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Asymptotic forms of two-electron wave functions with a monopole interaction

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The leading term in the Neumann expansion of $1/r_{12}$ is $1/r_>$, where $r_>$ signifies the greater of r_1 and r_2. Defining the monopole Hamiltonian (also called the radial-limit Hamiltonian) as the two-electron Hamiltonian with the replacement $1/r_{12}\rightarrow 1/r_>$, the author presents asymptotic forms of the eigenfunction of this operator. The bound-bound, bound-free, and free-free cases are treated. "Asymptotic" means here that $r_1\rightarrow\infty$, $r_2\rightarrow\infty$, but r_1/r_2 is not restricted.

I. INTRODUCTION

In the theoretical treatment of atomic-molecular processes in which the final state consists of an ionic core plus two free electrons, a long-standing problem has been how to account correctly for the mutual screening effects of the two free electrons. The effect of this screening will be most important for low-energy reactions and should show up vividly in differential as opposed to total cross sections. A wave function with these screening effects incorporated, then, would be useful for the treatment of low-energy electron-impact ionization of atoms and molecules[1-3] and also for the calculation of double-photoionization cross sections.[4-7]

In perturbation-theory (PT) or configuration-interaction (CI) approaches to this type of problem, one chooses an orthogonal basis set of bound and continuum orbitals, and it is not possible to choose continuum orbitals which are computed in correct asymptotic potentials for all states of the system under description. For example, the asymptotic effective charge in a Coulomb potential for a free electron is one for a singly-ionized state and something else for a doubly-ionized state, yet one basis set must, in principle, describe both situations. The signal that incorrect asymptotic forms are being used in the basis is the occurrence of singularities in certain matrix elements due to the long range of the Coulomb potential.[8] These singularities can evidently be integrated over in PT treatments,[7,8] but are more difficult to deal with in a CI approach.[9]

This two-free-electron screening problem is found at its simplest in two-electron systems, so we will consider only these. The term in the electron-electron interaction which gives rise to asymptotic Coulomb fields is just the first term in the Neumann expansion of $1/r_{12}$, i.e.,

$$1/r_{12} = 1/r_> + \cdots , \tag{1}$$

where $r_>$ is the greater of r_1 and r_2. The two-electron Hamiltonian with just this term included will be called the monopole Hamiltonian H_M, and evidently, eigenfunctions of H_M will always have proper asymptotic forms whether describing singly- or doubly-ionized states.

The eigenvalues of H_M for ground states have attracted some interest in the past. The problem reduces to a two-dimensional one, and various forms of variational wave functions have been employed[10] as well as a pure numerical treatment.[11] Calculations of phase shifts, using H_M as the Hamiltonian, have also been carried out for electron-hydrogen elastic scattering.[12]

We present in this paper asymptotic solutions to the Schrödinger equation, with H_M, for all possible two-electron states, i.e., bound-bound, bound-free, and free-free. "Asymptotic" means here that $r_1\rightarrow\infty$, $r_2\rightarrow\infty$, but r_1/r_2 can have any value. The asymptotic region is specified more closely below. The free-free states are of the greatest interest and may have immediate application by themselves, but the motivation of this investigation is to generate ultimately two-dimensional basis functions which are eigenfunctions of H_M and use them for a CI or PT treatment of continuum processes. Such basis sets have the virtue that there are no singular matrix elements of the interaction, not even in the element with four continuum functions. Some progress has been made in this direction, which will be reported in a later paper.

II. THEORY

The Hamiltonian, in atomic units, whose eigenvalues and eigenvectors we are seeking is given by

$$H_M = -\tfrac{1}{2}(\nabla_1^2+\nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_>}. \tag{2}$$

Because the interaction term $1/r_>$ is not able to transfer angular momentum between the two electrons, the individual angular-momentum quantum numbers of each electron are good quantum numbers. Thus the wave function factors into

a radial part times a product of spherical harmonics, or a linear combination of such terms. If both electrons have the same angular momentum, the wave function is just a simple product and we consider this case first. For simplicity we let $l_1 = l_2 = 0$. The case with the electrons carrying different angular momenta will be dealt with later.

