

On the Intensity of Total Scattering of X-Rays

I. Waller and D. R. Hartree

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To summarise the results obtained, we may say that the characteristic effects of an isolated force acting at the centre of the strip are not appreciable at a distance from the force equal to the width of the strip, when the force is longitudinal, or equal to $1\frac{1}{2}$ times the width of the strip when the force is transverse. The conditions at a "freely-supported" end may be closely imitated at any distance exceeding $1\frac{1}{2}$ times the width.

On the Intensity of Total Scattering of X-Rays.

By I. WALLER and D. R. HARTREE.

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Introduction and Summary.

We shall here investigate theoretically the intensity of total scattering of X-rays by atoms distributed at random, *e.g.*, the scattering by the atoms of a monatomic gas. In the scattered radiation we shall not include the characteristic X-rays excited by the incident radiation. The scattered radiation consists then partly of radiation having the same frequency as the incident radiation (coherent scattered radiation) and partly of radiation having other frequencies (incoherent scattered radiation).† For sufficiently high frequency of the incident radiation the incoherent scattered radiation is then nearly monochromatic for a given scattering angle, and consists practically entirely of radiation whose wave-length and intensity is given by the formulæ for the Compton effect for the scattering by free electrons. Generally, however, it must be taken into account that several frequencies occur in the scattered radiation for each direction of scattering. The total intensity of the scattered radiation for a given direction has therefore to be taken as a sum of the intensities of the different components, each having a definite frequency.

General expressions for the scattered radiation are given by a scattering formula derived by one of us.‡ In this formula "relativity corrections" are

† Each of the frequencies in the incoherent scattered radiation corresponds to a transition from the initial state of the scattering atom. The energies of the final states of these transitions may lie in either the discrete or the continuous range of possible energy values.

‡ Waller, 'Z. Physik,' vol. 51, p. 213 (1928).

neglected; for the intensity of scattering in the Compton effect for free electrons, this approximation, and a further one which we also make, lead to the classical Thomson formula. This means that our intensity formula gives a useful approximation only if the incident radiation is not too hard (*e.g.*, has a wave-length not shorter than about 1 Å., in which case the error arising from the approximation just mentioned should not exceed a few per cent.).

In § 1 of this paper we deduce from the general scattering formula just mentioned an expression for the total scattering of the atoms in a gas, approximately valid if the frequency of the incident radiation is essentially higher than the K-absorption frequency of the atoms. In § 2 we apply this formula to the special case of the scattering by helium atoms, taking the wave functions which correspond to the case of vanishing interaction. In order to calculate the scattered radiation in practical cases it is necessary to find approximate wave functions for the initial state of the atom and the application to the simple case of helium makes evident the necessity for using wave functions of the right symmetry properties. This means a complication of the problem which does not arise when we are concerned only with the coherent scattering. In § 3 it is then shown how in most practical cases such wave functions can be formed from wave functions for the separate electrons corresponding to vanishing resonance interaction (neglect of "exchange processes"). These considerations can be directly applied to wave functions for the separate electrons calculated according to a method developed by one of us† which have been found to give results in close agreement with experiment for the coherent scattering.‡ Using these wave functions we get (§ 4) the scattering formula in a more explicit form. In § 5 we treat more generally the relation between our formula for the total scattering and an approximate one which may be derived from consideration concerning the scattering by each electron separately. In § 6 our formula for the total scattering is evaluated numerically for the case of argon, and compared with the experimental results of Barrett.§ Since the wave-lengths used by Barrett are rather short so that for the experimental results "relativity effects" are appreciable, we cannot make a strict comparison. We actually compare the theoretical scattered intensity, given by our formulæ in terms of the *classical* intensity of scattering by a free electron, with the scattered intensity observed by Barrett, expressed in terms

† Hartree, 'Proc. Camb. Phil. Soc.', vol. 24, pp. 89, 114 (1928).

‡ James, Waller and Hartree, 'Roy. Soc. Proc.,' A, vol. 118, p. 334 (1928); James and Brindley, 'Roy. Soc. Proc.,' A, vol. 121, p. 155 (1928).

§ 'Phys. Rev.', vol. 32, p. 22 (1928).

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of the intensity of scattering of a free electron given by Dirac's formulæ.† The agreement seems to be satisfactory. The measurements of Barrett seem to be the only one suitable for a comparison with this theory.‡

§ 1. *Deduction of an Approximate Formula for the Total Scattering.*

We shall start from the general scattering formula published in a paper by one of us. The incident radiation may be assumed to consist of a monochromatic plane polarised X-ray wave, the electric vector of this wave being defined by the real part of

$$\mathbf{E}_0 e^{2\pi i \nu (t - \mathbf{s} \cdot \mathbf{r}/c)}. \quad (1)$$

We will consider the time $t = 0$ chosen so that \mathbf{E}_0 is real. \mathbf{r} is the vector distance from a fixed point, *e.g.*, the nucleus if the wave is scattered by an atom. \mathbf{s} is a unit vector in the direction of propagation of the incident wave.

It can formally be assumed that a state n of the scattering atomic system, atom or molecule, is represented by a single wave function Ψ_n , which is a function of the co-ordinates of the atomic system. The energy of the state n is denoted by E_n . The radiation scattered in any direction defined by the unit vector \mathbf{s}' consists of a number of components, each corresponding to a transition of the scattering system from its initial state n to a final state§ m . For any direction of scattering it is convenient to describe each component of the scattered radiation (at large distances from the scattering system) by a vector \mathbf{d} , which can be interpreted as the dipole moment which would give that radiation in that direction on the classical theory. The total radiation scattered in the direction \mathbf{s}' by atoms or molecules in the state n is then defined by two sums of such dipole moments

$$\sum_{E_m < E_n + h\nu} (\mathbf{d}_{nm} + \mathbf{d}_{nm}^*) + \sum_{E_m < E_n - h\nu} (\mathbf{d}_{mn} + \mathbf{d}_{mn}^*), \quad (2)$$

where the asterisk denotes the conjugate complex quantity. The frequencies of the components corresponding to the terms in the first and second of these sums are

$$\nu'_{nm} = (E_n - E_m)/h + \nu, \quad \nu'_{mn} = (E_n - E_m)/h - \nu. \quad (2')$$

† Dirac, 'Roy. Soc. Proc.,' A, vol. 3, p. 405 (1926).

‡ Prof. P. Scherrer has kindly informed us about recent measurements made by him and A. Stäger on the total scattering of X-rays by mercury vapour, but there are difficulties in applying the theory to the scattering by such a heavy atom.

§ The final states m will usually include states in which an electron is free, and whose energies belong to the continuous range of possible energy values. In the formal presentation of the theory it is convenient to deal with discrete energy values only; this seems to be justified for the purposes of this paper.

respectively. In the first set of components we can have $m = n$, so that $\nu'_{nm} = \nu$. This component gives the coherent scattered radiation.

