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THE EXTENSION OF THE X-RAY-DOUBLET LAWS INTO THE FIELD OF OPTICS

I. S. BOWEN AND R. A. MILLIKAN

ABSTRACT

Application of relativity formulas for x-ray doublets to ultra-violet spectra.—Evidence has been presented which indicates that many of the strongest lines in hot spark spectra are due to atoms stripped of all valence electrons excepting the one which in jumping between energy levels emits the radiation. For the L doublets due to atoms with but *one L electron*, Li(+), Be(2+), B(3+), C(4+), it is found that the frequency difference varies with atomic number Z in accordance with the relativity formula for x-ray doublets $\Delta\nu = K(Z-s)^4$, the constant K being .365 for the regular L series, and the screening constant s decreasing from 2.02 for Li(+) to 1.86 for C(4+). Other L doublets are attributed to atoms stripped of all but *three L electrons*, the same formula holding but giving values of s about 20 per cent greater. In the case of triplets, the frequency differences of the widest pairs give values of s for atoms stripped of all but *two or four L electrons* which agree well with values for only one, three or five L electrons, though tending to be somewhat greater. Similarly from M doublets and triplets ($K = .108$) of C and N, values of s were obtained for atoms with from one to three L electrons slightly greater than from the corresponding L lines. In the case of atoms with only *one M electron*, the values of s decrease from 7.45 for Na(+) to 5.74 for P(5+), corresponding values of s from N, O and P series of doublets being slightly larger; for atoms with only *two M electrons* (widest pair of triplets) and with only *three M electrons* (doublets) the values of s vary up to about 9. For doublets corresponding to outer transitions $3d_2-3d_1$, $4d_2-4d_1$ and $4f_2-4f_1$ the values of s come out close to 10. In the case of *irregular L and M doublets* corresponding to transitions from the $2s$ and $3s$ levels, the law for corresponding x-ray doublets also holds, the differences $(\sqrt{\nu_s}-\sqrt{\nu_p})$ increasing regularly and not very greatly with Z. All these facts are shown to agree well with what should be expected according to the *Bohr-Sommerfeld theory*; and the values of s give quantitatively the influence upon the effective nuclear charge of the addition of electrons in the valence shells. *New series terms.* The above relations enable the value of s for a given series for a given ionized atom to be predicted, and led to the discovery of an L doublet at λ1240 due to N(5+), and to the assignment of the following L doublets: λ990 to N(3+), λ1493 and 1744 to N(+), λ789 and λ658 to O(4+), and λ922 to O(2+). These results give us a *new method of predicting spectra* and of determining the state of ionization of atoms emitting certain lines.

Doublet frequency differences in extreme ultra-violet for $2p_2-2p_1$ terms due to B(3+) and C(4+) were measured by use of a special grating giving up to ten orders.

1. Introduction

In a recent paper we have brought forward evidence that many of the strongest lines in our hot-spark spectra are due to "stripped atoms," i.e., to atoms completely denuded of valence electrons save for the one which in jumping between different energy levels produces the radiation. Such atoms, because of the identity of their structure with the alkali metals must have, like the alkalies, two p levels and consequently must have lines the fine structure of which is that of a doublet.

In order to study the fine structure of the extreme ultra-violet lines which we have recently been engaged in bringing to light and classifying, it was necessary to obtain higher resolving power than had heretofore been used in this region. A special four inch grating of one meter focus kindly ruled for us by Dr. J. A. Anderson of the Mount Wilson Observatory in accordance with the method which we have previously described, was found to yield excellent spectra of our extreme ultra-violet lines in all orders up to and including the seventh, eighth, and even tenth, and enabled us with the use of a slit but .02 mm wide to obtain the separation of doublets no more than .15 A apart with an accuracy of about .01 A. Moreover, the discovery of a whole series of stripped atoms gave us the first good opportunity to compare in the optical region the spectra of atoms of identical structure but varying nuclear charge. Such atoms might be expected to reveal some regular progression of spectra with atomic number not unlike that shown in the x-ray field where the structures are also similar—in this case, however, because of the identity of the inner electron shells.

