we use a modification of a technique introduced by Fock[3] to study the three-electron atoms and ions themselves.

We are able to discover and make explicit the analytic structure of the wave function in two important regions of configuration space: that region in which the three electrons are near the nucleus, and that region in which the three electrons are near each other, but not necessarily near the nucleus. These are regions in which correlation effects are of great importance, and since the three-body effects discovered here surely obtain in many-electron situations their explicit structure has wide interest.

In Sec. II we discuss the coordinate systems that we intend to employ as well as the effect of spin when using a spin-free Hamiltonian. Section III is concerned with a simple, exactly solvable model atomic system obtained by requiring *all* interactions to be harmonic. In Sec. IV we treat a somewhat more realistic model obtained by replacing *only* the electron-nucleus Coulombic interactions by harmonic interactions, while retaining the Coulombic electron-electron interactions.

Section V discusses the actual atomic system by means of Z^{-1} perturbation theory. In Sec. VI we examine the nodal surface of the spatial eigenfunction in the vicinity of the nucleus, while in Sec. VII we discuss the effect of electron coalescence away from the nucleus.

The final section, Sec. VIII, is concerned with the relevance of the results obtained here to present computational efforts and to future researches.

II. SPIN RESTRICTIONS AND SPATIAL COORDINATES

Consider a system whose Hamiltonian is an operator on three (vector) spatial variables only, $H(1, 2, 3)$. It is well known[8,9] that a "spin-free" formulation of the corresponding eigenvalue problem is possible. It is perhaps less well known that this spin-free formulation may be cast into a form

lending itself to ready geometric interpretation (we shall exploit this feature later). Thus if Ψ represents the total wave function, a function of both space and spin variables, and if the states with $S = S_z = \frac{1}{2}$ (doublet states) are of interest, we may write the wave function as [4,10,11]

$$\Psi(\vec{1},\vec{2},\vec{3}) = \Phi(\vec{1},\vec{2}\,|\,\vec{3})\,\alpha(1)\alpha(2)\beta(3) - \Phi(\vec{1},\vec{3}\,|\,\vec{2})\alpha(1)\beta(2)\alpha(3) - \Phi(\vec{3},\vec{2}\,|\,\vec{1})\beta(1)\alpha(2)\alpha(3)\,, \tag{1}$$

where Φ is a function of the spatial variables only which satisfies the restrictions

$$\Phi(\vec{1},\vec{2}\,|\,\vec{3}) = -\Phi(\vec{2},\vec{1}\,|\,\vec{3})\,, \tag{2}$$

$$\Phi(\vec{1},\vec{2}\,|\,\vec{3}) = \Phi(\vec{1},\vec{3}\,|\,\vec{2}) + \Phi(\vec{3},\vec{2}\,|\,\vec{1}). \tag{3}$$

Restriction (2) is necessary and sufficient for the satisfaction of the Pauli principle, while restriction (3) is necessary and sufficient for Φ to represent a pure doublet state.

Owing to the independence of the spin functions in Eq. (1), the eigenvalue problem is equivalent to the pure spatial problem

$$H\Phi = E\Phi\,, \tag{4}$$

where Φ must obey Eq. (2) and Eq. (3). In this way we are able to effect a separation of the spatial and spin coordinates, insofar as the eigenvalue problem itself is concerned.

In the sections that follow, the Hamiltonian will always have the structure

$$H = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) + U(\vec{r}_1,\vec{r}_2,\vec{r}_3)\,, \tag{5}$$

and we find it convenient to utilize the following coordinate systems.

The ground state of the three-electron system is an $S(L=0)$ state, and hence depends on only six variables specifying the relative orientation of the three electrons and the nucleus. For such states we may write the Laplacian directly in terms of the interelectron coordinates $(r_1, r_2, r_3, r_{12}, r_{13}, r_{23})$. The result is[12,13]

$$\begin{aligned}\nabla_9^2 \equiv \nabla_1^2+\nabla_2^2+\nabla_3^2 = {}& \frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1 + \frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}r_2 + \frac{1}{r_3}\frac{\partial^2}{\partial r_3^2}r_3 + \frac{2}{r_{12}}\frac{\partial^2}{\partial r_{12}^2}r_{12} + \frac{2}{r_{13}}\frac{\partial^2}{\partial r_{13}^2}r_{13} + \frac{2}{r_{23}}\frac{\partial^2}{\partial r_{23}^2}r_{23} + \frac{r_{12}^2+r_1^2-r_2^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1\partial r_{12}} \\ & + \frac{r_{13}^2+r_1^2-r_3^2}{r_1 r_{13}}\frac{\partial^2}{\partial r_1\partial r_{13}} + \frac{r_{12}^2+r_2^2-r_1^2}{r_2 r_{12}}\frac{\partial^2}{\partial r_2\partial r_{12}} + \frac{r_{23}^2+r_2^2-r_3^2}{r_2 r_{23}}\frac{\partial^2}{\partial r_2\partial r_{23}} + \frac{r_{23}^2+r_3^2-r_2^2}{r_3 r_{23}}\frac{\partial^2}{\partial r_3\partial r} \\ & + \frac{r_{13}^2+r_3^2-r_1^2}{r_3 r_{13}}\frac{\partial^2}{\partial r_3\partial r_{13}} + \frac{r_{12}^2+r_{13}^2-r_{23}^2}{r_{12}r_{13}}\frac{\partial^2}{\partial r_{12}\partial r_{13}} + \frac{r_{12}^2+r_{23}^2-r_{13}^2}{r_{12}r_{23}}\frac{\partial^2}{\partial r_{12}\partial r_{23}} + \frac{r_{13}^2+r_{23}^2-r_{12}^2}{r_{13}r_{23}}\frac{\partial^2}{\partial r_{13}\partial r_{23}}\,.\end{aligned} \tag{6}$$

For some purposes it will be more convenient to use the full set of nine hyperspherical coordinates chosen as follows[4]:

$$\begin{aligned}&\rho^2 = r_1^2+r_2^2+r_3^2\,, \qquad 0 \le \rho < \infty \\ &r_3 = \rho\cos\chi_1\,, \\ &r_1 = \rho\sin\chi_1\cos\chi_2\,, \quad 0 \le \chi_1, \chi_2 \le \tfrac{1}{2}\pi \\ &r_2 = \rho\sin\chi_1\sin\chi_2\,,\end{aligned} \tag{7}$$

together with

$$\theta_1, \varphi_1, \theta_2, \varphi_2, \theta_3, \varphi_3\,,$$

the usual spherical angles of particles 1, 2, and 3. Then the Laplacian has the form[4]

$$\nabla_9^2 = \frac{1}{\rho^8}\frac{\partial}{\partial\rho}\rho^8\frac{\partial}{\partial\rho} - \frac{\Lambda_9^2}{\rho^2}\,, \tag{8}$$

where the generalized angular momentum operator $-\Lambda_9^2$ is

$$-\Lambda_9^2 = \frac{1}{\sin^5\chi_1\cos^2\chi_1}\frac{\partial}{\partial\chi_1}\sin^5\chi_1\cos^2\chi_1 \times \frac{\partial}{\partial\chi_1} - \frac{L^2(\theta_3,\varphi_3)}{\cos^2\chi_1} - \frac{\Lambda_6^2}{\sin^2\chi_1}\,. \tag{9}$$

In this last expression $-\Lambda_6^2$ is given by

$$-\Lambda_6^2 = \frac{1}{\sin^2\chi_2\cos^2\chi_2}\frac{\partial}{\partial\chi_2}\sin^2\chi_2\cos^2\chi_2 \times \frac{\partial}{\partial\chi_2} - \frac{L^2(\theta_1,\varphi_1)}{\cos^2\chi_2} - \frac{L^2(\theta_2,\varphi_2)}{\sin^2\chi_2}\,, \tag{10}$$

and $-L^2(\theta_i,\varphi_i)$ is defined to be

$$-L^2(\theta_i,\varphi_i) = \frac{1}{\sin\theta_i}\frac{\partial}{\partial\theta_i}\sin\theta_i\frac{\partial}{\partial\theta_i} + \frac{1}{\sin^2\theta_i}\frac{\partial^2}{\partial\varphi_i^2}\,. \tag{11}$$

We will also have occasion to use an orthogonal transformation of the $(\vec{r}_1,\vec{r}_2,\vec{r}_3)$ system defined by

$$\begin{aligned}&\vec{R}_1 = 3^{-1/2}(\vec{r}_1+\vec{r}_2+\vec{r}_3)\,, \qquad \vec{R}_2 = 2^{-1/2}(\vec{r}_1-\vec{r}_2)\,, \\ &\vec{R}_3 = 6^{-1/2}(2\vec{r}_3-\vec{r}_1-\vec{r}_2)\,.\end{aligned} \tag{12}$$

This will be called the center-of-mass system. Its utility arises from the fact that restrictions (2) and (3) concern only $\vec{R}_2$ and $\vec{R}_3$.

III. NODAL HYPERSURFACES IN A MODEL ATOMIC SYSTEM

Mathematically speaking, one of the simplest models of atomic systems obtains obtains from the following simple rule: Replace every Coulomb interaction by a corresponding harmonic interaction. We

will call this simple model the harmonic model. A similar model has been studied in the case of molecules.[14]

The Hamiltonian for the harmonic model of three-electron atomic systems is thus

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

in appropriate units.

For $^2S_{1/2}$ states, which are of interest here, the problem is to solve the eigenvalue equation

$$(H-E)\Phi = 0 , \quad (14)$$

with Φ chosen to obey restrictions (2) and (3) as well as to correspond to an $L = O(S)$ state. Use of the center-of-mass system of coordinates (12) allows (14) to be written

$$[-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2+\nabla_3^2)+\tfrac{1}{2}(R_1^2+R_2^2+R_3^2) - \tfrac{3}{2}\lambda(R_2^2+R_3^2)-E]\Phi = 0 , \quad (15)$$

where the subscripts on the Laplacians now refer to the new $\vec{R}$ coordinates. The eigenfunction Φ is separable in these coordinates and the separable solutions can be easily written down.

