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The Variation of the *K* Resonating Strength with Atomic Number

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The resonating strength of the *K*-shell or the effective number N_K of *K* electrons is less than 2 and varies with atomic number. It is determined in the present paper by an approximate theory using Hartree wave functions. The results are compared with N_k values obtained by anomalous dispersion, by computation from the most reliable absorption experiments, and by an approximate absorption theory of Hönl and Williams. Below atomic number 40 the present theory gives good results and allows of the determination of the N_k values which are needed in finding absolute x-ray wave-lengths from dispersion measurements.

THE general dispersion[1] formula gives the refractive index n at the frequency ν_i in terms of the electron number f as

$$n^2-1=\frac{N_e e^2}{\pi m Z}\int\frac{df(\nu)}{\nu_0^2-\nu_i^2}, \tag{1}$$

where ν_0 is the natural frequency of the electrons in the refracting material and N_e, e, m and Z have their usual meaning. If one assumes an absorption law of the form $\mu/\rho=c\lambda^n$, then for $n=3$, Eq. (1) can be written in the form

$$\lambda=\delta^{\frac{1}{2}}\left[\frac{\rho}{W}\cdot\frac{e}{m}\cdot\frac{F}{2\pi}\sum_1^s N_s\left\{1+\frac{1}{x_s^2}\ln\left(x_s^2-1\right)\right\}\right]^{-\frac{1}{2}} \tag{2}$$

and for $n=2.5$

$$\lambda=\delta^{\frac{1}{2}}\left[\frac{\rho}{W}\cdot\frac{e}{m}\cdot\frac{F}{2\pi}\sum_1^s N_s\left\{1+\frac{3}{2x_s^{\frac{3}{2}}}\times\left(\frac{\pi}{2}-\operatorname{ctn}^{-1}x_s^{\frac{1}{2}}-\tfrac{1}{2}\ln\frac{x_s^{\frac{1}{2}}+1}{|x_s^{\frac{1}{2}}-1|}\right)\right\}\right]^{-\frac{1}{2}} \tag{3}$$

where $\delta=1-\mu$; $x=\nu_i/\nu_0$; ρ is the density of the refracting substance and W its molecular weight, F is the Faraday constant; and N_s is the effective number of electrons in the s shell.

Equations of the type (2) and (3) have been used in calculating the absolute x-ray wave-lengths from dispersion measurements.[2–6] Various values of N_s have been used for the K electron shells and it is obvious that this factor affects the calculated wave-length considerably. The value of N_k for any element can be evaluated from the absorption law for that element. It can also be determined from theoretical considerations. The purpose of the present paper is to theoretically determine the value of N_k for those elements for which the Hartree wave functions are available and also to calculate the values of N_k for those elements on which good absorption measurements have been made.

DETERMINATION OF N_k FROM THEORY

In principle the true mass absorption coefficient and hence N_k can be calculated by evaluation of matrix elements for transitions to the continuous spectrum. This calculation is practical only when approximations are made. Starting out from a common point of view, Hönl,[7] Williams,[8] and Bethe[9] proceed by a method whose essential idea may be seen by reference to Fig. 1. The ejected K electron is treated as moving in a potential unchanged by its jump from the original energy $-E_k$ to the final energy $E=h\nu-E_k$. This potential is divided into two parts, one representing a pure inverse square force, the other being nearly constant in the region where the important contributions to the photoelectric matrix elements occur. The first, V_n, arises from the attraction of the nucleus diminished by the screening effect S of the other K electron. The remainder of the effect of the K electron is combined with the repulsion arising

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[1] See for example, Born and Jordan, *Elementare Quantenmechanik*, 1st Ed., p. 247.

[2] J. A. Bearden, Phys. Rev. **39**, 1 (1932).

[3] J. A. Bearden and C. H. Shaw, Phys. Rev. **40**, 1031 (1932).

[4] K. Shiba, Inst. of Chem. and Phys., Tokyo **19**, 97 (1932).

[5] J. A. Bearden and J. A. Wheeler, Phys. Rev. **43**, 1059 (1933).

[6] R. T. Birge, National Academy, Washington, 1934.

