and

$$\xi_0 - \xi_{\pm 1} = (0.219 \pm 0.001) \times 10^{-5} \text{ a.u.}, \qquad (14)$$

obtained by neglecting the effects of the nuclear motion.

The comparison indicates that these effects are of the order of 2 parts in 10^2 and 4 parts in 10^2, respectively, and thus must be considered in accurate work.

The differences remaining between the theoretical values (11) and (12) and experimental values (1) and (2), particularly in the case of $\langle \xi \rangle_{0,1}$, may be attributed, in part, to the neglect of the effects of small interactions between the electronic and nuclear motions.[13] These effects would tend to cancel out for $\langle \xi_0 \rangle_{0,1} - \langle \xi_{\pm 1} \rangle_{0,1}$ [see Eq. (4)].

[13] J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936); see also J. P. Auffray and J. W. Cooley, Phys. Rev. **124**, 137 (1961).

Elastic Scattering of Low-Energy Electrons by Atomic Hydrogen*

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The differential and total cross sections for elastic scattering of electrons by atomic hydrogen are calculated below the threshold for excitation of the second target quantum level (10.2 ev). A close-coupling approximation is used in which the total wave function is expanded in hydrogen eigenstates, and only terms corresponding to the $1s$, $2s$, and $2p$ states are retained; the wave function is symmetrized or antisymmetrized explicitly.

The coupled set of integro-differential equations resulting from the approximate wave function is integrated numerically on an IBM 709 computer, subject to standard boundary conditions, to yield the phase shift in each total spin and total angular-momentum state. The solution involves an iteration procedure to treat the integral terms, and a specialized integration scheme, including an asymptotic expansion of the solution, to overcome certain numerical difficulties associated with low-incident electron energy.

The results of this calculation agree reasonably well, in regions where comparison is possible, both with previous analyses and with experiment—although in states in which short-range correlation effects are important, the close-coupling expansion is seen to converge very slowly. It is suggested that this situation may be rectified either by including continuum hydrogen eigenstates in the wave function, or by replacing the close-coupling approximation by some different method, such as the alternative expansion suggested in the present work.

The most striking feature of our results is the appearance in many of the spin and angular-momentum states of pronounced, extremely narrow Breit-Wigner resonances at energies slightly below the second quantum excitation threshold. The resonance lying lowest in energy has been analyzed in most detail; it occurs in the singlet S state. It is found to have a full width at half maximum of 0.109 ev, and to be centered at 9.61 ev.

The long-range polarization effect is found to be dominant only at and very near zero energy for S and P states; for D states it is important up to 6 or 7 ev, and for F states it is of central importance for almost the entire range of energy below threshold.

The results of the calculation differ most from previous calculations at small scattering angles in the differential cross section, and in the existence of resonances near threshold. It is suggested that the former discrepancies can be resolved by differential cross-section measurements at angles of 30 deg and less, whereas the latter phenomenon requires electron-energy resolutions less than, or of the order of, 0.1 ev for experimental verification.

I. INTRODUCTION

IN this paper we describe our investigation of elastic electron-hydrogen collisions. This work was undertaken to bring to bear upon this problem calculational opportunities placed at the disposal of theorists by modern computing facilities, in the hope that certain discrepancies between theory and experiment may be resolved by the more nearly exact solutions now possible. These discrepancies are most serious for certain reaction processes[1] but here we examine the less complicated case of elastic scattering, which we intend to be the first of several investigations of problems of increasing complexity. Further, improvements in experimental techniques now make possible more complete and accurate data.[2] Our calculation is intended to make use of the data already available, as well as to point out where, and what kind of, new data would be useful.

In what follows we shall regard the proton as infinitely massive and therefore stationary during the interaction. Under such circumstances, the wave function for the electron-hydrogen system will depend only upon the coordinates of the bound and free electrons.

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[1] See, for example, A. E. Kingston, B. L. Moiseiwitsch, and B. G. Skinner, Proc. Roy. Soc. (London) **A258**, 245 (1960), and D. G. Hummer and M. J. Seaton, Phys. Rev. Letters **6**, 471 (1961).

[2] High-resolution electron-hydrogen scattering experiments have been proposed by Stephen Smith at the National Bureau of Standards, Washington, D. C.

The starting point in our analysis is an expansion of this wave function in eigenstates of the hydrogen atom. Having said this, we must immediately admit the complete impossibility of dealing with such an expansion containing, as it does, infinitely many terms. Our major approximation is to exclude from the expansion all continuum states of the hydrogen atom and all but a finite number of low-lying discrete states. This is frequently called the strong-coupling or close-coupling approximation.[3] The resulting expression for the wave function is explicitly symmetrized or antisymmetrized in accordance with the requirements of the exclusion principle, and we note (after the fact) that the additional terms included to satisfy these requirements simulate, to some extent, the effects of the omitted continuum states.

This approximate wave function leads, ultimately, to a set of coupled radial linear integro-differential equations, the number of which depends upon, among other things, the number of terms retained in the original expansion. These radial equations are solved numerically on an IBM 709 by means of techniques described below.

Analyses of the kind described above have been made by many authors over a period of many years.[4] For the history and development of the earlier work in this field, which generally involves the solution of a single equation, the reader is referred to the reviews given by Massey.[5] More recent work[6] has begun to utilize modern computing machines, and has, in some cases, dealt with sets of two coupled equations resulting from the retention of the $1s$ and $2s$ hydrogen states in the wave function. Our investigation follows in this tradition with, however, the scope of the work widened to the extent that the approximations involved can be refined and analyzed numerically. For example, the convergence of the total wave function in terms of hydrogen states can be examined by the straightforward procedure of noting the effect of including different numbers and different combinations of states. Analysis can also be made of the convergence in total angular-momentum states.

It is also worthwhile to emphasize the general nature of our procedure; it is applicable to a wide range of

energies both above and below the thresholds for excitation of the various hydrogen-atom quantum levels. Hence, we may chart the large scale behavior of the cross section as a function of incident electron energy and, in addition, learn something of its detailed structure at and near excitation energies. Finally, with little change, the method can be made to treat the collision of electrons with heavier atoms[7]—specifically, those in the alkali group, which are more amenable than hydrogen to experimental measurement.

A detailed analysis of our results leads to the conclusion that in certain regions of incident electron energy, notably near thresholds, and in states of particular symmetry, the expansion in eigenstates described above converges very slowly. We are thus led to propose, as a possible basis for future investigation, an alternative expansion which may provide a more satisfactory approach to the threshold problem.

In Sec. II we give the theory of the close-coupling approximation with explicit formulas expressing the cross sections in terms of the solutions of the coupled integro-differential equations. In Sec. III we give details of our method for solving the coupled integro-differential equations on an IBM 709. In Sec. IV we state our results and draw pertinent conclusions. In Sec. V we give a short comparison with the latest experimental results. In Sec. VI we discuss in some detail the alternative expansion mentioned above. Finally, in Sec. VII we make some general statements on the basis of our results.

II. THEORY OF THE CLOSE-COUPLING APPROXIMATION

The basic assumption of the close-coupling method is that the total wave function can be expanded in the antisymmetrized form

$$\Psi(\mathbf{r}_1\sigma_1\mathbf{r}_2\sigma_2)=\frac{1}{\sqrt{2}}\sum_{\Gamma}\left\{\psi_\Gamma(\mathbf{r}_1\sigma_1,\hat{r}_2\sigma_2)\frac{F_\Gamma(r_2)}{r_2}\right.$$
$$\left.-\psi_\Gamma(\mathbf{r}_2\sigma_2,\hat{r}_1\sigma_1)\frac{F_\Gamma(r_1)}{r_1}\right\}. \quad (1)$$

Here, in the notation of Percival and Seaton,[8] the representation is labeled $\Gamma=(nk_nl_1l_2LM_LSM_S)$ and is diagonal in the total orbital angular momentum L and the total spin S of the system; n and l_1 are the principal and angular-momentum quantum numbers, respectively, of the atomic electron; and l_2 and k_n are the orbital angular momentum and the wave number, respectively, of the scattered electron. The sum over Γ in Eq. (1) must in principle include the continuum states of the hydrogen atom. However, due to the additional difficulties that arise in the solution of the re-

[3] N. F. Mott, and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, New York, 1949), 2nd ed., p. 146.

[4] J. MacDougall, Proc. Roy. Soc. (London) **A136**, 549 (1932); P. M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933); S. Chandrasekhar and F. H. Breen, Astrophys. J. **103**, 41 (1946); and M. J. Seaton, Proc. Roy. Soc. (London) **A241**, 522 (1957).

[5] H. S. W. Massey, *Handbuch der Physik*, edited by E. Flügge (Springer-Verlag, Berlin, 1956), Vol. 36, p. 354. See also H. S. W. Massey, Revs. Modern Phys. **28**, 199 (1956).

[6] R. Marriott, Proc. Phys. Soc. (London) **72**, 121 (1958); T. L. John, Proc. Phys. Soc., (London) **76**, 532 (1960); K. Smith, W. F. Miller, and A. J. P. Mumford, Proc. Phys. Soc. (London) **76**, 559 (1960); K. Smith, Phys. Rev. **120**, 845 (1960); R. P. McEachran and P. A. Fraser, Can. J. Phys. **38**, 317 (1960); A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961); K. Smith and P. G. Burke, Phys. Rev. **123**, 174 (1961), and K. Smith, R. P. McEachran, and P. A. Fraser, Phys. Rev. **125**, 553 (1962).

[7] A. Salmona and M. J. Seaton, Proc. Phys. Soc. (London) **77**, 617 (1961).

[8] I. C. Percival and M. J. Seaton, Proc. Cambridge Phil. Soc. **53**, 654 (1957).

sulting equations for the functions $F_L(r)$,[9] the standard close-coupling approximation attempts to represent Ψ by including in the summation a few terms corresponding to discrete hydrogen states. In this paper we also adopt this approximation as our starting point and we shall, as far as possible from our results, point out where this is most likely to be in error, and, also, possible ways of improving the approximation.