With angular variables taken care of, the problem reduces to two dimensions. Introducing scaled variables, $\rho_i = Zr_i$, $i = 1, 2$, the Schrödinger equation, for an energy E, reduces to

$$\mathfrak{L}\Phi(\rho_1, \rho_2) \equiv \left(\frac{\partial^2}{\partial \rho_1^2} + \frac{\partial^2}{\partial \rho_2^2} + \frac{2}{\rho_1} + \frac{2\zeta}{\rho_2} + \epsilon \right) \Phi(\rho_1, \rho_2) = 0, \quad \rho_1 \leq \rho_2, \tag{3}$$

where $\zeta \equiv 1 - 1/Z$, $\epsilon = 2E/Z^2$, and $\Phi(\rho_1, \rho_2)$ is $\rho_1\rho_2$ times $\Psi(\rho_1, \rho_2)$, the eigenfunction. For $\rho_1 \geq \rho_2$, the variables ρ_1 and ρ_2 are interchanged in Eq. (3). This equation is to be solved subject to the boundary conditions

$$\Psi(\rho_1, \rho_2), \quad \frac{\partial \Psi(\rho_1, \rho_2)}{\partial \rho_1}, \quad \frac{\partial \Psi(\rho_1, \rho_2)}{\partial \rho_2} \tag{4a}$$

must be finite everywhere,

$$\Psi(\rho_1, \rho_2) \xrightarrow[\rho_1, \rho_2 \to \infty]{} 0 \quad \text{for bound states}, \tag{4b}$$

$$\left.\frac{\partial \Psi}{\partial \rho_1}\right|_{\rho_1 = \rho_2} - \left.\frac{\partial \Psi}{\partial \rho_2}\right|_{\rho_1 = \rho_2} = 0 \quad \text{(singlet states)}, \tag{4c}$$

$$\Psi(\rho_1, \rho_2)_{\rho_1 = \rho_2} = 0 \quad \text{(triplet states)}. \tag{4d}$$

The imposition of conditions (4a) and (4b) follows from general requirements of wave mechanics. Condition (4c) is necessary to ensure that the derivatives of $\Psi(\rho_1, \rho_2)$ are continuous at $\rho_1 = \rho_2$. Because the function $\Psi(\rho_1, \rho_2)$ is symmetric in ρ_1 and ρ_2, the slope normal to the $\rho_1 = \rho_2$ line must vanish. The spatial part of a triplet wave function is antisymmetric with respect to ρ_1 and ρ_2, and condition (4d) enforces this.

But now we are able to restrict the domain of ρ_1 and ρ_2 to $\rho_1 \leq \rho_2$ because we have boundary conditions along the $\rho_1 = \rho_2$ border. From here on, it is understood that $\rho_1 \leq \rho_2$, and we will no longer note it explicitly. Having the wave function in one half-plane, it is a simple matter to represent it in the other. For singlet functions $\Psi(\rho_1, \rho_2) = \Psi(\rho_2, \rho_1)$, while for triplets, $\Psi(\rho_1, \rho_2) = -\Psi(\rho_2, \rho_1)$.

We begin by looking at states in which one electron is bound and one is free. We consider scattering states of the type $1s - ks$, i.e., elastic scattering only. In the region $\rho_2 \gg \rho_1$ we write down the familiar scattering-type asymptotic form,

$$\Phi(\rho_1, \rho_2) \underset{\substack{\rho_2 \to \infty \\ \rho_2 \gg \rho_1}}{\sim} \rho_1 e^{-\rho_1} \rho_2^{i\zeta/k} e^{ik\rho_2} + \text{c.c.} \tag{5}$$

All constants which play no significant role in the development have been suppressed. The complex-conjugate term is noted specifically in Eq. (5) but will not be carried further as it adds nothing essential. The factor $\rho_2^{i\zeta/k}$ is present because the ρ_2 function must be an asymptotic solution to the Coulomb wave equation with effective charge ζ.