For our purposes it is sufficient to write the first two eigenfunctions corresponding to doublet S states. The ground state is described by the eigenfunction

$$\Phi_1 = N_1(r_{23}^2-r_{13}^2)\exp[-\tfrac{1}{2}(r_1^2+r_2^2+r_3^2) + \eta(\lambda)(r_{12}^2+r_{13}^2+r_{23}^2)] , \quad (16)$$

where $N_1 = N_1(\lambda)$ is a normalization constant and $\eta(\lambda) = \frac{1}{6}[1-(1-3\lambda)^{1/2}]$. We use interelectronic coordinates here for convenience. The energy of this state is

$$E_1(\lambda) = \tfrac{3}{2}+5(1-3\lambda)^{1/2} . \quad (17)$$

For $\lambda = 0$ this solution is degenerate with the eigenfunction

$$\Phi_2 = N_2[3(r_1^2-r_2^2)+(r_{23}^2-r_{13}^2)] \times\exp[-\tfrac{1}{2}(r_1^2+r_2^2+r_3^2)+\eta(\lambda)(r_{12}^2+r_{13}^2+r_{23}^2)] , \quad (18)$$

with eigenvalue

$$E_2(\lambda) = \tfrac{5}{2}+4(1-3\lambda)^{1/2} . \quad (19)$$

Although the model here is very simple, it has one feature worth looking at in some detail. The Φ_n for this model possess nodes when viewed in the full coordinate configuration space. We expect the spatial eigenfunctions for the actual (Coulombic) three-electron system to possess some type of analogous nodal structure as well, and so we will examine the nodal surfaces of Φ_1 (16) and Φ_2 (18) in order to gain familiarity with the concepts involved.

The nodal surface of Φ_1 is particularly simple. From (16) $\Phi_1 = 0$ (for finite r_i) occurs when

$$r_{23} = r_{13} . \quad (20)$$

If the positions of electrons $\vec{1}$ and $\vec{2}$, the α-spin electrons, are fixed in space (20) is satisfied when electron $\vec{3}$, the β-spin electron, moves in the plane which perpendicularly bisects $\vec{r}_{12}$. But if the positions of one α-spin electron and one β-spin electron, say electrons $\vec{2}$ and $\vec{3}$, are fixed in space, (20) is satisfied when the other α-spin electron, electron $\vec{1}$, moves on the surface of a sphere with its center at particle $\vec{3}$ and radius r_{23} (Fig. 1).

In the case of Φ_2 (19) the nodal surface is described by the equation

$$r_{13}^2 - r_{23}^2 = 3(r_1^2-r_2^2) . \quad (21)$$

For fixed α-spin electrons $\vec{1}$ and $\vec{2}$, (21) is satisfied when the β-spin electron $\vec{3}$ moves in a plane such that

$$\vec{r}_{12}\cdot(\vec{r}_1+\vec{r}_2+\vec{r}_3) = 0 . \quad (22)$$

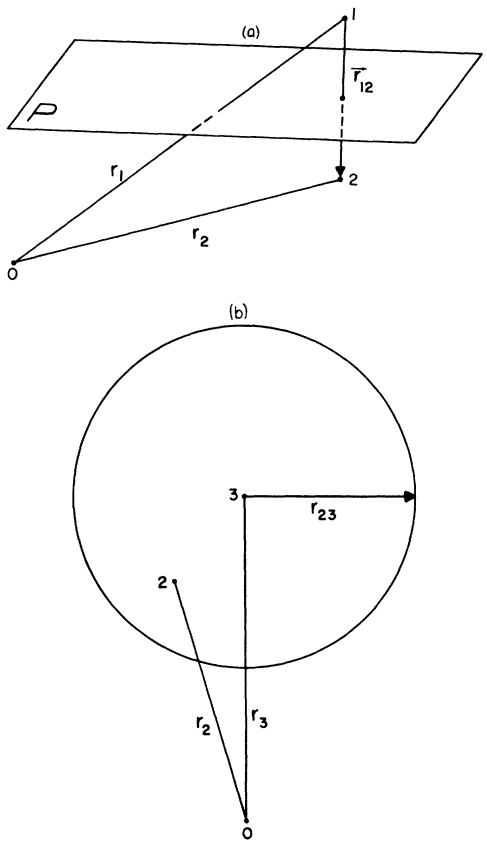

FIG. 1. (a) Surface P on which the lowest ^2S eigenfunction for the harmonic model [Eq. (16)] vanishes for fixed positions of α-spin electrons $\vec{1}$ and $\vec{2}$. The plane P is $(r_3 \mid r_{13} = r_{23})$. P perpendicularly bisects $\vec{r}_{12}$. The nucleus is indicated by 0. (b) Surface on which the lowest ^2S eigenfunction for the harmonic model [Eq. (16)] vanishes for fixed positions of one α-spin electron $\vec{2}$, and one β-spin electron $\vec{3}$. The sphere shown is centered at electron $\vec{3}$ and has radius r_{23}. The nucleus is indicated by 0.

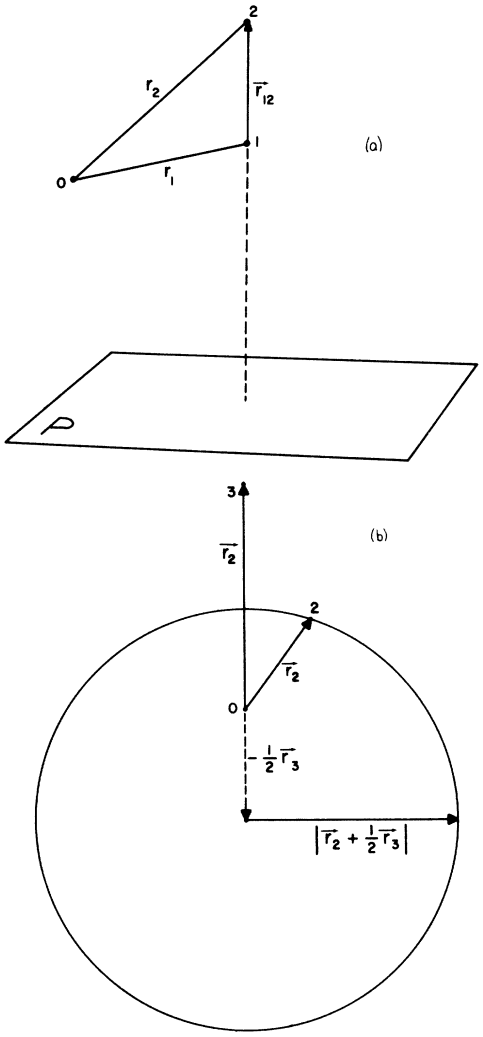

FIG. 2. (a) Surface on which the first excited ^2S eigenfunction for the harmonic model [Eq. (18)] vanishes for fixed positions of α-spin electrons $\vec{1}$ and $\vec{2}$. The plane P is $[\vec{r}_3 \mid \vec{r}_{12}\cdot(\vec{r}_1+\vec{r}_2+\vec{r}_3)=0]$ and is perpendicular to $\vec{r}_{12}$. The nucleus is indicated by 0. (b) Surface on which the first excited ^2S eigenfunction for the harmonic model [Eq. (18)] vanishes for fixed positions of one α-spin electron $\vec{2}$, and one β-spin electron $\vec{3}$. The sphere shown is centered at $-\frac{1}{2}\vec{r}_3$ and has radius $|\vec{r}_2+\frac{1}{2}\vec{r}_3|$. The nucleus is indicated by 0.

Thus the plane in which $\vec{3}$ moves has the vector to the center of mass of the three-electron triangle perpendicular to $\vec{r}_{12}$. If the positions of electrons $\vec{2}$ and $\vec{3}$ are fixed instead, electron $\vec{1}$ must move on a spherical surface with center $-\frac{1}{2}\vec{r}_3$ and radius $|\vec{r}_2+\frac{1}{2}\vec{r}_3|$ (Fig. 2).

Although the nodal characteristics are certainly not directly transferable from this simple model to the actual three-electron system, they are an indication of the kinds of features we can expect when we treat the true atomic system. It is especially significant to note that none of the nodal surfaces for the model are the same as would be obtained from a simple orbital product description (restricted Hartree-Fock) of this system.[15]

IV. ELECTRON-ELECTRON-ELECTRON COALESCENCE IN ANOTHER MODEL ATOMIC SYSTEM

A somewhat more realistic model atomic system is obtained by the following rule: Replace all nuclear-electron Coulomb interactions by harmonic interactions, but retain all Coulombic electron-electron interactions. We call this model the Hooke model for atomic systems. For two-electron systems this model has been studied both numerically[16] and analytically[17] (by perturbation theory).

The Hamiltonian for the Hooke model of three-electron atomic systems is

$$H=-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2+\nabla_3^2)+\tfrac{1}{2}(r_1^2+r_2^2+r_3^2)+\lambda\left(\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right) \tag{23}$$

in appropriate units.

The eigenvalue problem for $^2S_{1/2}$ states is once again to find those spatial functions Φ for which

$$(H-E)\Phi=0\ , \tag{24}$$

with Φ satisfying restrictions (2) and (3), and corresponding to a zero angular momentum state.

It is convenient to use the center-of-mass system of coordinates (12) here just as it was in Sec. III. Note that

$$\begin{aligned} r_{12}&=2^{1/2}R_2\ ,\\ r_{13}&=2^{-1/2}(R_2^2+3R_3^2-2\sqrt{3}\,R_2R_3\cos\Theta_{23})^{1/2}\ ,\\ r_{23}&=2^{-1/2}(R_2^2+3R_3^2+2\sqrt{3}\,R_2R_3\cos\Theta_{23})^{1/2}\ , \end{aligned} \tag{25}$$

where Θ_{23} is the angle between $\vec{R}_2$ and $\vec{R}_3$.

The eigenvalue problem (24) thus becomes

$$[-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2+\nabla_3^2)+\tfrac{1}{2}(R_1^2+R_2^2+R_3^2)+\lambda V(R_2,R_3,\cos\Theta_{23})-E]\,\Phi=0\ , \tag{26}$$

where

$$V(R_2,R_3,\cos\Theta_{23})=\frac{2^{-1/2}}{R_2}+\frac{2^{1/2}}{(R_2^2+3R_3^2-2\sqrt{3}\,R_2R_3\cos\Theta_{23})^{1/2}}+\frac{2^{1/2}}{[R_2^2+3R_3^2+2(3)^{1/2}R_2R_3\cos\Theta_{23}]^{1/2}}\ . \tag{27}$$

Let us concentrate on the ground-state solution of (26). For $\lambda=0$, there are two degenerate solutions of (26) corresponding in fact to the $\lambda=0$ limit of (16) and (18). In terms of the center-of-mass coordinates (12) these two eigenfunctions are proportional to

$$R_2R_3\cos\Theta_{23}\exp[-\tfrac{1}{2}(R_1^2+R_2^2+R_3^2)]\ , \tag{28}$$

$$R_1R_2\cos\Theta_{12}\exp[-\tfrac{1}{2}(R_1^2+R_2^2+R_3^2)] \ . \tag{29}$$

The perturbation V (27) is a function only of R_2, R_3, $\cos\Theta_{23}$ and thus never connects these degenerate states. In fact, the ground state for $\lambda>0$ corresponds to (28) alone (as it did in the previous model).

