JULY, 1932 REVIEWS OF MODERN PHYSICS VOLUME 4

Quantum Mechanics of Collision Processes

Part II

By Philip M. Morse
Massachusetts Institute of Technology

TABLE OF CONTENTS

Introduction

The ideas developed in the first part of this survey* will be applied here to the fundamental collision processes encountered in electric discharge in gases and in chemical dynamics: elastic scattering, excitation and ionization by impact, and the so-called collisions of the second kind. It is manifestly impossible to deal here with all the applications of collision theory which have appeared in the last few years. The following survey deals with a general discussion of some of the more important methods of treating these problems, and with applications of these methods which seemed apt to illustrate certain points.

All the processes mentioned above are essentially of the same type. Two systems (electron, atom or molecule) are initially in some specified quantum state and are approaching each other from infinity with a given relative kinetic energy. After some time we find that several different things can have happened to the systems: either the systems have passed by each other without influencing each other at all, or the systems have changed their direction of relative motion without changing their quantum state or relative kinetic energy (elastic scattering) or one or both systems are now in a higher quantum state with a correspondingly changed relative velocity (inelastic collision of the first kind, excitation, ionization), or one system is now in a lower quantum state while the other's state may be changed or not (collision of the second kind). Our problem is to determine the distribution-in-angle of each of the final scattered products, and the probability of occurrence of each of the processes.

Analytically, the problem can be attacked by two methods. For one method, the whole process is considered to be in equilibrium; that part of the wave function representing undisturbed relative motion being given by a plane wave multiplied by the wave functions appropriate for the initial quantum states of the two separate systems, and that part of the wave func-

---

* Condon and Morse, Rev. Mod. Phys. **3**, 43 (1931). Called hereafter Part I.

tion representing the scattered systems being given by outgoing radial waves multiplied by the appropriate wave functions for various final states of the systems. The interaction potential in the Schroedinger equation for the ensemble will then uniquely determine the relative amplitudes of plane and outgoing waves. From these amplitudes we can obtain the current of particles scattered in any final state per unit solid angle per unit current density of the initial stream, which gives us the distribution-in-angle of the scattered current. By integrating this over all directions we obtain the total scattered current for any final state per unit initial current density, a quantity of the dimensions of an area, which we call the effective cross section for the process considered.

Experimentally, of course, what is measured is not the effective cross section, but the absorption of a beam of system I particles by a gas composed of system II particles. The logarithmic absorption coefficient α, reduced to 0° C, and 1 mm mercury pressure, is related to the effective cross section q, expressed in units of the square of the first Bohr orbit radius for hydrogen, by the following equation

$$q = 1.005\alpha.$$

The other method of attack considers the process to be nonstationary. At time $t=0$ the system is in its initial state, represented by a plane wave multiplied by the systems' wave functions for the initial states. This state cannot be a stationary one, however, and after a short time the wave function must be represented by the initial function plus a number of others, each representing a possible final state. From the rates of increase of the various final functions we can calculate the corresponding effective cross sections.

These two methods, if carried out exactly, will of course both give the same answers. But the second method can seldom be carried through exactly. Consequently the first method will be used in most of the following.

§7. SCATTERING FROM A CENTRALLY SYMMETRIC POTENTIAL FIELD. EXACT SOLUTIONS

The simplest possible collision process we can consider is one in which one system is a single particle, and the other is a potential field symmetric about a fixed center. It will be worth while to investigate the solutions of this problem carefully; for, in most cases, we shall find we can reduce the more complicated problems to a set of simple elastic scattering problems, which can then be solved by the methods developed in this and the succeeding section.

The problem of the scattering of an electron wave from a field of force is analytically identical with the problem of the scattering of light from a region of varying index of refraction, and the methods already developed for optical scattering simply need to be adapted to the peculiarities of atomic fields. The methods used in this section were used by Mie and Debye for the scattering of light, while the methods used in the next section are similar to those used by Huygens and Kirchhoff.

The wave function for the present case has been discussed in Part I, section 4. It is a linear combination of the functions $\Phi_m(\phi)\ \Theta_{\lambda m}(\theta)\ R_\lambda(kr)/r$, where $\Phi\cdot\Theta$ is a normalized tesseral harmonic, and where R_λ satisfies the equation

$$\frac{d^2R_\lambda}{dr^2}+\left[k^2+2U(r)-\frac{\lambda(\lambda+1)}{r^2}\right]R_\lambda=0. \tag{1}$$

The coordinate r is the distance from the fixed center expressed in terms of the first Bohr orbit radius $(h^2/4\pi^2\mu e^2)$ as a unit. k^2 and $2U$ are respectively the initial kinetic energy and minus the potential energy of the particle in terms of the magnitude of the normal atomic energy $(2\pi^2\mu e^4/h^2)$ as a unit. We shall refer to these units later as atomic units. Expressed in them the U corresponding to a single proton at the fixed center acting on an electron, would be $1/r$. Charge density is in electrons per Bohr orbit radius cubed, and current density in electrons per second per Bohr orbit radius squared.

The case of the coulomb field, a/r, has been treated in Part I, section 5. In this case the scattered distribution-in-angle follows the classical Rutherford formula, and the total cross section is infinite. However most of the potential fields we shall deal with decrease with increasing r much more rapidly than a coulomb field does. Suppose U behaves like a/r^{n_0} for very small values of r, and approaches b/r^{n_∞} as r becomes very large. We shall see later that the total cross section is infinite if $n_0>2$ or if $n_\infty\leqq 2$. The cases actually encountered, however, have $n_0=1$ and n_∞ in most cases greater than 2, so most cross sections will be finite. R_λ for large values of r will then satisfy the equation

$$R_\lambda''+[k^2-\lambda(\lambda+1)/r^2]R_\lambda=0.$$

Therefore as r increases, R approaches the form

$$r^{1/2}(C_\lambda J_{\lambda+1/2}(kr)+D_\lambda J_{\lambda-1/2}(kr)). \tag{2a}$$

We can normalize R so that

$$R_\lambda \underset{r\to\infty}{\to} \frac{2\lambda+1}{k}\, i^\lambda e^{i\gamma_\lambda}\cos\left(kr-\pi(\lambda+1/2)+\gamma_\lambda\right) \tag{2b}$$

where $\tan\gamma_\lambda=(-1)^\lambda D_\lambda/C_\lambda$. The requirement that R_λ/r be finite at $r=0$ fixes the value of γ_λ. Then from part I section 4, the current per element of solid angle $d\omega$, for unit initial current density is

$$\frac{d\omega}{k^2}\sum_{\lambda,\lambda'=0}^{\infty}(2\lambda+1)(2\lambda'+1)P_\lambda(\cos\theta)P_{\lambda'}(\cos\theta)\sin\gamma_\lambda\sin\gamma_{\lambda'}\cos(\gamma_\lambda-\gamma_{\lambda'}) \tag{3a}$$

and the total cross section for elastic scattering is

$$q=\sum q_\lambda,\ \text{where}\ q_\lambda=(4\pi/k^2)(2\lambda+1)\sin^2\gamma_\lambda. \tag{3b}$$

Thus we see that the problem of scattering is solved when we have determined the values of the phase angle γ_λ as function of k, for the specified form of U.

When U becomes very much smaller than k^2 for $r \geqq r_0$, where r_0 is of the order of magnitude of unity, then it is possible to obtain a solution of Eq. (1) for $r \leqq r_0$ in the form of a power series in r. Setting

$$R_\lambda(r) = r^{\lambda+1} \sum_{n=0}^{\infty} a_{\lambda n} r^n; \text{ and } U = \sum_{k=0}^{\infty} v_k r^{k-1}$$

in (1), by equating powers of r we obtain values of a_n in terms of a_0 and the v_k's. Then, if r_0 is small enough that the series for $R_\lambda'(r_0)$ converges sufficiently rapidly for feasible calculation, we can obtain values of $R_\lambda(r_0)$ and $R_\lambda'(r_0)$. For values of r greater than r_0 our function becomes the expression given in (2a), and the requirement that the wave function be continuous in value and first derivative at $r = r_0$ fixes the relative value of C_λ and D_λ, and therefore of γ_λ.

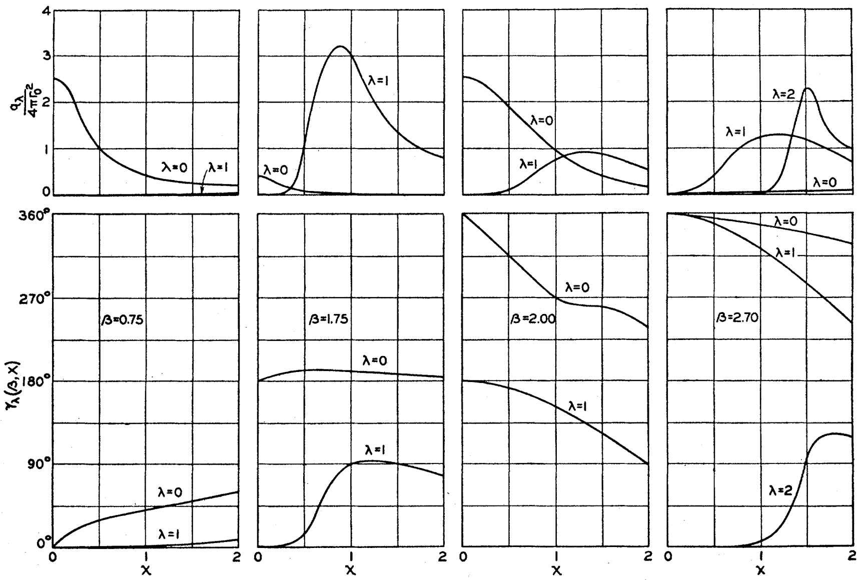

Fig. 1. Values of the phase angles $\gamma_\lambda(\beta, x)$ and reduced partial cross sections $q_\lambda/4\pi r_0^2$ as functions of the velocity parameter x, for the potential field given in Eq. (4a).

An example of this method has been calculated for the case[1] of a potential due to a nucleus of charge Ze surrounded by a spherical shell of charge $-Ze$ and of radius r_0. This gives

$$U = \begin{cases} (Z/r) - (Z/r_0) & (r \leqq r_0) \\ 0 & (r \geqq r_0). \end{cases} \tag{4a}$$

---

[1] Mensing, Zeits. f. Physik **45**, 603 (1927); Allis and Morse, Zeits. f. Physik **70**, 567 (1931). This method has also been used by Guth and Sexl, Zeits. f. Physik **66**, 577 (1930) to compute the emission of alpha-particles by radio-active nuclei, and by Taylor, Proc. Roy. Soc. **A134**, 103 (1931) in discussing the scattering of alpha-particles by helium atoms.

In this case it turns out that γ_λ is a function of only two parameters;

$$x = kr_0 \text{ and } \beta = (Zr_0/2)^{1/2}. \tag{4b}$$

The quantity x is proportional to the electronic velocity, and is the ratio of the circumference of the spherical shell to the de Broglie wave-length of the electron. The quantity β is the square root of the integral of the effective charge, rU, from r zero to r infinity, and is a sort of measure of the scattering power of the potential field.

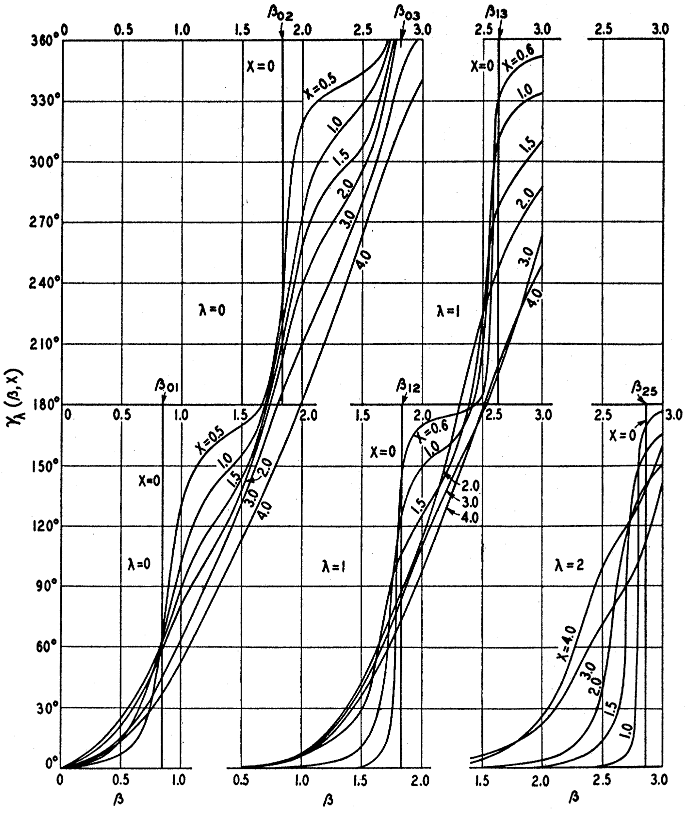

Fig. 2. Values of the phase angles $\gamma_\lambda(\beta, x)$ as functions of the field parameter β, for the potential given in Eq. (4a).

It is instructive to plot $\gamma_\lambda(\beta, x)$ as a function of x for several values of β. This is done in Fig. 1. We see that γ_0 starts from its initial values, 0° or 180° or 360°, at $x=0$, with the first power of x for small values of x, and therefore that q_0 can approach a finite value as k approaches zero. The γ_λ's for $\lambda>0$ all start out with powers of x higher than the first, and so all other q's become zero when k is zero (except in special cases, discussed below). When γ_λ is $(n+\frac{1}{2})\pi$, $\sin^2\gamma_\lambda$ is unity and q_λ is tangent to the curve $4\pi(2\lambda+1)/k^2$, so the value of q_λ oscillates between this curve and the k axis as k increases.

If we plot the γ's as functions of β for several values of x we see that $\gamma_\lambda(\beta, x)$ becomes more "step like" as smaller values of x are chosen. The values, $\beta_{n\lambda}$, of β for which $\gamma_\lambda(\beta, 0)$ changes discontinuously differ from one another by approximately unity (see Fig. 2). For these values of β q_λ approaches infinity as x approaches zero. The reason for this discontinuity can be seen when we consider the behavior of the quantized negative energy levels for the same potential field as the parameter β is varied. There will be a finite number of these levels for the form of U given in (4a), the lowest being a single level, $n=1$, $\lambda=0$, then next above coming a pair, $n=2$, $\lambda=0$ or 1, etc. If we start with a given value of β and watch the level labelled by the quantum numbers n and λ, we see that it rises as β decreases, eventually reaching the value zero and merging with the continuous allowed positive levels. The value of β where this level reaches the value zero is $\beta_{n\lambda}$, and q_λ for this value of β approaches infinity as x approaches zero. For all other values of β q_λ for decreasing k approaches a finite value if $\lambda=0$ or approaches zero if $\lambda\neq 0$.

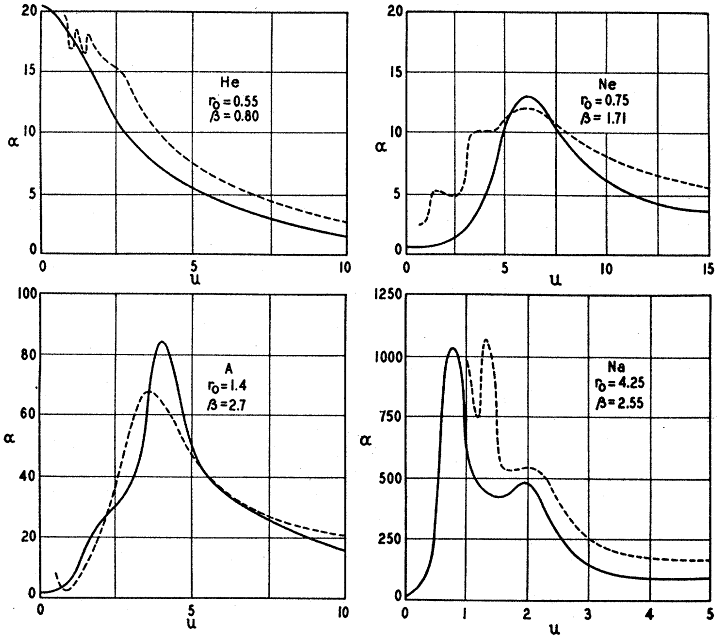

Fig. 3. Absorbtion coefficients, α, for various atoms as a function of electronic velocity in square root volts. Dotted lines are the experimental curves and solid lines are values computed by means of Eq. (4a).

Values of β can be chosen to fit the U given in (4) to some atomic potential curve. This seems to be best accomplished by choosing a value of β equal to the square root of the integral of the actual effective charge acting on the incoming electron. Fig. 3 shows the experimental curves of total cross section as dotted lines and the computed curves as full lines. The fit is remarkable, considering how very approximate is the correspondence between U and the actual atomic field.

This must mean that within certain limits a variation of the form of the scattering potential makes no difference on the shape of the corresponding cross-section curves, as long as β is kept constant during the variation. To satisfy ourselves that this is true we must obtain cross-section curves for a potential field of form different from Eq. (4) and compare them with the curves already computed.

When U has a more complex form than that given in (4) it is sometimes better to transform the dependent variable,[2] by setting

$$R_\lambda(r) = \frac{1}{(\Pi_\lambda(k, r))^{1/2}} \sin \int_0^r \Pi_\lambda(k, y)dy. \tag{5a}$$

The equation for $\Pi_\lambda(k, r)$ is

$$\Pi_\lambda{}^2 - (\Pi_\lambda)^{1/2} \frac{d^2}{dr^2}\left(\frac{1}{(\Pi_\lambda)^{1/2}}\right) = \left(k^2 + 2U - \frac{\lambda(\lambda+1)}{r^2}\right). \tag{5b}$$

We see that when r is large enough so that the right hand side of (5b) is sensibly equal to k^2 then Π_λ equals k, and for such values of $r \int \Pi_\lambda\, dy = kr + constant$. This constant is the area between the line $y = \Pi_\lambda(x)$, the line $y = k$, and the y axis.

We shall call the Π's for $U = 0$, $\Pi_\lambda{}^0$. They are the algebraic functions

$$\begin{aligned}
\Pi_0{}^0(k, r) &= k \\
\Pi_1{}^0(k, r) &= k\frac{k^2r^2}{k^2r^2+1} \\
\Pi_2{}^0(k, r) &= k\frac{k^4r^4}{k^4r^4+3k^2r^2+9} \\
\Pi_3{}^0(k, r) &= k\frac{k^6r^6}{k^6r^6+6k^4r^4+45k^2r^2+225} \\
&\cdots\cdots\cdots\cdots\cdots\cdots
\end{aligned} \tag{6a}$$

If we obtain the functions $\Pi_\lambda(k, r)$ for some form of U and some value of k, then we can find the phase angle γ_λ for this k and U by means of the equation

$$\gamma_\lambda = \int_0^\infty [\Pi_\lambda(k, r) - \Pi_\lambda{}^0(k, r)]dr \tag{6b}$$

Eq. (5b) for the Π's is of a form suitable for numerical integration, and so it is possible to obtain values of the γ's for any form of U.

---

[2] W. E. Milne, Phys. Rev. 35, 863 (1930); E. L. Hill, Phys. Rev. 38, 1258 (1931); L. A. Young, Phys. Rev 38, 1612 (1931): Rojansky and Wetzel, Phys. Rev. 38, 1979 (1931).

As an example of this method,[3] the form

$$U = Ze^{-2r/r_0}/r \tag{7}$$

was chosen, Here again the γ's turn out to be functions of the parameters x and β defined in (4b).

A set of typical curves showing Π_λ and $\Pi_\lambda{}^0$ is given in Fig. 4.

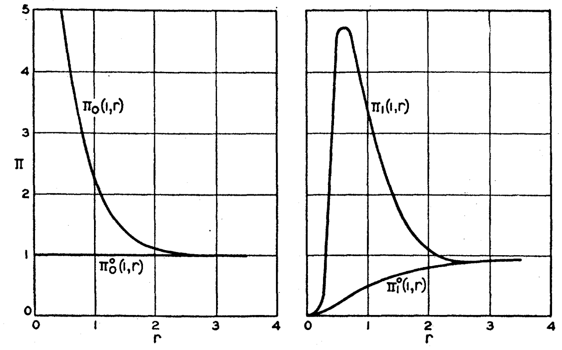

Fig. 4. Values of the functions $\Pi_\lambda(k, r)$ and $\Pi_\lambda{}^0(k, r)$ as a function of r for the potential function given in Eq. (7).

Fig. 5 shows curves for $\gamma_0(\beta, x)$ as a function of β. These curves show much the same characteristics as the curves in Fig. 2. Here also we have the values $\beta_{n\lambda}$, for which q_λ approaches infinity as k approaches zero, and where the quantized level labelled (n, λ) merges with the continuum of positive levels. These points, and the curves in general lie quite near to those given in Fig. 2, which indicates that the cross-section curves will be similar. Fig. 6 compares the cross-section curves for the two different forms of potential for the same values of β. The curves are quite closely alike, except that for very small values of x the curves for the U given in Eq. (7) are in general larger than the others. This is to be expected, since the second form of U is not limited to a finite region, but extends over all space; and it will affect very slow electrons to a greater extent than the first form of U, which is confined to a finite volume.