The electrons in the scattering system may be numbered $j = 1, 2, \dots, N$, and the position vector of the j th electron may be denoted by \mathbf{r} with components x_j, y_j, z_j . The co-ordinates of the nuclei may be denoted by $\mathbf{X}_l, \mathbf{Y}_l, \mathbf{Z}_l$ ($l = 1, 2, \dots, M$). In practice only the electrons will contribute appreciably to the scattered radiation. Taking this into account and making some formal alterations in the formulæ given in *loc. cit.*, we have the following formula for \mathbf{d}_{nm} ,

$$\mathbf{d}_{nm} = -\frac{\varepsilon^2}{8\pi^2\mu\nu\nu'_{nm}} \left[\mathbf{E}_0 \mathbf{D}_{nm} + \frac{h^2}{4\pi^2\mu} \sum_u \left\{ \frac{(\mathbf{E}_0 \cdot \mathbf{A}_{nu}) \mathbf{A}'^*_{mu}}{\nu_{nu} + \nu} + \frac{(\mathbf{E}_0 \cdot \mathbf{A}_{um}) \mathbf{A}'^*_{un}}{\nu_{mu} - \nu} \right\} \right] e^{2\pi i \nu'_{nm} t}, \quad (3)$$

where ε and μ are the charge and mass of the electron. Writing dv for the volume element of the configuration space of all particles (electrons and nuclei),[†] we have

$$dv = \prod_{j=1}^N dx_j dy_j dz_j \prod_{l=1}^M dX_l dY_l dZ_l, \quad (4)$$

$$\mathbf{D}_{nm} = \int \Psi_n^* \Psi_m \sum_{j=1}^N e^{\frac{2\pi i}{c}(\nu'_{nm} \mathbf{s}' - \nu \mathbf{s}) \cdot \mathbf{r}_j} dv, \quad (5)$$

$$\left. \begin{aligned} \mathbf{A}_{un} &= \int \Psi_u^* \sum_{j=1}^N e^{-\frac{2\pi i}{c} \nu \mathbf{s} \cdot \mathbf{r}_j} \text{grad}_j \Psi_n dv \\ \mathbf{A}'_{un} &= \int \Psi_u^* \sum_{j=1}^N e^{-\frac{2\pi i}{c} \nu'_{nm} \mathbf{s}' \cdot \mathbf{r}_j} \text{grad}_j \Psi_n dv \end{aligned} \right\}, \quad (6)$$

We shall assume the initial state n of the atomic system to be its normal state. We are then concerned only with the first sum in (2). We shall further assume that the frequency ν of the incident wave is essentially higher than the \mathbf{K} absorption frequency of the atoms in the system. Then the first term in the [] in (3) is the most important, and we shall calculate only that part of the scattered radiation which arises from this term in the expression for each \mathbf{d}_{nm} . This means that we put

$$\mathbf{d}_{nm} = -\mathbf{E}_0 \frac{\varepsilon^2}{8\pi^2\mu\nu\nu'_{nm}} \mathbf{D}_{nm}. \quad (7)$$

[†] For systems more complicated than single atoms each wave function depends on the co-ordinates of the nuclei as well as on those of the electrons, and cannot in general be written as a product of a function of the co-ordinates of the nuclei and a function of the co-ordinates of the electrons. In the following we will be mainly concerned with atoms, for which the co-ordinates of the nucleus can be disregarded.

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The intensity of the coherent scattered radiation is then given by

$$I_{\text{coh}} = I_{\text{cl}} |D_{nm}|^2, \quad (8)$$

I_{cl} being the intensity of the scattered radiation calculated according to the classical formula given by J. J. Thomson, and as far as the coherent scattering alone concerned, we get from this simple expression a satisfactory agreement with experimental results.†

It seems justifiable to assume that from (7) we can also get a proper approximation to the total scattering.‡ For the total intensity of all the components of the scattered radiation we get from (2) and (7)

$$I_{\text{tot}} = I_{\text{cl}} \sum_{E_m < E_n + h\nu} \left(\frac{\nu'_{nm}}{\nu} \right)^2 |D_{nm}|^2. \quad (9)$$

We shall now make the further assumption that all components giving an appreciable intensity have frequencies ν'_{nm} not very different from ν . This seems to be justified according to an earlier investigation of the scattering by an atom containing only one electron.§ We can then put $\nu'_{nm} = \nu$ in the right side of (9). For a similar reason we extend the summation over all states m . Writing D'_{nm} for the quantity obtained by putting $\nu'_{nm} = \nu$ in D_{nm} , that is

$$D'_{nm} = \int \Psi_n^* \Psi_m \sum_{j=1}^N e^{\frac{2\pi i \nu}{c} (\mathbf{s}' - \mathbf{s}) \cdot \mathbf{r}_j} dv, \quad (10)$$

we have to the approximation considered

$$I_{\text{tot}} = I_{\text{cl}} \sum_m |D'_{nm}|^2. \quad (11)$$

The quantities D'_{nm} defined by (10) can be interpreted as coefficients in an expansion in terms of wave functions; we have in fact

$$\Psi_n^* \sum_{j=1}^N e^{\frac{2\pi i \nu}{c} (\mathbf{s}' - \mathbf{s}) \cdot \mathbf{r}_j} = \sum_m D'_{nm} \Psi_m^*.$$

† See James, Waller and Hartree, *loc. cit.*

‡ A general discussion of the terms neglected in the approximation given by (7) is difficult, but for the one-electron problem it can be shown that they are small (*a*) for coherent scattering and $h\nu \gg$ ionisation energy, (*b*) for $h\nu/c \gg M_n$ where M_n is the mean momentum in the initial state (*cf.* Waller, 'Phil. Mag.', vol. 4, p. 1228 (1927)). It does not seem that there is likely to be any essential difference in order of magnitude of these terms for coherent scattering and incoherent scattering with ν'_{nm} nearly equal to ν .

§ Waller, 'Phil. Mag.', *loc. cit.*

Since the set of normal orthogonal functions Ψ_m^* must be assumed to be a complete set, we have

$$\begin{aligned}\sum_m |D'_{nm}|^2 &= \int \left| \Psi_m^* \sum_{j=1}^N e^{\frac{2\pi i \nu}{c}(\mathbf{s}' - \mathbf{s}) \cdot \mathbf{r}_j} \right|^2 dv \\ &= \int |\Psi_m^*|^2 \left| \sum_{j=1}^N e^{\frac{2\pi i \nu}{c}(\mathbf{s}' - \mathbf{s}) \cdot \mathbf{r}_j} \right|^2 dv.\end{aligned}\quad (12)$$

The total intensity of the scattered radiation is given by (11) and (12) to the approximation considered here.†

These formulæ are not necessarily restricted to the normal state of the atom (or molecule); they apply also to the scattering by an atomic system in any low state.

For an atom containing only one electron, it follows that

$$\sum_m |D'_{nm}|^2 = 1. \quad (13)$$

Thus to the approximation considered here, the total intensity of scattering by an atom containing a single electron is given by the Thomson formula for a free electron, which is a result found earlier. We will write R for the ratio of the intensity of total scattering by a many-electron atom to the classical intensity of scattering by a free electron. Then from (11) and (12) it follows that to this approximation where

$$R = I_{\text{tot}}/I_{\text{cl}} = \int |\Psi_m^*|^2 \left| \sum_{j=1}^N \exp(i\kappa \mathbf{r}_j) \right|^2 dv, \quad (14)$$

where

$$\kappa = 2\pi\nu(\mathbf{s}' - \mathbf{s})/c. \quad (14')$$

In the deduction of the general scattering formula a wave equation was used in which no account was taken of the spin of the electrons. In using this scattering formula we can therefore take the spin into account only as far as it is connected by Pauli's principle with the wave function in the co-ordinate space of the electrons. It seems justified to assume that we get in this way a proper approximation. The deduction just mentioned also rests on the assumption that we can represent each spectral term by one wave function. The validity of this assumption follows from the investigations on non-combining sets of wave functions, which we shall consider more closely in § 3.

† The possibility of devising a formula for the total scattering by a many-electron atom according to the same principle (use of "Vollständigkeits theorem") as had been used by Wentzel ('Z. Physik,' vol. 43, p. 1 (1927)) and one of us (J. Waller, 'Phil. Mag.,' *loc. cit.*) for a one-electron atom was first mentioned by Prof. W. Pauli in a discussion about this problem.

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Further approximations have been made in that relativity effects have been neglected and in putting $v'_{nm} = v$. The results may, therefore, be expected to apply best to the scattering of radiation of not too short a wave-length by the lighter atoms.

