A Note on the Scattering of Electrons from Atomic Hydrogen

A. Temkin
National Bureau of Standards, Washington, D. C.
(Received May 26, 1959)

The distortion of atomic hydrogen by a slowly moving electron at a large distance from the center of the atom is examined. The problem is the initial phase of a previously described method for the calculation of electron scattering which takes this distortion into account. The initial (static) problem is solved analytically and extended to include higher order effects of the interaction of the electron with the atomic cloud. The construction of a wave function to describe scattering starting from the solution of the static problem is clarified. This yields as an incidental result a new approximation of the second order perturbation energy associated with the above distortion. A short discussion of the present experimental results for this scattering process is included.

1. INTRODUCTION

AN earlier paper[1] presented a method for calculating the elastic scattering of slow electrons from atoms, with special emphasis on the distortion of the target by the incoming electron. Roughly speaking, the mechanism of accounting for this distortion is adiabatic in that the atom is assumed to follow the instantaneous motion of the scattered electron. Mathematically, however, there are several ways of formulating this idea, which have given rise to various "adiabatic" theories of scattering. When hydrogen is the target atom, the relationship of these methods becomes particularly clear. This introduction will be concerned with sketching and relating some of these various methods. Thereafter we shall be concerned with obtaining analytic results relevant to the method of I in the case of hydrogen and extending the method to include additional physical effects. The practical significance of the higher order corrections, it must be emphasized, is uncertain. This is because nonadiabatic effects are certainly important corrections.[2] These corrections, however, will be different for the different adiabatic theories.

Most of the methods which have been tried in the low-energy scattering problem can be related to each other within the framework of the variational form of the Schrödinger equation:

$$\delta \int \Psi^*(\mathbf{r}_1,\mathbf{r}_2)[H-E]\Psi(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = 0. \quad (1.1)$$

H is the complete Hamiltonian of the (two-electron) system in the field of the nucleus, E is the given total energy, and $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ is the desired wave function. The spin states of the electron pair can be treated separately by assigning the symmetry of the spatial wave function, $\Psi(\mathbf{r}_1,\mathbf{r}_2)$, under the permutation of $\mathbf{r}_1$ and $\mathbf{r}_2$ (symmetric for singlet and antisymmetric for triplet spin state). The wave function can also be treated separately for different values of the total orbital angular momentum. If the target hydrogen atom is in its ground state $(1s)$, then

the total orbital angular momentum is equal to the angular momentum of the (partial wave) of the bombarding electron.

The different methods can be classified according to the assumptions made regarding the structure of $\Psi(\mathbf{r}_1,\mathbf{r}_2)$. One of the simplest methods is to assume $\Psi(\mathbf{r}_1,\mathbf{r}_2)=u(\mathbf{r}_1)\Phi_0(\mathbf{r}_2)$, where $\Phi_0(\mathbf{r}_2)$ is the ground state of the hydrogen atom.[3] Note that this form is unsymmetrized and therefore does not distinguish between singlet and triplet scattering. The variation with respect to $u(\mathbf{r}_1)$ yields as its Euler-Lagrange equation the Schrödinger equation for an incident electron in the averaged central field of the unperturbed hydrogen atom. This method has accordingly been called by Bransden *et al.* the central field approximation.[4]

Morse and Allis[5] introduced a symmetrized form of the wave function (exchange approximation)

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=u(\mathbf{r}_1)\Phi_0(\mathbf{r}_2)\pm u(\mathbf{r}_2)\Phi_0(\mathbf{r}_1). \quad (1.2)$$

The resulting Euler-Lagrange equation is integrodifferential in nature and has been solved numerically. The symmetrization has a larger effect on the phase shift than it does on the energy levels of bound states.

To take into account the distortion of the atom by the incident electron, a potential energy term representing the interaction of the electron with an induced dipole in the atom has been added to the Euler-Lagrange equations of both the central field[6] and exchange approximations.[7] In the manner used by Bates and Massey this term is of the form $\alpha/(r_1^2+d^2)^2$, where α is the polarizability of the atom, and d is a cutoff parameter inserted to prevent this term from diverging at the origin. The addition of such a term to the equations arising from the exchange approximation has been called the exchange-adiabatic approximation by Martin *et al.*[8]

[1] A. Temkin, Phys. Rev. **107**, 1004 (1957). This paper will be referred to as I, and the equations referring to it will be prefixed by an I.

