PHYSICAL REVIEW A VOLUME 7, NUMBER 6 JUNE 1973

Self-Consistent-Field Calculations for the Elastic Scattering of Electrons from Hydrogenlike Systems*†

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(Received 9 October 1972)

A general formalism is presented for the description of elastic scattering of electrons from hydrogenlike atomic systems. The total wave function for the two-electron system is put forth as a multiconfiguration expansion in terms of suitably normalized orthogonal orbitals. These radial orbitals, as well as the coefficients of the expansion, are determined variationally via a system of coupled integrodifferential equations. The formalism is applied to the calculation of elastic electron-hydrogen scattering in the energy range below the first resonance for the ^1S state of the two-electron system. Accurate phase shifts are obtained with short expansions, as the newly introduced orbitals obtained by numerically integrating the integrodifferential equations account quite adequately for short-range correlation.

INTRODUCTION

Phase-shift calculations for the elastic scattering of electrons from one-electron atom or ion targets have been carried out by many workers.[1] The approach generally taken is to calculate an approximate total wave function of definite total angular momentum, parity, and spin. Such wave functions, called partial waves, represent standing-wave stationary-state solutions to the Schrödinger equation for a continuum state of the system consisting of the target atom (or ion) and the scattering electron. The partial wave contains an "open-channel" term consisting of an antisymmetrized product of the ground-state wave function of the target with an "open-channel orbital" used to describe the scattering electron, as well as a "bound part" which is square integrable in both electronic coordinates in the usual way. The open-channel term is, of course, not square integrable as the scattering orbital has sinusoidal dependence for large argument.

The scattering orbital is expressed in one of two ways. Some workers[2] use an analytic expansion in terms of known functions wherein the coefficients of this expansion, including the phase-shift parameter, are determined variationally via a system of linear algebraic equations. Other methods[3] allow complete variational freedom for the open-channel orbital and determine it via an integrodifferential equation. These latter methods have the additional advantage that, when properly formulated, they yield approximate phase shifts which are rigorous lower bounds to the true phase shift.[4]

The bound part of the partial wave plays a particularly important role in the description of correlated electronic motion which takes place in the vicinity of the target, and the most accurate phase-shift calculations to date employ wave functions for which the bound part depends explicitly upon the interelectronic separation.[5] This dependence is chiefly responsible for the high accuracy obtainable using such wave functions, yet, at the same time, it presents serious obstacles to calculations of electron scattering phenomena involving many-electron target atoms. This situation has led other workers, even in the case of scattering from atomic hydrogen, to express the entire partial wave solely in terms of products of one-electron functions.[6] These expansions are generally less efficient in terms of the expansion length needed to achieve a desired level of accuracy in the phase shift, yet a method of this type can be adapted with relative ease to problems involving scattering from more complex targets.[7]

Perhaps the most attractive of the methods which employ one-particle functions exclusively is the "close-coupling" technique,[8] where target eigenstates in excess of that needed to construct the open channel term are used with square-integrable "closed-channel orbitals" to construct the bound part of the partial wave. Hence, in the close-coupling method, the bound part is expressed in complete analogy with the open-channel term and the individual terms of the bound part are called "closed channels." This method is directly applicable to problems involving inelastic scattering and it is especially suited to describing the opening up of a new scattering channel. Moreover, the phase shift obtained from the close-coupling wave function is a rigorous lower bound to the true phase shift.[9]

In view of the many strong points of the close-coupling technique, it is most unfortunate that, except for very low scattering electron energies, the accuracy obtainable through its use is rather limited. This situation stems chiefly from the fact that the target eigenstates used to build the closed-channel terms are not spatially compact enough to allow an adequate description of close-range correlation. Attempts have been made to modify the close-coupling scheme by replacing some of the target eigenstates by other functions which are more compact spatially. Calculations of this type, called "pseudostate" calculations, have been carried out by Burke, Gallaher, and Geltman,[10] in the case of electron scattering from atomic hydrogen, using "pseudostates" derived by Damburg and Karule,[11] which account for the ground-state polarizability of the hydrogen atom. Their results indicate that the use of spatially compact pseudostates markedly improves the accuracy of the close-coupling scheme. Moreover, the desirable property of providing rigorous lower bounds on the phase shift is retained.

In the pseudostate calculations mentioned above, as well as in all close-coupling calculations, the open- and closed-channel orbitals are variationally determined by a system of coupled integrodifferential equations. The pseudostates, however, like the target eigenstates characteristic of the close-coupling method, have not been permitted to take part in the variational process. Seaton[12] has suggested that the pseudostates be determined on the same footing as the closed-channel orbitals. In the simpler problem of the elastic scattering of positrons from atomic hydrogen, Ruffine[13] determined a pseudostate variationally. In Ruffine's calculation, one closed-channel orbital and one pseudostate were determined along with the open-channel function by a system of differential equations. The results he obtained for the phase shift were quite good in comparison with calculations where full variational freedom was not permitted for the pseudostates.[14]

Another class of methods, which have been appropriately called "hybrid" methods,[14] append to a close-coupling wave function of one or several terms, an additional expansion in terms of known functions. In these methods, the open-channel orbitals and any closed-channel orbitals which may be present are determined from a system of integrodifferential equations, and a set of linear algebraic equations furnishes the coefficients of the expansion. In such calculations, the lower bound property of the phase shift is retained. Burke and Taylor[15] have used a method of this kind to combine the high accuracy of the Hylleraas–type expansion involving explicit dependence upon the interelectronic distances with the advantages of close coupling. Their method, which is in many respects ideal, is, unfortunately, not easily adapted to problems involving more complex target atoms. Gailitis,[16] using a single close-coupling term, has performed similar calculations wherein the appended expansion does not make use of explicit dependence on the interelectronic separation, and, for that reason, is less efficient than that of Burke and Taylor in terms of expansion length.

In this paper we present a method in which we append to the requisite open-channel term, a bound part consisting of a multiconfiguration expansion using a set of orthonormal orbitals. These orbitals are allowed to participate fully in the variational process. They are determined along with the open-channel orbital and the coefficients of the expansion by a system of coupled integrodifferential equations. The wave function so obtained can be written in the form of a pseudostate expansion in which the pseudostates are variationally optimal. Using this method, we have numerically integrated the equations for the ^1S state of the e-H system in the energy range below the first resonance, obtaining optimal orbitals and accurate phase shifts which are rigorous lower bounds to the true phase shift. The expansions are quite efficient with respect to the number of orbitals needed to achieve a desired level of accuracy. Close-range correlation is accounted for quite adequately as most of the orthonormal orbitals are large only in the neighborhood of the target. Polarization effects are automatically exhibited by the orbitals since the asymptotic behavior of the optimal orbitals is, in general, of a damped oscillatory character. The orbitals are, of course, energy dependent and as the scattering electron's energy approaches the threshold for target excitation, some of the optimal orbitals automatically assume the form of hydrogenic eigenstates. The method can also be viewed as an application to scattering problems of the multiconfiguration self-consistent-field method used with much success in bound-state atomic calculations.

FORMALISM

We consider the calculation of those continuum states of a two-electron system which describe a situation where one of the two electrons remains, on the average, in the vicinity of the nucleus with charge Z. The system is described by the usual nonrelativistic spin-independent Hamiltonian operator (in atomic units),

$$\mathcal{H}=-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2-r_1{}^{-1}Z-r_2{}^{-1}Z+r_{12}{}^{-1}. \qquad (1)$$

Here, r_1 and r_2 are, respectively, the distances of the two electrons from the nucleus and r_{12} is the interelectronic separation. The motion of the nucleus is neglected.

We wish to calculate $\psi_{LMSE}(\vec{r}_1, \vec{r}_2)$, which is the spatial part of the total two-electron wave function; it is to be understood as a real standing-wave solution of the Schrödinger equation:

$$\mathcal{H}\psi_{LMSE}(\vec{r}_1, \vec{r}_2)=E\psi_{LMSE}(\vec{r}_1, \vec{r}_2), \qquad (2)$$

where E is the fixed and given total energy of the system.

The invariance properties of $\mathcal{H}$ with respect to rotations and inversions as well as exchange of the electronic coordinates imply that ψ_{LMSE}, as is indicated by its labels, can be chosen to be an eigenfunction of the square of the total orbital angular momentum operator and of its z component, with eigenvalues $L(L+1)$ and M, respectively. The total spin quantum number S determines the symmetry of ψ_{LMSE} under coordinate exchange. When either of the coordinates $\vec{r}_1$ or $\vec{r}_2$ become large, the partial wave must "dissociate" into a product form consisting of the target ground state multiplied by a scattering orbital describing an electron of definite angular momentum. This implies that the inversion symmetry of ψ_{LMSE} is completely determined by the total orbital angular momentum quantum number L. Thus, only the "normal" spectral terms, which are the only ones occurring in one-electron spectra, are permitted. Wave functions of the opposite parity are excluded.

In the description to follow, considerable use will be made of the angular functions defined by[17]

$$Y_{LMll'}(\Omega_1, \Omega_2)=\sum_{m}\sum_{m'} C(l, l', L; m, m', M) \times Y_{lm}(\Omega_1)Y_{l'm'}(\Omega_2), \qquad -L\leq M\leq L \qquad (3)$$

where the $Y_{lm}(\Omega)$ are ordinary spherical harmonics and the $C(l, l', L; m, m', M)$ are Clebsch–Gordan coefficients. The permissible pairs (l, l') used in the specification of the $Y_{LMll'}$ are given by the set

$$\mathcal{V}_L=\{(l, l') \text{ such that } l+l' \text{ is even and } |l-l'|\leq L\leq l+l'\}. \qquad (4)$$

These pairs lie within and on the boundaries of the region of the l, l' plane bounded by the lines

$$\begin{aligned} l+l'&=L,\\ l-l'&=L, \qquad (5)\\ l'-l&=L. \end{aligned}$$

Pairs satisfying Eqs. (5) yet excluded from $\mathcal{V}_L$ because $l+l'$ is odd lead to angular functions with "abnormal" parity behavior. These ideas are illustrated in Fig. 1 for $L=0, 1, 2$.