§ 2. *Discussion of a Special Case.*

We will apply the formulæ (10) and (14) to the total scattering by a helium atom, as this simple case will illustrate the main points which arise in the treatment of a more general case.

We take the wave functions for the limit of vanishing interaction, when they can be written as sums of products of the wave functions of the two separate electrons, and consider first the scattering by a helium atom in an excited triplet state, for which the spins of the electrons are parallel, so the wave function must be antisymmetrical in the position co-ordinates of the two electrons.†

Thus for the initial state n we take

$$\Psi_n = \frac{1}{\sqrt{2}} [\psi_1(1) \psi_2(2) - \psi_2(1) \psi_1(2)], \quad (15)$$

and consider the scattering of the component of the radiation corresponding to a transition to state m with wave function

$$\Psi_m = \frac{1}{\sqrt{2}} [\psi_{m_1}(1) \psi_{m_2}(2) - \psi_{m_2}(1) \psi_{m_1}(2)]. \quad (16)$$

We will write

$$dx_j dy_j dz_j = dv_j.$$

$$\int \psi_a^*(j) \exp(i\mathbf{kr}_j) \psi_b(j) dv_j = f_{ab}. \quad (17)$$

All the ψ 's are orthogonal, as they are wave functions for one electron in the limit of vanishing interaction, so substituting (14'), (15), (16) in (10) and carrying out the integration we have

$$|D'_{nm}|^2 = 0 \quad \text{when } m_1, m_2 \text{ both different from 1 and 2} \quad (a)$$

$$= |f_{11} + f_{22}|^2 \quad \text{when } m_1 = 1, m_2 = 2 \text{ or } m_1 = 2, m_2 = 1 \quad (b)$$

$$= |f_{2, m_2}|^2, |f_{2, m_1}|^2 \quad \text{when } m_1 = 1, m_2 \neq 1, 2 \quad \left. \begin{array}{l} \text{or } m_2 = 1, m_1 \neq 1, 2 \text{ respectively} \end{array} \right\} (c)$$

$$= |f_{1, m_1}|^2, |f_{1, m_2}|^2 \quad \text{when } m_1 = 2, m_2 \neq 1, 2 \quad \left. \begin{array}{l} \text{or } m_2 = 2, m_1 \neq 1, 2 \text{ respectively} \end{array} \right\} (c)$$

$$= 0 \quad \text{when } m_1 = m_2 = 1 \text{ or } 2. \quad (d)$$

† Cf. Heisenberg, 'Z. Physik,' vol. 38, p. 411 (1926).

The result (a) indicates that the (to the approximation considered) incident radiation does not give rise to simultaneous transitions of both electrons; (b) gives the intensity of the coherent scattering, and (c) and (d) the intensities of components of the incoherent scattering. If only one electron were present, say with wave function ψ_1 , $|f_{11}|^2$ would be the intensity of coherent scattering [cf. (8)] and $|f_{1,m_1}|^2, |f_{1,m_2}|^2$ the intensities of two components of the incoherent scattering; the total intensity of incoherent scattering would be $1 - |f_{11}|^2$ by (13).

We see from (b) and (c) that for the scattering by a helium atom we must add the amplitudes of the coherent waves scattered by single electrons with the two wave functions ψ_1, ψ_2 present in the initial state of the atom, and must add the intensities of the incoherent waves scattered by these electrons, with one important exception. This exception is given by result (d), that (with anti-symmetrical wave functions) transitions to the states $m_1 = m_2 = 1$ or 2 cannot occur. For a single electron these transitions could occur, so if we wish to use the results for one electron to deduce the total scattering by a helium atom, we must take account of the fact that the corresponding component of the scattered radiation is absent. For one electron this component has the intensity $|f_{12}|^2$, so the total scattering by a helium atom is given by

$$\begin{aligned} R &= |f_{11} + f_{22}|^2 + 1 - |f_{11}|^2 + 1 - |f_{22}|^2 - 2|f_{12}|^2 \\ &= 2 + f_{11}f_{22}^* + f_{11}^*f_{22} - 2|f_{12}|^2. \end{aligned} \quad (18)$$

The same result follows by substituting (15) in (14); the object of the deduction here given is to show the origin of the term $-2|f_{12}|^2$. This term will in general be small when the frequency of the exchange of electrons 1 and 2 is small.

If the initial state has the symmetrical wave function

$$\Psi_n = \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)],$$

we find similarly

$$R = 2 + f_{11}f_{22}^* + f_{11}^*f_{22} + 2|f_{12}|^2.$$

In this case it should be noted that the probability of a transition to a state in which both electrons have the same space wave function is different from the probability of the corresponding transition of one electron if the presence of the other is neglected.

If we had taken the wave function $\Psi = \psi_1(1)\psi_2(2)$ for the initial state, we would have found

$$R = 2 + f_{11}f_{22}^* + f_{11}^*f_{22}.$$

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The difference between this and formula (18) shows that in calculating the total scattering by a many-electron atom it is necessary to consider carefully the question of the proper wave function by which to represent the initial state of the scattering atom. This question we now investigate.

§ 3. *On the Formation of Approximate Wave Functions of required Symmetry Properties for an Atom containing several Electrons.*

We consider an atom containing N electrons. The spin of the electrons is taken into account only as far as it is connected by Pauli's principle with the wave function in the co-ordinate space of the electrons.

Introducing external electric and magnetic fields as weak as we like, we may ensure that the system does not contain any degeneracy but that caused by the identity of the electrons. This means that from any wave function belonging to a characteristic of the Schrödinger equation (that is, to a spectral term) we can form by permutations of the electron numbers and linear combinations all wave functions belonging to the same term. All the wave functions of the atom can be grouped in a number of non-combining sets ("systems").†

We denote a wave function by $\Psi(1, 2, \dots N)$, j standing for x_j, y_j, z_j (the co-ordinates of one electron) ($1 \leq j \leq N$), and by $F(1, 2, \dots N)$ an arbitrary function or operator, symmetrical in all electron numbers $1, 2, \dots N$. Then, if Ψ' is a wave function belonging to another system, we have

$$\int \Psi'^* F \Psi dv = 0, \quad dv = \prod_{k=1}^N dx_k dy_k dz_k.$$

To each characteristic E_k in one of the systems belongs the same number f of linearly independent wave functions $\Psi_l^{(k)}(1, 2, \dots n)$, $l = 1, 2, \dots f$. According to Wigner (*loc. cit.*) these wave functions can be chosen in such a way that for any two terms E_k and $E_{k'}$ belonging to the same system

$$\int \Psi_l^{(k)*} F(1, 2, \dots n) \Psi_{l'}^{(k)} dv = C \delta_{ll'}, \quad \delta_{ll'} = \begin{cases} 1 & l = l' \\ 0 & l \neq l' \end{cases},$$

the value of C being independent of l and l' but, of course, dependent on F and k, k' . This equation is valid also for $k = k'$ (*i.e.*, $E_k = E_{k'}$). The normalisation condition means that $C = 1$ for $F = 1$. The expansion of $F(1, 2, \dots n) \Psi_l^{(k)}$

† Heisenberg, *loc. cit.*, and 'Z. Physik,' vol. 41, p. 239 (1927); Dirac, 'Roy. Soc. Proc.,' A, vol. 112, p. 661 (1926); Wigner, 'Z. Physik,' vol. 40, pp. 492, 883 (1926-7), and vol. 43, p. 624 (1927); Hund, 'Z. Physik,' vol. 43, p. 788 (1927); Delbrück, 'Z. Physik,' vol. 51, p. 181 (1928).

in terms of wave functions therefore involves only wave functions with the same suffix l , and has accordingly the form $F\Psi_l^{(k)} = \sum_{k'} A_{k'} \Psi_l^{(k')}$, so that an adequate representation of spectral terms by wave functions can be made by taking one of these wave functions $\Psi_l^{(k)}$ for each term, l being the same for all terms of the system. We can easily prove that for the evaluation of any matrix element $F_{kk'}$ of the symmetrical function $F(1, 2, \dots, n)$ we can just as well represent each term by the general wave function

$$\Psi_a^{(k)} = \sum_{i=1}^f a_i \psi_i^{(k)},$$

if the a_i 's are the same for all terms, and if, according to normalisation condition, $\sum_{i=1}^f |a_i|^2$ is equal to unity. We have in fact

$$\int \Psi_a^{(k)*} F \Psi_a^{(k)} dv = \sum_{i'} a_i a_{i'} \int \Psi_i^{(k)*} F \Psi_{i'}^{(k)} dv = C.$$

In evaluating the integral (14) for the total intensity scattered, we can therefore use for the initial state n any wave function which has the right symmetry properties.