In order to obtain a means of calculating the functions $F_\Gamma(r)$ in Eq. (1), we observe that the exact Ψ satisfies the Kohn-Hulthén[10] variational principle,

$$\delta\left\{\int \Psi^{LS*}(\nu)(H-E)\Psi^{LS}(\nu')d\tau_1 d\tau_2 - \tfrac{1}{2}A_{LS}{}^2 R_{\nu\nu'}{}^{LS}\right\}=0. \quad (2)$$

The $F_\Gamma(\nu)$ corresponding to $\Psi^{LS}(\nu)$ satisfy the boundary conditions [where we write Γ explicitly as $LS\nu'$; the meaning of ν is described following Eq. (4)]

$$F_{\nu'}{}^{LS}(\nu;r) \underset{r\to\infty}{=} \frac{A_{LS}}{k_{n'}{}^{\frac{1}{2}}}[\delta_{\nu\nu'}\sin(k_{n'}r-\tfrac{1}{2}l_2'\pi) \\ + R_{\nu\nu'}{}^{LS}\cos(k_{n'}r-\tfrac{1}{2}l_2'\pi)], \quad (3a)$$

for all channels ν' that are open, i.e., in which the wave function propagates. For all channels ν' that are closed,

$$F_{\nu'}{}^{LS}(\nu;r) \underset{r\to\infty}{=} 0. \quad (3b)$$

For all channels ν' both closed and open,

$$F_{\nu'}{}^{LS}(\nu;0)=0. \quad (3c)$$

In Eq. (2), the total Hamiltonian (H) of the system is given by[11]

$$H=-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2-\frac{1}{r_1}-\frac{1}{r_2}+\frac{2}{r_{12}}, \quad (4)$$

where $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$ is the interelectron distance. Also, E is the total energy, and $\Psi^{LS}(\nu)$ is that part of the wave function Ψ given by Eq. (1) that corresponds to the total orbital angular momentum L and the total spin S. The argument ν in $\Psi^{LS}(\nu)$ and also in $F_{\nu'}{}^{LS}(\nu;r)$ refers to the quantum numbers nl_1l_2, and denotes the one channel in Ψ^{LS} in which there is a component $\sin(k_n r-\tfrac{1}{2}l_2\pi)$, in addition to the $\cos(k_n r-\tfrac{1}{2}l_2\pi)$ term present in all open channels. The $R_{\nu\nu'}{}^{LS}$, elements of the

so-called R matrix, give the asymptotic amplitude of the cosine term in the open channels ν'. In Eq. (2) A_{LS} is a normalization constant, and, finally δ signifies arbitrary infinitesimal variations of the functions $F_{\nu'}{}^{LS}(\nu;r)$ contained in $\Psi^{LS}(\nu)$ about their correct values which, however, still satisfy the boundary conditions of Eq. (3).

If we carry out the manipulations implied by (2) and use the boundary conditions (3), we find that the functions $F_\nu{}^{LS}(r)$ must satisfy, for all ν,

$$\left[\frac{d^2}{dr^2}-\frac{l_2(l_2+1)}{r^2}+k_n{}^2\right]F_\nu{}^{LS}(r) \\ =2\sum_{\nu'}[V_{\nu\nu'}-W_{\nu\nu'}{}^{LS}]F_{\nu'}{}^{LS}(r). \quad (5)$$

The full complexity of this set of equations, first derived by Percival and Seaton,[8] is perhaps not evident in the form shown; in Appendix A, Eq. (ii) we give explicitly the potentials $V_{\nu\nu'}{}^L$ and $W_{\nu\nu'}{}^{LS}$, and it is seen that the latter are integral operators. Thus (5) is, in fact, a set of coupled integro-differential equations [see Eq. (6), below]. We note that the argument ν appearing explicitly in the F's as given in (3) has been omitted in (5); if there are n_a open channels there will be a n_a linearly independent solutions of (5). Appropriate linear combinations of these will yield n_a solutions that satisfy the boundary conditions (3), and in which ν ranges over all n_a open channels.

The scattering matrix S, as defined by Blatt and Biedenharn,[12] is given in terms of the R matrix by

$$S=(1+iR)/(1-iR).$$

The cross section can be written in the usual manner in terms of the S-matrix elements. We shall be concerned in this paper with the case in which only one channel is open. The R matrix then reduces to a single element, $\tan\delta^{LS}$, where δ^{LS} is the phase shift. The differential cross section in either spin state for elastic scattering is then

$$\sigma_S(\theta)=\left|\frac{1}{2ik}\sum_L(2L+1)[\exp(2i\delta^{LS})-1]P_L(\cos\theta)\right|^2,$$

and the total cross section is

$$\sigma_S{}^{tot}=\frac{4\pi}{k^2}\sum_L(2L+1)\sin^2\delta^{LS}.$$

Our procedure is then to decide which states we wish to include in expansion (1), this decision being dictated both by numerical expediency and by physical intuition and experience. The appropriate coupled Eqs. (5) are then set up and solved in the manner described in Sec. III.

[9] Among the difficulties involved when continuum functions are retained in the expansion are: first, the Coulomb wave functions which represent the continuum hydrogen states are difficult to obtain with sufficient accuracy; second, the arbitrary functions multiplying these continuum functions have, asymptotically, very rapidly increasing exponential parts, which make numerical accuracy difficult to obtain; and, third, the interpretation of the cross section is complicated by the fact that continuum functions contribute to the scattered flux.

[10] L. Hulthén, Kgl. Fysiograf. Sällskap. Lund, Förh. 14, 21 (1944). See also W. Kohn, Phys. Rev. 74, 1763 (1948).

[11] We adopt atomic units throughout this paper (see, for example, D. R. Hartree, The Calculation of Atomic Structures (John Wiley & Sons, Inc., New York, 1957), p. 5. In particular, the electron energy in electron volts is given by $E=13.6k^2$.

[12] J. M. Blatt and L. C. Biedenharn, Revs. Modern Phys. 24, 258 (1952).

III. METHOD OF SOLUTION OF THE INTEGRO-DIFFERENTIAL EQUATIONS

In this section we describe the method we adopt to solve the set of coupled integro-differential Eqs. (5). A preliminary discussion of some of these methods has been given elsewhere by Smith and Burke,[6] who deal with the simpler set of equations resulting from the retention of only the $1s$ and $2s$ states of hydrogen in the wave function. We shall describe here the extension to the general problem where an arbitrary number of states is included in expansion (1).

The set of equations given by (5) can be rewritten in the form

$$\frac{d^2F_i}{dr^2} = \sum_j V_{ij}(r)F_j(r) + \sum_j \int_0^\infty K_{ij}(rr')F_j(r')dr', \quad (6)$$

where $i, j = 1, 2, \cdots, n$. In (6) the $V_{ij}(r)$ represent the direct potentials, the energy, and the centrifugal barrier, whereas the $K_{ij}(rr')$ represent the exchange potentials. We suppose that the first n_a functions F_i $(1 \leqslant n_a \leqslant n)$ satisfy open-channel boundary conditions, and that the rest, n_b in number, satisfy closed-channel boundary conditions (see Eq. 3). We now define r_a such that the kernel $K_{ij}(rr') \approx 0$ for r or $r' \geqslant r_a$. For $r \geqslant r_a$, each of the $V_{ij}(r)$ can be written as a finite sum of inverse powers of r. We determine a solution of Eq. (6) by an iteration procedure to be described below for r in the range $0 \leqslant r \leqslant r_a$. For $r > r_a$, a general solution satisfying the asymptotic boundary conditions of Eq. (3) is completely specified by two arbitrary parameters for each open channel, and one arbitrary parameter for each closed channel; thus the solution in this region is determined by $n + n_a$ arbitrary parameters. In Appendix B we derive an asymptotic expansion that expresses the general solution in this region in terms of these parameters and the coefficients of the inverse powers of r that represent the V_{ij}. The accuracy of this asymptotic expansion depends upon energy as well as r, but in general improves as r increases. The procedure we use is to choose an $r_b \geqslant r_a$ that lies in a region in which this expansion is sufficiently accurate, and then integrate the equations inward numerically from r_b to r_a. At almost all energies considered, the asymptotic expansion gives sufficient accuracy using $r_b = r_a$. At certain energies, however, difficulties arise which are associated with threshold effects. Thus, at, and very near, zero energy it is necessary to introduce a modification of the asymptotic expansion (see Appendix B); at other thresholds the problem has not yet been treated in general, although the unappealing and time-consuming technique of taking r_b very large is usually available.

Since we require $F_i(0) = 0$ for all i, a solution of (6) is determined by n arbitrary parameters at the origin. If we were to proceed straight-forwardly—first taking an arbitrary set of n parameters as the starting values, and then carrying out a numerical integration of (6)

to $r = r_a$—we would immediately encounter a difficulty intimately related to the presence of the n_b closed channels. At large values of r one component of the solution in each closed channel is an increasing exponential that in simpler situations, would be eliminated by combining appropriately chosen linearly independent solutions. The value of r_a, however, is so large in the present case that the positive exponential grows to the extent that it overwhelms the other components of the solution; in particular, the decaying exponential component, the part that satisfies the boundary conditions at infinity, is lost. One might seek to circumvent this difficulty by integrating inward from $r = r_a$, choosing starting values in a way that eliminates the positive exponential at the outset. In general, this procedure is also doomed to failure since the integration will introduce some of the irregular solution at small r that, far from vanishing at the origin in accordance with the boundary conditions, is generally infinite there.

Thus, neither the conventional outward integration from the origin, nor the inward integration from the asymptotic region affords a means to solution. We adopt a compromise. We choose an intermediate value of r, hereafter referred to as r_0, where the offending terms in both the inward and outward integrations have not assumed significant proportions (this proves possible for all cases considered). We can then obtain n linearly independent solutions by outward integration from the origin to r_0, and also $n + n_a$ linearly independent solutions by inward integration from r_b to r_0. In general, these solutions will not be continuous at r_0, and must be matched there in the manner described below.