The total wave function can be expanded according to

$$\psi_{LMSE}(\vec{r}_1, \vec{r}_2)=(r_1r_2)^{-1}\sum \Phi_{LSE,ll'}(r_1, r_2) \times Y_{LMll'}(\Omega_1, \Omega_2), \qquad (l, l')\in\mathcal{V}_L. \qquad (6)$$

The biradial functions $\Phi_{LSE,ll'}$ can easily be shown to satisfy

$$\Phi_{LSE,ll'}(r_1, r_2)=(-1)^S\Phi_{LSE,l'l}(r_2, r_1). \qquad (7)$$

The asymptotic behavior of ψ_{LMSE} is summarized in the equations

$$\begin{aligned} \psi_{LMSE}(\vec{r}_1, \vec{r}_2)&\approx(r_1r_2)^{-1}\varphi_{1s}(r_1)\varphi_{kL}(r_2) \times Y_{LM0L}(\Omega_1, \Omega_2), \quad r_2\to\infty\\ \psi_{LMSE}(\vec{r}_1, \vec{r}_2)&\approx(-1)^S(r_1r_2)^{-1}\varphi_{kL}(r_1)\varphi_{1s}(r_2) \times Y_{LML0}(\Omega_1, \Omega_2), \quad r_1\to\infty \end{aligned} \qquad (8)$$

where $\varphi_{1s}(r)$ is the hydrogenic ground-state orbital

$$\varphi_{1s}(r)=2Z^{3/2}re^{-Zr} \qquad (9)$$

and

$$\varphi_{kL}(r)\approx A\sin[kr+k^{-1}(Z-1)\ln r+\eta], \quad r\to\infty. \qquad (10)$$

The function $\varphi_{kL}(r)$ is the scattering orbital; A is the amplitude, usually taken to be unity, k is the

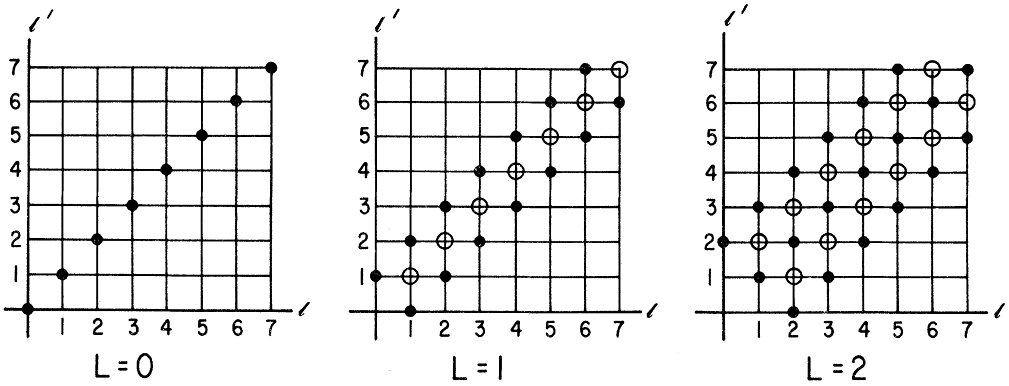


FIG. 1. Permitted pairs used in the construction of the angular two-particle functions $Y_{LMll'}(\Omega_1, \Omega_2)$, illustrated for $L=0, 1, 2$. Points indicated by ● are used for the "normal" terms for which $\mathcal{P}Y_{LMll'}=(-1)^L Y_{LMll'}$. Points indicated by ○ are used for the "abnormal" terms for which $\mathcal{P}Y_{LMll'}=(-1)^{L+1}Y_{LMll'}$.

wave number defined by

$$\tfrac{1}{2}k^2+\epsilon_{1s}=E\,,\qquad \epsilon_{1s}=-\tfrac{1}{2}Z^2\,, \tag{11}$$

and η is the phase shift.

The indices *LMSE*, being good quantum numbers, are constant for a given calculation; hence we suppress them on both ψ_{LMSE} and $\mathcal{V}_L$, writing, in view of Eqs. (6) and (7),

$$\psi(\vec{r}_1,\vec{r}_2)=(r_1r_2)^{-1}\sum\Phi_{ll'}(r_1,r_2)Y_{ll'}(\Omega_1,\Omega_2)\,,\quad\times(l,l')\in\mathcal{V} \tag{12}$$

$$\Phi_{ll'}(r_1,r_2)=(-1)^S\Phi_{l'l}(r_2,r_1)\,. \tag{13}$$

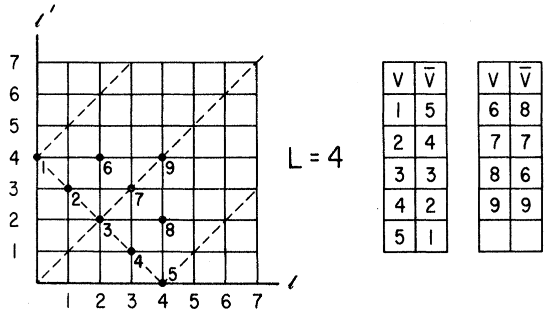
We turn now to the detailed consideration of the functions $\Phi_{ll'}(r_1, r_2)$. In practical calculations we use, instead of the infinite set $\mathcal{V}$, a finite subset $[\mathcal{V}]\subset\mathcal{V}$ which is arbitrary except that if (l, l') is included in it, so also is (l', l). For this chosen subset $[\mathcal{V}]$, we propose to determine the functions $\Phi_{ll'}$ variationally.

Since the set $[\mathcal{V}]$ contains a finite number of pairs (l, l'), it will be convenient to introduce the running index v which is in one to one correspondence with the pairs (l, l') belonging to $[\mathcal{V}]$. This correspondence can be set up in a variety of ways and a convenient choice is illustrated in Fig. 2 for $L=4$. We adopt the convention that $v=1$ corresponds to the "scattering term" $(0, L)$. Moreover, if v corresponds to (l, l'), we shall understand $\bar{v}$ to be that value of the running index corresponding to the exchanged pair (l', l). We indicate the correspondence by writing $v\rightarrow(l, l')$ and introduce V, the set of $v\rightarrow(l, l')$ for $(l, l')\in[\mathcal{V}]$.

We want to approximate $\Phi_{ll'}(r_1, r_2)$ by a finite bilinear expansion in functions of the single arguments r_1 and r_2. If a pair of such functions occurs in the construction of $\Phi_{ll'}$ then the member bearing the coordinate r_1 must vary for small argument as r_1^{l+1} while the function with argument r_2 behaves like $r_2^{l'+1}$ as r_2 approaches zero. This occurs because of the angular dependence of the function $Y_{ll'}(\Omega_1, \Omega_2)$ which accompanies $\Phi_{ll'}(r_1, r_2)$ in the expression (12) for the total wave function. Moreover, in order to satisfy the exchange condition Eq. (13), the functions used to describe $\Phi_{ll'}$ must be used with arguments exchanged to construct the function $\Phi_{l'l}$. With these facts in mind, we introduce functions φ_{vm} and $\varphi_{\bar{v}m}$, $m=1, 2, \ldots, N_v$, where, as $r\rightarrow0$,

$$\varphi_{vm}(r)\approx r^{l+1}\,,\qquad \varphi_{\bar{v}m}(r)\approx r^{l'+1}\,, \tag{14}$$

where $v\rightarrow(l, l')$ and $\bar{v}\rightarrow(l', l)$.



V	$\bar{V}$
1	5
2	4
3	3
4	2
5	1

V	$\bar{V}$
6	8
7	7
8	6
9	9

FIG. 2. Assignment of values for the running index v replacing the pair index $(l, l')\in[\mathcal{V}]$ for $L=4$. By convention $v=1$ corresponds to the pair $(0, L)$. The relationship between v and $\bar{v}$ is also illustrated. Note that the points corresponding to the indices v and $\bar{v}$ are symmetrically placed about the line $l=l'$. In this case the elements of the set V are the integers $1-9$.

As the notation indicates, the functions φ_{vm} depend upon *both* indices l and l'. We have introduced one set of functions for each point (l, l') of the set $[\mathcal{V}]$. To construct the functions $\Phi_{ll'}$ and $\Phi_{l'l}$, both sets of functions φ_{vm} and $\varphi_{\bar{v}m}$ are needed. In Fig. 2 for example, we use the products formed from $\varphi_{1m}(r_1)$ and $\varphi_{5n}(r_2)$, $m=1, 2, \ldots, N_1$; $n=1, 2, \ldots, N_5$; $N_1=N_5$, to construct $\Phi_{0,4}(r_1, r_2)$. All products are used which are not ruled out by the asymptotic behavior of the wave function. Note that in this example, $v=1\rightarrow(0, 4)$ and $\bar{v}=5\rightarrow(4, 0)$. The same functions with arguments interchanged are used to construct $\Phi_{4,0}(r_1, r_2)$, where $v=5\rightarrow(4, 0)$ and $\bar{v}=1\rightarrow(0, 4)$. Note that if $v\rightarrow(l, l')$ and $w\rightarrow(l, l'')$ with $l'\neq l''$, the two sets of functions $\varphi_{vm}(r)$ and $\varphi_{wn}(r)$ behave for small r like r^{l+1} according to Eqs. (14), yet these functions are, in general, completely different. This is a departure grom the usual orbital model; it is adopted because of the greater flexibility afforded to the wave function and the ease of implementation in the two-electron case.

