

THE DETERMINATION OF ELECTRON DISTRIBUTIONS FROM MEASUREMENTS OF SCATTERED X-RAYS

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ABSTRACT

A calculation based on classical electromagnetic theory is made of the intensity of the x-rays scattered by an atom in which the electrons are arranged with random orientation and with arbitrary radial distribution. Conversely *an expression is derived for the radial distribution of the electrons in an atom*, assuming that they have random orientation. This expression has the form of a Fourier integral, which can be evaluated from observed intensities of the scattered x-rays for different wave-lengths and angles.

A comparison of this calculation with Wentzel's quantum theory of x-ray scattering suggests the introduction of a certain correction factor to express more nearly the intensity of the modified rays. It is also noted that the interpretation of $\psi\bar{\psi}$ as a *probability of the occurrence of an electron* leads to the correct value for the intensity of total scattered x-rays.

As an example of the application of the new method of calculation, Barrett's experimental data for the scattering of x-rays by helium are analyzed to give *the distribution of the electrons in the helium atom*. The resulting distribution is in close agreement with the value calculated by Pauling on the basis of wave mechanics, but differs by more than the probable experimental error from the electron orbits given by Bohr's theory.

1. INTRODUCTION

IT IS well known that the intensity of the x-rays scattered at small angles may be considerably greater than is anticipated on the assumption that each electron in the scattering material acts independently of the other electrons. When the scattering of x-rays by solids and liquids is considered, at least a part of this "excess scattering" may be ascribed to the interference between the rays scattered by neighboring atoms. In the case of gases, however, such interference is negligible, since the phases of the rays scattered by neighboring molecules are random. It has nevertheless long been recognized¹ that groupings of the electrons in the atoms themselves should result in some excess scattering in the forward direction. Calculations of the intensity of the scattered x-rays for typical electron distributions have in fact been made by Debye,² Schott,³ the writer,⁴ Glocker⁵ and others. The converse problem of determining the electron distribution corresponding to an observed angular

¹ D. L. Webster, *Phil. Mag.* **25**, 234 (1913); C. G. Darwin, *Phil. Mag.* **27**, 325 (1914).

² P. Debye, *Ann. d. Physik* **46**, 809 (1915).

³ G. A. Schott, *Proc. Roy. Soc.* **96**, 695 (1920).

⁴ A. H. Compton, *Washington University Studies*, **8**, 98 (1921).

⁵ R. Glocker, *Zeits. f. Physik* **5**, 54 (1921).

distribution of scattered x-rays has not however been attempted. We shall in the present paper obtain a solution of this problem which applies to certain important cases, and illustrate its application by determining the electron distribution in atoms of helium.

Because of the very important information which can thus be obtained regarding atomic structures, the problem would doubtless have been long ago pressed to a solution had it not been for an obstinate theoretical difficulty. Calculations of the effect of interference on the intensity of x-ray scattering are based upon the classical electron theory and electrodynamics. In the course of these x-ray diffraction studies, however, it became evident⁶ that these classical theories are inadequate to supply a complete solution of the problem of the intensity of scattered rays. The problem was accordingly "laid on the table" until a new quantum dynamics should be developed which would be able to supply a more reliable solution. Recently Wentzel⁷ has shown how the wave mechanics may be applied to this problem, and from his discussion it appears that the classical electron theory itself should give results which are not greatly in error.

In the meantime, closely allied problems have been successfully attacked on the basis of classical electron theory. In our studies of the diffraction of x-rays by crystals, which is of course only a special case of the general problem of x-ray scattering, application of the usual wave theory has enabled us to arrive at satisfactory arrangements of the atoms in the crystals, and has recently been used to determine also electron distributions in the atoms.⁸ We have every reason to believe that the information supplied by this work regarding atomic arrangements is reliable, and even the electron distributions found by its use are too satisfactory to admit any major error in the method of analysis. Similarly the classical wave diffraction theory has been successfully applied to the x-ray study of molecular shapes and sizes of liquids,⁹ and very recently also to the study of interatomic distances in gaseous molecules.¹⁰ We are thus encouraged to undertake again a more detailed analysis of the scattering of x-rays by gases, on the basis of classical theory. The results of this analysis will then be compared with Wentzel's conclusions, to see what modifications are necessary in light of quantum mechanics.

