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EXPERIMENTAL ELECTRON DISTRIBUTIONS IN ATOMS OF MONATOMIC GASES

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Abstract

The radial electron distribution in the atoms of helium, neon, and argon is calculated from the writer's recent data for the intensity of x-rays scattered by gases. These curves are found to be in good agreement with similar curves derived from wave mechanics. They represent the electron distribution for the atom in a state of rest and hence show more detail than similar curves calculated with the aid of crystal reflection data. In the case of neon, the experimental data are sufficiently complete to separate the K and L electrons. The smaller radius of these levels in argon make such a resolution impossible for the wave-length of the x-rays used. A comparison of the U curve for argon and with the same curve for the chlorine ion from NaCl at 0°K shows the presence of zero point energy for the ion in the space lattice of the crystal.

Introduction

NOT long after it was shown that measurements of the diffraction of x-rays by crystals gave information regarding the positions of the atoms within the crystal, it was realized that these same data would also give an idea of the distribution of electrons within the atoms of which the crystal was composed. The first calculations of this kind were quite indirect, depending on making various guesses as to the function which would best represent the electron distribution and testing them out by comparing the resulting intensities with the experimental values.

Through the work of Bragg,[1] Compton,[2] Duane,[3] and others the trial and error method was replaced by a more direct calculation of the electron distribution involving the use of Fourier's series.

Although studies of this kind have led to a number of interesting results, there are certain inherent difficulties in the crystal method which can be only partially eliminated. I will briefly mention some of these limitations since they are indirectly connected with this problem.

In making measurements on single crystals difficult corrections for primary and secondary extinction must be made which decrease the precision of the measurement. However, in a large number of crystals the extinction may be reduced to a negligible quantity by grinding the crystal to a very fine powder, and wherever intensity permits, this method is generally employed.

The thermal motion of the atoms has a large effect on the intensity in the higher orders of reflection. If the data are used without correction for this motion the resulting distribution curves give a diffuse picture of the atom

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[1] W. H. Bragg, Phil. Trans. Roy. Soc. **215**, 253 (1915).

[2] A. H. Compton, X-rays and Electrons.

[3] W. Duane, Proc. Nat. Acad. Sci. **11**, 489 (1925).

with practically no detail. However, if a given type of thermal motion is assumed, it is possible to get the electron distribution curve corresponding to the atom at rest if measurements of the intensity are made for various temperatures.

Not all crystals permit of a solution for the structure factor corresponding to the individual atoms in the crystal. One difficulty in this connection is that of knowing the association of the valence electron. In analysing the reflection from crystals it has been generally assumed that the atoms exist as ions in the space lattice. It seems that this is not strictly true, but that the valence electron is part of the time associated with the parent atom. Because of this overlapping of the adjacent layers of atoms in the crystal, it does not seem possible by the crystal reflection method to analyse completely the electron distribution in the individual atoms.

In view of the difficulties associated with determining electron distribution from intensity measurements on crystals it is of considerable interest that measurements of the intensity of scattering of x-rays by monatomic gases gives data which are free from these objections. In such gases the interference effect takes place within the individual atoms and not between an atom and its neighbor. This means that thermal agitation and zero point energy play no part in the scattered intensity. One can also make intensity measurements to as small angles as the apparatus will permit and there is no doubt about the number of electrons effective in scattering at zero angle. Although these advantages have been realized for some time an obstacle has stood in the way of utilizing the data thus obtained.* Unlike the regular reflection of x-rays from crystals the intensity of scattering from gases is altered by the presence of the Compton effect. The difficulties which this introduced were only recently overcome by Compton[4] using the solution which Wentzel[5] and Waller[6] had obtained for the scattered intensity on the basis of wave mechanics.

Compton has shown that one can express the density of electrons in the atom by a Fourier integral of the form

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

where $U(r)$ represents the number of electrons per angstrom at a distance r from the center of the atom, Z is the atomic number, B depends on the intensity of scattering and is given by

$$B = 2\pi x\left\{\frac{S-1}{Z-1}\right\}^{1/2}$$

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* Rough estimates of electron distribution from data on diffuse scattering by "amorphous" substances have been made by A. H. Compton (Washington University Studies **8**, 98 (1921), X-rays and Electrons p. 79), which agree qualitatively with the results here obtained. A correction similar to that for the Compton effect was made by assuming that the size of the electron was comparable with the wave-length.

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

[5] G. Wentzel, Zeits. f. Physik **43**, 1 and 779 (1927).

[6] I. Waller, Phil. Mag. **4**, 1228 (1927).

where S is the scattering per electron** at $x = 4/\lambda \sin(\phi/2)$.

