

THE SCATTERING OF SLOW ELECTRONS BY NEUTRAL ATOMS*

BY EUGENE FEENBERG

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY

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ABSTRACT

A treatment of the $N+1$ electron Schroedinger equation describing the elastic scattering of an electron beam by an atom with N electrons in the outer shell which, in first approximation, leads to the equation

$$(\nabla^2 + k^2 + U(r))f(x, y, z) = 0,$$

widely used for the computation of low velocity elastic scattering cross-sections, in which $(\frac{1}{2})k^2$ is the kinetic energy of the incident electron and $(-\frac{1}{2})U(r)$ is the interaction energy of the atom and the incident electron including terms arising from the distortion of the atom by the field of the electron. The treatment is based on a wave function antisymmetric in the space-spin coordinates of all the electrons. A discussion of exchange interference and its application by Oppenheimer to supply a qualitative explanation of the Ramsauer effect. It is found that the exchange scattering amplitude as given by Oppenheimer requires modification. The modification greatly reduces the value of the exchange term in the elastic scattering amplitude. The tentative conclusion is reached that exchange interference is of minor importance in the complete explanation of the Ramsauer effect. A derivation of the relation

$$\iint F^* F d\Omega = 2\pi i/k(F(z/r) - F^*(z/r))_{z/r=1}$$

in which $F(z/r)$ is the elastic scattering amplitude and $\iint F^* F d\Omega$ is the total scattering cross-section. A simple generalization of this relation for electron energies great enough to produce excitation. Development of a new method of solving the scattering equation $(\nabla^2 + k^2 + U(r))f(x, y, z) = 0$ and application to computation of scattering amplitudes and cross-sections.

A BEAM of slow* electrons in a gas is gradually dissipated as a result of elastic collisions and consequent diversion of electrons from the beam. One type of scattering experiment measures the intensity of the scattered beam as a function of scattering angle; another the decrease in intensity of the incident beam and thus simply the total amount of scattering. The results are expressed in terms of an effective cross-section, a quantity which multiplied by the intensity of the incident beam gives the intensity of scattering per unit solid angle as a function of scattering angle and electron velocity. The goal of a scattering theory is the calculation of this effective cross-section.

Previous cross-section computations begin with the equation

$$(\nabla^2 + k^2 + U(r))f(x, y, z) = 0, \quad (1)$$

* By "slow" is meant that the kinetic energy W_e of the electrons is not great enough to produce excitation. Atomic units of length and energy are used throughout the paper.

in which $k^2 = 2W_e$ and $(-\frac{1}{2})U(r)$ is a statistical electron atom interaction potential. $f(x, y, z)$ is everywhere finite and for large values of r has the form

$$e^{-ikz} + (1/r)e^{-ikr}F(z/r),$$

a plane wave traveling along the z axis plus a spherical wave, with amplitude $F(z/r)$, scattered by the atom at the coordinate origin. The scattering cross-section per unit solid angle is then $F^*(z/r)F(z/r)$. Using (1) and suitable choice of the potential function Holtsmark and Faxen¹ have been very successful in explaining the Ramsauer effect. Allis and Morse² have recently developed a simple method of solving (1) and with a rather crude approximation to the interaction potential obtain fairly good agreement with experimental results for scattering in a number of gases and vapors.

This paper presents in section 1 a method of treating the Schroedinger equation describing the interaction of electron and atom which leads, in first approximation, to an equation of type (1) for the scattering function, the potential including terms arising from distortion of the atom by the field of the external electron. In section 2 is a discussion of the exchange interference phenomena predicted by Oppenheimer.³ It is found that the exchange term as given by Oppenheimer requires modification. This modification greatly reduces the magnitude of the exchange effect. An exact relation between the total scattering cross-section and the scattering amplitude in the direction of the incident wave is derived in section 3. A general method of solving (1) is developed in section 4.

SECTION 1. DERIVATION OF EQUATION (1)

Scattering in atomic hydrogen and alkali metal vapor. The scattering atom is represented as an electron in the potential field $-V(r)$ of the core. The normal state wave function $u_1(r)$ is then a solution of the differential equation

$$(\nabla^2 + 2W_1 + 2V(r))u_1(r) = 0, \quad (1.1)$$

with W_1 energy level of the normal state. The wave function $\psi(x_1, x_2)$ for the complete system consisting of neutral atom and external electron is a solution of the equation

$$(\nabla_1^2 + \nabla_2^2 + 2(W_1 + W_e) + 2(V(r_1) + V(r_2) - 1/r_{12}))\psi(x_1, x_2) = 0. \quad (1.2)$$

For simplicity of notation (x) is used as a symbol for (x, y, z) . In seeking a solution of (1.2) we adopt a scheme employed by Slater⁴ in the study of the helium atom. As a first approximation we assume that for every position r_2 of the incident electron the atomic electron has the same wave function as if the incident electron were permanently located at r_2 . This yields a wave function $u_1(x_1, x_2)$ for the atomic electron which is a solution of

$$(\nabla_1^2 + 2W + 2V(r_1) - 2/r_{12})u_1(x_1, x_2) = 0. \quad (1.3)$$

¹ Faxen and Holtsmark, Zeits. f. Physik **45**, 307 (1927).

