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The Probability of *KL* Ionization and X-Ray Satellites

ROBERT D. RICHTMYER, *Department of Physics, Massachusetts Institute of Technology*

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A theory of the multiple ionizations produced by a fast cathode electron in the target of an x-ray tube is developed, based on the Born approximation of collision theory. The effective cross section for $1s2s$ ionization of potassium by an incident electron having five times the energy required for K-ionization or $1s$-ionization of potassium, and the distribution of energy and of angular momentum among the three electrons after collision is shown in detail. The probability of $1s2p$ ionization is also estimated roughly by the same method, and the two taken together are shown to be roughly in agreement with the experimental value of the integrated satellite intensity for $K\alpha$ of potassium. The predicted variation of the relative intensity with atomic number is also shown to be in rough agreement with experiment.

THE weak "satellite" lines of x-ray spectra require for their explanation transitions between doubly ionized states of the atom, and at the present time there are two theories concerning the nature of these transitions. The older theory[1] assumes that both the ionizations occur in interior shells of electrons, and that in the transition only one electron of the atom changes its quantum numbers, or "jumps." The absence of the second electron modifies the energies of, and increases the multiplicities of the initial and final states in such a way that several satellites should be found on the short wave-length side of the diagram line produced by the corresponding transition between singly ionized states. The other theory[2] assumes that the initial doubly ionized state is of the somewhat more probable type in which one of the ionizations occurs in an inner electron shell, and the other in a shell not far below the outermost filled shell of the atom; and that in the transition two electrons jump simultaneously into the two vacant places. Since in this case the coupling between the electrons is not enough greatly to alter the energy levels, the frequency of the satellite should be equal to the sum of the frequencies of the two transitions taken separately.

It seems evident that according to contemporary quantum theory both these proposed mechanisms must produce satellite lines, although some or all of the lines produced by either may be far too weak to observe. The wave-lengths as predicted by either theory[3] agree roughly with experiment, but it is not possible to predict wave-lengths with sufficient accuracy to decide between the two theories by this means alone. Ramberg[4] and Bloch[5] have estimated the intensities as predicted by the double jump theory, and it seems likely that some, at least,

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[1] M. J. Druyvesteyn, Zeits. f. Physik **43**, 707 (1927).

[2] F. K. Richtmyer, J. Frank. Inst. **208**, 325 (1929).

[3] See Druyvesteyn, reference 1, H. C. Wolfe, Phys. Rev. **43**, 221 (1933), and Ramberg and Kennard, Phys. Rev. **46**, 1040 (1934) for the single jump theory, and Richtmyer reference 2 for the double-jump theory.

[4] E. Ramberg, Phys. Rev. **45**, 389 (1934).

[5] F. Bloch, Phys. Rev. **48**, 187 (1935).

of the lines are produced by double jumps. In this paper I consider intensities as predicted by the single jump theory. In 1927 Druyvesteyn[1] gave a rather crude semiclassical treatment of this problem, but since then nothing has been done with it.

The numbers of singly- and multiply-ionized atoms in the target are dependent upon the effective collision cross sections for single and multiple ionizations of an atom by a fast cathode electron, and for computing these cross sections we use the Born approximation of collision theory. Call the momentum vector (in atomic units) of the incident cathode electron $\mathbf{k}_0$. Then the cross section for collisions in which the atom is excited from the ground state to the nth state is

$$\Phi_n = \frac{k_n}{4\pi^2 k_0}\int \left| \int V_{0n}(r_0) e^{i(\mathbf{k}_0-\mathbf{k}_n)\cdot\mathbf{r}_0} d\tau_0 \right|^2 d\omega(\mathbf{k}_n) \qquad (1)$$

with

$$V_{0n}(r_0) = \int \Psi_n^*(r_j)\, U(r_0, r_j) \Psi_0(r_j) d\tau_j. \qquad (2)$$

