PHYSICAL REVIEW VOLUME 121, NUMBER 3 FEBRUARY 1, 1961

Application of the Method of Polarized Orbitals to the Scattering of Electrons from Hydrogen*

A. TEMKIN† AND J. C. LAMKIN
National Bureau of Standards, Washington, D. C.

(Received September 14, 1960)

The s-, p-, and d-wave scattering of slow electrons from atomic hydrogen is calculated by the method of polarized orbitals. Utilization of a transformation of Omidvar avoids the iterative procedure of solving the associated integro-differential equations. The s-wave scattering is smaller than that given by the exchange approximation, and the scattering lengths are within the upper bounds found by Rosenberg, Spruch, and O'Malley. The d-wave phase shifts are too small to explain a resonance in the total cross section. However, they are much larger than those of the exchange or Born approximation, and they give considerable structure to the differential cross-section curves. The p-wave phase shifts are not much increased by the polarization effects.

1. INTRODUCTION

THIS calculation is the concluding part of a study of the elastic scattering of electrons from atomic hydrogen via the method of polarized orbitals. This method, which was originally applied to the scattering of electrons from oxygen,[1] divides itself into two parts: a static and a dynamic problem. The static problem, which deals with determining $\Phi^{(\mathrm{pol})}$ (see below), was solved in a previous paper.[2] That paper contains the background and introductory material relevant to the present calculation. In particular the notation and units of II will be continued here. For completeness the definitions of most of the functions will be repeated. The only change will be the normalization of the function $u_{1s\to p}(r)$. (See Section 2.)

2. DERIVATION OF THE SCATTERING EQUATIONS

The static wave function which was derived in II is given by

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{u(\mathbf{r}_1)}{r_1}[\Phi_0(\mathbf{r}_2)+\Phi^{(\mathrm{pol})}(\mathbf{r}_1;\mathbf{r}_2)]$$
$$\pm\frac{u(\mathbf{r}_2)}{r_1}[\Phi_0(\mathbf{r}_1)+\Phi^{(\mathrm{pol})}(\mathbf{r}_2;\mathbf{r}_1)]. \quad (2.1)$$

The dynamic problem is concerned with the determination of the function $u(\mathbf{r})$, whose asymptotic form yields the desired phase shift. The function $\Phi_0+\Phi^{(\mathrm{pol})}$ is the asymptotic form of the first order perturbed ground-state wave function of the hydrogen atom due to the static influence of an electron at a distance r_1 from the nucleus. This perturbation is

$$\frac{2}{r_1}-\frac{2}{|\mathbf{r}_1-\mathbf{r}_2|}\cong\frac{2r_2}{r_1^2}P_1(\cos\theta_{12}),\quad r_1>r_2. \quad (2.2)$$

The approximation of the left-hand side of the above equation by the right-hand side is called the dipole approximation[1]; it is used in deriving (2.3). The higher multipoles in (2.2) give rise to additional terms which can also be calculated analytically[2,3]; however, they will not be included in this treatment. We repeat the definitions of the functions occurring in (2.1).

$$\Phi^{(\mathrm{pol})}(\mathbf{r}_1;\mathbf{r}_2)=\frac{-\epsilon(r_1,r_2)}{r_1^2}\frac{u_{1s\to p}(r_2)}{r_2}\frac{P_1(\cos\theta_{12})}{\pi^{\frac{1}{2}}}, \quad (2.3)$$

$$\epsilon(r_1,r_2)=1\quad\text{for}\quad r_1>r_2$$
$$=0\quad\text{for}\quad r_1<r_2, \quad (2.4)$$

$$\Phi_0(\mathbf{r})=\frac{u_{1s}(r)}{r}Y_{00}(\Omega)=2e^{-r}Y_{00}(\Omega), \quad (2.5)$$

$$u_{1s\to p}(r)=e^{-r}(\tfrac{1}{2}r^3+r^2). \quad (2.6)$$

(Note that $u_{1s\to p}$ is one half of the value defined in II.) The angular dependence of $u(\mathbf{r})$ is given by a spherical harmonic whose l value defines the order of the partial wave being considered.

$$u(\mathbf{r})=u_l(r)Y_{l0}(\Omega). \quad (2.7)$$

It was indicated in II that the usual way of deriving an equation for $u(r)$ was by using the variational principle for $H-E$:

$$\delta\int\Psi^*(H-E)\Psi d^3r_1d^3r_2=0.$$

---

* Work supported in part by the Office of Naval Research.

† Present address: National Aeronautics and Space Administration, Washington, D. C.

[1] A. Temkin, Phys. Rev. **107**, 1004 (1957). This paper will be referred to as I. In the past year we have learned that this method is in essence the same as the method of perturbed stationary states [N. Mott and H. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), 2nd ed., p. 153]. The differences lie in the application of the latter to heavy-particle scattering from atoms, where the adiabatic hypothesis was never in doubt, and where the problems of antisymmetrization do not arise. In addition, the method of polarized orbitals utilizes the Sternheimer method of finding the perturbed stationary state, which we have shown in reference 2 is a much more accurate and more feasible way of including the effects of first order perturbation theory.