Of more importance perhaps is the fact that the center-of-mass motion $\vec{R}_1$ of the model can be separated. Since restrictions (2) and (3) do not concern $\vec{R}_1$, the ground-state solution of (26) must have the form

$$\Phi=\pi^{-3/4}e^{-R_1^2/2}\psi(R_2,R_3,\cos\Theta_{23}) \ , \tag{30}$$

where the eigenvalue problem for ψ is

$$[-\tfrac{1}{2}(\nabla_2^2+\nabla_3^2)+\tfrac{1}{2}(R_2^2+R_3^2)+\lambda V(R_2,R_3,\cos\Theta_{23})-\epsilon]\psi=0 \ ,$$

$$\epsilon=E-\tfrac{3}{2} \ . \tag{31}$$

This reduces our problem to a pseudo-two-electron problem in only three variables, a situation we are more able to cope with mathematically.

Although the Hooke model is not expected to be accurate in its description of global properties of the actual (Coulombic) atomic system, it should be approximately correct in its description of certain local properties in configuration space. In particular, in the region of space where the three electrons coalesce away from the nucleus, the potential of (23) possesses the same singular terms as does the potential of the true Coulombic atom. These singular terms must certainly have dominant importance in "shaping" the wave function for the actual Coulombic atom in that region of space far enough removed from the nucleus. In this region of space for both the Hooke model and the actual Coulombic atom the role of the nuclear-electron interaction terms is to bind the electrons to the nucleus, while the interaction among the electrons in both cases is the same and serves to determine the local form of the wave function. We are thus led to study our model in the region $\vec{R}_1>0$, $\vec{R}_2$ and $\vec{R}_3$ small.

The factorization of the center-of-mass motion (30) allows us to consider any R_1, while the desire to study $\vec{R}_2$ and $\vec{R}_3$ small suggests we change coordinate systems slightly in (31). If we use an analog of the coordinates introduced by Fock[3] for two-electron systems

$$\begin{aligned} \rho^2&=R_2^2+R_3^2 \ , & \infty>\rho\geq 0 \\ \tan\tfrac{1}{2}\alpha&=R_2/R_3, & \pi\geq\alpha\geq 0 \\ \cos\theta&=\cos\Theta_{23} \ , & \pi\geq\theta\geq 0 \end{aligned} \tag{32}$$

the condition that R_2 and R_3 simultaneously be small corresponds to small ρ.

In terms of the coordinates (32) the Laplacian in (31) has the form[4]

$$\nabla_2^2+\nabla_3^2=\frac{\partial^2}{\partial\rho^2}+\frac{5}{\rho}\frac{\partial}{\partial\rho}-\frac{4}{\rho^2}\Lambda^2(\alpha,\theta) \ , \tag{33}$$

where the angular operator Λ^2 is

$$-\Lambda^2=\frac{1}{\sin^2\alpha}\left(\frac{\partial}{\partial\alpha}\sin^2\alpha\,\frac{\partial}{\partial\alpha}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\,\frac{\partial}{\partial\theta}\right). \tag{34}$$

The potential energy term in (31) is

$$\tfrac{1}{2}\rho^2+\frac{\lambda}{2^{1/2}\rho}\left(\csc\tfrac{1}{2}\alpha+\frac{2}{(2+\cos\alpha+3^{1/2}\sin\alpha\cos\theta)^{1/2}}+\frac{2}{(2+\cos\alpha-3^{1/2}\sin\alpha\cos\theta)^{1/2}}\right) \tag{35}$$

and we desire to find the solution of (31) for small ρ. Recall that the solution must be chosen to satisfy restrictions (2) and (3). (It is already guaranteed to correspond to a zero angular momentum state.)

Although we could proceed in the same way that Fock[3] did for the ground state of the two-electron atom, we choose to follow Hylleraas[18] instead. Thus we write (31) as

$$[\nabla_2^2+\nabla_3^2-\rho^2-(2^{1/2}\lambda/\rho)U(\alpha,\theta)+2\epsilon]\psi=0, \tag{36}$$

where

$$U(\alpha,\theta)=\csc\tfrac{1}{2}\alpha+\frac{2}{(2+\cos\alpha+3^{1/2}\sin\alpha\cos\theta)^{1/2}}+\frac{2}{(2+\cos\alpha-3^{1/2}\sin\alpha\cos\theta)^{1/2}}, \tag{37}$$

and observe that the Laplacian operator is formally of degree -2 in ρ.

We then formally expand ψ as

$$\psi=\psi_0+\psi_1+\psi_2+\cdots \tag{38}$$

(where the ψ_n forms a series of functions with ascending ρ order) and solve the equations ($\nabla_6^2=\nabla_2^2+\nabla_3^2$)

$$\nabla_6^2\psi_0=0, \tag{39}$$

$$\nabla_6^2\psi_1=(2^{1/2}\lambda/\rho)U(\alpha,\theta)\psi_0, \tag{40}$$

$$\nabla_6^2\psi_2=(2^{1/2}\lambda/\rho)U(\alpha,\theta)\psi_1-2\epsilon\psi_0, \tag{41}$$

$$\vdots$$

in turn for the ψ_n. The ψ_n are required to be finite, continuous, and square integrable over the surface of an appropriate sphere (not over all space), and must satisfy the symmetry restrictions (2) and (3). In general, this will lead to a formal solution of the original equation (36). It would be possible to make this formal solution an actual solution of the quantum-mechanical problem if the degrees of freedom remaining in the ψ_n could be chosen so that the resulting function is actually a member of the appropriate Hilbert space. We are not prepared to undertake a study of this complex point,

but will assume that such convergence can be obtained.

In Sec. V we will demonstrate this technique for two-electron systems where results are available by other means[3] and show that the present scheme leads to the known results.

All of the solutions of (39) are easily found[4] and the one corresponding to the ground state of this system is

$$\psi_0 = N\rho^2 \sin\alpha\cos\theta = 2NR_2R_3\cos\Theta_{23}, \tag{42}$$

where N is a constant not determined by this procedure. The equation for ψ_1 then becomes

$$(\nabla_2^2+\nabla_3^2)\psi_1 = 2^{1/2}N\lambda\rho U(\alpha,\theta)\sin\alpha\cos\theta. \tag{43}$$

ψ_1 should contain terms of at most ρ^3 order and there are no new homogeneous solutions to (43) with this characteristic. Thus, we need a particular solution to (43) which satisfies the auxiliary conditions (2) and (3). Such a particular solution is

$$\begin{aligned}\psi_1 &= 2^{-5/2}N\lambda\rho^3\{3^{-1/2}\sin^2\tfrac{1}{2}\alpha[(2+\cos\alpha-3^{1/2}\sin\alpha\cos\theta)^{1/2}-(2+\cos\alpha+3^{1/2}\sin\alpha\cos\theta)^{1/2}]-\sin\tfrac{1}{2}\alpha\sin\alpha\cos\theta\\ &\quad+3\sin\alpha\cos\theta[\sin\tfrac{1}{2}\alpha+\tfrac{1}{2}(2+\cos\alpha+3^{1/2}\sin\alpha\cos\theta)^{1/2}+\tfrac{1}{2}(2+\cos\alpha-3^{1/2}\sin\alpha\cos\theta)^{1/2}]\}\\ &= [N\lambda/(8\times3^{1/2})](r_{23}-r_{13})(r_{12}+r_{13}+r_{23})(3r_{13}+3r_{23}-r_{12}),\end{aligned} \tag{44}$$

where the last result is written in the more familiar interparticle coordinates. Our next task is to examine ψ_2, insofar as we are able. First, we write (41) using (42) and (44):

$$(\nabla_2^2+\nabla_3^2)\psi_2 = \tfrac{1}{2}N\lambda^2\rho^2U(\alpha,\theta)F(\alpha,\theta) - 2N\epsilon\rho^2\sin\alpha\cos\theta, \tag{45}$$

where

$$\begin{aligned}F(\alpha,\theta) &= 3^{-1/2}\sin^2\tfrac{1}{2}\alpha[(2+\cos\alpha-3^{1/2}\sin\alpha\cos\theta)^{1/2}-(2+\cos\alpha+3^{1/2}\sin\alpha\cos\theta)^{1/2}]-\sin\tfrac{1}{2}\alpha\sin\alpha\cos\theta\\ &\quad+3\sin\alpha\cos\theta[\sin\tfrac{1}{2}\alpha+\tfrac{1}{2}(2+\cos\alpha+3^{1/2}\sin\alpha\cos\theta)^{1/2}+\tfrac{1}{2}(2+\cos\alpha-3^{1/2}\sin\alpha\cos\theta)^{1/2}].\end{aligned} \tag{46}$$

The inhomogeneous part of (45) is now too complicated to expect a direct solution by simple methods. However, we can generate a solution in the following way. The angular operator Λ^2, (34), has the complete set

$$\Phi_{n,l}(\alpha,\theta) = N_{n,l}(\sin\alpha)^l C_{n-l}^{(l+1)}(\cos\alpha)P_l(\cos\theta), \qquad n=0,1,2,\ldots,\quad l=0,1,\ldots,n \tag{47}$$

of finite continuous square-integrable eigenfunctions.[4] The P_l are Legendre polynomials defined by

$$\frac{1}{(1+x^2-2x\cos\theta)^{1/2}} = \sum_{l=0}^{\infty}P_l(\cos\theta)x^l, \tag{48}$$

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

$$\frac{1}{(1+x^2-2x\cos\alpha)^{l}} = \sum_{n=0}^{\infty}C_n^{(l)}(\cos\alpha)x^n, \quad l\neq 0. \tag{49}$$

The eigenvalues of Λ^2 are

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

with degeneracy $n+1$, and the normalization constant is

$$N_{n,l} = 2^l l!\left(\frac{(2l+1)(n+1)(n-l)!}{\pi^3(n+l+1)!}\right)^{1/2}, \tag{51}$$

corresponding to the normalization

$$\pi^2\int_0^{\pi}d\alpha\int_0^{\pi}d\theta\sin^2\alpha\sin\theta\,\Phi_{n,l}\Phi_{m,k} = \delta_{n,m}\delta_{l,k}. \tag{52}$$

By virtue of the completeness of the set (47) we can expand the inhomogeneous part of (45) in terms of the $\Phi_{n,l}$ and we get

$$(\nabla_2^2+\nabla_3^2)\psi_2 = \rho^2\sum_{n=0}^{\infty}\sum_{l=0}^{\infty}R_{n,l}\Phi_{n,l}(\alpha,\theta), \tag{53}$$

where the $R_{n,l}$ are

$$R_{n,l} = \tfrac{1}{4}N\lambda^2\langle\Phi_{n,l}, UF\rangle_\Omega - \pi^{3/2}N\epsilon\,\delta_{1,1}, \tag{54}$$

the notation $\langle\ ,\ \rangle_\Omega$ implying angular integrations as in (52). Let us expand ψ_2 in the set $\Phi_{n,l}$ as well:

$$\psi_2 = \sum_{n=0}^{\infty}\sum_{l=0}^{\infty}\varphi_{n,l}(\rho)\Phi_{n,l}(\alpha,\theta). \tag{55}$$

