PHYSICAL REVIEW A VOLUME 25, NUMBER 1 JANUARY 1982

Asymptotic form of wave functions for two continuum electrons in a Coulomb field

P. L. Altick
Physics Department, University of Nevada, Reno, Nevada 89557
(Received 14 April 1981)

Within the framework of a partial-wave expansion, the Schrödinger equation for the asymptotic form of the wave function for two electrons in a Coulomb field is reduced to a set of first-order coupled differential equations in one variable ($r_< / r_>$). The solution of these equations is found both for the monopole interaction only, and the monopole and dipole interactions. The monopole result greatly simplifies an expression derived in an earlier paper. These results can be applied to the calculation of ionization processes for any atom or ion.

I. INTRODUCTION

The problem of correctly describing a quantum-mechanical state with two continuum electrons in a Coulomb field has attracted attention for a long time.[1,2] Wave functions for such states are needed for the calculation of electron-impact-ionization cross sections as well as double-photoionization cross sections.

For some applications, such as plasma modeling and diagnostics, total ionization cross sections are what is important. Current calculations use various approximate final states based on the Born approximation and motivated by intuition and physical reasoning.[3] Such calculations reproduce experimental data for isoelectronic sequences fairly well with some discrepancies. Still, since uncorrelated final states are used, the effect of such correlation on the results is not known and cannot be assumed to be negligible without further investigation.

More detailed data on the electron-impact-ionization process is provided by the work of Ehrhardt *et al.*,[4] Beaty *et al.*,[5] and the group at Flinders University.[6] These groups have measured differential cross sections which include energy and angle analysis for both outgoing electrons. The most successful theoretical description of the lower energy data is the application of the Coulomb-Born approximation,[7-9] but significant discrepancies with experiment remain. For higher energies, useful information can be obtained by analyzing the data in a distorted-wave impulse approximation.[6]

The focus of this paper is to consider the final state of electron-impact ionization of a hydrogen-like ion or of double photoionization of a helium-like ion. The asymptotic form of the wave function for such a state is studied. If only the monopole part of the electron-electron interaction is included, the asymptotic form is found exactly. This was done in an earlier paper,[10] hereafter called I. The results in that paper can be simplified significantly, and the simpler forms are presented here.

If the entire interaction between the electrons is included, the Schrödinger equation for the asymptotic form is reduced to a set of coupled, first-order, differential equations in one variable, $(r_</r_>)$. The solution of these equations for the combined monopole and dipole parts of the interaction is found and has a simple form. The results are immediately applicable to an ionization of any atom or ion as shown in Sec. III.

II. THE ASYMPTOTIC FORMS

The wave functions for two electrons in a Coulomb field of charge Z are written as eigenstates of total orbital angular momentum L and total spin S. Defining

$$\mathcal{Y}_{l_1,l_2,LM}(\Omega_1,\Omega_2) = \sum_{m_1 m_2} (l_1 m_1 l_2 m_2 | LM) Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_2) , \quad (1)$$

then

$$\Psi({}^{1,3}L,\vec{r}_1,\vec{r}_2) = \sum_{l_1 \le l_2}^{\infty} [\Phi_{l_1,l_2,L}(r_1,r_2)\mathcal{Y}_{l_1,l_2,LM}(\Omega_1,\Omega_2) \pm \Phi_{l_1,l_2,L}(r_2,r_1)\mathcal{Y}_{l_1,l_2,LM}(\Omega_2,\Omega_1)] \quad (2)$$

is a form with the proper symmetry. The plus sign defines the singlet function while the minus sign defines the triplet. In what follows, only the singlet case is considered. The extension to triplets is immediate.

The Φ's have no particular symmetry properties, but it is advantageous to write them as

$$\Phi_{l_1,l_2,L}(r_1,r_2) = {}^S\Phi_{l_1,l_2,L}(r_1,r_2) + {}^A\Phi_{l_1,l_2,L}(r_1,r_2) , \quad (3)$$

where ${}^S\Phi$ is symmetric under an interchange of r_1 and r_2 and ${}^A\Phi$ is antisymmetric. Also, let

$$^{S,A}\mathcal{Y}_{l_1,l_2,LM}(\Omega_1,\Omega_2)=\mathcal{Y}_{l_1,l_2,LM}(\Omega_1,\Omega_2) \pm\mathcal{Y}_{l_1,l_2,LM}(\Omega_2,\Omega_1) \qquad (4)$$