2. Characteristics of the Regular L Doublet in a One-Electron system

One particular group of stripped atoms which we had definitely brought to light was the following: Li_I, Be_{II}, B_{III}, C_{IV}.* The separations of the characterisitic doublets of lithium and beryllium (Li_I and Be_{II}) were obtainable from the literature.[1] We measured the B_{III} and the C_{IV} doublet separations, the former upon three different lines, the latter only upon the first line of the principal series at $\lambda = 1550$A, and thus obtained the first four numbers of the second column of Table I.

In seeking to find the law of progression of doublet separation we noticed that the fourth roots of the successive separations were in the ratios 1, 2, 3, 4, and accordingly were led to try out the relativity formula

* Li_I, Be_{II}, etc. mean singly ionized Li, doubly ionized Be, etc.

[1] See Fowler's report on Series in Line Spectra, p. 96, and Paschen-Götze's Seriengesetze der Linienspectra, p. 71.

for the doublet separation which works so amazingly well in the x-ray field and which we had also found to work well in predicting the doublet separation of the Mg L_{II} L_{III} level and Ca M_{II} M_{III} level.[2]

It will be recalled that the form of the relativity-doublet separation for the L_{II} L_{III} levels is[3]

$$\Delta\nu = .365\ (Z-s)^4 \tag{1}$$

and that for the M_{II} M_{III} levels

$$\Delta\nu = .108\ (Z-s)^4. \tag{2}$$

Using this formula to compute the value $(Z-s)$ we obtained the first four numbers in the third column of Table 1. The fourth column headed s was then obtained by subtracting the numbers in the $(Z-s)$ column from the successive values of Z (the atomic number), namely 3, 4, 5, 6. If the two electrons of the K "shell" acted exactly as though they were in the nucleus itself, the numbers in the s column should of course all be 2.

TABLE 1

Regular L and M doublets, one-electron systems

	$2p_2-2p_1$			$3p_2-3p_1$		
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.365}$	s	$\Delta\nu$	$\sqrt{\Delta\nu/.108}$	s
Li_I	.338	.981	2.019			
Be_{II}	6.61	2.063	1.937			
B_{III}	34.4	3.116	1.884			
C^{IV}	107.4	4.142	1.858	31.4	4.128	1.872
N_V	259.1	5.162	1.838			

They will be seen in all cases to be close to 2. That there is a regular progression in the value of s from 2 to about 1.84 as Z increases is to be expected from the necessary diminution in the perfectness of the screening of the nucleus by the two K electrons as the ratio of the distance from the nucleus to the outer L electron to the distance from the nucleus to the K electrons decreases. This ratio actually decreases from 12 to 1 for Li_I to 6 to 1 for C_{IV}.[4]

The application of the M doublet formula to the separation $\Delta\nu = 31.4$ of a pair of carbon lines at 5812 and 5801, which Fowler had already tentatively inferred might correspond to C_{IV} gave, as shown in columns 5, 6, 7, almost exactly the same value of s as had been obtained from the L doublet.

[2] Millikan and Bowen, Phys. Rev. **23,** pp. 13 and 21 (1924)

[3] See Sommerfeld's Atombau etc., 1923, English ed., Eqs. (6), (7) and (8) pp. 476-479; also p. 498, et seq.

[4] Since in the ideal case the distance from the nucleus is given by $a_n = n^2 a_1/z_{eff}$, for Li a for the L electron is $(4/1)a_1$ while for the K electron it is $\frac{1}{3}a_1$, i.e. the foregoing ratio is 12 to 1. For C_{IV} on the other hand a for the L electron is $(4/4)a_1$ while for the K electron it is $(1/6)a_1$, i.e. the foregoing ratio is 6 to 1.

