Probability of Double Jumps in X-Ray Spectra

E. G. RAMBERG,[1] *Heckscher Research Assistant, Cornell University*

(Received October 19, 1933)

By a suitable perturbation method, two-electron transition probabilities are computed for a number of double jumps, such as $2p, 4s \rightarrow 1s, 3s$ and $2p, 3d \rightarrow 1s, 3s$, in Na and Cu atoms. It is found that these probabilities are too small to account for the observed intensities of the x-ray satellites $K\alpha_{3,4}$. As a more general argument against the correctness of the double-jump hypothesis for the origin of the short wave-length x-ray satellites it is pointed out that the line structure due to two-electron transitions of the kind considered would consist of a symmetrical grouping of faint lines about the parent line, the stronger components being on the long wave-length side.

A NUMBER of considerations,[2] in particular the disagreement between the ionization potentials of x-ray satellites as predicted by the double ionization theory of Wentzel and Druyvesteyn with the experimental results of DuMond and Hoyt,[3] have lent support to the alternative view advanced by Richtmyer[4] that these satellites were due to transitions between the outer orbits of the atom taking place simultaneously with the inner transition normally producing the parent line. Conclusions reached in the present work are not in agreement with this view.

To test the last-mentioned hypothesis the strong satellites of $K\alpha_{1,2}$, $K\alpha_{3,4}$, were singled out for closer scrutiny. The parent line $K\alpha_{1,2}$ is known to be due to jumps of a $2p$ electron into a vacant $1s$ state. Now the outer field of an atom (atomic number Z) having lost a $1s$ electron resembles that of a singly ionized one of the next higher element (atomic number $Z+1$) very closely. Hence, assuming the double-jump hypothesis to be correct, we have to expect for the frequency of the satellite:

$$\nu_s(Z) \cong \nu_p(Z) + \nu_0(Z+1)^+,$$

where ν_p is the frequency of the parent line and ν_0 that corresponding to a transition in the outer atomic layers. Comparing, with due regard of the selection rules for multiple jumps, transitions in the optical term system of the ion of atomic number $Z+1$[5] with the observed frequency separations of satellite and parent line for element Z, we find that only transitions ending in a $3s$ or $3p$ level could yield separations of the right order of magnitude. Of these, again, we can expect the lowest members of the series, such as $4s \rightarrow 3s$, $4p \rightarrow 3p$, $3d \rightarrow 3s$ to occur most frequently, so that we can confine our attention to them.

If we suppose the satellites to originate in the above manner, the intensity ratio W of satellite and parent line is given by the product of two probability ratios, W_1, that for the excitation process necessary in each case, and W_2, that for the emission process. Thus we have for the line corresponding to $2p, 4s \rightarrow 1s, 3s$:

$$W = W_1 \cdot W_2 = \left\{ \text{Probability of } \begin{pmatrix} 1s \rightarrow \infty \\ 3s \rightarrow 4s \text{ or } \infty \end{pmatrix} \Big/ \text{Probability of } (1s \rightarrow \infty) \right\}$$
$$\times \left\{ \text{Probability of } \begin{pmatrix} 2p \rightarrow 1s \\ 4s \rightarrow 3s \end{pmatrix} \Big/ \text{Probability of } (2p \rightarrow 1s) \right\}.$$

[1] The present note gives results obtained in a thesis presented to the University of Munich.

[2] F. K. Richtmyer, J. Frank. Inst. **208**, 325 (1929); J. W. M. DuMond, Phys. Rev. **36**, 1015 (1930).

[3] J. W. M. DuMond and A. Hoyt, Phys. Rev. **36**, 799 (1930). For contrary evidence see D. Coster and W. J. Thijssen, Zeits. f. Physik **84**, 686 (1933).

[4] F. K. Richtmyer, Phil. Mag. **6**, 64 (1928).

[5] Optical terms refer to free atoms, x-ray observations to atoms bound in a crystal lattice; their comparison is justified below.

Both W_1 and W_2 depend principally on the closeness of the coupling between the electrons in the inner and outer shells of the atom, so that, if we find $W_2 \ll 1$, we are justified in assuming $W_1 \ll 1$ as well. W_2 does not depend on the nature of the excitation process and is, furthermore, easier to compute. Hence we confine our attention to it.