Using (50) and (52) we obtain an ordinary differential equation for the $\varphi_{n,l}$:

$$\left(\frac{d^2}{d\rho^2}+\frac{5}{\rho}\frac{d}{d\rho}-\frac{4n(n+2)}{\rho^2}\right)\varphi_{n,l} = R_{n,l}\rho^2, \tag{56}$$

which may be integrated directly. The homogeneous solutions are ρ^{2n} and ρ^{-2n-4}, and if $n\neq 2$, particular solutions are

$$-\frac{1}{4}\frac{R_{n,l}\rho^4}{(n-2)(n+4)}. \tag{57}$$

However, if $n=2$ then the particular solution must be

$$\tfrac{1}{12}R_{2,l}\rho^4\ln\rho. \tag{58}$$

Corresponding to $n=2$ there are three hyperspherical harmonics ($l=0,1,2$). They are

$$\Phi_{2,0} = \pi^{-3/2}(4\cos^2\alpha-1),$$

$$\Phi_{2,1} = 2^{1/2}3^{1/2}\pi^{-3/2}\sin 2\alpha\cos\theta, \tag{59}$$
$$\Phi_{2,2} = 2^{1/2}\pi^{-3/2}\sin^2\alpha(3\cos^2\theta - 1).$$

By symmetry ($\theta \to \pi - \theta$), $R_{2,0}$ and $R_{2,2}$ must be zero. The constant $R_{2,1}$ does not vanish by symmetry and, in fact, we compute this constant to be

$$R_{2,1} = -N\lambda^2\left(\frac{6323\pi^{1/2}}{2^{7/2}\times 7\times 5} - \frac{17\pi^{3/2}}{2^{3/2}\times 3^{1/2}} - \frac{2^{5/2}\pi^{3/2}}{5}\right)$$
$$= -2.67996\,N\lambda^2\,. \tag{60}$$

Thus we have discovered a three-body effect in the Hooke model atom which has primary importance when the three electrons coalesce. This type of logarithmic wave-function singularity (58) is analogous to the one first found by Fock[3] for the actual two-electron atom.

Writing out the wave function in interparticle coordinates we have

$$\psi = 3^{-1/2}N[(r_{23}^2 - r_{13}^2) + \tfrac{1}{8}\lambda(r_{23} - r_{13})(r_{12} + r_{13} + r_{23})$$
$$\times(3r_{13} + 3r_{23} - r_{12}) + (6\pi)^{-3/2}N^{-1}R_{2,1}(r_{23}^2 - r_{13}^2)$$
$$\times(r_{13}^2 + r_{23}^2 - 2r_{12}^2)\ln(r_{12}^2 + r_{13}^2 + r_{23}^2) + O(\rho^4)]\,. \tag{61}$$

We will see in Sec. VII that the form discovered here for the Hooke model has direct application to the actual (Coulombic) three-electron atom.

V. Z^{-1} PERTURBATION THEORY AND GROUND STATE OF THREE-ELECTRON ATOMIC SYSTEM

The Hamiltonian which describes the motion of three electrons in the vicinity of a fixed center of charge Z is

$$H = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - \frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_3}$$
$$+\lambda\left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right), \qquad \lambda = Z^{-1} \tag{62}$$

in Z-scaled atomic units. Obviously λ can serve as a natural perturbation parameter and with this partitioning of $H(=H_0+\lambda H_1)$ and the corresponding expansions of the spatial eigenfunction and eigenvalue

$$\Phi = \Phi_0 + \lambda\Phi_1 + \cdots\,,$$
$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \lambda^3 E_3 + \cdots \tag{63}$$

we are led to seek solutions of the set of equations[6,19–21]

$$(H_0 - E_0)\Phi_0 = 0\,, \tag{64}$$
$$(H_0 - E_0)\Phi_1 = (E_1 - H_1)\Phi_0\,, \tag{65}$$
$$\vdots$$

For the ground state of this atomic system, each of the Φ_n must obey restrictions (2) and (3) and must correspond to an $L = 0\,(S)$ state. The first equation in this hierarchy, (64), is separable in the coordinates $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}_3$ of the individual electrons, and the Φ_0 for the ground state is easily seen to be

$$\Phi_0(1,\,2\mid 3) = 2^{-1/2}[1s(1)2s(2) - 2s(1)1s(2)]\,1s(3), \tag{66}$$

where

$$1s = \pi^{-1/2}e^{-r}\,, \qquad 2s = \tfrac{1}{4}(2\pi)^{-1/2}(2-r)e^{-r/2} \tag{67}$$

are hydrogenic functions. It is, perhaps, not so clear that solutions to (65) in the form of appropriately chosen first-order two-electron functions (multiplied by hydrogenic functions) obtain. Nevertheless, it can be shown[6,19–21] that

$$\Phi_1(1,\,2\mid 3) = 2^{-1/2}[\,\psi_1^A(1\mid 3)2s(2) - \psi_1^A(2\mid 3)2s(1)]$$
$$+\tfrac{1}{2}[2\psi_1^B(1,\,2)1s(3) + \psi_1^B(1,\,3)1s(2) - \psi_1^B(2,\,3)1s(1)]$$
$$+\tfrac{1}{2}[\,\psi_1^C(2\mid 3)1s(1) - \psi_1^C(1\mid 3)1s(2)]\,, \tag{68}$$

where

$$\left(-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2} + 1\right)\psi_1^A(1\mid 2)$$
$$= \left(E_1^A - \frac{1}{r_{12}}\right)1s(1)1s(2)\,, \tag{69}$$

$$\left(-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{5}{8}\right)\psi_1^B(1,\,2)$$
$$= \left(E_1^B - \frac{1}{r_{12}}\right)\frac{[1s(1)2s(2) - 2s(1)1s(2)]}{2^{1/2}}\,, \tag{70}$$

$$\left(-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{5}{8}\right)\psi_1^C(1\mid 2)$$
$$= \left(E_1^C - \frac{1}{r_{12}}\right)\frac{[1s(1)2s(2) + 2s(1)1s(2)]}{2^{1/2}}\,. \tag{71}$$

The "A" label thus refers to the $1s^2\,{}^1S$ state of the two-electron atomic system, while "B" refers to the $1s2s\,{}^3S$ state, and "C" refers to the $1s2s\,{}^1S$ state. Note that $E_1^A = \frac{5}{8}$, $E_1^B = \frac{137}{729}$, $E_1^C = \frac{169}{729}$, and that the E_1 of (65) is

$$E_1 = E_1^A + \tfrac{3}{2}E_1^B + \tfrac{1}{2}E_1^C\,. \tag{72}$$

The problem now, at this level, has thus been reduced from a single three-electron problem to three two-electron problems.

Variational techniques[6,20,21] can now be used to calculate the ψ_1^A, ψ_1^B, and ψ_1^C if global properties of the system are of interest. We are here more interested in local properties of the wave function in configuration space, and thus we intend to study (69)–(71) by a method[18] essentially equivalent to that used by Fock[3] and then to relate these results to the three-electron system through Φ_1 (68).

We will use the Fock[3] coordinates

$$\rho^2 = r_1^2 + r_2^2\,, \qquad \infty > \rho \geq 0$$

$$\tan\tfrac{1}{2}\alpha = r_2/r_1 , \qquad \pi \geq \alpha \geq 0 \tag{73}$$

$$\cos\theta = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2} , \qquad \pi \geq \theta \geq 0$$

in our treatment and will analyze (69)–(71) for small ρ. In terms of (ρ, α, θ) the Laplacian has the same form (33) used in Sec. IV.

We treat (69) by writing a formal expansion of ψ_1^A as

$$\psi_1^A = \varphi_0^A + \varphi_1^A + \varphi_2^A + \varphi_3^A + \varphi_4^A + \cdots , \tag{74}$$

and determining the φ_n^A from the equations $(\nabla_6^2 = \nabla_1^2 + \nabla_2^2)$

$$\nabla_6^2 \varphi_0^A = 0 , \tag{75}$$

$$\nabla_6^2 \varphi_1^A = -(2/\rho)(\sec\tfrac{1}{2}\alpha + \csc\tfrac{1}{2}\alpha)\varphi_0^A + (2\pi^{-1}/\rho)(1 - \sin\alpha\cos\theta)^{-1/2} , \tag{76}$$

$$\nabla_6^2 \varphi_2^A = -(2/\rho)(\sec\tfrac{1}{2}\alpha + \csc\tfrac{1}{2}\alpha)\varphi_1^A + 2\varphi_0^A - 2\pi^{-1}E_1^A - 2\pi^{-1}(\sin\tfrac{1}{2}\alpha + \cos\tfrac{1}{2}\alpha)(1 - \sin\alpha\cos\theta)^{-1/2} , \tag{77}$$

$$\vdots$$

The results of solving these equations are [note that $\varphi_n^A(\vec{r}_1 \mid \vec{r}_2) = \varphi_n^A(\vec{r}_2 \mid \vec{r}_1)$ for singlet states]

$$\varphi_0^A(1 \mid 2) = N_A , \tag{78}$$

$$\varphi_1^A(1 \mid 2) = -N_A(r_1 + r_2) + \tfrac{1}{2}\pi^{-1} r_{12} , \tag{79}$$

$$\varphi_2^A(1 \mid 2) = \tfrac{1}{2}N_A(r_1 + r_2)^2 - \tfrac{1}{6}\pi^{-1}E_1^A(r_1^2 + r_2^2) - [(\pi - 2)/3\pi^2] r_1 r_2 \cos\theta \ln(r_1^2 + r_2^2) + (4\pi)^{-1} \sum_{n=0}^{\infty} \sum_{l=0}^{n} \frac{R_{n,l}^A}{(n-1)(n+3)} \rho^2 \Phi_{n,l}(\alpha, \theta) + a_1 r_1 r_2 \cos\theta , \tag{80}$$

$$\varphi_3^A(1 \mid 2) = -\tfrac{1}{6}N_A(r_1 + r_2)^3 + \tfrac{1}{18}\pi^{-1}E_1^A(2r_1^3 + 3r_1^2 r_2 + 3r_1 r_2^2 + 2r_2^3) + \tfrac{1}{24}\pi^{-1} r_{12}^3 - \tfrac{1}{2} a_1 (r_1 + r_2) r_1 r_2 \cos\theta + \chi_3^A(1 \mid 2) , \tag{81}$$

$$\varphi_4^A(1 \mid 2) = -[(\pi - 2)/60\pi^2](4r_1^2 + 5r_1 r_2 + 4r_2^2) r_1 r_2 \cos\theta \ln(r_1^2 + r_2^2) + a_2(3r_1^2 - r_2^2)(r_1^2 - 3r_2^2)\ln(r_1^2 + r_2^2) + a_3 r_1^2 r_2^2 (3\cos^2\theta - 1)\ln(r_1^2 + r_2^2) + O(\rho^4) . \tag{82}$$