Our procedure is then as follows. First we set the kernel term in (6) equal to zero, and evaluate the n inner solutions $F_i^{(0)i}(r)$, $j = 1, 2, \cdots, n$—and the $n + n_a$ outer solutions $G_i^{(0)i}(r)$, $j = 1, 2, \cdots, n + n_a$—where in each case the superscript in parentheses corresponds to the iteration number, and i is the channel index which runs from 1 to n, as in Eq. (6). We combine these solutions to form one continuous solution, i.e., one whose function and derivative are continuous at r_0 for each $i = 1, 2, \cdots, n$. We now use this continuous solution, denoted by $F_i^{(0)}(r)$, to evaluate the second term on the right-hand side of (6) for $0 \leqslant r \leqslant r_a$. Inserting this as an inhomogeneous term in the differential equation, we solve the equation once more to give one inner solution $\mathcal{F}_i^{(1)}(r)$ in the range $0 \leqslant r \leqslant r_0$, and one outer solution $\mathcal{G}_i^{(1)}(r)$ in the range $r_0 \leqslant r \leqslant r_a$. We add linear combinations of $F_i^{(0)i}(r)$ and $G_i^{(0)i}(r)$ to these inner and outer solutions in order to form a solution continuous at r_0; this solution we denote by $F_i^{(1)}(r)$. The iteration process is continued until we obtain convergence, i.e., until two consecutive iterates $F_i^{(n)}(r)$ and $F_i^{(n+1)}(r)$ are equal to within some predetermined amount.[13]

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[13] A possibility of avoiding this iteration procedure involves solving additional simultaneous differential equations, each one representing an exchange term. This method has been adopted

In achieving a continuous solution at each stage of the iteration by adding a linear combination of the $2n+n_a$ zero-order solutions $F_i^{(0)i}(r)$ and $G_i^{(0)i}(r)$, we have introduced $2n+n_a$ parameters, the coefficients multiplying these functions, but only $2n$ equations relating them—because of the demand for continuity of n functions and n derivatives. We use the other n_a degrees of freedom to impose n_a integral conditions on the first n_a functions to speed convergence (see below).[14] We thus solve the following set of $2n+n_a$ simultaneous equations at each stage of the iteration:

$$\sum_{j=1}^{n} a_j \int_0^{r_0} F_i^{(0)i}(r)dr + \sum_{j=1}^{n+n_a} b_j \int_{r_0}^{r_c} G_i^{(0)i}(r)dr$$

$$= C_i - \int_0^{r_0} \mathfrak{F}_i^{(n)}(r)dr - \int_{r_0}^{r_c} \mathcal{G}_i^{(n)}(r)dr,$$

$$\sum_{j=1}^{n} a_j F_k^{(0)i}(r_0) - \sum_{j=1}^{n+n_a} b_j G_k^{(0)i}(r_0)$$

$$= -\mathfrak{F}_k^{(n)}(r_0) + \mathcal{G}_k^{(n)}(r_0), \quad (7)$$

$$\sum_{j=1}^{n} a_j \frac{dF_k^{(0)i}(r)}{dr}\bigg|_{r_0} - \sum_{j=1}^{n+n_a} b_j \frac{dG_k^{(0)i}(r)}{dr}\bigg|_{r_0}$$

$$= -\frac{d\mathfrak{F}_k^{(n)}(r)}{dr}\bigg|_{r_0} + \frac{d\mathcal{G}_k^{(n)}}{dr}\bigg|_{r_0}$$

where the index i runs from 1 to n_a, and the index k runs from 1 to n. The C_i are constants described in full below. The resulting continuous solution is given by

$$F_i^{(n)}(r) = \mathfrak{F}_i^{(n)}(r) + \sum_{j=1}^{n} a_j F_i^{(0)i}(r), \quad 0 \leqslant r \leqslant r_0$$

$$\hspace{4cm} (8)$$

$$= \mathcal{G}_i^{(n)}(r) + \sum_{j=1}^{n+n_a} b_j G_i^{(0)i}(r), \quad r_0 \leqslant r \leqslant r_a,$$

with $i = 1, 2, \cdots, n$.

Equation (7) determines the n coefficients a_j and the $n+n_a$ coefficients b_j, which are used in (8) to construct the continuous solution. The first n_a functions of $F_i^{(n)}(r)$ satisfy, through Eq. (7), the integral condition

$$\int_0^{r_c} F_i^{(n)}(r)dr = C_i,$$

where $i = 1, 2, \cdots, n_a$. In general, r_c, which is otherwise arbitrary and can be adjusted to speed convergence,

by K. Omidvar, New York University Research No. CS-37 (unpublished), and by R. Marriott (reference 6). We have found this method difficult to incorporate into our procedure in a general way, because of the large number of extra equations required when more than one or two hydrogen states are included in Eq. (1).

[14] An equivalent criterion, which held the maximum of the unknown function constant in value for each iteration, was applied to the solution of a single integro-differential equation by R. A. Buckingham, S. J. Hubbard, and H. S. W. Massey, Proc. Roy. Soc. (London) **A211**, 183 (1952).

must satisfy the condition $0 < r_c \leqslant r_a$. We have written (7) for the case $r_c \geqslant r_0$. The modification for $r_c < r_0$ is obtained by dropping the last (integral) term on each side of the first equation, and by replacing r_0, the upper limit of the other integrals, by r_c in the first term on both sides. The real coefficients C_i, which are independent of iteration number, can also be chosen arbitrarily. Each linearly independent vector C_i generates a linearly independent solution $F_i^{(n)}(r)$. We thus obtain the complete set of solutions of Eq. (6), satisfying the boundary conditions (3), by using all n_a linearly independent vectors C_i which span the appropriate n_a-dimensional vector space.

The solution of the set of equations (6) is obtained numerically by replacing them with an equivalent set of difference equations and adopting the Runge-Kutta integration method.[15] For simplicity we use an equispaced grid in the r and r' variables over the whole range of integration. The integral terms are evaluated by a straightforward application of the trapezoidal rule. Convergence is usually most rapid with $r_c \approx 2$ atomic units (au) and $r_0 \approx 5$ au.[11] With only the 1s hydrogen state retained in the expansion (1), $r_a \approx 12$ au is satisfactory; with either the 2s and/or the 2p states included in addition, $r_a \approx 30$ au suffices; and with states from the third quantum level included, a somewhat larger value, about 37 au, is required. In all cases considered, a basic interval of 0.1 au proved to be sufficiently small to give the phase shifts correct to four decimal places.

We conclude this section with a brief description of the operating characteristics of the IBM 709 program. The code requires specification of: the atomic hydrogen states to be included in the expansion of the wave function, the total orbital angular momentum of the system, the total spin, the parity, and the incident electron energy. Also needed is information about the degree of convergence required, the interval of integration, and the number of intervals from the origin to the matching point and to the asymptotic region. With this information the code sets up and solves the equations for all linearly independent solutions. A typical run on the IBM 709 to solve, for example, the 1s-2s-2p $L=0$ equations for one total spin state and one energy below excitation of the second quantum level, requires 10 to 15 min—with convergence to one part in 10^4 in the phase shift—and involves four to six iterations.

IV. RESULTS

We have evaluated the singlet and triplet phase shifts for energies from $k^2 = 0$ to $k^2 = 0.75$ for the total angular-momentum states $L=0$, 1, 2, and 3 by using only the 1s-2s-2p states in the close-coupling approximation. This gives three coupled integro-differential equations for $L=0$, and four each for $L=1$, 2, and 3.

[15] F. B. Hildebrand, *Introduction to Numerical Analysis* (McGraw-Hill Book Company, Inc., New York, 1956), p. 233.

TABLE I. Phase shifts, in radians, calculated in the $1s\text{-}2s\text{-}2p$ close coupling approximation for singlet (δ^+) and triplet (δ^-) $L=0$, 1, 2, and 3 states. Entries for $k^2=0$ are the corresponding scattering lengths, in a.u. (atomic units). Phase shifts are accurate to within one or two in the last figure quoted.

k^2	$\delta_0{}^+$	$\delta_0{}^-$	$\delta_1{}^+$	$\delta_1{}^-$	$\delta_2{}^+$	$\delta_2{}^-$	$\delta_3{}^+$	$\delta_3{}^-$
0	6.7418	1.8931	...	...	...		...	...
0.01	2.4912	2.9355	0.0041	0.0079	0.0009	0.0009	...	...
0.02	2.2581	2.8451	...	...	...	...	...	...
0.03	2.0977	2.7748	...	...	...	...	...	...
0.04	1.9742	2.7153	...	...	...	...	...	...
0.05	1.8737	2.6630	0.0083	0.0477	0.0042	0.0047	...	...
0.10	1.5400	2.4616	0.0028	0.1013	0.0084	0.0096	0.0028	0.0028
0.15	1.3553	...						...
0.20	1.1987	2.1952	−0.0132	0.1970	0.0167	0.0194	...	...
0.25	1.0920	2.0956	...	...	...		...	...
0.30	1.0084	2.0108	−0.0374	0.2696	0.0249	0.0283	...	...
0.40	0.8876	1.8702	−0.0511	0.3208	0.0332	0.0366	0.0106	0.0104
0.50	0.8101	1.7568	−0.0585	0.3565	0.0424	0.0444	...	...
0.60	0.7707	1.6633	−0.0591	0.3824	0.0544	0.0520	...	...
0.65	0.7755	1.6222	...	...	...	...	...	...
0.67	0.7954	...	...	...	...	...	...	...
0.68	0.8202	...	...	...	...	...	...	...
0.69	0.8817	...	...	...	...	...	...	...
0.70	1.2396	1.5846	−0.0496	0.4159	0.0770	0.0594	0.0194	0.0199
0.71	3.001	1.575	...	...	...	...	...	...
0.72	...	...	...	...	...	...	...	...
0.73	3.8192	...	...	...	...	...	...	...
0.735	3.8377	...	...	...	...	...	...	...
0.74	3.8560	...	0.904	3.5380	0.1329	0.0624	0.0209	0.0219
0.745	3.8751	...	...	...	...	...	...	...

We present our results in Table I. The blanks in this table represent, in some cases, phase shifts that can be obtained with sufficient accuracy by interpolation. Other blanks represent phase shifts for which we have as yet been unable to obtain converged solutions, a situation occurring only at energies in the neighborhood of certain resonances which appear near the threshold for excitation of the second quantum level in hydrogen ($k^2=0.75$). These resonances, which appear in most of the angular momentum and spin states, are described in detail below.

Singlet S Phase Shift

The fact that the spatial part of the wave function is symmetric, and the absence of a centrifugal barrier are two characteristics of the singlet S state which imply that, on the average, the electrons are in closer proximity than in any other state. For this reason the interelectron interaction (e^2/r_{12}) plays its largest role here. But it is precisely this interaction which prevents the one-body approximation (that is, the approximation in which only the S state is retained in the expansion) from providing an exact solution to the scattering problem. For this reason, we expect that in the singlet S state the one-body approximation gains the most from the partial inclusion of correlation effects represented in the total wave function by the $2s$ and $2p$ states. Fortunately, in this state we have some rather accurate calculations of the phase shift by Schwartz,[16]

and also by Temkin,[17] for comparison. In Fig. 1 we show a plot of our $1s\text{-}2s\text{-}2p$ phase shift and the results of Schwartz and of Temkin, as well as those of John[6] ($1s$), and of Smith, McEachran, and Fraser[6] ($1s-2s$). Figure 1 shows, in addition, the phase shift given by Temkin from his solution of the spherically symmetric part of the singlet S equation. We expect both Schwartz's and Temkin's results to be accurate, because the former are derived on the basis of a variational treatment in which the trial function provides for a very thorough representation of the interelectron interaction, and the latter are obtained by a direct integration of the three-dimensional wave equation.