[7] H. Hönl, Zeits. f. Physik **84**, 1 (1933).

[8] E. J. Williams, Proc. Roy. Soc. **A143**, 358 (1934).

[9] H. Bethe, Handbuch der Physik, 2nd Ed., XXIV, Part I, p. 478.

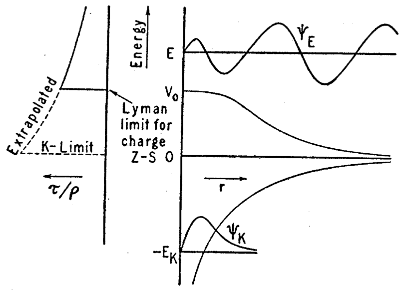

FIG. 1. Schematic diagram of potentials and wave functions for heavy element indicating how the hydrogenic photoelectric effect is extrapolated past the Lyman limit to give x-ray absorption.

from all the other electrons to give the potential V_e, which for large atomic number approximates a constant value V_0 in the K shell. Thus one may use hydrogenic wave functions corresponding to nuclear charge $Z-S$ and energies $-E_k-V_0$ and $E-V_0$ to approximate in the neighborhood of the K shell the actual wave functions ψ_k and ψ_E for energies $-E_k$ and E. The necessary matrix elements for hydrogenic functions have been calculated by Sugiura.[10] However, it is clear that the approximation used for ψ_E is not good outside of the region where V_e is constant, and it is just the behavior of ψ_E for large distances that determines the normalization factor by which the hydrogenic photoelectric absorption must be multiplied to give the desired value. Hönl and Bethe refer to approximate arguments based on the Wentzel-Kramers-Brillouin expression for the wave functions in the region where V_e varies and believe that the normalization factor is not changed much from unity by the variation of V_e.

When E lies between 0 and V_0, although ψ_E is in the continuous spectrum, the hydrogenic function approximating it is in the discrete spectrum, where of course there is no photoelectric absorption. Therefore Hönl and Williams are obliged to extrapolate the hydrogenic photoelectric absorption to wave-lengths considerably longer than the Lyman series limit to obtain the x-ray absorption all the way up to the K limit. This extrapolation is indicated schematically in the left-hand part of Fig. 1.

It is clear that in addition to the original assumption of a potential unaltered by the transition of a K electron, three approximations were made in the method of Hönl, Williams and Bethe:

(1) Obtaining absorption near K-limit by extrapolation.

(2) Normalization factor not accurately determined.

(3) No variation of V_e in the region where ψ_k is large.

In the region of relatively small atomic numbers (Si and O) important for absolute x-ray wave-lengths the use of assumption (3) may no longer be a good approximation.

The method used in the present work is quite different from the above method and is based upon the f sum rule[11] according to which a single electron in any fixed potential has for its transitions from a given initial state to all other states, both continuous and discrete, occupied and unoccupied, f values whose sum is unity. But N_k is defined as the strength of all permitted transitions of the K electrons, both continuous and discrete. According to the Pauli principle transitions to the occupied states of the atom are not permitted. Therefore

$$N_k=2(1-\sum_{\text{occupied states } n} f_{kn})$$

The advantage of using this relation is that to obtain N_k one needs to calculate only the strength of a few transitions in the discrete spectrum, where one has a much better knowledge of the wave functions than in the continuum. For example, the Hartree functions already take account of the variation of V_e with distance. The matrix elements involved in finding the f values given below were calculated from the wave functions of the states in question in a self-consistent field.

Strictly speaking, it is not right to apply the f sum rule to transitions probabilities calculated in this way, because slightly different potentials are used in calculating the different Hartree functions, whereas the sum rule assumes a fixed potential. On the other hand, the assumption of a fixed potential is wrong in itself. It would be of no advantage to recalculate the wave functions on the basis of a fixed potential

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[10] Sugiura, J. de physique 8, 113 (1927).

[11] R. L. Kronig and H. A. Kramers, Zeits. f. Physik 48, 174 (1928).

when the error arising from a fixed potential is of the same type as the error due to the self-consistent wave functions, both errors originating in the circumstance that a transition of one electron changes the wave function of all electrons. Proper allowance for this effect and for electron exchange would involve an amount of calculation not justified by increased accuracy of N_k.