The approximations to the functions $\Phi_{ll'}(r_1, r_2)$ are now given by

$$\Phi_v(r_1,r_2)=(r_1r_2)^{-1}\sum_m\sum_n\varphi_{vm}(r_1)\Gamma_{vmn}\varphi_{\bar{v}n}(r_2)\,, \tag{15}$$

where $v\rightarrow(l, l')$, $\bar{v}\rightarrow(l', l)$, and

$$\Gamma_{vmn}=(-1)^S\Gamma_{\bar{v}nm}\,. \tag{16}$$

In Eq. (15) the summations over m and n run from 1 to N_v and $N_{\bar{v}}$, respectively. Note that, evidently,

$$N_v=N_{\bar{v}}\,. \tag{17}$$

In case $l=l'$, so that $v=\bar{v}$, Eqs. (14) reduce to a single set, and Eqs. (15) and (16) still apply; $\Phi_v(r_1, r_2)$ becomes a quadratic form in the functions $\varphi_{vm}(r)$, $m=1, 2, \ldots, N_v$.

According to Eqs. (8), which indicate the asymptotic form of ψ, two of the orbitals introduced have a special significance. The orbital $\varphi_{1,1}(r)$ is the hydrogenic ground-state function $\varphi_{1s}(r)$, while $\varphi_{\bar{1},N_{\bar{1}}}(r)$ is the scattering orbital $\varphi_{kL}(r)$. We have adopted the convention that the fixed hydrogenic function is numbered *first* among the orbitals $\varphi_{1n}(r)$, $n=1, 2, \ldots, N_1$, and the continuum orbital $\varphi_{kL}(r)$ is numbered *last* among the functions $\varphi_{\bar{1}m}(r)$, $m=1, 2, \ldots, N_1$. All of the remaining orbitals $\varphi_{vm}(r)$, $m=1, 2, \ldots, N_v$; $v \in V$, are square-integrable functions. In scattering processes, φ_{1s} describes the target, φ_{kL} describes the scattered electron at large distances from the target, and the remaining orbitals describe interactions taking place in the vicinity of the target; these include polarization, correlated motion, and resonance formation.

In the expansion (15) for Φ_v, the continuum orbital $\varphi_{\bar{1},N_{\bar{1}}}$ can only be paired with the target eigenstate $\varphi_{1,1}$. This implies that

$$\Gamma_{\bar{1},N_{\bar{1}},n}=(-1)^S A\delta_{n1}=(-1)^S\Gamma_{1,n,N_{\bar{1}}}\,. \tag{18}$$

Because all possible products of square integrable orbitals are permitted in (15), some auxiliary conditions must be imposed upon the φ_{vm} to guarantee an unambiguous expression for Φ_v. Unique coefficients Γ_{vnm} can be specified only if some orthogonality and normalization requirements are placed upon the $\varphi_{vm}(r)$. Even with such requirements imposed, the square integrable φ_{vm} can only be determined up to a unitary transformation, and further specification is demanded. For these reasons we require that, for *fixed v*, the square-integrable functions (including φ_{1s} if $v=1$) shall satisfy the equations

$$\begin{aligned} \langle\varphi_{vm}|\varphi_{vn}\rangle &= \delta_{mn}\,, \\ -\langle\varphi_{vm}|h_v|\varphi_{vn}\rangle &= \omega_{vm}\delta_{mn}\,, \end{aligned} \tag{19}$$

where

$$2h_v=\frac{d^2}{dr^2}-l(l+1)r^{-2}+2Zr^{-1},\quad v\to(l, l')\,. \tag{20}$$

The particular choice of these conditions is dictated by the physical consideration that, as the incident electron's kinetic energy approaches the target excitation threshold, some of the $\varphi_{vm}(r)$ must become hydrogenic eigenfunctions. The conditions (19) allow this to happen in a natural way.

We wish to emphasize that the relations (19) apply only between functions bearing the same index v. Refer again to Fig. 2, where $v=2$ corresponds to the pair $(l, l')=(1, 3)$, while $v=7$ corresponds to the pair $(l, l')=(3, 3)$. The pair (3, 1) corresponds to $v=\bar{2}=4$. The two sets of functions

$$\varphi_{4n}(r),\quad n=1, 2, \ldots, N_4$$

$$\varphi_{7m}(r),\quad m=1, 2, \ldots, N_7$$

have the same behavior for small argument; all of these functions start out near $r=0$ proportional to r^4. The φ_{4n} form an orthonormal set which diagonalizes the operator h_4 in the Hilbert space available to them. According to Eqs. (19) with $v=7$, the functions φ_{7m} are also an orthonormal set and diagonalize the same operator in their Hilbert space, yet they have no orthogonality relations with the φ_{4n}.

The scattering orbital $\varphi_{\bar{1},N_{\bar{1}}}$ is required to be orthogonal to the rest of the functions $\varphi_{\bar{1}n}$:

$$\langle\varphi_{\bar{1}N_{\bar{1}}}|\varphi_{\bar{1}n}\rangle=0\,. \tag{21}$$

In Fig. 2, $v=1\to(0, 4)$, so that $\bar{v}=5\to(4, 0)$. If there are $N_5=N_1$ functions associated with the point (4, 0) then the continuum orbital is φ_{5,N_5} and is orthogonal to each function φ_{5m}, $m=1, 2, \ldots, N_5-1$. Note that all of the other points in the diagram correspond to sets of square-integrable functions only.

According to Eqs. (12) and (15), the partial wave can be written

$$\psi(\vec{r}_1, \vec{r}_2)=(r_1r_2)^{-1}\sum_v\sum_m\sum_n\varphi_{vm}(r_1)\times\Gamma_{vmn}\varphi_{\bar{v}n}(r_2)Y_v(\Omega_1, \Omega_2)\,. \tag{22}$$

To determine the functions $\varphi_{vm}(r)$ and the coefficients Γ_{vmn} we form the functional

$$L(\psi)=\int d^3\vec{r}_1\int d^3\vec{r}_2\psi^*(\mathcal{H}-E)\psi\,, \tag{23a}$$

and calculate the first variation of L:

$$\delta L(\psi)=2\int d^3\vec{r}_1\int d^3\vec{r}_2\,\delta\psi^*(\mathcal{H}-E)\psi-\int d^3\vec{r}_1\int_\infty d\sigma\left(\psi^*\frac{\partial\delta\psi}{\partial n_2}-\delta\psi\frac{\partial\psi^*}{\partial n_2}\right). \tag{23b}$$

From this expression we see that the function $\psi(\vec{r}_1, \vec{r}_2)$, for which $\delta L(\psi)$ vanishes for all variations $\delta\psi(\vec{r}_1, \vec{r}_2)$ such that the "surface term"

$$\int d^3r_1\int_\infty d\sigma\left(\psi^*\frac{\partial\delta\psi}{\partial n_2}-\delta\psi\frac{\partial\psi^*}{\partial n_2}\right) \tag{24}$$

also vanishes, must satisfy the Schrödinger equation (2).

We substitute $\psi(\vec{r}_1, \vec{r}_2)$ as given by Eq. (22) into Eq. (23a) and carry out the variation (23b) permitting only variations in the radial functions $\varphi_{vm}(r)$ and the coefficients Γ_{vmn}. These variations are restricted so that the surface term (24) is always zero. We introduce for convenience the functions $u_{vm}(r)$ defined by

$$u_{vm}(r)=\sum_n\Gamma_{vmn}\varphi_{\bar{v}n}(r)\,. \tag{25}$$

Note that according to Eq. (14),

$$u_{vm}(r)\approx r^{l'+1},\quad r\to 0\,. \tag{26}$$

According to Eqs. (22) and (25) we may write

$$\psi(\vec{r}_1, \vec{r}_2) = (r_1 r_2)^{-1} \sum_v \sum_m \varphi_{vm}(r_1) u_{vm}(r_2) Y_v(\Omega_1, \Omega_2)\,. \tag{27}$$

The variational condition that $\delta L(\psi)$ shall vanish for all permitted variations $\delta\psi$ leads to the system of equations

$$\begin{aligned}&[h_{\bar v} - X(\varphi_{vm}, \varphi_{vm}) - \omega_{vm} + E] u_{vm} \\ &\quad - \sum_w \sum_n{}' X(\varphi_{vm}, \varphi_{wn}) u_{wn} \\ &\quad + \delta_{v\bar 1} \langle \varphi_{\bar 1 m} | h_{\bar 1} | \varphi_{\bar 1 N_{\bar 1}} \rangle u_{\bar 1 N_{\bar 1}} = 0\,,\end{aligned} \tag{28}$$

for the functions $u_{vm}(r)$. Here, $v \rightarrow (l, l')$, $v \in V$, $w \in V$, $m = 1, 2, \ldots, N_v$; $n = 1, 2, \ldots, N_w$, but $(v, m) \neq (\bar 1, N_{\bar 1})$. The one-electron operator $h_{\bar v}$ is given by Eq. (20) and the prime in Eq. (28) indicates that the term

$$X(\varphi_{vm}, \varphi_{vm}) u_{vm}\,,$$

is not included in the summation. The auxiliary functions $X(\varphi_{vm}, \varphi_{wn})$ are defined by the equations

$$\begin{aligned}&X(\varphi_{vm}, \varphi_{wn}) = \sum_\nu C^\nu_{vw} X^\nu(\varphi_{vm}, \varphi_{wn})\,, \\ &X^\nu(\varphi_{vm}, \varphi_{wn}) = (2\nu+1)^{-1} \left[r^\nu \int_0^r \varphi_{vm}(s) s^{-\nu-1} \varphi_{wn}(s)\, ds \right. \\ &\qquad \left. + r^{-\nu-1} \int_r^\infty \varphi_{vm}(s) s^\nu \varphi_{wn}(s)\, ds \right],\end{aligned} \tag{29}$$

where

$$\begin{aligned}C^\nu_{vw} = {} & (-1)^{L+\nu}(2l+1)(2l'+1)(2p+1)(2p'+1) \\ & \times [C(l, p, \nu; 0, 0, 0) \\ & \times W(l, l'; p, p'; L, \nu) C(l', p', \nu; 0, 0, 0)]\,,\end{aligned} \tag{30}$$