Each system is characterised by the symmetry properties of the wave functions belonging to it, and it follows from Pauli's principle that only certain types of symmetry are actually possible. Using the notation of symmetry characters introduced by Hund (*loc. cit.*) we can represent any system allowed by Pauli's principle by the symbol

$$A(N - q, q) \quad (q \leq N/2) \quad (19)$$

known as the antisymmetry character of the system. This symbol means that from any wave function belonging to this system we can form a wave function antisymmetrical in $N - q$ electrons, and in the other q electrons by permutation of electron numbers and linear combination. Using the notation that a bar under the electron numbers indicated that the wave function is antisymmetrical in these electrons, this wave function can be written

$$\Psi(\bar{1}, \bar{2}, \dots, \bar{N - q}, \underline{N - q + 1}, \underline{N - q + 2}, \dots, \underline{N}) \quad (20)$$

The antisymmetry character (19) also means that by the procedure just mentioned we cannot form any wave function antisymmetrical in more than $N - q$ electron numbers, and the wave function (20) which is itself antisymmetrical in $N - q$ electrons and in the other q electrons, is known as the "antisymmetrical normal form" of the wave function of the system.†

† The "degree of degeneracy" of this system is $f = N!(N - 2q + 1)/q!(N - q + 1)!$ (Wigner, *loc. cit.*). The multiplicity of each "term" due to the spins is $N - 2q + 1$ (Heisenberg, Wigner, *loc. cit.*).

The simplest interpretation of q is this ; if the electrons are divided into two groups of opposite spin, $N - q$ and q are the numbers in the larger and smaller groups respectively.

If the solution of the wave equation involves a degeneracy of any kind other than that caused by the identity of the particles, the considerations just mentioned can no longer be applied directly.

Since the many-electron problem cannot be solved exactly, it is necessary to use an approximate wave function. A suitable approximation is provided by considering each electron to be in a stationary state in the field of the nucleus and remaining electrons. In this approximation the interaction of the electrons is taken into account in so far as it can be expressed by a static field acting on each electron, but its essentially dynamical character, involving the interchange of electrons, is neglected. We will express this by saying that we neglect the "resonance interaction."

In this way approximate wave functions for the single electrons are found, and from them we have to form a wave function for the whole atom with definite symmetry properties. This problem is closely related to some investigations by Heisenberg, Wigner and Delbrück (*loc. cit.*), who have studied the wave functions of an atom by treating any interaction as a perturbation. We shall here treat the problem in a different way which makes it possible in cases of practical importance to find directly wave functions of zero order of approximation which have the required symmetry characters.

The use of a static field acting on each electron as an approximate expression of the interaction of the electrons provides deviations from a Coulomb field, and in order that the wave functions for the single electrons in the limit of vanishing resonance interaction shall be non-degenerate, we can assume a homogeneous magnetic field in addition.

The various wave functions for the individual electrons in the atomic state considered will be written

$$\psi_{\alpha_1}(j), \psi_{\alpha_2}(j) \dots \psi_{\alpha_N}(j), \quad (21)$$

j denoting the space co-ordinates of a single electron. These wave functions (*i.e.*, the suffixes $\alpha_1, \alpha_2, \dots \alpha_N$) need not all be different, but according to Pauli's principle each one can be identical with not more than one other, and any two which are identical must be wave functions of electrons of opposite spin. Two electrons having the same space wave function and opposite spins may be called a "closed pair" ; we will write s for the number of closed pairs ; clearly

$s \leq q$. If there are s closed pairs, we can suppose the wave functions so numbered that $\alpha_1 \dots \alpha_{N-s}$ are all different, and

$$\alpha_{N-s+1} = \alpha_1, \quad \alpha_{N-s+2} = \alpha_2 \dots, \quad \alpha_N = \alpha_s.$$

In the limit of vanishing interaction, any wave function for the whole system can be expressed in the form†

$$\sum_{(a)} C_{(a)} \psi_{a_1}(a_1) \psi_{a_2}(a_2) \dots \psi_{a_N}(a_N), \quad (21)$$

$(a) = (a_1, a_2 \dots a_N)$ being any permutation of the electron numbers $1 \dots N$, and the $C_{(a)}$'s being constants. An expression of the form (21) will not generally have a definite symmetry character; on the other hand, if we take the resonance interaction of the electrons into account we must get perturbed wave functions of definite symmetry characters. We consider a set of perturbed wave functions belonging to a given term; these have a definite anti-symmetry character (19) and normal form (20); we wish to form wave functions of the type (21) which shall be the limit of these perturbed wave functions as the perturbation tends to zero; that is to say, we want to determine the coefficients $C_{(a)}$ in (21) so that this expression has the symmetry of this normal form.

Putting $N - q = p$ (we must have $p \geq q$, since $q \leq N/2$) we must have in the limit

$$\Psi(1, 2, \dots p, p+1, p+2, \dots p+q) = \sum_{(a)} C_{(a)} \psi_{a_1}(a_1) \psi_{a_2}(a_2) \dots \psi_{a_N}(a_N).$$

By arranging the factors in each product in the sum in such a way that the electron numbers have their natural order, we get

$$\begin{aligned} \Psi(1, 2, \dots p, p+1, p+2, \dots p+q) \\ = \sum_{(\beta)} C_{(\beta)} \psi_{\beta_1}(1) \psi_{\beta_2}(2) \dots \psi_{\beta_p}(p) \psi_{\beta_{p+1}}(p+1) \dots \psi_{\beta_{p+q}}(p+q) \end{aligned}$$

where $(\beta) = (\beta_1, \beta_2, \dots \beta_{p+q})$ is a permutation of the suffixes $(\alpha_1, \alpha_2, \dots \alpha_{p+q})$. We now permute $(1, 2, \dots p)$ into $(b) = (b_1, b_2, \dots b_p)$, multiply both sides of the equation by -1 if the permutation is an odd one, and sum for all permutations. This gives

$$\begin{aligned} p! \Psi(1, 2, \dots p, p+1, p+2, \dots p+q) \\ = \sum_{(\beta)} C_{(\beta)} \left[\sum_{(b)} (-)^{(b)} \psi_{\beta_1}(b_1) \dots \psi_{\beta_p}(b_p) \right] \psi_{\beta_{p+1}}(p+1) \dots \psi_{\beta_{p+q}}(p+q), \end{aligned}$$

† It is convenient to use Roman letters for the electrons and Greek letters as suffixes to distinguish the various wave functions for one electron.