[2] M. Mittleman and K. Watson, Phys. Rev. **113**, 198 (1959).

[3] J. Holtsmark, Z. Physik **55**, 437 (1929).

[4] Bransden, Dalgarno, John, and Seaton, Proc. Phys. Soc. (London) **71**, 877 (1958). This paper will be denoted as BDJS.

[5] P. M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933).

[6] J. Holtsmark, Z. Physik **66**, 47 (1930).

[7] D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) **A192**, 1 (1947).

[8] Martin, Seaton, and Wallace, Proc. Phys. Soc. (London) **72**, 701 (1958).

The procedure of I takes the distortion of the atom into account by modifying the Ansatz for the wave function in the variational principle (1.1) rather than by the addition of an *ad hoc* term in the one particle Euler-Lagrange equation. The modification consists of adding to $\Phi_0(\mathbf{r}_2)$ of Eq. (1.2) a function of $\mathbf{r}_2$ which depends parametrically on the position of the incident electron $\mathbf{r}_1$. (This method will accordingly be called the method of polarized orbitals.) The determination of this function is equivalent for large r_1 to first order perturbation theory for the distortion of the atomic cloud by an incident electron, as will be shown in Sec. 2. More specifically, the treatment of I only considered the dipole part of the interaction between the electron and the atom and determined the function numerically. This contribution can be found analytically in the case of hydrogen and the method can be extended to include higher multipoles. With this modified Ansatz, the Euler-Lagrange equation contains dipole and, if desired, higher multipole terms representing the interaction of the electron with the atomic cloud.

This multipole expansion is equivalent for large r_1 to the second order perturbation energy of a static electron with the atomic charge cloud. However the expansion is an asymptotic series unless one restricts the integrations over r_2 in deriving these terms. In Sec. 3 it will be shown that such a restriction yields an expansion which is convergent for all values of r_1. Although this series does not converge to the value of the second order energy, a numerical comparison with the latter (which has been calculated by Dalgarno and Lynn[9]) shows that it is a more accurate approximation than various other approximations which have been used.

An additional feature of the method of polarized orbitals is the appearance of exchange polarization terms in the Euler-Lagrange equations in addition to the dipole polarization potential. These terms arise because the function expressing the polarization of the atom also occurs with its arguments exchanged in the symmetrized form of the variational Ansatz [see Eq. (2.1)]. To include the effect of these terms in a treatment which does not utilize fully-antisymmetric wave functions, in the exchange-adiabatic approximation for example, would clearly require an admixture of excited states, which would be interpreted as nonadiabatic perturbations. Thus it is likely that the conditions for the validity of the Born-Oppenheimer approximation are less stringent when exchange is included than when there is no exchange.[2] The exchange polarization terms have been found to have an important effect on the phase shifts.[8]

Section 4 contains a remark concerning the current experimental situation.

[9] A. Dalgarno and N. Lynn, Proc. Roy. Soc. (London) **A70**, 223 (1957).

2. RELATION OF PERTURBATION THEORY TO THE DETERMINATION OF THE POLARIZED FUNCTION $\Phi^{(\mathrm{pol})}$

The method of I utilizes as the variational Ansatz the wave function

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

$$\pm \frac{u(\mathbf{r}_2)}{r_2}[\Phi_0(\mathbf{r}_1)+\Phi^{(\mathrm{pol})}(\mathbf{r}_2;\mathbf{r}_1)]. \quad (2.1)$$

Φ_0 is the ground state wave function of the hydrogen atom, and $\Phi^{(\mathrm{pol})}(\mathbf{r}_1;\mathbf{r}_2)$ represents the distortion of this state by an incoming electron at the *fixed* point $\mathbf{r}_1$. The determination of $\Phi^{(\mathrm{pol})}(\mathbf{r}_1;\mathbf{r}_2)$ was called the static problem. We shall now investigate its connection with perturbation theory.