2. INTENSITY OF THE X-RAYS SCATTERED BY A GROUP OF ELECTRONS HAVING A RANDOM ANGULAR DISTRIBUTION

Let us suppose that an atom has Z electrons whose distances from the nucleus are at any instant $r_1, r_2 \cdots r_s$, and whose angular distribution is random. We imagine that this atom is traversed by an x-ray wave propagated

⁶ A. H. Compton, Bull. Nat. Res. Council No. 20, p. 10 (1922).

⁷ G. Wentzel, Zeits. f. Physik **43**, 1 and 779 (1927).

⁸ For summaries of the latter work, *cf. e.g.*, A. H. Compton, "X-rays and Electrons," Chapter V, or W. L. Bragg, "Electrons et Photons," report of the Fifth Solvay Congress, Paris (1928).

⁹ For a summary of this work, *cf. e.g.*, G. W. Stewart, Phys. Rev. Supp., Jan., 1930.

¹⁰ P. Debye, L. Bewilogua and F. Ehrhardt, Phys. Zeits. **30**, 84 (1929); Ber. Sächsischen Ak. d. Wiss. zu Leipzig **81**, 29 (1929).

The intensity of the scattered ray at this instant is however proportional to E^2 , say bE^2 , or,

$$I_i = bA_e^2 \left\{ \sum_1^Z (\cos pt \cos x_n + \sin pt \sin x_n) \right\}^2. \quad (6)$$

When this expression is averaged over a complete cycle, from $t=0$ to $t=2\pi/p$, all the terms in the summation disappear except those of the form

$$\cos x_m \cos x_n + \sin x_m \sin x_n,$$

and we find for the intensity averaged over a cycle,

$$I_\alpha = \frac{1}{2} bA_e^2 \sum_1^Z \sum_1^Z (\cos x_m \cos x_n + \sin x_m \sin x_n). \quad (7)$$

For a single electron, this becomes

$$I_e = \frac{1}{2} bA_e^2. \quad (8)$$

As Thomson has shown,¹² for unpolarized x-rays

$$I_e = \frac{Ie^4}{2m^2R^2c^4} (1 + \cos^2 \phi), \quad (9)$$

where I is the intensity of the primary beam traversing the electron, e , m and c have their usual significance, and R is the distance from O to P . Equation (7) may thus be written,

$$I_\alpha = I_e \sum_1^Z \sum_1^Z (\cos x_m \cos x_n + \sin x_m \sin x_n). \quad (10)$$

Since we have assumed that the electrons have random angular distribution, we must now average this intensity over all angles α_n . The probability that any α will lie between α and $\alpha+d\alpha$ is for random orientation $\frac{1}{2} \sin \alpha d\alpha$. Writing then

$$x_n = z_n \cos \alpha_n, \quad (11)$$

where

$$z_n \equiv (4\pi r_n/\lambda) \sin(\phi/2), \quad (12)$$

the probable contribution to the intensity due to the orientations α_n is

$$dI_\alpha = I_e \left\{ \sum_1^Z \sum_1^Z \frac{1}{2} [\cos(z_m \cos \alpha_m) \cos(z_n \cos \alpha_n) + \sin(z_m \cos \alpha_m) \sin(z_n \cos \alpha_n)] \times \sin \alpha_m \sin \alpha_n d\alpha_m d\alpha_n + \sum_1^Z \frac{1}{2} [\cos^2(z_n \cos \alpha_n) + \sin^2(z_n \cos \alpha_n)] \sin \alpha_n d\alpha_n \right\}.$$

¹² J. J. Thomson, *Conduction of Electricity through Gases*, 2nd Ed., p. 325; or cf. "X-rays and Electrons," p. 60.

Integrating over all values of α_m and α_n this takes the simple form,

$$I_r = I_e \left\{ Z + \sum_1^Z \sum_1^Z \sum_{m \neq n} \frac{\sin z_m}{z_m} \frac{\sin z_n}{z_n} \right\}. \quad (13)$$

Equation (13) represents the scattering by electrons arranged at fixed distances r_1, r_2, \dots from the nucleus, but with random orientations.