The constants N_A and a_1 are not determined by this type of analysis. The constants $R_{n,l}^A$ are defined by

$$R_{n,l}^A = \langle \Phi_{n,l}(\alpha, \theta), R^A(\alpha, \theta) \rangle_\Omega , \tag{83}$$

where

$$R^A(\alpha, \theta) = (\sec\tfrac{1}{2}\alpha + \csc\tfrac{1}{2}\alpha)(1 - \sin\alpha\cos\theta)^{1/2} + 2(\sin\tfrac{1}{2}\alpha + \cos\tfrac{1}{2}\alpha)(1 - \sin\alpha\cos\theta)^{-1/2} \tag{84}$$

and the $\Phi_{n,l}$ are defined by (47). The integral $\langle , \rangle_\Omega$ in (83) refers to an angular integration [as in (52)]. The constants a_2 and a_3 are given by similar angular integrations, but we have not evaluated them explicitly. They are fixed numbers, however, and could be determined. It is even possible for them to be zero, but we feel that this is not very likely. The function χ_3^A [in (81)] is the solution to the equation

$$\nabla_6^2 \chi_3^A = \frac{2(\pi - 2)}{3\pi^2}(r_1 + r_2)\cos\theta \ln(r_1^2 + r_2^2) + \frac{\pi^{-1}}{r_{12}}(r_1 + r_2)^2 - (2\pi)^{-1}\rho(\sec\tfrac{1}{2}\alpha + \csc\tfrac{1}{2}\alpha) \times \sum_{\substack{n=0 \\ n\neq 1}}^{\infty} \sum_{l=0}^{n} \frac{R_{n,l}^A}{(n-1)(n+3)} \Phi_{n,l}(\alpha, \theta) . \tag{85}$$

Note that χ_3^A must contain the term

$$+[(\pi - 2)/6\pi^2](r_1 + r_2) r_1 r_2 \cos\theta \ln(r_1^2 + r_2^2)$$

as well as terms of order ρ^3. We will find, however, that we do not need χ_3^A for our particular application.

These results, (78)–(82), agree with similar results obtained by the use of Fock's original method.[3,22,23]

Applying a similar technique to (70) yields [$\varphi_n^B(\vec{r}_1, \vec{r}_2) = -\varphi_n^B(\vec{r}_2, \vec{r}_1)$ for triplet states]

$$\varphi_0^B(1, 2) = N_B(r_1^2 - r_2^2), \tag{86}$$

$$\varphi_1^B(1, 2) = -\tfrac{2}{3}N_B(r_1 - r_2)(r_1^2 + r_2^2 + \tfrac{5}{2} r_1 r_2) + \tfrac{1}{128}\pi^{-1}(r_1^2 - r_2^2) r_{12}, \tag{87}$$

$$\varphi_2^B(1, 2) = N_B[\tfrac{11}{48}(r_1^4 - r_2^4) + \tfrac{2}{3} r_1 r_2 (r_1^2 - r_2^2)] - (320\pi)^{-1}\Big\{E_1^B(r_1^4 - r_2^4) + \frac{1}{3}(r_1^3 - r_2^3) r_{12} + \frac{2(7\pi - 20)}{3\pi} \times (r_1^2 - r_2^2) r_1 r_2 \cos\theta \ln(r_1^2 + r_2^2) - \frac{1}{4}\rho^4 \sum_{\substack{n=0 \\ (n\neq 2)}}^{\infty} \sum_{l=0}^{n} \frac{R_{n,l}^B}{(n-2)(n+4)} \Phi_{n,l}(\alpha, \theta)\Big\} + b_1(r_1^2 - r_2^2) r_1 r_2 \cos\theta . \tag{88}$$

The constants N_B and b_1 are not determined by this anaylsis, but the $R_{n,l}^B$ are given by

$$R^B_{n,l} = \langle \Phi_{n,l}(\alpha, \theta), R^B(\alpha, \theta) \rangle_\Omega \,, \tag{89}$$

where

$$R^B(\alpha, \theta) = 5(\csc\tfrac{1}{2}\alpha \cos^{2}\tfrac{1}{2}\alpha - \sec\tfrac{1}{2}\alpha \sin^{2}\tfrac{1}{2}\alpha)(1 - \sin\alpha\cos\theta)^{1/2} + 11(\cos^{3}\tfrac{1}{2}\alpha - \sin^{3}\tfrac{1}{2}\alpha)(1 - \sin\alpha\cos\theta)^{-1/2}$$
$$+ 19(\sin\tfrac{1}{2}\alpha \cos^{2}\tfrac{1}{2}\alpha - \cos\tfrac{1}{2}\alpha \sin^{2}\tfrac{1}{2}\alpha)(1 - \sin\alpha\cos\theta)^{-1/2} \,, \tag{90}$$

and where the $\langle\,,\,\rangle_\Omega$ integration is the same angular integration as in (83). This state has also been analyzed by the Fock technique.[24,25]

Proceeding to analyze (71) we obtain

$$\varphi_0^c(1\,|\,2) = N_c \,, \tag{91}$$

$$\varphi_1^c(1\,|\,2) = -N_c(r_1 + r_2) + \tfrac{1}{4}\pi^{-1} r_{12} \,, \tag{92}$$

$$\varphi_2^c(1\,|\,2) = N_c[\tfrac{7}{16}(r_1^2 + r_2^2) + r_1 r_2] - \tfrac{1}{12}\pi^{-1} E_1^c(r_1^2 + r_2^2) - \frac{(\pi - 2)}{6\pi^2} r_1 r_2 \cos\theta \ln(r_1^2 + r_2^2)$$
$$+ (8\pi)^{-1} \sum_{\substack{n=0 \\ (n\neq 1)}}^{\infty} \sum_{l=0}^{n} \frac{R^A_{n,l}}{(n-1)(n+3)} \rho^2 \Phi_{n,l}(\alpha, \theta) + c_1 r_1 r_2 \cos\theta \,, \tag{93}$$

$$\varphi_3^c(1\,|\,2) = -\tfrac{1}{16} N_c(2r_1^3 + 7r_1^2 r_2 + 7r_1 r_2^2 + 2r_2^3) + \tfrac{1}{36}\pi^{-1} E_1^c(2r_1^3 + 3r_1^2 r_2 + 3r_1 r_2^2 + 2r_2^3)$$
$$+ \tfrac{1}{128}\, 3\pi^{-1} r_{12}^3 - \tfrac{1}{64}\pi^{-1} r_{12}(r_1^2 + r_2^2) - \tfrac{1}{2} c_1 (r_1 + r_2) r_1 r_2 \cos\theta + \tfrac{1}{2}\chi_3^A(1\,|\,2) \,, \tag{94}$$

$$\varphi_4^c(1\,|\,2) = -[(\pi - 2)/480\pi^2](13r_1^2 + 20r_1 r_2 + 13r_2^2) r_1 r_2 \cos\theta \ln(r_1^2 + r_2^2) + c_2(3r_1^2 - r_2^2)(r_1^2 - 3r_2^2)\ln(r_1^2 + r_2^2)$$
$$+ c_3 r_1^2 r_2^2 (3\cos^2\theta - 1)\ln(r_1^2 + r_2^2) + O(\rho^4) \,. \tag{95}$$

N_c and c_1 are undetermined, $R^A_{n,l}$ is given by (83), χ_3^A is the solution to (85), and the constants c_2 and c_3 have not been determined (but could have been).

Combining the results of (78)–(82), (86)–(88), and (91)–(95) according to (68) and expanding the result near the nucleus ($r_1^2 + r_2^2 + r_3^2 = 0$) we obtain

$$\Phi_1(1, 2\,|\,3) = \tfrac{1}{4}\pi^{-1/2}(\tfrac{1}{8}N_A + 6N_B + \tfrac{1}{8}N_c + \tfrac{1}{2}a_1 - c_1 - E_1^A/6\pi + E_1^C/6\pi)[(r_1^2 - r_2^2) + \tfrac{1}{3}(r_1^3 - r_2^3) - (r_1 + r_2 + r_3)(r_1^2 - r_2^2) + O(\rho^4)]$$
$$+ \tfrac{1}{4}\pi^{-1/2}(c_1 - \tfrac{1}{2}a_1)\{(r_{13}^2 - r_{23}^2) - \tfrac{1}{6}(r_1^3 - r_2^3) - (r_1 + r_2 + r_3)(r_{13}^2 - r_{23}^2) + \tfrac{1}{2}[r_{13}^2(r_1 + r_3) - r_{23}^2(r_2 + r_3)]$$
$$- \tfrac{1}{2}(r_1 - r_2)(r_1 + r_2 + r_3) r_3 + O(\rho^4)\}$$
$$+ \tfrac{1}{64}\pi^{-3/2}\{(r_{12} + r_{13} + r_{23})(r_1^2 - r_2^2) - \tfrac{1}{12}(r_{13}^3 - r_{23}^3) - \tfrac{1}{4}[2r_{12}(r_1^2 - r_2^2) + r_{13}(r_1^2 - r_3^2) + r_{23}(r_3^2 - r_2^2)] + O(\rho^4)\}$$
$$+ \tfrac{1}{4}\pi^{-1/2}\{(\pi - 2)/80\pi^2[(r_2^2 + r_3^2) r_2 r_3 \cos\theta_{23} - (r_1^2 + r_3^2) r_1 r_3 \cos\theta_{13}]\ln\rho^2 - (7\pi - 20)/240\pi^2$$
$$\times [2(r_1^2 - r_2^2) r_1 r_2 \cos\theta_{12} + (r_1^2 - r_3^2) r_1 r_3 \cos\theta_{13} + (r_3^2 - r_2^2) r_2 r_3 \cos\theta_2]$$
$$\times \ln\rho^2 + (a_2 - 2c_2)(r_1^2 - r_2^2)(3r_1^2 + 3r_2^2 - 10r_3^2)\ln\rho^2$$
$$+ (a_3 - 2c_3)[r_1^2 r_3^2(3\cos^2\theta_{13} - 1) - r_2^2 r_3^2(3\cos^2\theta_{23} - 1)]\ln\rho^2 + O(\rho^4)\} \,, \tag{96}$$

where $\rho^2 = r_1^2 + r_2^2 + r_3^2$.