for $l_1 \neq l_2$. For $l_1 = l_2$ and L even

$$^{S}\mathcal{Y}_{l,l,LM}(\Omega_1,\Omega_2)=\mathcal{Y}_{l,l,LM}(\Omega_1,\Omega_2)\,, \qquad (5a)$$

$$^{A}\mathcal{Y}_{l,l,LM}(\Omega_1,\Omega_2)=0\,, \qquad (5b)$$

while for $l_1=l_2$, L odd

$$^{S}\mathcal{Y}_{l,l,LM}(\Omega_1,\Omega_2)=0\,, \qquad (6a)$$

$$^{A}\mathcal{Y}_{l,l,LM}(\Omega_1,\Omega_2)=\mathcal{Y}_{l,l,LM}(\Omega_1,\Omega_2)\,. \qquad (6b)$$

Now

$$\Psi(^1L,\vec{r}_1,\vec{r}_2)=\sum_{l_1\leq l_2}^{\infty}[{}^{S}\Phi_{l_1,l_2,L}(r_1,r_2)\,{}^{S}\mathcal{Y}_{l_1,l_2,LM}(\Omega_1,\Omega_2) + {}^{A}\Phi_{l_1,l_2,L}(r_1,r_2)\,{}^{A}\mathcal{Y}_{l_1,l_2,LM}(\Omega_1,\Omega_2)]. \qquad (7)$$

This form is the most convenient for studying the asymptotic forms because

$$\int d\Omega_1 d\Omega_2\, {}^{S}\mathcal{Y}^{*}_{l_1,l_2,LM}(\Omega_1,\Omega_2)\,{}^{A}\mathcal{Y}_{l_1',l_2',L'M'}(\Omega_1,\Omega_2)=0\,,$$

$$\int d\Omega_1 d\Omega_2\, {}^{S}\mathcal{Y}^{*}_{l_1,l_2,LM}(\Omega_1,\Omega_2) \times P_n(\cos\theta_{12})\,{}^{A}\mathcal{Y}_{l_1',l_2',L'M'}(\Omega_1,\Omega_2)=0 \qquad (8)$$

for any values of the subscripts. The $P_n(\cos\theta_{12})$ is a Legendre polynomial and θ_{12} is the angle between $\vec{r}_1$ and $\vec{r}_2$. The last equation follows because $P_n(\cos\theta_{12})$ is a symmetric function of Ω_1 and Ω_2. Because of Eq. (8), the two terms in Eq. (7) uncouple in the Schrödinger equation.

The Hamiltonian is

$$H=T_1+T_2-\frac{Z}{r_1}-\frac{Z}{r_2}+\sum_{n=0}^{\infty}\frac{r_<^n}{r_>^{n+1}}P_n(\cos\theta_{12})\,. \qquad (9)$$

First, the asymptotic form retaining only the monopole, $n=0$, term in Eq. (9) will be found. For simplicity, let $L=0$. Other values of L will be considered at the end of this development. In this case only ${}^{S}\Phi_{l,l,0}(r_1,r_2)$ is present in the sum in Eq. (7) because ${}^{A}\mathcal{Y}_{l,l,00}(\Omega_1,\Omega_2)=0$. Further, each ${}^{S}\Phi_{l,l,0}(r_1,r_2)$ is decoupled and can be considered separately. Repeating some definitions made in I,

$$\rho_1=Zr_<\,,\quad \rho_2=Zr_>\,,\quad \zeta=1-1/Z\,,\quad \epsilon=2E/Z^2\,. \qquad (10)$$

The Schrödinger equation, in a.u., reduces to

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial\rho_1^2}+\frac{\partial^2}{\partial\rho_2^2}\right)-\frac{1}{\rho_1}-\frac{\zeta}{\rho_2}+\frac{l(l+1)}{2\rho_1^2} + \frac{l(l+1)}{2\rho_2^2}-\frac{\epsilon}{2}\right]{}^{S}\Phi_{l,l,0}(\rho_1,\rho_2)=0\,, \qquad (11)$$

but the angular momentum terms, going as $1/\rho_i^2$, will be ignored.