But except for these small values of x, the curves are very much alike. This indicates that for electrons of energies greater than one volt, say, the total cross section for elastic scattering from a potential field U is determined chiefly by the value of β, the square root of the integral $\int_0^\infty rU dr$, and depends only slightly on the particular shape of U. This explains the checks with experiment shown in Fig. 3, and shows that we are justified in computing atomic elastic cross sections by means of simplified potential functions.

Another method of determining γ_λ which is amenable to numerical integration is to consider the form (2a) to hold for all values of r, by making C and D functions of r.

---

[3] The computations were made on the Differential Analyser described by V. Bush, Jour. Frank. Inst. **212**, 447 (1931). The writer wishes to thank Dr. L. A. Young, and Mr. S. Caldwell for their help in these calculations.

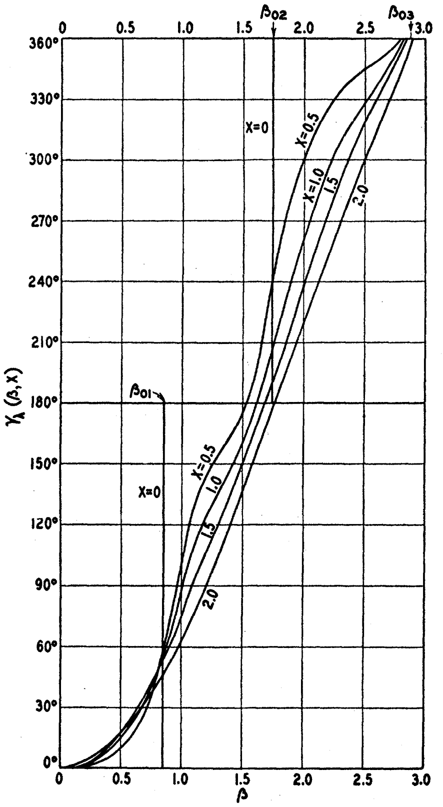

Fig. 5. Values of the phase angle $\gamma_0(\beta, k)$ as function of the field parameter β, for the potential field given in Eq. (7).

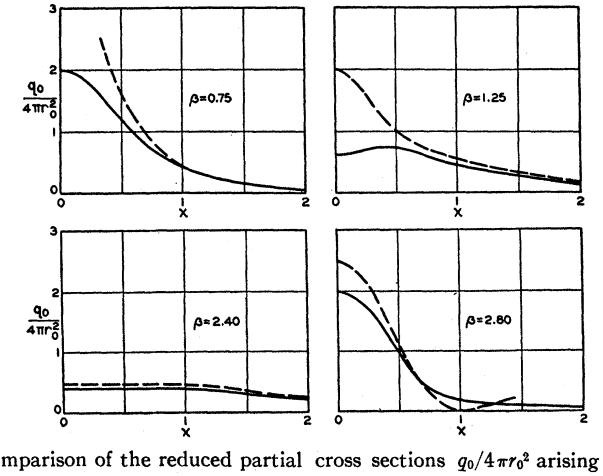

Fig. 6. Comparison of the reduced partial cross sections $q_0/4\pi r_0^2$ arising from the fields given in Eqs. (4a) and (7) as functions of the velocity parameter x, for the same values of the field parameter β. Solid lines correspond to Eq. (4a) and dotted lines to Eq. (7).

$$R_\lambda = r^{1/2}[c_\lambda(r)J_{\lambda+1/2}(kr) + d_\lambda(r)J_{-\lambda-1/2}(kr)]. \tag{8a}$$

Differential equations can then be obtained for c_λ and d_λ. Since R/r must be finite at $r=0$, we see that the initial conditions are that $c_\lambda(0)=1$, $d_\lambda(0)=0$. These c's and d's will approach constant values as r increases, and so

$$(-1)^\lambda \frac{d_\lambda(r)}{c_\lambda(r)} \xrightarrow[r\to\infty]{} \tan\gamma_\lambda$$

and therefore

$$q_\lambda = \frac{4\pi}{k^2}(2\lambda+1)\frac{d_\lambda^2(\infty)}{c_\lambda^2(\infty)+d_\lambda^2(\infty)}\,. \tag{8b}$$

This method has been applied to the Hartree potential functions for various atoms by Holtzmark.[4] The curves computed for the simple Hartree fields did not agree very well with experiment, but when a correction, in the form of a "polarization energy," was added the agreement was good.

In the above, it was tacitly considered that only elastic collisions could happen between a single particle and a potential field. This is not strictly true, however, for the particle may radiate light during the collision, and leave with a reduced kinetic energy. It is this process which gives rise to the continuous x-ray spectrum. It has been treated in a thorough manner by Sommerfeld[5] for the case of the coulomb field. The matrix elements of the electric moment are computed for the transition from a plane-wave-plus-scattered wave for some initial velocity, to another plane-plus-scattered wave for another direction and velocity. The intensities of the radiation arising from such a transition compare favorably with the experimental data. This process is important for electrons of energies of several thousand volts or larger, but can be completely neglected for electrons of energies of the order of a few hundred volts or less.

§8. SCATTERING FROM A CENTRALLY SYMMETRIC POTENTIAL FIELD. APPROXIMATE SOLUTIONS

We have seen in the foregoing section that the exact solution of the scattering problem involves a large amount of labor, and usually involves numerical integration; so that the cross sections and distributions-in-angle do not come out as analytic functions of the electronic velocity and constants of the field, but simply as a set of numerical values, each set for each different condition having to be calculated from the beginning. It is often better to obtain an approximate solution of the problem, giving answers in terms of known analytic functions than it is to obtain an exact solution which is unmanageable analytically. This is especially true in discussing complicated problems, where the results obtained for the various elementary problems must be combined to form a final solution. This section will be devoted to a

---

[4] Faxén and Holtzmark Zeits. f. Physik **45**, 307 (1927); Holtzmark, Zeits. f. Physik **48**, 231 (1928); **55**, 437 (1929); **66**, 49 (1930).

[5] Sommerfeld, Ann. d. Physik **11**, 257 (1931).

discussion of various approximation methods and to a few examples of the methods.

The chief question one asks of an approximate formula is; in what range is it valid? So a good portion of this section will be devoted to a discussion of the convergence of the approximation series developed.

If we know the solution of the radial Eq. (1) for some U_0 which has a form approximately like the actual U, i.e.,

$$U(r) = U_0(r) + U_1(r)$$

where U_1 is small compared to U_0, then (1) can be set in the form

$$R_\lambda'' + \left(k^2 + 2U_0 - \frac{\lambda(\lambda+1)}{r^2}\right) R_\lambda = -2U_1R_\lambda. \tag{9a}$$

This can be considered as an inhomogeneous equation, and we can apply the methods of Part I, page 61 to it. If U_0 goes to zero at least as fast as $1/r^2$ for large r then two independent solutions can be obtained for the homogeneous equation

$$y'' + \left(k^2 + 2U_0 - \frac{\lambda(\lambda+1)}{r^2}\right) y = 0 \tag{9b}$$

which behave like trigonometric functions for large r. Pick one of these solutions, $y_{\lambda 1}$, so that it is finite everywhere. Then multiply it by the appropriate constant so that

$$y_{\lambda 1} \underset{r\to\infty}{\rightarrow} \cos\left(kr - \pi\frac{\lambda+1}{2} + \Phi_\lambda\right). \tag{9c}$$

Then choose the other solution, $y_{\lambda 2}$, so that

$$y_{\lambda 2} \underset{r\to\infty}{\rightarrow} \sin\left(kr - \pi\frac{\lambda+1}{2} + \Phi_\lambda\right). \tag{9d}$$

These two solutions can be obtained, since we are supposed to know to solutions of (9b). We shall assume also that $U_0(r)$ does not go to infinity as fast as $1/r^2$ for vanishing r. Then we can show that if $y_{\lambda 1}$ behaves as $r^{\lambda+1}$ for small r, $y_{\lambda 2}$ will behave like $r^{-\lambda}$.

Then a solution of (9a) must satisfy the integral equation

$$R_\lambda(r) = a_\lambda y_{\lambda 1}(r) + \int_0^r K_\lambda(r, \mu) R_\lambda(\mu) d\mu \tag{10a}$$

where

$$K_\lambda(r, \mu) = \frac{2}{k}[y_{\lambda 1}(r)U_1(\mu)y_{\lambda 2}(\mu) - y_{\lambda 2}(r)U_1(\mu)y_{\lambda 1}(\mu)]. \tag{10b}$$

This is an integral equation of the second kind and its solution[6] is the series

$$R_\lambda(r) = a_\lambda \sum_{n=0}^{\infty} K_{\lambda,n}(r) \tag{10c}$$

---

[6] Bocher, Introduction to Integral Equations (Cambridge University Press, 1914) page 15.

where $K_{\lambda,0}(r)=y_{\lambda 1}(r)$, and $K_{\lambda,n}=\int_0^r K_\lambda(r,\mu)\,K_{\lambda,n-1}(\mu)\,d\mu$. This series is absolutely and uniformly convergent for all finite values of r, if $K_\lambda(r,\mu)y_{\lambda 1}(\mu)$ is finite for all values of $\mu \leqq r$; as long as $y_{\lambda 1}$ and $y_{\lambda 2}$ behave for vanishing r in the manner stated above.

We can rewrite (10c) in the form

$$R_\lambda(r) = \frac{2a_\lambda}{k}\left[y_{\lambda 1}(r) \sum_{n=0}^{\infty} F_{\lambda n 1}(r) - y_{\lambda 2}(r) \sum_{m=1}^{\infty} F_{\lambda m 2}(r) \right] \tag{11a}$$

where $F_{\lambda 01}=k/2$ and $F_{\lambda n1}(r)=\int_0^r U_1(\mu)y_{\lambda 2}(\mu)K_{\lambda,n-1}(\mu)d\mu$ and $F_{\lambda m2}(r)=\int_0^r U_1(\mu)y_{\lambda 1}(\mu)K_{\lambda,m-1}(\mu)d\mu$. For very large values of r, U_1 becomes so small that we can consider the F's as constants, and

$$R_\lambda(r) \underset{r\to\infty}{\longrightarrow} b_\lambda \cos\left(kr - \pi\frac{\lambda+1}{2} + \gamma_\lambda\right)$$

where

$$b_\lambda = \frac{2a_\lambda}{k}\left\{\left[\sum_{n=0}^{\infty} F_{\lambda n 1}(\infty)\right]^2 + \left[\sum_{m=1}^{\infty} F_{\lambda m 2}(\infty)\right]^2\right\}^{1/2}$$

and the phase angles γ_λ, which are to be inserted in (3a) and (3b) to determine the scattering, are

$$\gamma_\lambda = \Phi_\lambda + \tan^{-1}\left\{\frac{\sum_{m=1}^{\infty} F_{\lambda m 2}(\infty)}{\sum_{n=0}^{\infty} F_{\lambda n 1}(\infty)}\right\}. \tag{11b}$$

We have thus found a series solution for R_λ and for γ_λ which is as accurate as we please, if only we compute enough of the F's. In practice it is only feasible to compute at the most three F's, $F_{\lambda 01}$, $F_{\lambda 11}$ and $F_{\lambda 12}$, and so we must seek criteria telling how many F's must be used to obtain a required accuracy.

Let us examine the convergence of (10c) for the worst case, when $U_0=0$ and $U_1=U$. Then $y_{\lambda 1}=(\pi kr/2)^{1/2}\,J_{\lambda+1/2}(kr)$ and $y_{\lambda 2}=(-1)^\lambda(\pi kr/2)^{1/2}\,J_{-\lambda-1/2}(kr)$. For r less than $(\lambda+1)/k$, $y_{\lambda 1}$ can be represented approximately by the first term in its power series expansion

$$|\,y_{\lambda 1}| \leqq \frac{\pi^{1/2}(kr)^{\lambda+1}}{2^{\lambda+1}\Gamma(\lambda+3/2)}, \quad \text{also} \quad |\,y_{\lambda 2}| \leqq \frac{2^\lambda\Gamma(\lambda+\frac{1}{2})}{\pi^{1/2}(kr)^\lambda}.$$

Now suppose that we can find a number Z such that $|\,U|$ is less than Z/r for r less than some value r_0, and is negligible compared to k^2 for values of r greater than r_0. If this r_0 is finite, then the discussion of the convergence of (11b) for λ greater than kr_0-1 becomes simplified.

For then

$$|\,F_{\lambda n1}(\infty)\,| \leqq \frac{k}{2}\,\frac{(Zr_0)^n}{n!(\lambda+\frac{1}{2})(\lambda+1)\cdots(\lambda+n/2)}$$

$$|\,F_{\lambda m2}(\infty)\,| \leqq \frac{\pi Z}{2[\Gamma(\lambda+3/2)]^2}(kr_0/2)^{2\lambda+2}\frac{(Zr_0)^{n-1}}{(n-1)!(\lambda+1)\cdots(\lambda+(n+1)/2)}.$$

From this we see that the series of F's is absolutely convergent for all finite values of Z and of r_0 and that if $Zr_0/(\lambda+1)$ is smaller than our previously assigned limit of error, then only $F_{\lambda 01}$ and $F_{\lambda 12}$ need be considered in (11b). If this is not true, then we must compute the F's up to $F_{\lambda n1}$ and $F_{\lambda, n+1,2}$, where $\sum_{\nu=n+1}^{\infty}\Gamma(2\lambda+1)\cdot(2Zr_0)^{\nu}/(\nu!)\Gamma(2\lambda+\nu)$ is less than our assigned limit of error. No matter how large Zr_0 is, we can always do this.

Stated in another way; if we find that $|U(r)|$ is very much less than k^2 for $r \geqq r_0$ and is never greater than Z/r for $r \leqq r_0$, then our partial cross sections can be given by the formula

$$q_{\lambda} \sim \frac{16\pi}{k^4}(2\lambda+1)\left[\int_0^{\infty} U_1(\mu) y_{\lambda 1}{}^2(\mu) d\mu\right]^2 \tag{11c}$$

for every value of λ greater than some λ_0 where λ_0 is greater than kr_0-1 and is large compared to Zr_0-1.

When kr_0 is larger than $\lambda+1$ then our reasoning becomes somewhat more complicated, but it can be indicated here. The first maximum of $y_{\lambda 1}(r)$ comes at about $kr=\lambda+1$, and after than that the function behaves more or less sinusoidally. This means that the integrals $F_{\lambda n\nu}(r)$ start from zero at $r=0$, rise to the respective values $F_{\lambda n\nu}(\lambda+1/k)$ and then a further increase in r will only make a small change in the F's. The value of $F_{\lambda n\nu}(\infty)$ will therefore not be much different from $F_{\lambda n\nu}(\lambda+1/k)$, and we can safely say that if the series $\sum_n F_{\lambda n\nu}(\lambda+1/k)$ converges rapidly, then the series $\sum_n F_{\lambda n\nu}(\infty)$ will converge rapidly.

We can again use the first term in the expansion of the y's to give us an upper limit for the F's. We substitute $\lambda+1/k$ instead of r_0 in the formulas already obtained, and we see that instead of $Zr_0/(\lambda+1)$, Z/k must be small compared to unity in order that $F_{\lambda 01}$ and $F_{\lambda 12}$ alone give a satisfactory answer. Moller and Distel found this same criterion by quite other methods of reasoning.[7]

Our final statement of convergence is therefore the following: if k is much larger than Z then Eq. (11c) is a valid expression for the partial cross sections for all values of λ; but even if k is of the same order of magnitude or smaller than Z, (11c) will be valid for those values of λ much larger than Zr_0-1.

We notice also, from the equations for the F's, that $\sum_{\lambda=\lambda_0}^{\infty} q_{\lambda}$ $(\lambda_0+1 \gg Zr_0)$ is an absolutely convergent series. The above method of successive approximations is convenient for discussion of convergence, but it involves indefinite integrals, which are often extremely difficult to compute.

Born[8] has adapted the method used by Huygens and Kirchhoff for the diffraction of light to the scattering of electrons. This method is a successive approximation method involving definite integrals. The series obtained bears a close relationship to the series obtained above, but the integrals are usually much easier to handle.

---

[7] Møller, Zeits. f. Physik **66**, 513 (1930); Distel, Dissertation München, (1931).

[8] Born, Zeits. f. Physik **37**, 863 (1926); **38**, 803 (1926); Gött. Nach. page 146 (1926); Wentzel, Zeits. f. Physik **40**, 590 (1927).

We shall first show the relationship between the Born series and the series already developed, and thereby obtain convergence criteria for the Born method. Then we shall discuss the various applications of the method to specific problems.

To obtain the series, we notice that the general wave equation for the incoming particle

$$(\nabla^2 + k^2)\psi = -2U(r)\cdot\psi \tag{12}$$

is similar to a Helmholtz equation,[9] with $2U\psi$ corresponding to $4\pi\rho$. Therefore to satisfy (12), ψ must satisfy the integral equation

$$\psi(r) = f(r) + \int \psi(r')\cdot U(r')\frac{e^{ikR}}{2\pi R}dv'$$

where the integral is taken over all space. r stands for the coordinates r, θ, Φ; r' for r', θ', Φ' and R is the distance between the two points defined by the two sets. The function f is some solution of the equation $(\nabla^2+k^2)f=0$. dv' is the volume element $r'^2 \sin\theta' dr' d\theta' d\phi'$. We shall see later that the integral approaches zero for large values of r. Therefore f must represent the behavior of the electron at great distances from the scatterer, and thus for most experiments must represent the primary electron beam, e^{ikx}, where x is the direction of initial motion of the electron.

This integral equation can be stated in the form of a law of particle scattering.[10] If $2U(r)$ be the potential field on a particle (in atomic units), then each volume element dv scatters a wavelet whose amplitude at a distance R from the volume element is $(1/2\pi R)$ times the value of the potential function at the volume element, times the amplitude of the wave function at the volume element. This is the analogue of Huygens principle for particle waves.

If we set $f(r)$ equal to e^{ikx} then our equation becomes

$$\psi(r) = e^{ikx} + \int \psi(r')\cdot U(r')\frac{e^{ikR}}{2\pi R}dv'. \tag{13a}$$

The solution of this equation is

$$\psi(r) = \sum_{n=0}^{\infty} K_n(r) \tag{13b}$$

where $K_0(r)=e^{ikx}$, and $K_n(r)=\int K(r,r')\cdot K_{n-1}(r')dv'$. $K(r,r')=U(r')\cdot e^{ikR}/2\pi R$. This series represents ψ if it converges, so our first task is to obtain criteria for its convergence.

Certainly it diverges if $K_1(r)$ is infinite. This happens when $U(r)$ goes to infinity with decreasing r as fast as $1/r^2$ or faster.

A simple criterion for convergence can be obtained from the following considerations. Function K_1 is every where less than the integral $I(r)=$

---

[9] A. G. Webster, Partial Differential Equations of Mathematical Physics, (B. G. Teubner, Leipzig, 1927) page 220.

[10] Mott, Proc. Roy. Soc. **127 A**, 658 (1930).

$\int U(r')\cdot dv'/2\pi R$, and if U is a monotonic function of r, $I(r)$ is never greater than the integral

$$I(0) = 2\int_0^\infty U(r')r'dr'$$

Therefore $K_n(r) \leqq [I(0)]^n$, and so if $I(0)$ is less than unity series (13b) will certainly converge. This is in general too stringent a criterion, for the series of K's will often converge even though $I(0)$ is larger than unity, especially if k is large.