As an example of the application of this formula, consider the case of an atom with two electrons, both at a distance $r=a$ from the center, but with random orientations. We may write equation (13) in the form

$$S \equiv \frac{I_r}{ZI_e} = 1 + \frac{1}{Z} \sum \sum_{m \neq n} \frac{\sin z_m}{z_m} \frac{\sin z_n}{z_n}, \quad (14)$$

which in the present case becomes,

$$S = 1 + \left(\frac{\sin z_a}{z_a} \right)^2. \quad (15)$$

A graph of this expression is shown in Fig. 2 by the solid line. This may be compared with scattering by two electrons separated by a fixed distance $2a$, which is given by the expression¹³

$$S = 1 + \frac{\sin 2z_a}{2z_a}, \quad (16)$$

and is represented in the figure by the broken line.

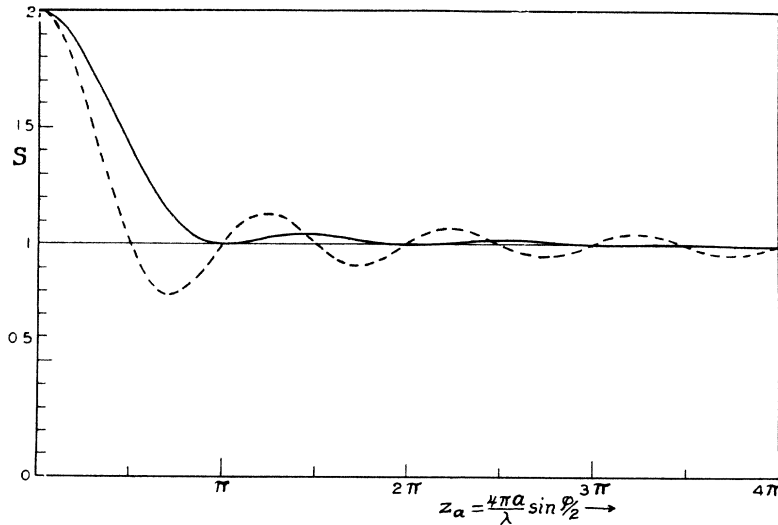


Fig. 2. Relative scattering per electron for an atom of two electrons. Solid line, both electrons at radius a and random orientation. Broken line, electrons at opposite ends of diameter $2a$.

¹³ P. Debye, reference 2, or "X-rays and Electrons," p. 72.

If the probability that any one electron shall lie between r and $r+dr$ is $u(r)dr$, and if this probability is the same for every electron, we have,

$$dI_s = I_e \left\{ Z + \sum \sum_{m \neq n} \frac{\sin kr_m \sin kr_n}{k^2 r_m r_n} u(r_m) u(r_n) dr_m dr_n \right\},$$

where

$$k \equiv z_m/r_m = (4\pi/\lambda) \sin(\phi/2). \quad (17)$$

Since $u(r_m)$ assumed the same for all electrons, the integral of this expression may be written,

$$I_s = I_e Z + I_e \sum \sum_{m \neq n} \left\{ \int_0^a u(r) \frac{\sin kr}{kr} dr \right\}^2,$$

where a is the maximum radius of the atom.

Since

$$\sum_1^Z \sum_{m \neq n}^Z 1 = Z^2 - Z,$$

$$I_s = I_e \left\{ Z + (Z^2 - Z) \left[\int_0^a u(r) \frac{\sin kr}{kr} dr \right]^2 \right\}. \quad (18)$$

For the relative scattering per electron we thus have

$$S = \frac{I_s}{ZI_e} = 1 + (Z - 1) \left\{ \int_0^a u(r) \frac{\sin kr}{kr} dr \right\}^2. \quad (19)$$

Expressions (13) or (18) may be applied to calculate the intensity of the rays scattered by an electron group, according as the electrons are at fixed distances from the center of the atom, or as they have a continuous radial distribution.

According to equation (18), I_s should never fall below ZI_e , since the term representing the interference is always positive. In this respect our calculation differs from that of Debye,² who considers electrons at fixed distances from each other, of which equation (16) is the simplest example.