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where $(-)^{(b)}$ means $+1$ or -1 according as (b) is an even or odd permutation of $(1, 2, \dots, p)$. Then permuting $(p+1, p+2, \dots, p+q)$ into

$$(b') = (b_{p+1}, b_{p+2} \dots b_{p+q})$$

we get in the same way

$$\begin{aligned} p! q! \Psi(1, 2 \dots p, p+1, p+2 \dots p+q) \\ = \sum_{(\beta)} C_{(\beta)} \left[\sum_{(b)} (-)^{(b)} \psi_{\beta_1}(b_1) \dots \psi_{\beta_p}(b_p) \right] \left[\sum_{(b')} (-)^{(b')} \psi_{\beta_{p+1}}(b_{p+1}) \dots \psi_{\beta_{p+q}}(b_{p+q}) \right] \\ = \sum_{(\beta)} C_{(\beta)} \begin{vmatrix} \psi_{\beta_1}(1) & \dots & \psi_{\beta_p}(1) \\ \vdots & & \vdots \\ \psi_{\beta_1}(p) & \dots & \psi_{\beta_p}(p) \end{vmatrix} \begin{vmatrix} \psi_{\beta_{p+1}}(p+1) & \dots & \psi_{\beta_{p+q}}(p+1) \\ \vdots & & \vdots \\ \psi_{\beta_{p+1}}(p+q) & \dots & \psi_{\beta_{p+q}}(p+q) \end{vmatrix}. \quad (22) \end{aligned}$$

The sum on the right side might contain terms corresponding to any permutation $(\beta) = (\beta_1 \dots \beta_{p+q})$ of $(\alpha_1 \dots \alpha_{p+q})$ (*i.e.*, of the suffixes of the wave functions of the separate electrons), including interchanges of one or more wave functions between the two determinants.

If $s = q$ we can from (22) definitely find a unique expression for

$$\Psi(1, 2, \dots, p, p+1, p+2, \dots, p+q)$$

for vanishing resonance interaction. The number of suffixes $\alpha_1 \dots \alpha_N$ which are different is $N - s$, and in the case of $s = q$ this number is equal to p , these different suffixes being $\alpha_1 \dots \alpha_p$. In any non-vanishing term of the sum on the right-hand side of (22), $\beta_1 \dots \beta_p$ must be all different, and also $\beta_{p+1} \dots \beta_{p+q}$. In the case $s = q$, $\beta_1 \dots \beta_p$ must therefore be a permutation of $\alpha_1 \dots \alpha_p$ and $\beta_{p+1} \dots \beta_{p+q}$ a permutation of $\alpha_{p+1} \dots \alpha_{p+q}$. We therefore get from (22)

$$\begin{aligned} p! q! \Psi(1, 2, \dots, p, p+1, p+2, \dots, p+q) \\ = \left[\sum_{(\beta)} \pm C_{(\beta)} \right] \begin{vmatrix} \psi_{\alpha_1}(1) & \dots & \psi_{\alpha_p}(1) \\ \vdots & & \vdots \\ \psi_{\alpha_1}(p) & \dots & \psi_{\alpha_p}(p) \end{vmatrix} \begin{vmatrix} \psi_{\alpha_{p+1}}(p+1) & \dots & \psi_{\alpha_{p+q}}(p+1) \\ \vdots & & \vdots \\ \psi_{\alpha_{p+1}}(p+q) & \dots & \psi_{\alpha_{p+q}}(p+q) \end{vmatrix} \end{aligned}$$

which means that

$$\begin{aligned} \Psi(1, 2, \dots, p, p+1, p+2 \dots p+q) \\ = A \begin{vmatrix} \psi_{\alpha_1}(1) & \dots & \psi_{\alpha_p}(1) \\ \vdots & & \vdots \\ \psi_{\alpha_1}(p) & \dots & \psi_{\alpha_p}(p) \end{vmatrix} \begin{vmatrix} \psi_{\alpha_{p+1}}(p+1) & \dots & \psi_{\alpha_{p+q}}(p+1) \\ \vdots & & \vdots \\ \psi_{\alpha_{p+1}}(p+q) & \dots & \psi_{\alpha_{p+q}}(p+q) \end{vmatrix} \quad (23) \end{aligned}$$

A being a constant.

If $s < q$, the number $N - s$ of different suffixes α is greater than p . We can by the method just mentioned get some information also in this case, *i.e.*, that Ψ can be expressed as a sum of products of two determinants of orders p and q .

It appears that the condition $s = q$, for which the wave function can be expressed as a single product of two determinants, is usually, and perhaps always, satisfied for the normal state of an atom or ion. For we have the rule, at first stated empirically from the results of the analyses of complex spectra,[†] and later given a theoretical basis by Heisenberg,[‡] that of the different multiplet arising from a set of electrons with given space quantum numbers, the term of greatest multiplicity generally lies deepest and for the deepest terms no exceptions are known.|| But this term is just the one for which the spins of all electrons not in closed pairs are parallel, which is the case $s = q$.

If for homopolar molecules we form an approximate wave function in terms of the unperturbed wave functions of the component atoms after the method of Heitler and London,[¶] the condition $s = q$ does not hold for them, as each homopolar bond essentially involves two electrons, not members of closed pairs, with different spins and *different* wave functions, one from each atom. This can be seen already by considering the normal electronic state of the hydrogen molecule. But another approximation would be to consider each of the binding electrons as in a stationary state in the field of the nuclei and other electrons of *both* atoms, and it might be found that with this approximation, the two electrons have the same wave function, in which case the condition $s = q$ would apply here also.

§ 4. *Application of Approximate Wave Functions to Formula for Total Scattering.*

It is more convenient now to distinguish the different wave functions of a single electron by numerical suffixes, or generally by single Greek letter suffixes. Those in the first determinant in (23) will be written $\psi_1, \psi_2, \dots \psi_p$, and those in the second determinant will be written $\psi_{p+1}, \psi_{p+2}, \dots \psi_{p+q}$. Also we will write $1; p$ as an abbreviation for "the electrons 1 to p "; and $dv_{1;p}$ for

[†] See F. Hund, "Linienspektren," p. 124.

[‡] Heisenberg, 'Z. Physik,' vol. 41, p. 239, especially p. 257.

|| Hund, *op. cit.*

[¶] 'Z. Physik,' vol. 44, p. 455 (1927); London, 'Z. Physik,' vol. 46, p. 455 (1928).

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the volume element of the co-ordinate space of these electrons, and will put

$$\Delta(1; p) = \begin{vmatrix} \psi_1(1) & \dots & \psi_p(1) \\ \vdots & & \vdots \\ \psi_1(p) & \dots & \psi_p(p) \end{vmatrix}, \quad \Delta'(p+1; p+q) = \begin{vmatrix} \psi_{p+1}(p+1) & \dots & \psi_{p+q}(p+1) \\ \vdots & & \vdots \\ \psi_{p+1}(p+q) & \dots & \psi_{p+q}(p+q) \end{vmatrix}, \quad (24)$$

so that the wave function (23) for an atom consisting of q closed pairs, and $p - q$ additional electrons all of the same spin, can be written

$$\psi = A \Delta(1; p) \Delta'(p+1; p+q). \quad (25)$$

If the wave functions $\psi_1 \dots \psi_p$ were different wave functions for a single electron in approximately the same field of force, they would be orthogonal; actually they are wave functions of a single electron in a field of force which is slightly different for different electrons, but it will be assumed for the present that they are exactly orthogonal, and departures from this will be considered later. In the case considered each of the wave functions in the second determinant is the same function of its arguments as a wave function in the first determinant, but in this section it will not be necessary to make use of this property.

In working with wave functions which involve such determinants, it is convenient to use the following notation. For a determinant of order p we write

$$\begin{aligned} \varepsilon_{\alpha\beta\gamma\dots\pi} &= 0 \quad \text{unless } \alpha\beta\gamma\dots\pi \text{ are all different,} \\ &= 1 \quad \text{if } \alpha\beta\gamma\dots\pi \text{ is an even permutation of } 1, 2, 3, \dots, p, \\ &= -1 \quad \text{if } \alpha\beta\gamma\dots\pi \text{ is an odd permutation of } 1, 2, 3, \dots, p, \\ \delta_{\alpha\beta} &= 1 \quad \text{if } \alpha = \beta, \\ &= 0 \quad \text{if } \alpha \neq \beta. \end{aligned}$$

Further it is convenient to adopt the convention that in a product or in a single term a repeated Greek letter suffix indicates summation over all relevant values of that suffix (this notation is suggested by the "summation convention" of the calculus of tensors†). The determinant $\Delta(1; p)$ can then be written

$$\Delta(1; p) = \varepsilon_{\alpha\beta\gamma\dots\pi} \psi_\alpha(1) \psi_\beta(2) \dots \psi_\pi(p), \quad (26)$$

the summations being over the values 1 to p for each of the repeated suffixes.