$v \rightarrow (l, l')$ and $w \rightarrow (p, p')$, and $C(l, p, \nu; 0, 0, 0)$ and $W(l, l'; p, p'; L\nu)$ are the well-known Clebsch–Gordan and Racah coefficients, respectively.[17] The index ν in Eqs. (29) and (30) has the range specified by the conditions

$$\begin{aligned}&|l - p| \leq \nu \leq l + p\,, \\ &|l' - p'| \leq \nu \leq l' + p'\,, \\ &(-1)^{l+p} = (-1)^\nu = (-1)^{l'+p'}\,.\end{aligned} \tag{31}$$

There is one differential equation for each independent radial function. We see from Eq. (28) that there is no equation for $u_{\bar 1 N_{\bar 1}}(r)$. This is so because its functional form is prescribed by the "dissociation" requirement and therefore cannot be varied. We obtain it from Eqs. (18) and (25):

$$u_{\bar 1 N_{\bar 1}}(r) = (-1)^S A \varphi_{1s}(r)\,. \tag{32}$$

We wish to call attention to the terms in Eq. (28) of the form

$$\delta_{v\bar 1} \langle \varphi_{\bar 1 m} | h_{\bar 1} | \varphi_{\bar 1 N_{\bar 1}} \rangle u_{\bar 1 N_{\bar 1}}\,.$$

These terms occur in the system (28) because of the orthogonality condition (21) imposed upon the scattering orbital $\varphi_{kL}(r)$. These terms would not appear at all if, instead of Eq. (21), we required

$$\langle \varphi_{\bar 1 m} | h_{\bar 1} + \tfrac{1}{2}k^2 | \varphi_{kL} \rangle = 0\,; \tag{33}$$

however, the resultant lack of orthogonality between φ_{kL} and the square integrable orbitals $\varphi_{\bar 1 m}$, $m = 1, 2, \ldots, N_1 - 1$, makes the determination of the functions $u_{vm}(r)$ more difficult in practice as the iterative scheme used to determine these functions is less stable when strict orthogonality is not maintained between the scattering orbital φ_{kL} and its square integrable companions. For this reason, condition (21) was adopted.

The system (28) is solved iteratively: approximate orbitals $u_{vm}(r)$ and $\varphi_{vm}(r)$ must be in hand. The quantity

$$\begin{aligned}S_{vm}(r) = {} & \sum_w \sum_n{}' X(\varphi_{vm}, \varphi_{wn}) u_{wn} \\ & + \delta_{v\bar 1} \langle \varphi_{\bar 1 m} | h_{\bar 1} | \varphi_{\bar 1 N_{\bar 1}} \rangle u_{\bar 1 N_{\bar 1}}\end{aligned} \tag{34}$$

is computed using these approximate functions and then used as a "source term" in Eq. (28) which is treated as a second-order ordinary differential equation for the function $u_{vm}(r)$. The "Coulomb potential" $X(\varphi_{vm}, \varphi_{vm})$ as well as the "orbital energies" ω_{vm} given by Eq. (19) are computed using approximate $\varphi_{vm}(r)$. Numerical integration of the differential equation then furnishes an improved function $u_{vm}(r)$. For the square-integrable functions, unique solutions, regular at the origin, are obtained. A unique improved continuum function $u_{1,1}(r)$ is also obtained if the condition of unit amplitude for large r is imposed.

Once the improved functions $u_{vm}(r)$ are obtained by numerical integration, a revised set of $\varphi_{\bar v m}(r)$ are furnished by constructing appropriate linear combinations of the $u_{vm}(r)$ which satisfy the conditions (19) and (21). The expansion coefficients Γ_{vmn} are obtained by projection:

$$\Gamma_{vmn} = \langle u_{vm} | \varphi_{\bar v n} \rangle\,, \qquad \begin{aligned}&m = 1, 2, \ldots, N_v\,, \\ &n = 1, 2, \ldots, N_v\,.\end{aligned} \tag{35}$$

The coefficients $\Gamma_{1,n,N_{\bar 1}}$ and $\Gamma_{\bar 1, N_{\bar 1}, n}$ are, of course, fixed with values given by Eq. (18). The Γ_{vnm}, so obtained, are forcibly symmetrized according to Eq. (16) so that the exchange condition (13) is satisfied as the iteration proceeds. From the symmetrized Γ_{vmn} and the revised $\varphi_{\bar v m}$, a further revised set of u_{vm} are constructed according to Eq. (25) and the source terms $S_{vm}(r)$ and the Coulomb potentials $X(\varphi_{vm}, \varphi_{vm})$ are recomputed. The process is repeated until convergence of the $\varphi_{vm}(r)$ and the Γ_{vmn} is achieved.

As is characteristic of self-consistent-field methods in general, Eqs. (28) are nonlinear in the orbitals φ_{vm} and the solution of the system must be obtained iteratively, in contrast to the "close-coupling" and "pseudostate" equations for which noniterative schemes for solution have been devised.[18] Nevertheless, the iterative scheme used in solving Eqs. (28) converges quite rapidly in practice and the functions φ_{vm} so obtained are variationally optimal.

The iterative process can be started by choosing for the square integrable $\varphi_{vm}(r)$ a suitable linear combination of Slater functions which satisfies Eqs. (19) and which spans the region of configuration space in the neighborhood of the target. The initial approximation to the scattering orbital $\varphi_{kL}(r)$ is taken to be

$$\varphi^0_{kL}(r)=u^0_{kL}(r)-\sum_n \langle u^0_{kL}|\varphi_{\bar{1}n}\rangle\varphi_{\bar{1}n}(r)\,, \tag{36}$$

where u^0_{kL} satisfies the "source free" equation

$$\left(\frac{d^2}{dr^2}+2Zr^{-1}-2X(\varphi_{1s},\varphi_{1s})+k^2\right)u^0_{kL}=0\,, \tag{37}$$

and the solution of Eq. (37) regular at the origin with unit amplitude at ∞ is chosen. The initial set of Γ_{vmn} can be taken as follows:

$$\begin{aligned}&\Gamma_{1,1,N_{\bar{1}}}=1=(-1)^S\Gamma_{\bar{1},N_{\bar{1}},1}\,,\\ &\Gamma_{vmn}=0\quad\text{all others.}\end{aligned} \tag{38}$$

Of course, other more accurate starting sets may be used if they are available. All that is necessary is that the approximate φ_{vm} satisfy the conditions (19) and (21) and the Γ_{vmn} satisfy the symmetry condition (16).

Equation (27) expresses the partial wave in terms of the functions φ_{vm} and u_{vm} where the u_{vm} are given by Eq. (25). We could have written instead

$$\begin{aligned}&\psi(\vec{r}_1,\vec{r}_2)=P\psi(\vec{r}_1,\vec{r}_2)+Q\psi(\vec{r}_1,\vec{r}_2)\,,\\ &P\psi(\vec{r}_1,\vec{r}_2)=(r_1r_2)^{-1}[\varphi_{1s}(r_1)F_{kL}(r_2)Y_{LM0L}(\Omega_1,\Omega_2)\\ &\qquad\qquad+(-1)^S\varphi_{1s}(r_2)F_{kL}(r_1)Y_{LMLO}(\Omega_1,\Omega_2)]\,,\\ &Q\psi(\vec{r}_1,\vec{r}_2)=(r_1r_2)^{-1}\sum_v\sum_m{}'\varphi_{vm}(r_1)u_{vm}(r_2)Y_v(\Omega_1,\Omega_2)\,,\end{aligned} \tag{39}$$

where P is a projection operator which projects ψ onto all states included in an ordinary close-coupling expansion of one term, and $Q=1-P$. The function $Q\psi$ contains only functions which are square integrable and the function $u_{vm}(r_2)$ which is paired with $\varphi_{vm}(r_1)$ is identical with the function $u_{vm}(r_2)$ appearing in Eq. (27) with the exception that if $L=0$ we require in (39) for $v=1\rightarrow(0,0)$,

$$\langle u_{1m}|\varphi_{1s}\rangle=0\,,\quad m=2,3,\ldots,N_1\,. \tag{40}$$

Thus, any component which u_{1m} may have had in Eq. (27), along $\varphi_{1s}(r)$, has been absorbed into $F_{k0}(r)$ in Eqs. (39). The function $P\psi$ is the complete open-channel part of the partial wave ψ.

TABLE I. Structure of the wave functions.

(l,l')	(0, 0)					(1, 1)			(2, 2)		(3, 3)
v	1					2			3		4
m	1	2	3	4	5	1	2	3	1	2	1
ψ_1	$1s$	ks									
ψ_2	$1s$	$2s$	ks								
ψ_3	$1s$	$2s$	ks			$2p$					
ψ_4	$1s$	$2s$	$3s$	ks		$2p$	$3p$		$3d$		
ψ_5	$1s$	$2s$	$3s$	ks		$2p$	$3p$	$4p$	$3d$		
ψ_6	$1s$	$2s$	$3s$	$4s$	ks	$2p$	$3p$	$4p$	$3d$	$4d$	$4f$

A system of coupled equations entirely equivalent to Eqs. (28) can be derived for F_{kL} and the u_{vm} in Eqs. (39), and the variationally determined total wave functions obtained from the two systems are identical. In particular, they yield the same phase shift. The arguments of Hahn, O'Malley, and Spruch[4] establish that for a wave function of the form of Eqs. (39) determined with full flexibility for the open-channel function $P\psi$, the calculated phase shift is a rigorous lower bound to the true phase shift in the elastic scattering energy range. Thus the phase shift determined by Eq. (28) is certainly a rigorous lower bound to the true phase shift in the energy range considered here.

