

## Radiation Probabilities, Auger Effect and Energy Level Widths for Au(79)

E. G. RAMBERG\* AND F. K. RICHTMYER†  
*Cornell University, Ithaca, New York*

(Received April 7, 1937)

The theory of energy level widths developed by Weisskopf and Wigner and by Wentzel is applied to the calculation of the energy level widths of Au(79). Radiation and Auger transition probabilities are determined separately with the aid of numerically integrated nonrelativistic eigenfunctions, the latter being calculated for electrons moving in the Fermi-Thomas field of Tl(81)<sup>++</sup>. Sources of error are considered, the major one being the nonrelativistic treatment. The band width due to the interaction of electrons in different atoms in the crystal lattice does not add materially to the level width of the *O<sub>I</sub>* and lower states.

Except for the *K* state, the Auger contribution to the width exceeds that of the radiation transitions. Where the majority of the significant Auger effects have been calculated (*L<sub>I</sub>*, *M<sub>I</sub>*, *N<sub>I</sub>*) the total calculated width is found to be appreciably in excess of the observed width, but of the same order. The results confirm the view that the contributions of radiation transitions and Auger effects to the level widths of the initial and final states of the atom suffice to explain the magnitude of the widths of the x-ray lines emitted by the heavy elements.

### I. INTRODUCTION

WITHIN recent years improvements in experimental techniques and measurements made by use of the two-crystal spectrometer have made it possible to obtain dependable estimates of the true shape and widths of spectral lines in extended regions of the x-ray spectrum. It has been found (1) that the shape, or contour, of lines agrees well within experimental error<sup>1</sup> with that predicted by either the classical or the quantum theory of radiative processes; but (2) that x-ray lines are in general much wider than either theory predicts.

Classically,<sup>2</sup> an emitting atom is treated as a damped harmonic oscillator whose energy at time *t* is proportional to  $e^{-2\pi\Gamma t}$ . A Fourier analysis of the emitted wave train gives a spectral energy distribution,  $J(\nu)d\nu$ , as follows:

$$J(\nu)d\nu = \frac{\Gamma}{2\pi} \frac{d\nu}{(\nu_0 - \nu)^2 + (\Gamma/2)^2} \quad (1)$$

where  $\nu_0$  is the frequency of the undamped

oscillator and  $\Gamma$  is the full width of the contour at half-maximum intensity.

In quantum theory, it is assumed that the probability that in unit time an atom in state *A* may pass, at time *t*, to any other state is equal to  $2\pi\Gamma_A$ . The mean life of state *A* is then given by  $1/(2\pi\Gamma_A)$ . Weisskopf and Wigner<sup>3</sup> have shown by a wave-mechanical treatment, that on these assumptions the spectral intensity distribution in a spectral line resulting from transitions from state *A* to state *B* is given by (1) provided we put

$$\Gamma \equiv \Gamma_A + \Gamma_B, \quad h\nu_0 \equiv E_A - E_B = h\nu_{AB},$$

where  $1/(2\pi\Gamma_A)$  and  $1/(2\pi\Gamma_B)$  are the mean lives, and  $E_A$  and  $E_B$  the atomic energies of states *A* and *B*, respectively. True line width, therefore, is an atomic phenomenon and is determined by the mean lives of the initial and the final states of the emitting atoms.

The mean life of any atomic state is determined by two factors: (1) the probability that, in unit time, the atom may pass spontaneously from that state to a state of lower energy with the emission of radiation (radiation transition); and (2) that it may change to a new state without the emission of radiation, the energy freed by filling a vacancy in an inner electron shell being used to expel a less tightly bound electron (Auger effect). The present work was undertaken to determine the relative importance of the several radiation and Auger transitions for different states of

\* At present with Electronic Research Laboratory, RCA Manufacturing Company, Camden, N. J.

† This research was made possible by a grant from the American Philosophical Society, F. K. R.

<sup>1</sup> The troublesome instrumental correction due to the finite resolving power of the spectrometer, is in general small compared to the total width of lines. See Parratt, *Rev. Sci. Inst.* **6**, 387 (1935).

<sup>2</sup> For an outline of the classical and of the quantum theory of line widths, including references to original sources, see "The Widths of the *L*-Series Lines and of the Energy Levels of Au(79)," by F. K. Richtmyer, S. W. Barnes and E. Ramberg, *Phys. Rev.* **46**, 843 (1934), hereinafter referred to as RBR.

<sup>3</sup> V. Weisskopf and E. Wigner, *Zeits. f. Physik* **63**, 54 (1930).

excitation; and also to ascertain whether the observed width of x-ray spectral lines could be thus explained. Au(79) was chosen as the element to be studied, since the measurements of RBR on its  $L$  series lines furnish adequate experimental data for comparison with theory.

## II. DEFINITIONS AND GENERAL FORMULAS

According to the above mentioned theory of natural line widths proposed by Weisskopf and Wigner the energy distribution in a spectral line of frequency  $\nu_{AB}$ , corresponding to a transition from atomic state  $A$  to atomic state  $B$ , is given by

$$J_{AB}(\nu)d\nu = \frac{(\Gamma_A + \Gamma_B)d\nu/(2\pi)}{(\nu_{AB} - \nu)^2 + [(\Gamma_A + \Gamma_B)/2]^2}. \quad (1')$$

$(\Gamma_A + \Gamma_B)$  is the width at half-maximum (or simply "the width") of the line on a frequency scale.  $\Gamma_A$  and  $\Gamma_B$  individually represent, but for a factor  $1/(2\pi)$ , the sum of the probabilities of all spontaneous transitions from state  $A$  or  $B$  respectively to any other state and will be termed, for convenience, the frequency widths of the energy levels  $A$  and  $B$ :

$$\Gamma_A = \frac{1}{2\pi\tau_A} = \sum'_{E_C \leq E_A} (C)\gamma_{AC}, \quad (2)$$

$$\Gamma_B = \frac{1}{2\pi\tau_B} = \sum'_{E_D \leq E_B} (D)\gamma_{BD},$$

where  $\tau_A$  is the mean life of state  $A$ ; and  $2\pi\gamma_{AC}$  is the probability in unit time of a transition from state  $A$  to any state  $C$ .  $E_C$  and  $E_A$  represent, respectively, the atomic energies for state  $C$  and state  $A$ . The sign "<" under the sum refers to the radiation transitions; the sign "=" to the Auger jumps. In order to calculate the magnitude of  $\Gamma_A$  for any particular level  $A$  we substitute for  $\gamma_{AC}$  the known expression for the transition probabilities in the form of matrix elements of the coordinates and of the electronic interaction energies:<sup>4</sup>

<sup>4</sup>G. Wentzel, *Handbuch der Physik*, Vol. 24, part 1 (1931): p. 779 for the dipole component and p. 783 for the quadrupole component of the radiative transitions; p. 736 for the Auger effects.