The form in Eq. (5) is a solution to Eq. (3) to $O(1/\rho_2^2)$, but cannot be extended to the region $\rho_1 \simeq \rho_2$ because it does not obey the boundary conditions (4c) or (4d). However, a function which obviously satisfies the boundary condition is given by a symmetrical version of (5),

$$\begin{aligned} \Phi(\rho_1, \rho_2) &\underset{\substack{\rho_1 \to \infty \\ \rho_2 \to \infty}}{\sim} \rho_1 e^{-\rho_1} \rho_2^{i\zeta/k} e^{ik\rho_2} \\ &\quad \pm \rho_2 e^{-\rho_2} \rho_1^{i\zeta/k} e^{ik\rho_1}, \\ &\sim \Phi'(\rho_1, \rho_2) \pm \Phi'(\rho_2, \rho_1), \end{aligned} \tag{6}$$

where the upper sign is for singlets and the lower for triplets. With $\Phi(\rho_1, \rho_2)$ given by Eq. (6),

$$\mathfrak{L}\Phi(\rho_1, \rho_2) \underset{\substack{\rho_1 \to \infty \\ \rho_2 \to \infty}}{\sim} \pm 2(\zeta - 1)\left(\frac{1}{\rho_2} - \frac{1}{\rho_1} \right) \Phi'(\rho_2, \rho_1) + O(\Phi/\rho_1^2, \Phi/\rho_2^2). \tag{7}$$

Now, except in the limit $\rho_1/\rho_2 \equiv R \to 1$, $\Phi'(\rho_2, \rho_1)$ vanishes exponentially compared to $\Phi(\rho_1, \rho_2)$ and so the second term in Eq. (6) can be neglected compared to the first. As $R \to 1$, the leading term in Eq. (7) becomes

$$\lim_{R \to 1} \frac{2(\zeta - 1)}{\rho_2} \left(1 - \frac{1}{R} \right) \Phi'(\rho_2, \rho_1) = 0. \tag{8}$$

Thus, for any R Eq. (6) is an asymptotic form, but only the first term need be retained, except in the region $\rho_1 \simeq \rho_2$.

For states of the type $1s - ns$, i.e., both electrons bound, we make the substitution

$$k \to i/\lambda,$$

where

$$\epsilon = -1 - (1/\lambda^2). \tag{9}$$

For all such states, including $1s^2$, $\lambda > 1$, and so the same analysis as just given goes through for this case also resulting in the asymptotic form

$$\begin{aligned} \Phi(\rho_1, \rho_2) &\underset{\substack{\rho_1 \to \infty \\ \rho_2 \to \infty}}{\sim} \rho_1 e^{-\rho_1} \rho_2^{\lambda\zeta} e^{-\rho_2/\lambda} \\ &\quad \pm \rho_2 e^{-\rho_2} \rho_1^{\lambda\zeta} e^{-\rho_1/\lambda}. \end{aligned} \tag{10}$$

However, in this case, we cannot exclude further terms of the type $2s - \lambda$'s, $3s - \lambda$'s, etc., so that the form in Eq. (10) does not appear to be imme-

diately useful.

We have yet to consider states in which both electrons are in the continuum. It proves advantageous in this situation to start by writing down a form in the region $\rho_1 \simeq \rho_2$. Suppose the asymptotic energies of the two electrons are $k_1^2/2$ and $k_2^2/2$, then we try the form

$$\Phi(\rho_1,\rho_2) \underset{\substack{\rho_1\to\infty\\ \rho_2\to\infty}}{\sim} \rho_1^{i/k_1} e^{ik_1\rho_1} \rho_2^{i\zeta/k_2} e^{ik_2\rho_2} \pm \rho_2^{i/k_1} e^{ik_1\rho_2} \rho_1^{i\zeta/k_2} e^{ik_2\rho_1} [1+Q(\rho_1/\rho_2)], \tag{11}$$

where Q is an as yet unspecified function of ρ_1/ρ_2.[13] Using exponentials in Eq. (11) is the most convenient in what follows. A more general expression would contain, in addition, terms containing complex conjugates of the forms given. These other terms would be necessary to match Eq. (11) to an inner wave function in an actual application, but they play no role in our treatment here so we don't introduce them. For this function to obey the slope condition Eq. (4c), we have

$$[(i\zeta/k_2\rho_2 + ik_2 - i/k_1\rho_1 - ik_1)Q]_{\rho_1=\rho_2} + \left.\frac{\partial Q}{\partial \rho_1}\right|_{\rho_1=\rho_2} - \left.\frac{\partial Q}{\partial \rho_2}\right|_{\rho_1=\rho_2} = 0. \tag{12}$$

We meet this condition to $O(1/\rho_2)$ by requiring that

$$\left. Q \right|_{\rho_1=\rho_2} = 0. \tag{13}$$

Since Q is a function solely of ρ_1/ρ_2, both derivatives of Q in Eq. (12) are of $O(1/\rho_2)$. In the triplet case, Eq. (13) ensures the exact satisfaction of condition (4d).