In next seeking in the hot spark spectrum of nitrogen for a doublet which might be the first term of the principal series of the stripped nitrogen atom, we found by a method to be considered later that this was to be expected at about 1240 A. Since we had taken no plate using high resolution in this region we sought the second order of the doublet at about 2480 and found a nitrogen pair which on the assumption that it was of the second order gave the $\Delta\nu$ and the s shown under N_V in the table. *There is thus brought to light a new procedure for the prediction of spectra and for the identification of the state of ionization of the emitting atom. This procedure will be shown in the following to be exceptionally effective.*

3. The Regular L Doublet in a Three-Electron system (B_I C_{II} N_{III} O_{IV})

The so-called Sommerfeld Law of Exchange states that all systems possessing an odd number of electrons, 1, 3, 5, etc., produce doublets while those possessing an even number give rise to triplets. The doublet due to the boron atom when possessed of three valence electrons (B_I) had already been recognized and its separation for the pair at 2497 found[5] to be $\Delta\nu=15.3$ while our own measurements on the pair at 2089 had given $\Delta\nu=15.8$ and on that at 1826 $\Delta\nu=16.2$. We took as the weighted mean 15.55 and then applied the L relativity formula precisely as in column 3, Table I, and obtained the results shown in the first row of Table II. That the value of the screening s here comes out 2.45 in place

Table II

Regular L and M doublets, three-electron systems

	$2p_2-2p_1$			$3p_2-3p_1$		
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.365}$	s	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.108}$	s
B_I	15.55	2.555	2.445			
C_{II}	66.76	3.678	2.322	10.8	3.161	2.839
N_{III}	179.3	4.708	2.292	36.04	4.273	2.727
O_{IV}	398.4	5.748	2.252			

of 1.88, its value for B_{III}, is to be expected since the two additional valence electrons in B_I must exert mutual repulsions and thus decrease the effective nuclear charge; *indeed the difference gives the first direct measurement of the influence upon the effective nuclear charge of the addition of electrons in the valence shell.*

Again we had already identified the 1335 carbon doublet as belonging to C_{II} since there was nothing but C_{II} and C_{IV} for it to belong to and its

[5] Fowler, Report on Series in Line Spectra, p. 155.

doublet separation was not correct for the latter,[6] (see Table I). Applying the relativity doublet formula to it as in column 2, Table I, there resulted the data given under C_{II} in Table II, the value of s coming out 2.322, precisely where it would be expected to come from the progression shown in the s column of Table I. It may be noted that the carbon line at 1036 is a doublet having the same separation as has 1335, and it is accordingly at once assignable to C_{II}.

Next, having already analyzed under high resolution the small number of ultra-violet lines due to nitrogen it was only necessary to try out the relativity formula upon the separations of the two doublet separations which alone had been found in nitrogen, namely the $\Delta\nu = 179.3$ belonging to the pair at 990, and the $\Delta\nu = 85.3$ belonging to the pairs at 1493 and 1744. The first mentioned pair gave the results shown under N_{III} Table II, while the second separation fits into the results given in Table III for N_I. *These results begin to show the fecundity of this method for the discovery of the nature of the atomic sources of given spectral lines.*

It is perhaps worthy of remark that the wave-lengths of the doublets at 1493 and 1744 are also inconsistent with their assignment to N_{III}. For in B_I, C_{II}, N_{III} we are dealing with identical structures save that the effective nuclear charge is progressing regularly from B_I to N_{III}. The corresponding wave-lengths should therefore progress systematically toward the violet. The strong lines in B_I are around 2000 A, those in C_{II} around 1300 so that, of the measured nitrogen doublets, the one at 990 is alone consistent with this progression.

Our preceding study of oxygen lines[7] under high resolution had revealed but one strong doublet, namely that at 787.74, 790.22, which also falls in about the position to be expected of an O_{IV} doublet from the proceeding progression. When the L relativity formula was applied to the separation of this doublet the results shown under O_{IV} in Table II were obtained. There is also another weak oxygen pair at 656.7, 658.4 which has this same separation and is therefore also a part of the O_{IV} spectrum.

The striking similarity in the progression of the values of s in Tables I and II is at once apparent and fits beautifully into the theory already given.

When the M_{II} M_{III} relativity formula Eq. (2) is applied to the doublet separation[8] $\Delta\nu = 10.8$ which Fowler has already assigned to C_{II} and to

[6] Fowler does not include the 1335 line among his C_{II} lines, but recent measurements in 4th and 5th orders show that it has the same doublet separation as the 1036 line, instead of the different separations which Simeon inferred from his lower resolution, and hence it must be included among the C_{II} lines.