$$\begin{aligned} \Gamma_A/R = & \sum_{E_C < E_A} (C) \frac{\alpha^3}{3} (\nu_{AC}/R)^3 \{ | (A | \sum_i x_i/a_0 | C) |^2 \\ & + | (A | \sum_i y_i/a_0 | C) |^2 + | (A | \sum_i z_i/a_0 | C) |^2 \\ & + \sum_{E_D < E_A} (D) \frac{\alpha^5}{240} (\nu_{AD}/R)^5 \{ | (A | \sum_i x_i^2/a_0^2 | D) |^2 \\ & + | (A | \sum_i y_i^2/a_0^2 | D) |^2 + | (A | \sum_i z_i^2/a_0^2 | D) |^2 \\ & + 3 | (A | \sum_i x_i y_i/a_0^2 | D) |^2 + 3 | (A | \sum_i y_i z_i/a_0^2 | D) |^2 \\ & + 3 | (A | \sum_i z_i x_i/a_0^2 | D) |^2 \\ & - (A | \sum_i x_i^2/a_0^2 | D) (A | \sum_i y_i^2/a_0^2 | D) \\ & - (A | \sum_i y_i^2/a_0^2 | D) (A | \sum_i z_i^2/a_0^2 | D) \\ & - (A | \sum_i z_i^2/a_0^2 | D) (A | \sum_i x_i^2/a_0^2 | D) \} \\ & + \sum'_{E_G = E_A} (G) 4\pi | (A | \sum_{i>k} a_0/r_{ik} | G) |^2, \quad (3) \end{aligned}$$

where  $(A | F | N) = \int \Psi_A^* F \Psi_N d\tau.$

$\Psi_A$  is the wave function of the atom in state  $A$ . The integration has to be carried out over the coordinates of all the atomic electrons. The first two terms in the expression (3) are the contributions to the level widths due to radiative transitions, dipole and quadrupole, respectively;<sup>5</sup> the last that due to Auger jumps;  $\alpha = 2\pi e^2/(ch)$  is the fine structure constant;  $a_0 = \hbar^2/(4\pi m e^2)$ , the radius of the Bohr orbit for normal hydrogen; and the subscripts  $i$  and  $j$  refer to the number of the atomic electrons.

The above formula is greatly simplified if we treat all of the electrons of the atom as moving in the same central field. We may then represent the atomic wave-function by a determinant<sup>6</sup> of

<sup>5</sup>The formula given assumes real wave functions.

<sup>6</sup>The sums of the squared absolute values of the matrix elements over the magnetic quantum numbers of states  $C$ ,  $D$  and  $G$  pertaining to given  $n_i$ ,  $l_i$ ,  $j_i$  are invariant under unitary transformations of the wave functions, so that this simplest form of an antisymmetrical wave function leads to the correct result.

individual electronic wave functions characterized by the quantum numbers  $n, l, j, m_j$ :

$$\Psi_A = \begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(z-1) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{A-1}(1) & \psi_{A-1}(2) & \cdots & \psi_{A-1}(z-1) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{A+1}(1) & \psi_{A+1}(2) & \cdots & \psi_{A+1}(z-1) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_z(1) & \psi_z(2) & \cdots & \psi_z(z-1) \end{vmatrix} / ((z-1)!)^{\frac{1}{2}}, \quad (4)$$

where  $\psi_i(1) = P_{l_i j_i m_i}(\vartheta_1, \varphi_1, \mu_1) f_i(r_1) / r_1$  (5)

and  $\int \psi_i(1) \psi_j(1) d\tau = \delta(i, j)$ . (6)

In greater detail the angular function (with spin) is given by<sup>7</sup>

$$P_{l_i m_i} = \{ \pm (l \pm m_i + \frac{1}{2})^{\frac{1}{2}} P_{l_i m_i - \frac{1}{2}}(\vartheta, \varphi) \delta(\frac{1}{2}, \mu) + (l \mp m_i + \frac{1}{2})^{\frac{1}{2}} P_{l_i m_i + \frac{1}{2}}(\vartheta, \varphi) \delta(-\frac{1}{2}, \mu) \} / (2l+1)^{\frac{1}{2}} \quad (7)$$

for  $j = l \pm \frac{1}{2}$ ,  $P_l^m$  being the associate Legendre function of order  $l$  and degree  $m$  normalized to 1.  $\mu$  indicates the spin of the electron. The angular function has the following property:

$$\sum_{\mu = \pm \frac{1}{2}} \int_0^{2\pi} \int_0^\pi P_{l_j m_j}^*(\vartheta, \varphi) P_{l_j' m_j'}(\vartheta, \varphi) \sin \vartheta d\vartheta d\varphi = \delta(l, j, m_j; l', j', m_j'). \quad (8)$$

If we substitute wave functions of the form (5) in the formula for the level width (3) we obtain:

$$\begin{aligned} \Gamma_A/R &= \sum_{E_C < E_A} (\alpha^3/3) (\nu_{AC}/R)^3 a(l_A j_A; l_C j_C) \\ &\times \left| \int_0^\infty f_A(r/a_0) f_C dr \right|^2 + \sum_{E_D < E_A} (\alpha^5/240) (\nu_{AD}/R)^5 \\ &\times b(l_A j_A; l_D j_D) \left| \int_0^\infty f_A(r/a_0)^2 f_D dr \right|^2 \\ &+ 4\pi \sum_{k, j, l_i} \sum_{\kappa, \kappa'} \{ c(l_k j_k, l_m j_m; l_i j_i, l_A j_A; \kappa \kappa') \\ &\quad E_i = -E_A + E_k + E_m \geq 0 \\ &\times (kmG^{*iA})(kmG^{\kappa' iA}) \quad (9) \\ &- d(l_k j_k, l_m j_m; l_i j_i, l_A j_A; \kappa \kappa') (kmG^{*iA})(kmG^{\kappa' A i}) \\ &+ e(l_k j_k, l_m j_m; l_i j_i, l_A j_A; \kappa \kappa') (kmG^{*A i})(kmG^{\kappa' iA}) \}. \end{aligned}$$

Here  $A$  refers to the initial vacancy;  $C, D, k$  and  $m$  to the vacancies in the several final states of the

atom; and  $i$  to the expelled electron in the case of an Auger transition. Furthermore

$$(kmG^{*iA}) = \int_0^\infty \int_0^\infty f_k(1) f_m(2) \times (\mathbf{a}_0 r_a^k / r_b^{k+1}) f_i(1) f_A(2) dr_1 dr_2 \quad (10)$$

with  $r_a = r_1, r_b = r_2$  for  $r_2 > r_1$ ,  
 $r_a = r_2, r_b = r_1$  for  $r_2 < r_1$ .

If we sum over the  $j$  values pertaining to a given value of  $l_C$  we find for the angular coefficients in the first sum

$$a(l_A; l_C) = \sum_{j_C} a(l_A, j_A; l_C, j_C) = (1 \pm 1/(2l_A + 1)) \delta(l_C, l_A \pm 1)/2. \quad (11)$$

Similarly, summing over  $j_D$  we find for

$$b(l_A; l_D) = \sum_{j_D} b(l_A, j_A; l_D, j_D)$$

the values given in Table I. To obtain the angular coefficients  $a$  and  $b$  for specific  $j$  values recourse must be had to the sum rules and the formulas of A. Rubinowicz<sup>8</sup> for relative quadrupole intensities.

The angular coefficients  $c, d$  and  $e$ , finally, may be evaluated for each special case by the formulas for integrals over three associated spherical harmonics given by Gaunt.<sup>9</sup> The number of terms in the last sum increases rapidly with the azimuthal quantum number of the initial vacancy,  $l_A$ ; for  $l_A = 0$  it reduces to three terms for given  $l$  and  $j$  values; for  $l_A = 1$  to eight terms. Thus for  $l_A = 0$  we can write for the contribution to  $\Gamma_A/R$  of the transition  $A \rightarrow k, m; i$ :

$$\begin{aligned} \Delta \Gamma_A/R &= 4\pi \{ c(l_m, l_m) (kmG^{l_m iA})^2 \\ &- d(l_m, l_k) (kmG^{l_m iA})(kmG^{l_k A i}) \\ &+ e(l_k, l_k) (kmG^{l_k A i})^2 \}. \quad (12) \end{aligned}$$

TABLE I. Values of the coefficients  $b(l_A; l_D)$ .