$\mathbf{k}_n$ is the momentum vector of the cathode electron after the atom has been excited; its magnitude is given by $k_n = (k_0^2 - 2E_n)^{\frac{1}{2}}$ where E_n is the energy of excitation of the atom, and its direction is the variable of integration $\omega(\mathbf{k}_n)$ in (1). r_0 refers to the three coordinates of the cathode electron; r_j (in which $j=1, 2, 3, \cdots, N$) refers to the coordinates of the N atomic electrons; $d\tau_0$ means integration over all space with respect to the coordinates of the cathode electron; and $d\tau_j$ means N-fold integration over all space with respect to the coordinates of the atomic electrons. The capital psi's are the complete atomic wave functions for the ground state and the nth excited state of the atom. $U(r_0, r_j)$ is the energy of interaction of the cathode electron with the atom. The outside integration in (1) is to be extended over the entire solid angle; that is, over all directions of scattering.

Let the excited state be a doubly ionized state in which a K electron and an L_{I} electron have been removed to "hyperbolic orbits" denoted by the quantum numbers k_1, l_1, m_1 and k_2, l_2, m_2, and represented by wave functions $\psi_{k_1 l_1 m_1}$ and $\psi_{k_2 l_2 m_2}$. We use N-rowed determinants of one-electron functions for Ψ_0 and Ψ_n, and if we retain only the first order of small quantities, we get

$$\begin{aligned} V_{0n} = \int\int \{ & \psi^*{}_{k_1 l_1 m_1}(r_1) \psi^*{}_{k_2 l_2 m_2}(r_2) \\ & - \psi^*{}_{k_1 l_1 m_1}(r_2) \psi^*{}_{k_2 l_2 m_2}(r_1) \} \\ & \cdot (1/r_{01} + 1/r_{02}) \varphi_1(r_1) \varphi_2(r_2) d\tau_1 d\tau_2 \end{aligned} \qquad (3)$$

in which φ_1 and φ_2 are the K and L wave functions, respectively, in the normal atom, $r_{01} = |\mathbf{r}_0 - \mathbf{r}_1|$, and $r_{02} = |\mathbf{r}_0 - \mathbf{r}_2|$. It is to be noted that the φ's are not quite orthogonal to the ψ's, because the removal of each electron from the atom alters the field in which the other one moves. However, φ_1 will be much more nearly orthogonal to the ψ's than will φ_2, and so we shall drop terms in $1/r_{02}$.

This V_{0n} is to be substituted into expression (1). We introduce the quantity $q = |\mathbf{k}_0 - \mathbf{k}_n|$, which is the magnitude of the change of momentum experienced by the cathode electron. We write the wave functions explicitly in terms of their angular and radial parts as

$$\begin{aligned} \psi_{klm} &= Y_l^m(\theta, \varphi) S_{kl}(r); \\ \varphi_1 = S_1(r)/(4\pi)^{\frac{1}{2}}; &\quad \varphi_2 = S_2(r)/(4\pi)^{\frac{1}{2}} \end{aligned} \qquad (4)$$

in which Y_l^m is a normalized spherical surface harmonic, the S's are solutions of Hartree's equations, and the continuous state functions $S_{kl}(r)$ are normalized so as to represent one particle per unit range of the momentum k. We then expand everything in sight in terms of spherical harmonics and Bessel functions, and boil down the result until we obtain

$$\Phi_n = \frac{16\pi^3}{k_0^2} \int_{k_0-k_n}^{k_0+k_n} \{ O_{k_2} I_{k_1 0}(q) - O_{k_1} I_{k_2 0}(q) \}^2 \frac{dq}{q^4} \qquad \text{for } l_1 = 0,\ l_2 = 0 \qquad (5a)$$

$$\Phi_n = \frac{32\pi^3}{k_0^2} (l_1 + \tfrac{1}{2}) O_{k_2}^2 \int_{k_0-k_n}^{k_0+k_n} [I_{k_1 l_1}(q)]^2 \frac{dq}{q^4} \qquad \text{for } l_1 \neq 0,\ l_2 = 0 \qquad (5b)$$

$$\Phi_n = 0 \qquad \text{for } l_2 \neq 0. \qquad (5c)$$

In these equations, O_k and $I_{kl}(q)$ have the following meanings:

$$O_k = \int \psi^*_{k00}\varphi_2(2)d\tau_2 = \int_0^\infty S_{k0}(r)S_2(r)r^2dr, \quad (6)$$

$$I_{kl}(q) = \frac{1}{(4\pi)^{\frac{1}{2}}}\int_0^\infty S_{kl}(r)S_1(r)J_{l+\frac{1}{2}}(qr)r^{\frac{3}{2}}dr. \quad (7)$$

