number of two, thirty-six electrons have a quantum number of three, etc.

On examining the data closely we find a systematic deviation of the calculated from the observed values. This deviation becomes most marked in the elements of low atomic number. It lies in the same direction as the well-known difference between the observed and calculated ionizing potentials of helium.

In order to see whether a better representation of facts can be obtained by supposing that the two inner electrons revolve in opposite directions in separate orbits, I have made the calculations on that basis. The only difference in formula 11 occurs in the terms representing the innermost orbit. The first two terms of equation 11 must be replaced by the single term.

$$(N-1)^2 (1 + \tfrac{1}{4}\beta'^2 + \tfrac{1}{8}\beta'^4 + \ldots) \qquad (12)$$

Column 5 of the table contains the results of the computations. It appears from the data of column 5 that the observed and calculated values differ from each other by amounts up to $4\tfrac{1}{2}\%$. A systematic variation exists which increases as the atomic weight decreases, and which lies in the opposite direction to that represented by the data of column 3.

[1] *Science*, May 21, 1920.

[2] Fall Meeting of the National Academy of Sciences, 1920; *Physic. Rev.*, March, 1921, p. 431.

[3] This can be proved easily for the particular case in question. For a proof of the theorem in a more general form see A. Sommerfeld, *Atombau und Spektrallinien*, Appendix 5.

ON THE CALCULATION OF THE X-RAY ABSORPTION FREQUENCIES OF THE CHEMICAL ELEMENTS (SECOND NOTE)

By William Duane

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In a note presented to the National Academy of Sciences[1] I have given some computations of the K critical absorption frequencies of the chemical elements based on the Rutherford-Bohr theory of the structure of atoms and the mechanism of radiation. In these computations I have assumed that the electrons were distributed in circular orbits, which did not lie in planes passing through the nucleus of the atom.

In order to estimate roughly the forces exerted on an electron in one orbit (A in the figure of the previous note) due to the electrons in the parallel orbit, I assumed that they were the same as if the charges of the electrons in the orbit BC were concentrated, half at the nearest point

in the orbit to A, and half at the furthest point in the orbit from A. In the computations presented in this note I assume that the forces are the same as if the electricity of the electrons in the orbit BC were uniformly distributed along the orbit. As in the previous note, I neglect the forces acting on an electron at A, due to the electrons in the orbits that are larger than the orbits $A\ B\ C\ D$, and assume that the forces due to the electrons in the orbits smaller than $A\ B\ C\ D$ are the same as if these electrons were concentrated at the nucleus of the atom.

The terms in the expression for the ratio of the critical absorption frequency to the Rydberg constant, ν/ν_0, due to the two innermost electrons, are the same as in the previous case (expressions 6 and 12 of the previous note). To get the correction term due to the electrons in the orbits outside of the inner orbit we proceed as follows: Equating to zero the horizontal components of the forces acting on an electron at A due to the nucleus and to the electrons inside and in the orbits $A\ B\ C\ D$, we get the equation

$$N'cos^3\alpha = \frac{n}{2\pi}\int_0^{\frac{\pi}{2}}\frac{d\theta}{(1 + tan^2\alpha\ sin^2\theta)^{3/2}}$$

where θ is half the angle made by the radius of the orbit BC drawn to any point in the orbit with the vertical.

Similarly, equating the centripetal acceleration of the electron at A to the centripetal force acting on it, due to the nucleus, to the electrons inside the orbits $A\ B\ C\ D$ and to the electricity of the orbit BC, and reducing, we get the equation

$$mv^2a = N'sin^3\alpha - nB - s_n, \qquad (14)$$

$$\text{where } B = \frac{tan^3\alpha}{2\pi}\int_0^{\frac{\pi}{2}}\frac{sin^2\theta\ d\theta}{(1 + tan^2\alpha\ sin^2\theta)^{3/2}} \qquad (15)$$

and where s_n is given by equation 9 of the previous note.