To satisfy the differential equation, Eq. (3), we have

$$\left(\frac{(1-\zeta)}{\rho_2} - \frac{(1-\zeta)}{\rho_1}\right)(1+Q) - \frac{1}{2}\left(\frac{\partial^2 Q}{\partial\rho_1^2} + \frac{\partial^2 Q}{\partial\rho_2^2}\right) - (i\zeta/k_2\rho_1 + ik_2)\frac{\partial Q}{\partial\rho_1} - (i/k_1\rho_2 + ik_1)\frac{\partial Q}{\partial\rho_2} = 0, \tag{14}$$

where terms of $O(1/\rho_1^2)$ have been neglected.[14]

We will find a solution to Eq. (14) valid in the asymptotic region defined by writing down the leading neglected terms. These are

$$1/\rho_2^2, \tag{15a}$$

$$1/\rho_1\rho_2, \tag{15b}$$

$$(\rho_2/\rho_1)^N \frac{1}{\rho_1^2}, \quad N \text{ some integer}. \tag{15c}$$

The region is thus that for which $\rho_1 \to \infty$, $\rho_2 \to \infty$, $1 \leq (\rho_2/\rho_1) \leq \alpha$, where α is an arbitrarily large number.

The ansatz for Q is

$$Q = a_0 + \sum_{n=1}^{\infty} a_n'(\rho_1/\rho_2)^n + \sum_{m=1}^{\infty} b_m'(\rho_2/\rho_1)^m. \tag{16}$$

This form is chosen because the second derivatives in Eq. (14) produce terms of the forms in Eq. (15), and thus these derivatives can be neglected. Furthermore, the terms in Eq. (14),

$$\frac{1}{\rho_1}\frac{\partial Q}{\partial\rho_1}, \quad \frac{1}{\rho_2}\frac{\partial Q}{\partial\rho_2}, \tag{17}$$

can also be neglected. Thus, with the following definitions,

$$\begin{aligned} \zeta_2 &\equiv (1-\zeta)/ik_1, \\ \zeta_1 &\equiv (1-\zeta)/ik_2, \\ x_1 &\equiv k_1\rho_1, \\ x_2 &\equiv k_2\rho_2, \end{aligned} \tag{18}$$

the Q equation becomes

$$\left(\frac{\zeta_2}{x_2} - \frac{\zeta_1}{x_1}\right)(1+Q) - \frac{\partial Q}{\partial x_1} - \frac{\partial Q}{\partial x_2} = 0. \tag{19}$$

Rewriting Q in terms of x_1 and x_2, i.e.,

$$Q = a_0 + \sum_{n=1}^{\infty} a_n\left(\frac{x_1}{x_2}\right)^n + \sum_{m=1}^{\infty} b_m\left(\frac{x_2}{x_1}\right)^m, \tag{20}$$

we note that $\partial Q/\partial x_1$ and $\partial Q/\partial x_2$ operating on the first series in Eq. (20) produce terms of the form x_1^p/x_2^{p+1} while the derivatives operating on the second series yield terms like x_2^p/x_1^{p+1}, so that in deriving recursion relations for the coefficients, the a_n and b_m do not appear in the same expression. This, of course, greatly simplifies finding the solution.

We now show the first few recursion relations among the a_n coefficients found by equating the total coefficient of various combinations of powers of x_1 and x_2 to zero:

Term	*Coefficient*
$1/x_2$	$\zeta_2(1+a_0) - a_1(1+\zeta_1) = 0$
x_1/x_2^2	$a_1(\zeta_2+1) - a_2(2+\zeta_1) = 0$
x_1^2/x_2^3	$a_2(\zeta_2+2) - a_3(3+\zeta_1) = 0$
x_1^p/x_2^{p+1}	$a_p(\zeta_2+p) - a_{p+1}(p+1+\zeta_1) = 0$

(21)

So the ratio of coefficients is

$$a_{p+1}/a_p = (\zeta_2+p)/(\zeta_1+p+1), \tag{22}$$

but this ratio is the same as for the hypergeometric function

$$F(1, \zeta_2; \zeta_1+1; x_1/x_2)\,. \tag{23}$$

Similarly, the series in $(x_2/x_1)^m$ can be written as

$$F(1, -\zeta_1; -\zeta_2+1; x_2/x_1)\,. \tag{24}$$

Finally, adjusting the constant term,

$$Q(x_1/x_2) = a_0 + (1+a_0)[-2 + F(1, \zeta_2; \zeta_1+1; x_1/x_2) + F(1, -\zeta_1, -\zeta_2+1, x_2/x_1)]\,. \tag{25}$$

