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Asymptotic Large-Z Atomic Wave Functions*

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A new technique for calculating wave functions for atoms and ions is developed. Formal asymptotic expansions with largeness parameter Z (nuclear charge) of the form $\psi=e^{-Zh}\Sigma a_nZ^{-n}$, where h and the set of a_n's are functions of the electron coordinates, are determined through first order in $1/Z$. In so doing, the Schrödinger equation for a general atomic system with N electrons is reduced to a set of first-order partial differential equations for successive a_n. These equations are then solved recursively. Screening and correlation are exhibited explicitly in the resulting asymptotic atomic wave functions. Applications made to the ground state of 2-electron systems show that the asymptotic wave function obeys the virial theorem through first order. Magnetic susceptibilities within 5% of the accepted values are obtained for helium and singly ionized lithium. Other expectation values, $\frac{1}{2}(s_1+s_2)$, s_{12}^2, and s_{12}, are found to be in excellent agreement with Pekeris's variational calculations utilizing many parameters. In the neighborhood of certain singular points the large-Z asymptotic solutions obtained by a "matching technique" are shown to satisfy the correct cusp conditions. In certain of these regions, $(\ln Z)/Z$ terms enter. The omission of such terms in ordinary variational-perturbation wave functions may result in a loss of accuracy when computing expectation values other than the energy.

ASYMPTOTIC WAVE FUNCTIONS FOR ATOMIC SYSTEMS

1. INTRODUCTION

RECENTLY, approximate ground-state solutions to the nonrelativistic Schrödinger equation for many-electron atoms have received considerable attention. Electron wave functions giving a reasonably correct description of the electron density throughout configuration space would facilitate calculation of weak-interaction effects. Of late, there have been refinements in the experimental measurements of magnetic susceptibility, electric polarizability, and quadrupole coupling of atoms. The utilization of more accurate wave functions would allow calculation of these effects to keep pace with experiment. More accurate atomic-scattering factors could also be obtained. In addition, if accurate excited-state wave functions were known, transition probabilities and optical-absorption and inelastic-scattering cross sections could be calculated with much greater precision.

The calculation of ground-state atomic wave functions is usually performed by either a Hartree (Hartree-Fock) calculation or by some other variational technique. It is well known that Hartree calculations usually give the energy of the ground state to within 1 percent.[1] However, these solutions do not incorporate interelectronic repulsion correctly since they describe each electron as moving in the average central field due to all the others, and these are distributed throughout their wave functions according to the statistical probability that they will be found at any one coordinate. Hence the electrons do not avoid one another because of their mutual Coulomb repulsion but tend to avoid regions of large average potential energy. Also such techniques are derived from a variational principle, and their application to excited states leads to problems of orthogonality.[2]

Generalized variational techniques such as Hylleraas or configuration-interaction expansions using a sufficiently large number of undetermined parameters give results for the upper bound to the energy to almost any desired accuracy for small atomic systems. For example, the ground state of helium has been computed to eight figures using a 39-parameter wave function[3] and to ten figures using a 1078-term wave function.[4] However, the wave functions so obtained are not uniformly convergent. This is further brought to light in the fact that the rigorous lower bound calculated with these wave functions does not usually agree with the upper bound in the last few figures. If the variational wave functions were a close approximation to the exact solution over most of the atomic configuration space, one might expect better agreement between the two limits. Furthermore, the number and type of correlation terms which may be included in the trial wave function are usually chosen *ad hoc*. Therefore the interpretation of the resulting variational wave function for a two- or three-electron system does not usually lead to any real insight into general electron-electron correlation effects. Since extensions of such expansions to atoms with many electrons must become hopelessly complex, some other techniques must be utilized to exhibit general correlation effects and give wave functions of some reliability for larger atomic systems.

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[1] Per-Olov Lowdin, *Recent Development of the Theory of the Electronic Structure of Atoms* (Quantum Chemistry Group, Uppsala University, Uppsala, Sweden, 1958).

[2] M. Cohen and A. Dalgarno, Rev. Mod. Phys. **35**, 506 (1963).

[3] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

[4] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959); **126**, 143 (1962).

In this paper, we develop the method of asymptotic expansions for obtaining atomic wave functions. We look for asymptotic large-Z (atomic number) wave functions of the form

$$\psi=e^{-Zh}(a_0+a_1Z^{-1}+a_2Z^{-2}+\cdots+). \qquad \text{(A)}$$

The energy is also expanded as a power series in Z of the form

$$E=-Z^2(C_0^2-Z^{-1}C_1^2+Z^{-2}C_2^2+\cdots+). \qquad \text{(B)}$$

Insertion of (A) and (B) into the Schrödinger equation for any atom leads to a set of lower order partial differential equations for h, a_0, and a_1. Although the energy parameters may be determinable in a self-consistent manner, we make use of the fact that C_0^2 and C_1^2 are known exactly for atomic systems.[5] C_2^2 may be determined from an experimental analysis of the binding energies of the isoelectronic series of interest.

In Sec. 2 of this paper, we apply our formalism to separable atomic systems and show that truncated asymptotic expansions are *exact* solutions to the separable problem. In Sec. 3, the partial differential equations for a general atomic system are solved recursively through the lowest orders. Screening and correlation are exhibited explicitly in the resulting atomic wave functions. The correlation effects are exhibited as a sum of 2-electron correlation functions which depend on the principal quantum numbers of the electrons involved.

Asymptotic solutions of form (A) (naturally with different largeness parameters) have been obtained previously for a wide class of electromagnetic-scattering problems[6] and fluid-dynamics problems. In those rare cases where an exact solution could be obtained by the method of separation of variables, a comparison between the asymptotic solution and the exact one has shown: (1) The leading term or terms of the asymptotic series represents the leading term or terms in the asymptotic expansion of the exact solution. (2) The asymptotic expansion including only a few terms is a very good approximation to the exact solution over most of the domain when the expansion parameter is of the order of 2 or greater. From (2) we expect our asymptotic expansion to be a good approximation to the exact solution even for atoms or ions of low atomic number. That this is the case is shown by the close agreement of our results of Sec. 4 for the angular correlation in the helium ($Z=2$) wave function away from isolated singularity points, with those obtained from a many-parameter variationally calculated wave function. From (1) we expect our asymptotic series to represent the leading terms in the asymptotic expansion in large Z of the exact solution. This is shown in part at the end of Sec. 4.

In Sec. 5, we calculate some first-order expectation values for the helium ground state utilizing our asymptotic expansions. Our helium wave function is shown to obey the virial theorem to first order. Magnetic susceptibilities within 5% of the accepted values are obtained for helium and singly ionized lithium.

In Sec. 7, we determine by a "matching technique" the asymptotic expansions for helium which are correct, within a small neighborhood of the singular points. The expansions are shown to satisfy the "cusp condition" at the origin exactly and the one at s_{12} (interelectron distance)$=0$ to leading order. Since the wave-function expansions in these regions have $(\ln Z)/Z$ terms, expectation values for operators other than the energy will include such terms in their high-Z expansions. Ordinary perturbation theory expansions[7] do not include such log terms.

2. ASYMPTOTIC SOLUTIONS FOR SEPARABLE ATOMIC SYSTEMS

The general Schrödinger equation for a system of a nucleus with charge Z surrounded by N electrons can be written in dimensionless form,

$$-\tfrac{1}{2}\sum_{i=1}^{N}\nabla_i^2\psi-\sum_{i=1}^{N}\frac{Z}{s_i}\psi+\Theta\sum_{i=1}^{N}\sum_{j>i}\frac{1}{s_{ij}}\psi=E\psi, \qquad (1)$$

where s_i is the distance in Bohr radii of the ith electron from the nucleus, E is the energy of the system in large rydbergs (approximately 27.2 eV), and Θ is set equal to zero when the electron-electron interaction is considered to be turned off and taken as one for the actual atomic problem. Let us consider the case when $\Theta=0$. The equation is then separable. That is, $\psi\approx\phi(s_1)\phi(s_2)\cdots\phi(s_N)$, where $\phi(s)$ satisfies

$$-\tfrac{1}{2}\nabla_s^2\phi-(Z/s)\phi-E_s\phi=0. \qquad (2)$$

The exact solution can then be represented by product wave functions of hydrogenic character. If the Pauli principle is invoked and the hydrogenic states are filled two at a time in the order of increasing energy, one builds up the periodic table with each element having its proper valence and the correct ground-state symmetry properties (assuming L-S coupling to be negligible). Thus the independent electron model certainly predicts some of the more important atomic properties correctly and must in some sense represent a first approximation to the true solution. The energies of such separable systems only include the Z^2 term and can therefore be written

$$E=-Z^2E_0 \text{ large rydbergs}. \qquad (3)$$

Each electron with a principal quantum number n contributes an amount $1/2n^2$ to E_0. The exponential behavior of the wave function for an independent elec-

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[5] C. W. Scherr, J. M. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).

[6] R. M. Lewis and J. B. Keller, New York University, EM Division, Research Report EM-194, 1964 (unpublished).

[7] A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **247**, 245 (1958); A. L. Stewart, Advan. Phys. **47**, 299 (1963); R. E. Knight and C. W. Scherr, Rev. Mod. Phys. **35**, 436 (1963).

tron in orbital n is given by

$$\phi\approx e^{-Zs/n}. \tag{4}$$

In the next section when the general problem is solved we will demand for $\Theta=0$, $C_1{}^2=0$, $C_2{}^2=0$, $\cdots$, $C_j{}^2=0$ that ψ go over to a product of separable wave functions each of which has an exponential behavior expressed by (4). In order to make complete contact with the known solution with the interaction turned off, we ask that each electron for the given state of the atom or ion has the same value of n with the interaction on or off.

In the remainder of this section as a simple illustration of the asymptotic expansion technique we apply it to the separable problem (2). Substituting the formal expansion

$$\phi=e^{-Zh(s)}\sum_{j=0}^{\infty}a_j(\mathbf{s})Z^{-j} \tag{5}$$

and (3) into (2), and taking the gradient

$$\nabla\phi=-Z\phi\nabla h+e^{-Zh}\sum_{j=0}^{\infty}Z^{-j}(\nabla a_j)$$

and Laplacian

$$\nabla^2\phi=(\nabla h)^2\sum_{j=0}^{\infty}a_jZ^{-j+2}-2\sum_{j=0}^{\infty}(\nabla h\cdot\nabla a_j)Z^{-j+1}$$

$$-\nabla^2h\sum_{j=0}^{\infty}a_jZ^{-j+1}+\sum_{j=0}^{\infty}Z^{-j}\nabla^2a_j,$$

we obtain, setting the coefficient of the Z^2 term equal to zero,

$$-\tfrac{1}{2}(\nabla h)^2a_0=-E_0a_0. \tag{6}$$

Since $h=h(s)$, the equation can be written

$$(\partial h/\partial s)^2=2E_0,$$

which admits the solution

$$h=(2E_0)^{1/2}s=\alpha_0s.$$

Setting the coefficient of the Z^1 terms equal to zero gives

$$-\tfrac{1}{2}(\nabla h)^2a_1+\alpha_0(\partial a_0/\partial s)+(\alpha_0/s)a_0-(a_0/s)=-E_0a_1. \tag{7}$$

The $(\nabla h)^2$ term cancels the E_0 term, and we are left with a homogeneous equation for a_0 of the form

$$\frac{\partial a_0}{\partial s}-\left[\frac{1}{\alpha_0}-1\right]\frac{a_0}{s}=0. \tag{8}$$