[7] Bowen and Millikan, Phil. Mag., 1924

[8] Fowler, Report on Series in Line Spectra, pp. 163 and 165

the further doublet separation $\Delta\nu = 36.04$ which he has assigned to N_{III}, we obtain the numbers shown in columns 5, 6, 7 of Table II.

The fact that the values of s computed from the M doublets for C_{II} N_{III} are considerably larger than the values computed from the L doublets, while in the case of C_{IV}, Table I, the M and L doublets yielded nearly identical values of s, finds very beautiful interpretation in terms of the shapes assigned to the respective orbits in the Bohr-Sommerfeld theory. For in C_{II}, for example, the M orbit is an ellipse which carries the electron revolving in it far out beyond the L orbits in which the other two valence electrons are found, and in consequence in this outer portion of its orbit the M electron is quite effectively screened from the nucleus by these other two valence electrons. This pushes up the value of the screening constant s beyond its value when the three valence electrons are all in L orbits and hence are never more than partially screened by their other two L neighbors. In the case of C_{IV}, however, whether the single valence electron is in the L or in the M orbit it is always far outside the region occupied by the two K electrons and hence experiences nearly complete screening in both cases.

4. Regular L Doublets in Five-and-higher-Electron Systems

The doublet arising from N_I has been referred to in the preceding. Its separation taken from the lines at 1493 and 1744 when substituted in the L relativity formula yields the values shown in Table III. There are here five electrons influencing one another in the L shell, and it will be seen that the screening s has risen as it should to 3.09. The O_{II} doublet shown in this table is somewhat uncertain for it corresponds to a weak

Table III

Regular L doublets, five-electron systems

	$2p_2-2p_1$		
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.365}$	s
N_I	85.3	3.910	3.090
O_{II}	240.0	5.064	2.936

pair at 921.1 and 923.1 published by us in connection with our exploring work and not strong enough to get with the use of our apparatus of high resolving power. Though the separation has not been determined with precision, the value of s fits quite satisfactorily into the scheme of progression of this quantity shown throughout our tables. Since in general the value of s starts high with small values of the effective nucleus and diminishes toward a limit as the effective nuclear charge increases, for

this five valence electron structure this limit may be estimated to be near 2.8 as compared with the 2.2 and 1.8 values for the three and the one electron systems, respectively.

For the eight-electron system constituting the completed L shell we have previously found[9] by applying the relativity equation to our data on the L doublet of Mg, and to Grotrian's data on the same doublet in neon, the values 3.1 and 3.2, respectively. All of these foregoing values of s are nicely consistent both with one another and with the fact that, when there are a whole group of shells completely filled with electrons, as is the case with atoms of high atomic number, the value of s which fits all the x-ray data obtained with such heavy atoms[10] is 3.5.

5. The Irregular L Doublet in Optical Spectra

Having found that the formula for the L_{II} L_{III} doublet in the x-ray field, i. e., the regular or relativity doublet, holds perfectly in the field of optical spectra, it is natural to try also in the latter field the validity of the law governing the irregular x-ray doublet, L_I L_{II}. This law was discovered by G. Hertz.[11] Stated graphically, it consists in the assertion that on the Moseley diagram the line corresponding to the series of L_I levels runs parallel to the line corresponding to the series of L_{II} levels. This means that $\sqrt{\nu_I}-\sqrt{\nu_{II}}=$constant. This law follows simply from the elementary Moseley equation

$$\nu/R=(1/n^2)(Z-\sigma)^2 \tag{3}$$

where the screening constant[12] σ is assumed to take on two different values σ_1 and σ_2 (representing the different amounts of screening experienced by electrons in the two different orbits), and the difference between these constants $\sigma_1-\sigma_2$ is, altogether naturally, assumed to be the same for different elements.[13] It follows simply from this law that the difference $\Delta\nu$ of the wave-numbers of the irregular doublet increases linearly with the atomic number, while in the regular doublet it increases as the fourth power.[13]

Now in the optical region since the L_{II} L_{III} levels correspond to the $2p_2$ $2p_1$ levels there is nothing for the L_I to correspond to save the $2s$ level, i. e., the $\Delta\nu$ of the irregular doublet should be $(2s-2p_2)$. The second

[9] Millikan and Bowen, Phys. Rev. **23**, 1 (1924)

[10] Sommerfeld, Atomic Structure and Spectral Lines, p. 501

[11] G. Hertz, Zeits. f. Phys. **6**, 84 (1921); see also Sommerfeld, English ed. p. 510

[12] In this Moseley equation it will be shown in the following paper that the screening constant must be given a considerably larger value than the screening constant s required for the relativity doublet, which in the x-ray field amounts to 3.5.