The boundary condition, Eq. (13), is satisfied by choosing a_0 so that $Q(k_1/k_2)=0$, i.e.,

$$a_0 = \frac{-[2 - F(1, \zeta_2; \zeta_1+1; k_1/k_2) - F(1, -\zeta_1; -\zeta_2+1; k_2/k_1)]}{[1 - F(1, \zeta_2; \zeta_1+1; k_1/k_2) - F(1, -\zeta_1; -\zeta_2+1; k_2/k_1)]}\,. \tag{26}$$

Eq. (25) is the primary result of this paper. With it we have an analytic form for the asymptotic wave function describing two electrons in the continuum interacting through the monopole term of $1/r_{12}$.

We next ensure that the expression for Q in Eq. (25) is defined for all physically possible values of the arguments, and then look at limiting forms.

There is no loss in generality in assuming

$$k_1/k_2 \leq 1\,. \tag{27}$$

The hypergeometric function is defined by analytic continuation for all complex values of its argument except for a cut running along the real axis from 1 to infinity. Thus there is no ambiguity in the evaluation of the function with argument x_1/x_2 except when $k_1=k_2$. The function with argument $x_2/x_1 \geq 1$ must, however, be defined as the limit in approaching the real axis from either above or below the cut. We find that by letting $k_2 \to k_2 - i\eta$, where η is infinitesimally small, that Q is defined everywhere without singularities. For instance, let $k_1=k_2$ and $\rho_1=\rho_2$, then $F(1, \zeta_2; \zeta_1+1; 1)$ is defined if

$$\mathrm{Re}(\zeta_1+1-\zeta_2-1)>0\,, \tag{28}$$

but

$$\mathrm{Re}(\zeta_1+1-\zeta_2-1) = \mathrm{Re}(\zeta_1-\zeta_2) \simeq (1-\xi)\eta/k_2^2 > 0\,. \tag{29}$$

The same situation also holds for $F(1, -\zeta_1; -\zeta_2+1; 1)$. When $|x_2/x_1|>1$, adding the imaginary part to k_2 means that the hypergeometric function is evaluated by approaching the real axis from below.

The most interesting limiting case is when $x_2/x_1 \gg 1$; i.e., $\rho_2/\rho_1 \gg 1$. By using an analytic continuation formula[15] we can write

$$Q \simeq -1 + (1+a_0)\frac{\Gamma(-\zeta_2+1)\Gamma(1+\zeta_1)}{\Gamma(\zeta_1-\zeta_2+1)}\left(-\frac{x_2}{x_1}\right)^{\zeta_1}. \tag{30}$$

So the entire wave function is

$$\Phi(\rho_1, \rho_2) \underset{\substack{\rho_1 \to \infty \\ \rho_2 \to \infty \\ \rho_2/\rho_1 \gg 1}}{\sim} \rho_1^{i/k_1} e^{ik_1\rho_1}\, \rho_2^{i\xi/k_2}\, e^{ik_2\rho_2} \pm (1+a_0)\frac{\Gamma(1-\zeta_2)\Gamma(1+\zeta_1)}{\Gamma(1+\zeta_1-\zeta_2)}\left(-\frac{k_2}{k_1}\right)^{\zeta_1} \times \rho_2^{i/k_1 + i(\xi-1)/k_2}\, e^{ik_1\rho_2}\, \rho_1^{i/k_2}\, e^{ik_2\rho_1}\,. \tag{31}$$

When this form is operated on by the differential operator in Eq. (3), we find

$$\mathfrak{L}\Phi(\rho_1, \rho_2) \sim O[(\rho_1/\rho_2)1/\rho_1]\,, \tag{32}$$

which is consistent with the approximations made in arriving at Eq. (31). If $k_1=k_2$, Eq. (31) reduces to just a simple product,

$$\Phi(\rho_1, \rho_2) \sim \rho_1^{i/k} e^{ik\rho_1}\, \rho_2^{i\xi/k} e^{ik\rho_2}\,. \tag{33}$$