However we can transform series (13b) and compare it with series (10c). From Part I page 67 we see that

$$e^{ikx} = \left(\frac{2\pi}{kr}\right)^{1/2}\sum_{\lambda=0}^{\infty}(\lambda+\tfrac{1}{2})\cdot i^\lambda\cdot J_{\lambda+1/2}(kr)\cdot P_\lambda(\cos\theta)$$

and from part I page 72, that

$$K_1(r) = \frac{2}{k}\sum_{\lambda=0}^{\infty}(\lambda+\tfrac{1}{2})\cdot i^\lambda\cdot P_\lambda(\cos\theta) \cdot\int_0^\pi \sin\theta' d\theta'\int_0^\infty \frac{e^{ikR}}{R}\cdot P_\lambda(\cos\omega)\cdot y_{\lambda 1}(r')\cdot r'dr'$$

where ω is the angle between r and r', and where

$$y_{\lambda 1}(r) = (\pi kr/2)^{1/2}J_{\lambda+1/2}(kr)$$

as before. Also we can expand the e^{ikR}/R in Bessel and Hankel functions[11]

$$\frac{e^{ikR}}{R} = \begin{cases} \dfrac{2}{k}\,\dfrac{1}{rr'}\displaystyle\sum_\lambda(\lambda+\tfrac{1}{2})\cdot P_\lambda(\cos\omega)\cdot y_{\lambda 1}(r)\cdot y_{\lambda 3}(r') & (r\leqq r') \\ \dfrac{2}{k}\,\dfrac{1}{rr'}\displaystyle\sum_\lambda(\lambda+\tfrac{1}{2})\cdot P_\lambda(\cos\omega)\cdot y_{\lambda 3}(r)\cdot y_{\lambda 1}(r') & (r\geqq r') \end{cases}$$

where

$$y_{\lambda 3} = i(\pi kr/2)^{1/2}H_{\lambda+1/2}{}^{(1)}(kr).$$

Then series (13b) can be separated into the double series

$$\psi(r) = e^{ikx} + \frac{4}{k^2 r}\sum_{\lambda=0}^{\infty}(\lambda+\tfrac{1}{2})\cdot i^\lambda\cdot P_\lambda(\cos\theta)\left[\sum_{n=1}^{\infty}L_{\lambda n}(r)\right]. \tag{14a}$$

Here

$$\begin{aligned} L_{\lambda 0}(r) &= y_{\lambda 1}(r) \\ L_{\lambda n}(r) &= r\int_0^\pi \sin\theta' d\theta'\int_0^\infty U(r')\cdot P_\lambda(\cos\omega)\frac{e^{ikR}}{R}L_{\lambda,n-1}(r')r'dr' \\ &= y_{\lambda 3}(r)\cdot F_{\lambda n 3}(r) + y_{\lambda 1}(r)\cdot F_{\lambda n 4}(r) \end{aligned} \tag{14b}$$

---

[11] G. N. Watson, Theory of Bessel Functions, (Cambridge University Press, 1922) page 365.

where

$$F_{\lambda n3}(r) = \int_0^r y_{\lambda 1}(r')\cdot U(r')\cdot L_{\lambda,n-1}(r')dr'$$

$$F_{\lambda n4}(r) = \int_r^\infty y_{\lambda 3}(r')\cdot U(r')\cdot L_{\lambda,n-1}(r')dr'.$$

If U decreases for large values of r faster than $1/r$, then $F_{\lambda n4}(r)\xrightarrow[r\to\infty]{}0$, and (14a) simplifies. Since

$$y_{\lambda 3}(r) \underset{r\to\infty}{\longrightarrow} \exp i(kr - \lambda\pi/2)$$

we have for very large values of r

$$\psi(r) = e^{ikx} + \frac{4}{k^2}\frac{e^{ikr}}{r}\sum_{\lambda=0}^{\infty}(\lambda+\tfrac{1}{2})P_\lambda(\cos\theta)\sum_{n=1}^{\infty}F_{\lambda n3}(\infty). \tag{14c}$$

Again, as in (3b), we can obtain the total cross section for scattering as

$$q = \sum_\lambda q_\lambda$$

where

$$q_\lambda = \frac{16\pi}{k^4}(2\lambda+1)\sum_{n=1}^{\infty}[F_{\lambda n3}(\infty)]^2. \tag{15}$$

The functions $F_{\lambda n3}$ and $F_{\lambda n4}$ bear a very close relationship to the functions $F_{\lambda n1}$ and $F_{\lambda n2}$ used in series (11a), for the case $U_0=0$, $U_1=U$. In fact, in this case $F_{\lambda 11}=F_{\lambda 13}$. It is thus not difficult to see that all the convergence criteria developed in the previous discussion can be used for series (15), and therefore for series (13b).

Therefore if we can find a Z such that $|U(r)|$ is never greater than Z/r for values of r less than some finite r_0, where $|U|$ is negligible compared to k^2 for values of r greater than r_0, then *the single term* $K_1(r)$ *is a valid approximation for series* (13b) *as long as* k *is much larger than* Z. If k is not much larger than Z, *Eq.* (11c) *will be a valid approximation for series* (15) *for those values of* λ *much greater than* Zr_0. The error involved by the neglect of the rest of the terms is in the first case of the order of Z^2/k^2, and in the second case of the order of $Z^2r^2{}_0/(\lambda+1)$.[2]

This first criterion has been stated in several different ways in the literature.

If we consider that $k=hv/2\pi e^2$, where v is the initial velocity of the particle in cm/sec., then our criterion becomes

$$\frac{Z}{k} = \frac{2\pi e^2 Z}{hv} \ll 1.$$

But $2\pi e^2 Z/h$ is the velocity in cm/sec. which the particle would have by the Bohr theory in the lowest quantized state of the potential field $-Ze^2/r$.

Therefore the first term in the approximation series is sufficient to express the scattering of a particle by a potential field $V(r)$, *if the particle's velocity is large compared to any velocity it could have by Bohr theory in any of the quantized states of the field* $-|V(r)|$.[7] Thus we see that the convergence depends on the particle's initial velocity and not on its energy or momentum.

If we consider the classical behavior of a particle of energy k^2 in the repulsive potential field $|2U(r)|$ (in atomic units), then the distance of closest approach of the particle to the force center, which we can call r_c, is the solution of the equation $|2U(r_c)| = k^2$. Since we have defined Z so that U is never greater than Z/r, then $Z \geqq r_c k^2/2$. If k is to be larger than Z, it must be larger than $r_c k^2/2$; which means that $2/k$ must be larger than r_c. But $2\pi/k$ is the de Broglie wave-length of the primary particle beam.

Therefore *the first term in the approximation series is valid if the de Broglie wave-length of the primary beam is large compared to* r_c.

If k is of the same order of magnitude as Z then the first approximation still holds if the electron has an angular momentum $h\lambda/2\pi$ such that $h\lambda/2\pi$ is great compared to $hZr_0/2\pi$, or great compared to $hkr_0/2\pi$. But the distance of closest approach to the center for electrons with such angular momentum is about equal to λ/k. From the last inequality we see that even if the electron's initial de Broglie wave-length is not large compared to r_c, the first approximation is valid if the particle has an angular momentum such that its approach to the center is greater than r_0.

The whole criterion can be summed up as follows: the scattering of a particle from a centrally symmetric field $V(r)$ can be expressed by the first term in one of the various approximation series given above, *if the particle's distance of closest approach to the scattering center (computed by classical methods for the field* $|V(r)|$*) either is much smaller than the de Broglie wave-length of the particle initially, or else is larger than the radius outside which* V *is negligible compared to the particle's initial energy.*

Having discussed the range of validity of the Born method, let us apply it to some specific cases.

It might be well to apply it first to a case we have solved exactly, so as to determine whether our criteria are dependable. If we use the field given in (7)

$$U(r) = \frac{Ze^{-2r/r_0}}{r}$$

and apply (11c) to obtain approximate values of the cross section we find[12]

$$F_{\lambda 11}(\infty) = F_{\lambda 13}(\infty) = \int_0^\infty U(w) \cdot y_{\lambda 1}^2(w) \cdot dw = \frac{\pi k Z}{2} \int_0^\infty e^{-2w/r_0} [J_{\lambda+1/2}(kw)]^2 dw$$
$$= \frac{Z}{2} Q_\lambda \left(\frac{2}{r_0^2 k^2} + 1 \right)$$

where Q_λ is a Legendre function of the second kind.[13] Therefore

---

[12] Watson, Theory of Bessel Functions, page 389.

$$q_\lambda \sim 16\pi r_0^2 \frac{\beta^4}{x^4}(2\lambda + 1)Q_\lambda\left(1 + \frac{2}{x^2}\right). \tag{16a}$$

Fig. 7 shows the relation between the curves obtained from (16a), (dotted lines) and the exact solutions (solid lines). These curves show that our criteria are the right ones, if we interpret the phrase *much smaller than* used in the criteria to mean less than half as large.

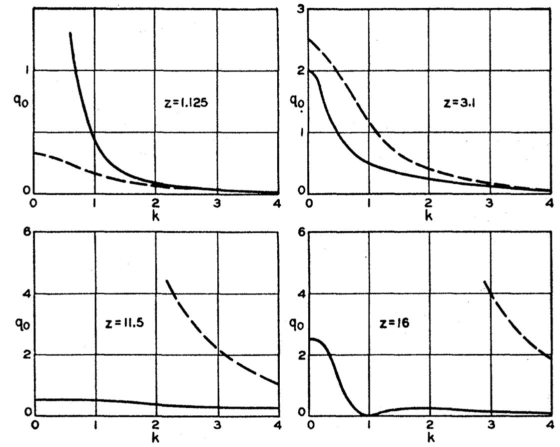

Fig. 7. Comparison of exact partial cross section q_0 for the field given in Eq. (7) with those given by approximate formula (16a) for the same field. The exact curves are shown as solid lines and the approximate ones as dotted lines.

To obtain the angular distribution, we remember that our wave function can be written as

$$\psi(r) \cong e^{ikx} + \frac{e^{ikr}}{r} f(\theta)$$

where $f^2(\theta)$ gives us the angular distribution of scattered current per unit solid angle. By using (14c) with only the terms $n=1$ included, we see that[14]

$$\begin{aligned} f(\theta) &\cong \frac{Z}{k^2}\sum_\lambda(2\lambda + 1)P_\lambda(\cos\theta)Q_\lambda\left(1 + \frac{2}{r_0^2k^2}\right) \\ &= 2Zr_0^2/(4 + \mu^2r_0^2) \end{aligned} \tag{16b}$$

where $\mu = 2k\sin(\theta/2)$. By integration of f^2 over all directions, or from (16a), by use of the formula

$$\sum(2\lambda + 1)[Q_\lambda(x)]^2 = 1/(x^2 - 1)$$

we obtain the total cross section

$$q \cong 4\pi r_0^2\beta^4/(1 + x^2). \tag{16c}$$

---

[13] Whittaker and Watson, Modern Analysis (Cambridge University Press 1927), page 316.

[14] Reference 13, page 322.

However, if we are only going to compute the first approximation, we can obtain the above formulas and others without expanding (13b) into a series involving zonal harmonics. If we only use the first two terms in the series, (13b) becomes

$$\psi(r) \cong e^{ikx} + \int e^{ikx'} U(r') \frac{e^{ikR}}{2\pi R} dv'$$

and if we only wish to find the value of ψ for large values of r, we can use the method of reasoning given in Part I page 71, and obtain

$$\psi(r) \cong e^{ikx} + \frac{e^{ikr}}{2\pi r} \int e^{i\boldsymbol{r}' \cdot (\boldsymbol{k}_i - \boldsymbol{k}_s)} U(r') dv' \tag{17a}$$

where $\boldsymbol{k}_i$ is a vector of length k in the direction of the primary beam, $\boldsymbol{k}_s$ is the corresponding vector in the direction of the scattered beam, at an angle θ to $\boldsymbol{k}_i$, and $\boldsymbol{r}'$ is the vector giving the position of the volume element dv' with respect to the force center. The vector $(\boldsymbol{k}_i - \boldsymbol{k}_s)$ has a length $\mu = 2k \sin(\theta/2)$, and we can use its direction for the pole of the spherical coordinates r, θ, ϕ. By integrating over the angles φ and ϑ we see that

$$\psi(r) = e^{ikx} + e^{ikr} f(\mu)/r \tag{17b}$$

where

$$\mu = 2k \sin(\theta/2) \text{ and } f(\mu) \cong 2 \int_0^\infty U(r) \frac{\sin \mu r}{\mu r} r^2 dr. \tag{17c}$$

Inserting $U = Ze^{-2r/r_0}/r$ makes $f(\mu) = 2Zr_0^2/(4 + \mu^2 r_0^2)$, which checks with (16b). The angular distribution of scattered current due to any potential $U(r)$ is therefore given by $f^2(\mu)$, where $f(\mu)$ can be computed by means of (17c), subject to our criteria of validity developed above.[15]

We can use these formulas to give us the elastic scattering of high velocity electrons from atoms. In the next section we shall see that exchange effects and polarization drop out for large initial velocities, and the elastic scattering simply becomes that due to the combined potential field of the nucleus and of the atomic electrons. In that case the potential due to a spherically symmetric atom of atomic number Z whose electrons are distributed with a density $\rho(r)$, is

$$U(r) = \frac{4\pi}{r} \int_r^\infty \rho(x) x^2 dx - 4\pi \int_r^\infty \rho(x) x dx.$$

The $\rho(r)$ is of course the sum of the squares of the atomic wave functions.

---

[15] The angular scattering from various kinds of fields has been computed by a number of workers. Among them are:

Massey, Proc. Roy. Soc. **127,** 671 (1930), alpha-particles from nuclei.

Mitchell, J. Frank. Inst. **207,** 753 (1929), electrons from Thomas-Fermi atomic potentials.

Møller, Zeits. f. Physik **62,** 54 (1929), alpha-particles from nuclei.

Mott, Proc. Roy. Soc. **124,** 425 (1929), fast electrons from bare nuclei, using the Dirac equation for the electron; Proc. Camb. Phil. Soc. **24,** 304 (1929), electrons from a Hartree. charge distribution in helium.

Sexl, Zeits. f. Physik **67,** 766 (1931), alpha-particles from nuclei.

Wentzel, Zeits. f. Physik **40,** 590 (1927), particles from a field of the type of Eq. (7).

When we insert this expression in (17c) and integrate by parts, we find that

$$\begin{aligned} f(\mu) &\cong \frac{8\pi}{\mu^2}\int_0^\infty \left(1 - \frac{\sin \mu r}{\mu r}\right)\rho(r)r^2dr \\ &= \frac{2Z}{u^2}[F(0) - F(\mu)] \end{aligned} \tag{18}$$

where

$$F(\mu) = \frac{4\pi}{Z}\int_0^\infty \rho(r)\frac{\sin \mu r}{\mu r}r^2dr,$$

and, of course, $F(0) = 1$.

We have thus obtained an expression for the elastic scattering of fast electrons from neutral atoms, in terms of the atomic number and the electron distribution. The function $F(\mu)$ is equal to the x-ray structure factor,[16] since $\mu = 4\pi \sin (\theta/2)/\lambda$, where λ is the electron's de Broglie wave-length. Therefore if we know the x-ray scattering from an atom, we can determine its electron scattering, and vice versa, within the ranges set by our criteria above.

We notice that no matter what the atomic charge density, our scattering function $f^2(\mu)$ depends on angle and velocity only through the product

$$\mu = 2k \sin (\theta/2) = 0.5425(E_v)^{1/2} \sin (\theta/2)$$

where E_v is the initial electronic energy, measured in volts. We can use this as a criterion for the validity of the approximation, for whenever the experimentally determined data are not a function of μ alone, then (17c) is no longer a valid expression for the angle distribution.

When μ becomes very large, $F(\mu)$ approaches zero (for $r\rho(r)$ goes to zero as r goes to zero), and the angle scattering approaches the Rutherford law

$$f_R(\mu) = 2Z/\mu^2.$$

Therefore the expression $1 - F(\mu)$ is equal to the ratio of the actual scattered amplitude to the Rutherford amplitude, $f(\mu)/f_R(\mu)$. This quantity, which we shall call $R(\mu)$, approaches unity as μ increases, and is the best form to which the experimental data can be reduced.

Curves of $R(\mu)$ are plotted for helium in Fig. 8 (solid line) and for neon in Fig. 9. The ρ's used were those obtained by variational methods.[17] The curve for the $r^2\rho(r)$ used for helium is shown by line A in Fig. 10. The presence of the two electronic shells in neon is clearly shown in the curve, the dotted line marked K giving the effect of the inner shell and that marked L the effect of the outer shell. This illustrates a general property of $R(\mu)$ which we can deduce from (18). The function $\sin \mu r/\mu r$ equals unity for $r = 0$, goes to zero

---

[16] A. H. Compton, X-Rays and Electrons (Van Nostrand, 1926) page 122. Wentzel, Zeits. f. Physik **43**, 1 and 779 (1927). See also Eq. (27a) et seg. For some applications of (18) to the structure of Molecules, see Mark and Weierl, Zeits. f. Physik **60**, 741 (1930), Mark and Weierl, Zeits. f. elekt. Chem. **36**, 675 (1930), Wierl, Ann. d. Physik **8**, 521 (1931).

[17] Eckart, Phys. Rev. **36**, 878 (1930); Zener, Phys. Rev. **36**, 51 (1930).

for $r=\pi/2\mu$, and thereafter oscillates with rapidly diminishing amplitude. Therefore by far the greatest part of the integral $F(\mu)$ comes for values of r less than $1/\mu$. This means that, very approximately, $ZR(\mu)$ represents the total charge present in the atom inside a sphere of radius $1/\mu$. The curve for neon shows that the average position of the electrons in the L shell is about 0.7 Bohr radii, and that the probability of these electrons being closer to the nucleus than 0.2 Bohr radii is negligible.

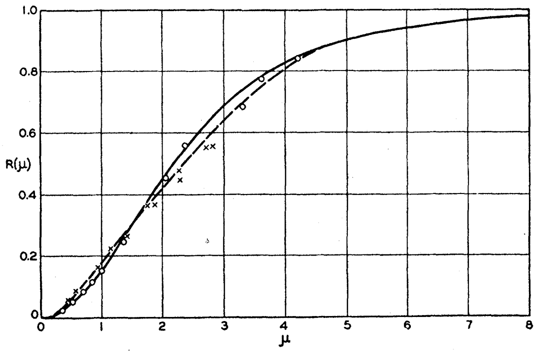

Fig. 8. Ratio $R(\mu)$ of the actual scattered amplitude $f(\mu)$ to the Rutherford amplitude $2Z/\mu^2$ as function of μ for helium. Solid line is the theoretical curve, circles are experimental points obtained by Dymond and Watson, and crosses those determined by McMillen.

When we use the experimental data available to check these curves, we must remember that we cannot be sure that formula (18) is valid unless k is much greater than Z. This means that we should use only data for electrons of energy greater than 13.6 Z^2 volts; or greater than 60 volts for helium, and greater than 1400 volts for neon. There are considerable such data for helium,[18] but none for neon.

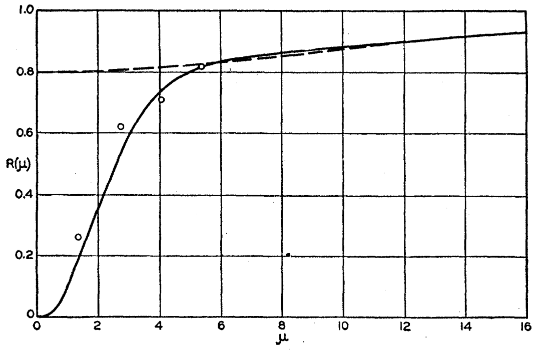

Fig. 9. Ratio, $r(\mu)$, of the actual scattered amplitude to the Rutherford amplitude as a function of μ for neon. The dotted line is the theoretical ratio for the K shell, solid line the theoretical ratio due to both K and L shells, and circles are the experimental points determined by Arnot.

---

[18] Dymond and Watson, Proc. Roy. Soc. **125**, 660 (1929); McMillen, Phys. Rev. **36**, 1034 (1930).

However, undoubtedly our criterion is too stringent, and even if k is a bit smaller than Z it may be that (18) still holds. In fact we can be reasonably sure that (18) is valid as long as the experimental data turn out to be a function of μ alone. Using this criterion we find that some of the data obtained by Arnot[19] for neon may possibly be expected to correspond with the curve in Fig. 9. The points are shown in the figure. We cannot say much about the check, for the data only cover a part of the curve.

Of course the absolute magnitude of the experimentally determined points is not usually known, the data being equal to $a^2f^2(\mu)$, where a is an unknown constant dependent on the dimensions of the particular apparatus used in making the measurements. The square root of the data is $af(\mu)$, however, and a can be determined by taking the average ratio between the experimental af and the theoretical f, for all the data from one source. Even if the theoretical curve is for a charge density which is not quite correct this method of determining a should be fairly accurate.

The experimental points for helium are shown in Fig. 8. We note that the data obtained by Dymond and Watson check the solid curve almost exactly, but that the data obtained by McMillen seem to require a flatter curve, something like the dotted line. It would be interesting to work back from this dotted curve to see what charge distribution it represents.

This can be done, and in every case that formula (18) is valid a unique answer can be obtained.

We notice that (17c) and (18) are both Fourier integrals, and can therefore be inverted,[20] giving

$$\begin{aligned} r^2\rho(r) &= \frac{Zr}{2\pi^2}\int_0^\infty \sin \mu r(1 - R(\mu))\mu d\mu \\ U(r) &= \frac{Z}{r} + \frac{1}{\pi r}\int_0^\infty \sin \mu r(f(\mu) - f_R(\mu))\mu d\mu . \end{aligned} \tag{19}$$

Applying the first formula to the dotted curve in Fig. 8, we obtain the curve marked B in Fig. 10 for the curve of $r^2\rho(r)$ computed from McMillen's data. The curve marked A is the theoretical curve, which fits Dymond and Watson's data very well, and curve C is the curve obtained by A. H. Compton[21] by a similar method from x-ray scattering data. The difference between the three curves is surprisingly small.

Eq. (19) must be used with care, however, for it assumes a knowledge of f from $\mu=0$ to $\mu=\infty$; and the form of the ρ or U obtained will sometimes be tremendously altered by a small change in the shape of the curve which must be assumed beyond the values of μ which are observed.

It might seem that by observing the deviation from the Rutherford scattering for very fast alpha-particles, one could determine the potential field of the nucleus. We should expect that formulas (19) would hold if the data turn

---

[19] Arnot, Proc. Roy. Soc. **133**, 615 (1931).

[20] Muskat, Phys. Rev. **35**, 1583 (1930); **38**, 23 (1931).

[21] A. H. Compton, Phys. Rev. **35**, 925 (1930).

out to be functions of μ only. Unfortunately this does not seem to be the case.[22] The scattering from Mg seems to start out as a function of μ for small values of μ, but this simple dependence seems to disappear for larger values; while no simple dependence is anywhere discernable for the other elements investigated. The attempts[23] to fit the magnesium curve by means of an assumed field, using formula (17c), have not been successful, and it seems that the more exact and more complicated methods discussed in section 7 must be used.[1] It would seem that the fields encountered inside the nucleus were just too large for the first approximation to be valid at the speeds at present available. Perhaps if sources of alpha-particles, of speeds two or three times greater than those now used, were obtainable, data could be gotten which would be amenable to the application of formulas (19).