Holtsmark, Zeits. f. Physik **48**, 231 (1928); **52**, 495 (1928-29); **55**, 437 (1929).

² Allis and Morse, Zeits. f. Physik **70**, 567 (1931).

³ Oppenheimer, Phys. Rev. **32**, 361 (1927).

⁴ Slater, Proc. Nat. Acad. Sci. **13**, 423 (1926).

In this equation r_2 is merely a parameter. The energy W depends on r_2 and is conveniently replaced by

$$W = W_1 - E(r_2) + V(r_2).$$

A first order perturbation calculation yields

$$E(r_2) = - \iiint u_1(r_1)(1/r_{12})u_1(r_1)d\tau_1 + V(r_2).$$

Higher approximations add a polarization term which outside the region of high charge density has the value $+a/2r_2^4$. (a is the polarizability of the atom). The approximate complete wave function must then have the form

$$\psi_{\pm}(x_1, x_2) = u_1(x_1, x_2)f_{\pm}(x_2) \pm u_1(x_2, x_1)f_{\pm}(x_1). \quad (1.4)$$

Both symmetric and antisymmetric solutions are admitted because we are treating a two-electron problem neglecting spin. Let

$$\begin{aligned} L(2) &= \nabla_2^2 + 2W_e + 2E(r_2) + \iiint u_1(x_1, x_2)\nabla_2^2 u_1(x_1, x_2)d\tau_1, \\ g(x_2, f) &= \iiint u_1(x_1, x_2) \left[\left(\nabla_1^2 u_1(x_2, x_1) - u_1(x_2, x_1) \right. \right. \\ &\quad \left. \left. \cdot \iiint u_1(x_3, x_1)\nabla_1^2 u_1(x_3, x_1)d\tau_3 \right) f(x_1) + 2\nabla_1 u_1(x_2, x_1) \cdot \nabla_1 f(x_1) \right] d\tau_1. \end{aligned}$$

Inserting $\psi(x_1, x_2)$ as given by (1.4) into equation (1.2), multiplying the resulting equation by $u_1(x_1, x_2)$ and integrating over (x_1) space, there results

$$Lf_{\pm}(x) = \mp \iiint u_1(x_1, x)u(x, x_1)Lf_{\pm}(x_1)d\tau_1 \mp g(x, f_{\pm}). \quad (1.5)$$

The integral in the right-hand member may conveniently be labelled an "exchange" term. The function g vanishes if the perturbed atomic wave functions are replaced by unperturbed functions. Thus it may be described as resulting from atomic distortion. With $f(x) = \sum_{i=1}^{\infty} f_i(x)$ the method of successive approximation yields

$$\begin{aligned} Lf_1(x) &= 0, \\ Lf_2(x) &= \mp \iiint u_1(x_1, x)u_1(x, x_1)Lf_1(x_1)d\tau_1 \mp g(x, f_1) \\ &= \mp g(x, f_1), \\ Lf_3(x) &= + \iiint u_1(x_1, x)u_1(x, x_1)g(x_1, f_1)d\tau_1 \mp g(x, f_2) \\ &\quad \cdot \quad \cdot \quad \cdot \\ &\quad \cdot \quad \cdot \quad \cdot \end{aligned}$$

Identifying $U(r)$ with $E(r) + (\frac{1}{2})\iiint u_1(x_1, x)\nabla^2 u_1(x_1, x)d\kappa_1$ the equation $Lf_1(x)$

$=0$ is identical with (1). At large distances from the scattering center $f_1(x)$ is to have the form of a plane wave plus a scattered wave. $\sum_{i=2}^{\infty} f_i(x)$ represents an additional scattered wave which however we may judge to be relatively small both from the form of g and from the success of calculations based on (1). It is clear that a procedure that neglects g must also neglect the "exchange" term. The "exchange" term appears first in the third approximation and is somewhat smaller than, but comparable with g . (1.5) and (1) differ essentially in that (1.5) involves atomic distortion both in the potential energy and in the right-hand member while (1) takes distortion into account only in the potential.

Scattering in the inert gases and in zinc, cadmium and mercury vapor. The atom is idealized as an outer shell of 2 or 8 electrons in the potential field $-V(r)$ of the core. We introduce the convention that $(1, 2, \dots, N; x_0)$ represents the space coordinates of electron 0 and the space and spin coordinates of electrons $1, 2, \dots, N$. Also $u_1(1, 2, \dots, N)$ with $N=2$ or 8 is the normal state wave function including spin and $u_1(1, 2, \dots, N; x_0)$ the solution of the equation

$$\left(\sum_1^N \nabla_i^2 + 2 \left(W_1 - E(r_0) + \sum_0^N V(r_i) - \sum_0^N 1/r_{ik} \right) \right) u_1(1, 2, \dots, N; x_0) = 0 \quad (1.6)$$

for which $u_1(1, 2, \dots, N; \infty) = u_1(1, 2, \dots, N)$ and

$$\sum_{\text{spin}} \int \dots \int u_1^*(1, 2, \dots, N; y_0) u_1(1, 2, \dots, N; x_0) d\tau_1 \dots d\tau_N = 1.$$