For the purpose of the computations the two electrons participating in the transition were thought of as moving in the centrally symmetric field of the atom core, made up of the nucleus and the remainder of the electrons of the atom and the charge of one electron distributed so as to compensate the effect of one of the moving electrons on the other. We thus treat the case of the free atom. There may be little justification for expecting results thus obtained to hold for atoms bound in a crystal lattice. However, once we assume that x-ray satellites are due to two-electron transitions of the kind considered, the experimentally observed fact that the $K\alpha$ satellite structure is only very slightly influenced by chemical combination[6] leads us to the conclusion that, as long as we are concerned only with orders of magnitude, the influence of the neighboring atoms may be left out of account. As the frequencies of satellite and parent line differ very little we can, disregarding retardation effects, regard the probability I of any transition as proportional to the square of the matrix element of the coordinates of the two electrons:

$$I \sim \left| \int U_a^*(\vec{r}_1+\vec{r}_2)\, U_b d\tau \right|^2. \tag{1}$$

Here U_a is the wave function of the initial and U_b that of the final state. To the zero approximation, i.e., with the linear combinations of products of one-electron wave functions appropriate for (j, j) coupling as wave functions of the system,[7] this matrix element vanishes for two-electron transitions. Hence, expanding U_a and U_b in terms of one-electron wave functions[8] and determining the coefficients by numerical integration, first order expressions were obtained for the matrix element in (1).

The one-electron wave functions themselves were found by numerical integration and adjustment of energy parameters from the Schrödinger equation for central field. The latter was obtained with the aid of a semi-empirical formula given by Slater.[9] Finally the probability of each of the double jumps considered as well as of the related one-electron jump were computed by summing the probabilities of all possible transitions between states making up the initial and final configurations of the atom.

Carrying out computations for the two electron transitions $2p$, $4s \to 1s$, $3s$ and $2p$, $3s \to 1s$, $4s$ in Na(11) and $2p$, $4s \to 1s$, $3s$ and $2p$, $3d \to 1s$, $3s$ in Cu(29) following results were obtained for the probability ratio W_2 of double and single jump:

Sodium:

$$I(2p, 4s \to 1s, 3s)/I(2p, 4s \to 1s, 4s) = 1 : 170, \tag{2a}$$

$$I(2p, 3s \to 1s, 4s)/I(2p, 3s \to 1s, 3s) = 1 : 320 \tag{2b}$$

Copper:

$$I(2p, 4s \to 1s, 3s)/I(2p, 4s \to 1s, 4s) = 1 : 4800, \tag{2c}$$

$$I(2p, 3d \to 1s, 3s)/I(2p, 3d \to 1s, 3d) = 1 : 18{,}000. \tag{2d}$$

As there are 10 $3d$ electrons in copper we have to multiply the ratio in (2d) by the factor 10, obtaining for the relative probability of double and single jumps the ratio 1 : 1800. The double jumps in (2a), (2c), and (2d) correspond to lines on the short wave-length side of the parent line. Here we must require the atom to be initially doubly excited, so that the probability ratio W_1 for the excitation process is itself $\ll 1$, probably of the same order of magnitude as W_2. The computed values of W_2 are themselves considerably

[6] For observations on Si(14) and S(16) see E. Bäcklin, Zeits. f. Physik **38**, 215 (1926).

[7] An analogous treatment for Russell-Saunders coupling led to the same results.

[8] See H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A136**, 289 (1932), esp. Eqs. (2) and (4).

[9] J. C. Slater, Phys. Rev. **36**, 57 (1930).

smaller than the measured or estimated intensity ratio for $K\alpha_{3,4}$ and $K\alpha_{1,2}$ (1 : 180 for Cu[10]; very much larger for Na). Hence we must conclude that the relative intensity $W = W_1 \cdot W_2$ predicted by the double jump hypothesis is far too low to account for the satellites $K\alpha_{3,4}$.

The case (2b) corresponds to a long wave-length satellite of $K\alpha_{1,2}$ with a separation from the parent line equal to that of the short wave-length satellite considered in (2a). In this case—(2b)—the initial states of parent line and satellite are identical, so that the expected intensity ratio here becomes simply $W = W_2$. As W_2 for (2b) and (2a) differs by less than a factor of 2, we must hence expect the long wave-length satellite to be far stronger than the corresponding short wave-length satellite. It is generally to be expected that, for every double jump which involves the filling of a newly created vacancy in the outer shells of the atom, there is another more frequently occurring double jump with the same outer transition taking place in the reverse direction. We conclude that the line structure due to double jumps of the type here considered consists, as in the Raman effect, of a symmetrical grouping of faint lines about the parent line, the more intense ones being on the long wave-length side, while the actually observed satellites lie on the short wave-length side. This last conclusion should hold for the bound as well as the free atom, though in the former case the double jump line structure might be replaced largely or even entirely by bands due to transitions from conduction levels and thus become still less observable.

The author wishes to express his thanks to Professor Sommerfeld for his interest and encouragement of this work, and Drs. K. Bechert and H. Bethe for many valuable suggestions. He is also greatly indebted to Professor F. K. Richtmyer, to whom he owes his interest in the subject, and Professor E. H. Kennard for many clarifying discussions.

[10] J. W. M. DuMond and A. Hoyt, Phys. Rev. **36**, 799 (1930).