Combining equation 14 with equation 2 of the previous note, representing the angular momentum law, we get an expression similar to equation 10 for the kinetic energy of the electron at A. Taking the sum of these expressions for all the electrons with one of the electrons of the inner orbit removed and with it in place, and substituting in formula 3, representing the frequency law, we get the equation for ν/ν_0

$$\frac{\nu}{\nu_0} = 2(N - .25)^2(1 + \tfrac{1}{2}\beta^2 + \tfrac{1}{8}\beta^4 + ..) - N^2(1 + \tfrac{1}{4}\beta'^2 + \tfrac{1}{8}\beta'^4 + ..)$$

$$+ \sum\frac{2n}{r^2}\ [N'sin^3\alpha - nB - s_n]^2$$

$$- \sum \frac{2n}{\tau^2} [(N'+1)sin^3\alpha' - nB' - s_n]^2 \tag{16}$$

where α is related to N' and n according to equation 13, and B is given by equation 15, and where α' and B' are obtained from the same equations by substituting $N'+1$ for N'. For purposes of computation I have performed the indicated integrations by graphical methods and plotted curves representing N'/n and B as functions of $tan^2\alpha$. The curves appear in the figure. The relation of N'/n to $tan^2\alpha$ is almost linear. By using these curves to determine the values of α and α' corresponding to various values of N'/n and $(N'+1)/n$, respectively, and then the values of B
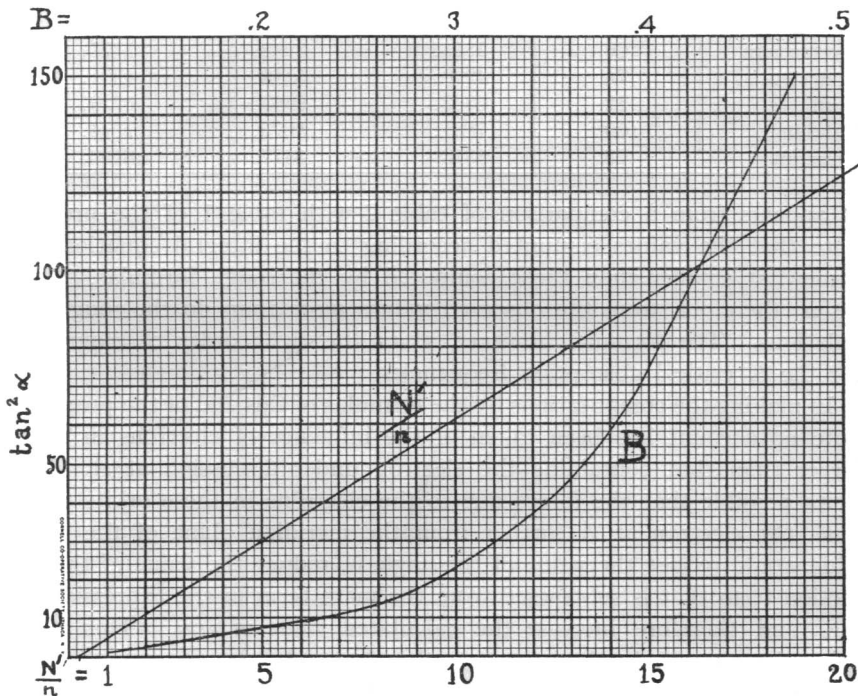
and B' corresponding to those values of α and α', the data of table 2 has been computed. Columns 3 and 5 in table 2 contain values computed on a distribution of electrons represented by the scheme

$$n_1 = 1, \quad n_2 = 4, \quad n_3 = 4, \quad n_4 = 9, \quad n_5 = 9, \quad n_6 = 16,$$
$$\tau_1 = 1, \quad \tau_2 = 2, \quad \tau_3 = 2, \quad \tau_4 = 3, \quad \tau_5 = 3, \quad \tau_6 = 4.$$

The data in column 5 has been computed under the assumption that the two electrons nearest the nucleus revolve in opposite directions in separate orbits, one outside the other; whereas for the data of column 3 they are supposed to revolve in the same orbit.