RESULTS

Calculations were carried out for the ^1S state of the system e-H in the energy range $\epsilon_{1s}\leq E\leq\epsilon_{2s}$, using wave functions of increasing complexity. In Hartrees,

$$E=\epsilon_{1s}+\tfrac{1}{2}k^2,\quad \epsilon_{1s}=-0.500\,,\quad \epsilon_{2s}=-0.125\,.$$

The wave functions used are labeled ψ_n, $n=1, 2, \ldots, 6$, and the orbital structure of these partial waves is exhibited in Table I. For example, the approximate total wave function ψ_3 has the form

$$\begin{aligned}\psi_3(\vec{r}_1,\vec{r}_2)=(r_1r_2)^{-1}\{&[\varphi_{1s}(r_1)u_{1s}(r_2)+\varphi_{2s}(r_1)u_{2s}(r_2)\\ &+\varphi_{ks}(r_1)u_{ks}(r_2)]Y_1(\Omega_1,\Omega_2)\\ &+\varphi_{2p}(r_1)u_{2p}(r_2)Y_2(\Omega_1,\Omega_2)\}\,.\end{aligned} \tag{41}$$

Here we have departed from the formal notation of the text and adopted instead a "spectroscopic" notation. Table I gives the "spectroscopic" label corresponding to the index pair (v, m) for each approximate wave function used. Thus for ψ_3,

$$\varphi_{1,1}=\varphi_{1s}\,,$$

$$\varphi_{1,2}=\varphi_{2s}\,,$$

$$\varphi_{1,3}=\varphi_{ks}\,,$$

and

$$\varphi_{2,1}=\varphi_{2p}\,.$$

In all of these wave functions, φ_{1s} is the hydrogen ground-state orbital and φ_{ks} is the scattering orbital. The spectroscopic label on a u function simply indicates which φ function is paired with it in the approximate partial wave given by Eq. (27).

Because the $u_{\nu m}$ are linear combinations of the $\varphi_{\bar{\nu} m}$ according to Eq. (25), the expression (27) for the total wave function is not manifestly symmetric in $\vec{r}_1$ and $\vec{r}_2$. These functions nevertheless possess complete exchange symmetry according to Eqs. (15) and (16);

$$\psi_n(\vec{r}_1, \vec{r}_2) = \psi_n(\vec{r}_2, \vec{r}_1), \quad n = 1, 2, \ldots, 6. \tag{42}$$

Only φ_{1s} among the functions $\varphi_{\nu m}$ used in the construction of the wave functions ψ_n has a prescribed form

$$\varphi_{1s}(r) = 2re^{-r}. \tag{43}$$

Exchange symmetry of the functions $\psi_n(\vec{r}_1, \vec{r}_2)$ then forces the function $u_{ks}(r)$ to have the identical form

$$u_{ks}(r) = \varphi_{1s}(r). \tag{44}$$

The function $\varphi_{ks}(r)$ and therefore $u_{1s}(r)$ have the asymptotic behavior: For $r \to \infty$,

$$\begin{aligned} \varphi_{ks}(r) &\approx \sin(kr + \eta), \\ u_{1s}(r) &\approx \sin(kr + \eta), \end{aligned} \tag{45}$$

where we have imposed unit amplitude normalization on the total wave functions. The remaining functions are square integrable.

The function ψ_1 is identical to the "one-state" close-coupling function $\psi_{1\,\mathrm{cc}}$ and reproduces the phase shifts determined by other workers as is illustrated in Table II. If we compare the two functions,

$$\begin{aligned} \psi_1(\vec{r}_1, \vec{r}_2) &= (r_1 r_2)^{-1}[\varphi_{1s}(r_1)u_{1s}(r_2) \\ &\quad + \varphi_{ks}(r_1)u_{ks}(r_2)]\, Y_1(\Omega_1, \Omega_2), \\ \psi_{1\,\mathrm{cc}}(\vec{r}_1, \vec{r}_2) &= (r_1 r_2)^{-1}[\varphi_{1s}(r_1)F_{1s}(r_2) \\ &\quad + F_{1s}(r_1)\varphi_{1s}(r_2)]\, Y_1(\Omega_1, \Omega_2), \end{aligned} \tag{46}$$

we note that $\psi_1(\vec{r}_1, \vec{r}_2)$ is not manifestly symmetrical in its arguments. The two functions are in fact identical and the connection between them is exhibited in the relations

$$\begin{aligned} \varphi_{ks}(r) &= F_{1s}(r) - \langle F_{1s} | \varphi_{1s} \rangle \varphi_{1s}(r), \\ u_{1s}(r) &= F_{1s}(r) + \langle F_{1s} | \varphi_{1s} \rangle \varphi_{1s}(r). \end{aligned} \tag{47}$$

The continuum function $F_{1s}(r)$ of the close-coupling model is determined from the differential equation

$$\begin{aligned} [h_1 - X(\varphi_{1s}, \varphi_{1s}) + \tfrac{1}{2}k^2]\, F_{1s} - X(\varphi_{1s}, F_{1s})\varphi_{1s} \\ + \langle \varphi_{1s} | h_1 + \tfrac{1}{2}k^2 | F_{1s} \rangle\, \varphi_{1s} = 0, \end{aligned} \tag{48}$$

where

$$h_1 = \frac{1}{2}\frac{d^2}{dr^2} + r^{-1}, \tag{49}$$

while the equation

$$[h_1 - X(\varphi_{1s}, \varphi_{1s}) + \tfrac{1}{2}k^2\,]u_{1s} - X(\varphi_{1s}, \varphi_{ks})u_{ks} = 0, \tag{50}$$

supplemented by the linkage relations

$$\begin{aligned} \varphi_{ks}(r) &= u_{1s}(r) - \langle u_{1s} | \varphi_{1s} \rangle \varphi_{1s}(r), \\ u_{ks}(r) &= \varphi_{1s}(r), \end{aligned} \tag{51}$$

determines the functions $u_{1s}(r)$ and $\varphi_{ks}(r)$. Note that no term proportional to $\varphi_{1s}(r)$ appears in Eq. (50). This is so because $\varphi_{1s}(r)$ is an eigenfunction of the operator h_1 and the two conditions (21) and (23) are, in this case, equivalent, so that the term

$$\langle \varphi_{1s} | h_1 | \varphi_{ks} \rangle u_{ks}(r),$$

does not appear in Eq. (50).

We next compare ψ_2 with the corresponding "two-state" close-coupling function $\psi_{2\,\mathrm{cc}}$. We have

$$\begin{aligned} \psi_2(\vec{r}_1, \vec{r}_2) &= (r_1 r_2)^{-1}[\varphi_{1s}(r_1)u_{1s}(r_2) + \varphi_{2s}(r_1)u_{2s}(r_2) \\ &\quad + \varphi_{ks}(r_1)u_{ks}(r_2)]\, Y_1(\Omega_1, \Omega_2), \end{aligned}$$

TABLE II. Phase shifts η for ${}^1S$ elastic scattering of electrons from hydrogen atoms.

k	ψ_1[a], $\psi_{1\,\mathrm{cc}}$[b]	$\psi_{2\,\mathrm{cc}}$[b]	ψ_2[a]	$\psi_{3\,\mathrm{cc}}$[b]	$\psi_{3\,\mathrm{ps}}$[c]	ψ_3[a]	15 term[d]	ψ_4[a]	50 term[d]	ψ_5[a]	ψ_6[a]	r_{12}[e]
0.1	2.396	2.404	2.420	2.491	2.529	2.537	2.539	2.548	2.550	2.549		2.553
0.2	1.871	1.878	1.894	1.974		2.043	2.047	2.060	2.060	2.061		2.067
0.3	1.508	1.519	1.533	1.596	1.657	1.673	1.673	1.688	1.690	1.690		1.696
0.4	1.239	1.257	1.266	1.302		1.390	1.389	1.405	1.408	1.409	1.411	1.415
0.5	1.031	1.046	1.062	1.093	1.155	1.172	1.174	1.189	1.192	1.194		1.202
0.6	0.869	0.89	0.906	0.93		1.006	1.013	1.029	1.032	1.035		1.041
0.7	0.744	0.77	0.791	0.817	0.875	0.882	0.902	0.919	0.921	0.924		0.930
0.8	0.651	0.70	0.716	0.773	0.823	0.799	0.857	0.875	0.877	0.879	0.883	0.886

[a] Present model wave functions.

[b] Close-coupling wave functions, Refs. 1 and 8.

[c] Pseudostate wave functions, Ref. 10.

[d] Analytic expansion wave functions, Ref. 19.

[e] Schwartz's Hylleraas-type wave functions, Ref. 5.

$$\psi_{2\,\mathrm{cc}}(\vec{r}_1, \vec{r}_2) = (r_1 r_2)^{-1}[\varphi_{\overline{1s}}(r_1)F_{1s}(r_2) + F_{1s}(r_1)\varphi_{\overline{1s}}(r_2) + \varphi_{\overline{2s}}(r_1)F_{2s}(r_2) + F_{2s}(r_1)\varphi_{\overline{2s}}(r_2)]\,Y_1(\Omega_1, \Omega_2)\,, \tag{52}$$

where

$$\begin{aligned} \varphi_{\overline{1s}}(r) &= \varphi_{1s}(r) = 2re^{-r}\,, \\ \varphi_{\overline{2s}}(r) &= 2^{-3/2}(2r - r^2)e^{-1/2r} \end{aligned} \tag{53}$$

are hydrogenic radial eigenfunctions.