If, in Fig. 1, we concentrate our attention upon energies less than $k^2\approx0.65$ and assume the Schwartz-Temkin results to be substantially correct, we see that our $1s\text{-}2s\text{-}2p$ curve has moved somewhat less than halfway from the one-body ($1s$) approximation towards the "correct" Schwartz-Temkin result; whereas the $1s\text{-}2s$ curve goes only half as far as the $1s\text{-}2s\text{-}2p$ result. Although this discrepancy is not large, we would like to understand whether it is due to the short-range correlation effects discussed above or to the long-range polarization terms in the potential arising from the multipole distortions of the target atom due to the field of the projectile electron. This latter effect is taken into account by methods such as the Bransden et al.[18] varia-

[16] C. Schwartz, in *International Conference on the Physics of Electronic and Atomic Collisions, 2nd, University of Colorado, Boulder, June, 1961* (W. A. Benjamin, Inc., New York, 1961), Paper I1, and also C. Schwartz, Phys. Rev. **124**, 1468 (1961).

[17] A. Temkin, in *International Conference on the Physics of Electronic and Atomic Collisions, 2nd, University of Colorado, Boulder, June, 1961* (W. A. Benjamin, Inc., New York, 1961), Paper I5, and also A. Temkin, Phys. Rev. Letters **8**, No. 3, A9 (1962).

[18] B. H. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, Proc. Phys. Soc. (London) **71**, 877 (1958).

tional approach, and the polarized orbital method of Temkin[19]; this effect is by no means limited to the singlet S state.

In order to throw more light on this problem we solved the singlet $L=0$ equations for a variety of closely coupled states, up to a maximum of five. We present these results in Table II. The most striking impression is that once all states corresponding to the second quantum level have been included, states of higher principal quantum number have almost negligible effect. It thus appears that convergence in closely coupled states becomes very slow. This slow convergence can probably be attributed to the short-range correlation effect, rather than to the long-range polarization. Our reasoning is as follows. The $2p$ state in the expansion of the wave function gives rise to about 66% of the α/r^4 polarization term.[20] On the other hand, we see that adding only the $2p$ state to the $1s$ state provides about 17.5% of the difference between the single-body approximation and the "correct" (Schwartz-Temkin) result. We expect, by direct comparison with the effect of the $2s$ state (which, of course, contributes nothing whatever to the polarization), that some fraction of the 17.5% must come from the short-range correlation. We are left with the conclusion that the polarization correction at these energies is very small. This conclusion
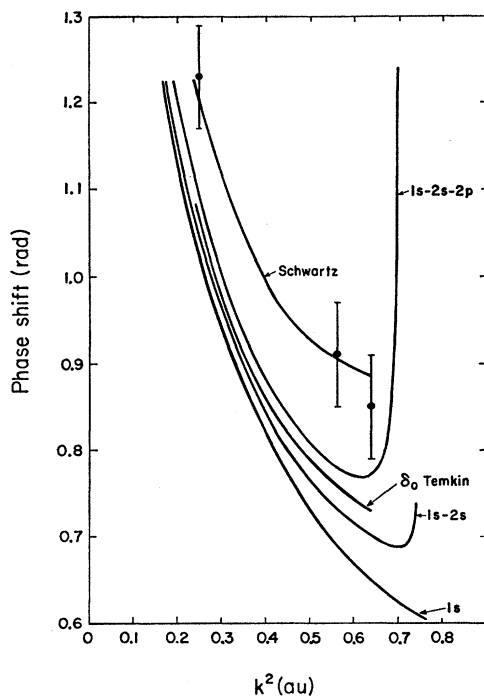

FIG. 1. The singlet S phase shift as a function of k^2, as given by various calculations. The points with their associated errors refer to the calculation of Temkin.[17]

[19] A. Temkin, Phys. Rev. 116, 358 (1959).
[20] L. Castillejo, I. C. Percival, and M. J. Seaton, Proc. Roy. Soc (London) A254, 259 (1960).

TABLE II. Singlet S phase shifts, in radians, at two values of k^2 for a number of combinations of closely coupled states. The corresponding results obtained by Schwartz[a] are also given. Phase shifts are accurate to within one or two in the last figure quoted.

States included	$k^2=0.55$	$k^2=0.60$
$1s$	0.7004	0.6704
$1s$-$2s$	0.7352	0.7115
$1s$-$2p$	0.7338	0.7040
$1s$-$2s$-$2p$	0.7846	0.7707
$1s$-$2s$-$2p$-$3s$	0.7894	0.7738
$1s$-$2s$-$2p$-$3p$	0.7920	0.7770
$1s$-$2s$-$2p$-$3d$	0.7841	0.7694
$1s$-$2s$-$2p$-$3s$-$3p$	0.7975	0.7814
Schwartz	0.908	0.894

[a] See reference 16.

is again borne out by the extremely small effect of the $3p$ state.

The results summarized in Table II also show that the $2s$ state gives a larger correction to the $1s$ phase shift than does the $2p$ state. This indicates that the $2s$ state is at least as effective as the $2p$ state in allowing for the short-range correlation, thereby providing another indication that the short-range correlation dominates the long-range polarization in its contribution to the phase shift. Further, the fact that the combined effect of the $2s$ and $2p$ states on the $1s$ phase shift is larger than the sum of the individual effects of the $2s$ and $2p$ states indicates that the $2s$-$2p$ coupling plays a significant role in elastic scattering. A similar, although smaller, effect can be observed in the influence of the $3s$ and $3p$ states on the $1s$-$2s$-$2p$ phase shift.

Two more points must be made concerning the range of energies below $k^2=0.65$. First, the contribution of the $3d$ state of hydrogen is so small that, within the accuracy of our calculation, it is essentially zero. Second, the apparent additivity of the effect on the phase shift due to different closely coupled states indicates that the effect of one state cannot be taken into account, except perhaps partially, by another—a fact which is consistent with the slow convergence of the series.

Our general conclusion is that the close-coupling approximation has been fully exploited with the use of the $1s$-$2s$-$2p$ states of hydrogen; very little is gained, at least at the energies considered here, by the inclusion of additional hydrogen eigenstates. Adding a term to the potentials to represent the long-range polarization also will not improve matters at these energies, other than fortuitously, unless this added term allows for short-range correlations as well, in the manner of a correct optical-model potential.[21]

We now come to the most striking feature of our results, that of the sharp increase in phase shift above $k^2=0.65$. Unfortunately, neither Schwartz[16] nor Tem-

[21] K. M. Watson, Phys. Rev. 105, 1388 (1957); M. Mittleman and K. M. Watson, Phys. Rev. 113, 198 (1959); B. A. Lippmann, M. Mittleman, and K. M. Watson, Phys. Rev. 116, 920 (1959); and B. A. Lippmann and H. M. Schey, Phys. Rev. 121, 1112 (1961).
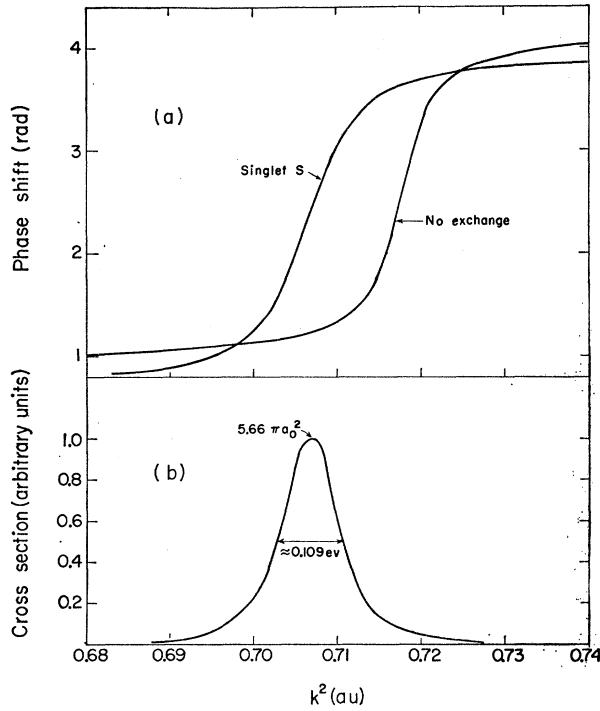
Fig. 2 (a). The singlet S phase shift and the no-exchange S phase shift as function of k^2, as given by the $1s$-$2s$-$2p$ close-coupling approximation in the neighborhood of resonance. (b) The corresponding resonant part of the singlet S cross section as a function of k^2.

kin[17] has carried his calculation into this energy region, although what may be a similar effect is evident at a somewhat higher energy in the $1s$-$2s$ results of Smith, McEachran and Fraser.[6] In Fig. 2(a) we show our singlet $L=0$ phase shift together with the nonexchange $L=0$ phase shift in the interval from $k^2=0.68$ to 0.74. As can be seen, both curves show a pronounced resonance behavior, with a definite flattening out before the threshold is reached (at $k^2=0.75$). Of course this is not a standard threshold effect,[22] although we believe that the effect is intimately connected with the new scattering channels that enter at $k^2=0.75$. It should be remarked here that this effect is not confined to the singlet S state; we observe similar effects in higher angular-momentum states. However, due to numerical difficulties in the solution of the coupled equations in the energy range of the supposed resonances, we are not yet able to analyze them as well as in this present case.