[2] A. Temkin, Phys. Rev. **116**, 358 (1959). This paper will be referred to as II.

[3] A. Dalgarno and A. Stewart, Proc. Roy. Soc. (London) **A238**, 269, 276 (1956).

Here H is the total Hamiltonian,

$$H=-\nabla_1^2-\nabla_2^2-\frac{2}{r_1}-\frac{2}{r_2}+\frac{2}{r_{12}}; \tag{2.8}$$

E the total energy (in rydbergs; 1 ry=13.6 ev),

$$E=-1+k^2; \tag{2.9}$$

and k^2 is the energy of the incident electron. The variational principle amounts to formally substituting (2.1) into the Schrödinger equation, multiplying on the left by $\Phi_0(\mathbf{r}_1)+\Phi^{(\mathrm{pol})}(\mathbf{r}_1;\mathbf{r}_2)$, and the integrating over all coordinates but r_1 (indicated here by dr_1^{-1}). One can readily see that this procedure will give rise to terms quadratic in $\Phi^{(\mathrm{pol})}$. Such terms are not in accord with first-order perturbation theory.[1] Consequently we will modify the variational approach and obtain our final scattering equations by projecting the Schrödinger equation on the known part of the asymptotic wave function[4]:

$$\int Y_{l0}^*(\Omega_1)\Phi_0^*(\mathbf{r}_2)(H-E)\Psi(\mathbf{r}_1,\mathbf{r}_2)dr_1^{-1}=0. \tag{2.10}$$

The integration of (2.10) is straightforward and yields the scattering equations for arbitrary l:

$$\begin{aligned}
&\left[-\frac{d^2}{dr_1^2}+\frac{l(l+1)}{r_1^2}-2e^{-2r_1}\left(1+\frac{1}{r_1}\right)-k^2\right]u_l(r_1)\\
&\pm u_{1s}(r_1)\left[-(1+k^2)\delta_{l0}\int_0^\infty u_{1s}(r_2)u_l(r_2)dr_2\right.\\
&\left.+\frac{2}{2l+1}\,y_l(u_{1s},u_l;1)\right]\\
&=\frac{\alpha_1(r_1)}{r_1^4}u_l(r_1)\pm u_{1s\to p}(r_1)\left\{-\tfrac{2}{3}(1+k^2)\delta_{l1}\right.\\
&\times\int_{r_1}^\infty\frac{u_{1s}(r_2)u_l(r_2)dr_2}{r_2^2}+4\left[\frac{l}{(2l+1)(2l-1)}r_1^{l-1}\right.\\
&\times\int_{r_1}^\infty\frac{u_{1s}(r_2)u_l(r_2)}{r_2^{l+2}}+\frac{(l+1)r_1^{l+1}}{(2l+1)(2l+3)}\\
&\left.\left.\times\int_{r_1}^\infty\frac{u_{1s}(r_2)u_l(r_2)dr_2}{r_2^{l+4}}\right]\right\}\\
&\pm\tfrac{4}{3}r_1^2e^{-r_1}\delta_{l1}\int_{r_1}^\infty\frac{u_{1s}(r_2)u_l(r_2)dr_2}{r_2^2}.
\end{aligned} \tag{2.11}$$

In (2.11) we have the additional definitions

$$y_l(u_{1s},u_l;1)=\frac{1}{r_1^{l+1}}\int_0^{r_1}r_2^lu_{1s}(r_2)u_l(r_2)dr_2+r_1^l\int_{r_1}^\infty\frac{u_{1s}(r_2)u_l(r_2)dr_2}{r_2^{l+1}}, \tag{2.12}$$

and

$$\alpha_1(r_1)=\frac{9}{2}-\frac{2}{3}e^{-2r_1}\left(r_1^5+\frac{9}{2}r_1^4+9r_1^3+\frac{27}{2}r_1^2+\frac{27}{2}r_1+\frac{27}{4}\right). \tag{2.13}$$

The scattering equation (2.11) has been arranged so that the polarization terms are on the right-hand side of the equation. The upper sign in these equations refers to the singlet scattering, and the lower sign to the triplet.

We shall have occasion to mention two sets of equations in addition to (2.11). The first is the "exchange approximation," obtained by dropping the right-hand side of (2.11). The second includes only the first term on the right-hand side. We shall refer to this as the "exchange-adiabatic" approximation. We shall also use this name to refer to calculations in which this first term is replaced by other assumptions about the form of $\alpha_1(r)/r^4$ providing they have the form α_1/r^4 at infinity. Both the exchange and exchange adiabatic approximations have been previously used by others, and they are discussed in reference 2. The solution of the complete equation (2.11) corresponds to the method of polarized orbitals.