Having measured the values of S the integral can be solved for $U(r)$. It is usually necessary to make part of the solution graphically, and for large values of x some algebraic curve can be fitted to B which will admit of direct integration to infinity. An example of this type of calculation has been given by Compton.

The intensity measurements on which this paper is based were recently made by the writer [7] and here only the electron distribution curves will be discussed.

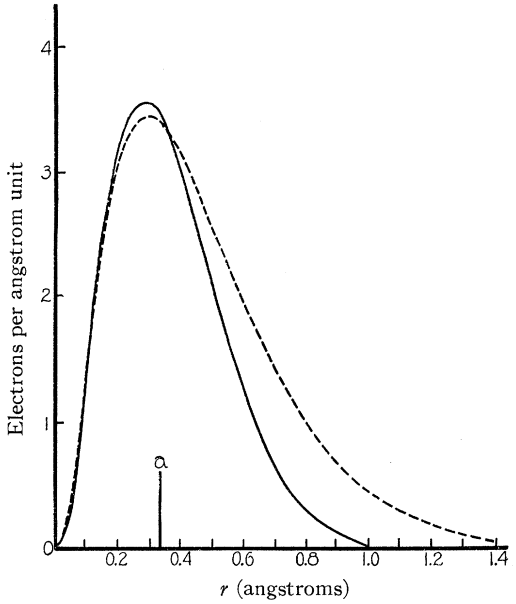

Fig. 1. Radial electron distribution in helium. Solid line from experiment, broken line from wave mechanics.

Helium

Calculations of electron distribution from measurements of the intensity of x-rays scattered by gases have been made by Compton using the experimental data of Barrett[8] for helium. He gets a distribution which is in good agreement with a corresponding curve worked out on the basis of wave mechanics. He has also shown[9] that the resulting distribution curves cannot be reconciled with Schrödinger's idea of a continuous distribution of electricity but are in excellent agreement with Heisenberg's interpretation of $\lambda\lambda^*$ as the probability of a discrete electron being present at a given point.

** S_x represents the classical value of the scattering per electron. Its relation to the experimental value can be found in refs. 7 and 5.

[7] E. O. Wollan, Phys. Rev. **37,** 862 (1931).

[8] C. S. Barrett, Phys. Rev. **32,** 22, (1928).

[9] A. H. Compton, Technology Review **33,** 19, (1930), Jour. Opt. Soc. **21,** 81, Fig. 6, (1931).

The solid line of Fig. 1 represents the electron distribution for helium as calculated from the writer's data. The maximum lies at a slightly smaller value of r than the above mentioned curve from the data of Barrett. Here the broken line represents the same function derived by Hartree[10] from wave mechanics. There is seen to be good agreement at least regarding the maximum and the inner part of the atom. At larger values of r the experimental curve indicates a less diffuse atom. The difference is perhaps within the experimental errors of the determination which rapidly become greater for larger values of r. The first Bohr orbit as calculated by Pauling[11] comes at 0.33A, slightly farther out than the maximum of either of these curves.

Although the data for helium here used are in fairly good agreement with those of Barrett they are slightly lower for all values of the scattering angle ϕ. This may be due to slight impurities which Barrett suspected in his helium. One advantage of the data used here is the fact that measurements were carried to smaller values of ϕ so that the B curve is more completely determined.

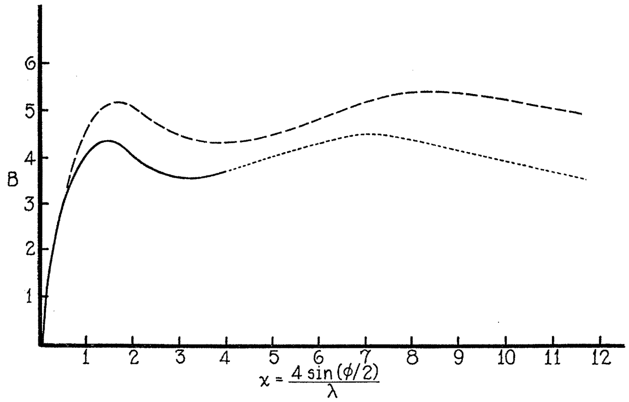

Fig. 2. Broken line B curve for Na^+ from wave mechanics, solid line experimental part of B curve for neon, dotted line shows how this curve was extrapolated to get electron distribution in neon.