In discussing the singlet S resonance, let us decompose the phase shift into two parts. We put

$$\delta_{\text{tot}} = \delta_{\text{res}} + \delta_{\text{pot}},$$

where δ_{pot} is the slowly varying (nonresonant) potential part of the phase shift. We then write

$$\sigma_{\text{tot}} = (\pi/k^2) |A_{\text{res}} + A_{\text{tot}}|^2,$$

[22] E. P. Wigner, Phys. Rev. 73, 1002 (1948). See also R. G. Newton, Ann. Phys. 4, 29 (1958).

where

$$A_{\text{res}} = \exp(2i\delta_{\text{pot}})[\exp(2i\delta_{\text{res}}) - 1],$$

and

$$A_{\text{pot}} = \exp(2i\delta_{\text{pot}}) - 1.$$

The resonant part of the singlet S cross section can now be defined by the expression

$$\sigma_{\text{res}} = (\pi/k^2) |A_{\text{res}}|^2 = (4\pi/k^2) \sin^2\delta_{\text{res}}.$$

In Fig. 2(b) we give a plot of σ_{res} as a function of k^2. By making a Breit-Wigner[23] fit to this cross section,

$$\sigma_{\text{res}} = \frac{4\pi}{k^2} \frac{\tfrac{1}{4}\Gamma^2}{(E - E_{\text{res}})^2 + \tfrac{1}{4}\Gamma^2},$$

we obtain $\Gamma = 0.109$ ev and $E_{\text{res}} = 9.61$ ev. The resonance associated with the nonexchange phase shift lies at a slightly higher energy, and is somewhat narrower.

We do not wish to comment further upon the mechanism of these resonances at this time. We are presently investigating this intriguing phenomenon, and any understanding of it we may gain will be set forth in a later publication.[23a]

Triplet S Phase Shift

The triplet S phase shift given by our calculation can be characterized by the fact that it agrees very well, on the one hand, with Schwartz's result,[16] and, on the other, with both the single-body ($1s$) and the $1s$-$2s$ values. The agreement with Schwartz indicates that the short-range correlation present in this state is well represented by our approximation. The agreement with the more restricted close-coupling approximations, in which only spherically symmetric hydrogen eigenstates are retained, supports our belief that the effect of the polarization potential is negligible at least in S states removed from thresholds (see Fig. 3).

In the triplet S state we carried out a search for a resonance similar to the one found in the singlet S state and though we have uncovered no equivalent effect, we note that our calculation does not converge in the energy region from $k^2=0.71$ to 0.74. This may be due to the fact that the nonexchange solution, which is used as the starting point in the iteration scheme [see Fig. 2(a)], is itself resonating in this region and, therefore, provides a poor first approximation to the triplet-state solution if the latter is not resonating.

The P Phase Shifts

We have plotted our singlet and triplet P phase shifts in Figs. 4(a) and 4(b), respectively. In the same figures

[23] G. Breit and E. P. Wigner, Phys. Rev. 49, 519, 642 (1936).
[23a] Note added in proof. It has been suggested to us by Professor H. S. W. Massey (private communication) that these resonances may occur in a multi-channel problem when at least one of the channels is closed. For example, in a two-channel problem below the threshold in one channel the resonance would be expected when the energy in the closed channel is at an eigenvalue for motion in that channel uncoupled from the first.

we also show: the Bransden et al.[18] phase shifts obtained from an adiabatic variational polarization potential; the Temkin-Lamkin[6] phase shifts obtained from their polarized orbital method; the results of Malik and Trefftz,[24] who solved the one-body exchange equations modified with a polarization potential; the $1s$ phase shift of John[6]; and, finally, the $1s$-$2s$ results of Smith, McEachran and Fraser.[6]

The first feature of our results which we would like to point out is the fact that the polarization again appears to play a relatively minor role away from thresholds. In fact, in this instance polarization is not a dominant effect for energies somewhat above $k^2 = 0.02$. This follows from the observation (see Fig. 4) that the singlet and triplet phase shifts, which would be identical if the potential arose solely from polarization effects, begin to deviate from each other at this very small energy. It is near this same small energy that the triplet phase shift departs from the k^2 dependence given by a polarization potential. The relatively unimportant nature of polarization phenomena in this case is also manifested by the fact that the $2p$ term in the total wave function provides, in the triplet state, only a small correction to the $1s$-$2s$ result; we suppose that only some fraction of this correction comes from polarization. In applying this assumption to the singlet case, we suppose that the large correction to the $1s$-$2s$ result, obtained by includ-
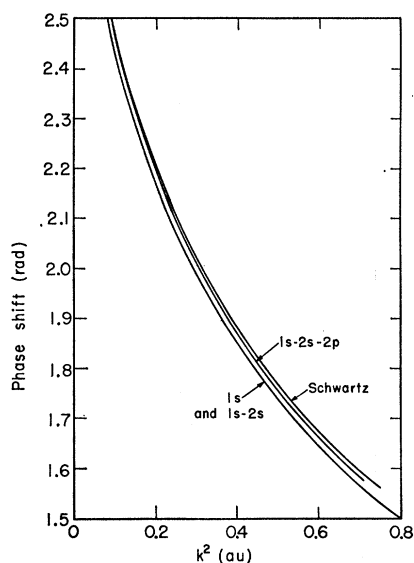

FIG. 3. The triplet S phase shift as a function of k^2, as given by various calculations

ing the $2p$ state, comes mainly from the extra short-range electron-electron correlation allowed for by the $2p$ state. If this is so, it seems surprising to us that the $2s$ state changes the $1s$ result so little, inasmuch as we
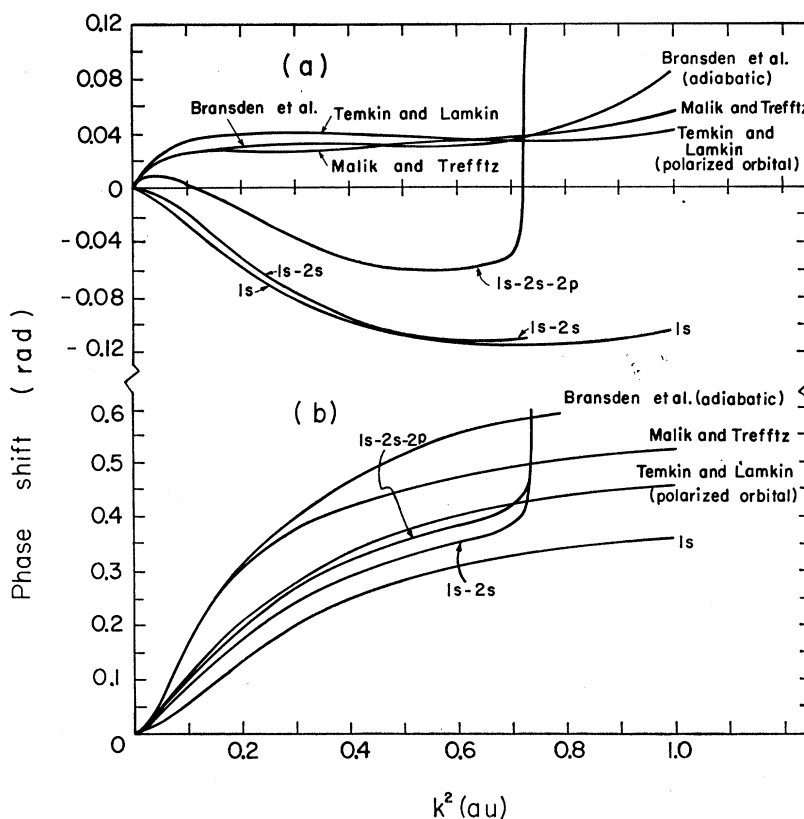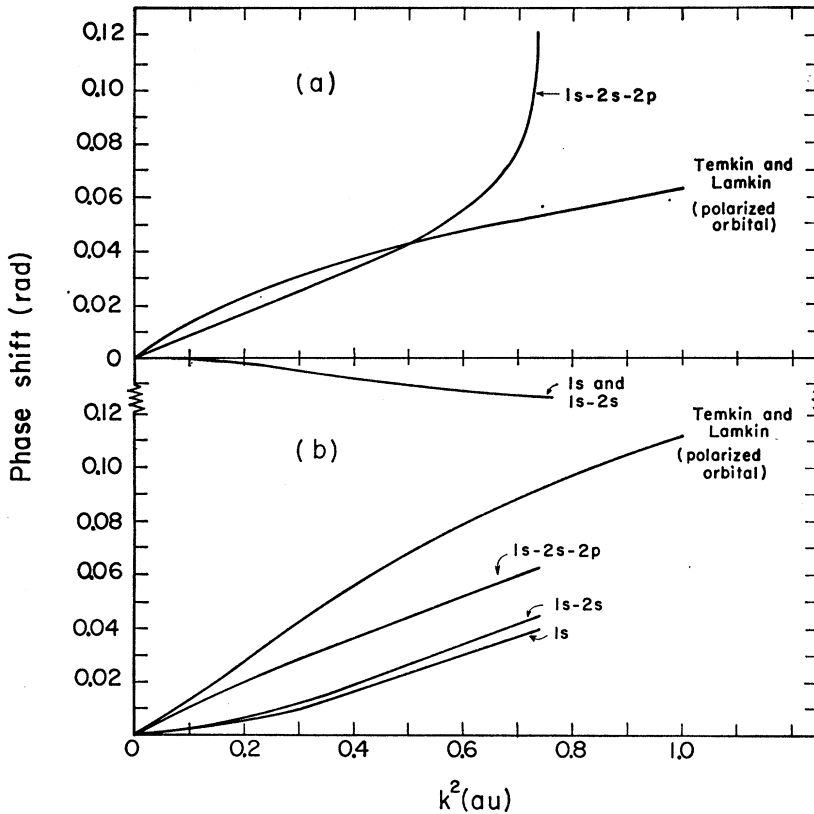

FIG. 4 (a). The singlet P phase shift as a function of k^2, as given by various calculations. (b) The triplet P phase shift as a function of k^2, as given by various calculations.

[24] F. B. Malik and E. Trefftz, Z. Astrophys. 50, 96 (1960).

FIG. 5 (a). The singlet D phase shift as a function of k^2, as given by various calculations. (b) The triplet D phase shift as a function of k^2, as given by various calculations.

learned from our singlet S result that the $2s$ state contributes as much as does the $2p$ state to the short-range correlation. Perhaps this is more evidence that the $2s$-$2p$ coupling term plays an important role in allowing for this correlation.

On the basis of the above argument, we believe that our results provide further evidence in support of the view of Martin et al.[25] that the adiabatic polarization potential provides a gross overestimate of the effect of the polarization potential.