† Eddington, 'Mathematical Theory of Relativity,' p. 50.

The following properties of the coefficients $\varepsilon_{a\beta\gamma\dots\pi}$ are required

$$\left. \begin{aligned} \varepsilon_{a\beta\gamma\dots\pi} \varepsilon_{a\beta\gamma\dots\pi} &= p! \\ \varepsilon_{a\beta\gamma\dots\pi} \varepsilon_{a'\beta\gamma\dots\pi} &= (p-1)! \delta_{aa'} \\ \varepsilon_{a\beta\gamma\dots\pi} \varepsilon_{a'\beta'\gamma\dots\pi} &= (p-2)! (\delta_{aa'} \delta_{\beta\beta'} - \delta_{a\beta'} \delta_{a'\beta}) \end{aligned} \right\}. \quad (27)$$

Since the wave functions $\psi_a \dots \psi_\pi$ are taken to be orthogonal, we have

$$\int \psi_a^*(j) \psi_\beta(j) dv_j = \delta_{a\beta} \quad (28)$$

where $dv_j = dx_j dy_j dz_j$; and if F is a function of the co-ordinates of any one electron, we will write

$$\int \psi_a^*(j) F(j) \psi_\beta(j) dv_j = F_{a\beta}, \quad (29)$$

and will write $F_{a\beta}^*$ for the conjugate of $F_{a\beta}$, it is the $\beta\alpha$ component of $[F(j)]^*$.

From (26) to (29) it follows that

$$\int |\Delta(1; p)|^2 dv_{1; p} = p! \quad (30)$$

$$\int |\Delta(1; p)|^2 F(j) dv_{1; p} = (p-1)! F_{aa} \quad (1 \leq j \leq p), \quad (31)$$

$$\begin{aligned} \int |\Delta(1; p)|^2 F(j) [F(k)]^* dv_{1; p} &= (p-2)! [F_{aa} F_{\beta\beta}^* - F_{a\beta} F_{a\beta}^*] \\ &\quad (j \neq k; 1 \leq j \leq p, 1 \leq k \leq p). \end{aligned} \quad (32)$$

The first of these results gives directly the normalisation of the wave function (25), viz.

$$A^2 p! q! = 1. \quad (33)$$

The formula (14) for the intensity of total scattering can be written

$$R = p + q + \sum_{j, k=1}^{p+q} \int |\Psi_n|^2 e^{i\mathbf{k}(\mathbf{r}_j - \mathbf{r}_k)} dv_{1; p+q}, \quad (34)$$

where Σ' denotes that the terms $j = k$ are omitted from the sum. There are two main types of terms in the sum according as the electrons j, k occur as arguments of wave functions in the same determinant or different determinants in (25) (i.e., according as these electrons have the same or different spin); in the former case the integral reduces to one of the type (32) and in the second to a product of two of type (31). We will write

$$\int \psi_a^*(j) \exp(i\mathbf{k}\mathbf{r}_j) \psi_\beta(j) dv_j = f_{a\beta},$$

(cf. (17)), and use suffixes without and with a dash to refer to wave functions in the first and second of the determinants (24) respectively. Then using (31), (32) the value of R found from (34) to be

$$R = p + q + (f_{\alpha\alpha} + f_{\alpha'\alpha'}) (f_{\beta\beta}^* + f_{\beta'\beta'}^*) - f_{\alpha\beta} f_{\alpha\beta}^* - f_{\alpha'\beta'} f_{\alpha'\beta'}^*. \quad (35)$$

We will require the result that the value of R given by (35) is invariant for certain orthogonal transformations of the wave functions ψ occurring in either determinant.

Suppose the coefficients $a_{\xi\alpha}$ define an orthogonal transformation of $\psi_1 \dots \psi_p$

$$\phi_\xi = a_{\xi\alpha} \psi_\alpha. \quad (36)$$

We are taking the ψ 's as orthogonal, and the condition that the ϕ 's should be orthogonal is therefore

$$a_{\xi\alpha} a_{\eta\alpha}^* = \delta_{\xi\eta}$$

whence also

$$a_{\xi\alpha} a_{\xi\beta}^* = \delta_{\alpha\beta}. \quad (37)$$

Corresponding to (29) we define matrix elements F' involving the wave functions ϕ by

$$F'_{\xi\eta} = \int \phi_\xi^*(j) F(j) \phi_\eta(j) dv_j,$$

and from (36), we find

$$F'_{\xi\eta} = a_{\xi\alpha}^* a_{\eta\beta} F_{\alpha\beta},$$

so by (37)

$$\begin{aligned} F'_{\xi\xi} &= a_{\xi\alpha}^* a_{\xi\beta} F_{\alpha\beta} = \delta_{\alpha\beta} F_{\alpha\beta} = F_{\alpha\alpha} \\ F'_{\xi\eta} F'_{\xi\eta}^* &= a_{\xi\alpha}^* a_{\eta\beta} F_{\alpha\beta} a_{\xi\gamma}^* a_{\eta\epsilon}^* F_{\gamma\epsilon}^* \\ &= \delta_{\alpha\gamma} \delta_{\beta\epsilon} F_{\alpha\beta} F_{\gamma\epsilon}^* = F_{\alpha\beta} F_{\alpha\beta}^*, \end{aligned}$$

so that each term in (35) is invariant for an orthogonal transformation of the ψ 's occurring in either determinant separately.

It may be emphasised that in (35) the sums indicated by the repeated suffixes are to be taken over the *wave functions* occurring in one or other determinant, not over the separate electrons. Indeed, the contributions to R expressed by the sum in (34) are essentially from *pairs* of electrons, not from single electrons, and the contribution from all pairs of electrons occurring as arguments of the wave functions in a single determinant are the same, and so are the contributions from all pairs of electrons which occur as arguments of the wave functions in different determinants. This arises from the form (25) used for the wave function of the whole system, in which we cannot associate any particular electron with any particular wave function, and conforms to

the principles of the quantum-mechanical treatment of the many-body problem, in which the interchange of the electrons plays an essential part.

Nevertheless it is convenient as a conventional manner of speaking to describe the behaviour of an atom in a way which does appear to assign each electron to a single wave function, as when we speak of an atom having 2 K-electrons, 6 L-electrons, etc. We can do this by relating electrons to wave functions by a single term in the expansion of the determinant, say by the product of the elements of the principal diagonal.

Then indicating these electrons by ordinary letter suffixes, and retaining the summation sign for them, (35) becomes†

$$R_1 = p + q + \left| \sum_{j=1}^{p+q} f_{jj} \right|^2 - \sum_{j=1}^{p+q} |f_{jj}|^2 - \left[\sum'_{j, k=1}^p + \sum'_{j, k=p+1}^{p+q} \right] |f_{jk}|^2. \quad (38)$$

This formulæ gives the theoretical value of R_1 the ratio of the total intensity of scattering by a many electron atom to the classical intensity of scattering by a free electron; to the approximation explained in §2. If R_F is the value of R for scattering by the same number $p + q$ of free electrons, then to the same approximation, $R_F = p + q$. $R - R_F$ may be called the “excess scattering” due to the space distribution of the electrons, and $(R/R_F) - 1$ the “excess scattering per electron.” It seems probable that R/R_F or $(R/R_F) - 1$ is the most suitable quantity in terms of which to make comparison with experiment, as the approximations made seem likely to have the same kind of effect on R and on R_F .