In the close-coupling function $\psi_{2\,\mathrm{cc}}$, both F_{1s} and F_{2s} are determined by solving coupled differential equations. Likewise, in ψ_2, u_{1s} and u_{2s} are similarly determined from the system

$$\begin{aligned} &[h_1 - X(\varphi_{1s}, \varphi_{1s}) + \tfrac{1}{2}k^2]u_{1s} - X(\varphi_{1s}, \varphi_{2s})u_{2s} - X(\varphi_{1s}, \varphi_{ks})u_{ks} = 0\,, \\ &[h_1 - X(\varphi_{2s}, \varphi_{2s}) + E + \langle\varphi_{2s}|h_1|\varphi_{2s}\rangle]u_{2s} - X(\varphi_{2s}, \varphi_{1s})u_{1s} - X(\varphi_{2s}, \varphi_{ks})u_{ks} + \langle\varphi_{2s}|h_1|\varphi_{ks}\rangle u_{ks} = 0\,, \end{aligned} \tag{54}$$

supplemented by the linkage relations

$$\begin{aligned} \varphi_{2s}(r) &= [u_{2s}(r) - \langle u_{2s}|\varphi_{1s}\rangle\varphi_{1s}(r)]N_{2s}^{-1}\,, \\ \varphi_{ks}(r) &= u_{1s}(r) - \langle u_{1s}|\varphi_{2s}\rangle\varphi_{2s}(r) - \langle u_{2s}|\varphi_{1s}\rangle\varphi_{1s}(r)\,, \end{aligned} \tag{55}$$

where

$$N_{2s} = (\langle u_{2s}|u_{2s}\rangle - \langle u_{2s}|\varphi_{1s}\rangle^2)^{1/2}\,. \tag{56}$$

The function ψ_2, involving only three pairs of functions, is somewhat more compact than $\psi_{2\,\mathrm{cc}}$. The important distinction, however, between the two functions is that in ψ_2, the orbital φ_{2s} is not arbitrarily prescribed. Table II compares the phase shifts obtained from both ψ_2 and $\psi_{2\,\mathrm{cc}}$ over a range of energies. As a benchmark for comparison we take the accurate Schwartz values. A small but significant improvement in η_2 over $\eta_{2\,\mathrm{cc}}$ is noted throughout the energy range considered, namely, $0.1 \leq k \leq 0.8$.

Figure 3 illustrates $\varphi_{2s}(r)$ for several values of k and also compares these functions with the hydrogenic orbital $\varphi_{\overline{2s}}(r)$. A dramatic departure from $\varphi_{\overline{2s}}$ is exhibited for all k values examined. The more compressed appearance of φ_{2s} suggests that it is describing the close-range interaction more adequately than is $\varphi_{\overline{2s}}$. The illustrated dependence of φ_{2s} on wave number shows that the compression increases toward low k values. Even for $k = 0.8$, which is fairly close to the $1s \rightarrow 2s$ excitation threshold, the appearance of φ_{2s} is still quite compact relative to $\varphi_{\overline{2s}}$. These results are in agreement with the "orbital energies"

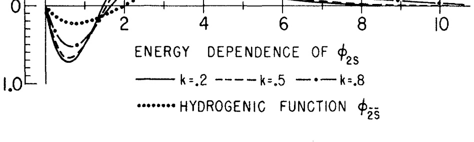


FIG. 3. Variation of φ_{2s} with scattering electron kinetic energy. Orbitals are taken from the wave function ψ_2.

TABLE III. Orbital energy of the $2s$ orbital for different k values.

k	$\omega_{2s}(\psi_2)$	$\omega_{2s}(\psi_2 + \varphi_{3s}u_{3s})$
0.2	0.191	0.026
0.5	0.117	−0.025
0.8	−0.031	−0.108

For the hydrogenic $2s$ orbital
$\omega_{\overline{2s}} = \epsilon_{2s} = -0.125$

$$\omega_{2s} = -\langle\varphi_{2s}|h_1|\varphi_{2s}\rangle\,, \tag{57}$$

which are given in Table III. For the hydrogenic function $\varphi_{\overline{2s}}$,

$$\omega_{\overline{2s}} = \epsilon_{2s} = -0.1250\,,$$

and we see from Table III that positive values of ω_{2s} are obtained for low k values indicating that considerable continuum contribution is present in the function φ_{2s}. On physical grounds, it might be expected that as k increases toward the $1s \rightarrow 2s$ excitation threshold of the atom core, the function φ_{2s} would tend to become the hydrogenic $\varphi_{\overline{2s}}$, while the function u_{2s} would expand to become a continuum orbital. This cannot happen for a wave function as simple in form as ψ_2. It is the exchange symmetry of ψ_2 which permits us to express u_{1s}, u_{2s}, and u_{ks} linearly in terms of φ_{ks}, φ_{2s}, and φ_{1s}, but ψ_2 with only three pairs of functions comprising it cannot exhibit proper behavior as threshold is crossed and still maintain its exchange symmetry. The difficulty is removed by adding an additional pair, $\varphi_{3s}(r_1)u_{3s}(r_2)$ to ψ_2. This gives a wave function of the form

$$\psi(\vec{r}_1, \vec{r}_2) = [\varphi_{1s}(r_1)u_{1s}(r_2) + \varphi_{2s}(r_1)u_{2s}(r_2) + \varphi_{3s}(r_1)u_{3s}(r_2) + \varphi_{ks}(r_1)u_{ks}(r_2)]\,Y_1(\Omega_1, \Omega_2)\,. \tag{58}$$

In this case, u_{2s} is a linear combination of φ_{1s}, φ_{2s}, and φ_{3s}. The orbital φ_{2s} is now free to become the hydrogenic function $\varphi_{\overline{2s}}$ as k increases and threshold is crossed, while φ_{3s} and u_{2s} will become continuum orbitals. The other orbital u_{3s} will go over into a constant multiple of the hydrogenic function $\varphi_{\overline{2s}}$ and the entire wave function will become equivalent (above threshold) to the close-coupling function $\psi_{2\,\mathrm{cc}}$.

Figure 4 illustrates the change in the form of

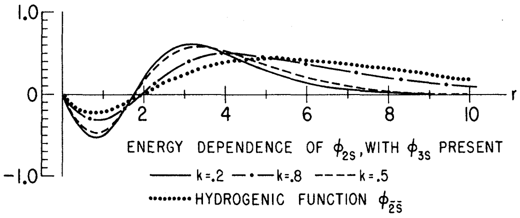


FIG. 4. Variation of φ_{2s} with scattering electron kinetic energy in the presence of φ_{3s}.

φ_{2s} when we add $\varphi_{3s}(r_1)u_{3s}(r_2)$ to ψ_2. Table III shows the effect that the addition of this term has upon the 2*s* "orbital energy" ω_{2s}. We note that the addition of the φ_{3s} orbital allows φ_{2s} to become less compact spatially and to relax toward larger values of r, although the compactness of φ_{2s} still persists markedly for low k values. The orbital energy ω_{2s} becomes lower throughout the examined energy range and as k approaches the $1s \rightarrow 2s$ excitation threshold, φ_{2s} bears a much stronger resemblance to the hydrogenic function $\varphi_{\bar{2}\bar{s}}$.

We discuss now the function ψ_3 which includes a term

$$(r_1 r_2)^{-1}\varphi_{2p}(r_1)u_{2p}(r_2)Y_2(\Omega_1,\ \Omega_2)\,, \tag{59}$$

designed to account for angular correlation. The index $v=2$ on $Y_2(\Omega_1, \Omega_2)$ corresponds to the pair index $(l, l')=(1, 1)$. The functions $u_{1s}(r)$, $u_{2s}(r)$, and $u_{2p}(r)$ are determined from the system of equations

$$\begin{aligned}
&[h_1 - X(\varphi_{1s},\ \varphi_{1s}) + \tfrac{1}{2}k^2\,]u_{1s} - X(\varphi_{1s},\ \varphi_{2s})u_{2s} \\
&\qquad - X(\varphi_{1s},\ \varphi_{ks})u_{ks}\ - X(\varphi_{1s},\ \varphi_{2p})u_{2p} = 0\,, \\
&[h_1 - X(\varphi_{2s},\ \varphi_{2s}) + \langle\varphi_{2s}|h_1|\varphi_{2s}\rangle + E]u_{2s} \\
&\qquad - X(\varphi_{2s},\ \varphi_{1s})u_{1s}\ - X(\varphi_{2s},\ \varphi_{ks})u_{ks} \\
&\qquad - X(\varphi_{2s},\ \varphi_{2p})u_{2p} + \langle\varphi_{2s}|h_1|\varphi_{ks}\rangle u_{ks} = 0\,, \\
&[h_2 - X(\varphi_{2p},\ \varphi_{2p}) + \langle\varphi_{2p}|h_2|\varphi_{2p}\rangle + E]u_{2p} \\
&\qquad - X(\varphi_{2p},\ \varphi_{1s})u_{1s}\ - X(\varphi_{2p},\ \varphi_{2s})u_{2s} \\
&\qquad - X(\varphi_{2p},\ \varphi_{ks})u_{ks} = 0\,,
\end{aligned} \tag{60}$$

supplemented by the linkage relations

$$\begin{aligned}
&\varphi_{2s}(r) = N_{2s}^{-1}[u_{2s}(r) - \langle u_{2s}|\varphi_{1s}\rangle\varphi_{1s}(r)\,]\,, \\
&\varphi_{ks}(r) = u_{1s}(r) - \langle u_{1s}|\varphi_{1s}\rangle\varphi_{1s}(r) - \langle u_{1s}|\varphi_{2s}\rangle\varphi_{2s}(r), \\
&\varphi_{2p}(r) = N_{2p}^{-1}u_{2p}(r)\,,
\end{aligned} \tag{61}$$

where

$$\begin{aligned}
&N_{2s} = (\langle u_{2s}|u_{2s}\rangle - \langle u_{2s}|\varphi_{1s}\rangle^2)^{1/2}\,, \\
&N_{2p} = \langle u_{2p}|u_{2p}\rangle^{1/2}\,.
\end{aligned} \tag{62}$$