Defining $\beta=(1/\alpha_0)-1$, our result for a_0 can be written

$$a_0=F(\theta,\phi)s^\beta.$$

Setting the coefficient of the zeroth power of Z equal to zero, an inhomogeneous equation for a_1 of the form

$$\partial a_1/\partial s-\beta(a_1/s)=(1/2\alpha_0)\nabla^2a_0 \tag{9}$$

results. In terms of the variable r_1 defined as $r_1=a_1/a_0$, Eq. (9) becomes

$$\partial r_1/\partial s=(1/2\alpha_0a_0)\nabla^2a_0, \tag{9.1}$$

which, for an S state $[F(\theta,\phi)=\text{const}]$, takes the form

$$dr_1/ds=\beta(\beta+1)/2\alpha_0s^2. \tag{9.2}$$

Equation (9.2) is immediately integrated and gives

$$r_1=-\beta(\beta+1)/2\alpha_0s, \tag{10}$$

where we have chosen the constant of integration equal to zero. Defining $r_2=a_2/a_0$, the equation for r_2 for an S state is

$$dr_2/ds=(1/2\alpha_0a_0)\nabla^2a_1. \tag{11}$$

Integrating, we finally obtain

$$r_2=(\beta+1)\beta^2(\beta-1)/8\alpha_0{}^2s^2. \tag{12}$$

Thus to second order in the expansion in inverse powers of Z, ϕ is of the form

$$\phi=e^{-Z\alpha_0s}s^\beta\left[1-Z^{-1}\frac{\beta(\beta+1)}{2\alpha_0s}+Z^{-2}\frac{(\beta+1)\beta^2(\beta-1)}{8\alpha_0{}^2s^2}+\cdots+\right]. \tag{13}$$

For the 1S orbital, $\alpha_0=1$, $(\beta=0)$, and the series truncates after the first term. For the 2S orbital, $\alpha_0=\frac{1}{2}$, and we obtain

$$\phi=e^{-Zs/2}s[1-2(Zs)^{-1}], \tag{14}$$

which is the exact 2S wave function. In the above manner, we can generate all the S states for one-electron systems. Choosing $F(\theta,\phi)$ in a_0 as one of the appropriate spherical harmonics and demanding truncation, we can generate the exact wave functions for the case when the angular momentum of the system is not equal to zero. Thus we observe the well-known fact that the exact solutions for the separable problem can be written as truncated asymptotic series of form (2). This simplicity arises because no interaction terms occur, and the energy in the separable case can be written $-Z^2E_0$. With interaction terms present, the energy is represented as an infinite expansion in decreasing powers of Z. This is one of the reasons no such truncation is possible in the general case.

3. ASYMPTOTIC SOLUTIONS FOR GENERAL ATOMIC SYSTEMS

We assume an asymptotic solution of Eq. (1) exists and is of the form

$$\psi=\exp[-Zh(s_1,s_2,\cdots,s_N)]\sum_{n=0}^{\infty}a_n(\mathbf{s}_1,\mathbf{s}_2,\cdots,\mathbf{s}_N)Z^{-n}. \tag{15}$$

The condition that our solution go over to the correct separable form with no interaction present indicates that there is no dependence of the function h on angular coordinates. Substituting Eq. (15) and the energy expansion[8]

$$E=-Z^2\sum_{w=0}^{\infty}(-1)^w Z^{-w}C_w{}^2 \tag{16}$$

into Eq. (1), we have, after cancelling out the exponential e^{-Zh} from both sides,

$$-\tfrac{1}{2}\sum_{n=0}^{\infty}\sum_{i=1}^{N}\left[(\boldsymbol{\nabla}_i h)^2 a_n Z^{-n+2}-[2\boldsymbol{\nabla}_i h\cdot\boldsymbol{\nabla}_i a_n+(\nabla_i{}^2 h)a_n]Z^{-n+1}+(\nabla_i{}^2 a_n)Z^{-n}\right]$$

$$-\sum_{n=1}^{\infty}\sum_{i=1}^{N}\frac{1}{s_i}a_n Z^{-n+1}+\sum_{n=0}^{\infty}\sum_{i=1}^{N}\sum_{j>i}\frac{1}{s_{ij}}a_n Z^{-n}=-Z^2\sum_{w=0}^{\infty}(-1)^w Z^{-w}C_w{}^2\sum_{n=0}^{\infty}a_n Z^{-n}. \tag{17}$$

Setting the coefficient of all Z^2 terms equal on both sides of the equation, we obtain an eikonal equation for h of the form

$$\sum_{i=1}^{N}(\boldsymbol{\nabla}_i h)^2=2C_0{}^2. \tag{18}$$

Since h is not a function of angles, Eq. (18) can be written

$$\sum_{i=1}^{N}\left(\frac{\partial h}{\partial s_i}\right)^2=2C_0{}^2. \tag{18a}$$

In order that our solution go over properly for the case of no electron-electron interaction, h must be of the form

$$h=\sum_{i=1}^{N}\frac{s_i}{n_i}, \tag{19}$$

where the ith electron is taken to be in a state with principal quantum number n_i. It then follows that each electron will contribute an amount $1/2n^2$ to $C_0{}^2$. Thus $C_0{}^2=E_0$ and is therefore determined since E_0 is known. For example, in the case of a filled shell atom whose outer shell has a principal quantum number N,

$$E_0=2\sum_{n=1}^{N}(1/2n^2)\sum_{l=0}^{n-1}(2l+1).$$

In more conventional perturbation theory techniques, the electron position coordinates in Eq. (1) are all multiplied by Z, and this results in a $1/Z$ appearing as the perturbation parameter multiplying the $1/s_{ij}$ term. It then follows immediately that the leading term of the energy expansion is the unperturbed energy obtained with $1/Z$ equal to zero, which is just the separable energy $-Z^2E_0$.

Equating coefficients of Z^1 terms on both sides of Eq. (17), we obtain

$$\sum_{i=1}^{N}\left[-\tfrac{1}{2}(\boldsymbol{\nabla}_i h)^2 a_1+\boldsymbol{\nabla}_i h\cdot\boldsymbol{\nabla}_i a_0+\tfrac{1}{2}(\nabla_i{}^2 h)a_0-\frac{1}{s_i}a_0\right]$$

$$=-C_0{}^2 a_1+C_1{}^2 a_0. \tag{20}$$

From Eq. (18), it follows that the coefficients of the a_1 terms on both sides of Eq. (20) are equal. The resulting equation for a_0 is therefore

$$\sum_{i=1}^{N}\left[\frac{1}{n_i}\frac{\partial a_0}{\partial s_i}+(1/n_i-1)\frac{1}{s_i}a_0\right]=C_1{}^2 a_0. \tag{21}$$

Equation (21) admits the general solutions

$$a_0=J_0\prod_{i=1}^{N}s_i{}^{-\omega_i}e^{\lambda_i s_i}, \tag{22}$$

where

$$\omega_i=1-n_i,\quad \lambda_i=n_iC_1{}^2/N,$$

and J_0 is an arbitrary function of angles and of the differences formed by taking the radial coordinates of any two electrons, multiplying each by its principal quantum number and then subtracting one from the other. Choosing J_0 as a product of the appropriate spherical harmonic functions of the angular coordinates of those electrons not in S states, our solution goes over correctly for the separable case. From the above form of the λ_i's, it follows that in any given ion or atom the shielding factor for any electron is approximately proportional to its average distance from the nucleus with the interaction turned off.

Equating coefficients of the zeroth power terms, we obtain an inhomogeneous equation for a_1 of the form

$$\sum_{i=1}^{N}\left[\frac{1}{n_i}\frac{\partial a_1}{\partial s_i}+\left(\frac{1}{n_i}-1\right)\frac{1}{s_i}a_1\right]-C_1{}^2 a_1$$

$$=-\Theta a_0\sum_{i=1}^{N}\sum_{j>i}\frac{1}{s_{ij}}+\tfrac{1}{2}\sum_{i=1}^{N}\nabla_i{}^2 a_0-C_2{}^2 a_0. \tag{23}$$

Making the substitution $a_1=r_1a_0$ and noting that both functions a_0 and a_1 satisfy the same homogeneous equation, we find Eq. (23) reduces to

$$\sum_{i=1}^{N}\frac{1}{n_i}\frac{\partial r_1}{\partial s_i}=-\Theta\sum_{i=1}^{N}\sum_{j>i}\frac{1}{s_{ij}}+\frac{1}{2a_0}\sum_{i=1}^{N}\nabla_i{}^2 a_0-C_2{}^2. \tag{24}$$

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[8] In the energy expansion (16) $C_w{}^2$ is taken as necessarily positive for $w=0$, 1, and 2.

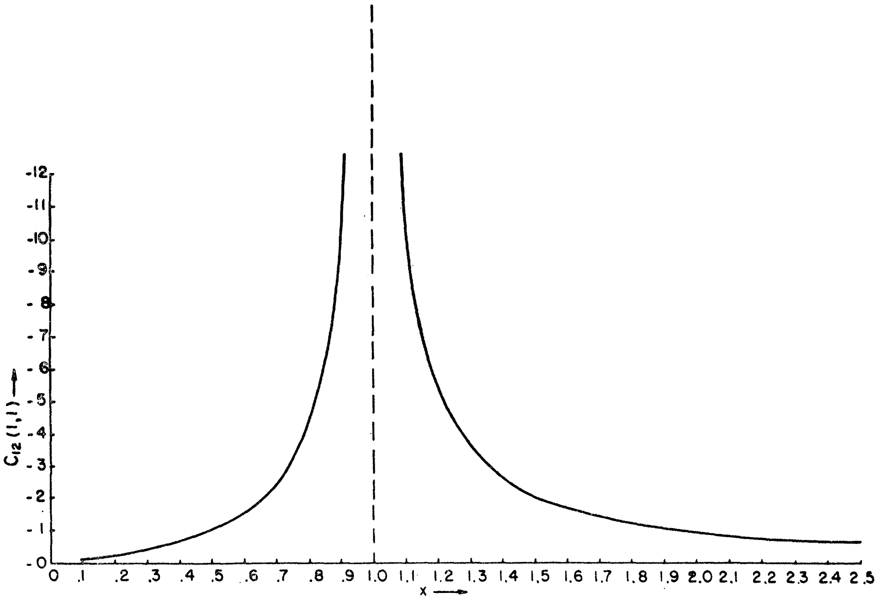

FIG. 1. The $1S^2$ correlation function $C_{12}(1,1)$ for the case that both electrons lie on the same side of the nucleus and on the same straight line passing through the nucleus ($\theta_{12}=0°$). x is the ratio of the radial electron distances s_2/s_1.

The solution to Eq. (24) can be written

$$r_1=\Theta\sum_{i=1}^{N}\sum_{j>i}C_{ij}+\tfrac{1}{2}\sum_{i=1}^{N}n_i\int\frac{\nabla_i^2 a_0}{a_0}ds_i-\sum_{i=1}^{N}\frac{C_2^2}{N}n_is_i,\tag{25}$$

where C_{ij} is the solution of

$$\frac{1}{n_i}\frac{\partial C}{\partial s_i}+\frac{1}{n_j}\frac{\partial C}{\partial s_j}=-\frac{1}{s_{ij}},\tag{26}$$

subject to the boundary condition that as either s_i or s_j goes to infinity or zero with the other held fixed, C_{ij} goes to zero. This condition follows, since C_{ij} represents the direct correlation term in our first-order solution. As the electrons go infinitely far apart from one another, the electron-electron interaction contribution to the wave function goes to zero. The solution of Eq. (26) is shown by standard techniques[9] to be of the form

$$C_{ij}=\frac{-n_jn_i}{Q_{ij}}\ln\left(\frac{s_{ij}Q_{ij}+(n_j-D_{ij}n_i)s_i+(n_i-D_{ij}n_j)s_j}{A_{ij}}\right),\tag{27}$$

where

θ_{ij} is the angle subtended at the nucleus between electrons i and j, $D_{ij}=\cos\theta_{ij}$,

$$Q_{ij}=(n_i^2+n_j^2-2D_{ij}n_in_j)^{1/2},$$

and

$$A_{ij}=[Q_{ij}+n_j-D_{ij}n_i][s_i-(n_j/n_i)s_j],\quad\text{for}\quad n_js_j<n_is_i.$$

It is obvious from (27) that C_{ij} depends only on the ratio s_i/s_j and the angle between the electrons.

It should be noted that in the analysis of this section we have tacitly assumed that no nonuniformities occur in performing the two limiting procedures $\Theta\to 0$, $Z\to\infty$.