The terms multiplied by the ±sign on the right-hand side of (2.11) are the exchange polarization terms, which arise because $\Phi^{(\mathrm{pol})}$, like the nonpolarization part of Ψ, occurs with its arguments interchanged in (2.1).

3. TECHNIQUE OF NUMERICAL SOLUTION OF THE SCATTERING EQUATIONS

In describing the numerical methods of integrating (2.11), we shall confine ourselves to the s-wave equation. The $l>0$ equations are handled in essentially the same way. This equation can be written [we suppress the subscript 0 of $u_0(r)$].

$$\begin{aligned}
&\left[-\frac{d^2}{dr^2}-2e^{-2r}\left(1+\frac{1}{r}\right)-\frac{\alpha_1(r)}{r^4}\right]u(r)\\
&\pm\left\{8re^{-r}\left[C_1+\frac{1}{r}\int_0^r r_2e^{-r_2}u(r_2)dr_2\right.\right.\\
&\left.-\int_0^r e^{-r_2}u(r_2)dr_2\right]-\frac{8}{3}re^{-r}(\tfrac{1}{2}r^3+r^2)\\
&\left.\times\left[C_2-\int_\epsilon^r\frac{e^{-r_2}u(r_2)dr_2}{r_2^3}\right]\right\}=0.
\end{aligned} \tag{3.1}$$

---

[4] The variational principle gives rise to an integral like (2.10) with $\Phi_0^*(\mathbf{r}_2)$ replaced by $\Phi_0^*(\mathbf{r}_2)+\Phi^{(\mathrm{pol})}(\mathbf{r}_1,\mathbf{r}_2)$.

The constants C_1 and C_2 are given by

$$C_1=\int_0^\infty [1-\tfrac{1}{2}(1+k^2)r_2]e^{-r_2}u(r_2)dr_2,$$
$$C_2=\int_\epsilon^\infty e^{-r_2}r_2^{-3}u(r_2)dr_2. \tag{3.2}$$

The last square bracket of (3.1) is just the integral $\int_r^\infty e^{-r_2}r_2^{-3}u(r_2)dr_2$. Since $u(r_2)$ describes an s wave $[u(r_2)\rightarrow r_2$ as $r_2\rightarrow 0]$, the integral is seen to diverge as r^{-1} (as $r\rightarrow 0$). However the factor on its left in (3.1) goes to zero as r^3; thus the product is zero in that limit. In practice the integral was broken up as in the last square bracket (3.1) with $\epsilon=2h$, h being the mesh size. This is exact; however the portion of the last integral for $r<\epsilon$ was neglected, the justification for this being the preceding argument. A meaningful phase shift must be independent of ϵ, and this was tested by varying h.

We found the procedure as described above quite satisfactory for the p- and d-wave equations using the trapezoidal rule for integrating the cumulative integral. In the case of the triplet s-wave equation, trouble was encountered with the trapezoidal rule. This difficulty was eliminated by replacing the divergent r_2^3 denominator in the last integrand of (3.1) by $(r_2^3+\Delta)$. In spite of the crudeness of this device, the phase shifts were found to be virtually independent of Δ when Δ was varied between 0.01 and 0.5.

The usual way of solving an equation like (3.1) is to take a guess at the constants, evaluate $u(r)$, evaluate the constants on the basis of $u(r)$, and iterate the procedure until convergence is obtained. Our experience in these matters indicated that the convergence can be slow and erratic even in the equations corresponding to the exchange approximation. The presence of the exchange polarization terms made it practically impossible to obtain (by iteration) a fully convergent $u(r)$. Therefore we shall describe a slight generalization of a method due to Omidvar[5] which completely avoids the iteration problem.

Let $u(r)$ of (3.1) be written

$$u(r)=u^{(0)}(r)+C_1u^{(1)}(r)+C_2u^{(2)}(r), \tag{3.3}$$

where C_1 and C_2 are those of (3.2). We assert that (3.1) is equivalent to the three equations

$$O_\pm u^{(0)}(r)=0, \tag{3.1a}$$
$$O_\pm u^{(1)}(r)\pm 8re^{-r}=0, \tag{3.1b}$$
$$O_\pm u^{(2)}(r)\pm[-(8/3)re^{-r}(\tfrac{1}{2}r^3+r^2)]=0, \tag{3.1c}$$

where

$$O_\pm u^{(i)}(r)$$
$$\equiv\left[-\frac{d^2}{dr^2}-2e^{-2r}\left(1+\frac{1}{r}\right)-\frac{\alpha_1(r)}{r^4}-k^2\right]u^{(i)}(r)$$
$$\pm\left\{8re^{-r}\left[\frac{1}{r}\int_0^r r^2e^{-r_2}u^{(i)}(r_2)dr_2-\int_0^r e^{-r_2}u^{(i)}(r_2)dr_2\right]\right.$$
$$\left.+\frac{8}{3}re^{-r}(\tfrac{1}{2}r^3+r^2)\int_\epsilon^r e^{-r_2}u^{(i)}(r_2)r_2^{-3}dr_2\right\}.$$

To prove the assertion, multiply (3.1b) by C_1 and (3.1c) by C_2 and add these equations to (3.1a) to obtain (3.1).