The stationary state wave functions of hydrogen will be written

$$\Phi_{nlm}(\mathbf{r}_2) = \frac{u_{nl}(r_2)}{r_2}Y_{lm}(\Omega_2). \quad (2.2)$$

[In this notation Φ_0 of (2.1) becomes Φ_{100}.] The $u_{nl}(r_2)$ satisfy

$$\left[-\frac{d^2}{dr_1^2}+\frac{l(l+1)}{r_2^2}-\frac{2}{r_2}-\epsilon_n\right]u_{nl}(r_2)=0, \quad (2.3)$$

where

$$\epsilon_n = -n^{-2}. \quad (2.4)$$

(Our units are lengths in Bohr radii: $a_0 = \hbar^2/me^2$, and energy in Rydbergs: $1\ \mathrm{ry} = (2ma_0^2/\hbar^2)^{-1}$.)

The perturbation potential due to an incident electron at $\mathbf{r}_1$ *including* its interaction with the nuclear charge is

$$V(\mathbf{r}_1,\mathbf{r}_2) = -\frac{2}{r_1}+\frac{2}{|\mathbf{r}_1-\mathbf{r}_2|}. \quad (2.5)$$

The first order perturbed wave function of electron 2 due to this potential is

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \Phi_{100}(r_2)-\sum_{n,l}{}' \frac{\langle nl0|V(r_1,r_2')|100\rangle}{\epsilon_n-\epsilon_1}\Phi_{nl0}(r_2). \quad (2.6)$$

In (2.6) the z axis of $\mathbf{r}_2$ has been taken along $\mathbf{r}_1$; $\mathbf{r}_2'$ is the variable of integration. In order to establish the correspondence with the static problem, we shall now write an approximate form of (2.6) consistent with the fact that we are interested in $\psi(\mathbf{r}_1,\mathbf{r}_2)$ for points $r_1>r_2$. The exact form of the matrix element in (2.6) is (for $l\neq0$)

$$\langle nl0|V(r_1,r_2')|100\rangle Y_{lm}(\Omega_2)$$

$$=\left[\frac{1}{r_1^{l+1}}\int_0^{r_1}u_{nl}(r_2')r_2'^{l}u_{10}(r_2')dr_2'\right.$$

$$\left.+r_1^l\int_{r_1}^{\infty}u_{nl}(r_2')\frac{1}{r_2'^{l+1}}u_{10}(r_2')dr_2'\right]\frac{2}{(4\pi)^{\frac12}}P_l(\cos\theta_2)$$

$$\equiv Q(r_1)\frac{2}{(4\pi)^{\frac12}}P_l(\cos\theta_2). \qquad (2.7)$$

In the limit $r_1\to\infty$ the second integral in (2.7) vanishes. Our approximation is

$$Q(r_1)\cong\frac{1}{r_1^{l+1}}\int_0^{\infty}u_{nl}(r_2')r_2'^{l}u_{10}(r_2')dr_2'$$

$$=\frac{1}{r_1^{l+1}}\langle nl|r_2'^l|10\rangle. \qquad (2.8)$$

[The $l=0$ term of (2.6) drops out in this approximation.] Calling the wave function resulting from (2.8) $\Phi(r_1,r_2)$, we have

$$\psi(r_1,r_2)\cong\Phi(r_1,r_2)$$

$$=\Phi_{100}(r_2)-\sum_{l=1}^{\infty}\frac{2}{r_1^{l+1}}\frac{P_l(\cos\theta_2)}{(4\pi)^{\frac12}}$$

$$\times\sum_{n=l+1}^{\infty}\frac{\langle nl|r_2'^l|10\rangle}{\epsilon_n-\epsilon_1}(u_{nl}(r_2)/r_2). \qquad (2.9)$$

It must be emphasized that $\Phi(r_1,r_2)$ is equal to $\psi(r_1,r_2)$ only in the limit $r_1\to\infty$, and it is meaningful as an approximation only when $r_1>r_2$.

It is well known that the summation in (2.6) for the first order perturbed wave function is a formal expansion of the solution of a differential equation for $\psi(r_1,r_2)$. This equation cannot be easily solved; however the equation corresponding to approximation (2.9) can be readily solved. This not only bypasses the necessity of performing the sum over n in (2.9), but it will enable us to establish the connection with the approach of I to the static problem.