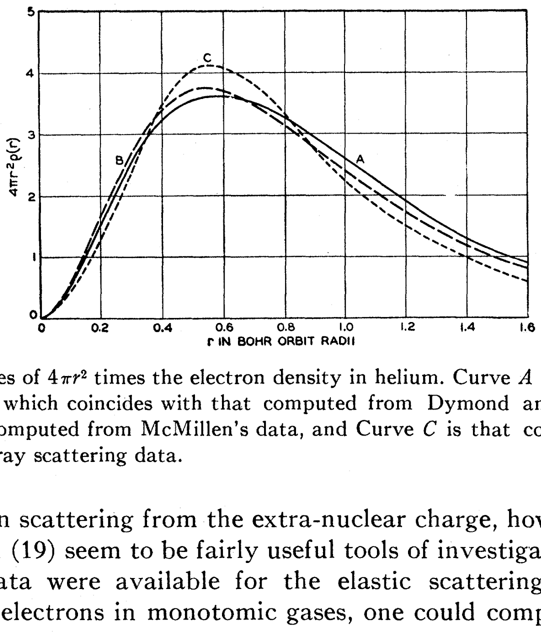

Fig. 10. Values of $4\pi r^2$ times the electron density in helium. Curve A is the approximate theoretical curve, which coincides with that computed from Dymond and Watson's data. Curve B is that computed from McMillen's data, and Curve C is that computed by A. H. Compton from x-ray scattering data.

For electron scattering from the extra-nuclear charge, however, formulas (17c), (18) and (19) seem to be fairly useful tools of investigation. If angular distribution data were available for the elastic scattering of one-to-ten thousand volt electrons in monotomic gases, one could compute the charge distribution inside the gas atoms quite easily.

§9. Scattering of Electrons by Atoms.

So far we have assumed that the effect of the scattering atom on the scattered particle can be represented by means of an effective potential field, and that the atom itself is not disturbed by the collision. This is, of course, not strictly true, in fact in many cases it is a very bad assumption to make; for the atom may be considerably disturbed by the collision. In this section

---

[22] Bieler, Proc. Roy. Soc. **105,** 434 (1924), scattering from Mg and Al.
Rutherford and Chadwick, Phil. Mag. **50,** 889 (1925), scattering from Mg and Al.
Rutherford and Chadwick, Phil. Mag. **4,** 605 (1927), scattering from He.
Riezler, Proc. Roy. Soc. **134,** 154 (1931), from Mg, Al, B and C.

[23] Massey, Møller and Sexl. See footnote 15.

we shall take into account the fact that the atom is made up of electrons which can be disturbed by the colliding particle, and shall try to see what effect this has on the scattered particle.

This is naturally a much more difficult task, and in general we shall have to be satisfied with approximate answers. Accordingly we shall be interested in criteria for the validity of these answers, and also in criteria indicating when we can safely substitute a potential field for the atom, and use the methods discussed in the previous sections.

The energy operator for a neutral atom of atomic number Z plus an extra electron is that of a negative ion. If we denote the coordinates of the extra electron by r_0, ϑ_0, and φ_0, and of the atomic electrons by r_σ, ϑ_σ and φ_σ, where σ runs from 1 to Z, and if we call the distance between the σth and τth electron $r_{\sigma\tau}$, the negative Hamiltonian for the system in atomic units is

$$H = \sum_{\sigma=0}^{Z}\left(\nabla_\sigma^2 + \frac{2Z}{r_\sigma}\right) - \sum_{\sigma=0}^{Z}\sum_{\tau=\sigma+1}^{Z}\frac{2}{r_{\sigma\tau}}\cdot$$

The incoming particle need not be an electron, of course, and the above Hamiltonian will be correct if we multiply ∇_0^2 by the ratio of the mass of the electron to the mass of the particle used.

The most obvious method of attack[24] is to consider the unperturbed atom, satisfying the Hamiltonian

$$H_0 = \sum_{\sigma=1}^{Z}\left(\nabla_\sigma^2 + \frac{2Z}{r_\sigma}\right) - \sum_{\sigma=1}^{Z}\sum_{\tau=\sigma+1}^{Z}\frac{2}{r_{\sigma\tau}} \tag{20a}$$

being perturbed by the potential

$$2U_0 = \frac{2Z}{r_0} - \sum_{\sigma=1}^{Z}\frac{2}{r_{0\sigma}} \tag{20b}$$

and to take the perturbation into account by a successive approximations method. The Schroedinger equation which must be satisfied is

$$[\nabla_0^2 + H_0 + 2U_0 + E]\Psi = 0. \tag{20c}$$

The energy of the system, E, must be made up of the initial kinetic energy of the incoming electron k_i^2, plus the energy of the atom in its initial state E_i.

After the collision the atom can be in any state labelled by the ensemble of quantum numbers ν (the initial state is the special case $\nu = i$), with energy E_ν and wave function $\psi_{\nu 0}$, where

$$(H_0 + E_\nu)\psi_{\nu 0} = 0.$$

The labels ν are arranged so that $\nu = 0$ is the normal state (usually but not necessarily the initial state), $\nu = 1$ the state with next lowest energy, etc.

---

[24] Born, Gött. Nach., page 146 (1926).

If the incoming particle is an electron, it is also possible that it will have changed places with the σth atomic electron during the collision. The final atomic wave function will then be $\psi_{\nu\sigma}$, where

$$(H_\sigma + E_\nu)\psi_{\nu\sigma} = 0$$

$$H_\sigma = \sum_{\alpha=0}^{Z}\left(\nabla_\alpha^2 + \frac{2Z}{r_\alpha}\right) - \sum_{\alpha=0}^{Z}\sum_{\tau=\alpha+1}^{Z}\frac{2}{r_{\alpha\tau}}(\alpha,\tau \neq \sigma). \tag{20d}$$

Thus $\psi_{\nu\sigma}$ is a function of all the electronic coordinates except those of the σth one; just as $\psi_{\nu0}$ is a function of all except the *zeroth electron*, the incoming one.

Some of these wave functions represent the various excited levels of the neutral atom, where the allowed energies form a discrete set, and the wave function decreases like a real exponential if we make any of the r_σ's very large. Others of the wave functions represent the ionized atom, where the allowed energies form a continuous set, and the wave functions decrease much more slowly than a real exponential as one or more of the r_σ's is made large; corresponding to the fact that one or more of the atomic electrons is free and leaving the atom. The set $\psi_{\nu\sigma}$ for a given σ and for all values of ν forms a complete orthogonal set of functions for all the electronic coordinates except those of the σth electron.

Consequently the function $U\Psi$ can be expanded in terms of the functions $\psi_{\nu0}$,

$$U\Psi = \sum_{\nu=0}^{\infty} a_\nu(r_0)\psi_{\nu0}; \quad a_\nu = \int \bar{\psi}_{\nu0} U\Psi dV_1 \cdots dV_Z$$

where the integral for a_ν is taken over all the atomic electronic coordinates. The summation sign indicates a sum over the discrete states and an integral over the continuous states.

Consequently our Eq. (20c) becomes

$$[\nabla_0^2 + H_0 + E_i + k_i^2]\Psi = -2\sum_{\nu=0}^{\infty} a_\nu(r_0)\psi_{\nu0}.$$

Considering this as an inhomogeneous equation for Ψ, we can show that it is equivalent to the integral equation

$$\Psi = \psi_{i0}e^{ik_ix_0} + \sum_{\nu=0}^{\infty}\psi_{\nu0}\int a_\nu(r')\frac{e^{ik_\nu R}}{2\pi R}dV' \tag{21a}$$

where the integral is taken over the coordinates r', ϑ' and φ', where $R = |r_0 - r'|$, as in Eq. (13a), and where k_ν^2 is the initial energy of the incoming electron minus the difference between the energies of the final and initial states of the atom,

$$k_\nu^2 = k_i^2 - (E_\nu - E_i). \tag{21b}$$

If the incoming particle is not an electron (21a) and the equations obtained from it will still be correct if r_0, r' and R are measured in the proper units. If the electron's charge and mass are e and m, and the particle's charge and mass are E and M, then the proper unit of length for the particle is me/ME times the unit of length for the electron, the Bohr orbit radius. Also the unit of energy for k^2 must be ME^2/me^2 times the unit of energy for the electron. If we wish to keep the units of atomic energy in atomic units, we must change (21b) to read

$$k_\nu^2 = k_i^2 - \frac{me^2}{ME^2}(E_\nu - E_i)$$

where E_ν and E_i are still given in atomic units, and the k^2's are in the units proper to the particle.

A solution of (21a) is

$$\Psi = \sum_{\nu=0}^{\infty} \psi_{\nu 0} \sum_{n=0}^{\infty} K_{n\nu}(r_0) \tag{22a}$$

where

$$K_{0\nu}(r) = e^{ik_i x}\delta_{i\nu}; \quad \delta_{i\nu} = \begin{cases} 0 & (\nu \neq i) \\ 1 & (\nu = i) \end{cases}$$

and

$$K_{n\nu}(r) = \sum_{\nu'} \int U_{\nu\nu'}(r')K_{n-1,\nu'}(r')\frac{e^{ik_\nu R}}{2\pi R}dV'. \tag{22b}$$

The function $U_{\nu\nu'}$ is the matrix element for the transition $\nu \rightarrow \nu'$,

$$U_{\nu\nu'}(r_0) = \int \bar{\psi}_{\nu 0} U \psi_{\nu' 0} dV_1 dV_2 \cdots dV_Z.$$

Let us defer the discussion of the convergence of the series (22a) until later in the section, and let us discuss the behavior of the first approximation to Ψ; i.e., the behavior of (22a) when we neglect all $K_{n\nu}$'s for n larger than unity.

The sum over ν divides naturally into two parts, that part where k_ν is real, where the initial kinetic energy of the incoming electron is greater than the energy required to raise the atom from its initial to its final state; and that part where k_ν is imaginary, where k_i^2 is less than the difference between E_ν and E_i. Suppose that ν_0 is the largest value of ν for which k_ν is real. If we have ordered our labelling correctly then k_ν will be real for all values of ν less than ν_0. If k_i is small (i.e., if the incoming electron is a slow one) ν_0 can be i, and the only state for which k_ν is real is the initial state (or, if the initial state is not the normal state, k_ν will be real for the initial state and for all lower states). If k_i is somewhat larger ν_0 may correspond to one of the quantized states above the initial one, and if k_i is large enough ν_0 will correspond to one of the continuous states representing an ionized atom.

At any rate we can represent our approximation by the expression

$$\Psi \cong \psi_{i0}e^{ik_i x_0} + \sum\nolimits_1 + \sum\nolimits_2$$

where

$$\Sigma_1 = \sum_{\nu=0}^{\nu_0} \psi_{\nu 0} \int U_{\nu i}(r') \frac{e^{i(k_i x' + k_\nu R)}}{2\pi R} dV' \tag{23}$$

$$\Sigma_2 = \sum_{\nu=\nu_0+1}^{\infty} \psi_{\nu 0} \int U_{\nu i}(r') \frac{e^{ik_i x' - \kappa_\nu R}}{2\pi R} dV'$$

and where $\kappa_\nu = i\kappa_\nu$.

The sum Σ_1 represents all the final states of the atom associated with an outgoing scattered current of the incoming particle. We notice that only those states are represented whose energies are smaller than $k_i^2 + E_i$. The sum Σ_2 represents those final states where the incoming particle is bound to the atom: there is no outward scattered current because the coefficient of R in the integral is real. If the incoming particle is not an electron, this second sum need not concern us very much, for we are not usually interested in the probability of formation of a molecular ion. If the incoming particle is an electron, however, this sum must be taken into account, fundamentally because we cannot distinguish between one electron and another.

However, we shall return to the question of Σ_2 later, after we have treated Σ_1, which is usually the most important part of the correction.

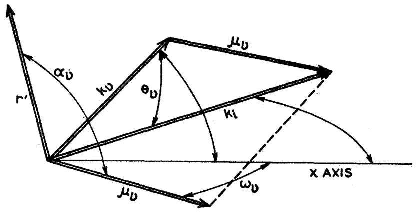

Fig. 11. Relation of initial, final, and recoil momentum vectors.

When r_0 is large, the terms in Σ_1 can be simplified by the method used in Part I, page 71, and already applied to Eq. (17a), Part II. The coefficient of $\psi_{\nu 0}$ becomes

$$\frac{e^{ik_\nu r_0}}{2\pi r_0} \int U_{\nu i}(r') e^{i\mathbf{r}' \cdot (\mathbf{k}_i - \mathbf{k}_\nu)} dV' \tag{24a}$$

where, as before, $\mathbf{k}_i$ is the vector representing the direction and wave number of the primary beam, and $\mathbf{k}_\nu$ represents the direction and wave number of the scattered beam corresponding to the νth final atomic state. (See Fig. 11.) The angle between the two is θ_ν. If we refer the direction of $\mathbf{r}'$ to the vector $\boldsymbol{\mu}_\nu = \mathbf{k}_i - \mathbf{k}_\nu$, we can take the angle between $\mathbf{r}'$ and $\boldsymbol{\mu}_\nu$ to be α_ν, and the angle between $\boldsymbol{\mu}_\nu$ and the x axis to be ω_ν. This vector $\boldsymbol{\mu}_\nu$ is proportional to the recoil momentum imparted to the atomic electrons, since $\mathbf{k}_i$ is proportional to the momentum of the incoming particle and $\mathbf{k}_\nu$ to its final momentum. We can expand the exponential

$$e^{i\mathbf{r}' \cdot \boldsymbol{\mu}_\nu} = \left(\frac{2\pi}{\mu_\nu r'}\right)^{1/2} \sum_{\lambda=0}^{\infty} (\lambda + \tfrac{1}{2}) i^\lambda J_{\lambda+1/2}(\mu_\nu r') P_\lambda(\cos \alpha_\nu)$$

where

$$\mu_\nu^2 = k_i^2 + k_\nu^2 - 2k_i k_\nu \cos\theta_\nu, \text{ and } \sin\omega_\nu = (k_\nu/\mu_\nu)\sin\theta_\nu.$$

It is best, however, to refer directions to the direction of the primary beam, the x axis. The vectors $\mathbf{x}$, $\boldsymbol{\mu}_\nu$, and $\boldsymbol{r}'$ form the corners of a spherical triangle whose sides are the angles α_ν, ω_ν and ϑ'. We can transform[25] $P_\lambda(\cos\alpha_\nu)$ into a combination of tesseral harmonics of ω_ν, ϕ_ν and of ϑ', φ',

$$e^{i\mathbf{r}'\cdot\boldsymbol{\mu}_\nu} = \left(\frac{2\pi}{\mu_\nu r'}\right)^{1/2}\sum_{\lambda=0}^{\infty}(\lambda+\tfrac{1}{2})i^\lambda J_{\lambda+1/2}(\mu_\nu r')$$

$$\cdot\sum_{m=0}^{\lambda}2\cos m(\phi_\nu-\varphi')\frac{(\lambda-m)!}{(\lambda+m)!}\cdot\sin^m\omega_\nu\cdot\sin^m\vartheta'\cdot P_\lambda^m(\cos\omega_\nu)\cdot P_\lambda^m(\cos\vartheta').$$

If $U_{\nu i}$ is spherically symmetric, then when we perform the integration in (24a) over the angles φ' and ϑ', all the terms in the sum become zero except the one for $\lambda=0$. Since $(\pi\mu_\nu r'/2)^{1/2}J_{1/2}(\mu_\nu r')=\sin(\mu_\nu r')$, the integral reduces to a simple Fourier integral of the same form as (17c).

If $U_{\nu i}$ is not spherically symmetric it can be expanded into a series of tesseral harmonics

$$U_{\nu i}(r') = \sum_{\lambda,m}e^{im\varphi'}\sin^m\vartheta'\,P_\lambda^m(\cos\vartheta')u_{\nu i\lambda m}(r')$$

where $u_{\nu i\lambda m}$ is a function of r' only. Substituting all these series into the series for Σ_1 we have

$$\Sigma_1 = \sum_{\nu=0}^{\nu_0}\psi_{\nu 0}\frac{e^{ik_\nu r_0}}{r_0}f_\nu(\omega_\nu,\mu_\nu) \tag{24b}$$

where

$$f_\nu = \sum_{\lambda,m}i^\lambda e^{im\phi_\nu}\sin^m\omega_\nu\,P_\lambda^m(\cos\omega_\nu)f_{\nu m\lambda}(\mu_\nu)$$

and

$$f_{\nu m\lambda} = \int_0^\infty u_{\nu im\lambda}(r)\cdot(2\pi/\mu_\nu r)^{1/2}J_{\lambda+1/2}(\mu_\nu r)r^2dr. \tag{24c}$$

Sum (24b) indicates that the incoming particle can be scattered from the atom, leaving the atom in any excited state whose energy is not farther above the initial atomic energy than the value of the particle's initial kinetic energy. The scattered current corresponding to the νth atomic state, per unit primary current density per unit solid angle, is given by $k_\nu f_\nu^2/k_i$. Note that the distribution-in-angle of the scattered current is given, not in terms of the direction angles, θ_ν and ϕ_ν, and magnitude k_ν, of the momentum of the scattered particle, but in terms of the direction angles ω_ν, ϕ_ν and magnitude μ_ν of the *recoil momentum*, the difference between the initial and final momentum of the particle, $\boldsymbol{k}_i-\boldsymbol{k}_\nu$. The dependence of f_ν on the angles of scattering, θ_ν and ϕ_ν, can be obtained from (24c) by remembering that

$$\mu_\nu = (k_i^2+k_\nu^2-2k_ik_\nu\cos\theta_\nu)^{1/2} \text{ and } \omega_\nu = \sin^{-1}\left(\frac{k_\nu}{\mu_\nu}\sin\theta_\nu\right).$$

---

[25] A. Sommerfeld, Wellenmechanischer Ergänzungsband, (Vieweg, 1929), page 103.

The smallest value of μ_ν will be for $\theta_\nu = 0$ and will be $k_i - k_\nu$, and the largest value will be for $\theta_\nu = \pi$ and will be $k_i + k_\nu$. Since the Bessel function in (24c) is an oscillating function, we can say in general that f_ν will decrease as μ_ν increases. When k_i is large (i.e., when the incoming particle has a large velocity) μ_ν will increase very rapidly as θ_ν increases, and so f_ν will decrease very rapidly. Therefore most of the scattered particles leaving the atom in a given excited state will be deflected only slightly from their initial direction if their initial velocity is great.

If we know the atomic wave functions we can say something more about the behavior of the f's. In general it is not a bad approximation to assume that these functions are a linear combination of the products

$$\Phi_{\nu 1}(r_1)\Phi_{\nu 2}(r_2) \cdots \Phi_{\nu Z}(r_Z)$$

where each Φ is a properly normalized product of some tesseral harmonic of ϑ_σ and φ_σ times a radial function $S_{\nu\sigma}(r_\sigma)$.

If the initial state of the atom has a wave function which is spherically symmetric in all the electronic coordinates, then by its definition, U_{ii} will be the potential due to the nucleus and to a symmetric electronic charge density given by the sum of the squares of the wave functions Φ. In this case, we can revert to the methods of the preceding section and use Eq. (18) for f_i. Therefore, to the approximation of these formulas the elastic scattering from an atom in a radially symmetric state can be computed by the means developed in the preceding two sections, if the electronic charge density used in computing the effective potential field U is computed from the wave function in the usual manner.

For those excited states where only one electron is excited, the function $U_{\nu i}(r_0)$ becomes the integral

$$\int \bar{\Phi}_\nu(r_\sigma)\Phi_i(r_\sigma)dV_\sigma/r_{0\sigma}$$

where Φ_i and Φ_ν are the wave functions of the changing electron in its initial and final states respectively. We have already assumed that the normal state was symmetric, so

$$\Phi_i(r) = N_i S_i(r).$$

The excited state, however, need not be symmetric,

$$\Phi_\nu(r) = N_\nu e^{im_\nu\varphi} \sin^{|m_\nu|}\vartheta \, P_{l_\nu}{}^{|m_\nu|}(\cos\vartheta)S_\nu(r).$$

Since we can expand $1/r_{0\sigma}$ into the series

$$\frac{1}{r_{0\sigma}} = \sum_{\lambda=0}^{\infty}\sum_{m=0}^{\lambda}\frac{(\lambda - m)!}{(\lambda + m)!}2\cos m(\varphi_0 - \varphi_\sigma)\,\sin^m\vartheta_0\,\sin^m\vartheta_\sigma$$

$$P_\lambda{}^m(\cos\vartheta_0)P_\lambda{}^m(\cos\vartheta_0)\begin{cases} r_0{}^\lambda/r_\sigma{}^{\lambda+1} & (r_\sigma \geqq r_0) \\ r_0{}^\lambda/r_0{}^{\lambda+1} & (r_0 \geqq r_\sigma) \end{cases}$$

the function $U_{\nu i}$ will be

$$U_{\nu i}(r_0) = - N_i N_\nu \frac{2\pi}{l_\nu + \frac{1}{2}} e^{-im_\nu \varphi_0} \sin^{|m_\nu|}\vartheta_0 \, P_{l_\nu}^{|m_\nu|}(\cos\vartheta_0) \cdot \left\{ \frac{1}{r_0^{l_\nu+1}} \int_0^r r^{l_\nu+2} S_\nu(r)\cdot S_i(r)\cdot dr + r_0^{l_\nu} \int_r^\infty S_\nu(r)\cdot S_i(r)\cdot \frac{dr}{r^{l_\nu-1}} \right\}. \tag{25a}$$

If we insert this value of $U_{\nu i}$ into (24c) we find, by partial integration, that the f_ν's given in (24b) are given by the formula

$$f_\nu(\omega_\nu, \mu_\nu) = 4\pi i^{l_\nu} N_i N_\nu e^{-im_\nu\phi_\nu} \sin^{|m_\nu|}\omega_\nu \, P_{l_\nu}^{m_\nu}(\cos\omega_\nu) \frac{1}{\mu_\nu^2} \int_0^\infty S_\nu(r)\cdot S_i(r) \left(\frac{2\pi}{\mu_\nu r}\right)^{1/2} \cdot J_{l_\nu+1/2}(\mu_\nu r) r^2 dr. \tag{25b}$$

This is a generalization of formula (18), but it can be dealt with in the same manner.