With regard to the accuracy of our calculation, we believe that our result is quite accurate for the triplet phase shift, being no more than about 0.02 to 0.03 rad below the correct value. This follows from the assumption that the short-range correlation effect is small in the triplet state, and is probably well taken into account by the inclusion of the $2s$ and $2p$ states. We note however, that the convergence in closely coupled states is not as good here as in the triplet S state. The singlet P phase shift is certainly not given to this accuracy by the $1s$-$2s$-$2p$ approximation, and it may well prove to be the case that the correct phase shift is positive, like the adiabatic polarization result (although for a different reason, since most calculations overestimate the polarizability α), over most of the energy range up to the $n=2$ threshold.

[25] V. M. Martin, M. J. Seaton, and J. B. G. Wallace, Proc. Phys. Soc. (London) 72, 701 (1958).

Above $k^2=0.70$ we observe, in both spin states, the start of what we assume to be sharp resonances in the phase shifts, although convergence difficulties have prevented our amassing enough data in this region to enable us to say much about their exact positions or widths.

The D and F Phase Shifts

We show our singlet and triplet D phase shifts in Figs. 5(a) and 5(b), respectively. In these figures we also show the Temkin-Lamkin[6] polarized orbital results and the $1s$ and $1s$-$2s$ close coupling values of John[6] and of Smith, McEachran, and Fraser.[6] The main feature of our results is that the long range polarization now begins to play a dominant role over the entire energy range below threshold. This is evidenced by the linear behavior of the phase shift as a function of energy (see Bransden et al.,[18] O'Malley et al.[26]), as well as by the large change induced in the phase shift in the close-coupling approximation by the inclusion of the $2p$ state.

In the singlet D phase shift there appears an appreciable deviation from linearity for $k^2>0.5$, and this effect becomes violent for $k^2\approx0.74$. For $L\geqslant2$ a cusp of the Wigner type would occur in derivatives of the phase shift higher than the first. The variation with energy which we observe is thus almost certainly too strong to be a normal threshold effect. We, therefore, suggest that this strongly energy-dependent behavior is due to

another resonance similar to that found in the singlet S state. Because it occurs in so high an angular-momentum state, this resonance must have a large effect on the value of the total cross section; however, indications are that its width is even narrower than the 0.1 ev of the singlet S resonance, so that rather sophisticated experimental techniques would be required to see it.

It is worthwhile to point out at this stage that the long-range polarization potential has destroyed the rapid convergence in angular-momentum states associated with short-range forces. However, it appears possible to calculate the higher partial waves quite accurately—up to energies close to the second quantum level—by use of an expression due to O'Malley et al.,[26]

$$\tan\delta_L = \frac{\pi\alpha}{8(L+\tfrac{3}{2})(L+\tfrac{1}{2})(L-\tfrac{1}{2})}k^2 + \cdots, \qquad (9)$$

which is valid for all $L \geqslant 1$ at small values of k. This is an expansion in k^2; exchange effects, being of short range, influence only the higher-order terms. Using the value 2.96 (which is 66% of the correct value, 9/2) for the polarizability α, and putting $k^2 = 0.1$, we find that Eq. (9) gives $\delta_2 = 0.0089$ and $\delta_3 = 0.0029$. These values agree remarkably well with our results (see Table I), which are obtained from the solution of the coupled equations. Therefore, we conclude that Eq. (9), the leading term
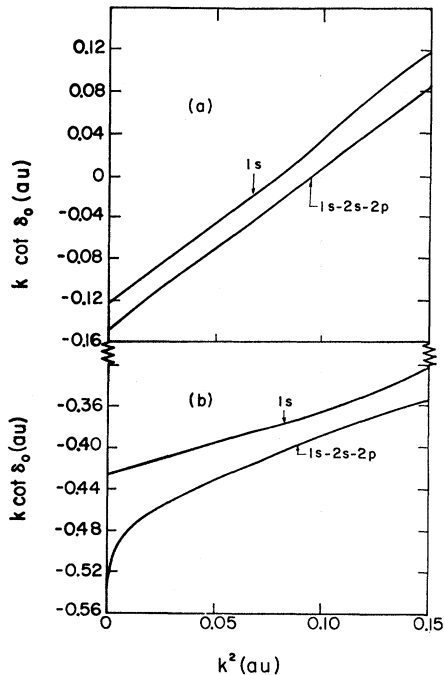

FIG. 6 (a). The singlet effective-range expansion in the 1s and the 1s-2s-2p close-coupling approximation. (b) The corresponding triplet effective-range expansion.

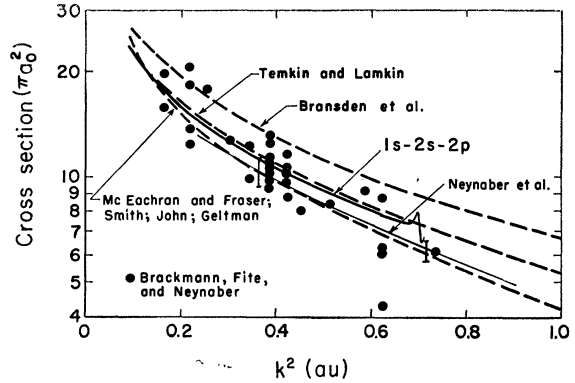[26] T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. 2, 491 (1961).

FIG. 7. Total cross section as a function of k^2, as given by various calculations, compared with experimental results (from Neynaber et al.[28]).

of the O'Malley et al.[26] expansion, provides a good approximation to the D phase shifts for $k^2 \lesssim 0.5$, and to the F phase shift for $k^2 \lesssim 0.75$ (see Table I). Further, this conclusion will probably be approximately correct even for an exact solution of the electron-hydrogen problem, since we feel our calculation reproduces the general features of an exact solution, if not all the details.

Zero-Energy Behavior of the S Phase Shifts

In Figs. 6(a) and 6(b) we plot the quantity $k \cot\delta_0$ as a function of k^2 for both the singlet and triplet phase shifts, respectively, as given by our calculation. Shown in the same figures are results of the 1s-exchange calculation. The triplet curve evidences strong nonlinear features near zero energy, due to the presence of terms in the effective range expansion whose dependence on energy (according to O'Malley et al.[26]) is given by k and $k^2 \ln k$. However, these terms seem to have little influence on the singlet effective-range expansion, which is nearly linear in k^2. Because the term in $k^2 \ln k$ is generally small, the behavior evidenced by $k \cot\delta$ in the singlet case is readily ascribed to the smallness of the coefficient of the term in k. This coefficient depends upon the reciprocal of the square of the relatively large singlet scattering length, which we find to be 6.742.

From the work of Spruch et al.,[27] we know that our value for the triplet scattering length $(a_T = 1.983)$ is an upper bound; and indeed, Schwartz, whose calculation we have taken as "correct," finds $a_T = 1.7686$.

V. COMPARISON WITH EXPERIMENT

In Fig. 7, on a plot taken from Neynaber et al.,[28] we show our result for the total cross section. Also shown

[27] L. Spruch and L. Rosenberg, Phys. Rev. 116, 1034 (1959). See also L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. 119, 164 (1960).

[28] R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, in International Conference on the Physics of Electronic and Atomic Collisions, 2nd, University of Colorado, Boulder, June, 1961 (W. A. Benjamin, Inc., New York, 1961), Paper G10; Phys. Rev. 124, 135 (1961).

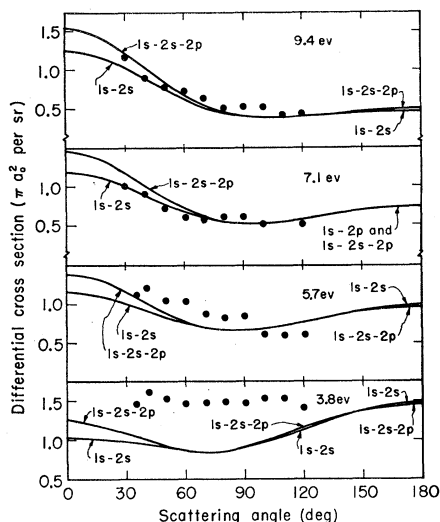FIG. 8. Differential cross section as a function of scattering angle in the $1s$-$2s$ and the $1s$-$2s$-$2p$ close-coupling approximation, at four incident electron energies. Circles indicate the experimental results of Gilbody et al.[31]

in the figure are the calculations of McEachran and Fraser,[6] Smith,[6] John,[6] Geltman,[29] Temkin and Lamkin,[6] and Bransden et al.[18]; and the experimental results of Brackmann et al.,[30] as well as of Neynaber et al. There is very little to choose between the results of several different calculations, from the point of view of agreement with experiment, although the P phase shifts obtained by Bransden et al. seem to give somewhat too large a cross section.

The high-energy end of our curve shows the effect of the singlet resonance at 9.61 ev, but we have been unable to extend the curve to 10.2 ev (which is the $n=2$ threshold) because we do not know the triplet S and P phase shifts in this region. We feel that the resonances are probably quite accurately given by our approximate solution of the electron-hydrogen problem, but it is clear that with present techniques it would be difficult to detect the singlet S resonance experimentally. The P state resonances, however, may be more easily observed, since they will have a much larger effect on the total cross section.

In Fig. 8 we compare the angular distributions predicted by both the $1s$-$2s$ and the $1s$-$2s$-$2p$ approximations with the experimental results of Gilbody et al.[31] If we assume that the experimental results are good, apart from an over-all normalization at the lower energies, then we observe that they do not distinguish between the two theoretical predictions, and the agreement with both is quite satisfactory. Because the two calculations deviate substantially only for small scatter-

[29] S. Geltman, Phys. Rev. 119, 1283 (1960).

[30] R. T. Brackmann, W. L. Fite, and R. H. Neynaber, Phys. Rev. 112, 1157 (1958).

[31] H. B. Gilbody, R. F. Stebbing, and W. L. Fite, Phys. Rev. 121, 794 (1961).

ing angles, measurements must be extended to angles of about 30 deg and less in order to distinguish between them.

VI. EXPANSION IN ORTHOGONAL STATES

Our work has shown certain inadequacies in the $1s$-$2s$-$2p$ close-coupling approximation that can be traced back to the fact that either very short-range or very long-range effects have not been treated adequately.

Although short-range correlations are not well represented by the $1s$-$2s$-$2p$ expansion, their representation by any close-coupling approximation composed exclusively of bound states would scarcely be better. The s and p states corresponding to $n>2$ resemble the $2s$ and $2p$ states for small values of r closely enough, so that an expansion in bound states is simply not sufficiently versatile to provide an adequate representation of short-range effects; their influence must be accounted for by functions markedly different from the bound-state terms at small r. Such functions are provided by terms coming from the continuum.