In first approximation $E(r_0) = V(r_0) - \sum_{\text{spin}} \int \dots \int |u(1, 2, \dots, N)|^2 \sum_1^N (1/|r_{0i} - r_e|) d\tau_1 \dots d\tau_N$. Higher approximations add a polarization term. The Schroedinger equation for the complete system is

$$\left(\sum_0^N \nabla_i^2 + 2 \left(W_1 + W_e + \sum_0^N V(r_i) - \sum_0^N 1/r_{ik} \right) \right) \psi(0, 1, \dots, N) = 0. \quad (1.7).$$

An approximate solution antisymmetric in the electron coordinates (including spin) is given by the sum of the functions obtained by cyclic permutations of the coordinates in the function $u_1(1, 2, \dots, N; x_0) f(x_0) \delta(0)$ ($\delta(0)$ is the spin function for the external electron):

$$\begin{aligned} \psi(0, 1, \dots, N) &= u_1(1, 2, \dots, N; x_0) f(x_0) \delta(0) \\ &+ u(2, \dots, N, 0; x_1) f(x_1) \delta(1) + \dots + u(0, 1, \dots, N-1; x_N) \delta(N) f(x_N). \end{aligned} \quad (1.8)$$

The antisymmetry of ψ results from the antisymmetry of u in the first N electrons and the fact that N is an even integer. Let

$$\begin{aligned} L &= \nabla^2 + 2W_e + 2E(r) \\ &+ \sum_{\text{spin}} \int \dots \int u_1^*(1, 2, \dots, N; x) \nabla^2 u_1(1, 2, \dots, N; x) d\tau_1 \dots d\tau_N, \end{aligned}$$

$$\begin{aligned}
g(x_0, f) = & N \sum_{\text{spin}} \delta(0) \delta(1) \int \cdots \int u_1^*(1, 2, \cdots, N; x_0) \left(\nabla_1^2 u_1(2, \cdots, N, 0; x_1) f(x_1) \right. \\
& + 2 \nabla_1 u_1(2, \cdots, N, 0; x_1) \cdot \nabla_1 f(x_1) - u_1(2, \cdots, N, 0; x_1) f(x_1) \\
& \left. \sum_{\text{spin}} \int \cdots \int u_1^*(1', \cdots, N'; x_1) \nabla_1^2 u_1(1^4, \cdots, N'; x_1) d\tau_1' \cdots d\tau_{N'} \right) \\
& \cdot d\tau_1 \cdots d\tau_N.
\end{aligned}$$

Combining (1.7) and (1.8), multiplying the resulting expression by $u^*(1, 2, \cdots, N; x_0) \delta(0)$, integrating over the space coordinates $(1, 2, \cdots, N)$ and summing over all spin coordinates, and finally applying the symmetry properties of u to simplify the result, we find

$$\begin{aligned}
Lf(x_0) = & -2 \left(\sum_{\text{spin}} \int \cdots \int u_1^*(1, \cdots, N; x_0) \nabla_0 u_1(1, \cdots, N; x_0) d\tau_1 \cdots d\tau_N \right) \cdot \nabla_0 f(x_0) \\
& - N \sum_{\text{spin}} \delta(0) \delta(1) \int \cdots \int u_1^*(1, \cdots, N; x_0) u_1(2, \cdots, N, 0; x_1) Lf(x_1) d\tau_1 \cdots d\tau_N \quad (1.9) \\
& - g(x_0, f).
\end{aligned}$$

We are free to multiply $u_1(1, \cdots, N; x_0)$ by a factor $e^{-i\gamma(x_0)}$ with γ an arbitrary real function. Determining γ so that the first integral on the right-hand side of (1.9) vanishes, (1.9) reduces to

$$\begin{aligned}
Lf(x_0) = & -N \sum_{\text{spin}} \delta(0) \delta(1) \\
& \int \cdots \int u_1^*(1, \cdots, N; x_0) u_1(2, \cdots, N, 0; x_1) Lf(x_1) d\tau_1 \cdots d\tau_N - g(x_0, f). \quad (1.10)
\end{aligned}$$

The discussion following Eq. (1.5) applies equally well here. Thus the problem of the validity of (1) is reduced to the problem of determining the order of magnitude of the distortion term $g(x, f)$. The success of Holtsmark's calculations on argon and krypton indicates that g is small. If g is neglected there remains the problem of computing the atomic potential. Perhaps the best that can be done here is to follow Holtsmark's procedure and fit more or less empirically a polarization term to the Hartree atomic potential. It seems reasonable to conclude that the use of equations of type (1) with proper choice of atomic potential for the description of electron scattering has considerable theoretical justification.

Solutions of the form (1.8) may be used to describe electron scattering by any atom with an even number of electrons in the outer shell. The particular integral values $N=2, 8$ are singled out because they define singlet normal states. For odd values of N greater than 1 the analysis is somewhat more complex, but leads to scattering equations very similar to (1.10), differing only in the form of the right-hand member.