By expanding Φ_0, Eq. (66), as

$$\Phi_0(1, 2\,|\,3) = \tfrac{1}{32}\pi^{-3/2}[(r_1^2 - r_2^2) + \tfrac{1}{3}(r_1^3 - r_2^3) - (r_1 + r_2 + r_3)(r_1^2 - r_2^2) + O(\rho^4)] \tag{97}$$

and combining this result with (96) we obtain an expansion of the three-electron atomic wave function

$$\Phi(1, 2\,|\,3) = \Phi_0(1, 2\,|\,3) + \lambda\Phi_1(1, 2\,|\,3) + O(\lambda^2) \tag{98}$$

correct to $O(Z^{-2})$ and $O(\rho^4)$. The terms of $O(\rho^3)$ in this result reflect the two-body interactions ("cusplike" behavior), while the terms of $O(\rho^4 \ln\rho)$ are manifestations of three-body effects (electron-electron-nucleus). The fact that the wave function has a leading-order ρ^2 term is a simple consequence of the restrictions [Eqs. (2) and (3)] imposed by the Fermi statistics and the requirement that Φ represent a pure spin state.

VI. NODAL HYPERSURFACE IN THREE-ELECTRON ATOM

In recent years it has become possible to perform variational calculations of the Hartree-Fock–type routinely for small atoms and molecules. However, it has also become clear that theoreticians must progress beyond the Hartree-Fock level and account for the correlation effects in these small systems if an *ab initio* theory is to be

used to explain experiment accurately. One of the more interesting attempts to include correlation effects directly in wave-mechanical calculations has been advocated recently by Boys and Handy.[26–28] The technique they introduce, called the transcorrelated method, expresses the wave function for an electronic system as the product of a "correlation function" C and an "orbital function" Φ:

$$C\Phi \ . \tag{99}$$

The correlation function C is required to be a completely symmetric function of the spatial variables and the orbital function Φ possesses the symmetry required by the Pauli principle and by the fact that the function $C\Phi$ should represent a pure spin state, as well as any other symmetry peculiar to the particular system being studied. In actual practice the orbital function Φ has taken the form of a simple antisymmetrized product of spin orbitals. This last restriction is imposed for computational convenience and is certainly not necessary to the general method.

This limitation on Φ (to a simple antisymmetrized product) can have one effect that may be unfortunate in certain cases. Since the function C is chosen to be positive and completely symmetric, it can possess no nodes. Thus the nodal hypersurfaces of the true wave function must be reflected in the orbital function Φ if equality of the approximate function $C\Phi$ and the exact function is to obtain. Let us examine the effect that limiting Φ to a simple antisymmetrized product has for the case of the ground state of the three-electron atomic system being studied in this paper. In spin-free terms the approximation (99) with Φ limited to a simple doubly filled orbital function would be

$$C(\vec{r}_1, \vec{r}_2, \vec{r}_3)[\varphi_1(r_1)\varphi_2(r_2) - \varphi_2(r_1)\varphi_1(r_2)]\varphi_1(r_3). \tag{100}$$

It is obvious that this function has a nodal surface at $r_1 = r_2$.

The question now arises as to the character of the true nodal surface for this system. The wave function, in general, for this state of a three-electron atomic system is a function of six variables and must obey Eqs. (2) and (3). It must also correspond to a solution of the Schrödinger equation, but Eqs. (2) and (3) alone partially dictate the nature of the nodal structure (since the Hamiltonian is a completely symmetric function). From Eq. (2) we can conclude that the exact eigenfunction possesses a nodal surface containing $\vec{r}_1 = \vec{r}_2$. We might at first guess that this is all we need to know, but the harmonic model studied in Sec. III indicates this is not the case.

We are not equipped mathematically to study the general nodal implications of Eqs. (2) and (3) taken together, but we can examine the character of the wave function for the ground state of our three-electron atomic system in the vicinity of the nucleus and determine the nature of the nodal structure in this region at least.

In Sec. V we obtained the leading-order terms (in ρ) of the wave function near the nucleus correct to $O(Z^{-2})$. We can do a little better than this by applying our expansion technique[18] directly to the Schrödinger equation

$$H\Phi(\vec{r}_1, \vec{r}_2 | \vec{r}_3) = E\Phi(\vec{r}_1, \vec{r}_2 | \vec{r}_3) \ , \tag{101}$$

where H is given by Eq. (61) and $\Phi(\vec{1}, \vec{2} | \vec{3})$ represents the exact spatial eigenfunction [not an orbital product as in (99)].

The result we obtain [the coordinate system given by Eq. (7) is relevant to this analysis] is

$$\begin{aligned}\Phi(\vec{r}_1, \vec{r}_2 | \vec{r}_3) = A\{&(r_1^2 - r_2^2) + \tfrac{1}{3}(r_1^3 - r_2^3) - (r_1 + r_2 + r_3)(r_1^2 - r_2^2) + \tfrac{1}{2}\lambda(r_{12} + r_{13} + r_{23})(r_1^2 - r_2^2) + \tfrac{1}{24}\lambda(r_{13}^3 - r_{23}^3) \\ &- \tfrac{1}{8}\lambda[2r_{12}(r_1^2 - r_2^2) + r_{13}(r_1^2 - r_3^2) + r_{23}(r_3^2 - r_2^2)] + O(\rho^4 \ln\rho)\} + B\{(r_{13}^2 - r_{23}^2) - \tfrac{1}{6}(r_1^3 - r_2^3) \\ &- (r_1 + r_2 + r_3)(r_{13}^2 - r_{23}^2) + \tfrac{1}{2}[r_{13}^2(r_1 + r_3) - r_{23}^2(r_2 + r_3)] - \tfrac{1}{2}(r_1 - r_2)(r_1 + r_2 + r_3)r_3 \\ &+ \tfrac{3}{8}\lambda(r_{12} + r_{13} + r_{23})(r_{13}^2 - r_{23}^2) - \tfrac{1}{8}\lambda(r_{12} + r_{13} + r_{23})(r_{13} - r_{23})r_{12} + O(\rho^4 \ln\rho)\} \ , \end{aligned} \tag{102}$$

where $\rho^2 = r_1^2 + r_2^2 + r_3^2$. We still do not know the values of A and B except that B must be of order λ [by Eqs. (96) and (98)] while A is of order λ^0. Their ratio is what matters here, and we estimate this ratio (in the particular case of the neutral atom, $\lambda = \frac{1}{3}$) to be

$$B/A \cong 0.04. \tag{103}$$

We obtained this estimate by calculating the ratio B/A for the simple wave function $C_1\Phi_1 + C_2\Phi_2$ where $\Phi_1 : 1s^2 2s$ configuration and $\Phi_2 : 1s2p^2$ configuration with the orbitals taken as scaled hydrogenics and by comparing this with the corresponding ratio calculated for the case

$$\Phi_1 = N_1(r_1^2 - r_2^2)\, e^{-\alpha\rho} \ ,$$

$$\Phi_2 = N_2(r_1 r_3 \cos\theta_{13} - r_2 r_3 \cos\theta_{23})\, e^{-\alpha\rho} \ ,$$

where $\rho^2 = r_1^2 + r_2^2 + r_3^2$ and α is a variational parameter. Since this latter function is a very poor wave

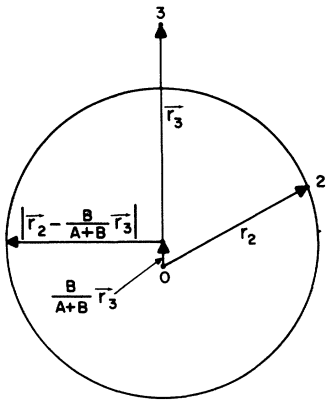

FIG. 3. Nodal character of the ground-state eigenfunction of the three-electron atom for sufficiently small ρ ($\rho^2 = r_1^2 + r_2^2 + r_3^2$). The positions of one α-electron $\vec{2}$, and one β-electron $\vec{3}$, are fixed. [See the discussion after Eq. (107).] The sphere shown is centered at $[B/(A+B)]\vec{r}_3$ and has radius $|\vec{r}_2 - [B/(A+B)]\vec{r}_3|$.

function from an energy standpoint and since the ratio B/A was of the same order of magnitude as in the former more accurate calculation ($B/A = 0.036$, hydrogenics; $B/A = 0.020$, hyperspherical) we have made the choice (103). The calculations to be mentioned below were checked with values of B/A in the range 0.02–0.04 and the same qualitative effect was noticed for each case.

We approach the nodal surface problem near the nucleus by considering the nodal structure of $\Phi(\vec{1}, \vec{2} \mid \vec{3})$ for $\rho < \rho_0$, where $\rho^2 = r_1^2 + r_2^2 + r_3^2$ and ρ_0 is a constant. If we choose ρ_0 small enough, then the wave function

$$\Phi(\vec{1}, \vec{2} \mid \vec{3}) = \rho^2 F_2(\Omega) + \rho^3 F_3(\Omega) + \cdots \tag{104}$$

is effectively described by the term $\rho^2 F_2(\Omega)$. Here Ω denotes the set of hyperspherical angles given by Eq. (7). Furthermore for small ρ_0 we can consistently consider the term $\rho^3 F_3(\Omega)$ as a perturbative effect in estimating the next-order behavior.

We thus first examine the nodal character of the term

$$\rho^2 F_2(\Omega) = A(r_1^2 - r_2^2) + B(r_{13}^2 - r_{23}^2) . \tag{105}$$

When $\rho^2 F_2 = 0$ we have ($A \neq 0$)

$$r_1^2 - r_2^2 = (B/A)(r_{23}^2 - r_{13}^2) . \tag{106}$$

For fixed-α-spin electrons $\vec{1}$ and $\vec{2}$, Eq. (106) is satisfied when electron $\vec{3}$ moves in a plane such that

$$\vec{r}_{12} \cdot [(1 + B/A)(\vec{r}_1 + \vec{r}_3) - 2(B/A)\vec{r}_3] = 0 . \tag{107}$$

If the positions of one α electron, say $\vec{r}_2$, and one β electron $\vec{r}_3$ are fixed, the quadratic equation (106) implies that the remaining α electron $\vec{1}$ is restricted to a spherical surface. In fact, this $\vec{r}_1$ sphere has its center at $[B/(A+B)]\vec{r}_3$ and its radius is $|\vec{r}_2 - [B/(A+B)]\vec{r}_3|$. In Fig. 3 we have drawn this nodal surface for particular fixed $\vec{r}_2$ and $\vec{r}_3$. To this order in ρ we have already discovered nodal surfaces different from those predicted by the orbital approximation[15] or by the simple transcorrelated model, Eq. (100).