Eq. (5c) shows that to our degree of approximation the L_{I} electron can be expelled only to states of zero angular momentum. The difference in appearance between (5a) and (5b) is due to an exchange effect between the two expelled electrons, which can take place only if the K electron is also expelled to a state of zero angular momentum. Exchange between the cathode electron and the atomic electrons is less important and has been neglected entirely.

In order, finally, to obtain the effective cross section for double ionization of the type in question (e.g., KL_{I}), the partial cross section as given by (5) must be integrated over all possible final states of the atom, that is over all possible hyperbolic orbits of the two expelled electrons. This requires a summation over l_1, and integrations in k_1 and k_2. The energetically possible final states will be given by the relations

$$\begin{gathered} k_1^2/2+k_2^2/2 \leqslant k_0^2/2 - W_K - W_L, \\ k_1 \geqslant 0, \quad k_2 \geqslant 0. \end{gathered} \quad (8)$$

These relations are approximate in that they assume that none of the three electrons involved stops in an optical orbit, but that all of them end up in states of positive energy. The relations require an integration of (5) over a 90° circle-sector in the k_1-k_2 plane. In the special case of $l_1=0$ only half of this sector is to be used, because of the symmetry properties of the wave functions. Otherwise the final states would be counted twice.

A completely numerical evaluation of the double-ionization cross section by this method would seem to be out of the question. One would have to obtain numerical solutions $S_{kl}(r)$ of Hartree's equation, then obtain the integrals O_k and $I_{kl}(q)$ by numerical integration, and then carry out the summation in l_1 and the integrations in q, k_1, and k_2 also numerically. One can approximate by taking the wave functions to be hydrogen-like functions, either corrected for external and internal screening, or uncorrected. Even then the amount of numerical work would be prohibitive, for one must still carry out the summation and the last three integrations numerically. We can further approximate, however, by replacing the product S_1S_{kl} by a function of simpler analytic form, but which is approximately equal to this product. Such a function must vary as r^l for small r, rise to a maximum for larger r, then become negative and have a much less pronounced minimum for still larger r, and after that be practically zero. Only the first maximum and first minimum of S_{kl} need be represented, because of the exponentially decreasing behavior of S_1. A function of the desired form, and which enables us to carry out the integration in q analytically is

$$S_1S_{kl} = (4\pi)^{\frac{1}{2}}(ar^l - br^{l+2})e^{-p^2r^2}. \quad (9)$$

The adjustable constants a, b, and p must be determined as functions of k_1 and l_1. For this purpose we suppose that the actual wave functions S_{kl} are solutions of the Schrödinger equation for a field of the form

$$V(r) = \begin{cases} V_0 - Z/r & \text{for } r \leqslant r_0 \; (=Z/V_0) \\ 0 & \text{for } r \geqslant r_0. \end{cases} \quad (10)$$

The solutions are hydrogen-like for small r, and essentially Bessel functions for larger r. The smooth joining at $r=r_0$ was carried out for energies greater than V_0 by means of the Wentzel-Kramers-Brillouin method. For small k the energies are less than V_0 and thus fall in a region which would be occupied by discrete levels if the Coulomb part of the field (10) were carried on out to infinity. For this case the smooth joining was carried out by means of some tables kindly supplied me by Professors Morse and Allis and which they had calculated in connection with their theory of the Ramsauer effect. V_0 and Z of the field (10) are chosen to make this field fit the actual atomic field in the neighborhood of the K shell,[6] and the K wave function S_1 is taken to be hydrogen-like with this same value of Z. Lastly a, b, and p are chosen so as to make the function (9) as nearly as possible equal to the product S_1S_{kl}. The method by which this was actually done is

