Interpretation of X-Ray Satellites

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Druyvestyn's explanation of the $K\alpha$ satellites has been put to the test of numerical calculation using the Hartree field in the case of potassium (Z=19). The $K\alpha$ satellites are attributed to transitions from states with one K and one L electron missing to states with two L electrons missing. Treating e^2/r_{12} as a perturbation and using the wave functions of the unperturbed Hartree wave equation, the energies belonging to the configurations 1s 2s, 1s 2p, 2s 2p, and $(2p)^2$ were calculated according to Slater's theory of complex spectra. The symbols describing the configurations refer to electrons missing from closed shells. The assumption of Russell-Saunders coupling is a justifiable approximation since the interchange energies turn out to be large compared with the spin-orbit interaction, which is measured by the $K\alpha_{1, 2}$ doublet separation. There are five allowed transitions which may be correlated with five characteristic $K\alpha$ satellites. $K\alpha_{5, 6}$ are not observed in

Line	ν/R obs.	 Transition 	ν/R calc.
$K \alpha'$	245.05	$1s \ 2p \ {}^{1}P \rightarrow (2p)^{2} \ {}^{1}S$	245.05
$K \alpha_3$	245.56	$1s \ 2s \ ^3S \rightarrow 2s \ 2p \ ^3P$	245.63
$K\alpha_4$	245.69	$1s \ 2s \ {}^1S \rightarrow 2s \ 2p \ {}^1P$	245.53
$K \alpha_5$		$1s 2p {}^{3}P \rightarrow (2p)^{2} {}^{3}P$	246.38
$K lpha_6$		$1s 2p {}^{1}P \rightarrow (2p)^{2} {}^{1}D$	246.15

potassium but appear in other elements as a doublet at higher frequency than $K\alpha_{3, 4}$. A small change in the interchange integrals would reverse the sequence of the frequencies calculated for $K\alpha_{3}$ and $K\alpha_{4}$ and likewise for $K\alpha_{5}$ and $K\alpha_{6}$. The reason for choosing the transitions assigned here is to make $K\alpha_{3}$ and $K\alpha_{5}$ appear as triplettriplet transitions, since these lines have fine structure. The strong lines, $K\alpha_{3, 4}$, which persist from Z=11 to Z=30, are due to an initial $KL(2_{1})$ ionization. The weak lines, $K\alpha'$ and $K\alpha_{5, 6}$, which appear from Z=11 only to Z=19 and Z=16, are due to an initial $KL(2_{2})$ ionization.

THE object of this paper was to put to the test of numerical evaluation in a special case the predictions of some of the theories of the origin of x-ray satellite lines.

On the hard side of the $K\alpha$ lines, satellites are observed over the atomic number range 11 to 30. Six satellites are observed, though not all are found for any one element, and are called $K\alpha'', K\alpha', K\alpha_3, K\alpha_4, K\alpha_5, K\alpha_6$, in order of increasing frequency. It was early suggested by Wentzel¹ that these lines might result from single electron transitions in atoms doubly ionized in the x-ray levels—thus analogous to spark lines in optical spectra. Experiments on excitation potential have shown that the details of Wentzel's scheme were wrong, since it called for double ionization in the K shell as the initial state for some of the satellites.

The experimental technique of measuring ionization potentials is so difficult that it has not been possible to prove whether energy enough for ionization in the K shell and in the L shell is necessary for the appearance of the $K\alpha$ satellites. Dumond and Hoyt² believe that the excitation potential of $K\alpha_{3, 4}$ in Cu (Z=29) is probably less than the sum of the K and L ionization energies, but this conclusion is based on an extrapolation and is not conclusive.

Druyvestyn³ has revised the theory of Wentzel. He assigns the following transitions to the $K\alpha$ satellites, where the symbol K means one electron missing from the K shell, etc. (see Table I). We

TABLE I.

Κα' Κα _{3, 4} Και 6	$KL(2_1)$ $KL(2_2)$ $KL(2_2)L(2_2)$	$ \xrightarrow{\rightarrow} L(2_2)L(2_1) \xrightarrow{\rightarrow} L(2_2)L(2_2) $ or $ L(2_2)L(2_2)L(2_2) $	1s 2s $1s 2p$ $1s (2p)$	$ \rightarrow 2p \ 2s \rightarrow (2p)^2)^2 \rightarrow (2p)^3 $
11000, 6	111(22)11((22) + H(22)H(22)H(22)	13 (4)) · (2P)

shall use hereafter the spectroscopic notation, 1s instead of K, etc. In support of these assignments, Druyvestyn has given a rather naive treatment of the theory of single and double ionization by electron impact according to which the relative intensities of the satellites and their falling off in intensity relative to the diagram

¹ Wentzel, Ann. d. Physik 66, 437 (1921).