TABLE 2

K CRITICAL ABSORPTION FREQUENCIES

CHEMICAL ELEMENT	ATOMIC NUMBER	FREQUENCIES DIVIDED BY RYDBERG CONSTANT, ν/ν_0		
		Calculated	Observed	Calculated
Magnesium	12	103.3	95.8	92.6
Sulphur	16	181.1	181.8	167.0
Calcium	20	290.0	297.5	272.0
Iron	26	510.1	523.8	484.0
Selenium	34	918.4	930.8	873.8
Molybdenum	42	1431.	1474.	1388.
Tin	50	2056.	2148.	1994.
Cerium	58	2854.	2970.	2796.
Dysprosium	66	3853.	3948.	3777.
Tungsten	74	4990.	5118.	4901.
Lead	82	6362.	6463.	6228.
Thorium	90	7891.	8075.	7774.
Uranium	92	8313.	8477.	8190.

It appears from a comparison of table 2 with table 1 of the previous note that the values computed according to the integral equations are somewhat smaller than those computed by the rough formulas. They differ, therefore, from the observed values more than do the rough calculations. The formula, however, gives the right order of magnitude for the K critical absorption frequencies.

In making the computations by the formulas of this and of the preceding note no account has been taken of the influence of electrons in orbits larger than that containing the electron under discussion at A. It is quite possible that the forces due to the electrons in these orbits would push the electron at A further from the meridian plane of the atom. This would reduce the value of the angle α, reduce the value of the correction term that is subtracted from the main term in the expression for ν/ν_0, and therefore increase the calculated value of ν/ν_0. This might bring the computed values closer to the observed. An accurate estimate of the correction, however, would be extremely difficult to obtain.

If we calculate the radius of an orbit from the above equations, we find that it contains as a factor the square of the quantum number of the orbit, as well as other quantities. This means that the orbits having the same quantum number do not differ very much in radii, but that when the quantum number changes there is a considerable difference in radii. In the above distribution of electrons four orbits have quantum numbers of two, and four have quantum numbers of three. The radii of the two quantum orbits do not differ very much from each other, and the radii of the three quantum orbits do not differ very much from each other, but the latter are much larger than the former. It follows from this that the

distribution of electrons described by the above equations consists of two electrons in an inner orbit: then two groups of eight electrons, each, each group on the surface of a sphere, the two spheres lying fairly close together. Considerably outside of these spheres are two spherical surfaces, each containing eighteen electrons and lying fairly close together. Thus the distribution corresponds approximately with that described in the Lewis-Langmuir theory of static atoms.

Bohr[2] has recently suggested an arrangement of orbits, one outside the other, that differs slightly from the arrangement adopted in the preceding calculations. He assumes that the three quantum orbit or orbits lie between the two quantum orbits, and that for those elements which have four quantum electrons the four quantum orbits lie between the two three quantum orbits. This arrangement of electrons may be represented by the scheme

$$n_1 = 2, \quad n_2 = 4, \quad n_3 = 9, \quad n_4 = 16, \quad n_5 = 9, \quad n_6 = 4,$$
$$\tau_1 = 1, \quad \tau_2 = 2, \quad \tau_3 = 3, \quad \tau_4 = 4, \quad \tau_5 = 3, \quad \tau_6 = 2.$$

In order to test this distribution of electrons I have calculated the critical absorption frequencies of the chemical elements that lie just above the inert gases in the chemical tables. The critical absorption wave-lengths have not been measured for all the inert gases themselves. In making the computations I have assumed that the distribution of the electrons is the same as that in the inert gases, and that in each case the extra electron has been taken over by the other chemical element which forms the chemical compound used in measuring the critical absorption wave-length. As a matter of fact, it makes very little difference what is done with this additional electron. Its influence on the critical absorption wave-length is, theoretically, very small. This distribution of electrons is the same as that employed above for all chemical elements up to and including argon ($N = 18$). I have, therefore, included in the computations only those chemical elements of higher atomic number than eighteen. In the case of niton ($N = 86$) the chemical element just above it is missing, and I have, therefore, calculated the critical absorption frequency for thorium. The data appear in table 3. As in tables 1 and 2 column 3 contains the data computed on the supposition that the two one quantum electrons revolve in the same orbit, whereas for the data of column 5 they are supposed to revolve in opposite directions in separate orbits, one just outside the other. It appears that the agreement between the calculated and observed values is much better for this distribution of electrons than for the preceding distributions, especially the data of column 3. Owing to the fact that the radius of the first three quantum orbits is much larger than that of the two quantum orbits inside them the correction for the mutual influence of these two and three quantum orbits becomes very small.