4. ASYMPTOTIC GROUND-STATE SOLUTIONS FOR 2-ELECTRON ATOMS

The ground state of a two-electron atomic system consists of a $1s^2$ configuration. Since both electrons are in orbitals with a principal quantum number of 1, we obtain

$$\omega_1=\omega_2=0,\quad \lambda_1=\lambda_2=\lambda=C_1^2/2,$$

and Eq. (22) for a_0 gives

$$a_0=e^{\lambda(s_1+s_2)}.\tag{28}$$

Operating on a_0 with the Laplacian, we obtain

$$\nabla_i^2a_0/a_0=2\lambda/s_i+\lambda^2.$$

Performing the integration in Eq. (25), we are led to the result

$$r_1=C_{12}(1,1)+\lambda\ln s_1s_2+\tfrac{1}{2}(\lambda^2-C_2^2)(s_1+s_2),\tag{29}$$

where $C_{ij}(n_i,n_j)$ refers to the correlation function when electron i is in an orbital with principal quantum number n_i and electron j is in an orbital with principal quantum number n_j. Equation (27) for $n_i=n_j=1$ gives

$$C_{12}(1,1)=-\frac{1}{2d}\ln\left(\frac{s_{12}+d(s_1+s_2)}{(1+d)|s_1-s_2|}\right),\tag{30}$$

with

$$d=(1-D_{12})/2\quad\text{and}\quad D_{12}=\cos\theta_{12}.$$

The isoelectronic energy expansion is well known for the case of 2-electron atomic systems.[10] In terms of large

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[9] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1962), Vol. 2.

[10] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Springer-Verlag, Berlin, 1957), p. 153. Also see Ref. 5.

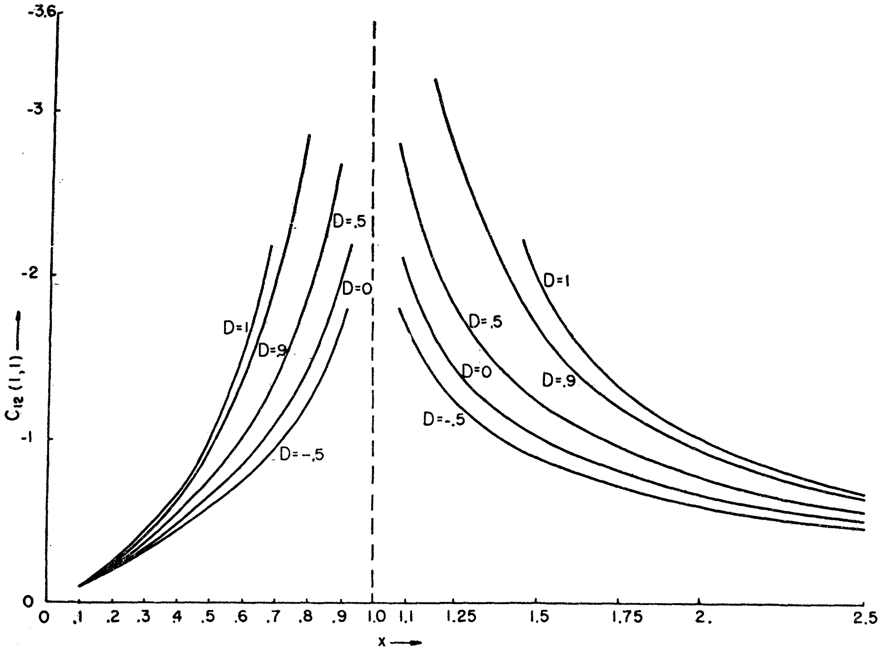

FIG. 2. The $1S^2$ correlation function $C_{12}(1,1)$ as a function of x for several values of θ_{12} (the angle subtended between the two electrons at the nucleus). $D=\cos\theta_{12}$.

rydbergs, we observe that $C_1^2=0.625$ and $C_2^2=0.15765$. Using these values, we obtain $\lambda=0.3125$, and the coefficient β of the s_1+s_2 term is -0.03. The first-order asymptotic wave function for a 2-electron atomic system is then

$$\psi_1=e^{-(Z-\lambda)(s_1+s_2)}\{1+Z^{-1}[C_{12}(1,1)+\lambda\ln(s_1s_2)+\beta(s_1+s_2)]\}. \quad (31)$$

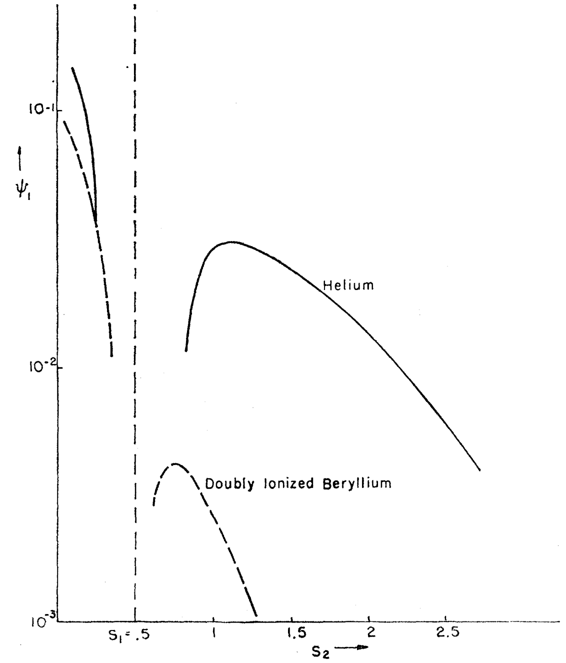

FIG. 3. The asymptotic solution ψ_1 [Eq. (31)] as a function of s_2 (Bohr radii) for the case of $\theta_{12}=0°$ and $s_1=0.5$ Bohr radii. Curves are drawn for helium and doubly ionized beryllium.

Since the value 0.3125 for our shielding parameter λ is exactly the value found by performing a variational calculation on a simple exponential product wave function, the leading term of ψ_1 is already well known. In Fig. 1, $C_{12}(1,1)$ is plotted as a function of x ($x=s_2/s_1$) for $\theta_{12}=0°$. This is the case when the two electrons are both on the same side of the nucleus and lie on a straight line which passes through it. We observe that C_{12} goes to zero as the electrons go infinitely far apart. As the electrons come near one another, C_{12} becomes more and more negative leading to a smaller value for ψ_1 and therefore to a decreased probability of finding the electrons close together. These are the correlation effects one expects physically.

In point of fact, C_{12} diverges logarithmically at $s_1=s_2$. For the case of $\theta_{12}=0°$, the divergence is stronger and a first-order pole occurs. This type of singularity at a point about which the asymptotic expansion changes character is common to many asymptotic solutions. For example, the WKB asymptotic solution of the simple harmonic oscillator diverges in the neighborhood of the classical turning point. The asymptotic solution also changes character about this point. Often one can obtain by a stretching technique an accurate nondivergent asymptotic solution in the transition region where the original asymptotic solutions diverged. For the harmonic oscillator, such a stretched solution is the Airy function. Simply stated, such singularity phenomena occur because the postulated form of the asymptotic expansion is not adequate to represent the asymptotic expansion of the true solution in this region due to problems of nonuniform convergence. This will be discussed further in Secs. 6 and 7 when we obtain the asymptotic expansion in the neighborhood of singular points. In another sense, one may sometimes think of the occurrence of such singularities as due to our conversion of a problem involving a second-order partial differential equation to one where a set of first-order equations are solved recursively. Somewhere in the process a boundary condition may be lost. In trying to recover the correct boundary value, the asymptotic solution overshoots the mark. Thus we do not expect our asymptotic expansion to be valid in some neighborhood of the points $s_1=s_2$. However, from the plots of our correlation function as a function of x, as shown in Fig. 2 for various angles, we expect radial correlation to be a general property of the helium ground-state system. That is, one should observe a reduced probability of finding two electrons having the same value of the radial coordinate. Strong radial correlation effects in the helium wave function have been discussed elsewhere.[11] We also observe from Fig. 2 that the correlation effect for any value of x decreases with decreasing D_{12} and therefore with increasing s_{12} as expected.

In Fig. 3, we compare ψ_1 for helium and doubly ionized beryllium for the case $s_1=0.5$, $\theta_{12}=0°$. It is physically unreasonable that the true helium wave function becomes negative in the neighborhood of $s_{12}=0$. We note from the figure that this phenomenon will occur much farther from the point $s_1=s_2$ in the case of helium than for doubly ionized beryllium. Therefore it is immediately obvious that our solutions become applicable closer to $s_1=s_2$ as Z becomes larger. As Z goes toward infinity, our solution ψ_1 will become applicable over almost all configuration space.

It should also be pointed out that 1S orbitals give rise to a logarithmic singularity when either electron goes into the nucleus. The region in the neighborhood of the nucleus in which this effect is large is small, even for $Z=2$. It is of the order of 0.3 Bohr radii for this case. A nondivergent asymptotic solution which is correct in the neighborhood of the origin can be found by a stretching technique. As our electrons go an infinite distance away from the nucleus, the usual nonconvergence problems arise in the wave function. Since this domain will not be of interest in computing expectation values, we do not trouble ourselves about it here. To avoid this problem, one has to use a density matrix formulation of the problem.

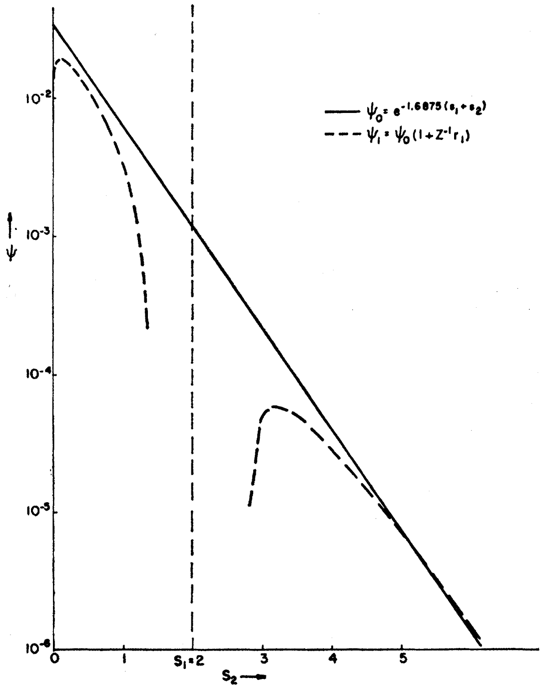

FIG. 4. Spatial correlation in helium. ψ_1 and ψ_0 (the leading term of ψ_1) as a function of s_2 for the case of $\theta_{12}=0°$ and $s_1=2.0$. Note the decrease in the wave function ψ_1 as electron 2 approaches electron 1.

In Fig. 4, we plot ψ_1 as a function of s_2 for the case $s_1=2$, $\theta_{12}=0°$. In the same figure, we plot the leading term of ψ_1, which is just a product of screened exponentials. We refer to this term as ψ_0. Note that ψ_1 becomes less than ψ_0 in the neighborhood of $s_{12}=0$ and larger than ψ_0 as the distance between electrons increases. Because of the compensating effects in the different regions, when a correct asymptotic description of the wave function in the immediate neighborhood of $s_{12}=0$ and the origin is used in conjunction with our asymptotic solution which is valid everywhere else, we expect the correct normalization constant multiplying ψ_1 will be only slightly changed from the normalization constant for ψ_0. Assuming ψ_1 to have the same normalization factor as ψ_0, we have calculated a correlation

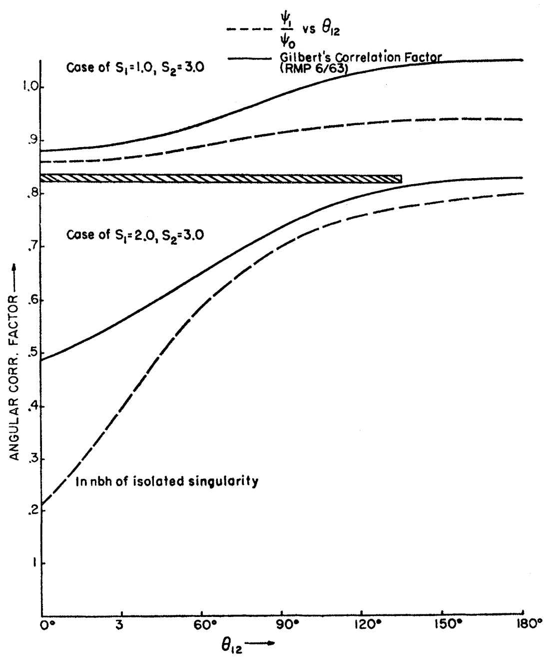

FIG. 5. Angular correlation effects in helium.