One can then verify that $\Delta\Phi\equiv\Phi_{100}(r_2)-\Phi(r_1,r_2)$ satisfies the differential equation

$$\left[-\nabla_2^2-\frac{2}{r_2}-\epsilon_1\right]\Delta\Phi=2\sum_{l=1}^{\infty}\frac{r_2^l}{r_1^{l+1}}\Phi_{100}(r_2)P_l(\cos\theta_2). \qquad (2.10)$$

This equation can be solved by expanding $\Delta\Phi$ in Legendre polynomials. Thus, letting

$$\Delta\Phi=\sum_{l=1}^{\infty}\frac{u_{1s\to l}(r_2)/r_2}{r_1^{l+1}}\frac{P_l(\cos\theta_2)}{(4\pi)^{\frac12}}, \qquad (2.11)$$

we can reduce (2.10) to the set of equations

$$\left[-\frac{d^2}{dr_2^2}-\frac{2}{r_2}+\frac{l(l+1)}{r_2^2}-\epsilon_1\right]u_{1s\to l}(r_2)=2r_2^l u_{1s}(r_2). \qquad (2.12)$$

(The spectroscopic notation $l=s$, p, $\cdots$ will be used interchangeably with $l=0$, 1, $\cdots$.) From (2.11) one can see that the dominant contribution to $\Delta\Phi$ comes from the $l=1$ term. The equation for it can be rewritten with the help of (2.3) in the form

$$\left[-\frac{d^2}{dr_2^2}+V_{1s\to p}(r_2)\right]u_{1s\to p}(r_2)=2r_2 u_{1s}(r_2), \qquad (2.13)$$

where

$$V_{1s\to p}(r_2)=\frac{1}{u_{1s}(r_2)}\left[\frac{d^2}{dr_2^2}u_{1s}(r_2)\right]+\frac{2}{r_2^2}. \qquad (2.14)$$

Equations (2.13) and (2.14) are a special case of the type of equations which Sternheimer[10] used in the calculation of atomic and ionic polarizabilities [see I (3.19) and I (3.21) for $n=1$, $l=0$, $l'=1$]. A solution of (2.13) which vanishes at $r_2=0$ and $r_2=\infty$ can be found[11]:

$$u_{1s\to p}(r_2)=2e^{-r_2}(\tfrac12 r_2^3+r_2^2). \qquad (2.15)$$

(Note that $u_{1s}(r_2)=2r_2 e^{-r_2}$.) Sternheimer's equations for higher multipoles is therefore equivalent to (2.12), the solution of which is

$$u_{1s\to l}(r_2)=2e^{-r_2}\left(\frac{r_2^{l+2}}{l+1}+\frac{r_2^{l+1}}{l}\right). \qquad (2.16)$$

Thus from (2.11)

$$\Phi(r_1,r_2)=\Phi_{100}(r_2)-\sum_{l=1}^{\infty}\frac{2}{r_1^{l+1}}$$

$$\times e^{-r_2}\left(\frac{r_2^{l+1}}{l+1}+\frac{r_2^l}{l}\right)\frac{P_l(\cos\theta_2)}{(4\pi)^{\frac12}}. \qquad (2.17)$$

Comparing this with (2.9), we see that Sternheimer's approach is equivalent to summing over n in that expression.

We can comment on the remark made above that the same procedure could in principle be followed in solving for the exact first-order wave function $\psi(r_1,r_2)$ of (2.6). The difficulty there is that one must use the complete decomposition of the perturbation $V(r_1,r_2)$, of

[10] R. M. Sternheimer, Phys. Rev. 96, 951 (1954).

[11] I am indebted to Mr. J. L. Hammersmith of the U. S. Naval Research Laboratory for the analytic solution of this equation. The solution, however, has been obtained by Foley, Sternheimer, and Tycko, Phys. Rev. 93, 734 (1954), and others, all in different contexts. [A bibliographical review is contained in L. C. Allen (unpublished).] Similarly (2.17) was independently obtained by A. Dalgarno and A. Stewart, Proc. Roy. Soc. (London) A238, 269, 276 (1956). The effectiveness of the differential equation approach to perturbation theory has also recently been stressed by C. Schwartz, Ann. Phys. 6, 156 (1959), in which this example has also been worked out.

which the right-hand side of (2.10) is only the part for $r_1 > r_2$. This gives rise to two equations of the type (2.12) for the two regions $r_1 > r_2$ and $r_1 < r_2$. The solutions in these two regions must be appropriately matched. This has been discussed in detail in Sec. 4 of I. The point here is that the approximation implicit in considering only (2.12) is more sharply defined in the perturbation theory approach through (2.8). From either point of view, however, the meaningfulness of (2.17) even as an approximation is certainly restricted to the region $r_1 > r_2$.