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[6] For potassium, $Z=18.5$, $V_0=37$, $r_0=0.50$; atomic units.

largely empirical, and since it is of no theoretical interest, it will not be described here.[7] The result is a set of graphs of a, b, and p as functions of k for various values of l. I believe that the fit is fully as good as the use of the Born approximation warrants. We now substitute (9) into (7), and put the resulting expression for $I_{kl}(q)$ into (5a) and (5b). In place of the integration variable q we introduce a new one given by $x=q^2/2p^2$, and we obtain

$$\Phi_n=\frac{\pi^3}{2k_0^2}\int_{u_1}^{u_2} e^{-x}\frac{[O_{k_2}(A_{k_10}+xB_{k_10})-O_{k_1}(A_{k_20}+xB_{k_20})]^2}{x^2}dx \quad \text{for } l_1=0, \tag{11a}$$

$$\Phi_n=\frac{\pi^3(l_1+\frac{1}{2})}{k_0^2 2^{l_1}}\int_{u_1}^{u_2} e^{-x}x^{l_1-2}[O_{k_2}(A_{k_1l_1}+xB_{k_1l_1})]^2dx \quad \text{for } l_1\neq 0, \tag{11b}$$

in which

$$A_{kl}=\frac{a}{p^{l+4}}+\frac{b(l+(3/2))}{p^{l+6}}; \quad B_{kl}=\frac{b}{2p^{l+6}}. \tag{12}$$

The integrals of (11) can be evaluated in terms of the exponential function and the exponential integral. The integration limits u_1 and u_2 depend on both k_1 and k_2 and are given by

$$u_1=\frac{(k_0-k_n)^2}{2p^2}, \quad u_2=\frac{(k_0+k_n)^2}{2p^2}. \tag{13}$$

k_n, the final momentum of the cathode electron, is given by conservation of energy as

$$k_n=(k_0^2-k_1^2-k_2^2-2W_K-2W_L)^{\frac{1}{2}} \tag{14}$$

in which W_K and W_L are the K and L ionization energies, respectively.

The calculation of the integrals O_k occurring in Eqs. (5) is by far the most important part of the work when the *relative* probability of double ionization is desired, since it is chiefly this factor which is responsible for the difference between the formulas for single ionization and for double ionization. In fact it can be shown that the relative probability can be roughly obtained from this quantity alone by integrating O_k^2 from $k=0$ to $k=$infinity. The other factors of (5) serve merely to give a variable weight to the various parts of this integration. O_k is to be contrasted with the integral $I_{kl}(q)$ in that it involves the L wave function of the atom while the latter involves the K wave function. For an actual atom the L wave function differs much more from a hydrogen-like wave function than does the K wave function. This means that although we may use hydrogen-like wave functions in connection with $I_{kl}(q)$, we cannot do so with O_k. The result of doing so depends in so sensitive a way on the effective nuclear charge and screening constant of the hydrogen-like functions that it seems best to use Hartree wave functions even in an approximate theory. The functions S_{k0} and S_2 of Eq. (6) were obtained by numerical solution of Hartree's equation, and then the integral O_k was obtained by numerical integration. This was carried out for the case of KL_{I} ionization of potassium. S_2 is just the $2s$ wave function as tabulated by Hartree, and the functions S_{k0} are positive-energy solutions of Hartree's equation for a potassium atom which has been ionized in the K and L_{I} shells. The results were checked by means of the identity

$$\int_0^\infty S_{k0}S_2dr=\frac{1}{W_{k0}-W_0}\int_0^\infty S_{k0}\delta VS_2dr \tag{15}$$

in which δV is the difference of the potential

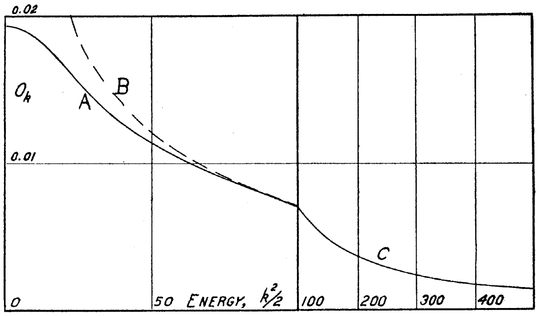

FIG. 1. The integral O_k for potassium. Curve A, computed by means of Hartree wave functions; curves B and C, computed by means of screened hydrogen-like wave functions. The energy is given in atomic units.