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[11] C. Schwartz, Phys. Rev. **126**, 1015 (1962).

TABLE I. Helium expectation values.

Operator	Expectation values Pekeris[a]	 Asymptotic	 Hylleraas[b]
$\frac{1}{2}(s_1^2+s_2^2)$	1.193	1.186	1.077
$\frac{1}{2}(s_1+s_2)$	0.9295	0.9453	0.8969
$\frac{1}{2}(1/s_1+1/s_2)$	1.68832	1.68750	1.689
s_{12}^2	2.516	2.600	2.327
s_{12}	1.422	1.547	1.372

[a] Pekeris' data is originally given to 10 figures. All values given in atomic units.

[b] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 224.

correction factor which is just the ratio of the two wave functions. In Fig. 5, we compare our results with those of Gilbert[12] who obtained this correction factor utilizing a many-parameter variationally determined Hylleraas-type wave function. In these plots, we are holding the radial coordinates s_1 and s_2 fixed while changing the distance between the electrons by varying the angle subtended at the nucleus by the two electrons (for $\theta_{12}=0°$ $s_{12}=s_1-s_2$; for $\theta_{12}=180°$, $s_{12}=s_1+s_{12}$). We expect physically the greatest correlation to occur for θ_{12} smallest. This is borne out by the curves. In the case of the $s_1=2$, $s_2=3$ example, we run into the s_1 approximately equal to s_2 distortion phenomena. Our correlation factor is too low for small angles as expected. However, outside of this region our results agree quite well with Gilbert's, and if we used the correct normalization constant for ψ_1, we expect that the agreement would be improved.

For large s_1 and s_2, it is known that the exact solution for helium has an exponential behavior given by

$$\psi\sim e^{-(-E)^{1/2}(s_1+s_2)}, \tag{32}$$

where E is the energy eigenvalue. Putting in the energy expansion for E in terms of the C's and expanding the exponential to first order in powers of $1/Z$, we obtain for Z large:

$$\psi\sim e^{-(Z-\lambda)(s_1+s_2)}[1+\tfrac{1}{2}Z^{-1}(\lambda^2-C_2^2)(s_1+s_2)].$$

Comparing our asymptotic expansion, Eq. (29), with this, we observe that it gives the correct high-Z asymptotic expansion of the exponential part of the exact wave function for the above case.

5. EXPECTATION VALUES FOR 2-ELECTRON ATOMIC SYSTEMS

In the previous section, we investigated the properties of the asymptotic helium wave function and found certain unphysical logarithmic divergences which occur at $s_i=0$, and $s_i=s_j$. However, these inaccuracies in our wave function have little effect on the expectation values of those operators which are relatively insensitive to the values of the wave function in the neighborhood of these points. Such operators as s_{12}^2, s_{12}, $\frac{1}{2}(s_1^2+s_2^2)$, $\frac{1}{2}(s_1+s_2)$, and $\frac{1}{2}(1/s_1+1/s_2)$ fall into the above class. Expectation value computations to first order in $1/Z$ were performed for these operators and our results, and a comparison with the "exact" results of Pekeris[4] for helium and singly ionized lithium are given in the Tables I and II. For helium we have also included calculations based on the two-parameter Hylleraas variational wave function containing a correlation term linear in s_{12}.

Our asymptotic calculations necessitated one numerical double integration over a finite domain for each expectation value. These integrations were performed on the 7094 computer using a trapezoidal-rule numerical integration scheme. Our numerical integration results are generally good to four figures. For the calculation of the nuclear magnetic shielding constant, $\frac{1}{2}(1/s_1+1/s_2)$, the results were extrapolated to six significant figures. The value of 1.68750 for this expectation value shows that ψ_1 satisfies the virial theorem to first order in $1/Z$.[13] Our result for the diamagnetic susceptibility, $\frac{1}{2}(s_1^2+s_2^2)$, of helium is within $\frac{1}{2}$ percent of the exact one.

In performing our computations, we form the product $\psi_1{}^*O\psi_1$, where O is the operator under consideration and calculate

$$\langle O\rangle_{\text{av}}=\int dV\psi_1{}^*O\psi_1\Big/\int dV\psi_1{}^*\psi_1 \tag{33}$$

to first order in $1/Z$. When performing integrations not involving terms dependent on s_{12} or D_{12}, it is convenient to choose

$$\int dV=(4\pi)^2\int_0^\infty\int_0^\infty ds_1ds_2\,s_1^2s_2^2.$$

For integrations involving correlation terms, we take[14]

$$\int dV=2\pi^2\int_0^\infty ds\int_0^s du\,u\int_0^u dt(s^2-t^2), \tag{34}$$

where $s=s_1+s_2$, $t=s_1-s_2$, and $u=s_{12}$ For operators of the form $O_j=\frac{1}{2}(s_1{}^j+s_2{}^j)$, the $\lambda(\ln s_1+\ln s_2)$ term is evalu-

TABLE II. Lithium$^+$ expectation values.

Operator	Expectation values Pekeris[a]	 Asymptotic
$\frac{1}{2}(s_1^2+s_2^2)$	0.4463	0.4624
$\frac{1}{2}(s_1+s_2)$	0.5728	0.5868
$\frac{1}{2}(1/s_1+1/s_2)$	2.6879	2.6875
s_{12}^2	0.9271	0.9925
s_{12}	0.8623	0.9307

[a] Pekiris' data is originally given to ten figures. All values given in atomic units.

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[12] T. L. Gilbert, Rev. Mod. Phys. **35**, 431 (1963).

[13] R. E. Knight and C. W. Scherr, Rev. Mod. Phys. **35**, 431 (1963).

[14] Reference 10, p. 147.

ated utilizing

$$\int_0^\infty dx\, e^{-kx} x^j \ln x = \frac{j![\Psi(j+1)-\ln k]}{k^{j+1}}, \qquad (35)$$

where

$$\Psi(j+1)=\int_0^\infty dy\, e^{-y} y^j \ln y = \frac{d}{dq}\ln\Gamma(q)\bigg|_{j+1},$$

and has been evaluated elsewhere.[15] Making a change of variables in the integral containing the C_{12} term,

$$u \to a = u/s\,,$$

$$t \to y = \{1-(u^2-t^2)^{1/2}/[(s^2-t^2)^{1/2}a]\}^{1/2}, \qquad (36)$$

the s integration can be performed separately, and what remains is a double integration over a finite domain of the form

$$C_j = 2\int_0^1 da\, a(1-a^2)\int_0^1 dy\, f_j(y,a)[\ln W(y,a)-\ln y]\,, \qquad (37)$$

with

$$W=([1-(1-y^2)a][2-y^2]/[1+(1-y^2)a])^{1/2}$$

and

$$f_j(y,a)=(O_j/s^j)/\{[1-(1-y^2)^2a^2]^{5/2}[2-y^2]^{1/2}\}\,.$$

The $\ln y$ term in Eq. (37) can be evaluated numerically by rewriting it

$$\int_0^1 dy\, f_j(y,a)\ln y$$

$$= -f_j(0,a)+\int_0^1 dy[f_j(y,a)-f_j(0,a)]\ln y\,. \qquad (38)$$

We obtain finally

$$\langle O_j\rangle_{\rm av} = \frac{(2+j)!}{2(2Z)^j}\bigg(1+\frac{1}{Z}\bigg[\lambda\{j+2[\Psi(3+j)-\Psi(3)]\}$$

$$+\frac{1}{2}\frac{5!}{2^5}C_0 - \frac{(6+j-1)!}{(2+j)!2^5}C_j\bigg]+O(1/Z^2)\bigg)\,. \qquad (39)$$

Similarly, expectation values of operators s_{12}^j are found to be of the form

$$\langle s_{12}^j\rangle_{\rm av} = \frac{(j+5)!}{(2Z)^j\times 2^5}\left(\frac{1}{j+3}-\frac{1}{3(j+5)}\right)\bigg[1+\frac{1}{Z}\bigg(\lambda\bigg\{j+4[\Psi(6+j)-\Psi(3)]-2\ln 4$$

$$+\frac{2I_j}{1/(3+j)-1/3(5+j)}\bigg\}+\frac{5!}{2\times 2^5}C_0-\frac{C_{s_{12}^j}}{1/(3+j)-1/3(5+j)}\bigg)\bigg], \qquad (40)$$

where $C_{s_{12}^j}$ has the same form as C_j except that O_j/s^j is replaced by a^j in the integrand and we have taken

$$I_j = \int_0^1 d\beta\, \beta^{2+j}\int_0^1 d\alpha(1-\alpha^2\beta^2)\ln(1-\alpha^2\beta^2)\,,$$

which can be evaluated analytically in terms of standard quadratures.

6. TECHNIQUE OF "MATCHED ASYMPTOTIC EXPANSIONS"

The asymptotic expansion for the ground state of helium has been found to diverge at certain singular points. We shall now discuss the technique of "matched asymptotic expansions" (stretching)[16,17] for obtaining an accurate nondivergent asymptotic solution in the neighborhood of any one of the singular points.

Let us consider the exact solution $\psi(Z; x_1,x_2,x_3)$ of our many-body problem with Hamiltonian H and a two-term formal asymptotic expansion ψ_1 obtained by the methods of Sec. 3. Suppose we want to determine the asymptotic expansion of ψ in the neighborhood of the point $x_1=0$ where ψ_1 blows up unphysically. Now although it has not been generally proven, we take

$$\psi_e(Z\ \text{large}) \to \psi_1\,,$$

where the subscript e indicates "the expansion of" and the arguments inside the parenthesis indicate the limiting procedures for obtaining the expansion. If more than one limiting process is involved, the limiting process farthest to the right is the first to be performed. Now when we evaluate ψ_1 as $x_1 \to 0$, we are performing the limit process

$$\psi_e(x_1\to 0,\ Z\ \text{large}) \to \psi_1(x_1\to 0) \to \text{divergence}\,.$$

However, near the point $x_1=0$ for Z large but finite, we really want to evaluate

$$\psi_e(Z\ \text{large},\ x_1\to 0)\,,$$

where

$$\psi_e(Z\ \text{large},\ x_1\to 0)\neq\psi_e(x_1\to 0),\ Z\ \text{large})\approx\psi_1(x_1\to 0)\,.$$

Let us consider a transformation of variables where we rewrite our operator H in terms of a new stretched variable ξ_1. That is,

$$x_1 \to \xi_1 = Z^j x_1\,,$$

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[15] H. T. Davis, *Tables of Higher Mathematical Functions* (Principia Press, Bloomington, Indiana, 1933).

[16] K. O. Friedrichs, Bull. Am. Math. Soc. **61**, 485 (1955).

[17] R. N. Buchal and J. B. Keller, Comm. Pure Appl. Math. **13**, 85 (1960).

where $j>0$ (j as yet otherwise unspecified),

$$H(Z;\, x_1,x_2,x_3) \rightarrow \bar{H}(Z;\, \xi_1,x_2,x_3).$$

Such a change of variables guarantees that when considering the Z dependence of terms in $\bar{H}$:

(A) Terms in H which go as $x_1^k(k>0)$ will be small when expressed in $\bar{H}$. On the other hand $k<0$ terms will be large. [Note that for x_1 small we expect terms $\sim x_1^k(k>0)$ in H to be small.] (B) Terms $\partial\psi/\partial x_1$ in H will be of magnitude $Z^j(\partial\psi/\partial\xi_1)$ in $\bar{H}$. This implies that if we look for a solution of the form $\psi\approx\phi\exp f(Z,\xi_1,x_2,x_3)$, the leading term of $\partial\phi/\partial x_1$ in the neighborhood of $x_1\approx 0$ will be of magnitude Z^j greater than the leading terms of $\partial\phi/\partial x_2$ or $\partial\phi/\partial x_3$ in this region when each is reexpressed as a function of ξ_1, x_2, and x_3. [Note again that for x_1 small we expect our boundary-layer solution to vary more rapidly with x_1 (have a larger partial derivative) than in the case of the asymptotic solution away from the singular point. The proper stretching accomplishes this.]