The important thing about (3.1a, b, c) is that they are uncoupled linear equations, each of which can be integrated out from the origin as any ordinary differential equation.

The method of solving such equations is straightforward. One expands about the origin in the form

$$u^{(0)}r=\sum_{i=1} a_0^{(i)}r^i.$$

The method of obtaining recursion relations for the $a_0^{(i)}$ is very well known.[6] Each $a_0^{(i)}$ eventually depends only on $a_0^{(1)}$. This coefficient is arbitrary corresponding to the arbitrariness in the normalization of the homogeneous equation (of which the phase shift is independent). We evaluated the first few $a_0^{(i)}$ analytically from which we could also evaluate the starting values of $u^{(0)}$ necessary for the outward numerical integration of the differential equation. A similar procedure was used on the inhomogeneous equations. The basic mesh was taken as $h=0.05$ and the equations were integrated to $r=20$.

When the $u^{(i)}(r)$ have been determined, the C_1 and C_2 can be determined as follows: Formal substitution of (3.3) into the two equations (3.2) yields two equations for C_1 and C_2 whose coefficients are integrals over the functions $u^{(i)}(r)$. These integrals can be evaluated once the $u^{(i)}(r)$ have been found, and the inhomogeneous equations for C_1 and C_2 can be uniquely solved for C_1 and C_2. With these known values, the final function $u(r)$ can be found from (3.3).

The phase shift in the case of an arbitrary angular momentum wave can be found from the formula

$$\delta_l=\tan^{-1}\left(\frac{j_l(kr)}{n_l(kr)}\right)-N\pi+Q\pi+\tan^{-1}\left(\frac{s_l}{f_l-\Delta_l}\right), \tag{3.4}$$

which, as is well known, is independent of r for values of r beyond which the potential is negligible. j_l and n_l are the regular and irregular spherical Bessel functions

---

[5] K. Omidvar, New York University Research Report No. CS-37 (unpublished). We are indebted to Dr. Omidvar for sending us a copy of his report and discussing his method with us. This method was also developed independently by I. Percival and R. Marriott. [See R. Marriott, Proc. Roy. Soc. (London) **72**, 121 (1958).]

[6] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957), p. 81.

defined in Morse and Feshbach.[7] s_l and Δ_l are functions of $x=kr$ defined in Blatt and Weisskopf.[8] f_l is r times the logarithmic derivative of the scattered function $u_l(r)$:

$$f_l=\frac{r(d/dr)u_l(r)}{u_l(r)}.$$

The arctangents in (3.4) are to be taken between $-\pi/2$ and $\pi/2$. N is the number of nodes in $n_l(kr)$; Q is the number of times (as a function of r) that the function $f_l-\Delta_l$ changes from positive to negative sign.[9]

The scattering lengths that we finally obtained using this procedure are practically the same as those obtained by us some time ago using the iterative method of solution.[10]

4. RESULTS AND DISCUSSION

Calculations have been carried out for s-, p-, and d-wave scattering and the results are given in Tables I, II, and III.

TABLE I. S-wave phase shifts in radians.

	Singlet (+)			Triplet (−)		
k	Exchange	Exchange adiabatic	Polarized orbital	Exchange	Exchange adiabatic	Polarized orbital
0[a]	8.10	6.5	5.8	2.35	1.9	1.9
0.01	3.0606	3.077	3.084±0.001	3.1181	3.123	3.123±0.001
0.05	2.746	2.821	2.855	3.024	3.048	3.046
0.1	2.396	2.522	2.583	2.907	2.949	2.945
0.2	1.870	2.025	2.114	2.679	2.737	2.732
0.3	1.508	1.654	1.750	2.461	2.528	2.519
0.4	1.239	1.374	1.469	2.257	2.329	2.320
0.5	1.031	1.157	1.251	2.070	2.146	2.133
0.75	0.694	0.815	0.908	1.679	1.764	1.745
1.00	0.543	0.666	0.758	1.391	1.480	1.460

[a] The $k=0$ entries are scattering lengths. Our numerical results for the phase shifts are uncertain by about 5 in the last place (except where otherwise indicated). The scattering lengths are defined as the negative of this quantity by many English authors. The exchange results for s and p waves check those of Omidvar (reference 5).

TABLE II. p-wave phase shifts in radians.

	Singlet			Triplet		
k	Exchange	Exchange adiabatic	Polarized orbital	Exchange	Exchange adiabatic	Polarized orbital
0.1	−0.0012	0.0052	0.00481	0.00214	0.0095	0.0090
0.3	−0.0241	0.0232	0.0322	0.0511	0.121	0.098
0.5	−0.0703	0.0133	0.0392	0.169	0.311	0.245
0.75	−0.1126	−0.00059	0.0347	0.304	0.407	0.390
1.0	−0.1059	0.0189	0.0428	0.358	0.503	0.453

TABLE III. d-wave phase shifts in radians.

