Double Electron Transitions in X-Ray Spectra

F. BLOCH, *Stanford University*

(Received May 2, 1935)

Elementary processes are considered, in which simultaneous transitions of an inner and an outer atomic electron result in the emission of one single light quantum. Considering the nuclear distance of the inner electron as small compared to that of the outer electron, formulae are developed for the probability of double transitions by dipole radiation. The occurrence of the Cu $K\alpha_3$ satellite is given as a possible illustration of the case, where the inner transition alone occurs by dipole emission; a special consideration applies in this connection to the probability of simultaneous inner ionization and outer excitation. For the case of a forbidden inner transition, the simultaneous emission of a light quantum and an outer electron (radiative Auger effect) is discussed.

1. INTRODUCTION

THE possibility of double electron transitions in x-ray spectra was first suggested by Richtmyer[1] in connection with the occurrence of the so-called "satellites" of x-ray spectral lines. According to his theory, the satellite line is due to the simultaneous transition of an inner and an outer electron from a higher to a lower energy level, so that the energy of the emitted quantum is the sum of both energy differences, while for the "parent" line only the transition of the inner electron should be responsible. An alternative explanation of the satellites has been given by Wentzel[2] and Druyvesteyn,[3] who attribute their appearance to the possibility of double ionizations of inner shells.

A quantitative theoretical justification of the double transition hypothesis has in the first place to explain a considerable probability of a simultaneous excitation of an outer electron and an ionization of an inner shell while for the double ionization a sufficiently frequent occurrence of such processes has to be explained.

Whereas it seems at first that at least one of these two theories must be wrong, one has to consider the possibility that both have a certain but different range of applicability. Indeed, the experimental evidence rather leads to the conclusion that one has to assume *different* mechanisms according to whether one considers the satellites of K or L lines. While the former occur only in the spectra of comparatively light elements, the latter show an irregular dependence[4] on the atomic number Z, being absent in the range from about $Z=50$ to $Z=70$, but occurring both for lower and higher atomic numbers.

Recently Coster and Kronig[5] have succeeded in giving a satisfactory explanation of the L satellites both as to their great intensities and their peculiar dependence on Z. They have to be understood as the result of a special process of double ionization, due to the Auger emission of an M electron and the simultaneous radiationless transition of an L electron from $(2p)$ to $(2s)$.

It is clear, however, that such an explanation cannot account for the satellites of the K series, and it seems to us that here, indeed, Richtmyer's point of view has to be taken into consideration. Some time ago, Ramberg[6] published arguments against the double transition theory, coming to the conclusion that such transitions should be expected to be far too improbable to account for the observed intensity of the $K\alpha$ satellites. In his considerations, however, decisive features are omitted which, as we will see, bring the theoretical intensity of the satellites quite close to the observed order of magnitude. Our main objection applies against his argument, that the ratio of the probabilities of double excitation (i.e., simultaneous ionization of the K shell and excitation of an outer level) to single excitation (i.e., mere ionization of the K shell) should be of the same order of magnitude as those of double transition to single transition. This would imply that the square of the latter ratio should give approximately the intensity ratio of satellite to parent line and would indeed turn out to be of far too

[1] F. K. Richtmyer, J. Frank. Inst. **208**, 325 (1929).
[2] G. Wentzel, Ann. d. Physik **66**, 437 (1921).
[3] M. J. Druyvesteyn, Zeits. f. Physik **43**, 707 (1927).
[4] F. K. Richtmyer and S. Kaufman, Phys. Rev. **44**, 605 (1933).
[5] D. Coster and R. de L. Kronig, Physica **2**, 1, 13 (1935).
[6] E. G. Ramberg, Phys. Rev. **45**, 389 (1934).

small an order of magnitude. Although, however, as Ramberg points out, both double excitation and double transition involve the coupling of an inner with an outer electron, there is nevertheless a radical difference between the two processes, making the former far more probable than the latter. While in the double transition the inner electron merely changes between two inner levels, for the double excitation an inner electron is completely removed, thus in a nonadiabatic process changing approximately the effective atomic number Z^* of an outer electron into Z^*+1. As we will point out later for the case of the Cu $K\alpha$ satellite, this has as a consequence that *if* the K electron is removed, there is not a small probability but almost *certainty* that at least one of the outer electrons will be excited; thus we understand also why in this case the satellite is found on the short wavelength side of the parent line and that there are not, as Ramberg would expect, two corresponding satellites on both sides, the more intense one lying on the long wavelength side.