[13] See Sommerfeld, English ed., pp. 511, 512

column of Table IV gives our observed series of frequencies for $(2s-2p_2)$. The third column shows the linear progression of these frequencies with atomic number, while the fourth column shows how nearly constant is the difference $\sqrt{\nu_s}-\sqrt{\nu_p}$.[14]

TABLE IV

Irregular L doublets, one-electron systems

	$2s-2p_2$		
	$\Delta\nu$	Diff.	$\sqrt{\nu_s}-\sqrt{\nu_p}$
Li_I	14903.8		39.470
		17023.8	
Be_{II}	31927.6		44.297
		16431.1	
B_{III}	48358.7		45.594
		16122.5	
C_{IV}	64481.2		46.068
		15973.9	
N_V	80455.1		46.276

The fact that $\sqrt{\nu_s}-\sqrt{\nu_p}$ is not quite constant but progresses systematically with atomic number is due to the same cause as the progression of s in Table I; for the difference in the screening by the K ring of an electron in the two different orbits here involved obviously must increase as the two L orbits approach nearer and nearer to the K shell.

The behavior, then, of the irregular doublet is beautiful confirmation of the conclusion arrived at from the behavior of the relativity doublet that both of the doublet laws first discovered in the x-ray field are equally applicable to the whole optical region.

6. THE REGULAR M DOUBLETS IN OPTICAL SPECTRA

The doublet separations of the $3p$ terms for Na_I, Mg_{II}, Al_{III} and Si_{IV} were already available from the work of Paschen,[15] Fowler[16] and others. These separations are given in the second column of Table V. The separation of the P_V doublet we had already measured.[9] The application of the M relativity formula (2) yielded the succession of values of s given in the fourth column. The altogether systematic progression of s shown in this column made it possible to locate what its value for S_{VI} would

[14] The numerical values of these frequency levels were obtained for Be, C and N as follows: The p levels being hydrogen like (circles according to Bohr) have frequencies which when divided by 1, 4, 16, etc., give practically the hydrogen L frequency and such slight variations as exist can be determined by linear extrapolation from our observed values in boron and lithium.

[15] Paschen, Ann. der Phys. **71,** 142 (1923)

[16] Fowler, Proc. Roy. Soc. **103,** 413 (1923)

of necessity be to within 3 or 4 hundredths at the most, and from this the doublet separation of S_{VI} is computable with an error of not more than .2 A. Also from the irregular doublet separation which, as was seen in Table IV, is the observed frequency, the frequencies and hence the wave-lengths of this doublet could be obtained. A glance at the second column of Table VI shows, since the linear progression at this point corresponds to the addition of approximately 17200, that the frequency of the $3s-3p_2$ line for S_{VI} should be about $88670+17200=105870$. Referring now to

TABLE V

Regular doublets for one electron outside K and L shells

	$3p_2-3p_1$			$4p_2-4p_1$		
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.108}$	s	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.0456}$	s
Na_I	17.18	3.550	7.450	5.49	3.312	7.688
Mg_{II}	91.55	5.394	6.606	30.5	5.085	6.915
Al_{III}	238	6.849	6.151	80.13	6.474	6.526
Si_{IV}	460	8.076	5.924	162.06	7.720	6.280
P_V	795	9.260	5.740			
S_{VI}	1279	10.428	5.572			
	$5p_2-5p_1$			$6p_2-6p_1$		
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.0234}$	s	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.0135}$	s
Na_I	2.49	3.213	7.787	1.50	3.246	7.754
Mg_{II}	14.07	4.954	7.046	7.6	4.869	7.131
Al_{III}	39.15	6.398	6.602			
Si_{IV}	75	7.528	6.472	41	7.421	6.579
	$3d_2-3d_1$			$4d_2-4d_1$		
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.036}$	s	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.0152}$	s
Mg_{II}	.99	2.289	9.711			
Al_{III}	2.28	2.820	10.180	1.28	3.029	9.971
	$4f_2-4f_1$					
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.0076}$	s			
Al_{III}	.38	2.659	10.341			
Si_{IV}	1.26	3.588	10.412			