3. DIRECT POLARIZABILITY POTENTIAL

The dipole part ($l=1$) of $\Delta \Phi$ of (2.11) is essentially the solution of the static problem of I, and thus it is the $\Phi^{(\text{pol})}$ of (2.1). The additional restriction $r_1 > r_2$ was incorporated in I by a prescription eliminating certain terms which arose in the Euler-Lagrange equations coming from the Ansatz (2.1).[12] This prescription can be succinctly incorporated in $\Phi^{(\text{pol})}$ itself by the use of the step function

$$\epsilon(r_1, r_2) = 1, \quad r_1 > r_2$$
$$= 0, \quad r_1 < r_2. \qquad (3.1)$$

$\Phi_1^{(\text{pol})}(\mathbf{r}_1; \mathbf{r}_2)$ can then be defined [the subscript 1 is added to indicate that we only include the $l=1$ term in (2.11)] by

$$\Phi_1^{(\text{pol})}(\mathbf{r}_1; \mathbf{r}_2) = -\frac{\epsilon(r_1, r_2)}{r_1^2} \frac{u_{1s \to p}(r_2)}{r_2} \frac{P_1(\cos\theta_{12})}{(4\pi)^{\frac{1}{2}}}, \qquad (3.2)$$

where θ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. The variational principle (1.1) with the wave function (2.1) then yields an Euler-Lagrange equation without any unwanted terms. It should be noted that in the exchange term of (2.1) the arguments of the step function in $\Phi_1^{(\text{pol})}(\mathbf{r}_2; \mathbf{r}_1)$ must also be interchanged.

Among the terms arising in the Euler-Lagrange equation for $u(r_1)$ is a direct polarizability potential of the form $-\alpha(r_1)/r_1^4$, with

$$\alpha_1(r_1) = \frac{2}{3} \int_0^\infty r_2 u_{1s}(r_2) u_{1s \to p}(r_2) \epsilon(r_1, r_2) dr_2$$

$$= \frac{2}{3} \int_0^{r_1} r_2 u_{1s}(r_2) u_{1s \to p}(r_2) dr_2$$

$$= \frac{9}{2} - \frac{2}{3} e^{-2r_1} \left(r_1^5 + \frac{9}{2} r_1^4 + 9 r_1^3 \right.$$
$$\left. + \frac{27}{2} r_1^2 + \frac{27}{2} r_1 + \frac{27}{4} \right). \qquad (3.3)$$

---

[12] The mathematical transcription of this restriction is confused in I. This confusion led to the retention of incorrect exchange polarization terms there, so that curve (b) in Fig. 3 of I is not quantitatively justified. However, as we used a smaller value of the polarizability and as the exchange polarization terms tend to offset the effects of the direct polarizability term,[8] it may be that the curve (a) or (b) is still a good estimate of the s-wave scattering from oxygen.

The value $\alpha_1(\infty)$ coincides, as it should, with the atomic polarizability $\alpha = 4.5 a_0^3$.

Disregarding its significance as a polarizability potential, one can consider the quantity $-\alpha_1(r_1)/r_1^4$ as a first approximation to the second order energy, $E_2(r_1)$, associated with the perturbation (2.5). A better approximation can be obtained by including higher l terms in (2.17) retaining in each the step function $\epsilon(r_1, r_2)$. This yields a new approximation to $E_2(r_1)$ which we shall call $E_2^A(r_1)$. One finds that

$$E_2^A(r_1) = -\sum_{l=1}^{\infty} \frac{\alpha_l(r_1)}{r_1^{2l+2}}, \qquad (3.4)$$