We believe also that there are other cases of double transitions. A particularly interesting one is associated with the occurrence of "forbidden" lines, and is brought to evidence by recent observations of Ross.[7] This mechanism can roughly be described in the following way: Instead of performing a forbidden radiative transition the atom is able to emit simultaneously a light quantum and an outer electron. The total system (consisting of inner + outer electron) can thus radiate by dipole emission (instead of quadrupole emission, as in the case of the forbidden line) and emit a continuum on the long wavelength side of the forbidden line, this type of "satellite" being more intense than the weak "parent" line.

A more quantitative discussion of the processes here considered would necessitate very accurate knowledge of atomic eigenfunctions and involve a great amount of numerical integration. We will restrict ourselves in the next sections to pointing out the main characteristics of the most interesting cases and estimating their probability under special conditions.

2. Probability of Double Transitions

We consider an inner electron 1 and an outer electron 2, assuming that the orbital dimensions of 1 shall be small compared with those of 2; in this case the eigenfunctions of 1 and 2 will overlap only very little, so that their exchange can be neglected. The presence of other atomic electrons shall be taken into account only insofar as they modify the potential field, in which 1 and 2 move, and as those transitions of 1 and 2 shall be excluded that lead to states occupied by any of the other electrons. This means that as "zero order" atomic eigenfunction we assume a function that can be written as a product of functions, each of them depending only on the coordinates of one electron.

Calling $\mathbf{r}_1$ and $\mathbf{r}_2$ the position vectors of electron 1 and 2 with components $(x_1y_1z_1)$ and $(x_2y_2z_2)$, respectively, we may expand the interaction energy of 1 and 2 in terms of the coordinates of 1 in the form:

$$e^2/|\mathbf{r}_1-\mathbf{r}_2| = e^2/r_2+v(\mathbf{r}_1,\mathbf{r}_2)=e^2/r_2+v'(\mathbf{r}_1,\mathbf{r}_2)+v''(\mathbf{r}_1,\mathbf{r}_2), \tag{1}$$

where

$$v'(\mathbf{r}_1,\mathbf{r}_2)=e^2(\mathbf{r}_1\mathbf{r}_2)/\mathbf{r}_2^3 \tag{2}$$

contains the terms that are linear, and

$$v''(\mathbf{r}_1,\mathbf{r}_2)=e^2/2[3(x_1x_2+y_1y_2+z_1z_2)^2/r_2^5-r_1^2/r_2^3] \tag{3}$$

contains the terms that are quadratic in the coordinates of 1, higher order terms being neglected. The term e^2/r_2 in (1) has to be taken as part of the nonperturbed potential of electron 2, representing the screening due to the presence of electron 1. The coupling energy $v=v'+v''$ shall be considered as a small perturbation. The nonperturbed eigenfunctions of 1 and 2 shall be generally designated by $u_\mu(1)$, $u_m(2)$, respectively, the corresponding energy levels by E_μ and E_m. Keeping only the terms linear in the matrix elements of v, we can write the eigenfunction of the initial state

[7] F. Bloch and P. A. Ross, Phys. Rev. **47**, 884 (1935).

$$\psi_{\alpha a}(1,2)=u_\alpha(1)u_\alpha(2)-\sum_{\mu,\ m\pm\alpha,\ a}\frac{v_{\mu m,\ \alpha a}}{E_\mu+E_m-E_\alpha-E_a}u_\mu(1)u_m(2) \tag{4}$$

and that of the final state

$$\psi_{\beta b}(1,2)=u_\beta(1)u_b(2)-\sum_{\mu,\ m\pm\beta b}\frac{v_{\mu m,\ \beta b}}{E_\mu+E_m-E_\beta-E_b}u_\mu(1)u_m(2). \tag{4a}$$

