Incoherent Scattering and the Concept of Discrete Electrons*

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Experiment has shown that scattered x-rays contain both a coherent and an incoherent portion. Classical electron theory provides a formula for scattering closely similar to that based on wave mechanics, but includes both coherent and incoherent components only if the atom consists of discrete electrons. From a comparison of the classical and wave-mechanics theories of scattering it is concluded that the most accurate classical analog of Schrödinger's $\psi\psi^*$ is the probability of occurrence of discrete electrons, and that a particular electron is associated with each particular function $\psi_n\psi_n^*$.

EXPERIMENT shows that two types of scattered x-rays occur, one of which is of the same wavelength as the primary rays and the other of greater wavelength. Definite phase relations occur between the unmodified rays scattered by neighboring portions of matter, whence these rays are described as *coherent*. The modified rays, differing from each other in wavelength, can have no fixed phase relations, and are described as *incoherent*. Theoretical descriptions of the origin of the two types of rays have been given on the basis of (1) photons, (2) wave mechanics and (3) classical electromagnetic theory. It is a point of no little interest that whereas according to wave mechanics both types of scattered rays are interpreted in terms of wave functions distributed continuously throughout space, according to classical electromagnetic theory discrete electrons are required if incoherent rays are to occur. A comparison of the various theories of scattering is thus helpful in understanding the realm within which the concept of the electron is applicable.

It was first recognized from a consideration of the interaction of atoms and photons[1] that in addition to coherent scattering, collisions should occur involving changes of the photon's energy, which would mean a change of frequency and hence incoherence. Whereas Compton and Debye concerned themselves primarily with electrons which were knocked free from the atom by the photon's impact, Smekal noted also that any possible energy change of the atom might give to the scattered photon a frequency described by

$$h\nu_s = h\nu + W_i - W_f, \qquad (1)$$

where W_i and W_f are the initial and final energies. In the hands of Jauncey and others[2] the concept of photons colliding with electrons moving within the atom has shown itself capable of describing in quantitative form the distribution of energy between the coherent and the incoherent rays.

According to the wave-mechanics theory,[3] under the influence of the field of the incident electromagnetic wave the characteristic functions for higher energy states of an atom assume finite values, and the radiation which it emits has the frequencies described by Eq. (1). If the final state of the atom is identical with the initial state i, the frequency is unchanged, and coherent radiation is emitted. In calculating this part of

* Based on an address presented at the Symposium on X-Ray Scattering at the St. Louis meeting of the Am. Phys. Soc., Dec. 1, 1934.

[1] A. H. Compton, Bull. Nat. Res. Council No. **20**, 19 (1922); Phys. Rev. **21**, 483 (1923); **24**, 168 (1924). P. Debye, Physik. Zeits. **24**, 161 (1923). A. Smekal, Naturwiss. **11**, 873 (1923).

[2] G. E. M. Jauncey, Phil. Mag. **49**, 427 (1925); Phys. Rev. **25**, 314 (1925). J. W. M. Dumond, Phys. Rev. **33**, 643 (1929). S. Chandrasekhar, Proc. Roy. Soc. **A125**, 231 (1929).

[3] This wave-mechanics theory includes the main features of the theory of dispersion by virtual oscillators introduced by H. A. Kramers, Nature **113**, 673 (1924); **114**, 310 (1924), and extended by H. A. Kramers and W. Heisenberg, Zeits. f. Physik **31**, 681 (1925), whose theory included the incoherent radiation of the frequency given by Eq. (1). E. Schrödinger's first wave-mechanical theory of scattering, Ann. d. Physik **81**, 109 (1926), was approximately equivalent to that of Kramers, giving only the coherent term. O. Klein, Zeits. f. Physik **41**, 407 (1927), in sections 5 and 6 of his paper, gives a detailed and lucid account of the origin of the coherent and incoherent radiation according to wave mechanics. This theory was extended by Wentzel, Zeits. f. Physik **43**, 1, 779 (1927), who first derived Eq. (6) from wave-mechanical principles. Eq. (3) is due to I. Waller, Phil. Mag. **4**, 1228 (1927); Zeits. f. Physik **41**, 213 (1928); and especially good for clarity of interpretation, I. Waller and D. R. Hartree, Proc. Roy. Soc. **A124**, 119 (1929), who corrected Wentzel's theory by taking into account the limitations of Pauli's exclusion principle.