² Dumond and Hoyt, Phys. Rev. 36, 799 (1930).

⁸ Druyvestyn, *Dissertation*, Groningen, 1928; Zeits. f. Physik **43**, 767 (1927).

line with increasing atomic number come out more or less right. The frequencies have not previously been calculated.

Langer⁴ has suggested that complex spectra are to be expected when two or more electrons are missing in inner shells and has pointed out that the transitions $1s 2s \rightarrow 2p 2s$, $1s 2p \rightarrow (2p)^2$ give rise to five lines and might account for the satellites.

We undertook to calculate the frequencies of these five lines for the case of potassium, Z=19. Heisenberg⁵ has shown that Slater's theory of complex spectra⁶ applies just as well to electrons missing from closed shells as to electrons present outside closed shells. Accordingly, we proceeded to calculate the energy levels of the configurations 1s 2s, 1s 2p, 2s 2p, and $(2p)^2$ according to Slater's theory. The levels predicted are (Slater,⁶ page 1315 and page 1316) given in Table II.

TABLE II.

1s 2s - 1s 2p -	$\begin{cases} {}^{1}S = J(100, 200) + K(100, 200) = F^{0}(10, 20) + G^{0}(10, 20) \\ {}^{3}S = J(100, 200) - K(100, 200) = F^{0}(10, 20) - G^{0}(10, 20) \\ {}^{1}P = J(100, 211) + K(100, 211) = F^{0}(10, 21) + \frac{1}{2}G^{1}(10, 21) \\ {}^{3}P = J(100, 211) - K(100, 211) = F^{0}(10, 21) + \frac{1}{2}G^{1}(10, 21) \\ {}^{1}P = J(200, 211) + K(200, 211) = F^{0}(20, 21) + \frac{1}{2}G^{1}(20, 21) \\ \end{cases}$
$(2p)^2$	$ \begin{array}{l} {}^{3}P=J(200,211)-K(200,211)=F^{0}(20,21)-\frac{1}{3}G^{1}(20,21)\\ ({}^{3}S=F^{0}(21,21)+10/25F^{2}(21,21)\\ {}^{4}D=F^{0}(21,21)+1(25F^{2}(21,21)\\ {}^{3}P=F^{0}(21,21)+1(25F^{2}(21,21)\\ \end{array} \end{array} $

The expressions in terms of F and G are found by substituting the values of a^k and b^k from the tables (Slater,⁶ page 1312) into the general expressions for J(nlm, n'l'm') and K(nlm, n'l'm')(Slater,⁶ p. 1311). The integrals F^k and G^k are defined (Slater,⁶ page 1311) as

$$F^{k}(nl, n'l') = e^{2} \int_{0}^{\infty} \int_{0}^{\infty} R_{nl}^{2}(r) R_{n'l'}^{2}(r') r_{a}^{k} / r_{b}^{k+1} r^{2} r'^{2} dr dr'$$

$$G^{k}(nl, n'l') = e^{2} \int_{0}^{\infty} \int_{0}^{\infty} R_{nl}(r) R_{n'l'}(r) R_{nl}(r') R_{n'l'}(r') r_{a}^{k} / r_{b}^{k+1} r^{2} r'^{2} dr dr'$$

Here R_{nl} is the solution of the radial part of the unperturbed wave equation for one electron. By r_a is meant the smaller and by r_b the larger of the values r and r'. We have dropped a factor $4\pi^2$ since we normalize R_{nl} to unity rather than to $1/(2\pi)^{1/2}$ as Slater does.⁷

The work which is being reported here was the calculation of the various F^k and G^k integrals required to determine the energy levels of the four configurations in which we are interested. The method used was numerical integration and the wave functions used were those of the Hartree self-consistent field⁸ for potassium. Having available the data on the self-consistent field of the potassium ion, i.e., potassium with the valence electron missing, we proceeded to solve the radial wave equation numerically, obtaining the wave functions R_{10} , R_{20} , R_{21} . The potential energy function in the wave equation in each case was that of the potassium ion less that of the particular electron whose wave function was to be found.

TABLE III.

$F^0(10, 20) = 6.38$	$G^0(10, 20) = 1.12$
$F^0(10, 21) = 7.50$	$G^{1}(10, 21) = 0.74$
$F^0(20, 21) = 4.76$	$G^1(20, 21) = 3.5$
$F^0(21, 21) = 5.44$	$F^2(21, 21) = 3.05.$

Using these wave functions, we calculated the following integrals in Table III. The numerical values given are in the customary ν/R units. The fact that the interchange integrals, the G's and F^2 , turn out to be large compared to the spin-orbit interaction energy, which is measured by the doublet separation of $K\alpha_{1, 2}$ and amounts to 0.23, shows that we are justified in neglecting the spin-orbit interaction and using as an approximation the Slater theory which assumes Russell-Saunders coupling.