We may assume furthermore, that not only the orbital dimensions of 1 shall be small compared with those of 2, but also, that the orbital dimensions of the final state β of electron 1 shall be small compared with those of the initial state α. In this case, the coupling energy v will practically act only on the initial state α, a and for the final state β, b, we can, instead of (4a) write approximately

$$\psi_{\beta b}(1,2)=u_\beta(1)u_b(2). \tag{5}$$

The emission of a light quantum with frequency

$$\nu=(E_\alpha+E_a-E_\beta-E_b)/h$$

will be mainly due to a radiative transition of 1. According to the general rules of the quantum theory of radiation[8] the probability for such a transition will then be proportional to the absolute square of

$$I_{\beta b}{}^{\alpha a}=\int\psi^{\alpha a*}\exp(i\mathbf{k}\mathbf{r}_1)(\mathbf{n},\operatorname{grad}_1)\psi_{\beta b}d\tau_1 d\tau_2, \tag{6}$$

where $\mathbf{n}$ is a unit vector, perpendicular to the direction of propagation of the emitted quantum and $\mathbf{k}$ its vector of propagation; $(\mathbf{n}\ \operatorname{grad}_1)$ stands for

$$n_x\partial/\partial x_1+n_y\partial/\partial y_1+n_z\partial/\partial z_1$$

and $d\tau_1$, $d\tau_2$ are the elements of the configuration space of 1 and 2, respectively. Using the expressions (4) and (5) and taking the functions $u(2)$ as orthogonal and normalized, we find for the "parent" line

$$I_\beta{}^\alpha=\int u_\alpha{}^*(1)\exp(i\mathbf{k}\mathbf{r}_1)(\mathbf{n},\operatorname{grad}_1)u_\beta(1)d\tau_1 \tag{6a}$$

and for the "satellite"

$$I_{\beta b}{}^{\alpha a}=\sum_\mu\frac{v_{\alpha a,\ \mu b}}{E_\alpha+E_a-E_\mu-E_b}\int u_\mu{}^*(1)\exp i(\mathbf{k}\mathbf{r}_1)(\mathbf{n},\operatorname{grad}_1)u_\beta(1)d\tau_1. \tag{6b}$$

The difference of frequency $\Delta\nu=(E_b-E_a)/h$ between parent line and satellite will always be so small that their intensity ratio will be given by the ratio of the absolute squares of (6a) and (6b). The discussion of (6a) and (6b) offers two entirely different aspects, according to whether the parent line is allowed or forbidden and they shall therefore be treated separately.

(a) Parent line allowed

If l_μ is the angular momentum (measured in units $h/2\pi$) of a state μ of electron 1, the well-known selection rules imply in this case that $l_\alpha-l_\beta=\pm1$. Similarly, in (6b) there will noticeably occur only states μ, for which $l_\mu-l_\beta=\pm1$. Both conditions together lead to the selection rule $l_\alpha-l_\mu=0,\ \pm2$. We may now split the matrix elements, occurring in (6b) into two parts, writing

$$v_{\alpha a,\ \mu b}=v'_{\alpha a,\ \mu b}+v''_{\alpha a,\ \mu b} \tag{7}$$

with
$$v'_{\alpha a,\ \mu b}=\int u_\alpha{}^*(1)u_a(2)v'(\mathbf{r}_1,\mathbf{r}_2)u_\mu(1)u_b(2)d\tau_1 d\tau_2 \tag{7a}$$

and
$$v''_{\alpha a,\ \mu b}=\int u_\alpha{}^*(1)u_a(2)v''(\mathbf{r}_1,\mathbf{r}_2)u_\mu(1)u_b(2)d\tau_1 d\tau_2, \tag{7b}$$

[8] Cf. e.g., G. Wentzel, *Handbuch der Physik*, 24, part 1, p. 743 f.f.

using for v' and v'' the expressions given in (2) and (3). Since (7a) contains the coordinates of 1 *linearly*, it leads only to a result different from zero, if $l_\alpha - l_\mu = \pm 1$. This condition contradicts the selection rule $l_\alpha - l_\mu = 0, \pm 2$, stated above and means that for the case of an allowed parent line, the terms (7a) will give *no* contribution to (6b). On the contrary, since v'' contains the coordinates of 1 in the *second* power, (7b) will generally be different from zero for $l_\alpha - l_\mu = 0, \pm 2$.