We now inquire into the effect of the cubic terms in ρ (104) on the spherical nodal surface just obtained. For fixed $\vec{r}_2$ and $\vec{r}_3$ we write Eq. (104) as

$$\Phi(1, 2 \mid 3) = f_2(\vec{r}_1) + f_3(\vec{r}_1) + \cdots , \tag{108}$$

where $\rho^2 F_2 \equiv f_2$, $\rho^3 F_3 \equiv f_3$ and only the dependence on $\vec{r}_1$ has been explicitly indicated. Let $\vec{r}_1^*$ denote those $\vec{r}_1$ for which $f_2(\vec{r}_1) = 0$ (the sphere discussed above and shown in Fig. 3). We wish to investigate the nodal character of $f_2 + f_3$, and so we write $\vec{r}_1 = \vec{r}_1^* + \delta\vec{r}_1$ and inquire into the effect produced by this change in $\vec{r}_1$. We have, including terms of $O(\rho^3)$,

$$f_2(\vec{r}_1^* + \delta\vec{r}_1) + f_3(\vec{r}_1^* + \delta\vec{r}_1) = f_2(\vec{r}_1^*) + \nabla f_2(r_1^*) \cdot \delta\vec{r}_1 + \cdots + f_3(\vec{r}_1^*) + \cdots = 0 . \tag{109}$$

But $\vec{r}_1^*$ is chosen so that $f_2(\vec{r}_1^*) = 0$ and the surface described by $f_2(\vec{r}_1^*) = 0$ is spherical. This means the gradient of f_2 evaluated on $\vec{r}_1^*$ is normal to the spherical surface and is constant in magnitude [$= |\nabla f_2(r_1^*)|$]. From Eq. (109) we have (neglecting higher-order terms)

$$\nabla f_2(\vec{r}_1^*) \cdot \delta\vec{r}_1 = -f_3(\vec{r}_1^*) . \tag{110}$$

This is the desired result. Equation (110) states that the change in the spherical nodal surface induced by the cubic terms (in ρ) is proportional to the value of the cubic terms on the original spherical nodal surface.

Thus, we fix $\vec{r}_2$ and $\vec{r}_3$ at various positions, evaluate the cubic terms implied by Eq. (102) on the spherical surface shown in Fig. 3, and obtain essentially the shift in the nodal surface. When we repeat this procedure for a wide variety of $\vec{r}_2$, $\vec{r}_3$ we find that the result indicates definite asphericity present in the nodal surface.

For example, if we fix $\vec{r}_2 = \vec{r}_3$ and evaluate the cubic terms on the original spherical surface, we arrive at Fig. 4. If this displacement were to correspond to a simple expansion or contraction plus translation of the original spherical surface we would expect a simple sine curve. To show that this does not obtain we have also plotted the difference between the actual result and the simple sine curve

$$0.220(1 - \sin\varphi) , \tag{111}$$

chosen to fit the maximum and minimum of the actual displacement curve. Note that the definite presence of higher harmonics (asphericity) is indicated.

In Fig. 5, we examine the case where $\vec{r}_2 = -2\vec{r}_3$. A displacement curve similar to the previous one

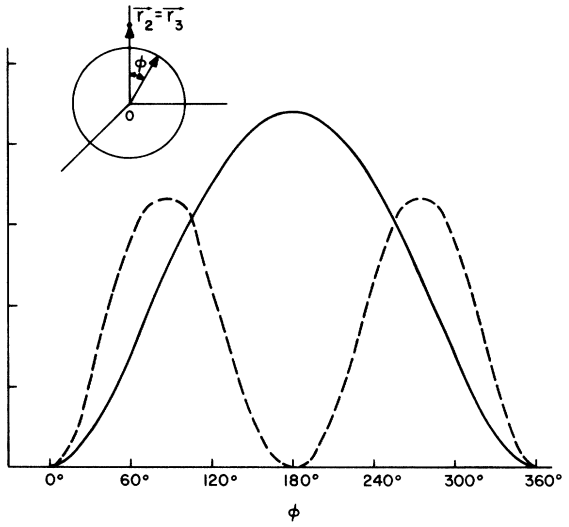

FIG. 4. Displacement of the spherical nodal surface near the nucleus as given by the cubic terms of Eq. (102), for the particular case $\vec{r}_2=\vec{r}_3$ (solid line). Also shown is the error made by Eq. (111) (dashed line). The two curves are not drawn to the same scale; the maximum error is about 15% of the actual displacement.

is found. The difference between the true displacement and that given by the simple sine curve,

$$-0.632\,(1+\sin\varphi)\,, \tag{112}$$

is also shown and indicates asphericity once more.

Finally, we fix $r_2=2r_3$, $\theta_{23}=\frac{1}{2}\pi$ and look at the displacement given by the cubic terms in two perpendicular planes. Figure 6 portrays the displacement in the plane containing $\vec{r}_2$ and $\vec{r}_3$, and also shows the difference between this displacement and that given by the sinusoidal representation

$$-0.693\sin\varphi\,. \tag{113}$$

Figure 7 shows the displacement in a plane containing $\vec{r}_3$ and perpendicular to $\vec{r}_2$. Also shown is the difference between the displacement curve and the curve

$$-0.689\sin\varphi\,. \tag{114}$$

Note that the difference curves shown in Figs. 4–7 have been scaled so as to be more legible. Also, we have not labeled the ordinate because the ultimate magnitude of the displacement depends on the choice of ρ_0.

These cases, and other similar cases considered, lead us to believe that the nodal hypersurface (corresponding to one fixed-α-spin and one fixed-β-spin electron) in general is definitely aspherical. Of course, our study here has been confined, of necessity, to small ρ only. But it is difficult to see why one would obtain qualitatively different results for any finite ρ.

Does this mean that we expect an approximation, like the simple transcorrelation approximation Eq. (100), to be seriously in error? The answer to this question probably depends on the meaning imparted to the word "seriously." The effect of the nodal surface is undoubtedly a small one [owing to the ratio (103)] as far as the total energy goes. But it may be that certain properties are much more sensitive to the nodal character of the approximation employed for the wave function, and for these properties the effect may be serious if very accurate results are desired. It would be very interesting to study this point in more detail.

VII. THREE-ELECTRON COALESCENCE AWAY FROM NUCLEUS

We now wish to examine the effect that bringing the three electrons together away from the nucleus has on the wave function for the atomic system described by the Hamiltonian of Eq. (62). This Hamiltonian may be written in the form (in appropriate units)

$$H=-\tfrac{1}{2}\,(\nabla_1^2+\nabla_2^2+\nabla_3^2)+U_0(\vec{r}_1,\,\vec{r}_2,\,\vec{r}_3)+\lambda V(\vec{r}_1,\,\vec{r}_2,\,\vec{r}_3), \tag{115}$$

where

$$U_0=-1/r_1-1/r_2-1/r_3\,,$$
$$V=1/r_{12}+1/r_{13}+1/r_{23}\,. \tag{116}$$

Since we wish to limit our considerations to the

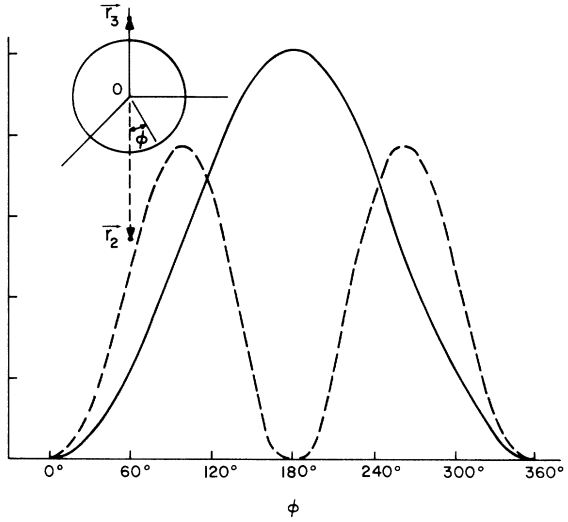

FIG. 5. Negative of the displacement of the spherical nodal surface near the nucleus as given by the cubic terms of Eq. (102), for the particular case $\vec{r}_2=-2\vec{r}_3$ (solid line). Also shown is the error made by Eq. (112) (dashed line). The two curves are not drawn to the same scale; the maximum error is about 7.6% of the actual displacement.

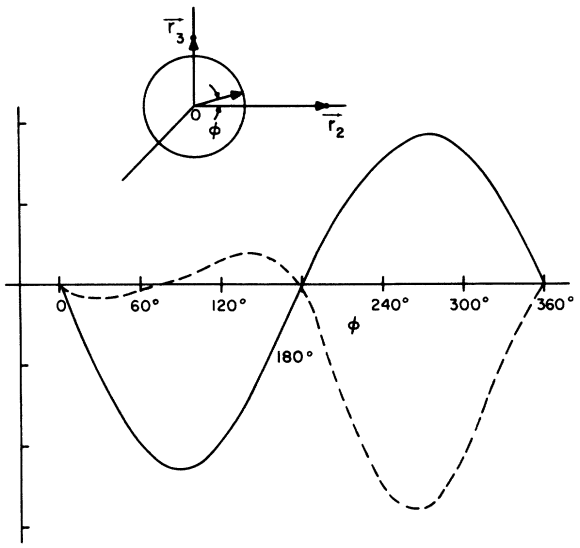

FIG. 6. Displacement of the spherical nodal surface near the nucleus as given by the cubic terms of Eq. (102), for the particular case $r_2 = 2r_3$, $\theta_{23} = \frac{1}{2}\pi$. The displacement drawn here (solid line) is in the plane containing $\vec{r}_2$ and $\vec{r}_3$. The error made by Eq. (113) is also shown (dashed line). The two curves are not drawn to the same scale; the maximum error is about 21% of the actual displacement.

particular situation where all three electrons are a finite distance away from the nucleus, it is convenient to introduce the center-of-mass coordinates (12). Note that

$$\begin{aligned} r_1^2 &= \tfrac{1}{3}R_1^2 + \tfrac{1}{2}R_2^2 + \tfrac{1}{6}R_3^2 + \tfrac{1}{3}\sqrt{6}\,R_1R_2\cos\Theta_{12} \\ &\quad - \tfrac{1}{3}\sqrt{2}\,R_1R_3\cos\Theta_{13} - \tfrac{1}{3}\sqrt{3}\,R_2R_3\cos\Theta_{23}\,, \\ r_2^2 &= \tfrac{1}{3}R_1^2 + \tfrac{1}{2}R_2^2 + \tfrac{1}{6}R_3^2 - \tfrac{1}{3}\sqrt{6}\,R_1R_2\cos\Theta_{12} \\ &\quad - \tfrac{1}{3}\sqrt{2}\,R_1R_3\cos\Theta_{13} + \tfrac{1}{3}\sqrt{3}\,R_2R_3\cos\Theta_{23}\,, \\ r_3^2 &= \tfrac{1}{3}R_1^2 + \tfrac{2}{3}R_3^2 + \tfrac{2}{3}\sqrt{2}\,R_1R_3\cos\Theta_{13}\,, \end{aligned} \tag{117}$$

and that the r_{ij} are given by Eq. (25). Θ_{ij} represents the angle between $\vec{R}_i$ and $\vec{R}_j$.