§ 5. *The Relation between the Scattering by a Many-electron Atom and that by a One-electron Atom.*

If we consider the j th electron alone, f_{jj} is the amplitude and $|f_{jj}|^2$ the intensity of the coherent scattering (*cf.* (8)) and since $R = 1$ for one electron (*cf.* (13)), $1 - |f_{jj}|^2$ is the intensity of the incoherent scattering.‡ If we tried to treat the scattering by a many-electron atom by adding the scattering by a number of independent single electrons, we would add the amplitudes of

† We have $f_{\alpha\alpha} + f_{\alpha'\alpha'} = f_{\beta\beta} + f_{\beta'\beta'} = \sum_j f_{jj}$. The term $\sum |f_{jj}|^2$ arises from the terms $\alpha = \beta$ and $\alpha' = \beta'$ in $f_{\alpha\beta} f_{\alpha'\beta'}^*$ and $f_{\alpha'\beta'} f_{\alpha\beta}^*$, the terms $\sum' |f_{jk}|^2$ arise from the terms $\alpha \neq \beta$ and $\alpha' \neq \beta'$ in these product-sums.

‡ These amplitudes and intensities are in terms of the amplitude and intensity of classical scattering by a free electron.

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the coherent waves scattered by the separate electrons, and the intensities of the incoherent waves, and obtain

$$R = \underbrace{\left| \sum_{j=1}^{p+q} f_{jj} \right|^2}_{\text{coherent}} + \underbrace{p + q - \sum_{j=1}^{p+q} |f_{jj}|^2}_{\text{incoherent.}} \quad (39)$$

This result is also obtained if the wave function of the many electron is taken as a single product of the separate wave function of the single electrons. The more exact formula (38) differs from this by including some negative terms involving all pairs of electrons with the same spin (or rather all pairs of wave functions in each determinant in (25)).

These terms arise because the incoherent radiation consists of components corresponding to different possible transitions of the atom from its initial state. When we express the many-electron problem as the sum of a number of one-electron problems, we allow each electron independently to have all the possible transitions of the one-electron problem, whereas actually in a many-electron atom some of these transitions of one electron cannot actually occur, as the final state would violate Pauli's exclusion principle. Thus some components of the incoherent scattered radiation which would be possible for a number of independent single electrons are missing from the radiation scattered from a many-electron atom, and it appears also that the intensities of other components may be altered.

This aspect of the negative terms in (38) which involve two wave functions has already been pointed out in § 2 in considering the simple case of He.

§ 6. *Approximate Wave Functions for the Single Electrons, Evaluation of Total Scattering in a Particular Case and Comparison with Experiment.*

We can make an approximation to the separate wave functions ψ by considering each as the wave function of an electron in a central non-Coulomb field of force (not necessarily the same for each electron). Taking spherical polar co-ordinates, origin at the nucleus, we have for the wave function of quantum numbers n, l, m

$$\psi = \chi_{n,l}(r) P_l^m(\cos \theta) e^{im\phi} \quad (40)$$

where P_l^m is an associated Legendre polynomial.

No two wave functions in one determinant are the same, *i.e.*, have all three quantum numbers n, l, m the same. If each of the $2(2l+1)$ wave functions of the same n, l but different m occurs in each determinant, we call the n, l group (conventionally, of electrons) "complete." It is convenient to have a

name for the $(2l + 1)$ wave functions in one determinant without those in the other (*i.e.*, for the $(2l + 1)$ electrons of the same n , l and same spin without those of the opposite spin), this will be called a "complete half group."

For a complete half-group, a change of the axis of the spherical harmonics corresponds to an orthogonal transformation of the ψ 's of this half-group† (such a transformation is in general impossible unless the half-group is complete), and since R is invariant for an orthogonal transformation of the ψ 's in either determinant, it follows that for an atom consisting of a number of complete half-groups the intensity of scattering in a given direction is independent of the orientation of the axis of the atom. This result would be expected as by a property of the spherical harmonics the charge distribution $\Sigma |\psi|^2$ is spherically symmetrical for a complete half-group, and so for an atom consisting of complete half-groups; but it does not hold in general if the wave function for the many-electron atom is taken as a single product of the wave functions for the different electrons. Its deduction here depends on the use of the wave function (25).

Since this result holds for atoms consisting of complete half groups, not only of complete groups, it applies to monatomic Na, K, ... vapours as well as to the inert gases and Hg vapour.

If we take the direction of $\mathbf{s}' - \mathbf{s}$ as the direction $\theta = 0$ and choose the axis of the spherical harmonics in the wave functions in this direction also, as we may do if the atom consists of complete half-groups, and write $2\mathfrak{S}$ for the angle of scattering so that $|\mathbf{s}' - \mathbf{s}| = 2 \sin \mathfrak{S}$, and also write $\mu = \cos \theta$, $\sigma = 4\pi \sin \mathfrak{S}/\lambda$, then

$$\kappa \mathbf{r} = \sigma \mu r,$$

so that

$$f_{jk} = \int \psi_j^* \psi_k e^{i\sigma \mu r} r^2 dr d\mu d\phi. \quad (41)$$

For any particular wave functions ψ_j , ψ_k the integrations in ϕ , μ can be carried out exactly, leaving only that in r to be evaluated numerically.‡ It is clear from (41) that for different wave-lengths λ and angles of scattering $2\mathfrak{S}$, f_{jk} and so R should be a function of $\sin \mathfrak{S}/\lambda$ only.

† The product of two spherical harmonics of different order vanishes on integration over a sphere, so any surface spherical harmonic can be expanded in surface spherical harmonics of the same order with another axis. The wave functions forming a half-complete group involve the same $\chi(r)$ and $(2l + 1)$ independent surface spherical harmonics of degree l ; thus the wave functions for a given n , l and one axis can be found from those of a half-complete group with any other axis by an orthogonal transformation.

‡ For a complete half-group $\Sigma |\psi_j|^2$ is spherically symmetrical, so Σf_{jj} can be calculated as if $|\psi_j|^2$ is spherically symmetrical for each electron, but $\Sigma |f_{jj}|^2$ cannot be so calculated.

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Since the wave functions involve the azimuth ϕ only through $e^{im\phi}$ the integration with respect to ϕ makes all f_{jk} zero except those for which ψ_j, ψ_k have the same m . Also the quantities f_{jk} ($j \neq k$) are likely to be most important when the electrons j and k have the same principal quantum number n , as then the principal maxima of ψ_j, ψ_k lie at approximately the same radius. So the chief terms involving two different wave functions are those for which n, m are the same and l different. Trial with the wave functions for a Coulomb field shows that the terms arising from wave functions with different principal quantum numbers are unlikely to contribute as much as 2 per cent. to R .

Values of $r\chi_{n,l}$ for any particular atom can be obtained by a method developed by one of us, of which the general idea is the solution of the wave equation of each electron in the field of the nucleus and of the charge distribution of the other electrons. The wave functions for which l and m are not both the same are orthogonal on account of the spherical harmonic factors, but two wave functions of the same l, m but different n are not exactly orthogonal as the functions $\chi_{n,l}$ for them are solutions of the wave equation in different central fields. This would bring in some additional terms both in the normalisation equation (33) and in the integrals occurring in the formula (34) for R . Estimation of these additional terms indicates that their effect on the calculated value of I is likely to be always small, probably less than 2 per cent.

In the calculated values of R which will be compared with experiment, these terms and the terms $|f_{jk}|^2$ where j and k refer to electrons with different principal quantum number n , will be omitted. It is possible that the total contribution to R from the terms so neglected would amount to 5 per cent., but it is probably much smaller.