The ansatz for ${}^{S}\Phi_{l,l,0}(\rho_1,\rho_2)$ in I is

$$ {}^{S}\Phi_{l,l,0}(\rho_1,\rho_2)\underset{\substack{\rho_1\to\infty\\ \rho_2\to\infty}}{\sim}\rho_1^{i/k_1}e^{ik_1\rho_1}\rho_2^{i\zeta/k_2}e^{ik_2\rho_2} + \rho_2^{i/k_1}e^{ik_1\rho_2}\rho_1^{i\zeta/k_2}e^{ik_2\rho_1}\left[1+Q\left(\frac{\rho_1}{\rho_2}\right)\right], \qquad (12)$$

with $k_1<k_2$ and the boundary condition

$$Q(1)=0\,. \qquad (13)$$

The case $k_1=k_2$ is especially simple and treated in I. Following the development in I, the differential equation for Q is

$$\left(\frac{\zeta_2}{k_2\rho_2}-\frac{\zeta_1}{k_1\rho_1}\right)\left[1+Q\left(\frac{\rho_1}{\rho_2}\right)\right]-\frac{1}{k_1}\frac{\partial Q}{\partial\rho_1}-\frac{1}{k_2}\frac{\partial Q}{\partial\rho_2}=0\,. \qquad (14)$$

This was found by consistently dropping terms of $O(1/\rho_i^2)$. The quantities ζ_2 and ζ_1 are prominent in the expressions found throughout this paper. They are given by

$$\zeta_1=(1-\zeta)/ik_2\,,\quad \zeta_2=(1-\zeta)/ik_1\,. \qquad (15)$$

Equation (14) can be written in one variable by defining

$$y=\rho_1/\rho_2\leq 1\,, \qquad (16)$$

and, also

$$1+Q(y)=\mathcal{S}(y)\,. \qquad (17)$$

With the variable change made, Eq. (14) becomes

$$\left(1-\frac{1}{y}\right)\mathcal{S}(y)+\left(\frac{y}{\zeta_2}-\frac{1}{\zeta_1}\right)\frac{d\mathcal{S}}{dy}=0\,, \qquad (18)$$

with the boundary condition $S(1)=1$. The solution to Eq. (18) is

$$\mathcal{S}(y)=y^{-\zeta_1}\left(\frac{1-\dfrac{\zeta_1}{\zeta_2}y}{1-\dfrac{\zeta_1}{\zeta_2}}\right)^{\zeta_1-\zeta_2}. \qquad (19)$$

This expression replaces Eq. (25) of I. The two are entirely equivalent—in fact, Eq. (19) was originally arrived at by simplifying Eq. (25) using continuation formulas for the hypergeometric functions. Since $y \leq 1$, and $\zeta_1/\zeta_2 = k_1/k_2 < 1$, the function $S(y)$ is analytic over the entire range of its argument. It has a modulus of 1 which was not obvious in its previous form. The asymptotic form is then

$$ {}^{S}\Phi_{l,l,0}(\rho_1,\rho_2) \underset{\substack{\rho_1\to\infty \\ \rho_2\to\infty}}{\sim} \rho_1^{i/k_1} e^{ik_1\rho_1} \rho_2^{i\zeta/k_2} e^{ik_2\rho_2} + \rho_2^{i/k_1} e^{ik_1\rho_2} \rho_1^{i\zeta/k_2} e^{ik_2\rho_1} \left(\frac{\rho_1}{\rho_2}\right)^{-\zeta_1} \left(\frac{1-\dfrac{\zeta_1\rho_1}{\zeta_2\rho_2}}{1-\dfrac{\zeta_1}{\zeta_2}}\right)^{\zeta_1-\zeta_2} . \tag{20} $$

For L even and $l_1 = l_2$, the same expression, Eq. (20), is valid. For L odd and $l_1 = l_2$, the right-hand side of Eq. (20) with a minus sign between the terms holds for ${}^{A}\Phi_{l,l,L}(\rho_1,\rho_2)$, while ${}^{S}\Phi_{l,l,L}(\rho_1,\rho_2)$ is not present in the expression for $\Psi({}^1L,\vec{r}_1,\vec{r}_2)$. For unequal l_1, l_2 both ${}^{S}\Phi_{l_1,l_2,L}(\rho_1,\rho_2)$ and ${}^{A}\Phi_{l_1,l_2,L}(\rho_1,\rho_2)$ are present in general. The treatment for ${}^{S}\Phi_{l_1,l_2,L}(\rho_1,\rho_2)$ is just the same as above, i.e., Eq. (20) is valid. For ${}^{A}\Phi_{l_1,l_2,L}(\rho_1,\rho_2)$, Eq. (20) is changed by the plus sign being replaced by a minus sign, and the understanding that ${}^{A}\Phi_{l_1,l_2,L}(\rho_1,\rho_2)$ changes sign as the $r_1 = r_2$ line is crossed. Asymptotic forms for all L are thus established for the monopole interaction.