Since the starting form, Eq. (11), was written down simply by analogy to the earlier cases, it may be well to give a physical interpretation to Eq. (31). The discussion is most easily carried on in terms of wave packets. A reasonable physical picture for large ρ_1 and ρ_2 is that of two packets emanating from the origin. The packet carrying the coordinate ρ_2 is at $\rho_2 \sim k_2 t$ for some large t and is traveling with a velocity k_2. The other packet is at $\rho_1 \sim k_1 t$ and has a velocity k_1. Since $k_2 > k_1$, ρ_2 is much greater than ρ_1, a condition consistent with the specification of the limiting form. Now packets formed from Eq. (31) give just this picture. The first term produces the desired packets while the second term suffers destructive interference for all $\rho_2 \gg \rho_1$.

The other limiting situation is when $\rho_1 \to \rho_2$. Here, we let

$$x \equiv k_1\rho_1/k_2\rho_2\,, \quad x_0 \equiv k_1/k_2\,, \quad \delta = \rho_2 - \rho_1\,, \tag{34}$$

and expand Q around x_0. The result is

$$\Phi(\rho_1,\rho_2)\underset{\substack{\rho_1\to\infty\\ \rho_2\to\infty\\ \rho_1\simeq\rho_2}}{\sim}\rho_2^{i/k_1+i\zeta/k_2}e^{i(k_1+k_2)\rho_2}[1-i(k_1+k_2)\delta-i(1/k_1+\zeta/k_2-iC)\delta/\rho_2] \tag{35}$$

for singlets and

$$\Phi(\rho_1,\rho_2)\underset{\substack{\rho_1\to\infty\\ \rho_2\to\infty\\ \rho_1\simeq\rho_2}}{\sim}\rho_2^{i/k_1+i\zeta/k_2}e^{i(k_1+k_2)\rho_2}[i(k_2-k_1)\delta+i(\zeta/k_2-1/k_1-iC)]\delta/\rho_2 \tag{36}$$

for triplets, where C is an involved constant.

We now briefly consider the alterations necessary when one or both of the electrons have angular momentum. The results are most simply presented for functions representing s-p configurations, so we will work only with these. Extension to other possible values of angular momenta is straightforward.

The basic form of the wave function is[16]

$$\Phi(\rho_1,\rho_2)=F(\rho_1,\rho_2)Y_{10}(\Omega_2)\pm F(\rho_2,\rho_1)Y_{10}(\Omega_1)\,. \tag{37}$$

When this form is used in the Schrödinger equation, one of the resulting radial equations is

$$\left(\frac{\partial^2}{\partial\rho_1^2}+\frac{\partial^2}{\partial\rho_2^2}+\frac{2}{\rho_<}+\frac{2\zeta}{\rho_>}-\frac{2}{\rho_2^2}+\epsilon\right)F(\rho_1,\rho_2)=0\,. \tag{38}$$

The other is found by interchanging ρ_1 and ρ_2. This is to be solved subject only to the conditions of finiteness and continuity. There is no boundary condition along the $\rho_1=\rho_2$ line in this case.

For the bound-bound case, evidently an acceptable asymptotic form for $1s$-np type function is

$$F(\rho_1,\rho_2)\underset{\substack{\rho_1\to\infty\\ \rho_2\to\infty}}{\sim}\rho_1 e^{-\rho_1}\rho_2^{\lambda\zeta}e^{-\rho_2/\lambda}\,, \tag{39}$$

where $\epsilon=-1-1/\lambda^2$ as before. But now, in contrast to the s-s case, this form is valid over the entire $\rho_1-\rho_2$ plane. When $\rho_1/\rho_2<1$, the above form is obviously correct. When $\rho_1/\rho_2>1$, the first term in Eq. (37) becomes exponentially small compared to the second and so the second term provides the asymptotic behavior. When $\rho_1/\rho_2\to 1+$, a similar result to that given in Eq. (8) is found to apply here also, so there are no remaining terms of $O(1/\rho_i)$ anywhere in the plane after operation on $F(\rho_1,\rho_2)$ with the differential operator.