SECTION 2. UNPERTURBED ATOMIC WAVE FUNCTIONS AND
EXCHANGE INTERFERENCE

Atomic hydrogen and alkali metals. Let the exact solution of the two electron scattering problem be written in the form

$$\psi(x_1, x_2) = u_1(r_1)f_{\pm}(x_2) \pm u_1(r_2)f_{\pm}(x_1) + R_{\pm}(x_1, x_2) \quad (2.1)$$

with $R_{\pm}(x_1, x_2)$ a remainder term quadratically integrable in (x_1, x_2) space. The condition $\iint u_1(r_1)R_{\pm}(x_1, x_2)d\tau_1 = 0$ is required for the unique determination of R and f . It is convenient to introduce the following definitions:

$$\begin{aligned} (1/r_1) &= \iiint u_1(r_2)(1/r_{12})u_1(r_2)d\tau_2, \\ V_1(r_1, r_2) &= 2(V(r_1) - 1/r_{12}), \\ U(r_1) &= \iiint u_1(r_2)V_1(r_1, r_2)u_1(r_2)d\tau_2 = 2(V(r_1) - (1/r_1)), \\ V_2(r_1, r_2) &= V_1(r_1, r_2) - U(r_1) = 2(1/r_1 - 1/r_{12}), \\ L &= \nabla^2 + k^2 + U(r). \end{aligned}$$

Combining (2.1) with (1.2) and following the usual procedure of integrating over the atomic wave function there results

$$\begin{aligned} Lf_{\pm}(x_1) &= \mp u_1(r_1) \iiint u_1(r_2)(L + V_2(r_2, r_1))f_{\pm}(x_2)d\tau_2 \\ &\quad + 2 \iiint u_1(r_2)1/r_{12}R_{\pm}(x_1, x_2)d\tau_2. \end{aligned} \quad (2.2)$$

The physical interpretation of (2.2) is immediate. Thus;

$$\begin{aligned} &Lf(x_1) - \text{electron in static field of atom} \\ &u_1(r_1) \iiint u_1(r_2)(L + V_2(r_2, r_1))f(x_2)d\tau_2 - \text{electron exchange,} \\ &2 \iiint u_1(r_2)1/r_{12}R(x_1, x_2)d\tau_2 - \end{aligned}$$

reaction of distorted atom on the external electron. The orthogonality of u and R must help to reduce the importance of this last term. The scattering problem as treated by Allis and Morse² is founded on the equation $Lf(x) = 0$, which implies complete neglect of exchange and atomic distortion. For the moment we neglect atomic distortion and study the equation

$$Lf_{\pm}(x_1) = \mp u_1(r_1) \iiint u_1(r_2)(L + V_2(r_2, r_1))f_{\pm}(x_2)d\tau_2. \quad (2.3)$$

The simplest procedure for the approximate solution of (2.3) is to replace

$f_{\pm}(x_2)$ in the right hand member by the plane wave e^{-ikz_2} which reduces (2.3) to

$$(\nabla_1^2 + k^2)f_{\pm}(x_1) = -U(r_1)f_{\pm}(x_1) \mp u_1(r_1) \iiint u_1(r_2)V_1(r_2, r_1)e^{-ikz_2}d\tau_2$$

yielding the scattering amplitude

$$F_{\pm}(z/r) = (1/4\pi) \int \dots \int u_1(r_2)e^{ikr_1\cos(r_1, r)} [V_1(r_1, r_2)u_1(r_2)f_{\pm}(x_1) \pm V_1(r_2, r_1)u_1(r_1)e^{-ikz_2}]d\tau_1d\tau_2 \quad (2.4)$$

which may be further simplified by substituting e^{-ikz_1} for $f(x_1)$. This is just the cross-section found by Oppenheimer³ and evaluated by Massey and Mohr.⁵ In words a simple approximation is substituted for $f_{\pm}(x_2)$ and the expression $(\dot{L} + V_2(r_2, r_1))f_{\pm}(x_2)$ is then evaluated. But this procedure is subject to the fundamental criticism: L contains a differential operator and therefore Lf is very sensitive to our choice of f . A slight change in $f(x_2)$ may lead to an entirely different final result. The following argument makes the criticism explicit and conclusive: We write $f(x) = \sum_{i=1}^{\infty} f_i(x)$ and solve (2.3) by successive approximation with

$$Lf_1(x_1) = 0,$$

$$Lf_2(x_1) = \mp u_1(r_1) \iiint u_1(r_2)(L + V_2(r_2, r_1))f(x_2)d\tau_2,$$

$$Lf_{i+1}(x_1) = \mp u_1(r_1) \iiint u_1(r_2)(L + V_2(r_2, r_1))f_i(x_2)d\tau_2.$$

Then

$$Lf_2(x_1) = \mp u_1(r_1) \iiint u_1(r_2)V_2(r_2, r_1)f_1(x_2)d\tau_2,$$

$$\begin{aligned} \iiint u_1(r_1)Lf_2(x_1)d\tau_1 &= \mp \iiint u_1(r_2)f_1(x_2) \iiint u_1(r_1)V_2(r_2, r_1)u_1(r_1)d\tau_1d\tau_2 \\ &= \mp 2 \iiint u_1(r_2)f_1(x_2)((1/r_2) - (1/r_2))d\tau_2 \\ &= 0. \end{aligned}$$

Thus

$$Lf_3(x_1) = \mp u_1(r_1) \iiint u_1(r_2)V_2(r_2, r_1)f_2(x_2)d\tau_2$$

and by induction

$$Lf_{i+1}(x_1) = \mp u_1(r_1) \iiint u_1(r_2)V_2(r_2, r_1)f_i(x_2)d\tau_2.$$

So finally

$$Lf_{\pm}(x_1) = \mp u_1(r_1) \iiint u_1(r_2)V_2(r_2, r_1)f_{\pm}(x_2)d\tau_2$$

⁵ Massey and Mohr, Proc. Royal Soc. A132, 605 (1931).