$l_A =$	0	1	2	3
$l_D$				
0			1/5	3/35
1		2/5		
2	1		2/7	
3		3/5		

<sup>8</sup> A. Rubinowicz, Zeits. f. Physik 65, 662-676 (1930).  
<sup>9</sup> J. A. Gaunt, Phil. Trans. Roy. Soc. London 228, 192 (1929); see also L. Pincherle, Nuovo Cimento 12, 85-86 (1935).

<sup>7</sup> J. H. Bartlett, Jr., Phys. Rev. 35, 230 (1930).

The arguments of the coefficients indicate the values of  $\kappa$  and  $\kappa'$  in (9). Similarly for  $l_A=1$  the contribution to the width is given by

$$\begin{aligned} \Delta\Gamma_A/R = & 4\pi \{ c(l_m-1, l_m-1)(kmG^{l_m-1}iA)^2 \\ & + c(l_m+1, l_m+1)(kmG^{l_m+1}iA)^2 \\ & - d(l_m-1, l_k-1)(kmG^{l_m-1}iA)(kmG^{l_k-1}Ai) \\ & - d(l_m-1, l_k+1)(kmG^{l_m-1}iA)(kmG^{l_k+1}Ai) \\ & - d(l_m+1, l_k-1)(kmG^{l_m+1}iA)(kmG^{l_k-1}Ai) \\ & - d(l_m+1, l_k+1)(kmG^{l_m+1}iA)(kmG^{l_k+1}Ai) \\ & + e(l_k-1, l_k-1)(kmG^{l_k-1}Ai)^2 \\ & + e(l_k+1, l_k+1)(kmG^{l_k+1}Ai)^2 \}. \end{aligned} \tag{13}$$

The calculated values of the coefficients for these two cases are tabulated in Tables II and III, respectively. Where two  $j$  values are indicated for a given state the coefficients pertaining to the separate  $j$  values have been added.

III. CALCULATION OF THE RADIAL WAVE FUNCTIONS AND MATRIX ELEMENTS

Having decided to make use of electronic wave functions calculated for a common central field it became necessary to determine what field might be most suitable. The Thomas-Fermi field for doubly ionized thallium,  $Tl^{++}(81)$ , was chosen since, for Auger electrons, it simulated most closely the field of a gold atom with two internal vacancies. For the most tightly bound electrons the error in the effective field is greatest. At the same time the fact that the atomic field itself is very strong makes this error relatively unimportant.

The Thomas-Fermi field for  $Tl^{++}(81)$  was obtained by numerical integration of the Thomas-Fermi equation, applying the boundary conditions for the ion prescribed by Sommerfeld.<sup>10</sup> The integration was performed inward, the ionic radius being adjusted until the boundary condition at the nucleus (the existence of a Coulomb field corresponding to a nuclear charge 81) was fulfilled. The effective ionic radius was found to be  $4.61 a_0$ .

With the potential field  $V$  thus determined the wave functions of all the electrons of the gold

<sup>10</sup> A. Sommerfeld, *Zeits. f. Physik* **78**, 283-308 (1932), Eqs. (1) to (3a).

TABLE II. Angular coefficients of Auger effect contributions to level width for  $l_A=0$ .

$l_k$	$j_k$	$l_m$	$j_m$	$l_i$	$\kappa$	$\kappa'$	$c(l_m, l_m)$	$d(l_m, l_k)$	$e(l_k, l_k)$
0	1/2	0	1/2	0	0	0	1	1	1
1	3/2	0	1/2	1	0	1	4	4/3	4/9
	1/2		1/2				2	2/3	2/9
1	3/2	1	3/2	0	1	1	8/27	4/27	8/27
	1/2		3/2				4/27	8/27	4/27
	3/2		1/2				4/27	8/27	4/27
	1/2		1/2				2/27	-2/27	2/27
1	3/2	1	3/2	2	1	1	16/27	20/27	16/27
	1/2		3/2				8/27	4/27	8/27
	3/2		1/2				8/27	4/27	8/27
	1/2		1/2				4/27	8/27	4/27
2	5/2	0	1/2	2	0	2	6	6/5	6/25
	3/2		1/2				4	4/5	4/25
2	5/2	1	3/2	1	1	2	24/45	12/75	24/125
	3/2		3/2				16/45	28/75	16/125
	5/2		1/2				12/45	24/75	12/125
	3/2		1/2				8/45	-4/75	8/125
2	5/2	1	3/2	3	1	2	12/15	16/25	36/125
	3/2		3/2				8/15	4/25	24/125
	5/2		1/2				6/15	2/25	18/125
	3/2		1/2				4/15	8/25	12/125
2	5/2	2	5/2	0	2	2	18/125	6/125	18/125
	3/2		5/2				12/125	24/125	12/125
	5/2		3/2				12/125	24/125	12/125
	3/2		3/2				8/125	-4/125	8/125
2	5/2	2	5/2	2	2	2	36/175	24/175	36/175
	3/2		5/2				24/175	36/175	24/175
	5/2		3/2				24/175	36/175	24/175
	3/2		3/2				16/175	4/175	16/175
2	5/2	2	5/2	4	2	2	324/875	500/875	324/875
	3/2		5/2				216/875	56/875	216/875
	5/2		3/2				216/875	56/875	216/875
	3/2		3/2				144/875	288/875	144/875
3	7/2	0	1/2	3	0	3	8	8/7	8/49
	5/2		1/2				6	6/7	6/49
3	7/2	1	3/2	2	1	3	16/21	12/49	48/343
	5/2		3/2				4/7	20/49	36/343
	7/2		1/2				8/21	16/49	24/343
	5/2		1/2				2/7	-6/343	18/343
3	7/2	1	3/2	4	1	3	64/63	88/63	64/343
	5/2		3/2				16/21	8/49	48/343
	7/2		1/2				32/63	8/147	32/343
	5/2		1/2				8/21	16/49	24/343
3	7/2	2	5/2	1	2	3	216/875	72/1225	216/1715
	5/2		5/2				162/875	306/1225	162/1715
	7/2		3/2				144/875	288/1225	144/1715
	5/2		3/2				108/875	-36/1225	108/1715
3	7/2	2	5/2	3	2	3	80/525	32/125	80/245
	5/2		5/2				24/125	88/525	24/245
	7/2		3/2				80/525	64/375	64/735
	5/2		3/2				16/125	32/525	16/245
3	7/2	2	5/2	5	2	3	16/35	24/49	80/343
	5/2		5/2				12/35	4/49	60/343
	7/2		3/2				32/105	8/147	160/1029
	5/2		3/2				8/35	16/49	40/343
3	7/2	3	7/2	0	3	3	32/343	8/343	32/343
	5/2		7/2				24/343	48/343	24/343
	7/2		5/2				24/343	48/343	24/343
	5/2		5/2				18/343	-6/343	18/343
3	7/2	3	7/2	2	3	3	24/343	0	24/343
	5/2		7/2				32/343	56/343	32/343
	7/2		5/2				32/343	56/343	32/343
	5/2		5/2				128/1029	56/1029	128/1029
3	7/2	3	7/2	4	3	3	576/3773	72/539	576/3773
	5/2		7/2				432/3773	72/539	432/3773
	7/2		5/2				432/3773	72/539	432/3773
	5/2		5/2				324/3773	36/539	324/3773
3	7/2	3	7/2	6	3	3	3200/11319	5000/11319	3200/11319
	5/2		7/2				800/3773	200/3773	800/3773
	7/2		5/2				800/3773	200/3773	800/3773
	5/2		5/2				600/3773	1200/3773	600/3773

atom ( $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 6s$ ) were calculated by integrating the equation

$$(d^2/dr^2 + E + 2V - l(l+1)/r^2)f = 0, \tag{14}$$

the energy parameter  $E$  being adjusted so as to satisfy the boundary conditions, in the manner suggested by Hartree.<sup>11</sup> In addition continuous