the scattering, only the ψ functions of the normal state o of the atom are therefore concerned. That is, the coherent scattering is identical with that from an atom having a continuous distribution of electric charge of density

$$\rho = -e\psi_0\psi_0^*. \tag{2}$$

If the final state differs from the initial state, the scattered ray is by Eq. (1) incoherent with the primary. The possible final states which may occur are all of those permitted by Pauli's exclusion principle, which is equivalent to the statement that an electron may be transferred to any level allowed by the selection rules, and not already occupied in the normal atom. Since the most probable transitions would in any case be those corresponding to complete ionization, this limitation is not stringent. It has the effect, however, of making the inner electrons of a Bohr atom less effective in incoherent scattering than are the outer ones.[4]

The formula thus developed by Waller[3] from wave mechanics may be written as

$$R_w \equiv \frac{I_a}{I_e} = \underbrace{(\sum_1^z f_n)^2}_{\text{content}} + \underbrace{\sum_1^z (1-f_n^2) - \sum_{mn}''(f_{mn}^2)}_{\text{incoherent}}. \tag{3}$$

[$\sum_{mn}''$ = sum over all pairs of electrons with the same spin, and $m \neq n$.]

Here I_a is the scattering by an atom, I_e that by an electron according to classical electron theory, f_n and f_{mn} are defined by the expressions,

$$f_n = \int\int\int \psi_n\psi_n^* e^{i\mathbf{k}\cdot\mathbf{r}} d\tau, \tag{4}$$

$$f_{mn} = \int\int\int \psi_m\psi_n^* e^{i\mathbf{k}\cdot\mathbf{r}} d\tau, \tag{5}$$

where ψ_n is Schrödinger's wave function corresponding to the nth electronic state in the normal atom, $\mathbf{k} = 2\pi(\mathbf{s}'-\mathbf{s})/\lambda$, where $\mathbf{s}'$ and $\mathbf{s}$ are unit vectors in the directions of the scattered and the primary rays respectively, $\mathbf{r}$ is the vector distance of the volume element $d\tau$ from the center of the atom and Z is the atomic number. Thus f_{mn} is the amplitude of the scattered wave due to the m to n transition, in terms of that due to a point charge electron as unity. The first term thus represents the scattering for the unchanged atom, which is coherent. The second term, as Wentzel shows, represents the scattering for all transitions for which $m \neq n$, and the third term takes account of those transitions which are disallowed by the Pauli exclusion principle. These terms thus describe the incoherent scattering.

In this theory, both radiation and atom are treated as distributed continuously through space. Its relation to the photon-electron theory described above corresponds to de Broglie's theorem of the equivalence of waves and particles. They may be considered as alternative views of the same phenomenon.[5]

It is noteworthy that classical electrical theory leads to a formula (Eq. (6)) almost identical with that derived from wave mechanics (Eq. (3)), but only if the atom is assumed to consist of discrete electrons. Woo's extension of Raman's classical theory[6] gives the expression,

$$R_c = (\sum_1^z f_n)^2 + \sum_1^z (1-f_n^2), \tag{6}$$

where f_n has the same significance as in Eq. (4) except that $\psi_n\psi_n^*$ is replaced by p_n, where $p_n d\tau$ is the probability that the nth electron will lie in the volume element $d\tau$. If we should assume on the other hand that $\sum p_n d\tau$ is the portion of the continuously distributed electric charge in the volume element $d\tau$, and that this volume element has the same ratio of charge to mass as does an electron, we should obtain merely[7]

[4] In most cases the effect of the negative term representing the Pauli exclusion principle is practically negligible. G. G. Harvey, P. S. Williams and G. E. M. Jauncey, Phys. Rev. **46**, 365 (1934), have recently shown, however, that in the diffuse scattering from crystals this term may become of experimental importance.