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[7] It is described in complete detail in the writer's M.I.T. Doctor's thesis, 1935.

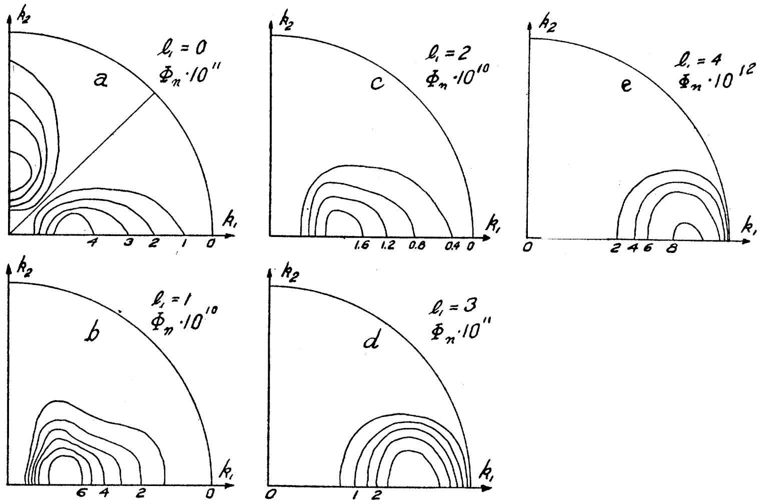

FIG. 2. Altitude charts of the partial cross section Φ_n, as a function of k_1 and k_2 for various values of l_1. Φ_n is zero along the k_2 axis and the circumference of the sector in charts *b*, *c*, *d*, and *e*, and along the 45° line and the circumference in chart *a*. Along the various curves it has the value indicated at the bottoms of the charts, multiplied by the proper power of 10.

functions for the normal and for the K-ionized atoms, W_0 is the energy parameter (a negative number) for the 2*s* wave function, and W_{k0} is the energy parameter (a positive number) for the function S_{k0}. For large values of k, or of energy, the numerical solution of Hartree's equation becomes increasingly difficult because of the rapid oscillations of the function S_{k0}, and a resort is had to hydrogen-like functions. For this purpose we use a screened Coulomb field of the type (10), choosing the constants V_0 and Z so as to fit the Hartree field near the L shell.[8] δV, which is the potential of a K electron in the atom, we take equal to $-\theta/r$, where θ is a constant, not far from unity, to be chosen by fitting the results onto the more accurate calculations of O_k with Hartree functions in the range of k for which both methods can be used. The results are shown in Fig. 1. In order to obtain a smooth joining of the two methods of calculation in the range $k^2/2$ equal to about 70 to 100 atomic units, it was necessary to take $\theta = 0.65$.

The results of the calculation with Eqs. (5) are shown in Fig. 2, consisting of altitude charts of the partial cross section Φ_n as a function of k_1 and k_2, for various values of l_1. It is seen that the most important contribution to the total cross section will come from $l_1 = 1$, and for rather small values of the kinetic energy of the expelled electrons. The incident energy of the cathode electron was taken for the calculations to be five times the K ionization energy of potassium, or 665 atomic units. This value was chosen to make possible comparison with the experimental work of Mrs. Pearsall, who used a tube voltage of five times the K excitation voltage.

The functions of Fig. 2 were integrated in polar coordinates over the 90° circle sectors, by using Simpson's rule, integrating first with respect to the angular coordinate, and then with respect to the radial coordinate. The results are added together to give a total double ionization cross section of 1.12×10^{-7} atomic unit, or 0.29 percent of the K cross section as determined by the same method. The analogous calculation for the $KL_{\text{II, III}}$ cross section was not actually carried out, but the result can be easily estimated, and is slightly less, per electron, than the KL_{I} cross section. If we remember that there are two[9] L_{I} electrons and six $L_{\text{II, III}}$ electrons in

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[8] This gives $Z = 13.1$, $V_0 = 10.2$, $r_0 = 1.28$; atomic units.