<sup>11</sup> D. R. Hartree, *Proc. Camb. Phil. Soc.* **24**, 89 (1928).

wave functions (with positive values for  $E$ , corresponding to the kinetic energy of the ejected Auger electron) were calculated from the differential equation and normalized by comparison with the asymptotic form of the wave function given by Kramers:<sup>12</sup>

$$f = (2/\pi)^{1/2} (E + 2V - l(l+1)/r^2)^{-1/2} \times \cos \left\{ \int_R^r (E + 2V(\rho) - l(l+1)/\rho^2)^{1/2} d\rho \right\}. \quad (15)$$

The lower limit of the integral was chosen so as

<sup>12</sup> H. A. Kramers, Zeits. f. Physik 39, 828 (1926).

to obtain coincidence of the zero points of the numerically integrated function and those of the asymptotic form. From a certain value of  $r$  on, i.e., where the variation of

$$(E + 2V - l(l+1)/r^2)^{-1/2}$$

was slow compared to that of the cosine, it proved to be convenient and sufficiently accurate to calculate the wave function from this asymptotic expression.

The energy parameter of the Auger electron was set equal to the difference between the measured x-ray term value of the initial vacancy

TABLE III. Angular coefficients of Auger-effect contributions to level width for  $l_A=1$ .

$j_A$	$l_k$	$j_k$	$l_m$	$j_m$	$l_i$	$c(l_m-1, l_m-1)$	$c(l_m+1, l_m+1)$	$d(l_m-1, l_k-1)$	$d(l_m-1, l_k+1)$	$d(l_m+1, l_k-1)$	$d(l_m+1, l_k+1)$	$e(l_k-1, l_k-1)$	$e(l_k+1, l_k+1)$
3/2	0	1/2	1	3/2	0	2			2/3				4/27
1/2		1/2		1/2									2/27
		1/2		3/2									4/27
		1/2		1/2		2			2/3				2/27
3/2	0	1/2	1	3/2	2		2/25					2/15	8/27
1/2		1/2		1/2			2/25					2/15	4/27
		1/2		3/2			4/25					4/15	8/27
		1/2		1/2								4/15	4/27
1/2	1	3/2	1	3/2	1		16/125				4/125	4	16/125
		1/2		3/2			8/125					4	8/125
		3/2		1/2		4			4/5	4/5		2	8/125
		1/2		1/2		2							24/125
1/2	1	3/2	1	3/2	3		24/125	2			36/125		24/125
		1/2		3/2			12/125						12/125
		3/2		1/2			0						0
		1/2		1/2									12/125
1/2	0	1/2	2	5/2	1								4/15
		1/2		3/2			6/49						32/105
1/2, 3/2	0	1/2	1	1/2, 3/2	0	2			2/3				2/9
					2		4/25						4/9
1/2, 3/2	1	1/2, 3/2	1	1/2, 3/2	1	6	24/125	2	4/5	4/5	4/125	6	24/125
					3		36/125				36/125		36/125
1/2, 3/2	2	3/2, 5/2	1	1/2, 3/2	0		4/25				4/15	4/9	54/343
					2	10	8/35	4/3	6/7	4/15		8/9	72/343
					4		72/175				12/245		72/343
1/2, 3/2	3	5/2, 7/2	1	1/2, 3/2	1		36/125			36/125		36/125	32/243
					3	14	112/375	6/5	8/9	24/125	10/189	54/125	40/243
					5		8/15				8/27		
1/2, 3/2	0	1/2	2	3/2, 5/2	1	4/9			4/9				4/9
					3		6/49						2/3
1/2, 3/2	2	3/2, 5/2	2	3/2, 5/2	1	8/9	54/343	4/35	12/35	12/35	18/1715	8/9	54/343
					3	4/3	8/49	4/5	8/35	8/35	48/735	4/3	8/49
					5		100/343				100/343		100/343
1/2, 3/2	3	5/2, 7/2	2	3/2, 5/2	0		6/49			6/35		6/25	80/567
					2	4/3	8/49	4/35	10/63	64/343	4/441	60/49	800/6237
					4	16/9	108/539	24/35	40/189	36/245	40/539	108/175	220/1053
					6		220/637				220/819		

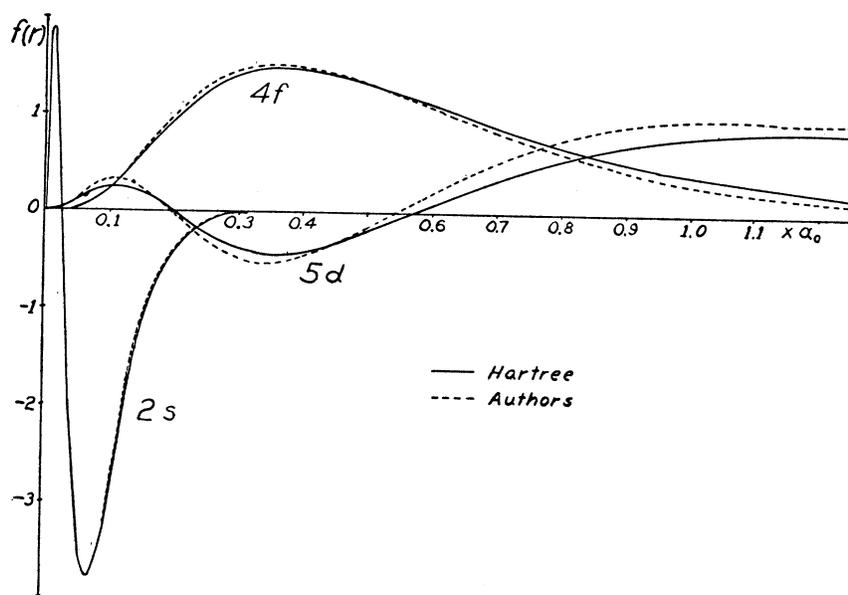


FIG. 1. Comparison of Hartree's functions for  $\text{Hg}^{++}$  with the authors' calculations.

for Au and the sum of the term value for the inner final vacancy for Au and that for the outer final vacancy for the next higher element, Hg. Since the value of the interaction matrix elements is in general not very sensitive to small changes in the energy parameter of the continuous function, only a limited number of continuous wave functions was calculated for a given azimuthal quantum number and that one was used whose energy parameter was closest to the prescribed value, as shown in Table V. In calculating the contribution to the width of the radiative transitions the actual line frequencies were substituted in the coefficients of the coordinate matrix elements (Eq. 9) in preference to the differences between the calculated energy parameters.

#### IV. SOURCES OF ERROR

Before giving the results of the calculations it is pertinent to summarize the principal sources of error. Perhaps the major defect, especially influential in the case of the radiation widths of the deepest energy levels, lies in the fact that the treatment given is nonrelativistic. Added to this is the practically unavoidable approximation that all the electrons move in a common central field. A comparison with Hartree's functions<sup>13</sup> for

<sup>13</sup> D. R. Hartree and W. Hartree, Proc. Roy. Soc. London **A149**, 210 (1935).