NEON

In calculating the electron distribution for the neon atom the extrapolation of the B curve becomes more difficult. Although B must approach zero for large values of x, it is still increasing at the largest values of x used in the experiments. As is evident from Fig. 2, the B curve must accordingly reach a maximum for some value of x greater than 4. To get as logical an extrapolation of this curve as possible, the F values corresponding to the electron distribution for the Na^+ ion calculated by James and Waller and Hartree[12] from wave mechanics were determined for large values of x. This curve is shown by the broken line in Fig. 2. The solid line represents the B curve from the experimental data and the dotted line shows how this curve was extrapolated to get the electron distribution in neon. Almost any reasonable extrapolation would

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[10] D. R. Hartree, Proc. Am. Phil. Soc. **24,** 89 (1928).

[11] L. Pauling, Proc. Roy. Soc. **A114,** 181 (1927).

give a distribution curve not far different from the one shown in Fig. 3 and in any case the *K* and *L* shells would be resolved. The electron distribution curve for neon is in good agreement with that for the Na^+ ion calculated from wave mechanics. The Na electrons are concentrated closer to the center of the atom as one would expect due to the larger nuclear charge.

In this case the x-ray instrument has an optical resolving power sufficient to show most of the details of the atom. The resolving power could be increased by measuring the intensity at larger angles or decreasing the wave-length of the radiation. These are the same factors which affect the resolving power of a microscope.

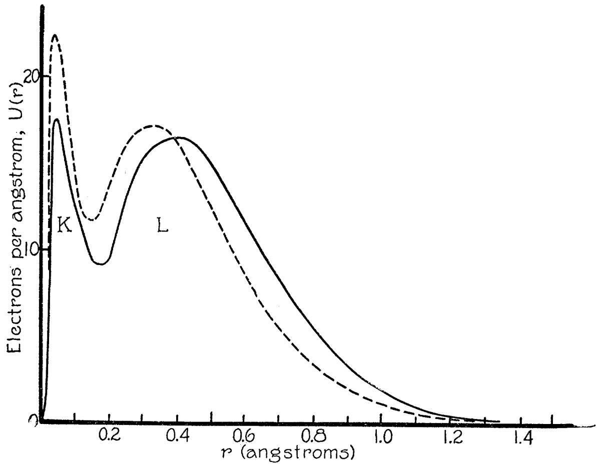

Fig. 3. Radial electron distribution curves. Solid line neon from experiment, broken line Na^+ from wave mechanics.

ARGON

An inspection of the *F* curve for argon and the corresponding curve from wave mechanics for $\frac{1}{2}(K^+ + Cl^-)$, Fig. 4, will show that the agreement is very satisfactory. One would therefore expect to get an electron distribution curve which would also agree with the corresponding wave mechanics curve.

If one extrapolates the experimental *B* curve as shown by the dotted line of Fig. 5 the *U* curve for argon shown in Fig. 6 is obtained. The points on the curve for values of r greater than 0.5A fluctuated somewhat and the dotted curve represents the mean values. This electron distribution curve does not show the detailed structure in the *K* and *L* shells that is present in the theoretical curve.[13] The difference must be due to a detailed structure in the *B* curve for larger values of x than those reached in these experiments.

Here is a case where the x-ray microscope did not have sufficient resolving power to bring out the finer structure of the atom. If the wave-length were decreased it is possible that a distinct resolution of the *K* and *L* electrons could be affected.

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[12] R. W. James, I. Waller and D. R. Hartree, Proc. Roy. Soc. **A118,** 334, (1928).

[13] R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121,** 155 (1928).

Fig. 7 shows a comparison of the electron distribution curve for argon with the similar curve derived from crystal reflection data for Cl^- at 0°K and 900°K. The electron distribution curves for the Cl^- ion were calculated from the data of James and Firth[14] for NaCl and the value at 0°K was gotten with the aid of the Debye-Waller temperature factor. The effect of thermal motion in the chlorine ion is quite apparent in the increased distance of the peaks of

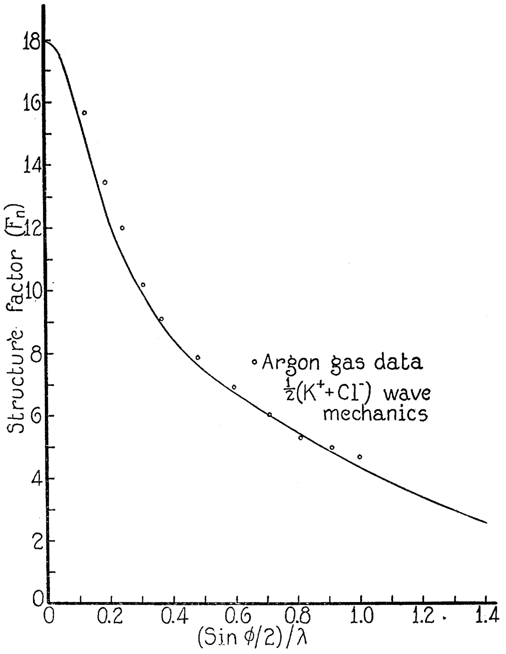

Fig. 4.