[9] Strictly speaking the two L_{I} electrons must be treated differently. We have tacitly assumed that the L_{I} electron has the same direction of spin as the K electron. For the other L_{I} electron this is not true and the exchange effect which we found for $l_1 = 0$ will be missing. However, since the contribution of $l_1 = 0$ to the total cross section is small, the two L_{I} electrons have practically the same chance of being expelled.

the atom, we conclude that the number of KL ionized atoms of the target is about 2.0 percent of the number of K ionized atoms. This number can be directly compared with experiments on the relative intensity of satellites after discussing the transition probabilities.

The intensity of a given line is proportional to the number of atoms of the x-ray target in the initial state and to the transition probability for the given line. It is with the former quantity that this paper deals primarily, but the transition probabilities must of course also be considered. The way in which they enter in can best be understood by considering the following example:

$$\text{Parent lines } (1s)\ {}^2S_{1/2}\rightarrow(2p)\ {}^2P_{3/2,\ 1/2}$$
$$\text{Satellites } (1s2s)\ {}^1S_0\ {}^3S_1\rightarrow(2p2s)\ {}^1P_1\ {}^3P_{012}.$$

The electron configurations represent electrons missing from completed shells. There are two parent lines (the $K\alpha$ doublet) and six satellites (including intercombination lines) allowed by the selection rules. The transition probability for a line is given by a constant numerical factor times the cube of the frequency times the squared modulus of the matrix element of the electric moment. These matrix elements are rather complicated, since the wave functions for the initial and final states are linear combinations of determinants of one-electron functions. But the available experimental data deal with the integrated intensity of the whole satellite structure, and it is possible to show that the sum of the satellite intensities for transitions $(1s2s)$ to $(2p2s)$ is in the same ratio to the sum of the parent line intensities as the total number of atoms in the initial configuration $(1s2s)$ to the total number in $(1s)$. In other words the presence or absence of the $2s$ electron does not affect the total probability that a $2p$ electron will drop into a vacancy in the $1s$ shell. This neglects the variation of the frequency-cubed factor from line to line and assumes that the one-electron wave functions for the $1s$ and $2p$ electrons are the same in the configurations $(1s)$ and $(2p)$ as in the configurations $(1s2s)$ and $(2p2s)$.

The general case of this theorem or sum-rule will now be stated, and is true to the same degree of approximation as the special case discussed above. A and B are the initial and final configurations for the parent lines. The configuration AC differs from A only in the addition or omission of certain electrons and the configuration BC differs from B only in the addition or omission of the same electrons. We consider those satellite lines which are due to transitions from AC to BC.

$$\text{Parent lines } A\rightarrow B$$
$$\text{Satellites } AC\rightarrow BC.$$

If the total number of atoms of the target in states of configuration A is the same as the total number of atoms of the target in states of AC, then the sum of the intensities of the parents is equal to the sum of the intensities of the satellites.

The final theoretical prediction which we make is then that if all the satellites of $K\alpha$ are due to KL ionization, the integrated intensity of the satellites of $K\alpha$ should be 2.0 percent of the sum of the intensities of $K\alpha_1$ and $K\alpha_2$, when the tube voltage is five times the K excitation voltage. Strictly speaking this assumes a thin target, but we hope that the correction for the use of a thick target will not be very great; and we compare our result with the experimental result of Mrs. Pearsall,[10] who found a relative intensity of 3.0 percent, for all of the satellites of $K\alpha$ of potassium taken together and referred to the total intensity of the parent doublet $K\alpha$. The agreement is not as good as we might wish, but would seem to show conclusively that some, at least, of the satellites are produced by single transitions in KL ionized atoms. There is reason to believe that the Born approximation should give a slightly low result in this case, and some of the satellites may be due to other double and multiple ionizations such as KL^2, KM, etc., so that it seems not impossible that all the satellites are in this case to be explained by the single jump theory.