$\text{Hg}^{++}$  in Fig. 1 makes it likely that the use of a common statistical field for all of the electron functions is not a major source of error.

For transitions involving the outermost levels the circumstance that in our observations we are dealing with atoms bound in a crystal lattice rather than with free atoms should lead to appreciable discrepancies owing to the modification of the electronic wave functions by the fields of the neighboring atoms. The widths of the electronic energy bands in the metal themselves are, it is true, negligible. Taking into account the twelve nearest neighbors of any one atom in a face-centered cubic structure, the width of the energy band becomes equal to 12 times the exchange integral  $A$  where<sup>14</sup>

$$A = \int \psi_0^*(\mathbf{r} - \mathbf{N})(V(\mathbf{r}) - U(\mathbf{r}))\psi_0(\mathbf{r})d\tau. \quad (16)$$

Here  $\mathbf{r}$  is the coordinate vector;  $\mathbf{N}$  the radius vector from the origin of  $r$  (the nucleus of the atom considered) to one of the nearest neighbors; and  $V(\mathbf{r}) - U(\mathbf{r})$  the difference between the lattice potential and that of the free atom. We can obtain an estimate of  $A$  by replacing the difference  $V(\mathbf{r}) - U(\mathbf{r})$  simply by  $U(\mathbf{r})$ . We then find

<sup>14</sup> A. Sommerfeld and H. Bethe, *Handbuch der Physik*, Vol. 24, part 2 (1933), p. 397.

for the width of the energy band of the 5s electrons of Au(79):

$$12A = 0.002 \text{ Rydberg (0.03 volt)}, \quad (17)$$

which is negligible compared with the observed line and level widths.

V. RESULTS FOR THE RADIATION TRANSITION PROBABILITIES

In Table IV are collected the calculated contributions  $\Delta\Gamma_R$  of the various radiation transitions to the energy widths  $\Gamma_R$  of the several energy levels of gold, the unit for  $\Gamma_R$  and  $\Delta\Gamma_R$  being the electron volt, corresponding to

$$(600\pi^2 m e^3 / h^2) \Gamma / R = 13.54 \Gamma / R.$$

For comparison, there are given in parentheses the relative transition probabilities deduced from the measurements by A. Jönsson,<sup>15</sup> Duane and

<sup>15</sup> A. Jönsson, Zeits. f. Physik 36, 426 (1926).

Stenström<sup>16</sup> and others reported by Compton and Allison.<sup>17</sup> In every case the probability of the strongest transition to a given level has been set equal to the calculated value and is indicated by a dash in parenthesis. It is seen that there is agreement between the present calculations and experiment as far as order of magnitude of the relative transition probabilities is concerned. It is equally evident that, except for the K level, the radiation widths of the levels are materially smaller than the observed widths, tabulated at the bottom of the table. These latter data are taken from RBR, with the exception of that for the K level which was extrapolated from the measurements of Richtmyer and Barnes<sup>18</sup> for W(74) assuming proportionality of the width with  $Z^4$ .

<sup>16</sup> Duane and Stenström, Proc. Nat. Acad. Sci. 6, 477 (1920).

<sup>17</sup> X-Rays in Theory and Experiment, p. 645.

<sup>18</sup> F. K. Richtmyer and S. W. Barnes, Phys. Rev. 46, 352 (1934).

TABLE IV. Relative probabilities of radiation transitions.\*

INITIAL VACANCY	K	L <sub>I</sub>	L <sub>II</sub>	L <sub>III</sub>	M <sub>I</sub>	M <sub>II</sub>	M <sub>III</sub>	M <sub>IV</sub>	M <sub>V</sub>	N <sub>I</sub>	N <sub>II</sub>	N <sub>III</sub>	N <sub>IV</sub>	N <sub>V</sub>	N <sub>VI</sub>	N <sub>VII</sub>
Final Vacancy	A = 5942 B = 5597	1057 934	1011.4 896.8	877.7 221.8	252.2	231.8	201.9	168.6	162.2	55.8	47.3	39.9	25.8	24.5	6.2	5.8 ← A 11.95 ← B
L <sub>II</sub>	16.63	0.0003														
L <sub>III</sub>	36.0	.0014														
M <sub>I</sub>			0.048 (.078)	0.027 (.050)												
M <sub>II</sub>	3.44	.41 (.57)			0.0002											
M <sub>III</sub>	6.98	.92 (-)	.003	.001	.0058											
M <sub>IV</sub>	.11	.020 (.007)	2.328 (-)	.138 (.145)		0.0081	0.0001									
M <sub>V</sub>	.17	.031 (.013)		1.283 (-)			.0018									
N <sub>I</sub>			.012	.008 (.015)		.0066	.0038									
N <sub>II</sub>	.83	.11 (.14)			.0186					0.0001						
N <sub>III</sub>	1.66	.22 (.19)			.0414	.0001		0.0003	0.0015	.0008						
N <sub>IV</sub>	.03		.465 (.429)	.030	.0001	.0646	.0040	.0012			0.00222	0.00006				
N <sub>V</sub>	.04	.01		.272 (.253)			.0371					.00073				
N <sub>VI</sub>			.003			.0007	.0004	.0706	.0030				0.00145	0.00006		
N <sub>VII</sub>				.001			.0004		.0600							.00119
O <sub>I</sub>			.003	.002 (.002)		.0015	.0009				.00050	.00027				
O <sub>II</sub>	.16	.02			.0040			.0002		.0006			.00014	.00001		
O <sub>III</sub>	.32	.04			.0081				.0003	.0011				.00011		
O <sub>IV</sub>			.051 (.041)	.003		.0082	.0005				.00054	.00003			0.00002	0.000001
O <sub>V</sub>				.030 (.013)			.0049					.00029				.000015
P <sub>I</sub>			.000	.000		.0002	.0001				.00006	.00003				
Total Radiation Width	66.38	1.78	2.913	1.796	.0782	.0900	.0536	.0723	.0648	.0026	.00332	.00141	.00159	.00137	.00002	.00002
Observed Width (RBR)	54.	8.7	3.7	4.4	15.5	10.7	12.1	4.2	3.5	11.7	8.5	6.5	6.8	5.9		5.4

\* At the top of the table line A gives the observed term value of the initial ionized state; and line B gives the calculated energy parameter—both in Ry. The data in the body of the table give, in electron volts, the computed contributions  $\Delta\Gamma_R$  to the width of the initial state arising from the several radiation transitions. The summation of each column gives, at the bottom of the table, the total computed radiation width  $\Gamma_R$  of the state. For comparison there are given the observed widths as reported by RBR.

TABLE V. Contribution of the Auger effect to the level widths.