3. COMPARISON WITH RESULTS OF QUANTUM MECHANICS.

Wentzel's equation (3a) for the intensity of the modified scattered rays¹⁴ may be written in the form

$$I_{unm} = I_e \left\{ \int \sum_n 4\pi r_n^2 \rho_n \frac{\sin kr}{kr} dr \right\}, \quad (20)$$

where $\sum \rho_n = \sum u_n$,² the electrical charge distribution in electronic units, the subscript indicating the n^{th} quantum number. Noting that $\sum 4\pi r^2 \rho_n$ is numerically equal to our $Zu(r)$, this may be written

$$I_{unm} = I_e \cdot Z^2 \left\{ \int u(r) \frac{\sin kr}{kr} dr \right\}^2. \quad (21)$$

¹⁴ G. Wentzel, reference 7, p. 781.

His equation (4a) for the intensity of the modified scattered rays (uncorrected for the change of wave-length) may similarly be written

$$I_{\text{mod}} = I_e \left\{ Z - \sum \left[\int 4\pi r^2 \rho_n \frac{\sin kr}{kr} dr \right]^2 \right\}. \quad (22)$$

The total intensity of the scattered rays thus becomes,

$$I_s = I_{\text{unm}} + I_{\text{mod}} \\ = I_e \left\{ Z - \sum \left[\int 4\pi r^2 \rho_n \frac{\sin kr}{kr} dr \right]^2 + Z^2 \left[\int u(r) \frac{\sin kr}{kr} dr \right]^2 \right\}. \quad (23)$$

This expression becomes identical with equation (18) if

$$4\pi r^2 \rho_n = u(r). \quad (24)$$

We have noted above that

$$\sum_1^Z 4\pi r^2 \rho_n = Zu(r), \quad (25)$$

whence relation (24) holds if

$$\sum_1^Z 4\pi r^2 \rho_n = Z \cdot 4\pi r^2 \rho_n, \quad (26)$$

i.e. if the charge distribution for every electron is the same. This is precisely the assumption on which equation (18) is derived. Wentzel, in his numerical calculation of equation (22) takes

$$\rho_n = u_n^2 \quad (27)$$

as the charge density for the n th electron, instead of

$$\rho_n = (1/Z) \sum_1^Z u_n^2, \quad (28)$$

which is the equivalent of (26). This introduces a slight difference between the results of his calculation and that of ours. It would seem however that relation (28) is in better accord with present interpretation of quantum mechanics than is (27), and if its validity is admitted, our classical equation (18) becomes identical with Wentzel's quantum equation (23).

This comparison shows that if we interpret $\sum u_n^2 dx dy dz$ as the electric charge in the volume element, the scattering which we calculate is the *unmodified* scattering (eq. 21). If, however, we interpret it as the probability that a discrete electron will be present in the volume element, as we have done in deriving equation (18), we calculate the *total* scattering. Since the total scattering is experimentally observed, it would seem that the latter interpretation has the better physical justification.

In his derivation of equation (22), Wentzel has assumed the limiting case of very long wave-lengths, for which the scattering by a free electron is identical with that calculated on the classical theory. For shorter wave-lengths

Breit¹⁵ and Dirac¹⁶ have shown that the intensity of the modified rays from free electrons is reduced in the ratio

$$\frac{I_{\text{mod}}}{I_{\text{class}}} = \left(\frac{\lambda}{\lambda'}\right)^3 = (1 + \gamma \text{vers } \phi)^3, \quad (29)$$

where λ and λ' are the wave-lengths of the primary and the modified ray respectively, and $\gamma = h/mc\lambda$. We may accordingly expect to get a closer approximation to the intensity of the modified scattering if we multiply equation (22) by equation (29), or using the equivalent part of equation (18),

$$I_{\text{mod}} = ZI_e(1 - F^2/Z^2)(1 + \gamma \text{vers } \phi)^{-3}. \quad (30)$$

Similarly¹⁷

$$I_{\text{unm}} = I_e F^2, \quad (31)$$

where

$$F \equiv Z \int_0^a u(r) \frac{\sin kr}{kr} dr, \quad (32)$$

which is identical with the so-called "atomic structure factor."

A convenient method of comparing the experiments with the theoretical calculations is thus to multiply the observed intensity of the modified rays by the factor $(1 + \gamma \text{vers } \phi)^3$, and add to the observed intensity of the unmodified rays. The resulting value

$$I_s' = I_{\text{mod}}(1 + \gamma \cos \phi)^3 + I_{\text{unm}} \quad (33)$$

may then be compared directly with the value of I_s derived by the classical equation (18).