TABLE 3

K CRITICAL ABSORPTION FREQUENCIES

CHEMICAL ELEMENT	ATOMIC NUMBER	FREQUENCIES DIVIDED BY RYDBERG CONSTANT, ν/ν_0		
		Calculated	Observed	Calculated
Potassium	19	262.0	266.0	243.7
Rubidium	37	1128.	1120.	1091.
Caesium	55	2649.	2648.	2591.
Thorium	90	8090.	8075.	7962.

In order to make the computations for chemical elements other than those in table 3 it appears to be necessary to make additional assumptions as to just how the elements are built up in increasing values of the atomic numbers. There is also some difficulty about the radii of the various orbits. In general, a two quantum orbit has a much smaller radius than a three quantum orbit.

The formulas of this and the preceding note contain no undetermined constants after the distribution of the electrons has been fixed; i.e., there is nothing in the equations which must be obtained from X-ray measurements themselves. The formulas are functions of numbers and of π except in the correction term for the change of mass of an electron with its velocity. The correction term is the only place where measured quantities appear. These quantities are the electron's charge e, Planck's action constant h, and the velocity of light c, and they may be regarded as having been determined by experiments other than X-ray measurements. In spite of this fact the formulas represent the observed values to within a few per cent. This is fairly close, considering the influences that have been neglected. Among the reactions that have been neglected we may mention the forces due to electrons in orbits outside the one considered, the fact that electrons inside these orbits have been supposed concentrated in the nucleus, forces due to the magnetic fields of the revolving electrons, the influence of electrons that may be out forming bonds with other chemical elements and which may not, therefore, take part in the energy changes, etc.

The fact that the various distributions considered give results that differ from each other by only a few per cent indicates that the calculation of the K critical absorption frequency is not a sensitive method of determining the *exact* distribution of the electrons. Further, other distributions than those considered may furnish more accurate values. The important point is that the distribution of electrons is what may be called the chemical distribution, and that the numbers of electrons in the orbits are related to their quantum numbers according to equation 4.

The calculation of the L and M, etc. critical absorption frequencies presents very great difficulties, for, if we suppose that an electron is removed from the second or third pair of orbits, it leaves this pair of orbits unbalanced. Just what would happen in this case is not clear, and it would require an additional assumption in order to complete the calculations. Definite general conditions of the dynamic equilibrium have not yet been found.

It may be, also, that orbits that are not circular would give better values than circular orbits. Computations of the frequencies on this basis present formidable difficulties. The fact, however, that the two quantum and three quantum orbits lie not in a plane, but in space of three dimensions may explain the appearance of three critical absorption wave-lengths in the L series, and six critical absorption wave-lengths in the M series, etc.

According to Sommerfeld's theory[3] the difference between two L absorption frequencies is due to the difference in shape of a circular and an elliptic orbit. His formula contains an undetermined constant. Professor Patterson and I have shown[4] that if we assume four electrons in the L orbit the undetermined constant is done away with, and that Sommerfeld's formula represents roughly the difference between the L_1 and L_2 absorption frequencies. It may be that a formula calculated on the basis of three dimensional orbits would give more accurate results.

I am greatly indebted to several of my assistants for carrying through many of the computations.

[1] These PROCEEDINGS, Sept., 1921, p. 260.
[2] *Nature*, March 24, 1921.
[3] *Atombau and Spektrallinien*, Chapter 5.
[4] These PROCEEDINGS, Sept., 1920, p. 517.

SEMI-COVARIANTS OF A GENERAL SYSTEM OF LINEAR HOMOGENEOUS DIFFERENTIAL EQUATIONS

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It is known[1] that the most general transformation of the dependent variables which converts the system of linear homogeneous differential equations

$$y_i^{(m)} + \sum_{l=0}^{m-1} \sum_{k=1}^{n} \binom{m}{l} p_{ikl} y_k^{(l)} = 0, \quad (i = 1, 2, \ldots, n), \quad (A)$$