the table of the ultra-violet sulphur lines which we have previously published,[9] a line is found at $\nu=105826$ within a half of an angstrom of the predicted spot. *Also the table contains another line at* $\nu=107105$, *between which and the foregoing line there exists the frequency separation given under* S_{VI} *in Table* V. These two lines are of small intensity, as is to be expected from the large number of electrons which have had to be detached in order to produce them. But the foregoing numbers illustrate

with how great certainty these two may be assigned to S_{VI} and in general how unerring is this method of predicting both the separation and the location of the doublet arising from a given type of ionization.

Column 5 of Table V shows the $4p$ instead of the $3p$ term separations, and column 7 shows the values of s determined from the relativity formula for the N_{II} N_{III} doublets, namely[17]

$$\Delta\nu = .0456\ (Z-s)^4. \tag{4}$$

That these values of s are nearly the same (the slight difference will be explained below) as those found for the $3p$ doublets is further evidence for the general correctness of the relativity equation for doublet separations. Still further evidence of the same kind is contained in Table V under the headings $5p$ and $6p$. Here are found the doublet separations of the $5p$ and $6p$ terms as given by Paschen and Fowler and the values of s obtained from the relativity formula as applied to these $5p$ and $6p$ terms, namely,

$$\Delta\nu = .0234\ (Z-s)^4; \tag{5}$$

$$\Delta\nu = .0135\ (Z-s)^4. \tag{6}$$

The slow, though slight progression in the value of s shown in $3p$, $4p$, $5p$ and $6p$, until in the $6p$ terms the doublet separations become too small to be accurately determined, is very illuminating.

Under the headings d_2-d_1 and f_2-f_1, Table V gives the doublet separations as obtained by Fowler and Paschen and the values of $(Z-s)$ and of s as computed by the relativity formulas, namely,

for the $3d$ ($M_{IV}M_V$) $\quad \Delta\nu = .0360\ (Z-s)^4$; (7)

for the $4d$ ($N_{IV}N_V$) $\quad \Delta\nu = .0152\ (Z-s)^4$; (8)

for the $4f$ ($N_{VI}N_{VII}$) $\quad \Delta\nu = .0076\ (Z-s)^4$. (9)

The data for the two irregular M doublets are given in Table VI.

Since in Table V we are dealing with but one structure, namely, a single electron in an orbit of higher quantum number than those corresponding to the K and L shells, and since this structure has both the K and L shell completely filled, the first with two and the last with eight electrons, it is obvious that *if the relativity formula corresponds to physical reality the screening constant s must come out 10 whenever the electron is in an orbit which remains everywhere far outside the L shell.* This last condition is satisfied by the $3d$, $4d$, and the $4f$ terms, since these are known to be *hydrogen-like*—to use a term which is independent of all theory. This hydrogen-like behavior is usually explained by the assumption (to be discussed later) that the s, p, d, f, etc. terms correspond to azimuthal quantum numbers 1, 2, 3, 4, etc., respectively; for this assumption makes

[17] Sommerfeld, English ed. p. 479

the $3d$ and $4f$ orbits circles, and the $4d$ orbit an ellipse which is nearly circular. *A glance at the values of s (Table V) computed from the relativity doublet formula for the 3d, 4d, and 4f terms shows that they are all equal to 10 within the limits of accuracy of the measurement of the separation of close doublets such as these are*, their doublet separation being from but .08A to .29A.