4. ANALYSIS OF SCATTERING DATA TO DETERMINE RADIAL ELECTRON DISTRIBUTION

If the distribution of the electrons is spherically symmetrical, as we have assumed, we may represent the probability that an electron will lie between r and $r + dr$ by a Fourier sine series of the form,

$$u(r) = A_1 r \sin \pi r/a + A_2 r \sin 2\pi r/a + \cdots + A_n r \sin n\pi r/a + \cdots \quad (34)$$

Substituting this value of $u(r)$ in equation (19) we get,

$$S = 1 + (Z - 1) \left[\sum_1^\infty \int_0^a \frac{A_n}{k} \sin \left(n\pi \frac{r}{a} \right) \sin (kr) dr \right]^2. \quad (35)$$

If the scattering I_s is evaluated for $k = n\pi/a$, i.e., by equation (17) for

$$\sin (\phi/2)/\lambda = n/4a, \quad (36)$$

¹⁵ G. Breit, *Phys. Rev.* **27**, 242 (1926).

¹⁶ P. A. M. Dirac, *Proc. Roy. Soc.* **111**, 405 (1926). This relation (29) presumably does not hold for wave-lengths so short that the velocity of the recoil electron approaches c . In this case the formula of Klein and Nishina presents a closer approximation.

¹⁷ It is interesting that the ratio $I_{\text{mod}}/I_{\text{unm}}$ is expressed by equations (30 and (31) in terms of interference. It was early suggested by the writer (*Phil. Mag.* **46**, 910 (1923)) that this ratio might be thus expressed, as an alternative to the more obvious description developed later by Jauncey, in terms of the ratio of the energy of recoil of the scattering electron to its binding energy in the atom. Wentzel⁷ shows that equivalent expressions of the ratio I_u/I_m may be made in terms of either interference or energy of recoil.

where a is an assumed maximum radius, all integrals in the sum of equation (35) vanish except the n th, giving

$$S_n = 1 + (Z - 1) \left[\frac{1}{4} \frac{a^2}{k^2} A_n^2 \right]. \quad (37)$$

Thus

$$A_n = \pm \frac{2k}{a} \left\{ \frac{S_n - 1}{Z - 1} \right\}^{1/2}. \quad (38)$$

Corresponding to each value of S_n we thus determine the n th term of the Fourier series (34), and thus eventually the value of $u(r)$.

Our series (34) has in it an arbitrary radius a , and in evaluating the series the data for only certain arbitrarily chosen values of k are employed. If this arbitrary radius is made large, the values of k which are used come closer together, and our series approaches the Fourier integral,

$$u(r) = r \int_0^\infty B \sin(\pi r x) dx, \quad (39)$$

where

$$x \equiv n/a = (4/\lambda) \sin(\phi/2), \quad (40)$$

according to equation (36), and

$$B \equiv A_n a = 2\pi x \left\{ \frac{S_x - 1}{Z - 1} \right\}^{1/2}. \quad (41)$$

If instead of the probable position of a single electron, we wish to find the probable number of electrons between r and $r + dr$, we have only to multiply $u(r)$ by the number of electrons per atom, giving by equation (34)

$$U(r) = Zu(r) = Zr \sum_1^\infty A_n \sin n\pi r/a, \quad (42)$$

or by (39),

$$U(r) = Zr \int_0^\infty B \sin(\pi r x) dx. \quad (43)$$

It is interesting to compare equation (42) with the similar series expressing the radial distribution of electrons in the atoms of a crystal,¹

$$U(r) = 8\pi \frac{r}{D^2} \sum_1^\infty nF_n \sin 2\pi n \frac{r}{D}. \quad (44)$$

We note that a of equation (42) corresponds to $D/2$ of (44), since both quantities represent the assumed outer limit of the atom. The series are accordingly identical if $2\pi(r/a^2)nF_n = ZrA_n$. Using the value of A_n given by (38), and noting that $D = 2a = (n\lambda/2) \sin \frac{1}{2}\phi$, this means that

$$F_n = Z \left\{ \frac{S_x - 1}{Z - 1} \right\}^{1/2}. \quad (45)$$

This expression enables us to compare the "F" curves obtained from crystal reflection with the data given by scattering experiments.

¹⁸ A. H. Compton, "X-rays and Electrons," p. 164. An integral identical in form with (43), but representing the electron distribution in atoms of a crystal, has been given by G. E. M. Jauncey and W. D. Claus, Phys. Rev. **32**, 20 (1928).