and the scattering amplitude is

$$F_{\pm}(z/r) = 1/4\pi \int \cdots \int u_1(r_2) e^{ikr_1 \cos(r_1, r)} [V_1(r_1, r_2) u_1(r_2) f_{\pm}(x_1) \pm V_2(r_2, r_1) u_1(r_1) f_{\pm}(x_2)] d\tau_1 d\tau_2. \quad (2.5)$$

The first integral represents direct scattering of the external electron; the second scattering by an exchange in which the external electron enters the atom and the atomic electron is scattered. This result differs from (2.4) essentially in the replacement of $V_1(r_2, r_1)$ by $V_2(r_2, r_1)$ in the exchange term, a substitution which greatly reduces the value of the exchange integral. For atomic hydrogen with f replaced by e^{-ikz} the exchange scattering amplitude in (2.5) is only $\frac{1}{2}$ as large as in (2.4) and 3 times as large as the direct scattering amplitude which is the same in both expressions.

The method which leads to (2.5) is quite general, although rigorous only for one electron systems with neglect of atomic distortion, and applies in particular to the inert gases, zinc, cadmium and mercury. For helium the scattering amplitude for collisions which raise the atom from normal state 1 to a singlet state s is

$$(1/4\pi) \int \cdots \int u_s^*(x_1, x_2) e^{ik_s r_0 \cos(r_0, r)} [V_1(r_0, r_1, r_2) u_1(x_1, x_2) f_1(x_0) - V_2(r_2, r_1, r_0) u_1(x_1, x_0) f_1(x_2)] d\tau_0 d\tau_1 d\tau_2 \quad (2.6)$$

and for a collision leaving atom in a triplet state t

$$(1/4\pi) \int \cdots \int v_t^*(x_1, x_2) e^{ik_t r_0 \cos(r_0, r)} V_2(r_2, r_1, r_0) u_1(x_1, x_0) f_1(x_2) d\tau_0 d\tau_1 d\tau_2 \quad (2.7)$$

in which

u_s is symmetric wave function of singlet state s ,
 v_t is antisymmetric wave function of triplet state t ,

$$V_1(r_0, r_1, r_2) = 4/r_0 - 2/r_{01} - 2/r_{02},$$

$$V_2(r_0, r_1, r_2) = V_1(r_0, r_1, r_2) - \int \cdots \int u_1(x_3, x_4) V_1(r_0, r_3, r_4) u_1(x_3, x_4) d\tau_3 d\tau_4 \\ = 4 \int \cdots \int u_1(x_3, x_4) (1/r_{03}) u_1(x_3, x_4) d\tau_3 d\tau_4 - 2/r_{01} - 2/r_{02},$$

f_1 is the scattering function for elastic collisions,

$$k_t^2 = 2(W_e + W_1 - W_l).$$

Thus the work of Massey and Mohr⁵ on singlet and triplet excitation probabilities in helium requires modification. This modification is simply the replacement of $V_1(r_2, r_1, r_0)$ in the exchange integrals by $V_2(r_2, r_1, r_0)$. A rough calculation shows that below the resonance potential the exchange scattering amplitude for elastic collisions is only 1/3 as large as the corresponding quan-

tity computed from Oppenheimer's scattering amplitude and yields a distribution in angle in much better agreement with the experimental results of Bullard and Massey.⁶ Possibly the difference is smaller for inelastic collisions.

Oppenheimer³ finds in the destructive interference of direct and exchange scattering amplitudes a qualitative explanation of the Ramsauer effect, i.e., the occurrence of a minimum in the scattering cross-section for very slow electrons. This qualitative explanation would appear very attractive were it not for the success of calculations based on (1). But the exchange scattering amplitudes for hydrogen and helium are much smaller than all previous considerations would indicate. Going from hydrogen to helium the ratio of exchange scattering amplitude to direct scattering amplitude falls from 3/1 to 3/2. For all atoms with atomic number greater than 2, the real and imaginary parts of the wave functions, plotted in phase space, will show regions of alternating positive and negative value. In general, the number of alternations in sign will increase with increasing atomic number. Merely because of this alternation in sign, the relative value of exchange and direct scattering amplitudes should decrease along the series helium, neon, argon, krypton. We must then tentatively come to a conclusion in harmony with the results of calculations based on (1): exchange interference is of minor importance in the complete explanation of the Ramsauer effect. It must be remembered, however, that the position and height of minima in the distribution in angle curves may depend markedly on small quantities which contribute very little to the total cross-section.

Returning to equation (2.2), the neglect of atomic distortion is a doubtful procedure because of the large polarizability of the alkali metals. The writer has in preparation a paper in which the remainder term $R_{\pm}(x_1, x_2)$ is computed by simple approximate methods. It is to be expected that the inclusion of atomic distortion in the calculation will lead to a smaller difference between symmetric and antisymmetric solutions than is implied by (2.5).