Having obtained the absolute value of the relative intensity, for one element, we can easily extend our results to neighboring elements by observing that according to our equations the result should vary roughly as the inverse cube of the effective nuclear charge near the L shell. This would be exactly the case if we used hydrogen-like wave functions throughout, and neglected external screening, thus setting $V_0=0$

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[10] Anna W. Pearsall, Phys. Rev. **48**, 133 (1935).

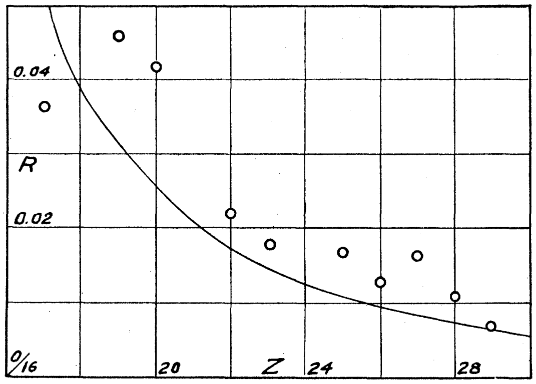

FIG. 3. The relative intensity of the $K\alpha$ satellites as a function of atomic number Z. R = integrated intensity of the satellites divided by the intensity of $K\alpha_1$. The circles are the experimental data of Mrs. Pearsall,[10] and the solid line gives the theoretical curve.

for both the K and L shells, and if we assumed a constant ratio between the effective nuclear charges near the K shell and near the L shell. In Fig. 3, therefore, we have compared the experimental values of relative intensity with the function $C/(Z-\sigma)^3$, in which σ is an internal screening constant which is practically independent of atomic number, and C is determined by our computation for potassium. The screening constant σ has the value $19-13$ or 6 for potassium according to our method of determining it by fitting the Hartree potential to a screened Coulomb potential near the L shell. Other ways of estimating this screening constant give a somewhat lower value. Slater's value,[11] as determined by fitting actual wave functions, is 3. We have compromised, and taken $\sigma=4.5$. The agreement between the experimental points and the theoretical curve is seen to be quite satisfactory, although the theory gives consistently slightly low values.

We can derive from our equations a greatly simplified formula for the relative probability of double ionization in one limiting case, and by means of this simplification show the connection between our theory and a formula which has already been used by Bloch (p. 192) for rough calculation of double ionization probabilities. If we were to compute the cross section for removing electron number one alone by the method followed in this paper for the double ionization, we should arrive at equations very similar to (11a) and (11b), but differing from those in the following respects: the exchange effect for $l_1=0$ is of course missing; the integral O_k is missing throughout; and the integration limits u_1 and u_2 are slightly different, due to a difference in Eq. (14). The limiting case we consider is that in which one of the electrons to be removed lies much deeper in the atom than does the other. In this case we need consider only a limited range of values of k_2—a range limited by the condition that $k_2^2/2$ must be of the order of magnitude of the ionization energy of the outer electron, and therefore by hypothesis small compared to the ionization energy of the inner electron. This limitation of the range of k_2 comes from the nature of the function O_k of Fig. 1. This quantity involves the wave function S_2 of the outer electron in the normal atom, and has the property that it rapidly approaches zero as the energy $k_2^2/2$ is made large compared to the ionization energy of this outer electron. When the range of k_2 is limited in this way, the *only* difference between (11b) and the corresponding equation for single ionization is the presence of the factor $O_{k_2}{}^2$, so that after integrating over all possible final states in each case, we get

$$\frac{\text{double ionization cross section}}{\text{single ionization cross section}} = \int_0^\infty O_k^2 dk. \qquad (16)$$

In order to get this result we have to consider Eq. (11a) a little further, because of the exchange effect which is present for the double ionization but not for the single ionization and which leads to cross product terms in the integrand of (11a) for double ionization but not for single ionization. However both $A_{k_1 0}$ and $B_{k_1 0}$ are practically zero for small values of k_1, and therefore the cross product terms are negligible in our limiting case, and Eq. (16) is established. In the case of KL ionization Eq. (16) gives a value which is about 25 percent too high as judged by our more exact calculation, but for KM and KN ionizations, etc., it should be much better.