[5] The photon theories of Jauncey and others are not in their present forms precisely equivalent to Eq. (3), though there is no apparent reason why they could not be so made. It seems possible from wave mechanics, however, to arrive more easily at a rigorously derived formula.

[6] The classical theory of coherent scattering by the electrons in an atom was first treated extensively by P. Debye, Ann. d. Physik **46**, 809 (1915). That incoherent scattering must occur was pointed out from classical principles by A. H. Compton, *X-Rays and Electrons*, p. 171 (1926), and the theory was developed independently by C. V. Raman, Ind. J. Phys. **3**, 357 (1928) and A. H. Compton, Phys. Rev. **35**, 925 (1930), leading to Eq. (9). Eq. (6) was derived by Y. H. Woo, Phys. Rev. **41**, 21 (1932), following an extension of Raman's theory by G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931).

[7] This result is implicit in Wentzel's wave-mechanics theory (reference 5), and is derived explicitly by A. H.

$$R_c' = (\sum_1^z f_n)^2. \qquad (7)$$

Since definite phase relations exist between the rays scattered by the various volume elements of charge, this expression represents coherent radiation. Raman has shown[6] that the second term of Eq. (6) arises from the fact that in an atom composed of discrete electrons the positions of these electrons are continually changing, giving variable phase relations. There is thus a portion of the radiation from each electron (represented by the nth term in the summation) which is incoherent with that from the rest of the atom.

To the last term in Eq. (3) there seems to be no exact classical analog. It represents constraints upon each electron's motion due to the presence of the other electrons. If an attempt were made to build an atom out of electrons according to classical principles, such constraints would necessarily arise, but they could not be expected to introduce a term in the scattering formula identical with that resulting from Pauli's exclusion principle. According to classical electron theory, electrons should partially shield each other from the action of the electric field of the primary wave due to (1) the electrostatic field of the displaced neighboring electrons, and (2) the radiation field resulting from this acceleration. The former effect is an aspect of refraction, the latter is an increase of the electrical inertia due to proximity of the electrons. Both effects are dimensionally different from the Pauli exclusion effect, and of a smaller order of magnitude.

Further differences arise if the wave-mechanical theory is developed in sufficient detail to take into account the recoil of the scattering electrons and the corresponding increase in wavelength of the incoherent rays. Here the classical analog of radiation pressure gives a term of entirely the wrong order of magnitude. Nevertheless even here a treatment of the change in wavelength as a Doppler effect has, in the hands of Jauncey and DuMond[2] shown that momenta can be properly ascribed to the electrons within the atom, thus emphasizing their discrete existence.

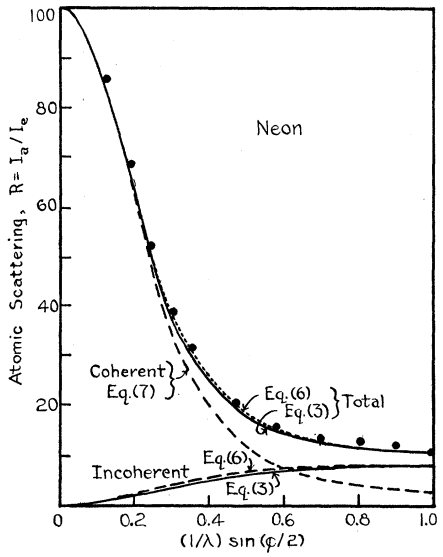

FIG. 1. Scattering of x-rays by neon. Experiments, Wollan. Theories based on Hartree electron distribution.

To a first approximation (Eq. (7)), a classical counterpart of the wave-mechanics atom is thus given by supposing the atom to consist of a continuously distributed charge of density given by Eq. (2). As will be seen from Fig. 1 this represents the most important part of the scattering at small angles. A second and much closer approximation (Eq. (6)) is obtained by replacing the continuous charge distribution with discrete electrons, the probability of occurrence of the nth electron being given by,

$$p_n d\tau = \psi_n \psi_n^* d\tau. \qquad (8)$$

Attempts to arrive at a still closer approximation by taking into account the constraints on the electron's motions cannot be expected to give the third term of Eq. (3).