Table I lists the f values, the source of the wave functions used in the calculations and the resulting values of N_k. The resultant values of N_k are plotted in Fig. 2 along with the results of Hönl and Williams and with the values of N_k obtained by integration of the absorption data tabulated in Table II.

TABLE I. *f values and the resulting values of N_K.*

Element	Z	Source of functions	f_{KL}	f_{KM}	f_{KN}	f_{KO}	N_K
Helium	2	[12]					2.00
Oxygen	8	Hartree and Black[13]	0.162				1.78
Chlorine	17	Hartree[14]	0.247	0.013			1.48
Copper	29	Hartree[14]	0.320	0.030			1.30
Caesium	55	Hartree[15, 15']	0.370	0.054	0.011	0.003	1.12

EFFECTIVE NUMBER OF ELECTRONS FROM EXPERIMENT

The relation between the oscillator strength, f, the frequency of the impressed radiation ν, and the true mass absorption coefficient τ/ρ, of that frequency can be written in the form[16]

$$df/d\nu=(mc/\pi e^2)\cdot m_a\tau/\rho \qquad (4)$$

where m_a is the mass of the given atom in grams. Experimentally τ/ρ can be divided into parts (τ_K/ρ), (τ_L/ρ), etc., whose relative magnitudes depend upon the number of electrons ejected from the K, L, $\cdots$ shells by the radiation.

Thus the effective number of electrons in the K shell can be defined in terms of observables:

$$N_K=\int df_K(\nu)$$
$$=1.875\times 10^{-4}W\int_0^{\lambda_k}(\tau_k/\rho)(d\lambda/\lambda^2). \qquad (5)$$

Here λ is the wave-length in A, and W is the atomic weight.

Using Eq. (5), various authors have calculated N_K from measurements of x-ray absorption. Houston[17] did this for a large number of elements. Owing to the errors in the experiments on which he based his calculations, the resultant N_K values showed wide fluctuations. However the results which were based on the best absorption data are in general agreement with the values obtained in the present work. More reliable determinations of (τ/ρ) are now available and the values of N_K obtained from these are shown in Table II and plotted in Fig. 2.

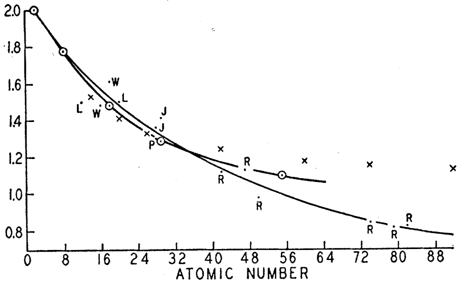

FIG. 2. Graph of theoretical and experimental values of N_K against atomic number. ⊙ = present theory; x = Hönl theory; · experimental points, R—Richtmyer, J—Jönsson, W—Woernle, L—Larsson, P—Prins.

It was necessary to extrapolate to short wave-lengths the total absorption coefficient as measured on the long wave-length side of the K limit and subtract from the actual absorption to obtain the effect (τ_K/ρ) produced by the K electrons alone. For the very light elements experiments are not available on account of the experimental difficulties at long wave-lengths.

Since the above calculations were made Grosskurth* has published measurements on the absorption coefficient for 16 elements for wave-lengths between 0.128A and 2.5A. From these results he obtains the absorption law

$$\mu/\rho=0.0166Z^{2.63}\lambda^{2.7377}$$

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[12] No upper shells are occupied in helium, and J. P. Vinti has shown that the effect of two-electron jumps is very small. Phys. Rev. **42**, 639 (1932).

[13] D. R. Hartree and M. M. Black, Proc. Roy. Soc. **A139**, 311 (1933).

[14] D. R. Hartree, Proc. Roy. Soc. **141**, 282 (1934).

[15] We are indebted to Professor Slater for sending us a photostat copy of Hartree's functions before their publication.

[15'] D. R. Hartree, Proc. Roy. Soc. **A143**, 506 (1934).

[16] Ladenburg, Zeits. f. Physik **4**, 451 (1921).