The multiplet energies obtained by substituting the values from Table III in the formulas

⁴ Langer, Cleveland Meeting, Phys. Rev. 37, 457 (1931).

⁵ Heisenberg, Ann. d. Physik 10, 888 (1931).

⁶ Slater, Phys. Rev. 34, 1293 (1929).

⁷ Condon and Shortley, Phys. Rev. **37**, 1026 (1931). Remark on normalization.

⁸ Hartree, Camb. Phil. Soc. Proc. 24, 89 (1927). Since the wave functions must have been worked out in the process of finding the self-consistent field, it would pay anyone who wished to do more work of this sort to obtain the complete solutions from Hartree for those atoms which have been studied by him. We had a table of the values of Z(r) as a function of r, sent to us by Miss Phillips at Berkeley and originally obtained by her from Hartree.

of Table II are perturbation energies—the perturbation being the electrostatic interaction e^2/r_{12} between two electrons present outside closed shells or missing inside closed shells-to be measured from the unperturbed levels which are, for each configuration, the sum of the ionization energies of the two electrons separately. In each of the transitions which we shall consider, one electron is common to the initial and final configurations while the change in the ionization energy of the other corresponds to the energy of the $K\alpha_{1, 2}$ doublet. Thus we must add 243.96, the ν/R value of the center of gravity of $K\alpha_{1,2}$, to the ν/R differences given by Table II to get the ν/R values predicted for the various allowed transitions.

In Table IV, we list the transitions that are allowed according to the spectroscopic rules in cases of Russell-Saunders coupling and the predicted ν/R values. We correlate these with the five $K\alpha$ satellites and list the ν/R values for those that are observed. The last column shows the transitions assigned by Langer to the various $K\alpha$ satellites. $K\alpha_{5, 6}$ are not observed in potassium but appear in other elements as a doublet at higher frequency than $K\alpha_{8, 4}$.

TABLE IV.

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Line obs. ν/R	Transition	ν/R calc.	Langer's assignment
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 1s \ 2p^{1}P \longrightarrow (2p)^{2} \ ^{1}S \\ 1s \ 2s^{3}S \ \longrightarrow 2s \ 2p^{3}P \\ 1s \ 2s^{3}S \ \longrightarrow 2s \ 2p^{3}P \\ 1s \ 2s^{3}S \ \longrightarrow 2s \ 2p^{1}P \\ 1s \ 2p^{3}P \longrightarrow (2p)^{2} \ ^{3}P \\ 1s \ 2p^{1}P \longrightarrow (2p)^{2} \ ^{1}D \end{array}$	$\begin{array}{r} 245.05\\ 245.63\\ 245.53\\ 246.38\\ 246.15\end{array}$	$1s 2s^{1}S \rightarrow 2s 2p^{1}P$ $1s 2p^{3}P \rightarrow (2p)^{2}{}^{3}P$ $1s 2s^{3}S \rightarrow 2s 2p^{3}P$ $1s 2p^{1}P \rightarrow (2p)^{2}{}^{1}S$ $1s 2p^{1}P \rightarrow (2p)^{2}{}^{1}D$

It will be noted that the frequency correlation would be better if we interchanged the transitions assigned to $K\alpha_3$ and $K\alpha_4$. Similarly, $K\alpha_6$ should have a higher frequency than $K\alpha_5$. But a small change in the interchange integrals, which were calculated much less accurately than the screening integrals, F^0 , would bring these frequencies into the right sequence. The reason for choosing the assignments as we have done is to make $K\alpha_3$ and $K\alpha_5$ appear as triplet-triplet transitions. These lines are generally diffuse and fine structure has been observed in them for some elements.

It is observed that $K\alpha_{3, 4}$ are much stronger than $K\alpha'$ and $K\alpha_{5, 6}$. Also the range of atomic numbers for which $K\alpha_{3, 4}$ are observed is 11 to 30, while for $K\alpha'$ it is 11 to 19 and for $K\alpha_{5, 6}$ it is 11 to 16. This correlates nicely with our assignment of $K\alpha_{3, 4}$ to one initial configuration, 1s 2s, and the other lines to the other initial configuration, 1s 2p. This suggests that a correct theory of double ionization *might* show a greater probability for the ionization $KL(2_1)$ than for the ionization $KL(2_2)$.

While the use of the Hartree atom is an approximation and we do not claim any high order of accuracy for our numerical work, it seems to us that the correlation between the observed and calculated behavior of the satellites is so striking as to make our interpretation seem very reasonable.

The satellite $K\alpha''$, which has been left entirely out of account here, lies much nearer to $K\alpha_{1, 2}$ than the rest and is assigned by Druyvestyn to a transition $KM \rightarrow LM$.

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