Considering now the entire interaction, the Hamiltonian can be written

$$ H = T_1 + T_2 - \frac{1}{\rho_1} - \frac{1}{\rho_2} + \frac{(1-\zeta)}{\rho_2}[1 + yP_1(\cos\theta_{12}) + y^2P_2(\cos\theta_{12}) + \cdots]. \tag{21} $$

To write the coupled equations for the ${}^{S}\Phi_{l_1,l_2,L}(\rho_1,\rho_2)$, found by equating the coefficient of each $P_r(\cos\theta_{12})$ to zero in the Schrödinger equation, it is convenient to define p_{nlr} coefficients by

$$ P_n(\cos\theta_{12})P_l(\cos\theta_{12}) = \sum_{r=|n-l|}^{n+l} p_{nlr} P_r(\cos\theta_{12}) . \tag{22} $$

In Eq. (22), $\Delta r = 2$. The p_{nlr} are, of course, essentially squares of $3-j$ coefficients and can be found in a number of places, e.g., Edmonds.[11]

For ${}^1S$ symmetry,

$$ \Psi({}^1S,\vec{r}_1,\vec{r}_2) = \frac{1}{4\pi}[{}^{S}\Phi_{0,0,0}(\rho_1,\rho_2)P_0(\cos\theta_{12}) - \sqrt{3}\,{}^{S}\Phi_{1,1,0}(\rho_1,\rho_2)P_1(\cos\theta_{12}) + \cdots (-1)^l(2l+1)^{1/2}\,{}^{S}\Phi_{l,l,0}(\rho_1,\rho_2)P_l(\cos\theta_{12}) + \cdots] , \tag{23} $$

and the coupled equations are

$$ \left(T_1 + T_2 - \frac{1}{\rho_1} - \frac{\zeta}{\rho_2}\right){}^{S}\Phi_{0,0,0}(\rho_1,\rho_2) + \frac{(1-\zeta)}{\rho_2}[-yp_{110}\sqrt{3}\,{}^{S}\Phi_{1,1,0}(\rho_1,\rho_2) + y^2p_{220}\sqrt{5}\,{}^{S}\Phi_{2,2,0}(\rho_1,\rho_2) + \cdots] = \frac{\epsilon}{2}\,{}^{S}\Phi_{0,0,0}(\rho_1,\rho_2) , \tag{24} $$

$$ \left(T_1 + T_2 - \frac{1}{\rho_1} - \frac{\zeta}{\rho_2}\right)\sqrt{3}\,{}^{S}\Phi_{1,1,0}(\rho_1,\rho_2) + \frac{(1-\zeta)}{\rho_2}\{-y[p_{101}\,{}^{S}\Phi_{0,0,0}(\rho_1,\rho_2) + p_{121}\sqrt{5}\,{}^{S}\Phi_{2,2,0}(\rho_1,\rho_2)] + y^2[p_{211}\sqrt{3}\,{}^{S}\Phi_{1,1,0}(\rho_1,\rho_2) + p_{231}\sqrt{7}\,{}^{S}\Phi_{3,3,0}(\rho_1,\rho_2)] + \cdots \} = \frac{\epsilon}{2}\sqrt{3}\,{}^{S}\Phi_{1,1,0}(\rho_1,\rho_2) . $$

$\cdot$
$\cdot$
$\cdot$

An asymptotic solution can be found by building upon the monopole solution. The monopole solutions, Eq. (20), consist of two terms. The first term will be called the "direct" term, and the second, the "symmetry" term as it owes its existence ultimately to symmetry and continuity requirements. When the entire interaction is present, each term must be treated separately.

The ansatz for the direct term is

$$ {}^{S}\Phi^{\rm dir}_{0,0,0}(\rho_1,\rho_2) = \rho_1^{i/k_1} e^{ik_1\rho_1} \rho_2^{i(\zeta/k_2+\alpha)} e^{ik_2\rho_2} f_0(y) , $$

$$ {}^{S}\Phi^{\rm dir}_{1,1,0}(\rho_1,\rho_2) = -\frac{1}{\sqrt{3}} \rho_1^{i/k_1} e^{ik_1\rho_1} \rho_2^{i(\zeta/k_2+\alpha)} e^{ik_2\rho_2} f_1(y) . \tag{25} $$

$\cdot$
$\cdot$
$\cdot$

The $-1/\sqrt{3}$ is added to cancel the like factors in Eq. (24). The changes from the monopole case consist of an added phase factor $\rho_2^{i\alpha}$ and a set of functions $f_i(y)$. The necessity of adding the phase factor has to do with analyticity requirements and will become clear as the development proceeds.