These f's can be computed if S_ν and S_i are known. In general the S's are finite polynomials whose terms are of the type $r^n e^{-ar}$, so that the integration indicated in (25b) can always be performed by a number of applications of the formula[26]

$$\int_0^\infty e^{-ar} J_{\lambda+1/2}(\mu r) r^{n-1/2} dr$$

$$= \frac{\mu^{\lambda+1/2}\Gamma(n+\lambda+1)}{2^{\lambda+1/2} a^{n+\lambda+1}\Gamma(\lambda+3/2)} F\left(\frac{n+\lambda+1}{2}, \frac{n+\lambda+2}{2}; \lambda+3/2; -\frac{\mu^2}{a^2}\right)\left(1+\frac{\mu^2}{a^2}\right)^{-n}$$

$$= \frac{\mu^{\lambda+1/2}\Gamma(\lambda+n+1)}{2^{\lambda+1/2}(\mu^2+a^2)^{1/2(\lambda+n+1)}\Gamma(\lambda+3/2)} F\left(\frac{n+\lambda+1}{2}, \frac{\lambda+1-n}{2}, \lambda+3/2; \frac{\mu^2}{\mu^2+a^2}\right)$$

where the F's are hypergeometric functions.

However the atomic energy E_ν is the same for all states having the same value of l_ν and total quantum number, but having different values of m_ν. In order to obtain the distribution-in-angle of all scattered particles having the same final velocity, we must sum the values of $|f_\nu|^2$ over all values of m_ν for the same l_ν and total quantum number. Several properties of the atomic wave function aid in making this total distribution-in-angle simpler: the radial factor, S_ν, is independent of m_ν, and the normalization factor N_ν for any value of m_ν equals $[(l_\nu - |m_\nu|)!/(l_\nu + |m_\nu|)!]^{1/2}$ times the normalization constant, $N_{0\nu}$, for $m_\nu = 0$. When this is taken into account, it turns out that the distribution-in-angle of all scattered particles leaving with the momentum k_ν is $k_\nu f_{0\nu}^2/k_0$, where

---

[26] Watson, Bessel Functions, page 385.

$$f_{0\nu}(\mu_\nu) = \frac{4\pi N_i N_{0\nu}}{\mu_\nu{}^2} \int_0^\infty S_\nu S_i \left(\frac{2\pi}{\mu_\nu r}\right)^{1/2} J_{l_\nu+1/2}(\mu_\nu) r^2 dr \tag{25c}$$

(unless the atomic energy levels are also degenerate in l_ν, in which case the $f_{0\nu}{}^2$ must be summed over all values of l_ν for the same total quantum number). We note that these f's are functions of μ_ν only, and thus correspond to the f's given by Eq. (18) for elastic collisions. Values of $f_{0\nu}$ as functions of μ_ν for hydrogenic wave functions are given in Fig. 12.

The f's have been computed in several ways for hydrogen and for helium, by Born,[24] Elsasser,[27] Bethe,[28] and by Massey and Mohr.[29]

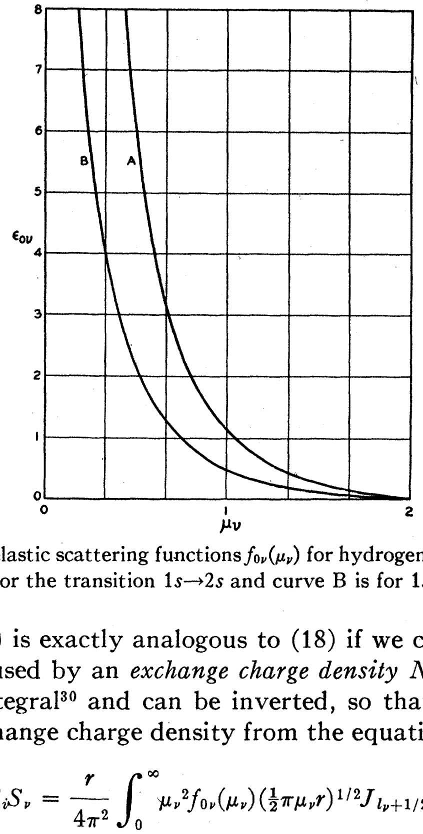

Fig. 12. Values of the inelastic scattering functions $f_{0\nu}(\mu_\nu)$ for hydrogenic wave functions. Curve A is for the transition $1s \rightarrow 2s$ and curve B is for $1s \rightarrow 2p$.

Expression (25c) is exactly analogous to (18) if we consider the inelastic scattering to be caused by an *exchange charge density* $N_i N_{0\nu} S_i(r) S_\nu(r)$. It is a Fourier-Bessel integral[30] and can be inverted, so that if we know $f_{0\nu}(\mu_\nu)$ we can find the exchange charge density from the equation

$$r^2 N_i N_{0\nu} S_i S_\nu = \frac{r}{4\pi^2} \int_0^\infty \mu_\nu{}^2 f_{0\nu}(\mu_\nu) (\tfrac{1}{2}\pi\mu_\nu r)^{1/2} J_{l_\nu+1/2}(\mu_\nu r) \mu_\nu d\mu_\nu \tag{25d}$$

a generalization of Eq. (19). There are not sufficient data on inelastic scattering at present to be able to use these formulas.

The probability of excitation to the state ν from the normal state i is obtained by integrating $k_\nu f_{0\nu}{}^2/k_i$ (where $f_{0\nu}$ is obtained from (25c)) over the

[27] Elsasser, Zeits. f. Physik **45**, 522 (1927).

[28] Bethe, Ann. d. Physik **5**, 325 (1930).

[29] Massey and Mohr, Proc. Roy. Soc. **132A**, 605 (1931).

[30] Watson, Bessel Functions, page 453.

angles ϕ_ν and θ_ν. This expresses the probability as an effective cross section in atomic units if the particle is an electron, or in the proper units given above if the particle is heavier than an electron. These *excitation functions* have been computed for hydrogen by Born,[24] Elsasser,[27] Bethe,[28] for hydrogen and helium by Massey and Mohr,[29] and for mercury by Penney;[31] and fair agreement is obtained with experiment.

Another method of dealing with (24a) which is useful in many cases is to integrate over dV_0' before we integrate over the coordinates of the atomic electrons.[28] If we remember our definition of $U_{\nu i}$, we see that the coefficient of $e^{ik_\nu r_0}/r_0$ is

$$f_\nu = \frac{1}{2\pi}\int \bar{\psi}_{\nu 0}\left(\frac{Z}{r_0} - \sum_{\tau=1}^{Z} \frac{1}{r_{0\tau}}\right)\psi_{i0} e^{i\boldsymbol{\mu}_\nu \cdot \mathbf{r}_0} dV_0 dV_1 \cdots dV_Z$$

Now by various limiting processes, one can show that

$$\frac{1}{2\pi}\int e^{i\mu_\nu r_0} dV_0/r_{0\tau} = \frac{2}{\mu^2} e^{i\boldsymbol{\mu}_\nu \cdot \mathbf{r}_\tau}.$$

When this is applied to the equation above, we have

$$f_\nu = \frac{2}{{\mu_\nu}^2}\int \bar{\psi}_{\nu 0}\left(Z - \sum_{\tau=1}^{Z} e^{i\boldsymbol{\mu}_\nu \cdot \mathbf{r}_\tau}\right)\psi_{i0} dV_1 \cdots dV_Z. \tag{26a}$$

When μ is small with respect to the size of the atom; i.e., when the momentum of the incoming particle is not altered much by the collision, then we need only consider the first two terms in the series expansion for the exponential, and since ψ_ν and ψ_i are orthogonal

$$f_\nu = \frac{2}{{\mu_\nu}^2}(\boldsymbol{\mu}_\nu \cdot \boldsymbol{M}_{\nu i}) \qquad (\mu_\nu \text{ small}) \tag{26b}$$

where $\boldsymbol{M}_{\nu i}$ is the dipole moment of the atom associated with the transition $\nu \rightarrow i$.

If k_i is very large, then for all states ν where (26a) is large enough to be worth considering k_ν is practically equal to k_i, and for all angles of scattering θ such that θk_i is much greater than $(k_i - k_\nu)$, $\boldsymbol{\mu}_\nu$ is nearly equal to $\mu = 2k_i \sin(\theta/2)$. In this case the current scattered at an angle θ corresponding to the ν'th final atomic state will be, approximately

$$|f_\nu|^2 = \frac{4}{\mu^4}|(\nu|G|i)|^2$$

where

$$(\nu|G|i) = \int \bar{\psi}_{\nu 0} G \psi_{i0} dV_1 \cdots dV_Z \text{ and } G = Z - \sum_\tau e^{i\boldsymbol{\mu}_\nu \cdot \mathbf{r}_\tau}.$$

---

[31] Penney, Phys. Rev. **39**, 467 (1932).

Then the *total* current scattered at an angle θ, for all states, including both elastically and inelastically scattered, will be

$$\frac{4}{\mu^4}\sum_{\nu=0}^{\infty}(i|G|\nu)(\nu|G|i) = \frac{4}{\mu^4}(i|G^2|i)$$

$$= \frac{4}{\mu^4}\int |\psi_i|^2\Big[Z^2 - 2Z\sum_{\tau}\cos(\mathbf{\mu}\cdot\mathbf{r}_\tau) + \sum_{\sigma,\tau}e^{i\mu\cdot(\mathbf{r}_\sigma-\mathbf{r}_\tau)}\Big]dV_1\cdots dV_Z \quad (27\text{a})$$

$$= \frac{4}{\mu^4}[Z^2 - 2Z^2F(\mu) + S]$$

where F is the x-ray structure factor for the initial state, and has been discussed in Eq. (18) *et seq.*

The function

$$S = \int |\psi_i|^2\sum_{\sigma,\tau}e^{i\mu\cdot(\ \sigma-r_\tau)}dV_1\cdots dV_Z$$

has been discussed[32] in connection with the incoherent scattering of x-rays. When we can represent the atomic wave function as a determinant

$$\psi_i = (1/Z!)^{1/2}|\Phi_s(r_\sigma)| \qquad (s,\sigma = 1, 2, \cdots, Z)$$

where the different Φ's are orthogonal (the spin coordinates must be taken into account) then S becomes

$$S = \int\sum_{s,t=1}^{z}|\Phi_s(r)|^2|\Phi_t(r')|^2e^{i\mu\cdot(\mathbf{r}-\mathbf{r}')}dVdV' + Z$$

$$-\int\sum_{s,t=1}^{z}\overline{\Phi}_s(r)\Phi_t(r)\overline{\Phi}_t(r')\Phi_s(r')e^{i\mu\cdot(\mathbf{r}-\mathbf{r}')}dVdV'.$$

The first part of this expression is just $Z^2F^2(\mu)$, and so (27a) becomes

$$\frac{4Z^2}{\mu^4}\left\{[1-F(\mu)]^2+\frac{S_i(\mu)}{Z^2}\right\} \quad (27\text{b})$$

where

$$F = \frac{1}{Z}\int\Big[\sum_{s=1}^{z}\rho_{ss}(r)\Big]e^{i\mu\cdot\mathbf{r}}dV = \frac{4\pi}{Z}\int_0^\infty\Big[\sum_s\rho_{ss}(r)\Big]\frac{\sin\mu r}{\mu r}r^2dr$$

and

$$S_i = Z - \int\Big[\sum_{s,t=1}^{z}\rho_{st}(r)\rho_{ts}(r')\Big]e^{i\mu.(\mathbf{r}'-\mathbf{r})}dVdV'$$

where the sum includes only those pairs of states s and t which have the same spins. ρ_{st} is the *exchange charge density* $\Phi_s\Phi_t$.

---

[32] Waller and Hartree, Proc. Roy. Soc. **124A,** 119 (1929); Heisenberg, Phys. Zeits. **32,** 537 (1931). Morse, Phys. Zeits. **33,** 443 (1932).

Expression S_i is already known in the theory of x-ray scattering, where it gives the angle distribution of the incoherent scattering. It has been computed for the Thomas-Fermi atomic charge distribution.[33] For hydrogen or helium in the normal state it is $Z-ZF^2(\mu)$, where the F is the form factor proper for hydrogen or helium. For heavier atoms it is a more complicated form of function, which is zero when μ is zero, and approaches the value Z as μ increases.[29]

The angle distribution of total scattered current from helium, obtained by (27b) is given by the solid curve in Fig. 13. The dotted curve marked *elastic* gives the distribution of elastically scattered current, given by (18).

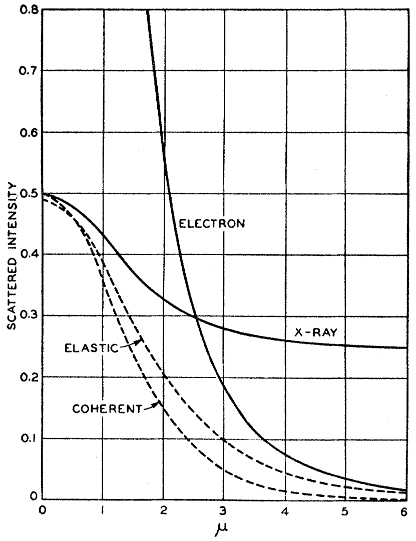

Fig. 13. Scattering of electrons from helium. Solid curve marked electron gives the total scattered electron current as a function of $\mu=2k\sin\theta/2$. Dotted curve marked elastic gives current of elastically scattered electrons. Solid curve marked x-ray gives the corresponding total x-ray scattering as a function of μ, and dotted curve marked coherent gives the x-ray coherent scattering.

The curve marked *x-ray* gives the angle distribution of scattered x-rays, both coherent and incoherent, from helium, given by the usual formula

$$Z^2F^2(\mu)+S_i(\mu).$$

The relationship between the two curves is apparent.

We have therefore obtained, in formula (27b), an expression for the total current scattered, per atom per unit solid angle per unit primary current, for high speed cathode-rays in terms of functions which are already in use in x-ray work. The de Broglie wave-length of the electron is used instead of the x-ray wave-length. The analogy with x-ray scattering is thus complete,

---

[33] Bewilogua, Phys. Zeits. **32,** 740 (1931).

and the methods developed [33,34] for the study of molecular structure by x-ray scattering can be used for their study by high speed cathode-ray scattering.[35]

For very high speed particles we are justified in neglecting sum Σ_2 in (23); but if the incoming particle is an electron, and it has an energy less than the ionization potential of the inner atomic electrons, then we cannot neglect Σ_2. Since Σ_2 does not oscillate as r_0 is increased (as Σ_1 does) it must represent the incoming electron being in a bound state. Since at least some of the atomic wave functions in Σ_2 represent ionized states, a part of Σ_2 must represent states where the incoming electron stays in the atom in some quantized state, and an atomic electron leaves in its stead. Sometimes the probability of this occurrence is relatively large, and cannot be neglected.

If the incoming particle is not an electron, the fact that Σ_2 were large would not bother us, for we could distinguish experimentally between the particle and an ejected electron, and Σ_1 would give us the distribution-in-angle of the scattered particle. If the incoming particle is an electron, however, Σ_1 is not a measurable quantity; for the experimentalist has no means of telling whether the electron which he catches is the one which he shot at the atom or is an atomic electron which had substituted itself for the original incoming one and come away at the speed which the original one would have had. All that he can measure is the total probability of both effects, and our theory must take this into account.[36]

After the substitution has taken place, the atomic wave function will not be a function $\psi_{\nu 0}$ of all the atomic electrons, but will be the similar function $\psi_{\nu\tau}$, with one of the atomic electron coordinates, the τ'th, replaced by the coordinates r_0 of the incoming electron. The equation for this function was given in (20d).

We have seen that that part of the wave function Ψ representing the atom excited to the ν'th state and the incoming electron scattered is approximately

$$\psi_{\nu 0}\frac{e^{ik_\nu r_0}}{r_0}f_\nu \tag{28a}$$

where

$$f_\nu = \frac{1}{2\pi}\int \bar{\psi}_{\nu 0}e^{-ik_\nu \cdot r_0}U_0\psi_{i0}e^{ik_i\cdot r_0}dV_0dV_1\cdots dV_Z.$$

We can show[37] that the part of the wave function representing the incoming electron trading places with the τ'th atomic electron and settling down to the ν'th state is approximately

---

[34] Debye, Phys. Zeits. **32**, 740 (1931).

[35] Kirchner, Ann. d. Physik **83**, 969 (1927); Mark and Wierl, Zeits. f. Physik **60**, 741 (1930); Wierl, Ann. d. Physik **8**, 521 (1931).

[36] Oppenheimer, Phys. Rev. **32**, 361 (1928).

[37] The method of time variation is perhaps the easiest method of demonstrating this. See Dirac, Quantum Mechanics (Oxford University Press, 1930), page 179. However, this form is not the best form to use for g. For a better form, see a discussion of Eq. (32c) later in this section.

$$\psi_{\nu\tau}\frac{e^{ik_\nu r_\tau}}{r_\tau}g_{\nu\tau} \tag{28b}$$

where

$$g_{\nu\tau} = \frac{1}{2\pi}\int \bar{\psi}_{\nu\tau}e^{-ik_\nu\cdot r_\tau}U_0\psi_{i0}e^{ik_i\cdot r_0}dV_0dV_1\cdots dV_Z.$$

This means that the sum Σ_2 can be represented in terms of a sum of such functions, plus a residual term; and therefore that the complete wave function is approximately

$$\Psi(r_0, r_1, \cdots, r_Z) \cong e^{ik_i\cdot r_0}\psi_{i0} + \sum_{\nu=0}^{\nu_0}\psi_{\nu 0}\frac{e^{ik_\nu r_0}}{r_0}f_\nu + \sum_{\tau=1}^{z}\sum_{\nu=0}^{\nu_0}\psi_{\nu\tau}\frac{e^{ik_\nu r_\tau}}{r_\tau}g_{\nu\tau} + O(r_0, \cdots, r_Z). \tag{28c}$$

The residue O represents states of the negative ion, where all the electrons are bound, etc. It must be taken into account in computing the total cross section, but it may be neglected when we deal with cross sections and angle distributions for specific transitions.

Since we cannot distinguish between different electrons travelling away from the atom with the same velocity, we must include the g_ν's as well as the f_ν when we compute the current scattered corresponding to the ν'th atomic state. This is quite important in a number of cases, for a number of transitions $i\rightarrow\nu$ involve changes in the symmetry of the wave functions (i.e., transitions from singlet to triplet states, etc.) such that f_ν is zero. If we neglected to include the g's, we would think that electron impact could not produce such transitions. However, we would be in error, for the g's corresponding to such a transition would not all be zero.

A further complication now arises: that of including the Pauli principle, for this must be taken into account wherever electrons have a chance of trading places. It turns out that when we do take it into account, the current corresponding to the ν'th state will not be a sum of the squares of f_ν and the g_ν's, but will be a sum of the squares of certain linear combinations of f_ν and g_ν's.[36]

Several simple illustrations will clarify the method of finding these combinations better than a general statement.

If the atom is hydrogen, there will only be one atomic electron, and the wave function (28c) will be

$$\Psi(r_0, r_1) \cong e^{ik_i\cdot r_0}\Phi_i(r_1) + \sum_{\nu=0}^{\nu_0}\Phi_\nu(r_1)\frac{e^{ik_\nu r_0}}{r_0}f_\nu + \sum_{\nu=0}^{\nu_0}\Phi_\nu(r_1)\frac{e^{ik_\nu r_1}}{r_1}g_\nu + O(r_0, r_1).$$

The Pauli principle states that every wave function involving electrons alone must be antisymmetric in form when the spin coordinate is included in the wave function. The correct wave function for hydrogen+electron must therefore be either

$$\frac{1}{2^{1/2}}\left[\Psi(r_0, r_1) + \Psi(r_1, r_0)\right]\left[\sigma_+(0)\sigma_-(1) - \sigma_-(0)\sigma_+(1)\right]$$

or one of the three products,

$$\frac{1}{2^{1/2}}\left[\Psi(r_0, r_1) - \Psi(r_1, r_0)\right]\left\{\begin{array}{l}[\sigma_+(0)\sigma_+(1)]\\ [\sigma_+(0)\sigma_-(1) + \sigma_-(0)\sigma_+(1)]\\ [\sigma_-(0)\sigma_-(1)]\end{array}\right.$$

where the σ's are the spin functions, and are orthogonal and normalized. There are three symmetric combinations of the spin functions, but only one antisymmetric combination.