We can therefore write (6b) in the form

$$I_{\beta b}{}^{\alpha a} = \sum_\mu \frac{v''_{\alpha a,\ \mu b}}{E_\alpha + E_a - E_\mu - E_b} \int u_\mu^*(1) \exp(i\mathbf{k}\mathbf{r}_1)(\mathbf{n}, \operatorname{grad}_1) u_\beta(1) d\tau_1. \tag{8}$$

The energy differences $E_\alpha - E_\mu$ of inner atomic levels will be big, compared with the outer atomic difference $E_a - E_b$, so that we will get a considerable contribution to the sum (8) only from the term $\mu = \alpha$, which simplifies our expression to

$$I_{\mu b}{}^{\alpha a} = \frac{v''_{\alpha a,\ \alpha b}}{E_a - E_b} \int u_\alpha^*(1) \exp(i\mathbf{k}\mathbf{r}_1)(\mathbf{n}, \operatorname{grad}_1) u_\beta(1) d\tau_1. \tag{8a}$$

Comparing (8a) with (6a) we find finally for the intensity ratio of satellite to parent line

$$|I_{\beta b}{}^{\alpha a}|^2 / |I_\beta{}^\alpha|^2 = |v''_{\alpha a,\ \alpha b}|^2 / (E_a - E_b)^2. \tag{9}$$

In the following section we shall discuss this formula for the case of the Cu $K\alpha_3$ satellite.

(b) Parent line forbidden

We will consider here only the special case of a forbidden line, for which $l_\alpha - l_\beta = 0, \pm 2$, so that (6a) vanishes. The situation is here just the inverse of case (a); the condition $l_\mu - l_\beta = \pm 1$ which is still necessary for the nonvanishing terms in (6b) implies here $l_\alpha - l_\mu = \pm 1, \pm 3$, a selection rule, which is only compatible with the terms (7a) but not with (7b). We obtain therefore

$$I_{\beta b}{}^{\alpha a} = \sum_\mu \frac{v'_{\alpha a,\ \mu b}}{E_\alpha + E_a - E_\mu - E_b} \int u_\mu^*(1) \exp(i\mathbf{k}\mathbf{r}_1)(\mathbf{n}, \operatorname{grad}_1) u_\beta(1) d\tau_1. \tag{10}$$

The main difference between (10) and (8) has to be seen in the circumstance that here the term with $\mu = \alpha$ gives no contribution, since the average value of the coordinates of 1 in the state α vanishes. The sum has therefore to be extended over "intermediate" states μ of the electron 1, different from α. Now the exclusion-principle formulated in the antisymmetry of the zero order eigenfunction demands that only such states μ shall be taken as are not occupied by any other electron and we have to investigate what possibilities there are left for μ. One of them is that μ refers to one of the optical levels of the atom; but the corresponding terms in (10) will generally appear with such small numerators and such big denominators that their contribution is negligible. Another possibility is $\mu = \beta$. The state β has certainly to be supposed unoccupied since otherwise it could not be the final state for electron 1; however, for $\mu = \beta$ the integral in (10) vanishes. The only remaining possibility is that μ refers to the state a, left unoccupied by the transition of electron 2 from a to b. This term will give the main contribution to (10), if the orbit of state a lies in deeper regions of the atom than those of optical levels. This assumption can and shall be made for further simplifications; it is not in contradiction to the distinction of "inner" and "outer" electrons, introduced in the beginning of this section since this distinction demands only the smallness of the orbital dimensions of α, compared with those of a. Omitting in (10) all terms, except the one with $\mu = \alpha$, we find thus

$$I_{\beta b}{}^{\alpha a} = [v'_{\alpha a,\ a b}/(E_\alpha - E_b)] \int u_a^*(1) \exp i(\mathbf{k}\mathbf{r}_1)(\mathbf{n}, \operatorname{grad}_1) u_\beta(1) d\tau_1. \tag{11}$$