with

$$\alpha_l(r_1) = \left\{ \frac{(2l+2)!(l+2)}{l(l+1)2^{2l+1}} - \frac{8(l+2)e^{-2r_1}}{l} \right.$$

$$\times \left[\frac{r_1^{2l+3}l}{2(l+1)(2l^2+5l+2)} + \frac{r_1^{2l+2}}{2(2l+2)} + \frac{r_1^{2l+1}}{2^2} \right.$$

$$+ \frac{r_1^{2l}(2l+1)}{2^3} + \frac{r_1^{2l-1}(2l+1)(2l)}{2^4}$$

$$\left. \left. + \cdots + \frac{(2l+1)!}{2^{2l+3}} \right] \right\}. \qquad (3.5)$$

This series converges for all values of r_1 as opposed to the series obtained by neglecting the step function. The latter may be obtained by letting $r_1 \to \infty$ in (3.5), giving the asymptotic series[13]

$$E_2^{(\text{asymp})}(r_1) = -\sum_{l=1} \frac{(2l+2)!(l+2)}{l(l+1)2^{2l+1}r_1^{2l+2}}, \qquad (3.6)$$

which is to be cut off at its smallest term.

Similarly the direct polarizability potential coming from the Ansatz

$$\Psi' \equiv (u(\mathbf{r}_1)/r_1)\psi(\mathbf{r}_1, \mathbf{r}_2) \pm (u(\mathbf{r}_2)/r_2)\psi(\mathbf{r}_2, \mathbf{r}_1), \qquad (3.7)$$

where ψ is the first order wave function given in (2.6), coincides with the second order energy, $E_2(r_1)$, which has been calculated by Dalgarno and Lynn.[9] The various polarizability potentials are given numerically in Table I, including in the last column the phenomenological $\alpha/(r_1^2 + d^2)^2$ potential with $d = 1.5$ as adopted by BDJS in their p-wave calculation. It should be noted that the entries under $E_2^A(r_1)$ contain only the first four terms of (3.4). Since the remaining terms make a positive contribution, column three is a lower limit of $E_2^A(r_1)$. One can convince oneself that $E_2(r_1)$ is an upper limit of $E_2^A(r_1)$. Therefore the agreement between $E_2^A(r_1)$ and $E_2(r_1)$ is even better than the numerical comparison in Table I would indicate.

---

[13] A. Dalgarno and J. Lewis, Proc. Phys. Soc. (London) **69**, 57 (1956).

TABLE I. Comparison of various direct polarization potentials. (Rigorous and approximate expressions of the second order perturbation energy.)[a]

r_1	$-r_1^4 E_2(r_1)$ from Dalgarno and Lynn[b]	$-r_1^4 E_2^A(r_1)$ from Eq. (3.4)	$r_1^4 E_2^{(asym)}(r_1)$ from Dalgarno and Lewis[c] Eq. (3.6)	$\alpha_1(r_1)$ Eq. (3.3)	$\alpha r_1^4/(r_1^2+d^2)^2$ $\alpha=4.5$, $d=1.5$
1	0.39862	0.194	2.25	0.146715	0.47605
2	2.24816	1.67	6.37504	1.27950	1.8432
3	4.16113	3.54	6.97685	2.81569	2.880
4	5.00429	4.60	5.69395	3.82265	3.4588
5	5.11606	4.92	5.37806	4.27378	3.78754
6	4.99838	4.92	5.0798	4.43395	3.986159
7	4.87067	4.84	4.89180	4.48256	4.11355
8	4.7751	4.77	4.78044	4.49574	4.19953
9	4.70745	4.707	4.71152	4.49902	4.26004
10	4.6659	4.665	4.662	4.49979	4.3044

[a] Columns 2 and 4 have been computed from Table I of reference 9. Column 3 includes the sum of 4 terms in (3.4).
[b] See reference 9.
[c] See reference 13.