INITIAL VACANCY	FINAL VACANCIES		EJECTED ELECTRON			CONTRIBUTION TO WIDTH		
			$l_i$	$E_{iRy}$ calc.	$E_{iRy}$ used	Present Calc. Ev.	With Hydrogen Functions <sup>21</sup>	
<i>K</i>	<i>L</i> <sub>I</sub>	<i>L</i> <sub>I</sub>	0	3785.6	3729.5	0.055	0.068	
		<i>L</i> <sub>II, III</sub>	1	3831.6 3974.1	3766.5	.193	.239	
	<i>L</i> <sub>II, III</sub>	<i>L</i> <sub>II, III</sub>	0	3877.4 4019.9	3803.5	.039	.051	
			2	4155.8	3803.5	.485	.610	
	Auger width contribution						> .772	
Radiation width contribution						66.38		
Calculated width of <i>K</i> level						> 67.15		
Observed width of <i>K</i> level						54		
<i>L</i> <sub>I</sub>	<i>L</i> <sub>III</sub>	<i>M</i> <sub>IV, V</sub>	1	3.7 10.5	6.97	.827		
			3		6.97	7.77		
			1	120.5	152.4	.147		
	<i>L</i> <sub>II</sub>	<i>N</i> <sub>III</sub>	0	3.4	5.35	.066		
			2		5.35	.130		
	<i>L</i> <sub>III</sub>	<i>N</i> <sub>II, III</sub>	0	129.3 137.1	130.0	.188		
			2		130.0	.047		
	<i>L</i> <sub>II</sub>	<i>N</i> <sub>IV, V</sub>	1	17.9 19.4	6.97	.200		
			3		6.97	.023		
	<i>L</i> <sub>III</sub>	<i>N</i> <sub>IV, V</sub>	1	151.6 153.1	152.4	.172		
			3		152.4	.758		
	<i>L</i> <sub>III</sub>	<i>N</i> <sub>VI, VII</sub>	2	171.9 172.3	197.9	.005		
			4		197.9	.698		
	<i>L</i> <sub>II</sub>	<i>N</i> <sub>VI, VII</sub>	2	38.2 38.6	25.05	.015		
			4			.555		
	<i>L</i> <sub>I</sub>	<i>L</i> <sub>II</sub>	<i>O</i> <sub>I</sub>	1	37.1	27.98	.047	
				1	170.8	175.0	.032	
		<i>L</i> <sub>III</sub>	<i>O</i> <sub>I</sub>	0	41.0	30.46	.042	
				2		30.46	.046	
		<i>L</i> <sub>III</sub>	<i>O</i> <sub>II, III</sub>	0	174.6	197.9	.015	
2					197.9	.001		
<i>L</i> <sub>II</sub>		<i>O</i> <sub>IV, V</sub>	1	45.3	34.46	.024		
			3		34.46	.002		
<i>L</i> <sub>III</sub>		<i>O</i> <sub>IV, V</sub>	1	179.0	175.0	.014		
			3		175.0	.090		
Auger width contribution						> 11.91		
Radiation width contribution						1.78		
Calculated width of <i>L</i> <sub>I</sub> level						> 13.69		
Observed width of <i>L</i> <sub>I</sub> level						8.7		
<i>M</i> <sub>I</sub>	<i>M</i> <sub>III</sub>	<i>N</i> <sub>II</sub>	0	0.2	5.35	.098		
			2		5.35	.466		
	<i>M</i> <sub>III</sub>	<i>N</i> <sub>III</sub>	0	8.0	10.76	.397		
			2		10.76	.668		
	<i>M</i> <sub>III</sub>	<i>N</i> <sub>IV, V</sub>	1	22.5 24.0	24.0	.817		
			3		24.0	.249		
	<i>M</i> <sub>II</sub>	<i>N</i> <sub>VI, VII</sub>	2	12.9 13.3	10.76	.496		
			4		19.17	.365		
	<i>M</i> <sub>III</sub>	<i>N</i> <sub>VI, VII</sub>	2	42.8 43.2	46.66	.490		
			4		46.66	.829		
	<i>M</i> <sub>II</sub>	<i>O</i> <sub>I</sub>	1	11.8	8.28	.207		
			1	41.7	42.66	.154		
	<i>M</i> <sub>II</sub>	<i>O</i> <sub>II, III</sub>	0	15.7	10.76	.120		
			2		10.76	.433		

TABLE V.—Continued.

INITIAL VACANCY	FINAL VACANCIES		EJECTED ELECTRON			CONTRIBUTION TO WIDTH	
			$l_i$	$E_{iRy}$ calc.	$E_{iRy}$ used	Present Calc. Ev.	With Hydrogen Functions <sup>21</sup>
$M_I$	$M_{III}$	$O_{II, III}$	0	45.6	40.18	.101	
			2		40.18	.257	
	$M_{II}$	$O_{IV, V}$	1	20.0	14.76	.123	
			3		14.76	.331	
			1	49.9	42.66	.149	
	$M_{III}$	$O_{IV, V}$	3		42.66	.089	
			1	20.4	15.965	.013	
			2	24.7	25.05	.670	
	$M_{IV, V}$	$N_{II, III}$	1	31.1			
			1	33.5	42.66	.162	
			3	41.3			
	$M_{IV, V}$	$N_{IV, V}$	3	39.9	42.66	.098	
			0	47.7			
			0	55.8	55.0	.095	
	$M_{IV, V}$	$N_{VI, VII}$	2	57.3			
			2	62.2	60.0	.148	
			4	63.7	60.0	.726	
	$M_{IV, V}$	$N_{VI, VII}$	1	76.1	80.0	.048	
			3	76.5			
			3	82.5	80.0	.426	
	$M_{IV, V}$	$O_I$	5	82.9			
			2	75.0	80.0	.451	
			2	81.4	85.0	.112	
	$M_{IV, V}$	$O_{II, III}$	1	78.9	80.0	.028	
			3	85.3			
			3		80.0	.016	
	$M_{IV, V}$	$O_{IV, V}$	0	83.2	85.0	.013	
			2	89.6			
2				85.0	.020		
$N_{VI, VII}$	$N_{VI, VII}$	4		85.0	.077		
		0	238.5	197.9	.003		
		0	238.9				
$M_{II}$	$M_V$	$N_I$	2	239.3	197.9	.007	
			4		197.9	.125	
			6		197.9	.157	
Auger width contribution						> 10.234	
Radiation width contribution						.078	
Calculated width of $M_I$ level						> 10.31	
Observed width of $M_I$ level						15.5	
$M_{II}$	$M_V$	$N_I$	1	0.9	1.87	.048	
			3		1.87	.046	
	$M_{III}$	$O_I$	0	11.5	10.76	.005	
			2		10.76	.978	
			1	15.4	14.76	.760	
	$M_{III}$	$O_{II, III}$	3		14.76	.034	
			0	3.3	10.76	.562	
			2	11.1			
	$M_{IV, V}$	$N_{II, III}$	2	9.7	10.76	1.767	
			4	17.5			
			4		19.17	.023	
	$M_{IV, V}$	$N_{IV, V}$	1	25.6	37.25	.728	
			3	27.1			
			3	32.0	37.25	.040	
	$M_{IV, V}$	$N_{VI, VII}$	5	33.5			
			0	45.9	37.25	.005	
0			46.3	55.0	.002		
$M_{IV, V}$	$N_{VI, VII}$	2	52.3	46.66	.440		
		4	52.7				
		4		46.66	6.05		
		6		46.66	.001		

TABLE V—Continued.