Instead of comparing the probability of such a double transition with the forbidden single transition $\alpha \rightarrow \beta$, it is more convenient to compare it with that of the single transition $a \rightarrow \beta$. Using (6a), we find for their ratio

$$R = |I_{\beta b}{}^{\alpha a}|^2 / |I_{\beta}{}^{a}|^2 = |v'_{\alpha a,\ ab}|^2 / (E_\alpha - E_b)^2. \tag{12}$$

In a paper, recently published with Ross,[7] we gave an illustration of case (b), applying to the continuum, observed on the long wavelength side of $K\beta_5$ of molybdenum. Here the final state b of the outer electron 2 has to be considered to lie in the continuous part of the energy spectrum, corresponding to an ejection of this electron. Instead of a well-defined satellite, we get then a continuous band; the separation of its short wavelength end from the parent line is given by the ionization energy of the ejected electron. Neglecting the binding forces, acting on the ejected electron (which is a good approximation except for the immediate neighborhood of the short wavelength limit of the continuum) we find from (12) for the relative intensity of the continuum lying within a frequency range $d\nu$:

$$dR = (8\pi m k_2 d\nu / h(I_\alpha + E)^2) \overline{|e^2 \int u_\alpha{}^*(1) u_a{}^*(2) [(\mathbf{r}_1 \mathbf{r}_2)/r_2{}^3] u_a(1) \exp i(\mathbf{k}_2 \mathbf{r}_2) d\tau_1 d\tau_2|^2}. \tag{13}$$

In this formula the horizontal line refers to the averaging over the different directions of the vector $\mathbf{k}_2$ with absolute value

$$k_2 = (2\pi/h)(2mE)^{\frac{1}{2}}.$$

$E = h\nu_{\alpha,\beta} - h\nu - I_a$ is the kinetic energy of the ejected electron with mass m, $\nu_{\alpha,\beta}$ the frequency of the forbidden parent line and I_α, I_a the ionization energies of the initial states of inner and outer electrons, respectively.

The details of the intensity distribution represented by (13) depend sensitively on the special shape of the eigenfunction $u_a(2)$. As general features, we may mention: vanishing for $E=0$ (short wavelength limit of the continuum) rapid approach of a maximum and slow falling off towards longer wavelengths.

The ratio of the total intensity of the continuum to that of the line $a \rightarrow \beta$ can be estimated to be of the order of magnitude

$$\int dR \cong (e^4/E_\alpha{}^2)(r_i/r_0{}^2)^2, \tag{14}$$

r_i and r_o being the radius of the initial orbits of inner and outer electrons, respectively.

3. Intensity of the Cu $K\alpha$ Satellite

The general formula (9) for the intensity ratio of a satellite to its strong parent line cannot be evaluated without further assumptions. We want to estimate its order of magnitude for the special case of the satellite $K\alpha_3$ of the Cu $K\alpha_1$ line, which has been carefully investigated by DuMond and Hoyt;[9] its separation from the parent line $K\alpha_1$ corresponds to an energy difference of about 35 e.v. The outer electronic configuration of Cu is of the type $(3d)^{10}\ (4s)^1$, the $4s$ electrons in the solid state being probably conduction electrons. After having removed one inner electron, the $3d$ electrons have to be compared with those of Zn, the element with the next higher atomic number; their ionization energy, the first ionization potential of the doubly ionized Zn equals 40 e.v.[10] Considering the $4s$ electrons in the metal as practically free, it seems therefore plausible to assume that Cu $K\alpha_3$ is due to a previous excitation of a $3d$ electron and emission of a $1s$ electron and a subsequent transition $2p,4s \rightarrow 1s,3d$.

As already indicated in the introduction, we want first to show that the simultaneous excitation of a $3d$ electron and a transition $1s \rightarrow \infty$ has a considerable probability; in fact, the expression

[9] J. W. M. DuMond and A. Hoyt, Phys. Rev. **36**, 799 (1930). The following considerations shall be regarded as an illustration of a possible double electron transition. That they cannot claim general validity is shown by the work of Coster and Thijssen on one of the K satellites of sulfur.

[10] Bacher and Goudsmit, *Atomic energy states*, page 525.