SECTION 3. A FUNDAMENTAL RELATION

Independent of the detailed structure of the scattering system there exists an exact and general relation connecting the total scattering cross-section, $\iint F^*(z/r)F(z,r)d\Omega$, with the scattering amplitude in the direction of the incident beam. This relation is

$$\iint FF^*d\Omega = (2\pi i/k)(F(z/r) - F^*(z/r)), \text{ with } z/r = 1. \quad (3.1)$$

Proof: Conservation of charge in a region G bounded by a surface S is expressed by the equation

$$\iint_S \left\{ \iiint_G \dots \iint_G (\psi^* \nabla_0 \psi - \psi \nabla_0 \psi^*) d\tau_1 \dots d\tau_N \right\} \cdot dS_0$$

⁶ Bullard and Massey, Proc. Royal Soc. A133, 637 (1931).

$$\begin{aligned}
& + \iint_S \left\{ \iiint_G \cdots \iint_G (\psi^* \nabla_1 \psi - \psi \nabla_1 \psi^*) d\tau_0 d\tau_2 \cdots d\tau_N \right\} \cdot dS_1 \\
& \quad \vdots \\
& + \iint_S \left\{ \iiint_G \cdots \iint_G (\psi^* \nabla_N \psi - \psi \nabla_N \psi^*) d\tau_0 \cdots d\tau_{N-1} \right\} \cdot dS_N = 0.
\end{aligned} \tag{3.2}$$

For r_0 large and the other coordinates of atomic dimensions ψ degenerates into the product of a normal state wave function $u_1(1, \dots, N)$ for the atom and the scattering function $f(x_0)\delta(0)$. Hence ψ can be written as a sum of terms of the form $\pm u_1(1, \dots, N)f(x_0)\delta(0)$ obtained by permutation of coordinates plus a remainder term $R(0, 1, \dots, N)$ which is quadratically integrable. With G a sphere centered at the origin,

$$\begin{aligned}
& \text{Limit}_{G \rightarrow \infty} \sum_{\text{spin}} \iint_S \left\{ \iiint_G \cdots \iint_G (\psi^* \nabla_0 \psi - \psi \nabla_0 \psi^*) d\tau_1 \cdots d\tau_N \right\} \cdot dS_0 \\
& = \text{Limit}_{G \rightarrow \infty} \left(\sum_{\text{spin}} \iiint_G \cdots \iint_G u_1^*(1, \dots, N) u(1, \dots, N) d\tau_1 \cdots d\tau_N \right) \\
& \quad \iint_S (f^* \nabla_0 f - f \nabla_0 f^*) \cdot dS_0 \\
& = \text{Limit}_{r \rightarrow \infty} \iint (f^* \partial f / \partial r - f \partial f^* / \partial r) r^2 d\Omega.
\end{aligned}$$

By (3.2)

$$\text{Limit}_{r \rightarrow \infty} \iint (f^* \partial f / \partial r - f \partial f^* / \partial r) r^2 d\Omega = 0. \tag{3.3}$$

For large values of r

$$\begin{aligned}
f & \cong e^{-ikz} + e^{-ikr}(1/r)F(z/r), \\
f^* \partial f / \partial r - f \partial f^* / \partial r & \cong -2ikz/r - 2ikkF^*F/r^2 \\
& \quad - (ik/r)(1+z/r)(e^{ik(r-z)}F^* + e^{-ik(r-z)}F) \\
& \quad + (1/r^2)(e^{ik(r-z)}F^* - e^{-ik(r-z)}F) \\
& \quad + \text{terms in } 1/r^3.
\end{aligned}$$

The intensity of the incident beam is proportional to k and intensity of the scattered beam to kF^*F/r^2 . Integrating over the surface of a sphere of radius r , we have

$$\begin{aligned}
\iint (f^* \partial f / \partial r - f \partial f^* / \partial r) r^2 d\Omega & = -2ik \iint F^* F d\Omega \\
& \quad - ikr \iint (1+z/r)(e^{ik(r-z)}F^* + e^{-ik(r-z)}F) d\Omega \\
& \quad + \text{higher order terms.}
\end{aligned}$$

Now

$$\begin{aligned}
& -ikr \iint (1+z/r)(e^{ik(r-z)}F^* + e^{-ik(r-z)}F)d\Omega \\
& = 2\pi \int_{-1}^1 (1+s) \left(F^* \frac{\partial}{\partial s} e^{ikr(1-s)} - F \frac{\partial}{\partial s} e^{-ikr(1-s)} \right) ds \\
& = 4\pi(F^*(z/r) - F(z/r)_{z/r=1} + \text{higher order terms}).
\end{aligned}$$

These results combined with (3.3) yield

$$\iint F^*F d\Omega = (2\pi i/k)(F(z/r) - F^*(z/r))_{z/r=1}.$$

Thus it is sufficient to compute the value of F in the direction of the incident beam in order to find the total scattering cross-section. The physical interpretation of (3.1) is simply that the scattered current is taken out of the incident beam. This occurs without decrease in the intensity of the incident beam because the infinite plane wave of finite amplitude represents an infinite electron current.

A simple generalization of (3.1) exists when the incident beam possesses sufficient energy to excite upper levels, but not enough for ionization. The cross-section for inelastic collisions must be added to the left-hand member. The right-hand member is unchanged. In this way the total scattering cross-section is expressed as a simple function of the scattering amplitude for elastic collisions.