The current scattered per unit solid angle per unit primary current density corresponding to the ν'th state is $(k_\nu/k_i)|f_\nu+g_\nu|^2$ when the first combination is used, and is $(k_\nu/k_i)|f_\nu-g_\nu|^2$ when the last three are used. The second function is three times as likely to occur as the first (since all four combinations are equally likely), and so the average current scattered is

$$\frac{k_\nu}{k_i}\left[\tfrac{1}{4}\,|f_\nu + g_\nu|^2 + \tfrac{3}{4}\,|f_\nu - g_\nu|^2\right]. \tag{29a}$$

In the case of the helium atom in the normal state, the atomic wave function is antisymmetric in the spin functions and symmetric in the space functions, and we have

$$\Psi(r_0; r_1, r_2) \cong \left\{e^{ik_i\cdot r_0}\psi_i(r_1, r_2) + \sum_{\nu=0}^{\nu_0}\left[\psi_\nu(r_1, r_2)\frac{e^{ik_\nu\cdot r_0}}{r_0}f_\nu + \psi_\nu(r_0, r_1)\frac{e^{ik_\nu r_2}}{r_2}g_\nu + \psi_\nu(r_0, r_2)\frac{e^{ik_\nu r_1}}{r_1}g_\nu\right] + O\right\}$$

where the ψ_ν's are the properly symmetrized space functions for the various singlet and triplet states. This function is symmetric in r_1 and r_2. The linear combinations which satisfy the Pauli principle are

$$\frac{1}{3^{1/2}}\left[\Psi(r_0; r_1, r_2)S_\pm(0) - \Psi(r_1; r_0, r_2)S_\pm(1) - \Psi(r_2; r_1, r_0)S_\pm(2)\right]$$

where

$$S_\pm(0) = \left[\sigma_+(1)\sigma_-(2) - \sigma_-(1)\sigma_+(2)\right]\sigma_\pm(0).$$

Both of these combinations give the same value for the scattered current corresponding to the ν'th state, so the average current scattered is

$$\frac{k_\nu}{k_i}\,|f_\nu - g_\nu|^2 \tag{29b}$$

which is quite a different form than that for the current scattered from hydrogen.

In the case of lithium, our functions are of the form

$$\Psi(r_0;r_1;r_2,r_3) \cong e^{ik_i\cdot r_0}\psi_i(r_1;r_2,r_3) + \sum_{\nu=0}^{\nu_0}\left[\psi_\nu(r_1;r_2,r_3)\frac{e^{ik_\nu r_0}}{r_0}f_\nu \right.$$
$$+\,\psi_\nu(r_0;r_2,r_3)\frac{e^{ik_\nu r_1}}{r_1}g_{\nu 1} + \psi_\nu(r_1;r_0,r_3)\frac{e^{ik_\nu r_2}}{r_2}g_{\nu 2}$$
$$\left. +\,\psi_\nu(r_1;r_2,r_0)\frac{e^{ik_\nu r_3}}{r_3}g_{\nu 2}\right] + O$$

where $\psi_i(r_1, r_2; r_3)$ is the space part of the wave function of the lithium atom in the normal state, with electrons 2 and 3 in the K shell. It is symmetric in r_2 and r_3, and therefore Ψ is also. As in the case of hydrogen, there can be one symmetric combination of the Ψ's, giving for current $(k_\nu/k_i)|f_\nu+g_{\nu 1}-g_{\nu 2}|^2$, and three antisymmetric combinations giving a current $(k_\nu/k_i)|f_\nu-g_{\nu 1}-g_{\nu 2}|^2$, so that the average scattered current is

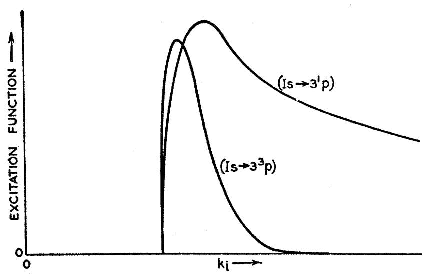

Fig. 14. Excitation functions for the transition ${}^1S\rightarrow{}^1P$ and ${}^1S\rightarrow{}^3P$ in helium as a function of electronic momentum k_i.

$$\frac{k_\nu}{k_i}\left[\tfrac{1}{4}\,|f_\nu + g_{\nu 1} - g_{\nu 2}|^2 + \tfrac{3}{4}\,|f_\nu - g_{\nu 1} - g_{\nu 2}|^2\right]. \tag{29c}$$

The proper combinations for the current scattered from more complex atoms can be worked out by a similar method.

The f's and g's have been calculated by Massey and Mohr[29] for hydrogen and helium, and by Penney[31] for mercury. Excitation functions, representing the probability of excitation by impact in terms of cross section, are obtained as functions of k_i by integrating the expressions above over all directions of the scattered current. Massey and Mohr show that in general excitations involving a change of magnetic quantum number m are relatively unlikely. Some of the excitation functions computed by Massey and Mohr are plotted in Fig. 14.

When we wish to find the range of validity for this first approximation we have been using in this section, we can apply the same methods as were used in section 8. We can show that the first approximation is valid for the f's when k_i is larger than Z, and therefore that we can use the same set of criteria used earlier. The discussion of the validity of the g's is much more complicated, but we can show that if the f's decrease approximately as Z/k_i for increasing k_i, the corresponding g's decrease as Z^2/k_i^2. This is due to the fact that we have a factor e^{ikr} in the integrations over two electronic coordinates, instead of over but one, as in the f's. Therefore for a k_i large enough that the f's will be valid, the g's will be smaller than the f's, and presumably the first approximation for the g's will be adequate.

The more rapid decrease of the g's than that of the f's is shown clearly by the excitation functions for helium. Due to the symmetry of the wave functions, the functions f for the transitions from the normal state to triplet states are identically zero; for transitions to singlet states they are not zero. Therefore the excitation functions for the triplet states, since they involve only a g, will decrease faster with increasing k_i than the functions for corresponding singlet states, which involve both f and g. This is shown in Fig. 14, and is more or less born out by experimental data.

Unfortunately we cannot be sure that by including the g's as we have done above we have improved our approximation, for as we have seen above the g's are roughly of the order of magnitude of the second approximation to the f's. In the case of the transitions where f is zero the g's are of definite value, but where the f's are not zero, then when k_i is large enough for the second approximation to the f's to be negligible compared to the first approximation, the g's are also negligible. In the case where the g's are not negligible compared to the f's, then we cannot be sure that the first approximation formulas we have been using for the f's will be valid.

As a matter of fact it does seem in some cases that by including the g's we obtain results even for small values of k_i which check experimental data. But the check is not good, and certainly not better than the check obtained by the exact methods of section 7 where exchange effects were not included.

Comparing the results obtained by this exact method with the experimental data we see that the check for the total cross section for elastic scattering is fairly good for all electronic velocities, but that the elastic angular distribution (and of course the inelastic scattering) is not good for small velocities. For instance the angle distribution curves for argon check for all energies greater than 16 volts, but the total cross-section checks for energies greater than one volt. The same number of electrons are scattered as the exact solution without exchange predicts, but these electrons are scattered in a different direction than this solution predicts.

This indicates that exchange effects are not very important in collision problems. They are completely negligible at high velocities, and for low velocities they are not important in the discussion of total cross sections for elastic scattering. For instance, exchange is not the cause of the Ramsauer effect; it is adequately explained by the exact methods of section 7, which disregards exchange. Exchange is important, however, in discussing the angular distribution of elastically scattered slow electrons, and in discussing inelastically scattered slow electrons.

It is in just this range, where exchange effects are important, that the approximate methods discussed so far are inadequate. It is therefore necessary to find a method for correcting the exact solutions given in section 7 for exchange.

The general method[36] for obtaining such a solution will be shown in detail for hydrogen. The generalization of the method for more complicated atoms will be clear.

The properly normalized wave function $\psi_{nlm}(r)$ for the hydrogen atom satisfies the equation

$$\left(\nabla^2 + \frac{2}{r}\right)\psi_{nlm}(r) = \frac{1}{n^2}\psi_{nlm}(r)$$

where n is a positive integer for the discrete states and is an imaginary quantity for the continuous states.

The equation which the system electron-plus-normal-atom must satisfy is

$$\left(\nabla_0^2 + \nabla_1^2 + \frac{2}{r_0} + \frac{2}{r_1} - \frac{2}{r_{01}}\right)\Psi = (1 - k_1^2)\Psi. \tag{30a}$$

We can assume that this equation is satisfied by one or the other of the combinations

$$\Psi = \sum_{n,l,m}\left[\psi_{nlm}(r_1)\chi_{\sigma nlm}(r_0) + (-1)^\sigma\psi_{nlm}(r_0)\chi_{\sigma nlm}(r_1)\right] \quad (\sigma = 0, 1)$$

where the sum includes the continuous states of the atom, and where the spin factors are not written. The state $\sigma = 1$ is three times as prevalent as the state $\sigma = 0$. These are the proper linear combinations for the perturbation we are to apply.

Substituting this in (30a), multiplying by $\psi_{nlm}(r_1)$ and integrating over the spin coordinates and the coordinates of electron one, we obtain the equations

$$\begin{aligned}\left(\nabla_0^2 + \frac{2}{r_0} + k_n^2\right)\chi_{\sigma nlm}(r_0) \\ = 2\sum_{n',l',m'} \int\bar{\psi}_{nlm}(r_1)\psi_{n'l'm'}(r_1)\frac{dV_1}{r_{01}}\cdot\chi_{\sigma n'l'm'}(r_0) \\ - (-1)^\sigma\sum_{n',l',m'}\int\bar{\psi}_{nlm}(r_1)\left(\nabla_1^2 + k_{n'}^2 + \frac{2}{r_1} - \frac{2}{r_{01}}\right)\chi_{\sigma n'l'm'}(r_1)dV_1\cdot\psi_{n'l'm'}(r_0)\end{aligned} \tag{30b}$$

where $k_n^2 = k_1^2 + (1/n^2) - 1$.

These equations cannot be solved exactly. However we can be sure that the function χ corresponding to the normal state of the atom is much larger than any other χ (since the normal state is the initial state). So we can neglect all except $\chi_{\sigma 100}$ in the sum over n', l' and m'.

We then obtain for the elastic scattering functions

$$H(r_0)\chi_{\sigma 100}(r_0) = -(-1)^{\sigma}\left[\int \bar{\psi}_{100}(r_1)H(r_1)\chi_{\sigma 100}(r_1)\cdot dv_1 + 2U_{\sigma 0}(r_0)\right]\psi_{100}(r_0) \tag{30c}$$

where

$$H(r) = \nabla^2 + 2V(100, 100; r) + k_1^2$$

$$V(nlm, n'l'm'; r_0) = \int \bar{\psi}_{nlm}(r_1)\left[\frac{1}{r_0} - \frac{1}{r_{01}}\right]\psi_{n'l'm'}(r_1)dV_1.$$

Since $\psi_{100}(r) = e^{-r}/\pi^{1/2}$, we have

$$V(100, 100; r) = e^{-2r}\left(1 + \frac{1}{r}\right).$$

Also

$$U_{\sigma 0}(r_0) = \int \bar{\psi}_{100}(r_1)\left[\left(\int \mid \psi_{100}(r_0) \mid {}^2\frac{dV_0}{r_{01}}\right) - \frac{1}{r_{01}}\right]\chi_{\sigma 100}(r_1)dV_1.$$

Eq. (30c) can be shown to be equivalent to

$$H(r)\chi_{\sigma 100}(r) = -2(-1)^{\sigma}U_{\sigma 0}(r)\psi_{100}(r). \tag{30d}$$

For suppose χ did satisfy (30d). Then the first integral on the right side of (30c) becomes zero, due to the form of $U_{\sigma 0}$, and therefore a solution of (30d) is also a solution of (30c).

If we insert the functional form of ψ_{100} in (30d), we obtain

$$H(r_0)\chi_{\sigma 100}(r_0)$$
$$= -2(-1)^{\sigma}\frac{\psi_{100}(r_0)}{\pi^{1/2}}\int e^{-r_1}\left[\frac{1}{r_1} - \frac{1}{r_{10}} - e^{-2r_1}\left(1 + \frac{1}{r_1}\right)\right]\cdot\chi_{\sigma 100}(r_1)dV_1. \tag{31a}$$

These integro-differential equations are too difficult to solve exactly; but we can obtain a fairly good approximation to the solution. Separate each χ into a series

$$\chi_{\sigma 100}(r) = \sum_{\lambda=0}^{\infty} a_{\sigma\lambda}P_{\lambda}(\cos\theta)R_{\sigma\lambda}(r)/r.$$

Then each equation separates into equations for the R's. Since

$$\int e^{-r_1}\chi_{\sigma 100}(r_1)\frac{dV_1}{r_{01}} = \frac{4\pi}{r_0}\sum_{\lambda=0}^{\infty}\frac{a_{\sigma\lambda}P_{\lambda}}{2\lambda + 1}\int e^{-x}R_{\sigma\lambda}(x)\xi_{\lambda}dx$$

$$\xi_{\lambda} = \begin{cases} x^{\lambda+1}/r_0^{\lambda} & (r_0 \geqq x) \\ r_0^{\lambda+1}/x^{\lambda} & (x \geqq r_0) \end{cases}$$

the equations for the R's become

$$\left[\frac{d^2}{dr^2} - \frac{\lambda(\lambda+1)}{r^2} + V(100,\,100;\,r) + k_1{}^2\right]R_{\sigma\lambda}(r)$$
$$= (-1)^{\sigma}\frac{8e^{-r}}{2\lambda+1}\left[\int_0^{\infty} e^{-x}R_{\sigma\lambda}(x)\xi_\lambda dx - \delta_{0\lambda}r\int_0^{\infty}(e^{-x} - e^{-3x} - xe^{-3x})R_{\sigma\lambda}(x)dx\right].$$

If we assume that the integral on the right is small compared to the terms on the left, and therefore that $R_{0\lambda}$ is nearly equal to $R_{1\lambda}$, then we have, to the second order of smallness

$$\left[\frac{d^2}{dr^2} - \frac{\lambda(\lambda+1)}{r^2} + V(100,\,100;\,r) + k_1{}^2\right]\tfrac{1}{2}(R_{0\lambda} + R_{1\lambda}) = 0. \tag{31b}$$

The solution for $\frac{1}{2}(R_{0\lambda}+R_{1\lambda})$ can be obtained by the methods discussed in section 7. The "scattering power," $\beta=(\int rVdr)^{1/2}$, of the potential $V(100,\,100;\,r)$ is 0.866. By our earlier discussion of this constant, we can expect that we could substitute a simpler form of V having a β equal to 0.866 for $V(100,\,100;\,r)$ in (31b) and obtain a function which would be very nearly equal to the correct average R. For instance we can take

$$V(100,\,100;\,r) = \begin{cases} \dfrac{2}{3} - \dfrac{1}{r} & (r \leqq 1.5) \\ 0 & (r \geqq 1.5) \end{cases}.$$

The solutions to this are known,

$$\tfrac{1}{2}(R_{0\lambda} + R_{1\lambda}) = y_{\lambda 1}(r) = \left(\frac{\pi kr}{2}\right)^{1/2}\left[\cos\gamma_\lambda J_{\lambda+1/2}(kr) + (-1)^\lambda \sin\gamma_\lambda J_{-\lambda-1/2}(kr)\right]$$
$$\xrightarrow[r\to\infty]{} \cos\left(kr - \pi\frac{\lambda+1}{2} + \gamma_\lambda\right)$$

for $r \geqq 3/2$. Values of the constant γ_λ can be obtained from Fig. 2 for $\beta=0.866$, as function of x (here $x=3k_1/2$). For r less than $3/2$ $y_{\lambda 1}$ can be represented by a power series[1] adjusted to fit the outer solution in value at $r=3/2$.

Returning to our equations for the R's, we find that

$$\left[\frac{d^2}{dr^2} - \frac{\lambda(\lambda+1)}{r^2} + V(100,\,100;\,r) + k_1{}^2\right]\tfrac{1}{2}(R_{0\lambda} - R_{1\lambda})$$
$$= \frac{8e^{-r}}{2\lambda+1}\left[\int_0^{\infty} e^{-x}y_{\lambda 1}(x)\xi_\lambda dx - \delta_{0\lambda}r\int_0^{\infty}(e^{-x} - e^{-3x} - xe^{-3x})y_{\lambda 1}(x)dx\right]. \tag{31c}$$

This is an inhomogeneous equation of the usual type. We obtained (31b) by assuming that $R_{0\lambda}-R_{1\lambda}$ was as small as possible over the whole range of r. The solution of (31c) which does this is

$$\begin{gathered}\tfrac{1}{2}(R_{0\lambda} - R_{1\lambda}) = h(r)y_{\lambda 1}(r) + g_\lambda(r)y_{\lambda 2}(r) \\ h(\infty) = 0\end{gathered} \tag{31d}$$

$$g_\lambda(\infty) = \frac{8}{k_1(2\lambda + 1)}\left[\delta_{0\lambda}\int_0^\infty xe^{-x}y_{\lambda 1}(x)dx\int_0^\infty (e^{-z} - e^{-3z} - ze^{-3z})y_{\lambda 1}(z)dz\right.$$
$$\left. - 2\int_0^\infty x^{\lambda+1}e^{-x}y_{\lambda 1}(x)dx\int_x^\infty e^{-z}y_{\lambda 1}(z)dz/z^\lambda\right].$$

The function $y_{\lambda 2}$ is the other solution of (31b), which becomes

$$\sin\left(kr - \pi\frac{\lambda + 1}{2} + \gamma_\lambda\right)$$

as r becomes very large. Therefore by adding the solutions of (31b) and (31c) we obtain

$$R_{\sigma\lambda}(r) \underset{r\to\infty}{\longrightarrow} (1 + g_\lambda^2(\infty))^{1/2}\cos\left(kr - \pi\frac{\lambda + 1}{2} + \gamma_{\sigma\lambda}\right)$$

where

$$\gamma_{\sigma\lambda} = \gamma_\lambda + (-1)^\sigma \tan^{-1} g_\lambda(\infty).$$

The constant γ_λ is given in Fig. 1 and g_λ can be computed from (31d). If we make

$$a_{\sigma\lambda} = \frac{2\lambda + 1}{(1 + g_\lambda^2(\infty))^{1/2}}\,\frac{1}{2k_1}\,i^\lambda e^{i\gamma_{\sigma\lambda}}$$

we will find the average current scattered to be

$$\frac{1}{4k_1^2}\sum_{\lambda,\lambda'}(2\lambda + 1)(2\lambda' + 1)P_\lambda(\cos\theta)\cdot P_{\lambda'}(\cos\theta)\left[\sin\gamma_{0\lambda}\sin\gamma_{0\lambda'}\cos(\gamma_{0\lambda} - \gamma_{0\lambda'})\right.$$
$$\left. + 3\sin\gamma_{1\lambda}\sin\gamma_{1\lambda'}\cos(\gamma_{1\lambda} - \gamma_{1\lambda'})\right] \tag{32a}$$

and the average total cross section to be

$$\frac{\pi}{k_1^2}\sum_\lambda(2\lambda + 1)\left[\sin^2\gamma_{0\lambda} + 3\sin^2\gamma_{1\lambda}\right] \tag{32b}$$

for elastic scattering.

If *both* γ_λ and $g_\lambda(\infty)$ are small compared to unity then (32a) will reduce to an equation similar to (29a) for $\nu = 1$; with this rather important difference: that whereas the f will reduce to a form quite like that given in (28a), the g will not be a form like that given by (28b), but will become

$$\frac{1}{2\pi}\int\bar{\psi}_i(r_0)e^{-ik'_i\cdot r_1}\left[\left(|\psi_i(r_2)|^2\frac{dV_2}{r_{12}}\right) - \frac{1}{r_{01}}\right]\psi_i(r_1)e^{ik_i\cdot r_0}dV_0dV_1. \tag{32c}$$

A general analysis similar to the above for more complex atoms indicates that Eqs. (29a, b, c, etc.) will be a better approximation if in the integral defining g_ν in (28b) we insert, not

$$U_0 = \frac{Z}{r_0} - \sum_\tau \frac{1}{r_{0\tau}}$$

but

$$U_0' = \int |\psi_{i0}|^2 \sum_\tau \frac{1}{r_{0\tau}} dV_1 \cdots dV_Z - \sum_\tau \frac{1}{r_{0\tau}} \cdot$$

This gives us somewhat better results than if we use the g given in (28b).

When γ_λ is large and $g_\lambda(\infty)$ small then (29a) is invalid and (32a) should be used. If both γ_λ and $g_\lambda(\infty)$ are large then neither equation holds well, but (32a) will have a better chance of being valid.