(9) has to be multiplied by this probability in order to obtain the true intensity ratio of satellite to parent line. Let $u_{b'}$ and u_b be the normalized eigenfunctions of one and the same $3d$ state in Cu and Zn, respectively. Then the probability that after having suddenly removed an inner electron, the electron will still be in its original $3d$ state, is obviously given by

$$1-\epsilon=|\int u_{b'}^*, u_b d\tau|^2.$$

ϵ is then the probability that the electron is *not* found in its original but in an excited state since all states with lower energy are occupied by other electrons. For the estimation of ϵ we assume that both states b' and b can be described by hydrogenic functions, but with different effective atomic numbers $Z^{*\prime}$ and Z'. We thus find for $l=Z$, $n=3$

$$\epsilon=1-[4Z^{*\prime}Z^*/(Z^{*\prime}+Z^*)^2].^7$$

Z^* and $Z^{*\prime}$ we choose such, that they account for the observed ionization energy of $3d$ electrons of Zn^{++} and Cu^+ respectively, the former being 40, the latter 20.2 e.v.[11] We obtain so

$$Z^*=3(40/13.5)^{\frac{1}{2}}=5.2, \quad Z^{*\prime}=3(20.2/13.5)^{\frac{1}{2}}=3.7$$

and $$\epsilon=0.2.$$

This means that for a specified one of the 10 $3d$ electrons there is a chance of about 1/5, that after having removed one inner electron we will find it in an excited state. Excluding the possibility that more than one of these electrons will be excitated, we have now to ask for the probability of having *any* one of them excited. Calling, for the moment, g the number of such equivalent electrons, we find for this probability

$$P=g\epsilon/(g-1)\epsilon+1$$

or with $g=10$, $\epsilon=0.2$, $P=5/7$. (15)

It is true that the assumptions which have led to this result, especially that of hydrogenic eigenfunctions, can give only rough approximations; nevertheless we may state that it is perfectly understandable that there is practical certainty for an outer excitation, the value (15) being rather close to unity and therefore only a satellite on the short wavelength side is observed. Of course we cannot exclude the possibility of a corresponding long wavelength satellite, but in any case we would expect it to be considerably weaker than the one on the short wavelength side.*

For the intensity ratio R of satellite to parent line, we have now

$$R=P|I_{\beta b}{}^{\alpha a}|^2/|I_\beta{}^\alpha|^2,$$

where in our case α stands for $(2p)$, β for $(1s)$, a for $(4s)$, b for $(3d)$. Since we only want to estimate the order of magnitude, we will leave out all factors of order of magnitude 1, and using (9), write R in the approximate form

$$R\leqq(e^4/(E_a-E_b)^2)[(r_i)^2/(r_0)^3]^2,$$

where r_i is of the order of magnitude of the radius of the $2p$ orbit, r_0 of the order of magnitude of the radius of either $4s$ or $3d$ of the doubly ionized Zn. From the corresponding ionization energies, we may assume

$$r_i\leqq a_0/8, \quad r_0\leqq a_0/2,$$

a_0 being the Bohr radius. Taking furthermore for E_b-E_a the energy, indicated by the separation from satellite to parent line, i.e., $E_b-E_a=35$ e.v. $\leqq 3I_0$ where I_0 is the ionization energy of hydrogen, we find approximately

$$R\leqq(1/8)^4/9(1/2)^6=1/576. \quad (16)$$

This result is only about a factor 3 times smaller than the observed ratio $R=1/180$, but it is naturally very unsure, because of the high power in which all possible errors appear. It shows, however, at least for the case of the Cu $K\alpha_3$ satellite, that the observed intensity lies entirely within the scope of the order of magnitude, theoretically to be expected and makes it plausible that here, indeed, we are faced with an emission by double electron transition.

[11] Reference 10, p. 180.

* If inner and outer excitation would *always* occur together, the satellite corresponding to the transition

$$2p(3d)^{10}\rightarrow 1s(3d)^9 4s$$

could of course not be observed, because the initial state would never be realized. One may object that nevertheless there should be a long wavelength satellite

$$2p(3d)^9\rightarrow 1s(3d)^8 4s.$$

It seems plausible, however, that the removal of a second (and even more so of a third, etc.) electron from the $3d$ level should occur with considerably smaller probability, so that this satellite should be expected to be quite weak. Besides it should not be exactly opposite to the long wavelength satellite discussed above.