In the asymptotic region $1/\rho_1^2$, $1/\rho_2^2$ and higher inverse powers are neglected. With the forms in Eqs. (25), Eqs. (24) become

$$\left(\frac{1}{\zeta_2}-\frac{1}{\zeta_1}y\right)\frac{df_0}{dy}+\frac{i\alpha}{\zeta_1}f_0-(yp_{110}f_1+y^2p_{220}f_2+\cdots)=0\,,$$
$$\left(\frac{1}{\zeta_2}-\frac{1}{\zeta_1}y\right)\frac{df_1}{dy}+\frac{i\alpha}{\zeta_1}f_1-[y(p_{101}f_0+p_{121}f_2)+y^2(p_{211}f_1+p_{231}f_3)+\cdots]=0\,. \quad (26)$$

.
.
.

It is emphasized that this set of equations contains only one variable, with a finite range. The only acceptable solutions to these equations will be analytic in the range $0\leq y\leq 1$. The equations contain a singular point at $y=\zeta_1/\zeta_2=k_1/k_2<1$. To investigate the solution in this region, let $z=(1-\zeta_2 y/\zeta_1)$ and expand all f_i around $z=0$, i.e.,

$$f_0(z)=d_{00}+d_{01}z+\cdots\,,$$
$$f_1(z)=d_{10}+d_{11}z+\cdots\,. \quad (27)$$

Such an expansion assumes an analytic form at $z=0$ and will be realizable for particular values of α. The equations for the d_{i0} are

$$\frac{i\alpha}{\zeta_1}d_{00}-\left[\frac{\zeta_1}{\zeta_2}p_{110}d_{10}+\left(\frac{\zeta_1}{\zeta_2}\right)^2p_{220}d_{20}+\cdots\right]=0\,,$$
$$\frac{i\alpha}{\zeta_2}d_{10}-\left[\frac{\zeta_1}{\zeta_2}(p_{101}d_{00}+p_{121}d_{20})+\left(\frac{\zeta_1}{\zeta_2}\right)^2(p_{211}d_{10}+p_{231}d_{30})+\cdots\right]=0\,. \quad (28)$$

By putting the determinant of the coefficients of the d_{i0} equal to 0, a secular equation for α is found. The values of α satisfying this equation allow the determination of the d_{i0} and thus ${}^S\Phi_{l,l,0}(\rho_1,\rho_2)$ which are analytic at $y=k_1/k_2$. For a particular α, there is just one arbitrary constant in the solution. By giving it a value, the $f_i(1)$, which enter the boundary condition, are all fixed.

In practice, the expression for the wave function Eq. (23) will have to be truncated at some l, and so the secular equation for α will have l roots, presumably all distinct, giving rise to l wave functions. This lack of uniqueness for an asymptotic form is familiar from close-coupling calculations where N linearly independent solutions exist for an N-channel scattering problem.

The boundary condition at $y=1$ comes into consideration when the symmetry terms are introduced. The form for the symmetry term is taken to be

$${}^S\Phi^{\rm sym}_{0,0,0}(\rho_1,\rho_2)=\rho_1^{i(\zeta/k_2+\alpha)}e^{ik_2\rho_1}\rho_2^{i/k_1}\times e^{ik_1\rho_2}y^{-\zeta_1'}\left(\frac{1-\frac{\zeta_1}{\zeta_2}y}{1-\frac{\zeta_1}{\zeta_2}}\right)^{\zeta_1'-\zeta_2}g_0(y)\,,$$

$${}^S\Phi^{\rm sym}_{1,1,0}(\rho_1,\rho_2)=-\frac{1}{\sqrt{3}}\rho_1^{i(\zeta/k_2+\alpha)}e^{ik_2\rho_1}\rho_2^{i/k_1}\times e^{ik_1\rho_2}y^{-\zeta_1'}\left(\frac{1-\frac{\zeta_1}{\zeta_2}y}{1-\frac{\zeta_1}{\zeta_2}}\right)^{\zeta_1'-\zeta_2}g_1(y)\,, \quad (29)$$

.
.
.

with $\zeta_1'=\zeta_1+i\alpha$. This form bears a strong resemblance to the symmetry term form for the monopole case. It is established in the Appendix. When Eqs. (29) are used in Eqs. (24) the resulting coupled equations for the $g_i(y)$ are similar in form to those for the $f_i(y)$ but the interchange of ζ_1 and ζ_2 pushes the singular point to $y=\zeta_2/\zeta_1>1$, outside the range, and so the equations have no singular points. The consequence of this is that there are N arbitrary constants in the solution for $Ng_i(y)$ and so the $g_i(1)$ can be chosen to match the $f_i(1)$, thus meeting the boundary condition.