It is noteworthy also that in order to get the closest classical analog to the wave-mechanical atom, we must assume that each electron has its own characteristic region within which it moves, i.e., $p_n \neq p_m$ (except where n and m differ only in the direction of the electron's spin). If each electron in the atom is assumed to have the same probability of occurrence at any point as every other electron, all the p_n's and hence all the f_n's will be alike (Eq. (4)), and Eq. (6) reduces to the form derived by Raman and

Compton and S. K. Allison in their *X-Rays in Theory and Experiment*, Van Nostrand, New York, 1935, p. 138.

Compton,[6]

$$R_c = Z^2 f^2 + Z(1-f^2), \quad (9)$$

where f is the common value of the structure factor for all of the electrons. This is no longer identical with the first two terms of Eq. (3), and is found[8] to be in somewhat less satisfactory agreement with the experiments.

Though we are accustomed to think of the Schrödinger ψ_n functions as distributed continuously throughout space, these functions are strictly speaking in $3n$-dimensional space. The apparent overlapping of the functions is merely a convenient 3-dimensional approximation. Thus the discreteness of the electrons in the classical theory corresponds on the wave-mechanics theory to equally discrete ψ_n functions, which are completely separated by being in different dimensions.

The closest classical analog to the wave-mechanical atom is thus one composed of discrete electrons, each of which has its own characteristic probability $\psi_n \psi_n^* d\tau$ of occurring within a given volume element.[9] It is accordingly proper not only to speak of electrons occurring within the atom, but also to distinguish each individual electron by the name of the corresponding quantum state. That is, K electrons are distinguishable from L electrons, etc. Thus for treatment of scattering problems, individual electrons grouped within the atom form the most nearly adequate classical picture corresponding to the continuous de Broglie waves of the wave-mechanics atom.

[8] G. Herzog, Zeits. f. Physik **69**, 207 (1931); E. O. Wollan, Rev. Mod. Phys. **4**, 241 (1932).

[9] Cf. A. H. Compton, Phys. Rev. **35**, 931 (1930), and Tech. Rev. Mass. Inst. **33**, 19 (1930). The conclusion there drawn was that the observed presence of incoherent scattering indicated that the discrete electron interpretation of $\psi\psi^*$ was necessary to bring agreement between theory and experiment. This argument was criticized by G. Herzog (reference 8), because of a supposed lack of agreement between the classical and quantum formulas, and because the concept of discrete electrons does not enter into the quantum theory of scattering. The statement that the best *classical* interpretation of $\psi\psi^*$ is the probability of occurrence of discrete electrons seems to be the legitimate conclusion from the considerations here advanced.

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The Arc Spectrum of Samarium and Gadolinium. Normal Electron Configurations of the Rare Earths

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A partial analysis which includes most of the low temperature lines is presented for Sa I and Gd I: 453 lines, 175 levels for Sa I; 71 lines, 35 levels for Gd I. The normal configuration and lowest state of Sa I is $4f^6 6s^2\ ^7F$; for Gd I is $4f^7 5d 6s^2\ ^9D$. It is also shown that the normal configuration for Tm I is probably $4f^{13} 6s^2$. There exists in the rare earth group the same type of variation of relative binding between the $4f$ and $5d$ electrons as exists between the s and d electrons in the long periods. In the rare earth group the $5d$ electron is most tightly bound at the beginning and middle of the group and has a minimum just before the middle and at the end of the group.

INTRODUCTION

THE region of the periodic table least investigated by spectroscopists is that occupied by the fourteen elements from cerium to lutecium, inclusive,—the so-called rare earths. With the exception of thulium, ytterbium and lutecium, the arc and spark spectra of the rare earths are of extreme complexity. Indeed, the number of lines obtained appears to depend only on the amount of exposure given. Even if one adheres to the strictest selection rules for L, S, J and parent terms, a fundamental electron transition in neutral gadolinium can yield more than 20,000 lines, and if only the J selection rule is retained, there is a possibility of more than 18,000,000 lines, whereas the identical electron jump in