Some numerical data for argon, calculated in this way, are given in the table, in such a form as to show the contributions to the total scattering from the various terms in (38) and from the various electron groups. It will be seen that in the range of values of $\sin \theta/\lambda$ covered by the calculations (and by the observations with which they will shortly be compared) the contribution from the M electrons to the excess scattering is very small; but they contribute to the term $p + q$ in (38), and so decrease the importance of the terms which depend on the atomic structure relative to the terms which would remain if all the electrons were free. The contribution from the term $|f_{jk}|^2$ ($j \neq k$), which arises from the use of the wave function (25) instead of the simple product of the wave functions of the single electrons, is of some interest. Its maximum value is about 1.4, and is probably about the same for any group of eight electrons consisting of two complete n, l groups with the same

n and $l = 0$ and 1. Its importance relative to the total scattering clearly decreases with the total number of electrons, and would be greater for neon than for argon.

Table.—Contributions to Total Scattering by Argon.

$\sin \vartheta/\lambda$.		0.522.	0.783.	1.044.	1.566.	2.088.	2.610.
Σf_{jj} j	2 K	1.96	1.90	1.83	1.65	1.44	1.20
	8 L	5.52	3.60	2.04	0.46	0.02	-0.02
	8 M	-0.11	0.16	0.18	0.04	0.00	0.00
	Total	7.37	5.66	4.05	2.15	1.46	1.20
$(\Sigma f_{jj})^2$ j		54.2	32.0	16.4	4.6	2.1	1.4
$\Sigma (f_{jj}^2)$ j	2 K	1.91	1.81	1.68	1.36	1.03	0.75
	8 L	3.95	1.97	1.03	0.39	0.15	0.04
	8 M	0.05	0.00	0.00	0.00	0.00	0.00
	Total	5.91	3.78	2.71	1.75	1.18	0.79
$\Sigma'' (f_{jk}^2)$ jk		8 L	1.30	0.90	0.17	0.01	0.00
R/R _F		3.61	2.50	1.71	1.15	1.05	1.04

$$R = 18 + I \left[\left(\Sigma_j f_{jj} \right)^2 - \Sigma_j (f_{jj}^2) - \Sigma_{jk}'' (f_{jk}^2) \right], R_F = 18.$$

Σ''_{jk} = sum over all pairs of electrons with same spin and $j \neq k$.

For a homopolar molecule the complete wave function is more complicated than a single product of two determinants, as has already been mentioned (see end of §3). Also the charge distribution of the electrons concerned in a homopolar band becomes concentrated to some extent between the atoms,† so may contribute appreciably to the excess scattering at angles of scattering at which for an atom the contribution from these electrons is negligible. There is also the possibility of an appreciable effect from the coupling of electronic and nuclear motions.

On account of the uncertainty of the effect of the binding electrons on the scattering by diatomic molecules, it is most satisfactory to compare theory and experiment for a monatomic gas or vapour, and moreover for one not too heavy, since for the heavier atoms the proportion of incoherent radiation is small, and it is known that, with the approximation to the wave functions ψ here

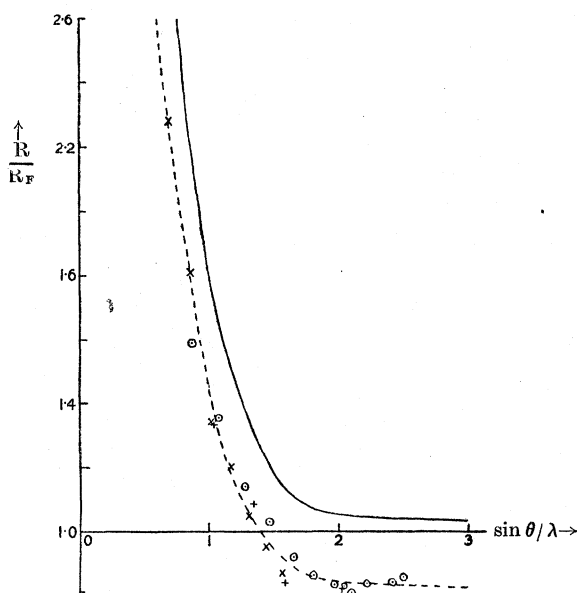
† See London, 'Z. Physik,' vol. 46, p. 455, fig. 3 (1928).

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used, the theory leads to results in close agreement with experiment for the coherent scattering.†

The most suitable case for comparison of theory and experiment seems to be that of argon, for which Barrett‡ has recently obtained experimental results, and such a comparison is made in the figure. A strict comparison is not



Curves showing Theoretical and Observed Variation of R/R_F with $\sin \theta/\lambda$ for total scattering of X-rays by Argon.

Observed values : \odot , $\lambda = 0.39$. $+$, $\lambda = 0.48$. \times , $\lambda = 0.49$ Å.U.

possible, as for the short wave-lengths used by Barrett "relativity effects" are appreciable, whereas they are neglected in the derivation of the theoretical formula. We can try to allow for this by comparing theoretical and observed values of the ratio R/R_F , and such a comparison is made in the figure.

The values of R for the experimental points were taken from the figures in Barrett's paper, R_F was calculated from Dirac's formula (formula (1) and curves Q of Barrett's paper) and for different wave-lengths R/R_F is plotted

† James, Waller and Hartree, *loc. cit.*

‡ Barrett, *loc. cit.* Barrett mentions that He, the other monatomic gas for which he has made experiments, may have contained impurities; the probable impurities contain so many more electrons per molecule than He that a small amount of impurity would give quite a large excess scattering. The argon is mentioned as 95 per cent. pure, but the probable impurities have only a small effect on the excess scattering (5 per cent. Ne might make the observed value 3 per cent. low).

against $\sin \vartheta/\lambda$. The theoretical values of R have been calculated from formula (38), and for R_F the classical value 18 has been taken (*cf.* Table) corresponding to the fact that the approximations made in deriving (38) lead to classical scattering when applied to a free electron. As has been mentioned, it is probable that the effects of these approximations on R and on R_F should be of the same kind so that the effect on R/R_F should not be so large as the effect on either separately.

The experimental results agree closely with the theoretical result that R/R_F should be a function of $\sin \vartheta/\lambda$ only. Whether this should still be true when relativity effects are included is not certain; in the experimental results there is a suggestion of a small consistent difference between different wave-lengths at the larger angles of scattering which might be such a relativity effect.

Barrett's results give relative values of R/R_F for different angles of scattering and for different gases, but not absolute values, so it may be necessary to multiply them by a constant factor throughout. The broken curve in fig. 1 is the theoretical curve with all its ordinates multiplied by 0.80, and it will be seen that it agrees very well with the points plotted from Barrett's observed values; this suggests that these values should be multiplied by a factor about $1/0.80 = 1.25$ to convert them to absolute values. This, however, cannot be considered as certain, as the suggested correction is no greater than the relativity effect on R_F at large angles, and it is only an assumption, though it seems a reasonable one, that R/R_F is less affected by relativity effects than R_F itself.

The rapid increase of R/R_F with decreasing $\sin \vartheta/\lambda$ beginning about $\sin \vartheta/\lambda = 1.8$ is due to contributions from the L electrons, and it is satisfactory that theory and experiment agree about the place at which this increase starts.

This comparison of experiment with theory suggests firstly the desirability of making experiments for monatomic gases with longer wave-lengths, for which the uncertain relativity effects for the many electron atom would be smaller, and for which also the excess scattering would be larger at a given angle of scattering; and secondly the value of absolute measurements if the experimental difficulties could be overcome.

In conclusion one of us (D.R.H.) wishes to express his thanks to the International Education Board for a Fellowship during the tenure of which this work was done, and to Prof. Bohr for the privilege of working at the Institut for teoretisk Fysik at Copenhagen.