Returning now to the values of s shown under $3p$, the fact that these are less than 10 may be taken as a demonstration that the electrons in these $3p$ orbits (which are ellipses by all types of theory) actually do penetrate to inner regions of the atom where the screening from the nucleus by the ten inmost electrons is very imperfect. Also the progression of this value of s from 7.45 to 5.57 in accordance with the progression Na_I, Mg_{II}, Al_{III}, Si_{IV}, P_V, S_{VI} is explained precisely as was the similar progression in Table I; that is, the screening becomes less and less perfect as the radiating electron draws closer and closer to the nucleus in comparison with the distance from this nucleus of the whole L group of

TABLE VI

Irregular M doublets, one-electron systems outside K and L shells

	$3s-3p_2$			$3p_1-3d_2$		
	$\Delta\nu$	Diff.	$\sqrt{\nu_s}-\sqrt{\nu_p}$	$\Delta\nu$	Diff.	$\sqrt{\nu_p}-\sqrt{\nu_d}$
Na_I	16956.2		47.089	12199.5		45.649
		18713.2			23529.9	
Mg_{II}	35669.4		55.666	35729.4		69.307
		18010.4			26307.8	
Al_{III}	53679.8		59.759	62037.2		82.074
		17600.2			26585.8	
Si_{IV}	71280		62.277	88623		89.382
		17390			25345	
P_V	88670		64.115	113968		93.077
		17156				
S_{VI}	105826		65.522			

electrons. Again, that the s values under $4p$ are all slightly higher than those under $3p$ is due to the fact that the $4p$ orbits are larger than the $3p$, and hence are slightly more perfectly screened from the nucleus by the ten electrons in the two inner shells.

The foregoing explanation of the progression of the values of s shown under $3p$ (Table V) accounts also completely for the progression of the value of $(\sqrt{\nu_p}-\sqrt{\nu_d})$ in the $(3p_1-3d_2)$ portion of Table VI. For the screening of the $3d$ orbits was found above to be 10 while that of the $3p$ orbits varies from 7.45 in Na_I to 5.57 in S_{VI}. Now since as the atomic number Z changes, $\sqrt{\nu_p}-\sqrt{\nu_d}$ should be constant if the difference in the two screening values corresponding to the $3p$ and the $3d$ terms remained

constant, it must of course progress as the difference between the two values of s for the d terms and the p terms progresses from $(10-7.45)$ to $(10-5.57)$; i. e., it should increase in going from Na_I to S_{VI} just as it is found to do in Table VI. A similar cause must be responsible for the progression of $(\sqrt{\nu_s}-\sqrt{\nu_p})$ shown under $(3s-3p_2)$ in Table VI.

Table VII shows the doublet separations and the s values computed from them by the relativity formula, for the similar three electron systems Al_I, Si_{II}, P_{III}. Precisely as shown in Tables I and II the addition of two electrons to the atoms Al_{III}, Si_{IV}, P_V treated in Table V causes in each an increase in s as worked out in Table VII for Al_I, Si_{II}, P_{III}.

TABLE VII

Regular doublets for three-electron systems outside K and L shells

	$3p_2-3p_1$			$4p_2-4p_1$		
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.108}$	s	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.0456}$	s
Al_I	112.01	5.673	7.327	15.22	4.274	8.726
Si_{II}	280.5	7.136	6.864	60	6.022	7.978
P_{III}	556	8.468	6.532			

Just as in the L doublets the value of s progressed from 1.8 (Table I) for one electron to 3.0 for five electrons (Table III), so in the M doublets, Tables V and VII reveal the value of s rising from 5.57 for one electron to 6.53 for three electrons. Continuing this same progression our former data[9] showed s for the eight electrons of calcium to be equal to 7, while in the x-ray field it is 8.3 for the full eighteen electrons.[18]

7. The Relativity-Doublet Separations Applied to Triplets

The unexpected success of the relativity formula is nowhere more strikingly shown than in its application to the separations of the components of triplets as well as doublets. Thus in Be_{II}, for example, Paschen[19] gives the separation of the wider components of the $2p$ triplet terms at 2.34 A. This separation substituted in the relativity formula (1) yields at once $(Z-s)=1.591$ and hence $s=4-1.591=2.409$. When it is remembered that s for Be_{II} was found above to be 1.937 and that Be_{II} has an L shell containing but one electron, while Be_I has one containing three *it will be recognized not only that the relativity fourth-power law works well here, but also that the numerical value of s,* 2.41, *is about right.* Similarly, Fowler has already given the separation of the widest pair of the C_{III} $3p$ triplet as $\Delta\nu=13.0$. Applying the M doublet relativity