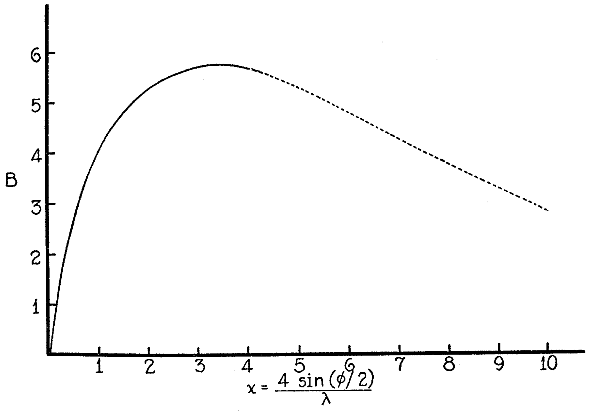

Fig. 5. Experimental and extropolated portion of *B* curve from which electron distribution in argon was determined.

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[14] R. W. James and Elsie M. Firth, Proc. Roy. Soc. **A117,** 62 (1927).

electron density from the center of the atom as the temperature increases from 0° to 900°K. Similarly, the fact that the chlorine peak for 0°K is at a considerably greater distance than the argon peak, is strong evidence for zero point motion of the chlorine ions.* James and Firth have reached the same conclusion by comparing their observed crystal reflection data with that calculated from wave mechanics. The present evidence however avoids the assumption of any theory of atomic structure.

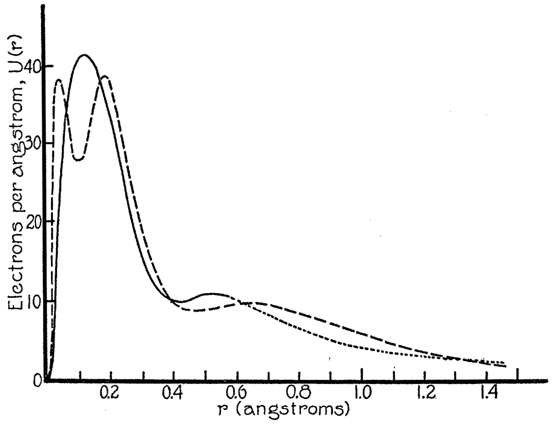

Fig. 6. Radial electron distribution curves. Solid line argon, broken line average of K^+ and Cl^- ions from wave mechanics.

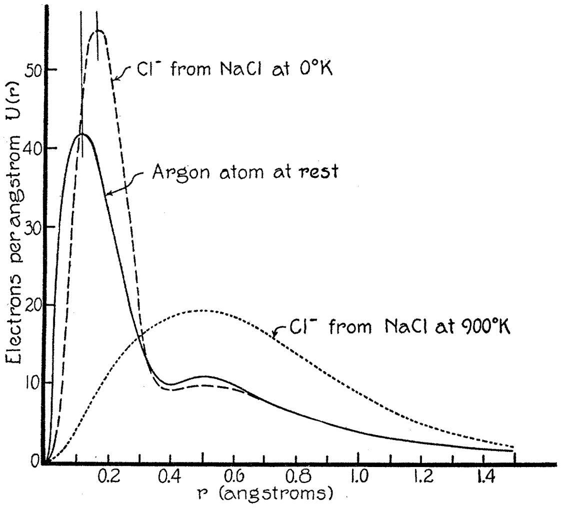

Fig. 7. Electron distribution curves showing effect of thermal agitation and zero point energy.

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* A suggestion of zero point energy was made on the basis of preliminary scattering data from argon by A. H. Compton, Technology Review **33**, 19 (1930).

CONCLUSION

The application of intensity measurements of x-rays scattered by gases to the determination of electron distribution curves gives results which are in agreement with those derived from wave mechanics. The curves represent the electron distribution for the atom in a state of rest and hence show greater detail than similar curves derived from crystal reflection data.

The difference between the electron distribution in argon and Cl^- at 0°K is good evidence for the existence of zero point energy.

The *B* curves and the electron distribution curves of neon and argon show a relation of optical resolving power to the wave-length and aperture analogous to that of a microscope. The information regarding the structure of the atom which one gets in this way is probably as reliable as would be gotten if an optical system could be devised to handle x-rays as can be done for visible light.

The writer takes pleasure in acknowledging the assistance and helpful suggestions which he has received from Professor A. H. Compton.