The treatment of long-range polarization phenomena is also little improved by the inclusion of additional bound states, for, as Castillejo et al.[20] have pointed out, even an expansion which includes all bound states will provide only 86% of the polarizability. Once again, continuum functions must be retained in the expansion to overcome the difficulty.

Continuum functions, suggested above as a solution to both the short- and long-range problems are, in fact, extremely awkward to deal with. We, therefore, introduce a new expansion of the wave function—one that simulates some effects of the continuum functions, but at the same time avoids their disagreeable features. We propose replacing (1) by the expression

$$\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2)$$

$$= \frac{1}{\sqrt{2}}(1-P_{12})\left\{ \sum_\Gamma \psi_\Gamma(\mathbf{r}_1\sigma_1\hat{r}_2\sigma_r)\frac{F_\Gamma(r_2)}{r_2} \right.$$

$$\left. + \sum_\Lambda \chi_\Lambda(\mathbf{r}_1\sigma_1\hat{r}_2\sigma_2)\frac{G_\Lambda(r_2)}{r_2} \right\}. \quad (10)$$

Here P_{12} is the space and spin exchange operator, and Γ has the same significance as in Eq. (1). Also, Λ represents $(mp_1p_2LM_LSM_s)$, where p_1 and p_2 are the orbital angular momentum of the bound and free electrons, respectively, and m distinguishes atomic states of different radial dependence corresponding to the same p_1. In general, mp_1 is a linear combination of hydrogen states which can contain both bound and continuum contributions. To simplify the analysis we require that the hydrogen states nl_1 included in Γ, and the additional states mp_1 of Λ, together constitute an orthonormal (though not necessarily complete) set.

When (10) is substituted for the wave function in the

Schrodinger equation, or used in an expression equivalent to (2), the resulting set of equations is given by

$$\left(\frac{d^2}{dr^2}-\frac{l_2(l_2+1)}{r^2}+k_n^2\right)F_\nu^{LS}(r)$$

$$=2\sum_{\nu'}\left[V_{\nu\nu'}{}^L-W_{\nu\nu'}{}^{LS}\right]F_{\nu'}{}^{LS}(r)$$

$$+2\sum_{\mu'}\left[V_{\nu\mu'}{}^L-W_{\nu\mu'}{}^{LS}\right]G_{\mu'}{}^{LS}(r),$$

$$\left(\frac{d^2}{dr^2}-\frac{p_2(p_2+1)}{r^2}+\gamma^2\right)G_\mu^{LS}(r)$$

$$=2\sum_{\nu'}\left[V_{\mu\nu'}{}^L-W_{\mu\nu'}{}^{LS}\right]F_{\nu'}(r)$$

$$+2\sum_{\mu'}\left[V_{\mu\mu'}{}^L-W_{\mu\mu'}{}^{LS}\right]G_{\mu'}{}^{LS}(r),$$

(11)

where the potentials V and W are as given in Appendix A. The solution (11) is no more difficult to obtain than that of (5), although the potentials are more difficult to evaluate.

The point to this approach is that a few terms judiciously chosen in both sums of (10) may be sufficient to obtain reasonably accurate results for electron-hydrogen scattering and reaction processes. For example, we might retain only one term in the Γ sum, and one in the Λ. The single $F_\nu(r)$ function would then represent scattering from the $1s$ state of hydrogen, whereas the term from the Λ sum could be chosen to have a p state ($l=1$) angular dependence and a radial dependence which would give rise, asymptotically, to the *total* α/r^4 polarization potential. Such a term would obviously receive contributions from the continuum states.

We conclude this section by remarking that no assessment of the worth of the alternative expansion (10) has been attempted here, and ultimately its utility must be ascertained by direct calculation.

VII. CONCLUSIONS

We have investigated the elastic scattering of electrons by atomic hydrogen for incident electron energies below the threshold for excitation of the second quantum level. From our results we draw the following conclusions:

1. The close-coupling approximation in which only the $1s$, $2s$, and $2p$ eigenstates of hydrogen are included, gives, in general, an adequate representation of elastic scattering over the whole energy region below threshold. The approximation is least successful in the singlet S state where the short-range interelectron correlation is largest. Even here the results obtained agree reasonably well with the "correct" results of Schwartz[16] and of Temkin,[17] having halved the error incurred by the single-body ($1s$) approximation. However, scarcely any im-

provement results from the inclusion of additional bound states with $n>2$ in the close-coupling expansion. We take this as an indication of very slow convergence. A better representation of short-range correlation, and of long-range polarization as well, requires either the inclusion of continuum states in the close-coupling approximation, or (perhaps more convenient numerically) an alternative expansion such as that suggested in Sec. VI.

2. At energies close to, but somewhat below, the second quantum-level excitation, the $1s$-$2s$-$2p$ close-coupling expansion indicates the existence of extremely narrow resonances in nearly all angular-momentum and spin states. Such resonances are, of course, entirely absent in the one-body approximation. On the basis of this fact, we are led to the not unexpected conclusion that at incident electron energies near the threshold for excitation of a target level it is imperative that all eigenstates corresponding to this level be present in the close-coupling expansion.

3. Earlier work has shown the importance of the $2s$-$2p$ coupling on the $1s$-$2s$, $1s$-$2p$, and $2s$-$2p$[1,32] reaction cross sections. Our work indicates this coupling is significant even for elastic scattering.

4. The long-range polarization effects play a decisive role in scattering at or near zero energy, and the energy range in which such effects are important increases with total angular momentum. Inclusion of the $2p$ state in the close-coupling approximation allows for only 66% of the asymptotic polarization, and improvements can probably result only from some scheme such as that suggested in Sec. VI, wherein an orthogonal p state is included with a radial dependence chosen to give the full asymptotic polarization. We believe, however, that the $1s$-$2s$-$2p$ expansion utilized in the present work will indicate the range of energy in which polarization is important. We find that for $L=0$ and 1 the polarization potential is important only for $k^2<0.05$; for $L=2$ it is important for $k^2<0.5$; and for $L=3$ it dominates for $k^2<0.75$. Our results indicate that some of the earlier work which allows for polarization, either by including *ad hoc* terms in the Schrodinger equation or by correcting the single-body approximation with a variational method, overestimates, for $L=0$ and 1, the region in which the polarization figures importantly in the scattering. This may be due to the fact that such analyses, in effect, carry the polarization potential to values of r that are too small.

5. Our results for the total cross section agree with experiment reasonably well, as do those of many earlier calculations. The same is true for the differential cross section except that, at small scattering angles, deviations among theoretical predictions exist and might be

[32] N. A. Kroll and E. Gerjuoy, in *International Conference on the Physics of Electronic and Atomic Collisions, 2nd, University of Colorado, Boulder, June, 1961* (W. A. Benjamin, Inc., New York, 1961), Paper B4.

resolved by measurements—so far lacking—at angles less than, and of the order of, 30 deg.

To make possible an experimental search for the resonances we find below the $n=2$ threshold, electron-energy resolution $\lesssim 0.1$ ev will be required.

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APPENDIXES

A. An Alternative Expansion

The expansion implied by Eq. (10) for each LS component of the wave function is given by

$$\Psi^{LS}(\mathbf{r}_1,\mathbf{r}_2)$$
$$= (1\pm P_{12})\Bigg[\sum_\nu \frac{1}{r_1 r_2}P_{nl_1}(r_1)F_{nl_1l_2}(r_2)\mathcal{Y}_{Ll_1l_2}{}^{ML}(\hat{r}_1,\hat{r}_2)$$
$$+\sum_\mu \frac{1}{r_1 r_2}R_{mp_1}(r_1)G_{mp_1p_2}(r_2)\mathcal{Y}_{Lp_1p_2}{}^{ML}(\hat{r}_1\hat{r}_2)\Bigg], \quad (A1)$$

where

$$\mathcal{Y}_{Ll_1l_2}{}^{ML}(\hat{r}_1\hat{r}_2)= \sum_{m_1m_2} C_{l_1l_2}(LM_L; m_1m_2)Y_l{}^{m_1}(\hat{r}_1)Y_l{}^{m_2}(\hat{r}_2),$$

and $Y_l{}^m(\hat{r})$ is the usual spherical harmonic.[12] Also, $\nu=nl_1l_2$ and $\mu=mp_1p_2$. All functions P and R are normalized to unity and are orthogonal for the same orbital angular-momentum quantum numbers. The P functions are reduced hydrogen-atom wave functions, and the R functions are arbitrary apart from the above orthonormality conditions and the following boundary conditions:

$$R_{mp}(r)\sim\alpha r^{p+1} \text{ for small } r,$$

and

$$R_{mp}(r)\sim 0 \text{ for large } r.$$

The operator P_{12} in Eq. (A1) is the space-exchange operator and the $+$ and $-$ signs go with the singlet and triplet spin states, respectively.

Substituting (A1) into a variational principle equivalent to that given by Eq. (2), or, alternatively, operating on (A1) with $H-E$ when H is given by Eq. (4), and then premultiplying by either $P_{nl_1}(r_1)\mathcal{Y}_{Ll_1l_2}{}^{ML}(\hat{r}_1,\hat{r}_2)$ or $R_{mp_1}(r_1)\mathcal{Y}_{Lp_1p_2}{}^{ML}(\hat{r}_1,\hat{r}_2)$, and integrating over $d\mathbf{r}_1 d\hat{r}_2$, we

derive the set of coupled integro-differential equations for the F and G functions given by Eq. (11).