Thus we see that stretching is a way of ordering the terms in H in the neighborhood of $x_1\approx 0$. When considering $\bar{H}$, this ordering is expressed simply by the dependence of the various terms on a single parameter Z. We can again look for solutions of the standard asymptotic form (15). The resulting system of partial differential equations (P.D.E.) to be solved is naturally simpler than the original problem. However, because of our ordering the equations are only applicable near $x_1=0$. Let us call the formal two-term asymptotic solution to the stretched problem $-\Psi(Z;\,\xi_1,x_2,x_3)$. We expect that if j has been chosen correctly that Ψ is an asymptotic expansion of ψ which is valid for Z large, s_1 small. Since $\xi_1=Z^jx_1$ the solution

$$\Psi(\xi_1 \text{ large})$$

corresponds to $\psi_e(x_1$ small, Z large), and therefore we expect

$$\Psi(\xi_1 \text{ large}) \rightarrow \psi_1(x_1 \text{ small}).$$

This is called the "matching condition." Only the correct value of j will allow this condition to be satisfied even though certain constants and/or functions in Ψ are determined from it. Once it is satisfied, the solution Ψ for ξ_1 small obviously corresponds to ψ_e (Z large, x_1 small) and is therefore the desired asymptotic expansion in the neighborhood of $x_1\approx 0$. Another important consideration in determining the requisite value of j is that we expect at least some of the operators present in the P.D.E. for r_1 of the original asymptotic expansion will also be present in the P.D.E. for m_1, the coefficient of the first-order term in Ψ. In addition, we also expect some second-order partial derivative terms to appear in the equation for m_1. For the case of ψ_1 becoming divergent at $x_1=0$, $x_2=0$, it may be necessary to perform different stretchings on variables x_1 and x_2, but essentially the same considerations go through for understanding the "matching principle." From physical considerations, one can usually ascertain whether ψ varies more rapidly (its partial derivative is greater) with respect to one variable than the other in the neighborhood of the singular point. It is then the former variable which receives the greater stretching.

In the foregoing we have introduced the idea of stretching and have indicated how the matching principle is fulfilled. We now state more explicitly the form of the matching principle[18] utilized in this paper:

"The two-term expansion of ψ_1 (when it is expressed in terms of stretched variables) in powers of $1/Z$ is equal to the two-term expansion of Ψ (when it is expressed in terms of ordinary variables) in powers of $1/Z$."

For the case that ψ_1 is singular at $x_1=0$, defining

$\tilde{\psi}_1(Z;\,\xi_1,x_2,x_3)=\psi_1(Z;\,\xi_1/Z^j,x_2,x_3)$,

$\tilde{\psi}_{1E}=\tilde{\psi}_1$ (expanded for Z large, keeping 2 largest orders),

$\tilde{\Psi}(Z;\,x_1,x_2,x_3)=\Psi(Z;\,Z^jx_1,x_2,x_3)$,

and

$\tilde{\Psi}_E=\tilde{\Psi}$(expanded for Z large, keeping 2 highest orders),

where a tilde over a symbol indicates it has been reexpressed in terms of unnatural variables, the "matching principle" asserts

$$\tilde{\Psi}_E=\tilde{\psi}_{1E}.$$

7. SOLUTIONS IN THE NEIGHBORHOOD OF SINGULAR POINTS

Before we begin our investigation, we would like to summarize the notation used in this section.[19]

ψ_1: The helium ground-state asymptotic wave function obtained in Sec. 4 is written in terms of ordinary variables as

$$\psi_1=e^{-Zh}[1+(1/Z)r_1].$$

$\tilde{\psi}_1$: When ψ_1 above is rewritten in terms of the stretched variables associated with the singular point under investigation, it is denoted by

$$\tilde{\psi}_1=[1+(1/Z)\tilde{r}_1]\exp(-Z\tilde{h}),$$

where $\tilde{r}_1$ is written in terms of $\tilde{d}_1$.

$\tilde{\psi}_{1E}$: $\tilde{\psi}_{1E}$ is the expansion of $\tilde{\psi}_1$ in powers of $1/Z$, keeping only the two leading terms.

$\tilde{r}_{1E}$: $\tilde{r}_{1E}$ is the expansion of $\tilde{r}_1$ in powers of $1/Z$, keeping only the leading term.

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[18] Van Dyke, *Perturbation Methods in Fluid Mechanics* (Academic Press Inc., New York, 1964), p. 90.

[19] In region Ib, these definitions are modified slightly by including an $m_{1/2}$ term in Ψ.

Ψ: The asymptotic solution of the stretched problem in terms of stretched variables is denoted by

$$\Psi=[1+m_1/Z]\exp(-Zh')$$

where $h'=h$ for regions I and they are not equivalent in regions II.

$\tilde{\Psi}$: When Ψ is written in terms of unstretched variables, we denote it by

$$\tilde{\Psi}=[1+\tilde{m}_1/Z]\exp(-Z\tilde{h}').$$

$\tilde{\Psi}_E$: $\tilde{\Psi}_E$ is the expansion of $\tilde{\Psi}$ in powers of $1/Z$, keeping only the two leading terms.

$\tilde{m}_{1E}$: $\tilde{m}_{1E}$ is the expansion of $\tilde{m}_1$ in powers of $1/Z$, keeping only the leading term.

Our helium ground-state asymptotic solution ψ_1 diverges in the following regions:

Ia $(t=0,\ u\neq 0)$,
Ib $(u=0,\ s\neq 0)$,
IIa $(s_1=0,\ s_2\neq 0)$,
IIb $(s_1=0,\ s_2=0)$.

To find the correct asymptotic solutions for regions I we rewrite the 2-electron Schrödinger equation in coordinates s, t, u as

$$u(s^2-t^2)\left(\frac{\partial^2\psi}{\partial s^2}+\frac{\partial^2\psi}{\partial u^2}+\frac{\partial^2\psi}{\partial t^2}\right)+2s(u^2-t^2)\frac{\partial^2\psi}{\partial s\partial u}$$
$$+2t(s^2-u^2)\frac{\partial^2\psi}{\partial u\partial t}+4su\frac{\partial\psi}{\partial s}+2(s^2-t^2)\frac{\partial\psi}{\partial u}-4ut\frac{\partial\psi}{\partial t}$$
$$+4Zsu\psi-(s^2-t^2)\psi+Eu(s^2-t^2)\psi=0,\quad(41)$$

with E given as before by (16). Regions Ia and Ib are considered removed from the origin. Thus we do not have to consider any stretching in s and expect that the exponential dependence on s (shielding effect) will be the same for the Ia and Ib solutions as for the original asymptotic solution. Therefore we look in regions Ia and Ib for stretched solutions of the form[20]

$$\Psi=e^{-(Z-\lambda)s}[1+m_1/Z+m_2/Z^2+\cdots+].\quad(42)$$

In the Appendix, we have substituted the above into Eq. (41) and have kept terms through order $1/Z$ considering $\psi=\psi(s,t,u)$. Certain terms automatically cancel one another in Eq. (A1). These terms are enclosed in curly brackets and need not be considered further. Now consider the general double stretching

$$\xi=Z^k t,\quad \gamma=Z^j u.$$

Under each term of Eq. (A1), we express the order of that term in Z when considered as a function of ξ, γ, and Z in terms of the j, k of the transformation. For the case $j=0$, $k=0$ (no stretching), the largest terms are of order Z^0, and, equating them equal to zero, we obtain

$$us^2[\lambda^2-2(\partial m_1/\partial s]-ut^2[\lambda^2-2(\partial m_1/\partial s)]$$
$$-2s[u^2-t^2]\partial m_1/\partial u+4\lambda su-s^2+t^2$$
$$-C_2{}^2[us^2-ut^2]=0.\quad(43)$$

It is a simple matter to show that this equation is satisfied by the r_1 [Eq. (29)] of our original asymptotic expansion. We will indicate this as expansion A. The terms in Eq. (A1) entering the leading equation for expansion A [Eq. (43)] are indicated by writing an A under the term. The A follows the j, k order of the term and is set off from it by a semicolon. Since there is one term, $-s^2$ in (A1), which is independent of j and k, it is necessary that other terms in (A1) which depend on j and k are also of order Z^0, if we are to be able to equate the coefficient of this power of Z equal to 0. For the region Ia, no stretching is required on the s_{12} variable and $j=0$, $k=\frac{1}{2}$ are the proper values of j and k. For the case $j=1$, $k=\frac{1}{2}$, we obtain the expansion in region Ib. For both cases, the P.D.E. to be satisfied by m_1 is found by setting the coefficient of the Z^0 terms equal to zero. The terms entering the equation for m_1 in region Ia have a Ia written under them in Eq. (A1). Similarly, those entering in region Ib have a Ib written under them. When a term enters the equation for m_1 in a few regions, these regions are written below the term and are set off from one another by commas. Note that of the four differential operator terms present in A, two are present in Ia and one is present in Ib. If, for example, we had chosen $j=1$, $k=1$ as the proper stretching in Ib, none of the differential operator terms present in A would have entered the equation for m_1. Needless to say, pursuance of the $j=1$, $k=1$ solution for m_1 would have indicated that no match with the asymptotic expansion A was possible.

We now write down the P.D.E. for m_1 in region Ia as

$$\frac{\partial^2 m_1}{\partial\xi^2}-2\frac{\partial m_1}{\partial s}-2\frac{u}{s}\frac{\partial m_1}{\partial u}=\frac{1}{u}-\frac{4\lambda}{s}(\lambda^2-C_2{}^2),\quad(44)$$

where $\xi=Z^{1/2}t$. Now we have r_1 of expansion A which can be written

$$r_1(s,t,u)=\lambda\ln\left(\frac{s^2-t^2}{4}\right)+\tfrac{1}{2}[\lambda^2-C_2{}^2]s$$
$$-\frac{1}{2d}\ln\left[\frac{u+ds}{(1+d)|t|}\right],\quad(45)$$

where $d=[(u^2-t^2)/(s^2-t^2)]^{1/2}$. This is immediately seen by referring to Eq. (29) and rewriting it in terms of the variables s, t, and u. Following our prescription at the

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[20] Ψ here is taken as the general expansion, but only terms through m_1 will be of importance in satisfying the "matching theorem."

end of Sec. 6,

$$\tilde{r}_1=\lambda\ \ln\tfrac{1}{4}s^2\left(1-\frac{\xi^2}{Zs^2}\right)+\tfrac{1}{2}(\lambda^2-C_2{}^2)s$$
$$-\frac{1}{2\tilde{d}_1}\ln\left[\frac{s_{12}+\tilde{d}_1 s}{(1+\tilde{d}_1)\,|\,\xi/Z^{1/2}|}\right],$$

with

$$\tilde{d}_1(Z;\,\xi,s,u)=d\left(Z;\frac{\xi}{Z^{1/2}},\,s,\,u\right)=\frac{u}{s}\left(\frac{1-\xi^2/Zu^2}{1-\xi^2/Zs^2}\right)^{1/2}.$$

Expanding for large Z,

$$\frac{1}{2\tilde{d}_1}\approx\frac{1}{2}\left(\frac{s}{u}\right)\left[1+\frac{1}{2Z}\xi^2\left(\frac{1}{u^2}-\frac{1}{s^2}\right)+O\left(\frac{1}{Z^2}\right)\right],$$

$$\tilde{d}_1 s\approx u\left[1+\frac{\xi^2}{2Z}\left(\frac{1}{s^2}-\frac{1}{u^2}\right)+O\left(\frac{1}{Z^2}\right)\right],$$

we obtain

$$\tilde{r}_{1E}\sim\lambda\ \ln\frac{s^2}{4}+\tfrac{1}{2}[\lambda^2-C_2{}^2]s+\frac{s}{2u}\left\{\ln\frac{|\xi|}{Z^{1/2}}\right.$$
$$\left.-[\ln 2u-\ln(1+u/s)]\right\}+O((\ln Z)/Z).\qquad(46)$$