INITIAL VACANCY	FINAL VACANCIES		EJECTED ELECTRON			CONTRIBUTION TO WIDTH	
			$l_i$	$E_{iRy}$ calc.	$E_{iRy}$ used	Present Calc. Ev.	With Hydrogen Functions <sup>21</sup>
				Auger width contribution		>11.49	
				Radiation width contribution		.09	
				Calculated width of $M_{II}$ level		>11.58	
				Observed width of $M_{II}$ level		10.7	
$M_{III}$	$M_{IV, V}$	$N_{VI, VII}$	0	16.0	19.95	.011	
				16.4			
			2	22.4	19.95	.031	
				22.8			
			4		19.95	4.41	
			6		19.95	.000	
				Auger width contribution		>4.45	
				Radiation width contribution		.05	
				Calculated width of $M_{III}$ level		>4.50	
				Observed width of $M_{III}$ level		12.1	
$N_I$	$N_{II, III}$	$N_{VI, VII}$	2	1.0	5.35	.296	
				1.4			
			4	8.4	5.35	2.451	
				8.8			
	$N_{III}$	$O_I$	1	7.3	6.97	.357	
	$N_{II}$	$O_{II, III}$	0	3.8	5.35	.107	
			2		5.35	1.091	
	$N_{III}$	$O_{II, III}$	0	11.2	10.76	.196	
			2		10.76	1.331	
	$N_{II}$	$O_{IV, V}$	1	8.1	6.97	.135	
			3		6.97	2.128	
	$N_{III}$	$O_{IV, V}$	1	15.5	14.76	.140	
			3		14.76	1.565	
	$N_{IV, V}$	$N_{IV, V}$	0	2.2	5.35	.016	
				3.7			
			2		5.35	.055	
			4		5.35	.122	
	$N_{IV, V}$	$N_{VI, VII}$	1	22.5	24.0	.005	
				22.9			
			3	23.8	24.0	.049	
				24.2			
			5		24.0	.458	
	$N_{IV, V}$	$O_I$	2	21.4	25.05	.495	
				22.7			
	$N_{IV, V}$	$O_{II, III}$	1	25.3	24.0	.095	
				26.6			
			3		24.0	.314	
	$N_{IV, V}$	$O_{IV, V}$	0	29.6	30.46	.018	
				30.9			
			2		30.46	.051	
			4		25.05	.038	
	$N_{VI, VII}$	$N_{VI, VII}$	0	42.1	40.18	.00004	
				42.5			
			2		40.18	.00002	
			4		46.66	1.156	
			6		46.66	.129	
	$N_{VI, VII}$	$O_I$	3	41.2	42.66	.463	
	$N_{VI, VII}$	$O_{II, III}$	2	45.1	46.66	.034	
			4		46.66	.251	
	$N_{VI, VII}$	$O_{IV, V}$	1	49.4	42.66	.009	
			3		42.66	.011	
			5		37.25	.035	
				Auger width contribution		>13.601	
				Radiation width contribution		.003	
				Calculated width of $N_I$ level		>13.60	
				Observed width of $N_I$ level		11.7	

TABLE VI. Comparison of Pincherle's computed values of widths of  $L$  levels with the observed values of RBR. Widths are given in electron volts.

LEVEL	PINCHERLE'S COMPUTED WIDTHS			OBSERVED BY RBR	AUTHORS' VALUE FROM TABLE V
	Radiation	Auger	Total		
$L_I$	1.0	5.5	6.5	8.7	13.7
$L_{II}$	0.9	2.2	3.1	3.7	—
$L_{III}$	1.6	2.6	4.2	4.4	—

## VI. RESULTS FOR THE AUGER EFFECT PROBABILITIES

Owing to the rapidly increasing complexity, mentioned in Section II, of the calculation with increasing azimuthal quantum number of the initial vacancy, extensive calculations have been made only for the  $s$  states,  $L_I$ ,  $M_I$  and  $N_I$  in particular. For the  $K$  and  $M_{II, III}$  levels the contributions of only a few Auger effects were calculated which, owing to the relative closeness of the coupling of the participating electrons as well as the low velocity of the ejected electron, could be expected to be relatively probable. In Table V are given in the several columns, the level symbols of the initial vacancies, those for the two final vacancies, the azimuthal quantum number characterizing the state of the ejected Auger electron, its correct energy in Rydbergs,<sup>19</sup> the energy parameter of the continuous wave function used in the calculation, and finally the calculated contribution to the width in electron volts. All the calculated Auger contributions for a given initial state are added together and, augmented by the radiation width given in Table IV, are compared with the experimental data of RBR.

## VII. DISCUSSION AND COMPARISON WITH EARLIER WORK

An inspection of Table V reveals that the Auger effect is responsible for the great discrepancy between the observed level widths and the calculated radiation widths. The credit for first suggesting that the Auger effect is primarily

<sup>19</sup> These values have been determined with the aid of the tables of term values in M. Siegbahn, *Spektroskopie der Röntgenstrahlen* (Springer, 1932).

responsible for this discrepancy and for applying Wentzel's<sup>20</sup> considerations regarding the variation of the Auger-effect probabilities with atomic number belongs to L. Pincherle.<sup>21</sup> In a later paper<sup>22</sup> the same writer has given numerous Auger effect probabilities for initial vacancies in the  $K$ ,  $L_I$  and  $L_{II, III}$  shells computed with hydrogenic wave functions without screening; in this approximation the probability of a given Auger transition becomes independent of the nuclear charge of the emitting element. Values thus obtained are given for comparison in the last column of Table V in the case of the  $K$  shell Auger effects. In a final paper, on the intensity of the  $L$  lines of gold,<sup>23</sup> Pincherle examines the factors determining the observed line intensities making use of radiation widths calculated with relativistic wave functions and the previously reported Auger transition probabilities. He compares the results with measurements of Jönsson<sup>24</sup> and RBR and concludes that the agreement between theory and experiment is satisfactory. Pincherle's computed values are shown in Table VI along with the observed values of RBR and the value for  $L_I$  from Table V. Pincherle's values for total width are smaller than the observed values of RBR; the reverse is the case throughout in the present calculations.

A further treatment of the Auger effect, for silver with the initial vacancy in the  $K$  shell, has been given by E. H. S. Burhop.<sup>25</sup> Burhop uses hydrogenic wave functions with effective nuclear charges determined by Slater.<sup>26</sup> The calculations are carried out rigorously for the cases in which the two final vacancies are in the  $L$  shell. The

<sup>20</sup> G. Wentzel, *Zeits. f. Physik* **43**, 524 (1927).

<sup>21</sup> L. Pincherle, *Atti Accad. Lincei* (Ser. VI) **20**, 29–35 (1934). Pincherle's papers did not come to the attention of the authors until the calculations here reported were practically completed. The present work, however, does not involve a duplication of Pincherle's calculations, since the latter obtained Auger effect probabilities for the  $K$  and  $L$  shells only. His calculations furthermore were carried out by means of hydrogenic wave functions, while the present ones are based on wave functions calculated from a statistical field approximating the real field of the gold atom.

<sup>22</sup> L. Pincherle, *Nuovo Cimento* (N.S.) **12**, 81–92 (1935).

<sup>23</sup> L. Pincherle, *Nuovo Cimento* (N.S.) **12**, 162–170 (1935); *Physica* **2**, 596–605 (1935).

<sup>24</sup> A. Jönsson, *Zeits. f. Physik* **36**, 426 (1926).

<sup>25</sup> E. H. S. Burhop, *Proc. Roy. Soc. London* **A148**, 272 (1935).

<sup>26</sup> J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

remaining  $K$  Auger effect probabilities are calculated making use of a plane wave for the ejected electron. As the behavior of the wave function of the latter in the interior of the atom is of primary importance, the figures thus obtained give at best the order of magnitude of the transition probabilities.

The relativistic theory of Dirac and Møller has been applied by Massey and Burhop<sup>27</sup> to the calculation of  $K$  Auger effect probabilities and radiative transition probabilities for gold, using screened hydrogen wave functions. In Table VII we compare their results calculated relativistically and nonrelativistically, with the values obtained in the present work. Our values are in approximate agreement with the nonrelativistic results of Massey and Burhop, though they are somewhat smaller throughout. The relativistic treatment evidently increases the contribution of the Auger effects and decreases that of the radiation transitions. This need not apply generally, however; in particular not to the complex transitions (involving higher azimuthal quantum numbers) which, according to Table V, contribute the largest share to the width of the higher levels.