The definition of the quantities occurring in Eqs. (5) and (11) are

$$k_n{}^2=2E-2E_n, \quad \gamma^2=2E,$$

$$V_{\nu\nu'}{}^L(r)=-\frac{\delta_{\nu\nu'}}{r}+\sum_\lambda f_\lambda(l_1l_2l_1'l_2'; L)y_\lambda(P_{nl_1}P_{n'l_1'}; r),$$

$$V_{\nu\mu'}{}^L(r)=\sum_\lambda f_\lambda(l_1l_2p_1'p_2'; L)y_\lambda(P_{nl_1}R_{m'p_1'}; r),$$

$$V_{\mu\nu'}{}^L(r)=\sum_\lambda f_\lambda(p_1p_2l_1'l_2'; L)y_\lambda(R_{mp_1}P_{n'l_1'}; r),$$

$$V_{\mu\mu'}{}^L(r)=-\frac{\delta_{\mu\mu'}}{r}+\sum_\lambda f_\lambda(p_1p_2p_1'p_2'; L)$$
$$\times[\delta_{\lambda 0}\Delta_{p_1'}(R_{mp_1}R_{m'p_1'})+y_\lambda(R_{mp_1}R_{m'p_1'}; r)],$$

$$W_{\nu\nu'}{}^{LS}F_{\nu'}{}^{LS}(r)= (-)^{1-S}\sum_\lambda g_\lambda(l_1l_2l_1'l_2'; L)$$
$$\times[\delta_{\lambda 0}(E_n+E_{n'}-E)\Delta(P_{nl_1},F_{\nu'})$$
$$+y_\lambda(P_{nl_1}F_{\nu'}; r)]P_{n'l_1'}(r),$$

$$W_{\nu\mu'}{}^{LS}G_{\mu'}{}^{LS}(r)= (-)^{1-S}\sum_\lambda g_\lambda(l_1l_2p_1'p_2'; L)$$
$$\times[\delta_{\lambda 0}(E_n+L_{p_1'}-E)\Delta(P_{nl_1},G_{\mu'})$$
$$+y_\lambda(P_{nl_1}G_{\mu'}; r)]R_{m'p_1'}(r),$$

$$W_{\mu\nu'}{}^{LS}F_{\nu'}{}^{LS}= (-)^{1-S}\sum_\lambda g_\lambda(p_1p_2l_1'l_2'; L)$$
$$\times\{\delta_{\lambda 0}[\Delta_{l_2'}(R_{mp_1},F_{\nu'})$$
$$+(E_{n'}-E)\Delta(R_{mp_1},F_{\nu'})]$$
$$+y_\lambda(R_{mp_1}F_{\nu'}; r)\}P_{n'l_1'}(r),$$

$$W_{\mu\mu'}{}^{LS}G_{\mu'}{}^{LS}(r)= (-)^{1-S}\sum_\lambda g_\lambda(p_1p_2p_1'p_2'; L)$$
$$\times\{\delta_{\lambda 0}[\Delta_{p_2'}(R_{mp_1},G_{\mu'})$$
$$+(L_{p_1'}(r)-E)\Delta(R_{mp_1},G_{\mu'})]$$
$$+y_\lambda(R_{mp'}G_{\mu'}; r)\}R_{m'p_1'}(r), \quad (A2)$$

where we have written

$$L_l(r)=-\frac{1}{2}\Big(\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}+\frac{2}{r}\Big),$$

$$\Delta_l(A,B)=\Delta(A,L_lB),$$

$$\Delta(A,B)=\int_0^\infty A(r)B(r)dr,$$

and

$$y_\lambda(AB; r) = \frac{1}{r^{\lambda+1}} \int_0^r A(r')B(r')r'^\lambda dr'$$
$$+ r^\lambda \int_r^\infty \frac{A(r')B(r')}{r'^{\lambda+1}} dr'.$$

The f_λ and g_λ functions are defined by

$$f_\lambda(l_1 l_2 l_1' l_2'; L) = (l_1 l_2 L | P_\lambda(\hat{r}_1 \hat{r}_2) | l_1' l_2' L),$$

and

$$g_\lambda(l_1 l_2 l_1' l_2'; L) = (-)^{l_1+l_2-L}(l_1 l_2 L | P_\lambda(\hat{r}_1 \hat{r}_2) | l_2' l_1' L).$$

As an example of a possible use of this extended expansion, consider the case mentioned in Sec. VI, where we retain one P function and one R function, the form of the latter being chosen to give the full polarization potential experienced by the scattered function F_{1s} in the asymptotic region.

The coupled equations describing F and G reduce, in the asymptotic region, to

$$\left(\frac{d^2}{dr^2} + k^2\right)F_{1s}(r) = -\frac{2}{\sqrt{3}}\frac{A}{r^2}G(r),$$

and

$$\left(\frac{d^2}{dr^2} - \frac{2}{r^2} + \theta^2\right)G(r) = -\frac{2}{\sqrt{3}}\frac{A}{r^2}F_{1s}(r).$$

$\qquad$ (A3)

It is shown by Castillejo et al.[21] that Eq. (A3) is equivalent to the following equation for $F_{1s}(r)$:

$$\left(\frac{d^2}{dr^2} + k^2 + \frac{\alpha}{r^2}\right)F_{1s}(r) = 0, \qquad (A4)$$

where

$$\alpha = \left(\frac{2}{\sqrt{3}}\right)^2 \frac{A^2}{k^2 - \theta^2}.$$

Now, from Eq. (A2) we have

$$A = \int_0^\infty rF_{1s}(r)G(r)dr, \quad k^2 - \theta^2 = 2\Delta_1(R,R) - 2E_1. \quad (A5)$$

Our requirement is that $\alpha = 4.5$, the polarizability of hydrogen. If we assume a radial form for R, such as

$$R(r) = (ar^2 + br^3)\exp(-\mu r),$$

we can determine a and b as functions of μ by using Eq. (A5) and the normalization condition $\int_0^\infty R^2(r)dr = 1$. Having obtained an analytic form for $R(r)$, we can solve Eq. (11), assured that the asymptotic region is correctly represented. In the triplet case, where a lower bound for the scattering length exists, we can plot the scattering length obtained from Eq. (11) as a function of μ, and choose the minimum in the curve as the best value.

B. An Asymptotic Expansion

In the region where the exchange terms are negligible the coupled differential equations can be written, according to Sec. III, in the form

$$\frac{d^2 F_i}{dr^2} = \sum_{j=1}^n V_{ij}(r)F_j(r), \qquad (B1)$$

where $i, j = 1, 2, \cdots, n$. Here V_{ij} includes the direct potential, the centrifugal barrier, and the energy term as follows:

$$V_{ij}(r) = \sum_{\lambda=1}^{m_{ij}} \frac{a_{ij}^\lambda}{r^{\lambda+1}} - k_i^2 \delta_{ij} + \frac{l_i(l_i+1)}{r^2}\delta_{ij}. \qquad (B2)$$

In Eq. (B2) we use the fact that each element of the direct potential can be written as a finite sum of inverse powers of r, starting with a power no higher than -2.

We now assume that there are m_a separate and independent wave numbers k_κ, $\kappa = 1$ to m_a above threshold, and m_b separate and independent wave numbers $\alpha_\tau = |k_\tau|$, $\tau = 1$ to m_b below threshold. We note that each k_κ and α_τ may include more than one channel; thus, for example, channels corresponding to the $2s$ and $2p$ states have the same k_κ (or α_τ).

We write our asymptotic expansion for each F_i in Eq. (B1) in the form

$$F_i(r) = \sum_{\kappa=1}^{m_a} \left(\sin k_\kappa r \sum_{p=0}^\infty \alpha_p^{i\kappa} r^{-p} + \cos k_\kappa r \sum_{p=0}^\infty \beta_p^{i\kappa} r^{-p} \right)$$
$$+ \sum_{\tau=1}^{m_b} \exp(-\alpha_\tau r) \sum_{p=0}^\infty \gamma_p^{i\tau} r^{-p}. \quad (B3)$$

Substituting (B3) into (B1), and equating the coefficients of $\sin(k_\kappa r)/r^p$, $\cos(k_\kappa r)/r^p$ and $\exp(-\alpha_\tau r)/r^p$ for all relevant κ, τ, and p, we obtain the following recursion relations for the α, β, and γ coefficients in (B3)

$$[(k_i^2 - k_\kappa^2)\alpha_p^{i\kappa} + (p-1)(p-2)\alpha_{p-2}^{i\kappa} + 2k_\kappa(p-1)\beta_{p-1}^{i\kappa}]$$
$$= \sum_{i=1}^n \sum_{\lambda=1}^{m_{ij}} a_{ij}^\lambda \alpha_{p-\lambda-1}^{i\kappa},$$

$$[(k_i^2 - k_\kappa^2)\beta_p^{i\kappa} + (p-1)(p-2)\beta_{p-2}^{i\kappa} - 2k_\kappa(p-1)\alpha_{p-1}^{i\kappa}]$$
$$= \sum_{j=1}^n \sum_{\lambda=1}^{m_{ij}} a_{ij}^\lambda \beta_{p-\lambda-1}^{i\kappa}, \quad (B4)$$

$$[(k_i^2 + \alpha_\tau^2)\gamma_p^{i\tau} + (p-1)(p-2)\gamma_{p-2}^{i\tau} + 2\alpha_\tau(p-1)\gamma_{p-1}^{i\tau}]$$
$$= \sum_{j=1}^n \sum_{\lambda=1}^{m_{ij}} a_{ij}^\lambda \gamma_{p-\lambda-1}^{j\tau},$$

where $i = 1$ to n, $\kappa = 1$ to m_a, and $\tau = 1$ to m_b. A particular solution of (B1) given by (B4) is defined uniquely by

specifying the $2n+n_a$ parameters

$$\alpha_0^{i\kappa(i)}, \beta_0^{i\kappa(i)}, \quad \text{where} \quad i=1 \text{ to } n_a;$$

$$\gamma_0^{i\tau(i)}, \quad \text{where} \quad i=n_a+1 \text{ to } n; \qquad \text{(B5)}$$

here we mean, by the notation $\kappa(i)$ and $\tau(i)$, that κ (or τ) which is determined by channel i. In terms of the values (B5), all the remaining α, β, and γ are given by (B4), thus determining the F_i by means of (B3).

Near any threshold, i.e., at any energy for which some k_κ^2 or α_τ^2 is less than about 0.005, expansion (B3) provides a good representation of Eq. (i) only for excessively large values of r. This difficulty arises from the inability of a sine, cosine, or exponential function to simulate the straightline behavior manifested in the asymptotic region by the solution near threshold. We overcome this difficulty at zero energy by dropping the term in (B3) whose wave number k_κ or α_τ is close to zero, and by adding to each F_i in (B3) a term

$$r \sum_{p=0}^{\infty} \delta_p^i r^{-p}, \qquad \text{(B6)}$$

where δ_0^i and δ_1^i are arbitrary parameters for that i which corresponds to the zero-energy channel—that is, for $i=1$. This gives, upon substituting (B6) into (B1) and equating coefficients, the additional recursion relations

$$p(p-1)\delta_p^1 = \sum_{j=1}^{n} \sum_{\lambda=1}^{m_{ij}} a_{ij}\delta_{p-\lambda+1}^j. \qquad \text{(B7)}$$

This procedure enables us to obtain a solution at zero energy.