5. TESTS OF THE METHOD OF ANALYSIS

Before applying equation (43) to the interpretation of experimental data, it will be of interest to study its application to certain cases where the solution is known.

a. Consider the intensity distribution described by equation (15). From equations (15) and (41) we have

$$B = \pm (2/a) \sin \pi xa. \quad (46)$$

Substituting this value in (43), since $Z = 2$,

$$U = 4(r/a) \int_0^\infty \sin(\pi ax) \sin(\pi rx) dx. \quad (47)$$

This integral is zero,¹⁹ except when $r = a$, in which case its value becomes infinite, indicating a concentration of the electrons at the distance $r = a$ from the nucleus, in accord with the original assumption on which (15) was based.

b. An atom of four electrons, each of whose probability of lying between r and $r + dr$ is $u(r) = 2r/a^2$ between $r = 0$ and $r = a$, and is zero beyond $r = a$.

By equation (19) we find,

$$S = 1 + 3 \left\{ \frac{2(1 - \cos \pi xa)}{\pi^2 x^2 a^2} \right\}^2. \quad (48)$$

From (41) then,

$$B = \pm \frac{4}{\pi x a^2} (1 - \cos \pi xa),$$

and equation (39) becomes,

$$u(r) = 4 \frac{r}{a} \left\{ \int_0^\infty \frac{\sin \pi rx}{\pi ax} dx - \int_0^\infty \frac{\cos \pi ax \sin \pi rx}{\pi ax} dx \right\}. \quad (49)$$

The value of the integrals is²⁰ $1/2a$ for $[r < a]$, and 0 for $[r > a]$, whence

$$\begin{aligned} u(r) &= 2r/a^2 & [r < a], \\ &= 0 & [r > a], \end{aligned} \quad (50)$$

as initially assumed.

These tests check the accuracy of the mathematical analysis. They of course say nothing, however, regarding the validity of our physical assumptions of spherical symmetry and of independence of the positions of the various electrons in the atomic groups.

6. ELECTRON DISTRIBUTION IN HELIUM

The formulas that have been developed above are directly applicable only to the scattering of x-rays by gases, in which case the interference effect due to neighboring molecules is negligible. In the case of the noble gases we are also free from interference between adjacent atoms, since the gases are mona-

¹⁹ At any point when $r \neq a$ the integral is strictly speaking indeterminate; but its average value over a finite range of x is zero.

²⁰ B. O. Peirce, "A Short Table of Integrals" (1910) nos. 484 and 485.

tomic, and according to current theories the probable electron distributions should be spherically symmetrical as we have assumed in our calculations. Fortunately recent experiments by Barrett²¹ supply sufficient information regarding the scattering by helium to yield valuable information.

In Barrett's Fig. 7 he compares the scattering by helium with that by hydrogen, which he finds identical with that calculated from the Breit-Dirac quantum formula for the range investigated. With an effective wave-length of 0.49A, he finds that helium and hydrogen scatter equally, within experimental error, at angles greater than 60°, but that at 40°, 30° and 20° the scattering by helium is greater by the ratios 1.025, 1.08 and 1.26 respectively. These values are indicated by the circles in Fig. 3, where $S \equiv I_s/ZI_e$ is plotted against x . At sufficiently small angles the phase difference between the rays from the two electrons in helium must be negligible, in which case our theory demands that the value of S must approach 2. For small values of x the phase

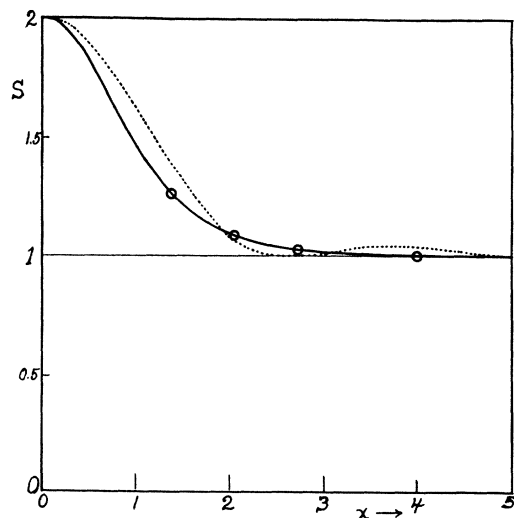


Fig. 3. Solid line, relative scattering by helium, based on Barrett's data (circles). Broken line, calculated scattering by Bohr type helium atom.

differences are small quantities of the first order; but the amplitudes, being proportional to the cosines of the phase differences, are affected only in the second order of small quantities.²² Thus the S curve must leave the $x=0$ axis parallel to the x axis, and must initially be of a parabolic form.²³ We can thus interpolate the S curve between $x=0$ and $x=1.4$ with some degree of assurance as indicated by the solid line.