[17] R. A. Houston, Phil. Mag. **2**, 512 (1926).

[18] Prins, Zeits. f. Physik **47**, 479 (1928).

[19] Larsson, Dissertation, Uppsala, 1929.

* K. Grosskurth, Ann. d. Physik **20**, 197 (1934).

for the short wave-length side of the K absorption limit and

$$\mu/\rho = 0.0097Z^{2.895}\lambda^{2.7377}$$

for the long wave-length side. Calculation of N_K values have been made using this law. The value obtained for atomic number 82 is 35 percent higher than that obtained from Richtmyer's result and for atomic numbers about 16 the values are 20 percent lower than those obtained from Woernle's and Larsson's results. This law gives values which agree better with those calculated from theory for high atomic numbers than those obtained from Richtmyer's results. However, for low atomic numbers they deviate from both theoretical N_K values and those calculated from previous absorption measurements. On account of this, and also the fact that most of Grosskurth's measurements deviate so much from his absorption law, we have not included these values of N_K in the graph of Fig. 2.

A second method of determining N_K experimentally is the anomalous dispersion of x-rays near the K-absorption edge. The theory is given by Prins,[18] who obtains in this way $N_K = 1.3$ from experiments on Fe. Larsson[19] gets 1.5 for Ca and Si in the same way. These values are included in Fig. 2.

DISCUSSION

The theoretical points obtained in this paper diverge systematically from experiment for high atomic number, though not quite so strongly as those of Hönl. The discrepancy would be removed if the f value for transition from K level to L level were actually higher than calculated. Relativity effects are appreciable for high atomic numbers ($\alpha = 55/137$ for Cs) but apparently do not explain the divergence, since for an unscreened nucleus of charge 55 the relativistic f values are somewhat smaller than the classical ones, as is seen in Table III. The reasons for the failure of the theory for large atomic number are not clear, but are probably connected with the considerable change in the distribution of the other electrons and in the potential arising from them that must take place when one K electron is removed, as well as with the fact that a central field is admittedly an approximation.

TABLE II. *Values of N_K obtained by integration of absorption data.*

Method	Symbol	Reference	Results of absorption measurements		El	Z	N_K
			K side of edge	L side of edge			
Absorption measurements	R	20	$375\lambda^3+1$	$50\lambda^3+1$	Mo	42	1.12
	R	20	$545\lambda^3+1$	$70\lambda^3+1$	Ag	47	1.13
	R	20	$575\lambda^3+1$	$90\lambda^3+1$	Sn	50	0.97
	R	20	$1870\lambda^3+0.8$	$330\lambda^3+0.8$	W	74	0.85
	R	20	$2230\lambda^3+0.85$	$395\lambda^3+0.85$	Au	79	0.80
	R	20	$2570\lambda^3+0.7$	$476\lambda^3+0.7$	Pb	82	0.81
	W	21	$43.54\lambda^{2.6}$	$3.86\lambda^{2.7}$	A	18	1.61
	W	21	$29.29\lambda^{2.7}$	$2.28\lambda^{2.8}$	S	16	1.48
	J	22	$123.1\ \lambda^{2.76}$	$15.25\lambda^{2.76}$	Ni	28	1.36
	J	22	$132.4\ \lambda^{2.75}$	$15.46\lambda^{2.74}$	Cu	29	1.41
Experiments on dispersion	P	18			Fe	26	1.3
	L	19			Ca	20	1.5
	L	19			Si	14	1.5

TABLE III.

Transition	Non-relativistic	Relativistic
$f_{sp_{3/2}}$	0.277	0.258
$f_{sp_{1/2}}$	0.139	0.128
sum $=f_{KL}$	0.416	0.386

Below atomic number 40 the theoretical curve agrees fairly well with experiment and allows of a determination of the N_k values of low atomic number needed for the determination of absolute x-ray wave-lengths. This application was the incentive for the present investigation.

We are indebted to Professor G. Breit for several discussions.

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[20] F. K. Richtmyer, Phys. Rev. **27**, 1 (1926).

[21] B. Woernle, Ann. d. Physik **5**, 475 (1930).

[22] E. Jönsson, Uppsala Universitets Arsskrift (1928).