As a specific example of a solution to Eqs. (24), the monopole and dipole terms in the interaction are retained in the Hamiltonian. This is accomplished by putting $p_{nlr}=0$ for $n\geq 2$. The $f_i(y)$ are now given by

$$f_0(y)=C_0e^{-i\alpha\zeta_2 y/\zeta_1}\,,$$
$$f_1(y)=C_1e^{-i\alpha\zeta_2 y/\zeta_1}\,. \quad (30)$$

.
.
.

When these are inserted in Eqs. (24), the result is a set of linear equations for the C_i, namely,

$$i\frac{\zeta_2}{\zeta_1^2}\alpha C_0 - p_{110}C_1 = 0\,,$$
$$i\frac{\zeta_2}{\zeta_1^2}\alpha C_1 - p_{101}C_0 - p_{121}C_2 = 0\,, \quad (31)$$
$$i\frac{\zeta_2}{\zeta_1^2}\alpha C_2 - p_{112}C_1 - p_{132}C_3 = 0\,.$$
$$\vdots$$

These equations have a nontrivial solution for α determined by the vanishing of the coefficient matrix. If C_N is the last coefficient retained, this is an $N\times N$ tridiagonal matrix and convenient methods exist to find its eigenvalues.[12] For $N=2$ or 3,

$$\alpha = \begin{cases} \pm\frac{k_1}{k_2^2}(1-\zeta)(p_{110}p_{101})^{1/2} = \pm\frac{k_1}{k_2^2}\frac{(1-\zeta)}{\sqrt{3}}\,, & N=2 \\ 0,\quad \pm\frac{k_1}{k_2^2}(1-\zeta)(p_{110}p_{101}+p_{121}p_{112})^{1/2} = \pm\frac{k_1}{k_2^2}(1-\zeta)(\tfrac{3}{5})^{1/2}\,, & N=3\,. \end{cases} \quad (32)$$

Once C_0 is chosen, C_1 and C_2 follow immediately and the direct-term solution is complete.

The details of the symmetry term treatment are given in the Appendix. As shown there, it is convenient to introduce a quantity $\beta=\zeta_2^3/\zeta_1^3\alpha$. The $g_i(y)$ defined by Eqs. (29) are then given by

$$g_i(y) = C_i' e^{-i\beta\zeta_1 y/\zeta_2}\,, \quad (33)$$

with the phase factor also changed slightly to

$$y^{-\zeta_1'}\left(\frac{1-\frac{\zeta_1}{\zeta_2}y}{1-\frac{\zeta_1}{\zeta_2}}\right)^{\zeta_1'-\zeta_2'}\,, \quad (34)$$

where ζ_1' is as given earlier and

$$\zeta_2' = \zeta_2 + i\beta\,. \quad (35)$$

The C_i' obey equations identical to Eqs. (31) with the substitution of $\zeta_1\beta/\zeta_2^2$ for $\zeta_2\alpha/\zeta_1^2$. The boundary condition is met by imposing

$$C_0 e^{-i\alpha\zeta_2/\zeta_1} = C_0' e^{-i\beta\zeta_1/\zeta_2}\,, \quad (36)$$

and the same condition for other C_i and C_i' follows automatically (see the Appendix) completing the solution.

For $L\neq 0$, the only significant change is in the definition of the p_{nlr} coefficients. The relevant coefficient now is

$$\int d\Omega_1 d\Omega_2\, {}^{S,A}\mathcal{Y}^*_{l_1,l_2,LM}(\Omega_1,\Omega_2)P_n(\cos\theta_{12}) \times {}^{S,A}\mathcal{Y}_{l_1',l_2',LM}(\Omega_1,\Omega_2) = {}^{S,A}p(l_1,l_2,l_1',l_2',L,n)\,. \quad (37)$$

The evaluation of the p's is straightforward and can be found in Edmonds.[11] The symmetric and asymmetric cases produce different p's. The ansatz for a particular ${}^{S,A}\Phi_{l_1,l_2,L}(\rho_1,\rho_2)$ is

$${}^{S,A}\Phi_{l_1,l_2,L}(\rho_1,\rho_2) \underset{\substack{\rho_1\to\infty\\ \rho_2\to\infty}}{\sim} \rho_1^{i/k_1}e^{ik_1\rho_1}\rho_2^{i(\zeta/k_2+\alpha_L)}e^{ik_2\rho_2}f_{l_1,l_2,L}(y) \pm \rho_1^{i(\zeta/k_2+\alpha_L)}e^{ik_2\rho_1}\rho_2^{i/k_1}\,e^{ik_1\rho_2}y^{-\zeta_1'}\left(\frac{1-\frac{\zeta_1}{\zeta_2}y}{1-\frac{\zeta_1}{\zeta_2}}\right)^{\zeta_1'-\zeta_2'} g_{l_1,l_2,L}(y)\,. \quad (38)$$