There are additional effects in the distortion of the wave function of the orbital electron, 2, by the potential (2.5) which can be evaluated in higher order perturbation theory. The effects of these additional corrections upon the energy have also been investigated by Dalgarno and Lewis.[13] They show that in the asymptotic region (large r_1) these terms make only a small contribution to the energy. For example, third order perturbation theory yields as its first term one proportional to r_1^{-7}, and fourth order starts as r_1^{-8}. This shows, however, that the corrections to the polarization potential in the asymptotic region from each order of perturbation theory are expressible, as in second order perturbation theory, as a series in inverse powers of r_1. It is clear that the sequence of terms to be added to the dipole polarization potential as corrections should be characterized only by the inverse power of each term rather than the order of perturbation of theory from which it arises. Thus r_1^{-7} term of third order perturbation theory should be included before r_1^{-8} of second order perturbation theory, and the latter should be included simultaneously with the r_1^{-8} correction of fourth order perturbation theory.

This consideration that the various orders of perturbation theory get intermixed in the region of large r_1 probably applies even more forcefully in the region of small r_1. Furthermore in this region the nonadiabatic corrections will have their most important effect. Thus the Ansatz (3.7) for the complete wave function is not necessarily better than (2.1). The physical approximation which led us to the generalized form of (2.1) in I was that the main effect on the phase shift in the region of smaller r_1 was dominated by the interaction of the scattered wave with the nuclear charge. According to this assumption it should not make much difference in the phase shift whether one uses Ψ' or Ψ in the variational principle as long as these functions are appropriately symmetrized. For as poor as these functions may be in the regions $r_1 \cong 0$, $r_2 \cong 0$, $r_1 \cong r_2$, they are likely to be better approximations of the exact wave function if they have the correct symmetry than other-

wise. This implies then that it is not the exact form of the direct polarization potential for small values r_1 (as long as the potential vanishes in some reasonably fast way as $r_1 \to 0$) but rather its accuracy for larger values of r_1 and *the consistent incorporation of the exchange polarization terms* which are important for the adiabatic description of scattering. It is in this latter respect that the exchange-adiabatic approximation (which includes no exchange polarization terms) falls short.

4. THE EXPERIMENTAL SITUATION

The experimental situation at the present time is uncertain because of an apparent discrepancy between the results of Bederson, Malamud, and Hammer,[14] and Brackmann, Fite, and Neynaber.[15] The former find a resonance in the total elastic scattering cross section with a peak value of $100\pi a_0^2$ at an incident electron energy of 3 ev. The most extensive calculations for the scattering in the energy range of these experiments are those of Massey and Moisiewitsch[16] (s-wave) and BDJS[5] (s- and p-wave). The latter also include an estimate of the contribution of the higher waves based on the Born approximation, which yields a negligible amount at these energies. Brackmann et al.[15] have looked at the scattering in a right circular cone at 90° to the incident beam. The spread in their data is such that there is agreement with the calculated values of both Massey and Moisiewitsch and BDJS, the agreement with the latter being somewhat better. The extrapolation of the experimental results to the total cross section necessitates some assumption about the scattering in the other parts of the scattering sphere. However, the resonance of Bederson et al. at 3 ev is about 30% higher than the maximum possible for s- and p-wave alone.[17] If one assumes that the difference is due to d-wave scattering, then one can show that there is a d-wave phase shift which will give approximate consistency among the phase shifts of BDJS,[5] the data of Brackmann et al.,[15] and those of Bederson et al.[14] At slightly higher energies exact consistency can be obtained. For example, at incident energy of 5 ev, if η_l^- and η_l^+ represent the triplet and singlet scattering phase shifts, respectively, measured in radians, then it may be verified that the phases $\eta_0^-=1.91$, $\eta_1^-=0.45$, $\eta_0^+=1.09$, $\eta_1^+=0.04$, taken from BDJS, and $\eta_2^-=2.16$, $\eta_2^+=0.98$ will give a total cross section $\sigma=50\pi a_0^2$ in accord with Bederson et al.,[14] and will give a cross

[14] Bederson, Malamud, and Hammer, Bull. Am. Phys. Soc. 2, 122 (1957); Technical Report No. 2, Electron Scattering Project, College of Engineering, New York University (unpublished).
[15] Brackmann, Fite, and Neynaber, Phys. Rev. 112, 1157 (1958).
[16] H. S. W. Massey and B. L. Moisiewitsch, Proc. Roy. Soc. (London) A205, 483 (1951).
[17] Kazem Omidvar, New York University Research Report No. CX-37 (unpublished); Bull. Am. Phys. Soc. 4, 281 (1959), has given a phenomenological, nonadiabatic method to account for the BMH resonance. It should also be pointed out that the results of BMH, although well known to the workers in the field, have not as yet been published.