In order to satisfy the matching principle, $\tilde{m}_{1E}$ obtained from m_1 of Eq. (44) must be equal to $\tilde{r}_{1E}$ given by Eq. (46). Choosing

$$m_1=\lambda\ \ln s^2+\tfrac{1}{2}[\lambda^2-C_2{}^2]s$$
$$-(s/2u)[\ln 2u-\ln(1+u/s)+M_1],\qquad(47)$$

and substituting into Eq. (46), we find M_1 satisfies the heat-flow equation

$$\partial^2 M_1/\partial\xi^2=2(\partial M_1/\partial s).\qquad(48)$$

To complete the match we expect for large ξ

$$M_1=-\ln\xi+\sum a_j(s)\xi^{-j}\quad\text{with}\quad a_{-|j|}=0.\qquad(49)$$

Substituting (49) into (48) we obtain

$$\frac{1}{\xi^2}+\sum_{j\neq 2}(j-2)(j-1)a_{j-2}\xi^{-j}-\sum_j 2\frac{\partial a_j}{\partial s}\xi^{-j}=0.\qquad(50)$$

Thus $a_0=$ constant. Since ψ must be even in t and therefore in ξ we next set the coefficients of ξ^{-2} in (50) equal to 0 obtaining

$$-2(\partial a_2/\partial s)+1=0,\qquad(51)$$

which has the solution

$$a_2=\tfrac{1}{2}s.\qquad(52)$$

For higher values of j, we find recursively

$$a_j=\frac{(j-2)(j-1)}{2}\int ds\ a_{j-2}.\qquad(53)$$

Defining $w=s/\xi^2$, we observe that for ξ large, w small, we can write

$$M_1=-\ln\xi+a_0+\tfrac{1}{2}w+\tfrac{3}{4}w^2+\cdots+.\qquad(54)$$

Therefore we look for a general solution of (48) of the form

$$M_1=-\ln\xi+a_0+\phi(w),\qquad(55)$$

with

$$\phi(w)\approx\tfrac{1}{2}w+\tfrac{3}{4}w^2+\cdots+\qquad(55\text{a})$$

for w large. Substituting, we obtain

$$\frac{d^2\phi}{dw^2}+\frac{1}{2}\left[\frac{3}{w}-\frac{1}{w^2}\right]\frac{d\phi}{dw}=-\frac{1}{4w^2},\qquad(56)$$

which has the general solution

$$\phi=C_1\int dw\ w^{-3/2}e^{-1/2w}$$
$$-\frac{1}{4}\int dw\ w^{-3/2}e^{-1/2w}\int^w dw'\frac{e^{1/2w'}}{w'^{1/2}}.\qquad(57)$$

Substituting $V=1/2w$, we obtain

$$\phi=-C_1\int\frac{dV}{V^{1/2}}e^{-V}-\frac{1}{4}\int\frac{dV}{V^{1/2}}e^{-V}\int^V\frac{du\,e^u}{u^{3/2}}.\qquad(58)$$

Now the homogeneous term would admit odd powers of ξ which is unphysical. Therefore we set $C_1=0$. Now we write our solution

$$\phi=-\frac{1}{4}\int\frac{dV}{V^{1/2}}e^{-V}g(V),\qquad(59\text{a})$$

with

$$g(V)=\int_{-\infty}^{V}\frac{du}{u^{3/2}}e^u.\qquad(59\text{b})$$

The lower limit on integral (59b) has been chosen so that no contributions from partial integrations will result from it. For V large, w small, we partially integrate to higher negative powers of V, giving

$$g(V)\approx e^V\left(\frac{1}{V^{3/2}}+\frac{3}{2}\frac{1}{V^{5/2}}+\frac{3\times 5}{2^2}\frac{1}{V^{7/2}}+\cdots+\right),\qquad(60)$$

which results in

$$\phi(V)\approx\tfrac{1}{4}\sum_{n=1}\frac{1\times 3\times 5\times\cdots\times(2n-1)}{(2^{n-1})n}\frac{1}{V^n},\qquad(61)$$

which gives as its leading terms

$$\phi(V)\approx\frac{1}{4V}+\frac{3}{16V^2}+\cdots+=\frac{w}{2}+\frac{3}{4}w^2+\cdots+,\qquad(62)$$

which is the previously obtained expansion (55a). We can now write

$$m_1=\lambda\ \ln s^2+\tfrac{1}{2}(\lambda^2-C_2{}^2)s -(s/2u)[\ln 2u-\ln(1+u/s)-\ln\xi+a_0+\phi(w)]. \quad (63)$$

We rewrite $w=s/\xi^2=s/Zt^2$. Thus for Z large, w is small, and $\phi(w)$ is given by (62). Therefore

$$\tilde{m}_1\approx\lambda\ \ln s^2+\tfrac{1}{2}(\lambda^2-C_2{}^2)s -\frac{s}{2u}[\ln 2u-\ln(1+u/s)-\ln\xi+a_0] -\frac{1}{Z}\frac{s}{4ut^2}+O\left(\frac{1}{Z^2}\right). \quad (64)$$

Truncating (64) according to the prescription at the end of Sec. 6 to obtain $\tilde{m}_{1E}$, we note that for $\tilde{m}_{1E}$ to match $\tilde{r}_{1E}$ we must choose

$$a_0=\tfrac{1}{2}\ln Z. \quad (65)$$

Now that we have determined M_1 completely, to obtain the expansion near $\xi=0$ we partially integrate (59b) to increasing powers of V, obtaining

$$g(V)=e^V\left[-\frac{2}{V^{1/2}}+4V^{1/2}\left(1-\tfrac{2}{3}V-\frac{2^2}{3\times 5}V^2+\cdots+\right)\right], \quad (66)$$

which leads to

$$\phi(V)\approx\tfrac{1}{2}\ln V-V+\sum_{j=2}\frac{2^{j-1}V^j}{[1\times 3\times\cdots\times(2j-1)](j)}. \quad (67)$$

In terms of our variables ξ and s,

$$\phi\approx\tfrac{1}{2}\ln\frac{\xi^2}{2s}-\frac{1}{2}\frac{\xi^2}{s}+O\left(\frac{\xi^4}{s^2}\right),$$
$$\phi\approx\ln\xi-\tfrac{1}{2}\ln 2s-\frac{1}{2}\frac{\xi^2}{s}. \quad (68)$$

Substituting into (55) for ξ^2/s small, we obtain

$$M_1\approx-\tfrac{1}{2}\ln 2s+\tfrac{1}{2}\ln Z-\tfrac{1}{2}(\xi^2/s), \quad (69)$$

and our solution m_1 no longer shows the singularity for t small which appeared in the original asymptotic expansion r_1. Thus the correct solution to be used in region Ia is

$$m_1=\lambda\ \ln\tfrac{1}{4}s^2+\tfrac{1}{2}(\lambda^2-C_2{}^2)s+\frac{s}{2u}\left[-\tfrac{1}{2}\ln Z-\ln 2u +\ln\left(1+\frac{u}{s}\right)+\tfrac{1}{2}\ln 2s+\frac{1}{2}\frac{Zt^2}{s}+O\left(\frac{Zt^2}{s}\right)^2\right]. \quad (70)$$

Now let us consider region Ib. We choose the stretching

$$\xi=Z^{1/2}t,\quad \gamma=Zu.$$

Therefore

$$\tilde{\psi}_1=e^{-(Z-\lambda)s}\left\{1+\frac{1}{Z}\left(\lambda\ln\left[\frac{s^2}{4}\left(1-\frac{\xi^2}{Zs^2}\right)\right] +\tfrac{1}{2}(\lambda^2-C_2{}^2)s+\tilde{C}_{12}\right)\right\}, \quad (71)$$

with

$$\tilde{C}_{12}=-\frac{1}{2\tilde{d}_1}\ln\left[\frac{\gamma/Z+\tilde{d}_1 s}{(1+\tilde{d}_1)\,|\xi/Z^{1/2}|}\right]$$

and

$$\tilde{d}_1=\left[\frac{\gamma^2/Z^2-\xi^2/Z}{s^2-\xi^2/Z}\right]^{1/2}. \quad (71a)$$

For large Z,

$$\tilde{d}_1\approx\frac{i\xi}{Z^{1/2}s}\left[1+\frac{1}{2Z}\left(\frac{\xi^2}{s^2}-\frac{\gamma^2}{\xi^2}\right)\right],$$

leading to

$$\tilde{C}_{12}\approx-\frac{Z^{1/2}\pi}{4}\frac{s}{|\xi|}+\frac{1}{2}\left(\frac{su}{\xi^2}+1\right). \quad (72)$$

Truncating (keeping three terms this time), we find

$$\tilde{\psi}_{1E}=e^{-(Z-\lambda)s}\left\{1-\frac{1}{Z^{1/2}}\frac{\pi}{4}\frac{s}{|\xi|}+Z^{-1}\left[\lambda\ \ln\tfrac{1}{4}s^2+\tfrac{1}{2}(\lambda^2-C_2{}^2)s +\frac{1}{2}\left(\frac{s\gamma}{\xi^2}+1\right)\right]+O\left(\frac{1}{Z^{3/2}}\right)\right\}. \quad (73)$$

Now from the Appendix we see that the equation for m_1 in region Ib takes the form

$$\frac{\partial^2 m_1}{\partial\gamma^2}+2\frac{\xi}{\gamma}\frac{\partial^2 m_1}{\partial\gamma\partial\xi}+2\left(\frac{\xi^2}{\gamma s}+\frac{1}{\gamma}\right)\frac{\partial m_1}{\partial\gamma}-\frac{1}{\gamma}=0. \quad (74)$$

Using a power series construct as in case Ia, we are led to an m_1 of the form

$$m_1=a_0(s)+\gamma\chi(w), \quad (75)$$

where $w=\xi^2/s$ as before. Substituting (75) into (74), we find that $\chi(w)$ satisfies

$$4w(d\chi/dw)+2[w+1]\chi-1=0, \quad (76)$$

which has the solution

$$\chi=C\frac{1}{w^{1/2}}e^{-w/2}+\frac{1}{4w^{1/2}}e^{-w/2}\int_{-\infty}^{w}\frac{1}{w^{1/2}}e^{w/2}dw. \quad (77)$$

In order that our solution be even in t, we choose $C=0$. For w large, we integrate by parts to obtain

$$\chi(w)\approx\frac{1}{2w}\left[1+\frac{1}{w}+O\left(\frac{1}{w^2}\right)\right]. \quad (78)$$

For Z large, w large, comparison with (73) indicates that one should take

$$a_0=\lambda\ \ln\tfrac{1}{4}s^2+\tfrac{1}{2}(\lambda^2-C_2{}^2)s+\tfrac{1}{2} \tag{79}$$

in order to match everything except the $1/Z^{1/2}$ term.