	Singlet			Triplet		
k	Exchange	Exchange adiabatic	Polarized orbital	Exchange	Exchange adiabatic	Polarized orbital
0.1[a]						
0.3	−0.000570	0.0108	0.0113	0.000763	0.0123	0.0118
0.5	−0.00397	0.0249	0.0266	0.00698	0.0371	0.0350
0.75	−0.0123	0.0387	0.0456	0.0274	0.0824	0.0746
1.00	−0.0176	0.0493	0.0627	0.0555	0.128	0.112

[a] The d-wave phase shifts at $k=0.1$ were still changing significantly at $r=20$. In all cases they were much smaller in absolute value than at $k=0.3$. Recent calculations of the exchange-approximation d-wave phase shifts by T. L. John (to be published) are in agreement with our results.

We shall discuss first the s-wave results. The s-wave scattering lengths (a) may be deduced from the $k=0.01$ phase shifts (δ) using the well-known formula[11]

$$k\cot\delta=-1/a+\cdots+\tfrac{1}{2}r_0k^2+\cdots. \tag{4.1}$$

r_0 is the effective range. [It is assumed that all terms beyond the first term in (4.1) have a negligible effect on a at this energy. The significance of the dots between the first and second terms on the right-hand side of (4.1) will be explained below.] For the polarized orbital approximation these are seen to be $a_+=5.8$ and $a_-=1.9$ in the singlet and triplet cases, respectively. These are slightly below the upper bounds set by Rosenberg, Spruch, and O'Malley (RSO).[12] The remaining two approximations give singlet scattering lengths which are greater than the singlet upper bound. That the exchange adiabatic approximation gives an $a_+=6.5$ is in marked contrast to the results of Staver[13] who obtained a value of $a_+=3.47$. His calculation corresponds to the exchange adiabatic approximation with the usual kind of polarization potential for r large; this potential, however, approaches infinity (as $-r^{-1}$) as $r\rightarrow 0$. The small scattering length is therefore due to the exaggerated strength of his polarization potential near the origin. An apparently similar result was obtained by Martin, Seaton, and Wallace[14] with a

---

[7] P. M. Morse and H. Feshbach, *Methods of Thoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 622.

[8] J. B. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons, Inc., New York, 1952), p. 332.

[9] Most references give formulas only for the tangent of the phase shift. A phase shift obtained by inverting such a formula is undefined modulo π. The absolute phase, which includes the correct number of multiples of π, is gotten by comparing $u_l(r)$ to the unperturbed $krj_l(kr)$ from the origin to where $u_l(r)$ achieves its asymptotic form. Multiples of π in the phase shift correspond to extra nodes in $u_l(r)$ relative to $krj_l(kr)$. Formula (3.4) can be considered an operational means of making this comparison to get the absolute phase shift.

[10] This solution was as close as we could come, using the iterative procedure, to a self-consistent solution. The programming of this approach was done by Mr. J. L. Hammersmith of the U. S. Naval Research Laboratory, September, 1958.

[11] See reference 8, p. 62.

[12] L. Rosenberg, L. Spruch, and T. O'Malley, Phys. Rev. **119**, 164 (1960). Their upper bounds for the singlet and triplet scattering lengths are $a_+=6.23a_0$, $a_-=1.91a_0$, respectively. We should like to thank Dr. Spruch for valuable discussions. These results assume only that the H^- ion has one bound state, and this of singlet spin.

[13] T. B. Staver, Arch. Math. Naturvidenskab **B51**, 29 (1951).

[14] V. M. Martin, M. J. Seaton, and J. B. G. Wallace, Proc. Phys. Soc. (London) **72**, 701 (1958). The effect of the polarization potential $V_p(r)$ on the exchange approximation scattering lengths is proportional to $\int_0^\infty V_p(r)u_0^2(r)dr$, where $u_0(r)$ is the s-wave radial function. For $u_0(r)$ these authors used the "exchange-approximation" function, whereas correctly one should use the exchange-adiabatic $u_0(r)$ calculated with the polarization potential $V_p(r)$. The s-wave function (in any of these approximations) has a node around $r=5$. The effect of the added attraction $V_p(r)$ is to pull this node closer to the origin and effectively decrease $u_0(r)$ in the region $r=1$ to 5 where the main contribution to the integral arises. The effect of the decrease is emphasized because $u_0(r)$

polarization potential which in fact vanished at the origin. This similarity of results led them to the conclusion that the exchange adiabatic approximation itself is not good and overestimates the effects of polarization near the origin. We have indicated in footnote 14 that MSW's result is due to an unjustified approximation in evaluating the effects of the exchange adiabatic potential rather than to the potential itself. The similarity with Staver's singlet result is an unfortunate coincidence. We therefore conclude, by virtue of the closeness of our exchange adiabatic results with the polarized orbital results, that the former approximation can give quite satisfactory results with a judiciously chosen potential. It is worth noting that MSW, using a variational calculation with wave functions similar to (2.1), have also obtained scattering lengths very close to those in Table I. This corroborates the assertion made in reference 2 that correctly symmetrized wave functions containing the same kind of adiabatic distortion at large distances will give rise to phase shifts which are relatively insensitive to how these distortions die off at small distances. This assertion, however, must be restricted to s waves. The higher partial waves become increasingly more sensitive to the form of the adiabatic potential in the nonasymptotic region.