This S curve can be transformed into a B curve by the help of equation (41), giving the result shown in Fig. 4. Here again the values given by the experimental data are shown by the circles.

²¹ C. S. Barrett, Phys. Rev. **32**, 22 (1928).

²² This may be seen by finding the maximum value of E from equation (5) for small values x_n . This maximum is unaffected to the first power of x_n , but is reduced by terms containing x_n^2 .

²³ These conclusions are valid only if the atom is not of infinite extent.

For values of x greater than 3 the experiments suggest that B gradually approaches zero.²⁴ The values of the integral U are not much affected by the exact manner of this approach as long as it is slow and continuous. For con-

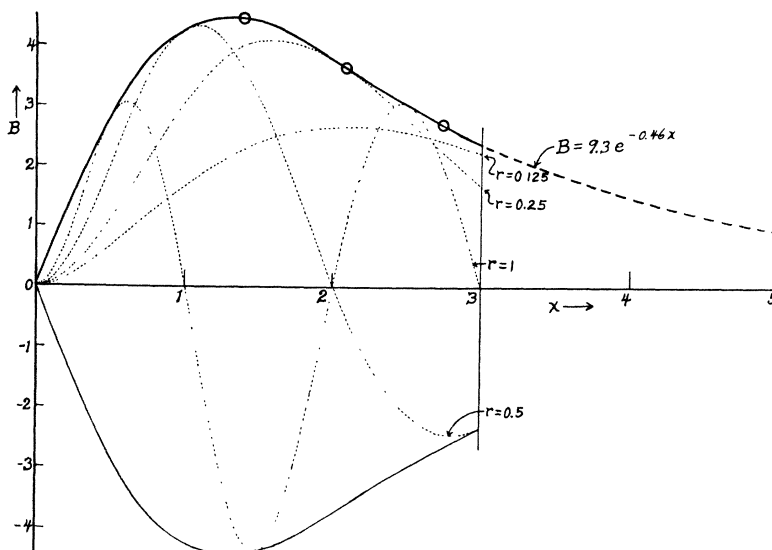


Fig. 4.

venience, therefore, we may assume that beyond some arbitrary value of x , say x_1 , B may be expressed by

$$B = be^{-ax} \quad [x > x_1]. \quad (51)$$

In order that at $x = x_1$ the values of B and dB/dx shall be continuous, we must have

$$a = - \left(\frac{1}{B} \frac{dB}{dx} \right)_{x_1} \quad (52)$$

and

$$b = B_1 e^{ax_1} \quad (53)$$

In order to evaluate $U(r)$ for a definite value of r we must determine the integral,

$$\Phi = \int_0^{\infty} B \sin(\pi r x) dx. \quad (54)$$

This may be separated into two parts,

$$\Phi_1 \equiv \int_0^{x_1} B \sin(\pi r x) dx, \quad (55)$$

and

$$\Phi_2 \equiv \int_{x_1}^{\infty} B \sin(\pi r x) dx. \quad (56)$$

²⁴ B must approach zero for large values of x unless the electron density at the center of the atom is infinite.

The first part Φ_1 may be evaluated graphically, by plotting $B \sin(\pi r x)$ for various values of r , as indicated by the dotted lines of Fig. 4, and integrating from O to x_1 with a planimeter. Φ_2 may be determined by substituting in equation (56) the value of B given in equation (51) and integrating, which gives

$$\Phi_2 = B_1 \frac{a \sin \pi r x_1 + \pi r \cos \pi r x_1}{a^2 + \pi^2 r^2}. \quad (57)$$

From Fig. 4 we find for helium, if $x_1 = 3$, $B_1 = 2.36$ and $a = 0.46$, whence the value of Φ_2 may be determined for any desired value of r .