In Table II we compare the phase shifts obtained using ψ_3 with those obtained from the "three-state" (1*s*-2*s*-2*p*) close-coupling wave function $\psi_{3\,\mathrm{cc}}$ and also with those obtained from the function $\psi_{3\,\mathrm{ps}}$ which differs from $\psi_{3\,\mathrm{cc}}$ in that the hydrogenic 2*p* eigenstate has been replaced by the function

$$\varphi_{2p'}(r) = (32/129)^{1/2}r^2(1+\tfrac{1}{2}r)e^{-r}\,, \tag{63}$$

derived by Damburg and Karule to account fully for the ground-state polarizability of the hydrogen atom.[11] The wave function $\psi_{3\,\mathrm{ps}}$ is that used by Burke, Gallaher, and Geltman in their "pseudostate" calculations.[10] Note that the pseudostate $\varphi_{2p'}$ is quite compact spatially; its exponential dependence being characteristic of the hydrogen ground state rather than of the 2*p* eigenstate. Table II indicates that ψ_3, which employs variationally optimal orbitals φ_{2p} and φ_{2s}, yields more accurate phase shifts over most of the energy range examined. Only for $k=0.8$ does $\psi_{3\,\mathrm{ps}}$ yield a more accurate value than ψ_3, and this is understandable because ψ_3 depends upon φ_{2p} through the single term (59) where u_{2p} is proportional to φ_{2p} according to Eq. (61), while $\psi_{3\,\mathrm{ps}}$ depends upon functions of p symmetry according to

$$[\varphi_{2p'}(r_1)F_{2p'}(r_2) + F_{2p'}(r_1)\varphi_{2p'}(r_2)]\,,$$

so that $\psi_{3\,\mathrm{ps}}$ enjoys an advantage with respect to its description of radial correlation which becomes more important as k approaches the excitation threshold. The close-coupling function $\psi_{3\,\mathrm{cc}}$ also enjoys this advantage over ψ_3 and it also has the correct form for crossing threshold, yet even at $k=0.8$ the use of a single optimal term (59) in ψ_3 is sufficient to produce a more accurate phase shift. The deficiency of ψ_3 with respect to radial correlation can be overcome by the addition of an additional orbital of p symmetry. This has been done using the wave function ψ_4 where the third quantum level has been included and additional optimal orbitals φ_{3s}, φ_{3p}, and φ_{3d} have been employed. The results of these calculations are listed in Table II.

One of the drawbacks of the pseudostate approach is the difficulty in choosing proper pseudostates. In the work of Burke *et al.*,[10] calculations were reported where a compact pseudostate $\varphi_{3d'}$ of d symmetry was included in the pseudostate expansion but that the phase shifts obtained from the 1*s*-2*s*-2*p*′-3*d*′ expansion were virtually indistinguishable from the 1*s*-2*s*-2*p*′ results. This situation does not imply that functions of d symmetry are unimportant, but indicates the difficulty encountered in choosing suitable pseudostates. In this connection, for $k=0.5$, we performed a calculation where we began with the optimal function ψ_3 and added additional optimal orbitals φ_{3s}, φ_{3p}, and φ_{3d}. These were added one at a time in order to see what effect each of these orbitals would have

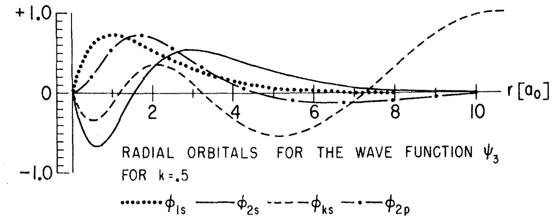


FIG. 5. Optimal orbitals from the wave function ψ_3.

on the phase shift η_3 given by ψ_3. In this context, it is to be remembered that the addition of a new orbital to a wave function of the present model entails a reoptimization of all previous orbitals, a characteristic feature of self-consistent-field calculations. For $k = 0.5$,

$$\psi_3 \rightarrow \eta_3 = 1.1724\,,$$

$$\psi_3 + \varphi_{3s} \rightarrow \eta_{3+3s} = 1.1748\,,$$

$$\psi_3 + \varphi_{3p} \rightarrow \eta_{3+3p} = 1.1794\,,$$

$$\psi_3 + \varphi_{3d} \rightarrow \eta_{3+3d} = 1.1788\,. \qquad (64)$$

We see from these results that although φ_{3s} contributes less than φ_{3p} or φ_{3d} in increasing the phase shift, each orbital contributes significantly and none can be ruled out on the grounds that its effect would be too small. It seems clear that choosing pseudostates is a process which requires extreme care and that it is much more effective to determine them via the variational principle.

The optimal orbitals φ_{2s}, φ_{ks}, and φ_{2p} used in ψ_3 are illustrated for $k = 0.5$ in Fig. 5. Figure 6 illustrates an interesting feature, namely, that the variationally determined orbitals φ_{2s} and φ_{2p} have damped oscillatory behavior for large argument. This effect is particularly striking in the case of the function $\varphi_{2p}(r)$, for which the oscillations damp out with an amplitude proportional to r^{-2}. The corresponding oscillations in the orbital $\varphi_{2s}(r)$ fall off like r^{-4}. The source of this behavior is to be found

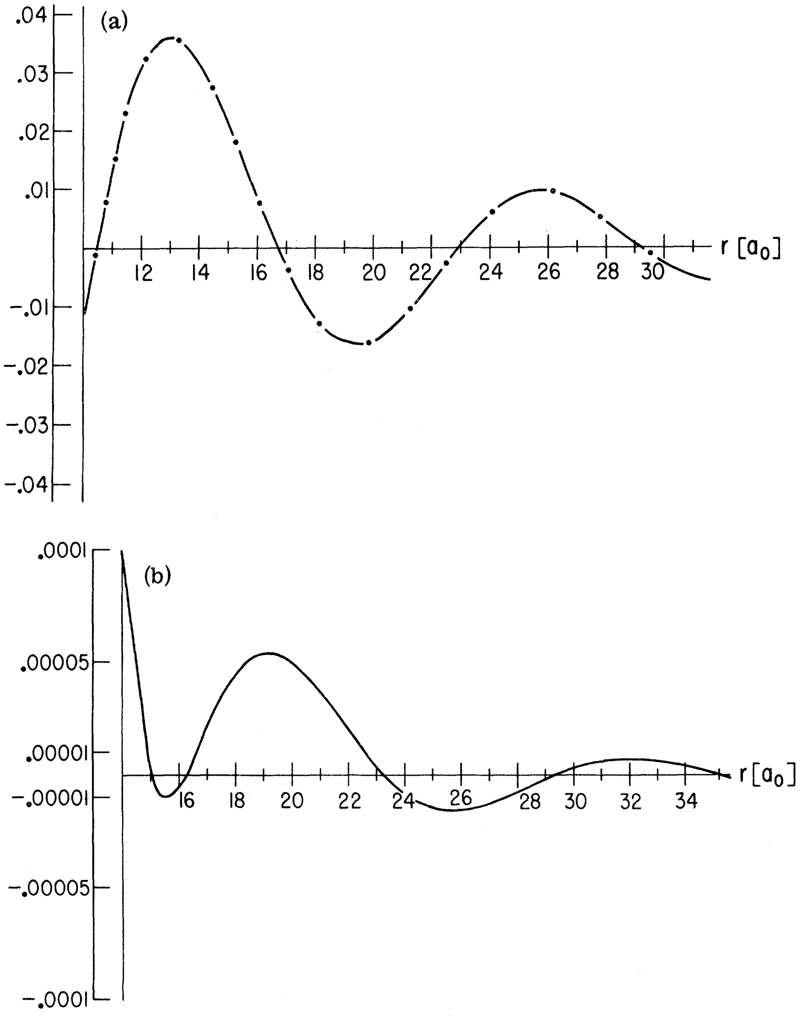


FIG. 6. (a) Oscillatory behavior of $\varphi_{2p}(r)$ in the region $10 \leq r \leq 32$ a.u. (from the wave function ψ_3 for $k = 0.5$). Oscillations damp out as r^{-2}. (b) Oscillatory behavior of $\varphi_{2s}(r)$ in the region $14 \leq r \leq 35$ a.u. (from the wave function ψ_3 for $k = 0.5$). Oscillations damp out as r^{-4}.

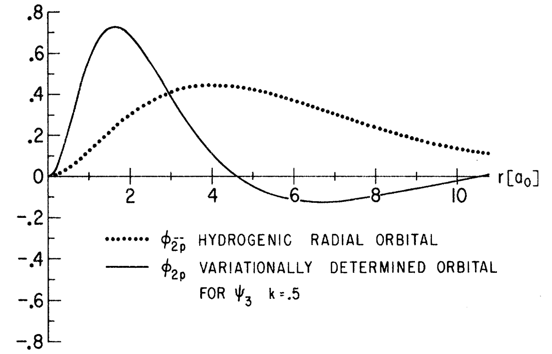


FIG. 7. Comparison of φ_{2p} with the hydrogenic eigenstate $\varphi_{\overline{2p}}$. The optimal orbital φ_{2p} is taken from the wave function ψ_3 for $k=0.5$.

TABLE IV. Comparison of present model phase shifts with rigorous limits for $k=0.4$.

Wave function	Orbitals	$\eta(^1S)$	Limit[a]
ψ_2	$1s\ 2s\ ks$	1.266	1.270 s
ψ_3	$1s\ 2s\ ks\ 2p$	1.390	1.403 sp
ψ_4	$1s\ 2s\ 3s\cdot ks\ 2p\ 3p\ 3d$	1.405	1.411 spd
ψ_5	$1s\ 2s\ 3s\ ks\ 2p\ 3p\ 4p\ 3d$	1.409	1.411 spd
ψ_6	$1s\ 2s\ 3s\ 4s\ ks\ 2p\ 3p\ 4p\ 3d\ 4d\ 4f$	1.411	1.413 $spdf$

[a] Reference 20.

in the coupling terms present in the differential system (60).

The term

$$X(\varphi_{2p},\ \varphi_{1s})u_{1s}\ , \tag{65}$$

is responsible for the oscillatory behavior of u_{2p} and hence φ_{2p}. For large r,

$$X(\varphi_{2p},\ \varphi_{1s}) \approx C^1_{2,1}\langle\varphi_{2p}|r|\varphi_{1s}\rangle r^{-2}\ , \tag{66}$$

and according to Eq. (45) we see that (65) is a driving term proportional to

$$r^{-2}\sin(kr+\eta)\ ,$$

and accounts for this dependence in the tail behavior of φ_{2p}.