When this is used in the Schrödinger equation, the result is a set of coupled equations for the $f_{l_1,l_2,L}(y)$ similar to Eq. (26) except the p_{nlr} are replaced by the more general p's of Eq. (37). Thus the procedures followed in the ${}^1S$ case are successful here also, and the asymptotic forms for different L have the same appearance.

For the triplet case, Eq. (7) is replaced by an expression which is antisymmetric in the spatial variables. Otherwise the entire development is unchanged.

III. EXTENSION TO N ELECTRON ATOMS AND IONS

The asymptotic wave functions found here can be used for the study of electron-impact ionization or double photoionization of any atom. The extension from two electron atoms is immediate. Consider the final state of an ionized atom. If the two free electrons are a long way from the residual ion, the wave function is written as a product of the ion wave function, L_I and S_I good quantum numbers, and the two-electron continuum wave function, L_c and S_c good quantum numbers. The two sets of angular momenta are coupled to form a total L and S. One term in the wave function is thus written

$$\Psi_I(S_I, L_I, \vec{x}_1, \vec{x}_2, \cdots, \vec{x}_{n-2})\Psi_c({}^{1,3}L_c, \vec{x}_{n-1}, \vec{x}_n), \tag{39}$$

where Ψ_I is the ion wave function, properly symmetrized, and Ψ_c is the function given by Eq. (2) with the small alteration that $\vec{x}_i$ now represents the spin variable as well as the space variable and so Ψ_c is the function in Eq. (2) multiplied by a suitable spin function. This expression is, of course, appropriate for r_{n-1}, r_n becoming large. To form an antisymmetric wave function with respect to all coordinates, it is necessary to add to Eq. (39), products with permuted electron indices such that every possible electron pair is represented in Ψ_c. The signs in this linear combination can be easily chosen using Slater determinants as a guide. This symmetrized wave function, then, has a proper asymptotic form for any pair of electrons in the continuum and provides a starting point for calculations.

IV. CONCLUSION

Within the framework of partial waves, asymptotic forms for two continuum electrons in a Coulomb field have been investigated. The forms for a monopole interaction and for a monopole plus dipole interaction are found explicitly while a set of first order coupled differential equations in one variable is derived for the general case. These forms are valid for $r_1 \to \infty$, $r_2 \to \infty$, but r_1/r_2 is not restricted.

These wave functions can be applied to the calculation of ionization processes for any atom or ion. To perform the calculations, suitable ways of extending these functions to small values of r_1 and r_2 must be developed.

APPENDIX: TREATMENT OF THE SYMMETRY TERM

Let

$$\mathcal{S}_\alpha(y) = y^{-\zeta_1'}\left(\frac{1-\frac{\zeta_1}{\zeta_2}y}{1-\frac{\zeta_1}{\zeta_2}}\right)^{\zeta_1'-\zeta_2}, \tag{A1}$$

and $G_i(y) = \mathcal{S}_\alpha(y) g_i(y)$. When the forms in Eq. (29) are put in Eqs. (24), the result is

$$\begin{aligned}
&\left(\frac{1}{\zeta_1} - \frac{1}{\zeta_2}y\right)\frac{dG_0}{dy} + \frac{\zeta_1'}{\zeta_1}\frac{G_0}{y} - G_0 \\
&\quad - (y p_{110} G_1 + y^2 p_{220} G_2 + \cdots) = 0, \\
&\left(\frac{1}{\zeta_1} - \frac{1}{\zeta_2}y\right)\frac{dG_1}{dy} + \frac{\zeta_1'}{\zeta_1}\frac{G_1}{y} \\
&\quad\vdots \\
&\quad - G_1 - [y(p_{101}G_0 + p_{121}G_2) \\
&\quad\quad + y^2(p_{211}G_1 + p_{231}G_3)\cdots] = 0.
\end{aligned} \tag{A2}$$