Similar remarks and arguments apply to the bound-free case. For the free-free situation, let

$$F(\rho_1,\rho_2)\underset{\substack{\rho_1\to\infty\\ \rho_2\to\infty}}{\sim}\rho_2^{i/k_1}e^{ik_1\rho_2}\rho_1^{i\zeta/k_2}e^{ik_2\rho_1} \tag{40}$$

for $\rho_1>\rho_2$. For $\rho_1<\rho_2$, we try

$$F(\rho_1,\rho_2)\underset{\substack{\rho_1\to\infty\\ \rho_2\to\infty}}{\sim}\rho_2^{i/k_1}e^{ik_1\rho_2}\rho_1^{i\zeta/k_2}e^{ik_2\rho_1}[1+Q(\rho_1/\rho_2)]\,, \tag{41}$$

where $Q\big|_{\rho_1=\rho_2}=0$ as before. Thus $F(\rho_1,\rho_2)$ is a continuous function with continuous first derivatives at $\rho_1=\rho_2$ to $O(1/\rho_2)$—the departure from perfect continuity coming from derivatives of Q. To get $F(\rho_1,\rho_2)$ in Eq. (41) to satisfy the differential equation, we are faced with exactly the same situation as in the s-s case; i.e., Q satisfies Eq. (14). So $Q(\rho_1/\rho_2)$ is the same function as previously found, namely that given by Eq. (25). Thus, the asymptotic form for the s-p case is established.

We note that addition of angular momentum does not change the asymptotic forms of the wave functions because angular momentum provides an effective potential that goes as $1/\rho^2$ for large ρ. On the other hand, the symmetry requirements of the radial wave function change from the s-s case due to the presence of spherical harmonics in the complete wave function, and it is these symmetry requirements which lead to distinct results for the s-s vs the s-p cases.

III. CONCLUSION

Asymptotic forms of two-electron eigenfunctions of the monopole Hamiltonian have been presented in Eqs. (6), (10), (11), (39), and (41). These forms are also correct if a short-range core potential is added to the Hamiltonian and so could be used for the description of processes taking place in heavier atoms as well as two-electron atoms. The wave function for two free electrons is manifestly nonseparable due to the double requirements of proper screening and proper symmetry. The form of this function is not as simple as could be hoped for; on the other hand, the properties of the hypergeometric function have been investigated extensively so their evaluation in particular cases is quite feasible.

It would be interesting to see the impact of using these proper asymptotic wave functions rather than intuitively constructed functions in, say, electron ionization calculations. Work is now underway to find practical means of generating monopole eigenfunctions over the entire r_1-r_2 plane to be used in such calculations.

[1]E. Schubert, A. Schuck, K. Jung, and S. Geltman, J. Phys. B 12, 967 (1979) and references therein.
[2]M. Lal, A. N. Tripathi, and M. K. Srivastava, J. Phys. B 12, 945 (1979) and references therein.
[3]M. Schulz, J. Phys. B 6, 2580 (1973).
[4]S. L. Carter and H. P. Kelly, Phys. Rev. A 16, 1525 (1977).
[5]P. Winkler, J. Phys. B 10, 1693 (1977).
[6]S. L. Carter and H. P. Kelly, J. Phys. B 8, 1887 (1976).
[7]T. N. Chang and R. T. Poe, Phys. Rev. A 12, 1432 (1975).
[8]H. P. Kelly, Phys. Rev. 131, 684 (1963).
[9]P. L. Altick, Phys. Rev. 179, 71 (1969).
[10]P. L. Altick, J. Phys. B 5, 1059 (1972) and references therein.
[11]C. G. Barraclough and J. P. Mooney, J. Chem. Phys. 54, 35 (1971).
[12]A. Tempkin, Phys. Rev. 126, 130 (1962).
[13]Since $k_1\rho_1$ and $k_2\rho_2$ must be large for Eq. (11) to be valid, we exclude either k_1 or k_2 being zero.
[14]It may appear inconsistent to satisfy the boundary condition to $O(1/\rho)$ and the differential equation to $O(1/\rho^2)$. This is not a fundamental difficulty because by adding a term b_0/ρ_2 to Q the singlet boundary condition can be matched to $O(1/\rho^2)$ while the rest of the development is unaffected. The added term is evidently the leading term in an asymptotic series, which is currently being investigated.
[15]*Handbook of Mathematical Functions, NBS, AMS-55,* edited by M. Abramowitz and I. A. Stegun (U.S. Govt. Printing Office, Washington, D.C., 1965).
[16]G. Breit, Phys. Rev. 35, 569 (1930).