Since $X(\varphi_{2s},\ \varphi_{1s})$ decays exponentially for large r according to Eq. (29) and the orthogonality between φ_{2s} and φ_{1s}, the direct coupling term involving the continuum function u_{1s} does not function as a driving term which can affect the tail behavior of φ_{2s}. Since u_{ks} falls off as e^{-r}, the oscillatory behavior of u_{2s} and hence of φ_{2s} can only come from the coupling to u_{2p} through the term

$$X(\varphi_{2s},\ \varphi_{2p})u_{2p}\ . \tag{67}$$

As we have seen, for large r, and some constant α,

$$u_{2p}(r) \approx \alpha r^{-2}\sin(kr+\eta)\ , \tag{68}$$

while

$$X(\varphi_{2s},\ \varphi_{2p}) \approx C^1_{1,2}\langle\varphi_{2s}|r|\varphi_{2p}\rangle r^{-2}\ , \tag{69}$$

so that (67) is a source term which for large r is proportional to

$$r^{-4}\sin(kr+\eta)\ ,$$

and accounts for this dependence in the tail behavior of φ_{2s}. These asymptotic damped oscillations represent polarization effects and it is interesting to note that such effects make themselves known directly upon the form of the optimal orbitals and that this comes about automatically in the present method.

Figure 7 illustrates the difference between the function φ_{2p} and the hydrogenic eigenfunction $\varphi_{\overline{2p}}$, where

$$\varphi_{\overline{2p}}(r) = (2\sqrt{6})^{-1}r^2e^{-1/2r}\ . \tag{70}$$

Note that the variationally determined orbital φ_{2p} has its peak much closer to the target atom than does the hydrogenic function $\varphi_{\overline{2p}}$. This illustration is for $k=0.5$.

Considerable continuum contribution is present in $\varphi_{2p}(r)$ as is indicated by its orbital energy

$$\omega_{2p} = +0.182\ ,\quad k=0.5\ ,$$

which is to be compared with the values

$$\epsilon_{2p} = -0.125\ ,\quad \omega_{2p'} = -0.081$$

characteristic of the hydrogenic eigenstate $\varphi_{\overline{2p}}$ and the Damburg and Karule pseudostate $\varphi_{2p'}$, respectively.

Some idea of the efficiency of the present model wave functions can be obtained by comparing the phase shifts obtained using ψ_3 with those obtained recently by Chung and Chen.[19] These workers used a wave function of the form

$$\psi(\vec{r}_1,\ \vec{r}_2) = (r_1r_2)^{-1}\{\varphi_{1s}(r_1)G_{1s}(r_2) + G_{1s}(r_1)\varphi_{1s}(r_2)$$

TABLE V. Expansion coefficients for ψ_4, $k=0.5$.

v	m	n	Γ_{vmn}
1	1	1	1.217
1	1	2	−0.859
1	1	3	0.746
1	1	4	1.000
1	2	2	−0.134
1	2	3	−0.029
1	2	4	0
1	3	3	−0.032
1	3	4	0
2	1	1	−0.085
2	1	2	−0.075
2	2	2	0.178
3	1	1	−0.031

TABLE VI. Orbital energies for the orbitals of the wave function ψ_4, $k = 0.5$.

Label	v	m	ω_{vm}
$1s$	1	1	-0.5000
$2s$	1	2	-0.0654
$3s$	1	3	$+1.0887$
$2p$	2	1	-0.1120
$3p$	2	2	$+0.2088$
$3d$	3	1	$+1.2299$

$$+ Q\sum_{n}\sum_{\mu\nu} A^{n}_{\mu\nu}(r_1^{\nu} r_2^{\mu} e^{-(\alpha r_1+\beta r_2)} + r_1^{\mu} r_2^{\nu} e^{-(\beta r_1+\alpha r_2)})P_n(\cos\Theta_{12})\}. \quad (71)$$

In the summation, six terms of s type and nine terms of p type were included. The open-channel function used was

$$G_{1s}(r) = (\sin kr + \tan\eta \cos kr)(1 - e^{-\sigma r}) + \sum_{m} d_m r^m e^{-\sigma r}, \quad (72)$$

and Q is the projection operator,

$$Q = [1 - |\varphi_{1s}(r_1)\rangle\langle\varphi_{1s}(r_1)|][1 - |\varphi_{1s}(r_2)\rangle\langle\varphi_{1s}(r_2)|]. \quad (73)$$

The coefficients $A^{n}_{\mu\nu}$ and d_n as well as the open-channel parameter σ were calculated for each energy value considered in the range $0.1 \leqslant k \leqslant 0.8$. The other nonlinear parameters α and β were determined and used over the entire energy range. The phase shifts obtained with this wave function are compared with those obtained with ψ_3 in Table II. These results show that the present model wave functions are quite efficient with respect to the number of terms needed to produce phase shifts of comparable accuracy.

Further calculations were carried out with the more elaborate wave functions ψ_4, ψ_5, and ψ_6. The results of these calculations are presented in Table II where it is seen that accurate phase shifts are obtainable with short expansions within the present model; the most elaborate wave function used in these calculations, namely, ψ_6, is constructed from only 11 optimal orbitals.

Another indication of the efficiency of the present model wave functions is obtained by comparing our results with the exhaustive variational bound calculations performed for $k = 0.4$ by Aronson, Hahn, Henry, Kleinman, and Spruch[20] where they obtained limiting values of $L = 0$ phase shifts obtainable when the angular symmetry of the one-particle functions used in the expansion of the total wave function is required to be less than a specified value. Thus, had we used only orbitals of s symmetry in the construction of ψ, then according to Aronson *et al.* the best phase shift obtainable would be $\eta_s = 1.270$, (for ^1S, $k = 0.4$). Using ψ_2 which uses only the optimal orbitals φ_{ks} and φ_{2s} we already obtain $\eta_2 = 1.266$. Table IV compares present model phase shifts with these rigorous limits.

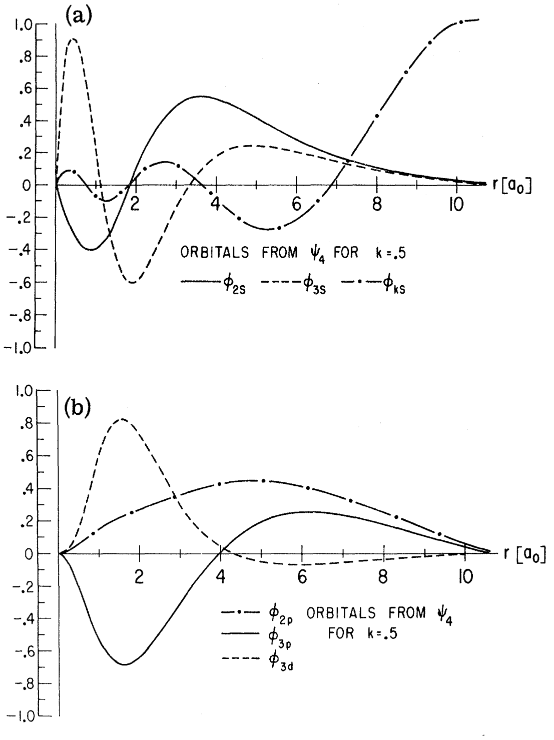


FIG. 8. (a) Optimal orbitals of a symmetry from the wave function ψ_4 for $k = 0.5$. (b) Optimal orbitals of p and d symmetry from the wave function ψ_4 for $k = 0.5$.

In Fig. 8 the optimal orbitals from ψ_4 are illustrated for $k = 0.5$. Table V gives the expansion coefficients Γ_{vmn} for this wave function. Finally, Table VI presents the corresponding orbital energies.

ACKNOWLEDGMENTS

Appreciation is expressed to Professor C. C. J. Roothaan for sponsoring this research and for many helpful discussions. Thanks are also due to Deborah Rosenblatt for encouragement during the particularly vexing period when the computer program used in these calculations was being debugged.

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*Research supported in part by the Advanced Research Projects Agency through the U. S. Army Research Office (Durham), under Contract Nos. DA-31-124-ARO-D-447 and ARPA-S-D-89 and by the National Science Foundation under Grant Nos. NSF-GP-27138 and NSF-GP-15216.

†Submitted in partial fulfillment of the requirements for the Ph.D., Department of Physics, University of

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PHYSICAL REVIEW A VOLUME 7, NUMBER 6 JUNE 1973

Cross Sections for *K*-Shell Ionization by 2-MeV-Electron Impact

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(Received 16 February 1973)

A systematic study of the cross sections for *K*-shell ionization by 2.0-MeV-electron impact has been made as a function of atomic number. The cross sections for 32 elements from V ($Z = 23$) to Bi ($Z = 83$) were first measured relative to each other, and then were normalized to 43 b at Sn ($Z = 50$). Thus systematic errors usually associated with absolute measurements were minimized and did not obscure minor variations in the Z dependence of the cross sections. The measured values drop from 353 b at V to 9.9 b at Bi. The general trend of the Z dependence of the data is in agreement with theoretical predictions of Kolbenstvedt. However, variations in cross sections by as much as 30% from one element to the next are not accounted for by the theory.

I. INTRODUCTION

The subject of inner-shell ionization by relativistic electrons has not been studied in any great detail either theoretically or experimentally. This is evidenced by both the lack of rigorous relativistic calculations for *K*-shell ionization and the sparsity of cross-section measurements. Specifically, *K*-shell ionization cross sections have been measured for only seven elements in the MeV energy range, and most of these measurements were at or below 2 MeV.[1–4] A series of experiments has also been performed in the extreme relativistic range of electron energies from 150 to 900 MeV, in which *K*-shell ionization cross sections were measured for eight elements ranging from Cu to Bi.[5] Within the experimental error limits of these measurements, the dependence of the *K*-shell ionization cross section on the electron energy has been found to be a smooth function. This feature is in agreement with the predictions of all existing theoretical approaches.[6–8]

Theoretical treatments of *K*-shell ionization by electrons are in the majority of cases completely nonrelativistic[9] and hence not applicable to the present experiment. In the work of Arthurs and