The factor $\mathcal{S}_\alpha(y)$ is common to all G_i. When the derivative of $\mathcal{S}_\alpha(y)$ is evaluated and $\mathcal{S}_\alpha(y)$ is factored out, the resulting equations for the $g_i(y)$ are

$$\begin{aligned}
&\left(\frac{1}{\zeta_1} - \frac{1}{\zeta_2}y\right)\frac{dg_0}{dy} - (y p_{110} g_1 + y^2 p_{220} g_2 + \cdots) = 0, \\
&\left(\frac{1}{\zeta_1} - \frac{1}{\zeta_2}y\right)\frac{dg_1}{dy} - [y(p_{101}g_0 + p_{121}g_2) \\
&\quad + y^2(p_{211}g_1 + p_{231}g_3) + \cdots] = 0. \\
&\vdots
\end{aligned} \tag{A3}$$

These equations resemble strongly Eqs. (26) for the f_i. The differences are ζ_1 and ζ_2 are interchanged and α is not present. There are no singular points.

For the specific solution when the monopole and dipole terms only are kept, it is convenient to use still another variation of $\mathcal{S}(y)$ given by

$$\mathcal{S}_\beta(y) = y^{-\zeta_1'}\left(\frac{1-\frac{\zeta_1}{\zeta_2}y}{1-\frac{\zeta_1}{\zeta_2}}\right)^{\zeta_1'-\zeta_2'}. \tag{A4}$$

The only difference between $\mathcal{S}_\alpha$ and $\mathcal{S}_\beta$ is the appearance of ζ_2' in the exponent. Its definition is

$$\zeta_2' = \zeta_2 + i\beta. \tag{A5}$$

Using $\mathcal{S}_\beta$ in place of $\mathcal{S}_\alpha$ the g_i equations become

$$\begin{aligned}
&\left(\frac{1}{\zeta_1} - \frac{1}{\zeta_2}y\right)\frac{dg_0}{dy} + \frac{i\beta g_0}{\zeta_2} - y p_{110} g_1 = 0, \\
&\left(\frac{1}{\zeta_1} - \frac{1}{\zeta_2}y\right)\frac{dg_1}{dy} + \frac{i\beta g_1}{\zeta_2} - y(p_{101}g_0 + p_{121}g_2) = 0. \\
&\vdots
\end{aligned} \tag{A6}$$

The solutions are

$$g_i(y) = C_i' e^{-i\beta\zeta_1 y/k_2} , \qquad \text{(A7)}$$

with the C_i' found from

$$i\frac{\zeta_1}{\zeta_2^2}\beta C_0' - p_{110} C_1' = 0 ,$$

$$i\frac{\zeta_1}{\zeta_2^2}\beta C_1' - p_{101} C_0' - p_{121} C_2' = 0 . \qquad \text{(A8)}$$

$$\vdots$$

The boundary condition is

$$C_i e^{-i\alpha\zeta_2/k_1} = C_i' e^{-i\beta\zeta_1/k_2} . \qquad \text{(A9)}$$

Choose C_0 and C_0' such that Eq. (A9) is satisfied, then it will be satisfied for any i provided

$$\beta = \frac{\zeta_2^3}{\zeta_1^3}\alpha . \qquad \text{(A10)}$$

With the value for β, Eqs. (A8) become identical to Eqs. (31) and so

$$\frac{C_i}{C_0} = \frac{C_i'}{C_0'} \qquad \text{(A11)}$$

holds for all i.

[1]M. R. H. Rudge, Rev. Mod. Phys. 40, 564 (1968), and earlier references therein.
[2]A. Temkin, Phys. Rev. Lett. 16, 835 (1966).
[3]S. M. Younger, Phys. Rev. A 22, 111 (1980).
[4]H. Ehrhardt, K. Jung, and E. Schubert, in *Coherence and Correlation in Atomic Collisions* (Plenum, New York, 1980), p. 41, and earlier references therein.
[5]E. C. Beaty, K. H. Hesselbacher, S. P. Hong, and J. H. Moore, J. Phys. B 10, 611 (1977). For experimental work very close to threshold see also S. Cvejanović and F. M. Read, J. Phys. B 7, 1841 (1974).
[6]I. Fuss, I. E. McCarthy, C. J. Noble, and E. Weigold, Phys. Rev. A 17, 604 (1978), and earlier references therein.
[7]S. Geltman and M. B. Hildalgo, J. Phys. B 7, 831 (1974).
[8]S. Geltman, J. Phys. B 7, 1094 (1974).
[9]M. Lal, A. N. Tripathi, and M. K. Srivastava, J. Phys. B 12, 945 (1979).
[10]P. L. Altick, Phys. Rev. A 21, 1381 (1980).
[11]A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, New Jersey, 1957).
[12]See, for example, J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Clarendon, Oxford, 1965).