The fact that singlet exchange adiabatic result gives a phase shift above the RSO upper bound, whereas the polarized orbital result is *below* this bound is the best indication we have yet had that the exchange polarization terms are meaningful. On the assumption that the significance of these terms continues to energies greater than zero, and on the basis of the result of Ohmura and Ohmura (see below), we feel that we can justifiably say that our s-wave phase shifts are correct to within 10%, and that the correct singlet scattering lengths are probably between our result and the RSO bound. The relative accuracy of higher partial waves is almost certainly not so great. However, since the polarizability causes a more drastic change in these results relative to results in which no long-range polarization is included, we feel that these results are also valuable. In particular we are confident that the change in sign of the singlet p- and d-wave phase shifts predicted by our polarization calculations relative to the exchange calculation is real. A quantitative justification for these assertions obviously depends on a more rigorous theory of scattering. A preliminary report of such a theory has recently appeared.[15]

A singlet scattering length, $a_+=6.17$, has been obtained by Ohmura and Ohmura.[16] Their calculation utilizes a series expansion for $k\cot\delta$ about the bound-state wave function of the H$^-$ ion. This is to be contrasted with the ordinary effective-range expansion which is about the zero-energy scattered wave function. The former may be written

$$\lim_{k\to 0} k\cot\delta = -\gamma+\tfrac{1}{2}\rho\gamma^2+O[\gamma^4]. \tag{4.2}$$

The quantities γ and ρ may be deduced with great accuracy from the Perkeris wave function of the H$^-$ ion.[17] γ is the square root of the H$^-$ electron affinity; from Perkeris' calculation $\gamma=0.2355883$, and Ohmura and Ohmura find $\rho=2.646$. The point of the Ohmura calculation is to equate the above with the ordinary effective-range expansion (4.1) in the limit $k\to 0$. They

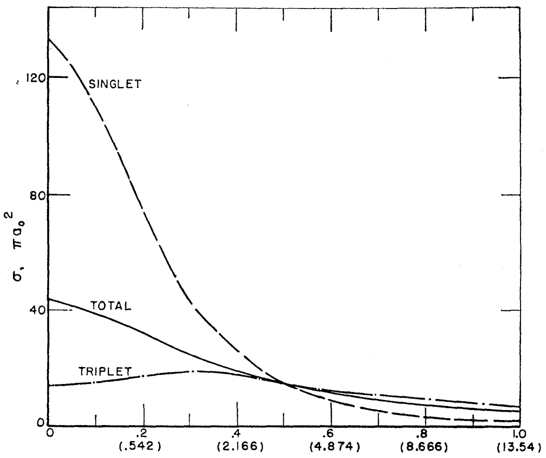

FIG. 1. Polarized orbital integrated cross sections vs k. (k^2 is the energy of the incident electrons in rydbergs; 1 ry = 13.6 ev.) Results include s-, p-, and d-wave phase shifts.

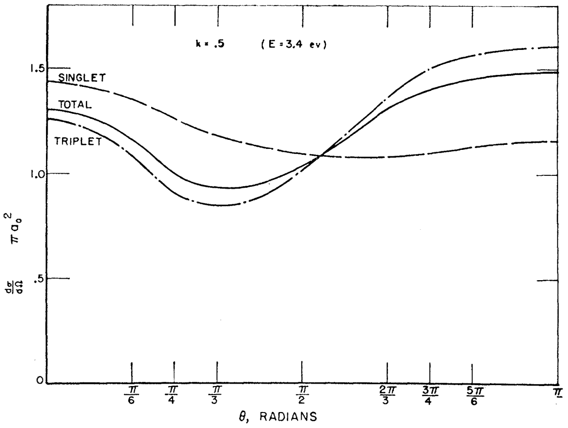

FIG. 2. Pol. orbital differential cross sections, $d\sigma/d\Omega$, for $k=0.5$ ($k^2=3.4$ ev).

---

appears squared in the integrand. We have utilized our own exchange-adiabatic functions in this integral and found that the integral is decreased enough so that the exchange scattering lengths are in approximate accord with our exchange-adiabatic results.

[15] A. Temkin, Phys. Rev. Letters **4**, 566 (1960). Dr. Bederson has informed us that his group intends to measure the spin flip cross section. This will allow for the determination of the relative sign of the singlet and triplet phase shifts.