For inelastic scattering we can take

$$\chi_{\sigma nlm}(r) = \sum_{\lambda,\mu} e^{i\mu\phi} \sin^{|\mu|}\theta P_\lambda^{|\mu|}(\cos\theta) \frac{R_\sigma(nlm, \lambda\mu; r)}{r} \cdot$$

The integrals on the right hand side of (30b) become

$$2[V(nlm, 100; r_0)\chi_{\sigma 100}(r_0) - (-1)^\sigma U_\sigma(nlm, 100; r_0)\psi_{100}(r_0)]$$

where

$$U_\sigma(nlm, 100; r_0) = \int \bar{\psi}_{nlm}(r_1)\left[\left(\int |\psi_{100}(r_0)|^2 \frac{dV_0}{r_{01}}\right) - \frac{1}{r_{01}}\right]\chi_{\sigma 100}(r_1) dV_1 .$$

For convenience, we can define a quantity $u_\sigma(nlm, \lambda\mu; r)$, such that

$$2[V(nlm, 100; r)\chi_{\sigma 100}(r) - (-1)^\sigma U_\sigma(nlm, 100; r)\psi_{100}(r)]$$
$$= \sum_{\lambda,\mu} u_\sigma(nlm, \lambda\mu; r) e^{i\mu\phi} \sin^{|\mu|}\theta P_\lambda^{|\mu|}(\cos\theta) .$$

The u's can be computed, since we know the V's and U's. The equation for the R's becomes

$$\left[\frac{d^2}{dr^2} - \frac{\lambda(\lambda+1)}{r^2} + V(nlm, nlm; r) + k_n^2\right] R_\sigma(nlm, \lambda\mu; r) = r u_\sigma(nlm, \lambda\mu; r) . \quad (33a)$$

The finite solution of the homogeneous equation we shall call $y_\sigma(nlm, \lambda\mu; r)$, and arrange its magnitude so that it shall become, for large r, $\cos(k_n r + e)$, where the phase angle e is determined by the V. Then for R to represent only an outgoing wave, the solution of the inhomogeneous equation will become for large values of r

$$R_\sigma(nlm, \lambda\mu; r) \xrightarrow[r\to\infty]{} \frac{ie^{i(k_n r + e)}}{k_n} \int_0^\infty y_\sigma(nlm, \lambda\mu; x) \cdot u_\sigma(nlm, \lambda\mu; x) \cdot x dx . \quad (33b)$$

Substituting this back in the series for $\chi_{\sigma nlm}(r)$ we can obtain the angular distribution and total cross section for the various inelastic collisions.

The method sketched above for hydrogen can be applied for the more complex atoms. The computations become considerably more tedious, but no new difficulties arise as long as the atomic wave functions are known. The computations for hydrogen have not even been completed as yet.

However, calculations of this or a similar[38] sort must be carried through before the theory of scattering of slow electrons can be said to be satisfactorily treated.

§10. COLLISION OF ATOM AND ATOM

The theory of collision of two atoms is one aspect of the theory of diatomic molecules, an aspect which is in a rather unsatisfactory state of development at present. Since the subject is so complex and since the experimental data are so meager that they do not serve to discriminate between the various methods of attack devised to date, only a discussion of the fundamental ideas involved, and a brief sketch of a few of the methods devised will be given here.

In considering the motions of two nuclei of charges $Z_a e$ and $Z_b e$ and masses M_a and M_b, and of a number of electrons, we can refer the positions of the electrons to the nucleus they happen to be near. Let $\rho_{ia}, \vartheta_{ia}, \varphi_{ia}$ be the coordinates of the i'th electron referred to the nucleus a, and $\rho_{jb}, \vartheta_{jb}, \varphi_{jb}$ refer to nucleus b. Then we can refer the motions of the two nuclei with their respective electrons to the center of gravity of the system, calling the internuclear distance r and giving its direction in space by the angles θ and ϕ. The motion of the system's center of gravity can be left out of the discussion. All these coordinates will be in atomic units.

What is done[39] in setting up the Schroedinger equation for the system is essentially the following. We first deal with the kinetic and potential energy of the electrons. The potential energy is made up of three terms; one term $-V_a(\rho_a)$ depending solely on the potential energy of the nucleus a and its surrounding electrons, another corresponding term $-V_b(\rho_b)$, and an interaction term $-V_{ab}(r, \rho)$, involving the effect of one nucleus and its electrons on the other. This last energy depends on r as a parameter. It vanishes as r goes to infinity. The kinetic energy operator for the electrons will be the sum of the Laplacians for each electron referred to coordinates *fixed in space.* These coordinates may as well be referred to one or the other nucleus, by considering the nucleus as momentarily fixed in space. The direction of the axes of these coordinates must of course remain the same, irrespective of the direction of r. The electronic kinetic energy term is therefore the sum of the Laplacians in the coordinates where the positions of the nuclei are simply parameters.

The kinetic energy of the nuclei relative to each other is given by m/M times the Laplacian in the coordinates r, θ, ϕ. Here m is the electronic mass and M is the reduced mass $M_a M_b/(M_a + M_b)$. The nuclear potential energy is of course $2Z_a Z_b/r$.

---

[38] Feenberg, Phys. Rev. **40**, 40 (1932).

[39] Born and Oppenheimer, Ann. d. Physik **84**, 457 (1927); Rosen, Thesis M. I. T. (1931).

Therefore the Schroedinger equation for the system is

$$\left(\sum \nabla_{\rho_a}{}^2 + \sum \nabla_{\rho_b}{}^2 + V_a + V_b + V_{ab} + \frac{m}{M}\,\nabla_r{}^2 - \frac{2Z_aZ_b}{r}\right)\Psi = \frac{1}{2\pi i}\,\frac{\partial\Psi}{\partial t} \quad (34a)$$

where the time t is measured in units of the period of oscillation corresponding to the unit of energy. The unit is 3.04×10^{-16} sec.

What is next done is to separate off the small terms $m\nabla_r{}^2/M$, and to solve the equation

$$\left[\sum \nabla_{\rho_a}{}^2 + \sum \nabla_{\rho_b}{}^2 + V_a + V_b + V_{ab} - \frac{2Z_aZ_b}{r} + E_\nu(r)\right]\psi_\nu(r, \rho) = 0 \quad (34b)$$

The coordinate r is here only a parameter, and the wave function $\psi_\nu(r, \rho)$, properly normalized, gives the behavior of the electrons when the two nuclei are held a distance r apart. There will be a large number of allowed wave functions corresponding to the different allowed states of this clamped molecule, each state labelled by an ensemble of quantum numbers ν. The energy of the clamped molecule, $E_\nu(r)$ is different for different ν's and depends on r as a parameter. It is the so-called molecular potential function.

When we obtained (34b) from the correct Eq. (34a) we arbitrarily assumed that the operators dependent on r could be separated from those dependent on the ρ's, and therefore that we could obtain a solution of (34a) as a product of a function dependent only on the ρ's times a function depending only on r. Actually we see that the function ψ which should only depend on the ρ's also depends on r, so (34a) is not separable. But usually the ψ's only vary very slowly as r changes, so that we can say that (34a) is almost separable (if the phrase has any meaning).

We can see that a solution of the form of a product $\psi_\nu(r, \rho)\chi_\nu$ will almost satisfy (34a) if χ be taken as a function of t, r, θ and ϕ alone. For χ must satisfy the equation

$$\psi_\nu\left[\nabla_r{}^2 - \frac{M}{m}E_\nu(r) + \frac{1}{\psi_\nu}(\nabla_r{}^2\psi_\nu + 2\nabla_r\psi_\nu \cdot \nabla_r)\right]\chi_\nu = \frac{M}{2\pi i m}\,\psi_\nu\,\frac{\partial\chi_\nu}{\partial t}\cdot \quad (35a)$$

The only term depending on the ρ's is the one involving the Laplacian and gradient of the ψ_ν. Since ψ_ν varies slowly with r this term is small; and moreover $\nabla_r{}^2\psi_\nu$ and $\nabla_r\psi_\nu$ are proportional to ψ_ν for considerable ranges of values of the ρ's. This means that the term in brackets is a small term which varies quite slowly with r and with the ρ's, so we can average over the ρ's by multiplying the equation by ψ_ν and integrating over the ρ's. We then obtain

$$\left[\nabla_r{}^2 + \frac{M}{m}\,V_{\nu\nu}(r) + \epsilon_{\nu n}\right]\chi_{\nu n}(r) = 0$$

if we solve for the steady state by assuming that $\partial\chi/\partial t = -2\pi i\epsilon_{\nu n}\chi$. The potential $V_{\nu\nu}(r)$ is given by a diagonal element of the matrix

$$V_{\mu\nu}(r) = \int \bar{\psi}_\mu \left[- E_\nu(r)\cdot\psi_\nu + \frac{m}{M}(\nabla_r{}^2\psi_\nu + 2\nabla_r\psi_\nu\cdot\nabla_r)\right] d\tau \tag{35b}$$

where $d\tau$ is the volume element for all the electronic coordinates. Therefore

$$V_{\nu\nu}(r) = - E_\nu(r) - \frac{m}{M}\int |\nabla_r\psi_\nu|^2 d\tau$$

$$V_{\mu\nu}(r) = \frac{m}{M}\int \bar{\psi}^\mu \nabla_r{}^2\psi_\nu d\tau + 2\int \bar{\psi}_\mu \nabla_r\psi_\nu d\tau\cdot\nabla_r .$$

When the two atoms are bound together and the χ's are only large within a limited range of r, then this approximation is valid and the allowed vibrational and rotational energies can be found from this equation for $\chi_{\nu n}$.

If the two nuclei are not bound together, but come from infinity, collide and go away from each other again, then this approximation is not the proper method of attack, for we shall see that it is just this nonseparability, the effect of the motion of the nuclei on the electrons, which produces a transition from one state to another at collision.[40] We must assume that our correct solution is the product $\psi_i\chi_i$ for the initial state plus a sum of other $\psi_\nu\chi_\nu$'s for the final states.

$$\Psi = \psi_i\chi_i + \sum_\nu \psi_\nu\chi_\nu .$$

The insertion in (34a) gives

$$\left\{\psi_i\left[\nabla_r{}^2 - \frac{M}{m}\left(E_i + \frac{1}{2\pi i}\frac{\partial}{\partial t}\right)\right] + [\nabla_r{}^2\psi_i + \nabla_r\psi_i\cdot\nabla_r]\right\}\chi_i(r,t)$$

$$+ \sum_\nu\left\{\psi_\nu\left[\nabla_r{}^2 - \frac{M}{m}\left(E_\nu + \frac{1}{2\pi i}\frac{\partial}{\partial t}\right)\right] + [\nabla_r{}^2\psi_\nu + \nabla_r\psi_\nu\cdot\nabla_r]\right\}\chi_\nu(r,t) = 0.$$

We can solve this approximately by considering χ_i to be much greater than all the other χ's. Then multiplying through by $\bar{\psi}_i$ integrating over $d\tau$ and neglecting the small χ's we obtain

$$\left[\nabla_r{}^2 + \frac{M}{m}\left(V_{ii} - \frac{1}{2\pi i}\frac{\partial}{\partial t}\right)\right]\chi_i(r) = 0. \tag{36b}$$

Similarly an equation for χ_ν can be obtained

$$\left[\nabla_r{}^2 + \frac{M}{m}\left(V_{\nu\nu} + \frac{1}{2\pi i}\frac{\partial}{\partial t}\right)\right]\chi_\nu(r) = - \frac{M}{m}V_{\nu i}(r)\chi_i(r). \tag{36c}$$

The $V_{\nu\nu}$'s, the molecular potential energy functions, are well known.[41] Many of them can be computed from band spectra data. There is a different function for every electronic state of the molecule. Some energy functions have minima, indicating the posibility of a stable molecule for such states;

[40] Rice, Phys. Rev. **38,** 1943 (1931); London, Zeits. f. Physik **74,** 143 (1932).

[41] Mulliken, Rev. Mod. Phys. **4,** 73 (1932).

while others have no minima, showing that these states cannot have a stable molecule. If we consider a neutral molecule, then, as we increase r, many of the wave functions ψ_ν approach the wave functions for two separate neutral atoms, each in some atomic state, having energies $E_{\nu a}$ and $E_{\nu b}$ respectively. The corresponding potential function $-V_{\nu\nu}$ approach the asymptotic values $(E_{\nu a}+E_{\nu b})$ more rapidly than $1/r^6$. In general the potential functions of several molecular states, some with minima and some without, can approach the same asymptotic value.

The states which separate into neutral atoms are called nonpolar states. However there are some states whose wave functions ψ_ν separate into the wave functions of a positive and a negative ion for large r. These states are called polar states, and the corresponding potential functions $-V_{\nu\nu}$ approach their asymptotic values $(E_{\nu a}+E_{\nu b})$ no faster than $2/r$.

Now let us set our energy scale such that $-V_{ii}(\infty)=(E_{ia}+E_{ib})=0$. Then if we allow $\partial\chi_i/\partial t=-2\pi i k_i^2\chi_i$, the resulting equation

$$\left[\nabla_r^2+\frac{M}{m}(V_{ii}+k_i^2)\right]\chi_i(r)=0 \tag{37a}$$

is the equation for two atoms approaching each other with an initial kinetic energy k_i^2. Likewise (36c) becomes

$$\left[\nabla_r^2+\frac{M}{m}(V_{\nu\nu}-W_\nu+k_\nu^2)\right]\chi_\nu(r)=\frac{M}{m}V_{i'}(r)\chi_i(r) \tag{37b}$$

where $W_\nu=-(E_{\nu a}+E_{\nu b})$ and is thus the difference between the initial and final atomic energy. Therefore $V_{\nu\nu}-W_\nu$ approaches zero as r goes to infinity, and the final kinetic energy of the system is $k_\nu^2=k_i^2+W_\nu$. If W_ν is positive, the system gains kinetic energy by the collision, if W_ν is negative it loses kinetic energy.

Eq. (37a) can be solved by the exact methods of section 7 or the approximate methods of section 8. The solution will be a plane wave in the direction of original motion plus an outgoing scattered wave. This gives us the scattering due to elastic collisions.

A solution of the left side of (37b) equal to zero gives another plane-plus-scattered wave, with the direction of the plane wave not necessarily in the same direction as the initial wave. Suppose $\chi_\nu(r,\Phi)$ be the particular solution of the left side of (37b) equal to zero whose plane wave is pointed in a direction at an angle Φ to that of the plane wave of χ_i. Then the solution of (37b) which is only an outgoing wave will be of the form

$$\frac{e^{ik_\nu r}}{r}F_\nu(\Phi)$$

for large values of r. $F_\nu(\Phi)$ gives the amplitude of the wave scattered in a direction at an angle Φ to the primary beam. It can be computed by the formula

$$\begin{aligned} F_\nu(\Phi) &= \frac{M}{4\pi m}\int \bar{\chi}_\nu(r,\ \Phi)V_{\nu i}(r)\chi_i(r)dV_r \\ &= \frac{1}{4\pi}\int \bar{\chi}_\nu(r,\ \Phi)\bar{\psi}_\nu(r,\ \rho)\,\nabla_r^2[\psi_i(r,\ \rho)\chi_i(r)]dV_r d\tau. \end{aligned} \tag{37d}$$

Usually (37a) is solved by expanding χ into a series

$$\chi_i = \frac{2}{k_i}\sum_{\lambda=0}(\lambda+\tfrac{1}{2})i^\lambda e^{i\gamma_\lambda}P_\lambda(\cos\theta)y_{i\lambda}(k_ir)/r$$

where y is the solution which remains finite everywhere, and which goes to $\cos(k_ir-\pi\lambda+1/2+\gamma_\lambda)$ at large r's. The homogeneous part of (37b) can be solved in the same manner. Then

$$F(\Phi) = \frac{2}{k_ik_\nu}\sum_\lambda(\lambda+\tfrac{1}{2})P_\lambda(\cos\Phi)\int_0^\infty y_{\nu\lambda}(k_\nu r)V_{\nu i}(r)y_{i\lambda}(k_ir)dr$$

an equation similar to (14c). The total cross section for this collision of the second kind is

$$q_{i\nu} = \frac{4\pi}{k_i^3k_\nu}\sum_\lambda(2\lambda+1)\left[\int_0^\infty y_{\nu\lambda}(k_\nu r)V_{\nu i}(r)y_{i\lambda}(k_ir)dr\right]^2 \tag{37e}$$

to the first approximation. This equation is similar to (11c). This is only true if $V_{\nu i}$ is a function of r alone. If $V_{\nu i}$ is a function of θ also, then terms will enter involving integrals of products of $y_{\nu\lambda}$ and $y_{i\lambda'}$ where λ is different from λ'.

The essential difference between electron-atom and atom-atom collision is emphasized by the difference between expression (28a) (or its generalization when plane-plus-scattered wave functions $\bar{\chi}_\nu(r,\ \Phi)\chi_i(r)$ are substituted for the approximate $\exp i\boldsymbol{r}\cdot(\boldsymbol{k}_i-\boldsymbol{k}_\nu)$) and expression (37d). In the electron scattering the perturbing energy is the electrostatic interaction between the atom and the incoming electron, whereas in atom scattering the perturbing energy is the relative kinetic energy of the atoms themselves, as evidenced by the operator ∇_r^2 in the integral.

As long as the q in (37e) is small compared to the elastic cross section, then the approximations we have made are valid, and (37d) and (37e) will express the scattering by collisions of the second kind, fairly well.[42]

This approximate expression for $q_{i\nu}(k_i^2)$ serves to demonstrate a fundamental relationship between this cross section and that for the exact reverse process, where the atoms come together in the state ν with kinetic energy k_ν and leave in state i with energy k_i. The only difference in the expression will be that outside of the summation sign we will have $4\pi/k_ik_\nu^3$ instead of $4\pi/k_i^3k_\nu$, and therefore

$$k_i^2q_{i\nu}(k_i^2) = k_\nu^2q_{\nu i}(k_\nu^2),\quad k_\nu^2 = k_i^2+W_\nu. \tag{37f}$$

---

[42] Frenkel, Zeits. f. Physik **58**, 794 (1929); Morse and Stueckelberg, Ann. d. Physik **9**, 579 (1931).

This relation has been obtained from an approximate[43] solution but its validity is more fundamental than this; it must be true for the exact solution. Klein and Rosseland first obtained it by appeal to the principle of detailed balance.[44]

But to get back to the discussion of the validity of (37d and e). In many cases there will be at least one q which will be large, and the approximation method will not be satisfactory for this one transition. This will happen if some $V_{\nu i}$ is abnormally large, and this will occur whenever the potential function V_{ii} is nearly equal to some one $V_{\nu\nu}$ inside the range of r where $\nabla_r \psi_i$ is appreciable in value. In other words there will be a large probability of transition from one state i to another whose potential function comes close to V_{ii}, and transitions to other states will be relatively unimportant.

For instance if the potential functions for the normal nonpolar state of the molecule (a, b) and for a polar state (a^+, b^-) were as shown in Fig. 15, then,

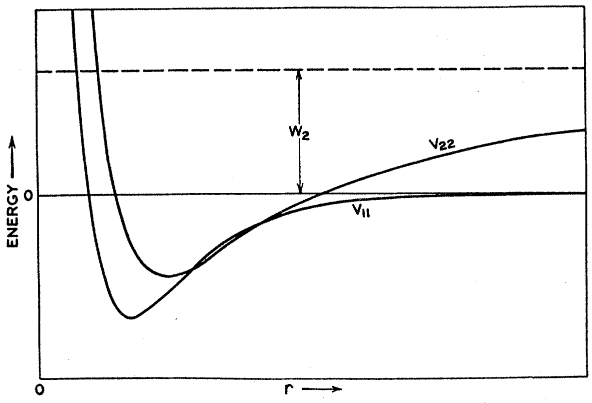

Fig. 15. Molecular potential functions for a polar and a nonpolar state which intercombine to a considerable extent.

unless other selection rules prevent it, when we shoot atom a at atom b there will be a very good chance to find atom b without one electron after collision. And of course, by (37f) if we shot a positive ion a at a negative ion of b, there would be a good chance that both atoms would be neutral after the collision. Other cases could be found where the state whose $V_{\nu\nu}$ comes close to V_{ii} would be one where the atoms were excited instead of ionized.

If only one $V_{\nu\nu}$ comes close to V_{ii} then we can disregard the other possible final states and just deal with the two. If more than one $V_{\nu\nu}$ is close the problem becomes considerably complicated, but it probably can be solved along lines similar to the following.

If we label state i by the number one and the other state which interacts strongly by number two, then, neglecting all other states in (36a), multiply-

---

[43] Morse and Stueckelberg, Ann. d. Physik **9**, 589 (1931); Goldstein, Comptes Rendus, **192**, 732 (1931).

[44] Klein and Rosseland, Zeits. f. Physik **4**, 46 (1921).

ing by $\bar{\psi}_1$ or $\bar{\psi}_2$ and integrating over the electronic coordinates, we obtain the two equations

$$\begin{aligned}\left[\nabla_r^2 + \frac{M}{m}V_{11}(r) - \frac{M}{2\pi i m}\frac{\partial}{\partial t}\right]\chi_1(r) &= -\frac{M}{m}V_{12}(r)\chi_2(r)\\ \left[\nabla_r^2 + \frac{M}{m}V_{22}(r) - \frac{M}{2\pi i m}\frac{\partial}{\partial t}\right]\chi_2(r) &= -\frac{M}{m}V_{21}(r)\chi_1(r).\end{aligned} \tag{38}$$

We must now try to find out what sort of functions these V's are.

If we can solve Eq (34b) then we can find[40] expressions for the V's by means of (35b). As was pointed out above, the diagonal elements are the molecular potential energy functions. The nondiagonal elements depend simply on the variation of ψ with r. For large values of r, ψ_ν is a product of unperturbed atomic wave functions $u_\nu v_\nu$, where

$$\begin{aligned}[\textstyle\sum \nabla_{\rho_a}^2 + V_a(\rho_a) + E_{\nu a}]u_\nu(\rho_a) &= 0\\ [\textstyle\sum \nabla_{\rho_b}^2 + V_b(\rho_b) + E_{\nu b}]v_\nu(\rho_b) &= 0.\end{aligned} \tag{39a}$$

The function ψ does not change much from this until r becomes small and the atomic wave functions begin to overlap appreciably. As r decreases beyond this point ψ changes considerably, and finally when r is zero ψ is the wave function for an atom of nuclear charge Z_a+Z_b. This means that the nondiagonal elements of the matrix V are zero for large values of r, and remain zero until r equals the sum of the "atomic radii." If r is further decreased these elements rise suddenly from zero, and remain finite as r decreases to zero. If V_{11} comes very close to V_{22} then V_{12} may become quite large.