The functions ψ_{k00} of (6) form a part of a complete orthogonal set. If we summed O_k^2 over all the members of this set, we should have, by a theorem in the theory of orthogonal functions,

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[11] J. C. Slater, "Analytic Atomic Wave Functions," Phys. Rev. **42**, 33 (1932).

just $\int|\varphi_2|^2 d\tau$ or unity. The integral in k of (16) is a summation of O_k^2 over some of these functions, and therefore equal to unity minus the summation over the rest of the functions, which are just the ones occupied by electrons in the atom, so that

$$\frac{\text{double ionization cross section}}{\text{single ionization cross section}}$$
$$=1-\left|\int\psi_2{}^*\varphi_2 d\tau\right|^2-\sum_{n,\,l,\,m}\left|\int\psi_{nlm}{}^*\varphi_2 d\tau\right|^2 \quad (17)$$

in which the summation is to be extended over all the electrons of the atom except electrons numbers 1 and 2 themselves. This formula, with the summation missing, is the one which was used by Bloch in his "order of magnitude" calculations connected with the double-jump theory of satellites. The summation would probably be quite important in quantitative work.

The author wishes to express his gratitude to Professor Philip M. Morse of Massachusetts Institute of Technology for much helpful guidance and many valuable suggestions received from him during the course of this investigation.

Note added in proof: Dr. L. G. Parratt of Cornell University has kindly sent the writer some unpublished data of his on the relative intensities of the satellites of $K\alpha$. These were taken with a two-crystal spectrometer and an ionization chamber. They are more accurate than the data of Mrs. Pearsall, and cover a wider range of atomic numbers. When plotted on the graph of Fig. 3, the points so determined are somewhat closer to the theoretical curve, but still slightly above it. However, Parratt's experiments are so much better than my theory, that a more detailed comparison at this time is not worth while.

Since the manuscript was submitted for publication, the writer has had the privilege of discussing the subject on several occasions with Professor J. R. Oppenheimer. Professor Oppenheimer suggests that the interaction of the two *expelled* electrons may be of more importance than one might perhaps think at first. This interaction was of course entirely neglected in the theory, since Hartree wave functions were used for the doubly ionized state of the atom. This point cannot be quantitatively investigated until further calculations are made.

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An Apparent Failure of the Photon Theory of Scattering

ROBERT S. SHANKLAND, *Ryerson Physical Laboratory, The University of Chicago*

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A test has been made of the photon theory of the scattering of high frequency radiation. The pairs of scattered photons and recoil electrons predicted by this theory have been looked for by means of specially designed Geiger-Müller counters. Coincident discharges in the electron and photon counters were recorded by means of a vacuum tube amplifying and adding circuit. The scatterers used were air, aluminum, beryllium, filter paper and paraffin. The radiation was the gamma-rays from radium C. Experiments were performed with the counters set at various angles, some where the photon theory predicts coincidences, and others where coincidences should not be expected. The experiments uniformly gave fewer coincidences in the correct positions than were expected, and those observed could in every case be accounted for as chance coincidences due to the finite resolving time of the apparatus. It has not been found possible to bring the results of these experiments into accord with the photon theory of scattering. The wave-mechanical theory of the scattering process has not yet been extended to include the gamma-ray region so that it is impossible to compare this theory with the present experiments. Unless it is shown that the two theories disagree in the gamma-ray region it does not seem possible to reconcile the present experiment with the Bothe-Geiger and Compton-Simon experiments.

INTRODUCTION

THE discovery of the change in wave-length of x-rays when scattered by loosely bound electrons led A. H. Compton[1] to develop a photon theory based on the concept of light quanta to account for this phenomenon. This theory accounted for the interaction between radiation and matter by picturing the process as a mechanical collision between a light corpuscle and an electron which obeyed the laws of conservation of energy and momentum. At about the same time a virtual radiation theory was

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[1] A. H. Compton, Phys. Rev. **21**, 483 (1923).