[16] T. Ohmura and H. Ohmura, Phys. Rev. **118**, 154 (1960). This work is based on T. Ohmura, Y. Hara, and T. Yamanouchi, Progr. Theoret. Phys. (Kyoto) **20**, 82 (1958).

[17] C. L. Perkeris, Phys. Rev. **112**, 1649 (1958).

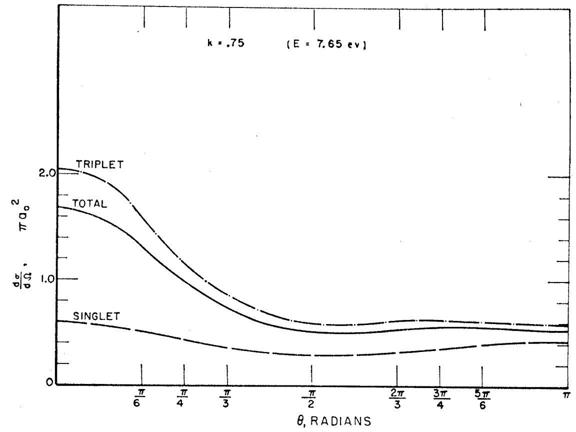

FIG. 3. Pol. orbital differential cross sections for $k=0.75$ ($k^2=7.65$ ev).

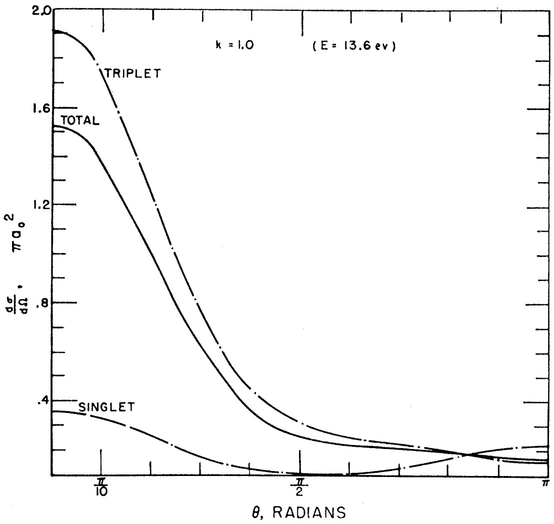

FIG. 4. Pol. orbital differential cross sections for $k=1.00$ ($k^2=13.6$ ev).

get the above value for a_+, and from (4.2) one would expect the error in a_+ to be of the order of γ^2, which would be of the order of one percent. Spruch, O'Malley, and Rosenberg[18] have shown that if one considers the scattering of a particle from an α/r^4 potential, then, in the effective-range expansion, r_0 becomes infinite. This is indicative of the fact that the effective-range expansion is altered and a term proportional to k appears between the constant and quadratic terms in (4.1). It has not been shown that the same thing holds in the electron-hydrogen case, however if an α/r^4 term appears in the potential for the scattered wave (and this is a basic consequence of the method of polarized orbitals), then it is extremely likely that a similar alteration will take place in that case also. The appearance of the k term is of course indicative of the series (4.1) being slowly convergent. In the limit that $\gamma \to 0$, however, the two series, (4.1) and (4.2), become identical. Since γ is in fact small, the series cannot be too different, which would indicate that (4.2) is also slowly convergent. We therefore expect that the error in Ohmura's scattering length is of order γ, i.e., of about 5%.

The polarized orbital phase shifts are larger for all partial waves than those corresponding to the exchange approximation. In the case of the s waves this means that the phase shifts are closer to π; thus the predicted cross-section curve (Fig. 1) is lower for small energies than the exchange approximation results and those of some of the more elaborate calculations in which no long-range polarization was included.[19] Figure 1 contains the p- and d-wave contributions also, but their effect is small at these energies. The total cross section, σ_{total}, is related to the singlet (σ_s) and triplet (σ_t) cross sections by

$$\sigma_{\text{total}}=\tfrac{1}{4}(3\sigma_t+\sigma_s). \tag{4.3}$$

All of these cross sections are in principle measurable.

The p-wave phase shifts are small, as they are in most of the other calculations so that distinguishing the p-wave predictions of various calculations on the basis of scattering experiments will probably be a long time in forthcoming. Some information about the singlet p-wave shifts from the photodetachment of electrons from H^- may be attainable. However, since that cross section is much more sensitive to the ground-state wave function of the H^- ion, conclusions about the phase shifts determined from presently available continuum functions on the basis of the agreement of calculated results with experiment[20] would seem to be unwarranted.

The d-wave calculation was made to test whether these phase shifts were large enough to explain the apparent discrepancy between the experimental results of Brackmann, Fite, and Neynaber[21] and Bederson, Malamud, and Hammer.[22] As was explained in II, a large d-wave phase shift could interfere destructively with the s wave in the cone of observation of BFN to explain their small observed cross section but interfere constructively in the remaining parts of the scattering sphere to explain the resonance in the observations of BMH. Our calculated phase shifts are at least an order of magnitude smaller than those required to explain this discrepancy.[2] Nevertheless they are many times larger than those of the exchange approximation. (In

---

[18] L. Spruch (private communication). (See footnote 12.)