It is also convenient to introduce the coordinates [cf. Eq. (32)]

$$\begin{aligned} &\rho^2 = R_2^2 + R_3^2\,, \quad \infty > \rho \geq 0 \\ &\tan\tfrac{1}{2}\alpha = R_2/R_3,\ \pi \geq \alpha \geq 0 \end{aligned} \tag{118}$$

in place of R_2 and R_3 because our interest here lies in that region of configuration space where R_2 and R_3 are simultaneously small (ρ small). In terms of these coordinates (R_1, ρ, α, Θ_{12}, Θ_{13}, Θ_{23}) we have

$$H = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - 3\sqrt{3}/R_1 + \lambda V(\rho, \alpha, \Theta_{23}) + H'\,, \tag{119}$$

where

$$H' = 3\sqrt{3}/R_1 - 1/r_1 - 1/r_2 - 1/r_3 \sim O(\rho^2/R_1^3)\,,$$

$$\begin{aligned} V = (1/\rho)[&2^{-1/2}\csc\tfrac{1}{2}\alpha \\ &+ 2^{1/2}(2 + \cos\alpha + 3^{1/2}\sin\alpha\cos\Theta_{23})^{-1/2} \\ &+ 2^{1/2}(2 + \cos\alpha - 3^{1/2}\sin\alpha\cos\Theta_{23})^{-1/2}]\,. \end{aligned}$$

We now treat the Schrödinger equation

$$(H - E)\,\Phi = 0 \tag{120}$$

by perturbation theory, with H' as the perturbation. Owing to the order of H' in both ρ and R_1, we expect the effect of this perturbation to be particularly small when R_1 is large and ρ is small. Thus if we set

$$H = H_0 + H' \tag{121}$$

and expand the wave function and energy similarly ($\Phi = \Phi_0 + \Phi_1 + \cdots$, $E = E_0 + E_1 + \cdots$), we are led to the zeroth-order problem

$$(H_0 - E_0)\,\Phi_0 = 0\,. \tag{122}$$

We now observe that the center-of-mass motion $\vec{R}_1$ may be separated off, and for the ground state ($\Theta_{23} = \theta$) we have

$$\Phi_0 = 3^{9/4}\pi^{-1/2}\,e^{-3^{3/2}R_1}\,\psi(\rho, \alpha, \theta)\,, \tag{123}$$

where ψ is the solution to

$$[-\tfrac{1}{2}(\nabla_2^2 + \nabla_3^2) + \lambda V - \epsilon]\,\psi = 0\,, \tag{124}$$

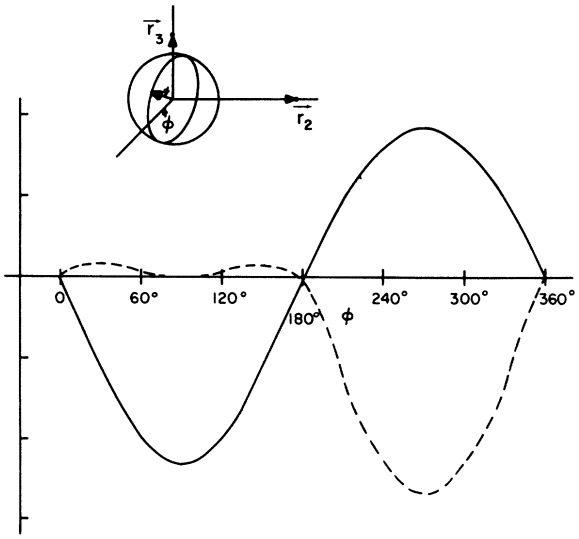

FIG. 7. Displacement of the spherical nodal surface near the nucleus as given by the cubic terms of Eq. (102), for the particular case $r_2 = 2r_3$, $\theta_{23} = \frac{1}{2}\pi$. The displacement drawn here (solid line) is in the plane containing $\vec{r}_3$ and perpendicular to $\vec{r}_2$. The error made by Eq. (114) is also shown. The two curves are not drawn to the same scale; the maximum error is about 19% of the actual displacement.

with $\epsilon = E_0 + \frac{27}{2}$. The Laplacian in (124) has previously been given by Eqs. (33) and (34).

Proceeding to analyze Eq. (124), following Eqs. (38)–(61) *step by step* ($V = 2^{-1/2} U/\rho$), we find *exactly* the same result, Eq. (61) (to this order in ρ). Thus we have (in interparticle coordinates)

$$\psi = 3^{-1/2} N \{(r_{23}^2 - r_{13}^2) + \tfrac{1}{8}\lambda (r_{23} - r_{13})(r_{12} + r_{13} + r_{23}) \times (3r_{13} + 3r_{23} - r_{12}) + (6\pi)^{-3/2} N^{-1} R_{2,1}(r_{23}^2 - r_{13}^2) \times (r_{13}^2 + r_{23}^2 - 2r_{12}^2) \ln(r_{12}^2 + r_{13}^2 + r_{23}^2) + O(\rho^4)\}, \quad (125)$$

where $R_{2,1}$ is given by Eq. (60).

This result reinforces the intuitive notion introduced in Sec. IV that, as long as the electrons were not in the immediate vicinity of the nucleus, the main effect of the nuclear-electron interaction terms is to bind the electrons to the nucleus.

In that region of configuration space where $R_1 > 0$ and $R_1 \gg \rho$, the perturbation H' affects the wave function only in higher-order terms (than $\rho^4 \ln \rho$), and Φ_0 (123) should thus exhibit precisely the behavior of the exact wave function to this ρ order.

VIII. DISCUSSION

Of the features of electron correlation in three-electron atoms and ions that we have examined in this paper, perhaps the most interesting is the nodal structure of the spatial wave function. We have been able to study the problem only in a relatively crude way, confining ourselves to simple models and to a study of the actual atomic system near the nucleus. The real importance of the nodal structure in actual calculations, both of the energy and of various properties is yet to be decided. It would be extremely interesting to study the nodal surface implied by large configuration interaction treatments or by direct analysis using r_{ij} (Hylleraas) coordinates, and then to determine just what the convergence properties of the simple transcorrelated method are (where the nodal surfaces are incorrectly placed).

It should also prove interesting to study the nodal characteristics of simple molecular systems and to correlate the nodal surfaces with those of the atom to clarify the effect of chemical bond formation. In this connection, nodal surfaces for a hydrogen atom in a static magnetic field have recently found application to exciton magneto-optical spectra in semiconductors.[29] Here the simple idea of conservation of the number of nodal surfaces leads to an appealing interpretation of the fine structure of the observed spectra of GaSe.

The fact that the exact expansion of the wave function in the vicinity of the nucleus can be rather easily obtained may be of some use to those who perform large variational calculations on this three-electron system, both by offering suggestions as to the type of terms of dominant importance and by checking the convergence in one region of configuration space.

The explicit form of the various logarithmic singularities in the wave function are interesting as well, since these terms represent the leading-order three-body effects in the wave function. The universality of these terms for all atoms and molecules is worth mentioning, and, for example, whenever two α-spin electrons and one β-spin electron coalesce, away from other particles, terms of the form $\rho^4 \ln\rho$ must be present in the wave function ($\rho \sim$ small distance variable for the coalescence). There is one further three-body effect to be examined: that present when three α-spin electrons coalesce away from other particles. We have not investigated this effect, but feel that it certainly produces nonanalytic terms of higher order than $\rho^4 \ln\rho$. Computationally speaking, variational calculations have probably not yet progressed to the point where direct incorporation of the various three-electron logarithmic terms is currently required. However, they may be of some importance as the ability to perform highly accurate calculations improves, since the inefficient representation of these singular terms is probably responsible for the ultimate slowness of the wave-function convergence, even in applications using direct r_{ij} coordinates.

It would also be interesting to explore the nature of true four-body effects in small systems, but this may have to await development of new approaches to the quantum-mechanical theory.

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Evaluation of Approximations to Hartree-Fock Exchange*

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Approximations to the Hartree-Fock (HF) exchange energy density have been derived directly from the HF exchange energy density. The approximations involving two free parameters take the form of a Kohn-Sham-Gaspar (KSG) exchange energy density plus inhomogeneity corrections. The approximation including lowest-order inhomogeneity corrections only is equivalent to the approximation recently proposed by Herman, Van Dyke, and Ortenburger. An approximation including the next-higher-order inhomogeneity corrections with no additional parameters is also derived. The approximations have been evaluated by direct comparison with the actual HF exchange energy density for Ar and Cu^+. The optimum choices of parameters in the case of the approximation including lowest-order inhomogeneity corrections are in excellent agreement with the corresponding values found by Herman *et al.* and are independent of the atomic system considered. The approximation including higher-order inhomogeneity corrections did not significantly improve the approximation including lowest-order inhomogeneity corrections. However, the higher-order approximation is of interest in that it does lead to an angular-momentum-dependent exchange potential.

I. INTRODUCTION

Simplified forms of the Hartree-Fock (HF) model of a many-electron system have been used in a variety of applications. In particular, approximations to the exchange terms of the HF model along lines similar to that originally proposed by Slater[1] have received considerable attention.[2-10] Exchange approximations derived in this paper are similar to approximations which have been previously suggested. One purpose of this paper is to present simple derivations of the Kohn-Sham-Gaspar[3] (KSG) and Herman–Van Dyke–Ortenburger[2] (HDO) exchange approximations. The derivations are of interest in themselves in that they provide insight into the exchange approximations mentioned above and readily lend themselves to generalization.

Common to all work on exchange approximations has been the difficulty of evaluating a given approximation. For example, total energy has been offered as a criterion for evaluating exchange approximations.[2] A similar approach has been to compare various matrix elements or combinations of matrix elements to those obtained from HF calculations.[6] As far as they go, these methods of comparison do enable a judgment to be made as to the relative merits of a given approximation. However, it is often difficult to decide why one approximation is "better" than another for one set of matrix elements while the converse may be true for another set. Obviously, a simple easily visualized comparison scheme in itself would be a useful addition to the literature of exchange approximations.

A second objective of this paper is to present evaluations of exchange approximations in atoms obtained from a very simple but highly informa-