SECTION 4. A METHOD OF COMPUTING THE SCATTERING FUNCTION

We have for solution the differential equation

$$(\Delta^2 + k^2 + U(r))p(x) = -U(r)e^{-ikz}, \quad (4.1)$$

derived from (1) by the substitution $f(x) = p(x) + e^{-ikz}$, in which

$$\text{Limit } r^3 U(r) = 0,$$

$$\text{Limit } rU(r) = \text{constant} \neq 0,$$

subject to the boundary conditions:

$$p(x) \text{ everywhere finite,}$$

$$p(x) \cong e^{-ikr}(1/r)F(z/r) \text{ for large values of } r.$$

All the difficulties of solving (4.1) arise from the potential term $U(r)$ in the differential operator. For sufficiently high electron velocities $\Delta^2 + k^2 + U(r)$ is replaced by $\Delta^2 + k^2$, an approximation not permitted in the velocity range considered in this paper. We follow a well-known procedure and introduce a function $G(r)$ with the following properties:

$$(\Delta^2 + k^2 + U(r))G(r) = 0,$$

$$\text{Limit } r^2 G(r) = 0,$$

$$\text{Limit } r^2 dG/dr = -1,$$

$$\text{Limit } rG(r)e^{ikr} = \text{constant}.$$

Then

$$\begin{aligned} G(r_{12})(\Delta_2^2 + k^2 + U(r_2))p(x_2) - p(x_2)(\Delta_2^2 + k^2 + U(r_2))G(r_{12}) & \quad (4.2) \\ = -G(r_{12})[U(r_2)e^{-ikz_2} + p(x_2)(U(r_2) - U(r_{12}))] & \quad (4.2) \\ = \Delta_2 \cdot [G(r_{12})\Delta_2 p(x_2) - p(x_2)\Delta_2 G(r_{12})] & \end{aligned}$$

and

$$p(x_1) = (1/4\pi) \iint G(r_{12})[U(r_2)e^{-ikz_2} + p(x_2)(U(r_2) - U(r_{12}))] d\tau_2, \quad (4.3)$$

an integral equation for the unknown function $p(x)$. In deriving (4.3) a surface integral was discarded which may be written

$$\text{Limit}_{r_2 \rightarrow \infty} r_2^2 \iint [G(r_{12})\partial p(x_2)/\partial r_2 - p(x_2)\partial G(r_{12})/\partial r_2] d\Omega.$$

As a result of the boundary conditions on G and p the integrand vanishes with the inverse third power of r_2 and the value of the limit is zero.

We require a proof that there exists a function $G(r)$ with the stated properties. Assume $G(r) = v(r, k)(1/r)e^{-ikr}$ with $v(0, k) = 1$ and limit $rdv/dr = 0$. $v(r, k)$ is then a solution of the differential equation

$$(d^2/dr^2 - 2ikd/dr + U(r))v(r, k) = 0. \quad (4.4)$$

This is readily transformed into the integral equation

$$v(r, k) = v(\infty, k) + (1/2ik) \int_{\infty}^r (1 - e^{2ik(r-r')})U(r')v(r', k)dr' \quad (4.5)$$

which may be solved by the method of successive approximation with the result

$$\begin{aligned} v(r, k) = v(\infty, k) & \left[1 + (1/2ik) \int_{\infty}^r (1 - e^{2ik(r-r')})U(r')dr' \right. \\ & + (1/2ik)^2 \int_{\infty}^r (1 - e^{2ik(r-r')})U(r') \int_{\infty}^{r'} (1 - e^{2ik(r'-r'')})U(r'')dr''dr' \\ & \left. + \dots \right]. \end{aligned} \quad (4.6)$$

By (4.6)

$$\begin{aligned} |v(r, k)| \leq |v(\infty, k)| & \left[1 + \int_r^{\infty} r'U(r')dr' \right. \\ & \left. + \int_r^{\infty} r'U(r') \int_{r'}^{\infty} r''U(r'')dr''dr' + \dots \right] \end{aligned}$$

and therefore

$$|v(r, k)| \leq |v(\infty, k)| \exp\left[\int_r^{\infty} r'u(r')dr'\right]$$

Thus the series (4.6) is absolutely convergent uniformly in r and k . $v(\infty, k)$ is defined by the boundary condition $v(0, k) = 1$ or by the equation

$$\begin{aligned}
1/v(\infty, k) &= 1 + (1/2ik) \int_{\infty}^0 (1 - e^{-2ikr})U(r)dr \\
&+ (1/2ik)^2 \int_{\infty}^0 (1 - e^{-2ikr})U(r) \int_{\infty}^r (1 - e^{2ik(r-r')})U(r')dr'dr + \dots \quad (4.7)
\end{aligned}$$

Clearly $v(\infty, k)$ can never vanish and provided only that $v(\infty, k)$ is finite, the function $v(r, k)(1/r)e^{-ikr}$ possesses all the properties required of $G(r)$.