[19] B. H. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, Proc. Roy. Soc. (London) **A70**, 223 (1957) contains a fairly complete list of references.

[20] S. J. Smith and D. S. Burch, Phys. Rev. Letters **2**, 165 (1959); Phys. Rev. **116**, 1125 (1959).

[21] R. T. Brackmann, W. L. Fite, and R. H. Neynaber, Phys. Rev. **112**, 1157 (1958), hereafter referred to as BFN.

[22] B. Bederson, H. Malamud, and J. Hammer, Technical Report No. 2, Electron Scattering Project, College of Engineering, New York University (unpublished). This will be referred to as BMH.

the triplet spin state they are of opposite sign.) This demonstrates very vividly that the long-range polarization potential has a proportionately larger effect on the higher partial waves. The results are in accord with the argument of Bransden *et al.*,[19] that the dipole polarizability make the $l>0$ phase shifts approach zero as k^2 (as $k\rightarrow 0$) rather than k^{2l+1} as predicted by the Born approximation with no r^{-4} potential present. The (relatively) large d-wave shifts, although they do not indicate any resonance in the total cross-section curve, do give considerable structure to the differential cross section even for as low an energy as 3 ev (see Figs. 2, 3, and 4).

(After this work was done, measurements of the angular distribution were completed at General Atomic Division of General Dynamics by Gilbody, Stebbings, and Fite.[23] We are indebted to them for advance communication of their results. Both the shape and absolute values of their angular distributions seem to be in satisfactory agreement with our differential cross-section curves. A more detailed analysis of this experiment and the ability to estimate the error in the absolute value may allow one to distinguish between the polarized orbital results and other calculations.)

---

[23] H. B. Gilbody, R. F. Stebbings, and W. L. Fite, following paper [Phys. Rev. 121, 794 (1961)].

PHYSICAL REVIEW VOLUME 121, NUMBER 3 FEBRUARY 1, 1961

Collisions of Electrons with Hydrogen Atoms. VI. Angular Distribution in Elastic Scattering*

H. B. Gilbody, R. F. Stebbings, and Wade L. Fite
John Jay Hopkins Laboratory for Pure and Applied Science, General Atomic Division of General Dynamics Corporation, San Diego, California

(Received September 28, 1960)

The angular distribution of electrons scattered elastically by hydrogen atoms has been determined for electron energies below 10 ev. The elastically scattered electrons arising from the interaction of crossed electron and modulated hydrogen-atom beams were examined over an angular range extending from 30° to 120°. The results are discussed with reference to other recent experimental and theoretical developments.

I. INTRODUCTION

THE elastic scattering of electrons by atoms and molecules has been of widespread interest for many years, particularly in the fields of astrophysics and gaseous electronics. Following the development of quantum mechanics in the mid-1920's, it was natural that the elastic scattering of electrons by atomic hydrogen should become the subject of many theoretical investigations. The wave functions of the target atom are completely and exactly known, so that calculated cross sections should be somewhat more accurate than in more complex scattering problems. A review of the theoretical work on this problem, however, reveals a considerable variation in results, depending on the scattering approximations used in the calculations. Clearly, it was desirable to carry out experiments on elastic scattering by atomic hydrogen to determine which of the calculations were superior.

The chemical instability of the hydrogen atom made experimentation in this area difficult, but by 1955 the development of modulated-beam techniques and crossed-beam experiments permitted the first experimental studies to be made. In these experiments a beam of atomic hydrogen, produced either by thermal dissociation in a tungsten furnace or in a high-frequency gas discharge tube, was crossed with a beam of electrons, and the electrons scattered by the beam were detected. These electrons gave rise to a signal which occurred at the beam modulation frequency and in a specified phase, while electrons scattered by the background gas gave rise to a dc signal plus noise at the modulation frequency.

The first experiment, to measure the cross section for scattering of electrons at angles greater than about 7°, was carried out by Bederson, Malamud, and Hammer[1] (BMH). The results of their experiments were surprising, in that they exceeded all of the theoretical predictions.

This immediately refocused attention on the elastic-scattering problem, and a fundamental question arose in regard to the scattering theory. This question concerned the role of the partial cross sections higher than the s-wave cross section. At low energies the quantization of angular momentum dictates that partial cross sections for $l>0$ be rather small, and most of the theoretical work prior to 1958 had been carried out for s-wave contributions only. It was conceivable that higher partial cross sections were significant—that forward scattering could be more prominent than had been

---

* This research was supported by a joint General Atomic-Texas Atomic Energy Research Foundation program on controlled thermonuclear reactions.

[1] B. Bederson, H. Malamud, and J. Hammer, Bull. Am. Phys. Soc. 2, 122 (1957). See also New York University Technical Report No. 2, 1958 (unpublished).