Now for t small, w small, one can integrate (77) to higher powers of w to obtain

$$\chi(w)=\tfrac{1}{2}\sum_{n=0}(-1)^n\frac{1}{3\times5\times\cdots\times(2n+1)}w^n. \tag{80}$$

We now note that if we had included an $m_{1/2}/Z^{1/2}$ term in expansion (42), $m_{1/2}$ would have satisfied the homogeneous part of Eq. (74), and any function $m_{1/2}(s,\xi)$ is an acceptable solution. We shall now show that $m_{1/2}$ cannot enter our asymptotic solution in the neighborhood of $\xi\approx0$. Let us first write down our asymptotic solution in region Ib as

$$\psi\approx e^{-(Z-\lambda)s}\left\{1+\tfrac{1}{2}u\left[1-\frac{1}{3}\left(\frac{Zt^2}{s}\right)+O\left(\frac{Zt^2}{s}\right)^2\right]\right.$$
$$\left.+\frac{m_{1/2}(s,\xi)}{Z^{1/2}}+Z^{-1}[\lambda\ \ln\tfrac{1}{4}s^2+\tfrac{1}{2}(\lambda^2-C_2{}^2)s+\tfrac{1}{2}]\right\}. \tag{81}$$

From Part B of Sec. 6, we expect that in region Ib

$$\frac{\partial\psi}{\partial u}(\xi,\gamma,s)\approx O(Z^{1/2})\frac{\partial\psi}{\partial t}(\xi,\gamma,s). \tag{82}$$

One observes that

$$\frac{\partial\psi}{\partial t}\approx e^{-(Z-\lambda)s}\left[-\frac{1}{12s}Ztu+\frac{1}{Z^{1/2}}\frac{\partial m_{1/2}}{\partial t}\right]$$
$$=e^{-(Z-\lambda)s}\left[-\frac{\xi\gamma}{12s}\frac{1}{Z^{1/2}}+\frac{1}{Z^{1/2}}\frac{\partial m_{1/2}}{\partial t}\right] \tag{83a}$$

and

$$\partial\psi/\partial u\approx\tfrac{1}{2}e^{-(Z-\lambda)s}. \tag{83b}$$

Now assume $m_{1/2}(s,\xi)$ is expressible as a power series about $\xi=0$. For jth order term in series $(m_{1/2}{}^j)$,

$$\partial m_{1/2}{}^j/\partial t\approx Z^{j/2}t^{j-1}=j\xi^{j-1}Z^{1/2}. \tag{84}$$

This would contribute a term of order Z^0 in $\partial\psi/\partial t$, in addition to the term already present of order $Z^{-1/2}$, and condition (82) would not then be fulfilled. Thus in the vicinity of $\xi\approx0$, $m_{1/2}$ must vanish identically and therefore will not contribute to (81). Thus, finally, for the solution in region Ib, we write

$$\psi\approx e^{-(Z-\lambda)s}\left\{1+\tfrac{1}{2}u\left[1-\frac{1}{3}\left(\frac{Zt^2}{s}\right)+O\left(\frac{Zt^2}{s}\right)^2\right]\right.$$
$$\left.+Z^{-1}[\lambda\ \ln\tfrac{1}{4}s^2+\tfrac{1}{2}(\lambda^2-C_2{}^2)s+\tfrac{1}{2}]\right\}. \tag{81a}$$

Now according to a theorem proved by Kato,[21] the exact wave function satisfies the cusp condition at $u=0$ of the form

$$\left.\frac{1}{\psi}\frac{\partial\psi}{\partial u}\right|_{u=0,t=0}=\frac{1}{2}. \tag{85}$$

Performing these operations on our solution (81a), we find that

$$\left.\frac{\partial\psi/\partial u}{\psi}\right|_{u=0,t=0}=\tfrac{1}{2}[1-Z^{-1}(\lambda\ \ln\tfrac{1}{4}s^2+\beta s+\tfrac{1}{2})]. \tag{86}$$

Therefore, in the limit that $Z\rightarrow\infty$, this cusp condition is identically satisfied.

In order to obtain our expansion for one or both of the electrons near the origin, it is convenient to rewrite the Schrödinger 2-electron equation in terms of variables s_1, s_2, u.

$$\frac{\partial^2\psi}{\partial s_1{}^2}+\frac{2}{s_1}\frac{\partial\psi}{\partial s_1}+\frac{\partial^2\psi}{\partial s_2{}^2}+\frac{2}{s_2}\frac{\partial\psi}{\partial s_2}+2\frac{\partial^2\psi}{\partial u^2}+\frac{4}{u}\frac{\partial\psi}{\partial u}$$
$$+\frac{(s_1{}^2-s_2{}^2+u^2)}{s_1u}\frac{\partial^2\psi}{\partial s_1\partial u}+\frac{(s_2{}^2-s_1{}^2+u^2)}{s_2u}\frac{\partial^2\psi}{\partial s_2\partial u}$$
$$+2\left(E+\frac{Z}{s_1}+\frac{Z}{s_2}-\frac{1}{u}\right)\psi=0. \tag{87}$$

For the case that electron 1 is near the nucleus, let us assume an integral stretching of the form $\xi_1=Zs_1$ is correct. Noting that in terms of u, s_1, and s_2, d in r_1 is expressed as

$$d=\{[u^2-(s_2-s_1)^2]/4s_1s_2\}^{1/2}, \tag{88}$$

we can write

$$\tilde{\psi}_1=e^{-(Z-\lambda)s_2}e^{-\xi_1}e^{\lambda\xi_1/Z}\left\{1+Z^{-1}\left[\lambda\left(\ln\frac{\xi_1}{Z}+\ln s_2\right)\right.\right.$$
$$\left.\left.+\tfrac{1}{2}(\lambda^2-C_2{}^2)(\xi_1/Z+s_2)+\tilde{C}_{12}\right]\right\}, \tag{89}$$

with

$$\tilde{C}_{12}=-\frac{1}{2\tilde{d}_1}\ln\left[\frac{u+\tilde{d}_1(\xi_1/Z+s_2)}{(1+\tilde{d}_1)(s_2-\xi_1/Z)}\right]$$

and

$$\tilde{d}_1=\left[\frac{u^2-(s_2-\xi_1/Z)^2}{4(\xi_1/Z)s_2}\right]^{1/2}. \tag{89a}$$

For large Z,

$$\tilde{d}_1\approx\frac{Z^{1/2}}{2}\left[\frac{u^2-s_2{}^2}{\xi_1s_2}\right]^{1/2}, \tag{89b}$$

which leads to an expansion for Z large of the form

$$\tilde{C}_{12}\approx-\frac{2}{Z}\left[\frac{\xi_1}{u+s_2}\right]+O\left(\frac{1}{Z^2}\right). \tag{90}$$

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[21] T. Kato, New York University Research Report CX-25, 1956 (unpublished).

Therefore, truncating to two orders,

$$\tilde{\psi}_{1E}=e^{-(Z-\lambda)s_2}e^{-\xi_1}\left\{1+\frac{1}{Z}\left[-\lambda \ln Z+\lambda\xi_1+\lambda \ln\xi_1+\lambda \ln s_2+\tfrac{1}{2}(\lambda^2-C_2^2)s_2\right]\right\}. \tag{91}$$

This suggests that we look for a solution of the stretched equation of the form

$$\Psi=e^{-(Z-\lambda)s_2}e^{-\xi_1}(1+Z^{-1}[m_1^{(1)}(\xi)+m_1^{(2)}(s_2)]+Z^{-2}m_2+\cdots+). \tag{92}$$

Making this ansatz and substituting into the stretched P.D.E.,

$$Z^2\left[\frac{\partial^2\psi}{\partial\xi_1^2}+\frac{2}{\xi_1}\frac{\partial\psi}{\partial\xi_1}\right]+\frac{\partial^2\psi}{\partial s_2^2}+\frac{2}{s_2}\frac{\partial\psi}{\partial s_2}+2\frac{\partial^2\psi}{\partial u^2}+\frac{4}{u}\frac{\partial\psi}{\partial u}+\frac{\xi_1}{u}\frac{\partial^2\psi}{\partial\xi_1\partial u}-Z^2\frac{s_2^2}{\xi_1 u}\frac{\partial^2\psi}{\partial\xi_1\partial u}+Z^2\frac{u}{\xi_1}\frac{\partial^2\psi}{\partial\xi_1\partial u}$$

$$+\left[\frac{s_2}{u}-\frac{1}{Z^2}\frac{\xi_1^2}{us_2}+\frac{u}{s_2}\right]\frac{\partial^2\psi}{\partial s_2\partial u}+2\left[-Z^2(C_0^2-Z^{-1}C_1^2+Z^{-2}C_2^2+\cdots+)+\frac{Z^2}{\xi_1}+\frac{Z}{s_2}-\frac{1}{u}\right]\psi=0, \tag{93}$$

we obtain, from setting the coefficient of $Z^{(1)}$ terms equal to zero,

$$\frac{\partial^2 m_1^{(1)}}{\partial\xi_1^2}+\left[\frac{2}{\xi_1}-2\right]\frac{\partial m_1^{(1)}}{\partial\xi_1}=-C_1^2. \tag{94}$$

A solution of this equation is

$$m_1^{(1)}=\lambda\left[\xi_1+\ln\xi_1-\frac{1}{2\xi_1}-\frac{1}{2}\int_{-\infty}^{\xi_1}\frac{d\xi_1 e^{2\xi_1}}{\xi_1^2}+C\right], \tag{95}$$

where C is a constant to be determined.

From setting the coefficient of the $Z^{(0)}$ terms equal to zero, we obtain

$$-2\left[\frac{\partial m_1^{(2)}}{\partial s_2}-\frac{\lambda}{s_2}+\tfrac{1}{2}(C_2^2-\lambda^2)\right]+\frac{\partial^2 m_2}{\partial\xi_1^2}+2\left[\frac{1}{\xi_1}-1\right]\frac{\partial m_2}{\partial\xi_1}$$

$$-C_2^2+C_1^2[m_1^{(1)}+m_1^{(2)}]+\frac{1}{\xi_1 u}[u^2-s_2^2]\left[\frac{\partial m_2}{\partial u}+\frac{\partial^2 m_2}{\partial u\partial\xi_1}\right]-\frac{2}{u}=0. \tag{96}$$

Choosing to set the first parenthesis itself equal to zero, we obtain

$$m_1^{(2)}=\lambda \ln s_2+\tfrac{1}{2}[\lambda^2-C_2^2]s_2. \tag{97}$$

For Z large, we can rewrite

$$\tilde{m}_1^{(1)}\approx\lambda\left[Zs_1+\ln Zs_1-\frac{1}{2Zs_1}-\frac{1}{2Z}\right.$$

$$\left.\times\int_{-\infty}^{Zs_1}ds_1\,(e^{2Zs_1}/s_1^2)+C\right], \tag{95a}$$

and performing the usual truncation procedure,

$$\tilde{m}_{1E}^{(1)}\approx\lambda[Zs_1+\ln Zs_1+O(1/Z)+C]. \tag{95b}$$

Considering (97) and (95b) in (92), we observe that the matching condition with (91) is made if we choose

$$C=-\ln Z. \tag{98}$$

Thus the matched stretched solution is

$$\Psi=e^{-(Z-\lambda)s_2}e^{-\xi_1}\left\{1+Z^{-1}\left[\lambda \ln s_2+\tfrac{1}{2}(\lambda^2-C_2^2)s_2\right.\right.$$

$$\left.\left.+\lambda\left(\xi_1+\ln\xi_1-\frac{1}{2\xi_1}-\frac{1}{2}\int_{-\infty}^{\xi_1}\frac{d\xi e^{2\xi}}{\xi^2}-\ln Z\right)\right]\right\}. \tag{99}$$

To obtain the expansion for s_1 small, we integrate by parts to higher powers of ξ to obtain

$$\Psi=e^{-(Z-\lambda)s_2}e^{-\xi_1}\{1+Z^{-1}[-\lambda \ln Z+\lambda \ln s_2$$

$$+\tfrac{1}{2}(\lambda^2-C_2^2)s_2-\lambda(\tfrac{1}{3}\xi_1^2+O(\xi_1^3))]\},$$

and therefore

$$\Psi\approx e^{-(Z-\lambda)s_2}e^{-Zs_1}(1-\lambda Z^{-1}[\tfrac{1}{3}(Zs_1)^2+O(Zs_1)^3]$$

$$+Z^{-1}[-\lambda \ln Z+\lambda \ln s_2+\tfrac{1}{2}(\lambda^2-C_2^2)s_2]\}, \tag{100}$$

for the case of s_1 small (in region IIa). Thus the correct asymptotic expansion has no divergences at $s_1=0$. The solution shows the expected physical characteristic that for one electron very near to the origin the shielding effect of the outer electron upon it goes to zero.