Apart from the fact that, except for the  $K$  level, the Auger effect appears to be the primary factor determining the level widths our calculations indicate the following:

(1) The widths of the  $L_I$ ,  $M_I$ , and  $N_I$  levels<sup>28</sup> are found to lie between 10 and 15 electronvolts, in good agreement with the measurements of RBR. In general the calculated contributions appear to be too large. It should also be pointed out that any revision of measured line and level widths<sup>29</sup> would probably be in the direction of a decrease in observed widths.

(2) Comparing the relative probabilities of individual Auger processes, we find that, in general, those are most probable for which the ejected electron has a relatively low energy. For very high energies of the latter—high compared to its potential energy in the region where the

TABLE VII. Contributions to the width of the  $K$  level, in electron volts.

RADIATION TRANSITION	MASSEY AND BURHOP		AUTHORS NON- RELATIVISTIC
	Relativistic	Nonrelativistic	
$K \rightarrow L_{III}$	28.7	37.6	36.0
$K \rightarrow L_{II}$	13.4	18.8	16.6
$K \rightarrow L_I L_{III}$	0.249	0.156	0.129
$K \rightarrow L_I L_{II}$	0.258	0.078	0.064
$K \rightarrow L_I L_I$	0.047	0.069	0.055

wavefunctions of the remaining electrons participating in the transition are large—the Auger probability must necessarily be small due to the oscillatory character of the wave function of the ejected electron in this region.

(3) Comparing different levels having the same total quantum number, we should expect a considerable decrease in width with increasing azimuthal quantum number. Thus in passing from  $M_I$  to  $M_{II}$ , several transitions which contribute substantially to the width of  $M_I$  drop out—for example, transitions of the type  $M_I \rightarrow M_{II} N_{VI, VII}$  and  $M_I \rightarrow M_{II} O_I$ . (See Table V.) The relatively small decrease in mean kinetic energy of the electrons expelled by the remaining Auger processes does not appreciably increase their respective probabilities and their contributions to the width of  $M_{II}$ .<sup>30</sup>

(4) No commensurate decrease in width should be expected in passing from the lower to the higher level of a relativistic doublet—for example from  $M_{II}$  to  $M_{III}$  or from  $M_{IV}$  to  $M_V$ , since in such cases the angular coefficients ( $c(0, 0)$  in Table III) of the largest interaction integrals vanish.

These indications are in accord with observation.

The present results, being confined to a single element, give no immediate information about the variation of the line widths or level widths with atomic number,  $Z$ . This variation will be determined by (1) the approximate constancy of Auger-transition probabilities with change of  $Z$  and (2) the proportionality of the radiation-

<sup>27</sup> H. S. W. Massey and E. H. S. Burhop, Proc. Roy. Soc. London **A153**, 661 (1936).

<sup>28</sup> The uncalculated Auger effects for these levels correspond to ejected electrons of high energy (for  $L_I > 540$  Ry). Such transitions have very low probability and contribute very little to the level widths.

<sup>29</sup> For recent work on this subject see L. G. Parratt, Rev. Sci. Inst. **6**, 387 (1935).

<sup>30</sup> This slightly higher probability arises from the fact that Auger electrons expelled with  $M_{II}$  ionization as the initial state have, for a given final state of double ionization, a somewhat lower kinetic energy than if  $M_I$  ionization be the initial state. See the immediately preceding paragraph.

transition probabilities with  $Z^4$ .<sup>20</sup> For Kr(36) Auger observed that, for the  $K$  shell, the probability of radiation transitions is approximately equal to that for Auger transitions. This leads to a theoretical curve giving level widths as a function of atomic number, of substantially the same character as the curve given by Zinn for the variation of absorption-limit widths.<sup>31</sup> Zinn finds approximate constancy of the  $K$  widths for

<sup>31</sup> W. H. Zinn, Phys. Rev. **46**, 659 (1934), Fig. 6.

elements below Ge(32) and near fulfillment of a fourth power law for the heavier elements.

The principal conclusion of the work here reported is that we feel justified in stating that within the present accuracy of experimental and theoretical studies, the widths of the principal x-ray lines of the heavier elements may be regarded as having a purely atomic origin with the Auger effect playing a dominant role for all but the  $K$  series.

JUNE 1, 1937

PHYSICAL REVIEW

VOLUME 51

### Satellite Structure of $L\alpha$ and $L\beta_2$ of Au(79)

F. K. RICHTMYER\* AND E. G. RAMBERG†

*Cornell University, Ithaca, New York*

(Received April 7, 1937)

Assuming the correctness of Coster and Kronig's hypothesis of the origin of the satellites accompanying  $L\alpha$  and  $L\beta_2$ , the separations and relative intensities of these satellites are calculated for Au(79) by means of the theory of complex spectra. Making use of data on the mean life of the states involved in the transitions and on the probability of the Auger effect producing the initial state for the satellite emission, contours of the satellite

structure are obtained and compared with patterns previously measured with the two-crystal spectrometer. Within the limitations of the theoretical treatment as well as the experimental material the agreement, both with regard to intensity distribution and relative intensity of parent lines and satellites, is satisfactory and confirms Coster and Kronig's theory.

COSTER and Kronig<sup>1</sup> have suggested the following sequence of processes for the production of x-ray satellites, such as those accompanying  $L\alpha$  ( $L_{III} \rightarrow M_{IV, \nu}$ ) or  $L\beta_2$  ( $L_{III} \rightarrow N_{IV, \nu}$ ), the intensity of which varies rapidly with atomic number in certain atomic number ranges:

(1) By electron or x-ray bombardment, the atom is initially ionized by the expulsion of an electron from the  $L_I$  shell (in the case of the satellites of  $L\alpha$ , for example).

(2) By a radiationless transition (Auger effect) the atom passes over into a doubly-ionized state, with one vacancy in the  $L_{III}$  shell and another in the  $M_{IV, \nu}$  shell.

(3) The vacancy in the  $L_{III}$  shell is then filled by an electron from the  $M_{IV, \nu}$  shell (or from the  $N_{IV, \nu}$  shell for the satellites of  $L\beta_2$ ). The radia-

tion emitted by this transition has a slightly higher frequency than  $L\alpha$  (or  $L\beta_2$ ) on account of the diminution of screening occasioned by the absence of the  $M_{IV, \nu}$  electron expelled by the Auger transition.

Auger transitions  $L_I \rightarrow L_{III} M_{IV, \nu}$  are possible only when the energy difference between the  $L_I$  and the  $L_{III}$  levels exceeds the energy of the  $M_{IV, \nu}$  level (for the element of next higher atomic number). But when there is such excess energy, the transitions have a high probability. A study of x-ray term tables shows that within the atomic number range  $52 < Z < 73$ , approximately,<sup>2</sup> the Auger transitions  $L_I \rightarrow L_{III} M_{IV, \nu}$  cannot occur. Both above and below this range, they are possible.

It is within this range of atomic numbers that the satellites of both  $L\alpha$  and  $L\beta_2$  are so weak as

\* This research was made possible by a grant from the American Philosophical Society. F. K. R.

† At present with Electronic Research Laboratory, RCA Manufacturing Company, Camden, New Jersey.

<sup>1</sup> D. Coster and R. de L. Kronig, Physica **2**, 13 (1935).

<sup>2</sup> "Approximately," because the screening effect of an  $L_{III}$  electron on the  $M_{IV, \nu}$  shell is somewhat less than unity.