section of $1.4\pi a_0^2$ in the cone of observation of Brackmann *et al.*, which is within their experimental spread of points. The destructive interference between the *s* and *d* waves at right angles to the incident beam is such as to reduce the scattering there relative to the forward and backward directions by a factor of twenty. These *d*-wave phase shifts, however, are at least an order of magnitude larger than what is expected on the basis of the Born approximation.[5] A calculation of the phase shifts using the method of polarized orbitals is in progress here.

The importance of complete experimental results can be appreciated when one realizes that the assumptions regarding the structure of the wave function that have thus far been made in the scattering problem are still extremely crude compared to what has been done in the bound-state problem.

Lifetime of the 2S State of Atomic Hydrogen*

WADE L. FITE, R. T. BRACKMANN, DAVID G. HUMMER, AND R. F. STEBBINGS
John Jay Hopkins Laboratory for Pure and Applied Science, General Atomic Division of General Dynamics Corporation, San Diego, California
(Received May 25, 1959)

A sensitive test for any mixing of the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ state of atomic hydrogen is the measurement of the rate for single-quantum decay of the 2S atom to the ground state. A new upper limit of this decay rate has been determined. A section along a beam of 2S atoms, produced by electron excitation of a ground-state atom beam, was viewed by an iodine-vapor-filled ultraviolet photon counter, which responds to the Lyman-alpha radiation of the single-quantum decay process. From the counts observed when an electrostatic quenching field was superposed on the counter's field of view, the necessary experimental parameter (product of 2S atom current and counter efficiency) was determined. With the field removed, a portion of the remaining counts could be ascribed to quenching on collision of the 2S atoms with residual gases in the vacuum chamber, the quenching cross sections for which were measured. The decay rate not ascribable to known quenching effects was 420 sec^{-1}. Since unknown quenching effects may have been operative, this figure must be considered only as an upper limit for the natural single-quantum decay rate.

I. INTRODUCTION

RECENTLY Salpeter pointed out that if a permanent electronic electric dipole moment were to exist, one manifestation of it would be a shortening of the lifetime of the $2S_{\frac{1}{2}}$ metastable state of atomic hydrogen.[1] Its presence would mix the metastable state with the $2P_{\frac{1}{2}}$ state, and the lifetime would be intermediate between the $\frac{1}{8}$ sec associated with the two-photon decay[2] of the 2S state and the 1.6×10^{-9}-sec lifetime of the *P* state. Clearly, by measuring a lower limit of the natural lifetime of the $2S_{\frac{1}{2}}$ atom for single-quantum decay, an upper limit for the strength of any perturbation of a fundamental kind, such as that produced by an electronic electric dipole moment, becomes, in principle, determinable. The present paper describes an experiment which yielded a lower limit of 2.4 msec for the lifetime of the 2S atom and in which the cross sections for quenching the metastable atoms in collisions with several common gases were determined.

II. EXPERIMENTAL APPROACH

A schematic diagram of the experiment is shown in Fig. 1. A beam of ground-state hydrogen atoms was produced from a furnace source and a fraction of these were excited by electron impact to the 2S state, in a manner similar to that used by Lamb and Retherford.[3] In the present case, however, the initial ground-state hydrogen atom beam was modulated at 100 cps by a chopper wheel so that ac as well as dc measuring techniques could be used. The 2S atom beam was then passed through two successive electrostatic-field quenching regions. In the second of these regions, the field was produced by a pair of parallel plates, a known portion of the region between them being viewed by an iodine-vapor-filled ultraviolet photon counter.[4] Since the range of this counter is from 1050 A to 1270 A, the detected

[1] E. E. Salpeter, Phys. Rev. **112**, 1642 (1958).
[2] J. Shapiro and G. Breit, Phys. Rev. **113**, 179 (1959).
[3] W. E. Lamb, Jr., and R. C. Retherford, Phys. Rev. **79**, 549 (1950).
[4] Brackmann, Fite, and Hagen, Rev. Sci. Instr. **29**, 125 (1958).