The cusp condition at $s_1=0$ satisfied exactly by the correct wave function is

$$\left.\frac{1}{\psi}\frac{\partial\psi}{\partial s_1}\right|_{s_1=0}=-Z. \tag{101}$$

Now for our asymptotic solution (100),

$$\frac{\partial\psi}{\partial s_1}=-Z\psi+e^{-(Z-\lambda)s_2}e^{-Zs_1}[-\tfrac{2}{3}Z\lambda s_1+O(s_1^2)], \tag{102}$$

which in the limit $s_1=0$ becomes

$$\left.\frac{\partial\psi}{\partial s_1}\right|_{s_1=0}=-Z\psi(s_1=0). \tag{103}$$

Our asymptotic solution identically satisfies this cusp condition.

In region IIb, we perform additional integral stretching on s_2 and u. We define $\xi_1=Zs_1$, $\xi_2=Zs_2$, and $\gamma=Zu$. One can readily show that for this case

$$\begin{aligned}\tilde{\psi}_{1E}=e^{-(\xi_2+\xi_1)}(1+Z^{-1}[&-2\lambda\ln Z+\lambda(\xi_1+\xi_2)\\&+\lambda(\ln\xi_1+\ln\xi_2)+C_{12}(\xi_1,\xi_2,\gamma)]),\end{aligned} \tag{104}$$

with

$$C_{12}(\xi_1,\xi_2,\gamma)=-\frac{1}{2d}\ln\left(\frac{\gamma+d(\xi_1+\xi_2)}{(1+d)|\xi_2-\xi_1|}\right)$$

and

$$d=\left(\frac{\gamma^2-(\xi_2-\xi_1)^2}{4\xi_1\xi_2}\right)^{1/2}.$$

Transforming Eq. (87) to new coordinates, we obtain the usual "perturbation theory" equation in the form

$$\begin{aligned}\frac{\partial^2\psi}{\partial\xi_1^2}+\frac{2}{\xi_1}\frac{\partial\psi}{\partial\xi_1}+\frac{\partial^2\psi}{\partial\xi_2^2}+\frac{2}{\xi_2}\frac{\partial\psi}{\partial\xi_2}+2\frac{\partial^2\psi}{\partial\gamma^2}+\frac{4}{\gamma}\frac{\partial\psi}{\partial\gamma}+\frac{(\xi_1^2-\xi_2^2+\gamma^2)}{\xi_1\gamma}\frac{\partial^2\psi}{\partial\xi_1\partial\gamma}+\frac{(\xi_2^2-\xi_1^2+\gamma^2)}{\xi_2\gamma}\frac{\partial^2\psi}{\partial\xi_2\partial\gamma}&\\+2\left[(-C_0^2+Z^{-1}C_1^2-Z^{-2}C_2^2+\cdots+)+\frac{1}{\xi_1}+\frac{1}{\xi_2}\right]\psi-\frac{1}{Z}\frac{2}{\gamma}\psi=0.&\end{aligned} \tag{105}$$

We look for a solution of (105) of the form

$$\Psi=e^{-(\xi_1+\xi_2)}(1+Z^{-1}[m_1^{(1)}(\xi_1)+m_1^{(2)}(\xi_2)+M_1(\xi_1,\xi_2,\gamma)]+Z^{-2}m_2(\xi_1,\xi_2,\gamma)+\cdots+). \tag{106}$$

Substituting (106) into (105), one finds that $m_1^{(1)}$ and $m_1^{(2)}$ satisfy equations of the form (94) in their respective variables. Therefore, from the analysis for region IIa, it follows that $m_1^{(1)}$ and $m_1^{(2)}$ will be matched with the first three terms of the coefficient of $1/Z$ in Eq. (104). We find the remaining equation satisfied by M_1 to be

$$\begin{aligned}\frac{\partial^2M_1}{\partial\xi_1^2}+2\left[\frac{1}{\xi_1}-1\right]\frac{\partial M_1}{\partial\xi_1}+\frac{\partial^2M_1}{\partial\xi_2^2}+2\left[\frac{1}{\xi_2}-1\right]\frac{\partial M_1}{\partial\xi_2}+2\frac{\partial^2M_1}{\partial\gamma^2}+\frac{4}{\gamma}\frac{\partial M_1}{\partial\gamma}-\left[\frac{\xi_1^2-\xi_2^2+\gamma^2}{\xi_1\gamma}+\frac{\xi_2^2-\xi_1^2+\gamma^2}{\xi_2\gamma}\right]\frac{\partial M_1}{\partial\gamma}&\\+\left[\frac{\xi_1^2-\xi_2^2+\gamma^2}{\xi_1\gamma}\right]\frac{\partial^2M_1}{\partial\xi_1\partial\gamma}+\left[\frac{\xi_2^2-\xi_1^2+\gamma^2}{\xi_2\gamma}\right]\frac{\partial^2M_1}{\partial\xi_2\partial\gamma}=-\frac{2}{\gamma}.&\end{aligned} \tag{107}$$

Since we have already taken proper care of the functions depending only on either variable ξ_1 or ξ_2 near the origin with our choice of $m_1^{(1)}$ and $m_1^{(2)}$, we expect that near the origin

$$M_1=C\gamma+O(\gamma l), \tag{108}$$

where C is a constant to be determined and l represents one of the fundamental smallness distances γ, ξ_1, or ξ_2. Substitution of (108) into (107) gives $C=\frac{1}{2}$. Although we have not shown the matching condition fulfilled for M_1 with C_{12}, we have determined the leading term of M_1 near the origin. Thus for region IIb, keeping only the leading terms of $m_1^{(1)}$ and $m_1^{(2)}$, we have

$$\begin{aligned}\psi\approx e^{-Zs_1}e^{-Zs_2}[1&-2\lambda(\ln Z/Z)+\tfrac{1}{2}u\\&-\tfrac{1}{3}\lambda Z(s_1^2+s_2^2)+O(\gamma l/Z)],\end{aligned} \tag{109}$$

assuming no other constants are brought in by matching M_1. Note that (109) identically satisfies the cusp condition (101) for s_1 or s_2 equal to zero. The cusp condition at $u=0$ is exactly satisfied in the limit that $Z\rightarrow\infty$. Thus, in the neighborhood of the origin,

$$\psi\approx1-Z(s_1+s_2)+u/2-2\lambda(\ln Z)/Z+O(l^2), \tag{109a}$$

in the limit of infinite Z, our ψ gives correct[22] behavior. This is to be compared with perburbation theory where the coefficient of the u term near the origin does not go over to its exact theoretical value in the infinite Z case.[23] Since ordinary perturbation theory assumes at the outset no $\ln Z$ terms are present in the wave-function expansion, whereas we have shown that in certain spatial regions they must be included, it is not surprising that the perturbation theory wave functions and expectation values calculated from them will show certain failings.

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[22] V. Fock, Izv. Akad. Nauk SSSR, Ser. Fiz. **18**, 161 (1954).

[23] Reference 13, p. 435.

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APPENDIX: ORDERING OF TERMS FOR j, k COORDINATE STRETCHING

The values of j, k for the regions A (no stretching), Ia, and Ib are, respectively, $(j=0, k=0)$, $(j=0, k=\frac{1}{2})$, and $(j=1, k=\frac{1}{2})$. Equation (A1) is as follows:

$$
\begin{aligned}
&us^2\Bigg[\{Z^2\}+\{Z(m_1-2\lambda)\}+\underset{(-j;\,\mathrm{A},\,\mathrm{Ia})}{\lambda^2}-\{2\lambda m_1\}+\{m_2\}-\underset{(-j;\,\mathrm{A},\,\mathrm{Ia})}{2\frac{\partial m_1}{\partial s}}\\
&\qquad+\frac{1}{Z}\bigg(\underset{(-j-1)}{2\lambda m_2}-\underset{(-j-1)}{2\frac{\partial m_2}{\partial s}}+\underset{(-j-1)}{2\lambda\frac{\partial m_1}{\partial s}}+\underset{(-j-1)}{\frac{\partial^2 m_1}{\partial s^2}}+\underset{(2k-j-1;\,\mathrm{Ia})}{\frac{\partial^2 m_1}{\partial t^2}}+\underset{(j-1;\,\mathrm{Ib})}{\frac{\partial^2 m_1}{\partial u^2}}\bigg)\Bigg]\\
&-ut^2\Bigg[\{Z^2\}+\{Z(m_1-2\lambda)\}+\underset{(-2k-j;\,\mathrm{A})}{\lambda^2}-\{2\lambda m_1\}+\{m_2\}-\underset{(-2k-j;\,\mathrm{A})}{2\frac{\partial m_1}{\partial s}}\\
&\qquad+\frac{1}{Z}\bigg(\underset{(-2k-j-1)}{2\lambda m_2}-\underset{(-2k-j-1)}{2\frac{\partial m_2}{\partial s}}+\underset{(-2k-j-1)}{2\lambda\frac{\partial m_1}{\partial s}}+\underset{(-2k-j-1)}{\frac{\partial^2 m_1}{\partial s^2}}+\underset{(-j-1)}{\frac{\partial^2 m_1}{\partial t^2}}+\underset{(j-2k-1)}{\frac{\partial^2 m_1}{\partial u^2}}\bigg)\Bigg]\\
&+2su^2\Bigg[-\underset{(-j;\,\mathrm{A},\,\mathrm{Ia})}{\frac{\partial m_1}{\partial u}}+\frac{1}{Z}\bigg(\underset{(-j-1)}{\frac{\partial^2 m_1}{\partial s\partial u}}-\underset{(-j-1)}{\frac{\partial m_2}{\partial u}}+\underset{(-j-1)}{\lambda\frac{\partial m_1}{\partial u}}\bigg)\Bigg]-2st^2\Bigg[-\underset{(j-2k;\,\mathrm{A},\,\mathrm{Ib})}{\frac{\partial m_1}{\partial u}}+\frac{1}{Z}\bigg(\underset{(j-2k-1)}{\frac{\partial^2 m_1}{\partial s\partial u}}-\underset{(j-2k-1)}{\frac{\partial m_2}{\partial u}}+\underset{(j-2k-1)}{\lambda\frac{\partial m_1}{\partial u}}\bigg)\Bigg]\\
&+2ts^2\underset{(j-1;\,\mathrm{Ib})}{\left(\frac{1}{Z}\frac{\partial^2 m_1}{\partial u\partial t}\right)}-2tu^2\underset{(-j-1)}{\left(\frac{1}{Z}\frac{\partial^2 m_1}{\partial u\partial t}\right)}+4su\Bigg[\underset{(-j;\,\mathrm{A},\,\mathrm{Ia})}{-\{Z\}+\lambda-\{m_1\}}+\frac{1}{Z}\bigg(\underset{(-j-1)}{\frac{\partial m_1}{\partial s}}-\underset{(-j-1)}{m_2}+\underset{(-j-1)}{\lambda m_1}\bigg)\Bigg]\\
&+\underset{(j-1;\,\mathrm{Ib})}{2(s^2}-\underset{(j-2k-1)}{t^2)}\frac{1}{Z}\frac{\partial m_1}{\partial u}+4Zsu\left(\{1\}+\left\{\frac{m_1}{Z}\right\}\right)-\underset{(0;\,\mathrm{A},\,\mathrm{Ia},\,\mathrm{Ib})}{s^2}\bigg(1+\underset{(-1)}{\frac{m_1}{Z}}\bigg)+\underset{(-2k;\mathrm{A})}{t^2}\bigg(1+\underset{(-2k-1)}{\frac{m_1}{Z}}\bigg)-\underset{(-j-1)}{4ut\frac{1}{Z}\frac{\partial m_1}{\partial t}}\\
&+us^2\big[-\{Z^2\}+Z(-\{m_1\}+\{C_1^2\})+\{C_1^2m_1\}-\{m_2\}-\underset{(-j;\,\mathrm{A},\,\mathrm{Ia})}{C_2^2}\big]\\
&\qquad-ut^2\big[-\{Z^2\}+Z(-\{m_1\}+\{C_1^2\})+\{C_1^2m_1\}-\{m_2\}-\underset{(-j-2k)}{C_2^2}\big]=0. \qquad \text{(A1)}
\end{aligned}
$$