However, it is often impossible to solve (34b) exactly to find the wave function ψ, so an approximate method of determining the V's must be found. The simplest approximation is to assume that $\psi_\nu = u_\nu v_\nu$ for all values of r. This will not satisfy (34b) exactly, but we can satisfy it on the average if we make $-E_\nu$ equal to the diagonal element $U_{\nu\nu}$ of the matrix

$$-U_{\mu\nu}(r) = \int \bar{u}_\mu \bar{v}_\nu \left(E_{\nu a} + E_{\nu b} + \frac{2Z_aZ_b}{r} - V_{ab}\right) u_\nu v_\nu d\tau. \tag{39b}$$

If we try to solve (34a) by setting $\psi = \Sigma u_\nu v_\nu \chi_\nu$ we will finally obtain equations of exactly the same form as (38), where to this approximation, the V's are not given by Eq. (35b), but are equal to the U's given in Eq. (39b). The diagonal elements of the U's are not much different from the diagonal elements of the V's given in (35b), but the nondiagonal elements of the U's are in general larger than the corresponding V's. This means that this approximation for Ψ is not as good as the previous one involving the ψ's. However, if all the nondiagonal elements of U are small except one pair, U_{12} and U_{21}, and if we can solve (38) exactly for this pair of states, then it will not matter much which approximation we use. If we must solve (38) by approximation methods, then this last approximation will not be as good as the one using the ψ's, since it makes the perturbation energy larger.

Thus we have developed two methods of obtaining the matrix elements $V_{\mu\nu}$ to be used in Eq. (38). We can solve for ψ from (34b), and use (35b) to obtain the V's. Or we can consider ψ_ν to be simply $u_\nu v_\nu$, in which case $V_{\mu\nu}$ is approximately equal to the element $U_{\mu\nu}$ given in (39b)

There are several methods of solving for the χ's, if just two states *mix up*. Essentially what we wish to know is the ratio of χ_1 to χ_2, which will give the probability of transition. We can do this in two ways; one by considering the state changing with time, starting all in state 1 at time $t=-\infty$ and ending up at time $t=+\infty$ partly in state 1 and partly in state 2. Or we can consider the steady state and find out what proportion of the two states is needed to have equilibrium.

The first method is valuable if we wish to make a wave packet out of the χ's, and to treat the motion of the atoms as classical motion. This is possible because the mass of the atoms prevents their packets from dispersing too rapidly. Let the solutions of the equations

$$\begin{aligned} \left(\nabla_r^2 + \frac{M}{m} V_{11} - \frac{M}{2\pi i m}\frac{\partial}{\partial t}\right)\Phi_1(r,t) &= 0 \\ \left(\nabla_r^2 + \frac{M}{m} V_{22} - \frac{M}{2\pi i m}\frac{\partial}{\partial t}\right)\Phi_2(r,t) &= 0 \end{aligned} \tag{38b}$$

be two normalized wave packets whose centers of gravity will travel in the same manner as classical mechanics would give for the motion of a particle of mass M in one or the other of the potential fields $-V_{11}$ or $-V_{22}$. Suppose we arrange that at $t=0$ both packets are at their most condensed state, have the same shape, have their velocities in the same direction, and are at the same place, a distance λ from the origin. By properly directing the x axis and the velocities of the packets, we can arrange it so that for large negative values of time both packets will be diffuse *blobs*, the center of gravity of Φ_1 travelling parallel to the x axis with a velocity proportional to k_1, and that of the other travelling at an angle to the x axis with a velocity proportional to k_2. The x coordinates of the center of gravity of each will be large and negative. The packets will both condense and approach each other as they come toward the origin, until at time $t=0$ they will coincide, and will both be at their nearest to the origin. After this instant the packets will separate and each move away from the origin along lines at an angle to the x axis, each packet becoming more diffuse as it goes.

If we now set $\chi_1 = a_1(t)\ \Phi_1(r,t)$ and $\chi_2 = a_2(t)\ \Phi_2(r,t)$, where, for normalization $|a_1|^2+|a_2|^2=1$; set this in (38), multiply by $\bar\Phi_1$ or $\bar\Phi_2$ and integrate over dV, we will have two equations for the a's.[45]

$$\begin{aligned} \dot a_1 &= 2\pi i V(t) a_2 \\ \dot a_2 &= 2\pi i \bar V(t) a_1 \end{aligned} \tag{40a}$$

where

$$V(t) = \int \bar\Phi_1(r,t) V_{12}(r)\Phi_2(r,t)dV$$

---

[45] Zener and Rosen, Phys. Rev. **40,** 502 (1932).

and $\int \bar{\Phi}_2 V_{21} \Phi_1 dV$ must equal $\bar{V}(t)$ in order that $|a_1|^2 + |a_2|^2$ does not change with time.

The function $V(t)$ depends on V_{11}, V_{22}, on V_{12} and on the packets' minimum distance from the origin λ. It will be a maximum at $t=0$, since here the packets overlap completely, and it will be more or less symmetrical about the point $t=0$. Its maximum value will decrease as λ increases since V_{12} is only large if r is small. If the shape of V_{11} is similar to V_{22} and k_1 equals k_2 (the case of exact resonance), then $V(t)$ will stay large the longest of any case since the packets will stay superimposed forever. The value of $V(t)$ will then be given by its *classical value*, i.e., if we force the atoms to move as they would do classically in a potential field $-V_{11}$ then the interaction between the atoms, $V_{12}(r)$, as a function of time (since r is a function of time classically) will be the classical value of $V(t)$. However if V_{11} is not the same as V_{22} or if k_2 is different from k_1, then the two packets will not overlap for long, and $V(t)$ will drop to zero faster than its classical value as $|t|$ increases. The greater the difference between k_1 and k_2 (i.e., the farther away from resonance) the faster $V(t)$ will fall away from its maximum value at $t=0$.

If we set $a_1=1$ and $a_2=0$ at time $t=-\infty$, then the value of $|a_2|^2$ at $t=+\infty$ gives the probability that a transition has occurred during the collision. The total probability of collision for all values of λ, expressed as a cross section, is

$$q_{12} = 4\pi\left(\int_0^\infty a_2^2 \lambda^2 d\lambda\right)_{(t=\infty)}.$$

To investigate the problem thoroughly we should try other cases where the packets do not coincide exactly at $t=0$, or do not have the same direction of velocity, and see what probability there will be of transitions occurring then. However if the packets do not coincide at their nearest approach they will never interact very much, and $V(t)$ will never be large, and these cases can be neglected. In other words, there is a sort of Franck-Condon principle holding for these transitions.

The only place where V_{12} can be large is where V_{11} is near V_{22}[40] and this is the place where Φ_1 is nearly equal to Φ_2. This means that $V(t)$ is real over that part of the range of t where it is the largest, and if we consider it to be real for all values of t we will make but a small error.

If $V(t)$ is real, the solution of (40a) is

$$\begin{aligned} a_1 &= \cos 2\pi \int_{-\infty}^{t} V(t)dt \\ a_2 &= i \sin 2\pi \int_{-\infty}^{t} V(t)dt \end{aligned} \tag{40b}$$

and so the probability of the transition 1→2 occurring during the collision is

$$p_{12} = |a_2|^2_{(t=\infty)} = \sin^2 2\pi A, \quad A = \int_{-\infty}^{\infty} V(t)dt. \tag{40c}$$

This expression for the probability of transition is rather difficult to obtain for any particular case, but it is useful in demonstrating several general properties of collisions of the second kind.

If A is small enough that $\sin^2 2\pi A = 4\pi^2 A^2$ then the q_{12} obtained from (40c) will reduce to a form similar to the approximate expression (37e), as it should.

However, as A increases p_{12} does not increase indefinitely, for of course it cannot be greater than unity. When $A = 1/4$, the collision is certain to result in a transition, but when $A = 1/2$ it is certain *not* to result in a transition; and so on, p_{12} oscillating between unity and zero as A increases. Of course when we integrate over λ to obtain the total cross section q_{12} much of this oscillation irons out. However, since A goes rapidly to zero when λ becomes larger than the sum of the atomic radii, R, some of this periodicity remains.

For exact resonance $(k_1 = k_2)$ V has its classical value. We can say that $V(t)$ is zero as long as the packets' centers of gravity are farther away from the origin than R, and has a value W when the centers are closer than R. The length of time the centers will be closer than R to the origin can be taken as T, where T is a function of λ, being zero when λ is greater than R. Then A is[46] simply $WT(\lambda)$ and $q_{12} = 4\pi\int_0^R \sin^2(2\pi WT(\lambda))\lambda^2 d\lambda$.

If the resonance is not exact, then $V(t)$ drops off faster with increasing $|t|$ than its classical value does, and so A will decrease, becoming smaller and smaller as k_2 differs more and more from k_1. Thus, in general, the maximum value of A will be its value at resonance. The relation between the q's on one side of resonance $(k_2 > k_1)$ and those on the other side $(k_2 < k_1)$ is given by the Klein-Rosseland equation (37f).

The other method of solving Eqs. (38) is to consider both χ's to be in a steady state, i.e., both to have a time factor of the sort $\exp 2\pi i k_1^2 t$. Then (38) becomes

$$\begin{aligned} \left[\nabla_r^2 + \frac{M}{m}(V_{11} + k_1^2)\right]\chi_1(r) &= -\frac{M}{m}V_{12}\chi_2(r) \\ \left[\nabla_r^2 + \frac{M}{m}(V_{22} + k_1^2)\right]\chi_2(r) &= -\frac{M}{m}V_{21}\chi_1(r). \end{aligned} \tag{41a}$$

This can be solved for several special cases.

At large distances $V_{22} = V_{11} + W_2$ where W_2 is the difference between the atomic energies in state one and in state two. Suppose this relation were true for all values of r. Then (41a) becomes

$$\begin{aligned} \left[\nabla_r^2 + \frac{M}{m}(V_{11} + k_1^2)\right]\chi_1 &= -\frac{M}{m}V_{12}\chi_2 \\ \left[\nabla_r^2 + \frac{M}{m}(V_{11} + k_2^2)\right]\chi_2 &= -\frac{M}{m}V_{21}\chi_1 \end{aligned} \tag{41b}$$

where as before $k_2^2 = k_1^2 + W_2$.

---

[46] Zener, Phys. Rev. **38**, 277 (1931).

Suppose we set

$$V_{12} = V_{21} = \begin{cases} W & (r < R) \\ 0 & (r > R) \end{cases} \tag{42a}$$

as we did just above.

If we separate our functions into the series

$$\begin{aligned} \chi_1 &= \sum a_{1\lambda} P_\lambda(\cos\theta) R_{1\lambda}(r)/r \\ \chi_2 &= \sum a_{2\lambda} P_\lambda(\cos\theta) R_{2\lambda}(r)/r. \end{aligned}$$

Then we have

$$\left[\frac{d^2}{dr^2} - \frac{\lambda(\lambda+1)}{r^2} + \frac{M}{m}(V_{11} + k_1^2)\right] R_{1\lambda} = -\frac{M}{m} V_{12} R_{2\lambda} \tag{42b}$$

and a similar one for $R_{\lambda 2}$

Suppose we call $y_{\lambda 1}(kr)$ the solution of the homogeneous equation

$$\left[\frac{d^2}{dr^2} - \frac{(\lambda+1)\lambda}{r^2} + \frac{M}{m}(V_{11} + k^2)\right] y_{\lambda 1}(kr) = 0$$

which remains finite everywhere.

Let it be normalized so that

$$\lambda_{\lambda 1}(kr) \underset{r\to\infty}{\longrightarrow} \cos\left[kr - \pi\frac{\lambda+1}{2} + \gamma_\lambda(k)\right].$$

Also let $y_{\lambda 3}$ be the solution which is infinite at the origin and which becomes

$$y_{\lambda 3}(kr) \underset{r\to\infty}{\longrightarrow} \exp i\left[kr - \pi\frac{\lambda+1}{2} + \gamma_\lambda(r)\right].$$

Then the solution of (42b) for r less than R is

$$\begin{aligned} R_{1\lambda} &= \alpha_\lambda y_{\lambda 1}(p_1 r) + C_1 \beta_\lambda y_{\lambda 1}(p_2 r) \\ R_{2\lambda} &= C_2 \alpha_\lambda y_{\lambda 1}(p_1 r) + \beta_\lambda y_{\lambda 1}(p_2 r) \end{aligned} \tag{42c}$$

where

$$\left.\begin{matrix} p_1^2 \\ p_2^2 \end{matrix}\right\} = \tfrac{1}{2}\left[k_1^2 + k_2^2 \pm \left\{(k_1^2 - k_2^2)^2 + 4W^2\right\}^{1/2}\right]$$

and

$$C_1 = W/(k_1^2 - p_2^2);\; C_2 = W/(k_2^2 - p_1^2).$$

The solution for (43b) for r greater than R is

$$\begin{aligned} R_{1\lambda} &= y_{\lambda 1}(k_1 r) + \eta_{1\lambda} y_{\lambda 3}(k_1 r) \\ R_{2\lambda} &= \eta_{2\lambda} y_{\lambda 3}(k_2 r) \end{aligned}$$

for if $a_{1\lambda}=a_{2\lambda}=(2\lambda+1)i^{\lambda}e^{i\gamma_{\lambda}(k1)}/k_1$ then χ_1 will be a plane-plus-scattered wave, and χ_2 will be a scattered wave. By joining the R's at $r=R$ in magnitude and slope we determine the constants α_λ, β_λ, $\eta_{1\lambda}$, and $\eta_{2\lambda}$ as functions of k_1, k_2 and W and R. As a matter of fact all we need solve for is the value of $\eta_{2\lambda}$, for the probability of the transition 1→2 during collision in terms of a cross section is

$$q_{12} = \frac{4\pi}{k_1k_2}\sum_{\lambda}(2\lambda+1)\eta_{2\lambda}^2. \tag{42d}$$

If we work this out for some specific form of V_{11}[47] we find that as we increase W from zero as long as A is less than either k_1^2 or k_2^2 q is given quite accurately by the formula

$$q_{12} = \frac{4\pi}{k_1^3k_2}\left(\frac{p_2^2-p_1^2}{k_2^2-k_1^2}\right)^2\sum_{\lambda=0}^{\infty}(2\lambda+1)\left[\int_0^\infty \bar{y}_{\lambda 1}(p_1r)V_{12}y_{\lambda 1}(p_2r)dr\right]^2. \tag{42e}$$

When we compare this with the expression (37e) which we obtained by straightforward approximation methods, we see that the approximation method formula will hold for fairly large interaction energies if instead of k_1 and k_2 we use p_1 and p_2.

Thus to obtain a better value for q, for any form of V_{12}, than would be given by (37e), we can find an equivalent W and R for the V_{12} and by means of these compute values of equivalent p's, which can then be substituted in (42e). An equivalent W and R can be found by solving the equations $WR=\int_0^\infty V_{12}dr$ and $WR^2=2\int_0^\infty V_{12}rdr$. This is equivalent to the method of obtaining the equivalent scattering power β for the scattering of electrons by atoms. The q obtained by means of (42e) will be valid unless V_{12} becomes very large.

However, if W is larger than k_1^2 or k_2^2 then (42e) no longer holds, and $\eta_{2\lambda}$ oscillates as W increases, just as we saw in (40b) that a_2 oscillates as A increases, and just as we saw in (3b) and Fig. 2 that q_λ oscillates as β increases. The periods are different for the different λ's so that when we sum $\eta_{2\lambda}^2$ over λ to obtain the cross section some of this oscillation will iron out just as it did when we integrated the p_{12} of (40c) over λ, and just as it did when we summed the q_λ of (3b) over λ. However some of this oscillation will remain.

We find that when λ is greater than $k_1R(m/M)^{1/2}$ the quantity $\eta_{2\lambda}$ becomes very small (for the corresponding $y_{\lambda 1}$ is very small for r less than R). This means that in our sum (42d) we need only sum over λ for those λ's less than $k_1R(m/M)^{1/2}$. It often means that η_{20} is the only η appreciably different from zero, and the computations are correspondingly simplified.[48] This again is closely analogous to the case of the wave packet method, given in equation (40c), where A is zero for λ larger than R.

In the case of exact resonance a special method can be devised[49] for the

---

[47] Stueckelberg. To be published shortly. The writer wishes to thank Dr. Stueckelberg for letting him read the manuscript of his paper.

[48] Rice, Phys. Rev. **38,** 1945 (1931).

[49] London, Zeits. f. Physik **74,** 150 (1932).

solution of (42b). One then finds that the equations for the functions $\frac{1}{2}(\chi_1+\chi_2)$ and $\frac{1}{2}(\chi_1-\chi_2)$ are homogeneous equations. If we again express these functions as sums of spherical harmonics we can solve for the sum and difference of the R's, and obtain the finite solutions, which go to

$$\begin{aligned} \tfrac{1}{2}(R_{1\lambda}+R_{2\lambda}) &\to \cos\left(k^2-\pi\frac{\lambda+1}{2}+\gamma_{+\lambda}\right) \\ & \qquad\qquad\qquad\qquad (k=k_1=k_2) \\ \tfrac{1}{2}(R_{1\lambda}-R_{2\lambda}) &\to \cos\left(k^2-\pi\frac{\lambda+1}{2}+\gamma_{-\lambda}\right). \end{aligned}$$

Since χ_1 must be a plane-plus-scattered wave, and χ_2 must be a scattered wave, then b_λ times the sum solution plus c_λ times the difference must equal $\cos\,(kr-\pi\ \lambda+1/2)+d_\lambda \exp(ikr)$; and b_λ times the sum minus c_λ times the difference must equal $e_\lambda \exp(ikr)$. From this we see that

$$e_\lambda = \tfrac{1}{2}\exp\left[i\left(\gamma_{+\lambda}+\gamma_{-\lambda}-\frac{\pi\lambda}{2}\right)\right]\sin\,(\gamma_{+\lambda}-\gamma_{-\lambda})$$

and, since the coefficients $a_{1\lambda}$ and $a_{2\lambda}$ in the expansion must be equal to $(2\lambda+1)i_\lambda/k$, we have for the cross section for exact resonance

$$q_{12} = \frac{4\pi}{k^2}\sum_\lambda (2\lambda+1)\tfrac{1}{4}\sin^2(\gamma_{+\lambda}-\gamma_{-\lambda}). \tag{43}$$

However, this case of exact resonance is not particularly important by itself. It is better to solve (41b) exactly for all cases, including resonance.

We are now in a position to discuss the general behavior of the cross sections for collisions of the second kind. These cross sections are dependent on three parameters; the initial relative kinetic energy of the two atoms k_1^2 the difference between the final and the initial kinetic energies $k_2^2-k_1^2=W_2$ (which is also the difference between the initial and final atomic energies), and the size (and of course shape) of the interaction potential V_{12}. For a given pair of atoms and pair of states (i.e., a given V_{12} and W_2) we will find q_{12} to be quite small for large values of k_1, and to decrease as k_1 increases. If we decrease k_1, we may find that q increases monotonously, or we may find it comes to a maximum value, and then decreases again, as in the case of the Ramsauer effect in elastic scattering of electrons.

In general, for V_{12} and k_1 fixed, q_{12} is a maximum at exact resonance, ($W_2=0$) being sometimes many hundred times the kinetic theory cross section for elastic collision. The cross section q_{12} decreases as W_2 increases. This is easily seen by means of the approximate solution (42e), for the greater the difference between k_1^2 and k_2^2, the greater the difference between p_1 and p_2, the quicker the y's will get out of phase, and the smaller the integral will be. We can also see this fact from the wave packet point of view. When V_{12} is very large, this may no longer be exactly true; q may increase at first as W_2 increases from zero, but q must eventually decrease and ultimately vanish when W_2 gets large enough. The relation between the q for a given k_1, V_{12} and W_2

and the q for the same V_{12}, an initial energy $k_1^2+W_2$ and a W_2 equal to minus the first W_2, is given by the Klein-Rosseland relationship (37f).

For a given k_1 and W_2, q_{12} will start from zero as V_{12} starts from zero, will increase according to (42e) at first as V_{12} increases, and then as V_{12} gets still larger, will oscillate, much in the same manner as the cross sections for elastic collision oscillate as the scattering power of the atom, β, is increased. (See the discussion in section 7.)

Considerable work has been done in developing special methods for the determination of cross sections for particular types of transition, some of them involving the collision of molecules.[50] The results obtained, however, are not interesting enough to discuss here.

There is a very considerable need for further study of collisions of the second kind, both experimentally and theoretically. The theory of these collisions must be the basis of any discussion of the dynamics of chemical reaction, and its results will be of value in the study of discharge in gases. It is to be hoped that considerable development will be made shortly.

---

[50] Fermi, Zeits. f. Physik **40,** 399 (1926), Excitation of Rotation.

Zener, Phys. Rev. **37,** 556 (1931), and Oldenberg, Phys. Rev. **37,** 194 (1931), Excitation of Rotation and Vibration.

Beutler and Eisenschimmel, Zeits. f. Elekt. Chem. **36,** 746 (1930), Permanence of Spin during Collision.

Rice, Zeits. f. phys. Chem. **7B,** 226 (1930) and Chem. Rev. **10,** 125 (1932), General Problems.

Kallmann and London, Zeits. f. phys. Chem. **2B,** 207 (1929), Adiabatic relative Motion of the Atoms.