As typical examples, we have the following values (Table I):

TABLE I.

r	Φ_1	Φ_2	$\Phi = \Phi_1 + \Phi_2$	$U = Zr\Phi$
1.125A	5.75	1.64	7.39	1.85
0.25	8.16	-0.42	7.74	3.87
0.5	3.14	-0.35	2.79	2.79
1.0	0.86	-0.70	0.16	0.32

The resulting values of U plotted against r are shown in Fig. 5 by the solid line.

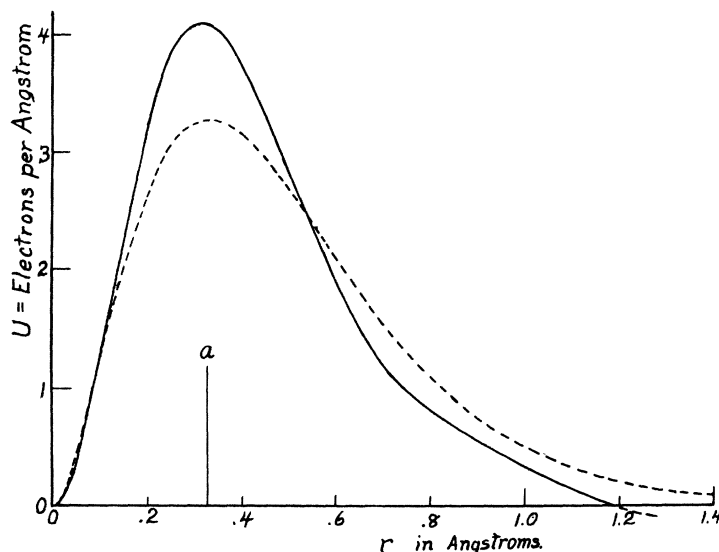


Fig. 5. Radial electron distribution in helium. Solid line, based on Barrett's x-ray scattering data. Broken line, Pauling's calculation from wave mechanics. a = radius of Bohr orbits.

It is of great interest to compare the "observed" distribution with that calculated theoretically. According to the Bohr-Sommerfeld theory, the elec-

trons in helium should both traverse approximately circular orbits with unit angular momentum, the radius of the orbits being given by

$$a = h^2/[4\pi^2e^2m(Z - s)]. \quad (58)$$

where h , e , m and Z have their usual significance, and s is the "screening constant" of each electron on the other, having a value²⁵ of approximately $s = 0.39$. Using the usual values of the constants, we thus find $a = 0.33A$. It will be seen that this value falls very close to the radius of maximum electron density as shown in Fig. 5.

If we assume that the two electrons are on a spherical surface of fixed radius $r = 0.33A$, the intensity of the scattered rays should be given by equation (15). The values of s thus calculated are shown by the dotted line Fig. 3. The differences between this dotted curve and the experimental points are considerably greater than the probable experimental error. Yet it is not impossible that a combination of heterogeneous x-rays such as Barrett used and the presence of incoherent rays (Compton scattering) at the large angles might flatten out the dotted curve to resemble the experimental one.

The distribution found from this analysis of Barrett's scattering data is however in striking agreement with that calculated on Schrödinger's wave mechanics. Thus Pauling²⁵ has shown that the radial electron distribution in helium can be expressed to a close approximation by

$$U(r) = Zr^2X^2, \quad (59)$$

where for helium in the normal state he finds,

$$X = u_{1,0} = -2\left(\frac{Z - s}{a_0}\right)^{3/2} e^{-\xi/2} \quad (60)$$

$$a_0 = h^2/4\pi^2e^2m = 0.53A,$$

$$Z = 2$$

$$s = \text{screening const} = 0.39$$

$$\xi = 2(Z - s)r/a_0.$$

Substituting these values in equation (59) we get the U curve shown by the dotted line of Fig. 5. The striking similarity between this distribution predicted by the quantum theory and that coming from our interpretation of the scattering experiments is the more convincing when it is noted that there are no arbitrary constants available to make the two curves correspond. This agreement is a strong argument in favor of a continuous electron distribution, as predicted by the wave-mechanics, as opposed to the Bohr quantum theory of definite orbits.

²⁵ Cf. e.g. L. Pauling, Proc. Roy. Soc. **A114**, 181 (1927).