(4.3) now becomes

$$\begin{aligned}
p(x_1) &= (1/4\pi) \iint \int v(r_{12}, k)(1/r_{12})e^{-ikr_{12}}[U(r_2)e^{-ikz_2} \\
&+ p(x_2)(U(r_2) - U(r_{12}))]d\tau_2. \quad (4.8)
\end{aligned}$$

This yields immediately the exact value of $p(x)$ at the origin. For with $r_1=0$ the factor $(U(r_1) - U(r_{12}))$ vanishes leaving

$$\begin{aligned}
p(0) &= (1/4\pi) \iiint v(r, k)(1/r)U(r)e^{-ik(r+z)}d\tau \\
&= (\frac{1}{2}) \int_0^{\infty} rU(r)v(r, k) \int_{-1}^1 e^{-ikr(1+s)}dsdr \\
&= (1/2ik) \int_{\infty}^0 (1 - e^{-2ikr})U(r)v(r, k)dr \\
&= v(\infty, k) - 1. \quad (4.9)
\end{aligned}$$

and at the origin the scattering function $f(x)$ has the value $v(\infty, k)$:

$$f(0) = 1 + p(0) = v(\infty, k). \quad (4.10)$$

The scattering amplitude is

$$F(z/r) = (1/4\pi) \iint \int e^{ikr_1 \cos(r_1, r)} [e^{-ikz_1} + p(x_1)]U(r_1)d\tau_1. \quad (4.11)$$

$p(x_1)$ appears under the integral on the right multiplied by a factor $U(r_1)$ which possesses a pole of the first order at the origin and decreases quite rapidly for large values of r_1 . Thus an approximation to $p(x)$ highly accurate in the neighborhood of the origin is essential for the computation of the scattering amplitude. If $p(x)$ is small compared to unity at the origin the term in $p(x_1)$ may be neglected and there remains just Born's⁷ first order scattering amplitude which agrees very well with experimental results down to surprisingly low velocities. From (4.9) the condition for the validity of the Born first order scattering amplitude is

$$|v(\infty, k) - 1| \ll 1. \quad (4.12)$$

In (4.7) both real and imaginary parts of $1/v(\infty, k)$ are given by series of al-

⁷ Born, Zeits. f. Physik **38**, 803 (1926); Goett. Nach. 146 (1926).

ternating positive and negative terms and provided that the absolute value of the first integral is less than unity, the successive iterated integrals decrease steadily in absolute value. (4.12) is then satisfied when

$$\left| \int_0^{\infty} (1 - e^{-2ikr})U(r)dr \right| \leq k. \quad (4.13)$$

For atomic hydrogen and helium

$$U(r) = (2Z/r)e^{-2\alpha r}(1 + \alpha r),$$

$Z=1$, $\alpha=1$ hydrogen, $Z=2$, $\alpha=27/16$ helium. The evaluation of (4.13) yields

$$Z^2 \left[(\alpha/(\alpha^2 + k^2) + (2/k) \tan^{-1}(k/\alpha))^2 + (k/(\alpha^2 + k^2) + (1/k) \lg_e(1 + k^2/\alpha^2))^2 \right] \leq 1 \quad (4.14)$$

and the Born first order scattering amplitude is valid in the energy range $W_e \geq 200$ volts for hydrogen, $W_e \geq 400$ volts for helium. Below these energies $p(x_1)$ cannot be neglected in the evaluation of (4.11).

We rewrite (4.8) in the form

$$p(x_1) = (1/4\pi) \iiint G(r_{12}) [U(r_{12})e^{-ikz_2} + f(x_2)(U(r_2) - U(r_{12}))] d\tau_2$$

which suggests the approximation

$$\begin{aligned} p_1(x_1) &= (1/4\pi) \iiint G(r_{12})U(r_{12})e^{-ikz_2} d\tau_2 \\ &= (1/4\pi) e^{-ikz_1} \iiint G(r)U(r)e^{-ikz} d\tau \\ &= (v(\infty, k) - 1) e^{-ikz_1}, \end{aligned} \quad (4.15)$$

valid for small values of r_1 and accurate at the origin. With this approximation for $p(x_1)$ the scattering amplitude becomes

$$F(z/r) = [v(\infty, k)/4\pi] \iiint e^{ik(r_1 \cos(\theta_1, r) - z_1)} U(r_1) d\tau_1, \quad (4.16)$$

again the Born first order scattering amplitude except for the multiplying factor $v(\infty, k)$. The distribution in angle predicted by the Born formula is then valid for electron energies smaller than calculated from (4.14), in agreement with experimental results. It is to be expected that the total cross-section computed from (4.16) will agree with experiment over a wide range of electron energy than does the distribution in angle. Further investigation of the function $v(\infty, k)$ is necessary.

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Note added in proof (supplementing section 2):

(2.6) has been evaluated for elastic collisions using an analytic approximation to f_1 . The results are in qualitative agreement with the measurements of Bullard and Massey⁶ and Ramsauer and Kollath (Ann. d. Physik, vol. 12, no. 5, 1932). A careful solution of the helium exchange scattering equation by numerical integration is in progress. Incomplete results indicate quantitative agreement with the measurements of Ramsauer and Kollath. The general effect of including exchange is to greatly increase the variation of scattering intensity with angle. For the other rare gases, neon, argon, krypton, exchange is small and becomes important only in the neighborhood of the cross-section minimum. The theory predicts for sufficiently low velocities a scattering intensity symmetric about the direction of right angle scattering. The scattering intensity does not tend toward spherical symmetry with decreasing electron velocity. These effects arise from the presence of p electrons in the scattering atom. The series of argon curves in the work of Ramsauer and Kollath strikingly exhibits both effects. A derivation and discussion of the exchange scattering equations for the rare gases together with calculations for helium will appear later.