[18] Sommerfeld, English ed. p. 507

[19] Paschen-Götze, loc. cit.[1]

formula (2) there results $s=2.69$, which is altogether consistent with the value of s for C_{II} given above, namely 2.839, for the latter system has one more electron than has C_{III}. Finally, our nitrogen triplet[7] at 1134 shows, in the case of its widest components, a separation of 44.2 which yields with the use of the M doublet formula $s=2.493$, just a trifle below that of C_{III} as it should be in view of the sort of progression shown in all the foregoing tables.

Table VIII shows similarly the progression of the values of $\Delta\nu$ for the structure C_I, N_{II}, O_{III}, the first C_I being taken from our measurements on the triplet lines 1561.3 and 1010.2, the second N_{II} from our measurements[7] on the 916 nitrogen line, and the O_{III} from our measurements[7] on the lines at 507 and 703A.

Since it is a four-electron group which is here being studied, the value of s should of course be a stage higher than its value for the three-electron group shown in Table II, as it is indeed found to be. Also in this three-electron structure of Table II the progression of s with atomic member has almost ceased so that it is not surprising that this progression scarcely appears in Table VIII.

TABLE VIII

Regular L triplets, four-electron systems

	$2p_2-2p_1$		
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.365}$	s
C_I	27.8	2.95	3.05
N_{II}	82.1	3.873	3.127
O_{III}	199.7	4.836	3.164

Finally, Table IX shows a similar application of the M and N relativity formulas to the widest pair of the triplets of Mg_I, Al_{II}, C_{III} and P_{IV}. The values of s in this table are all seen to be consistent with those given for the structure shown in Table V, which has one less electron and hence shows everywhere a smaller value of s.

TABLE IX

Regular triplets, two-electron systems outside K and L shells

	$3p_2-3p_1$			$4p_2-4p_1$		
	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.108}$	s	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.0456}$	s
Mg_I	40.9	4.410	7.590	4.1	3.079	8.921
Al_{II}	125.5	5.837	7.163	29.18	5.029	7.971
Si_{III}	257	6.982	7.018			
P_{IV}	439	7.982	7.018			

In all of these applications of the relativity-doublet formula we have chosen the widest pair of the three triplet lines. It is obvious that since the three lines of these triplets always maintain about the same relation to one another as the apparent nuclear charge progresses, so far as all progressions or relative values are concerned, the relativity formula must work just as well for the other pair. Had we chosen it we should simply have found everywhere a somewhat larger value of s. Thus, in Be_I, for example, this choice would simply have changed the final value of s obtained from 2.409 to 2.832 and similarly for the other triplets.

TABLE X

Values of screening constant s

	From L lines					From M lines		
Electrons in outer shell:	one	two*	three	four*	five	one	two*	three
Li	2.019	——	——	——	——		——	——
Be	1.937	2.41	——	——	——			——
B	1.884		2.445	——	——			
C	1.858		2.332	3.05	——	1.872	2.69	2.84
N	1.838		2.292	3.13	3.09		2.49	2.73
O			2.252	3.16	2.94			

	M			N			O	P
Electrons in outer shell:	one	two*	three	one	two*	three	one	one
Na	7.45	——	——	7.69	——	——	7.79	7.75
Mg	6.61	7.59	——	6.92	8.92	——	7.05	7.13
Al	6.15	7.16	7.33	6.53	7.97	8.73	6.60	
Si	5.92	7.02	6.86	6.28		7.98	6.47	6.58
P	5.74	7.02	6.53					
S	5.57							

*Values computed from the widest pair of triplet lines in each case.

For convenience of reference, the values of the screening constants are collected in Table X, which also shows strikingly the regular progression of the values from element to element and from one-electron to two-electron systems, etc.

NORMAN BRIDGE LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
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