

SOME CONSPICUOUS SUCCESSES OF THE BOHR ATOM
AND A SERIOUS DIFFICULTY

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ABSTRACT

Some consequences to the Bohr theory of extending the formulas for x-ray doublets to optical spectra.—The extension of the laws for x-ray doublets to ultra-violet spectra has given values of the screening constant in agreement with the Moseley-Bohr formula. This extension means a considerable simplification but it implies the identification of the L_I, L_{II}, L_{III} x-ray levels with the *s*, *p*₂, *p*₁ terms of optical series, respectively. This would make *p*₂*p*₁ correspond to 2₁2₂ orbits (whereas they are always both assigned to 2₂ orbits) and would also assign both *s* and *p*₂ to the 2₁ orbits. In this case, the screening constant must, contrary to the natural assumption, be much more affected by orientation of orbit (inner quantum number) than by the shape of the orbit (azimuthal number). This seems to require either discarding the relativity explanation of *p*₂*p*₁ and L_{II}L_{III} doublets and with it all relativity effects in electronic orbits or introducing a dissymmetry not heretofore contemplated in atomic models, abandoning Bohr's interpenetration ideas and his assignment of azimuthal quantum numbers.

1. COMPARISON OF THE VALUES OF THE SCREENING CONSTANTS
OBTAINED BY DIFFERENT METHODS

THE tables shown in the preceding article show that the relativity formula¹

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

is capable of predicting the known values of *s*, namely 2 for L orbits, 10 for M orbits, etc., so long as the orbits from which the value of $\Delta\nu$ is obtained are far outside the screening electrons. This is illustrated by the fourth column of Table I of that article, and by the data under 3*d*, 4*d*, and 4*f* in Table V.

TABLE I
Screening constants computed with the Moseley-Bohr formula

	2 <i>p</i> ₁		3 <i>d</i> ₁		4 <i>t</i> ₁	
	<i>ν</i>	<i>s</i>	<i>ν</i>	<i>s</i>	<i>ν</i>	<i>s</i>
Li _I	28582.5	1.979287	12203.1	1.999586	6856.1	2.000180
B _{III}	257545	1.936062	109870	1.998183	61742	1.999637
	3 <i>p</i> ₁		3 <i>d</i> ₁		4 <i>t</i> ₁	
	<i>ν</i>	<i>s</i>	<i>ν</i>	<i>s</i>	<i>ν</i>	<i>s</i>
Na _I	24475.65	9.583189	12276.18	9.996595	6860.37	9.999868
Mg _{II}	85506.44	9.351841	49776.0	9.979519	27467.4	9.998792
Al _{III}	175536.11	9.205732	113496.68	9.949042	61841.56	9.997219
Si _{IV}	292377	9.103155	203705	9.912615	109923	9.996612

¹ The *K* in this formula is the difference between two terms of the form (a^2/n^4) [$\frac{1}{4} + (n-k)/k$]. See Sommerfeld, p. 476

Again, so long as attention is confined to the same sorts of remote orbits, the simple Moseley-Bohr formula, namely,

$$\nu = (R/n^2)(Z-s)^2 \quad (2)$$

likewise yields these same known values of s , as is seen from Table I in which the B_{III} terms represent our own measurements, while the remaining term-values are taken from Fowler and Paschen.

The success of both these purely theoretical formulas in leading in the field of optical spectra to the known values of s is a significant discovery and constitutes evidence in favor of the validity of the theoretical conceptions underlying both formulas.

When, however, the orbits considered approach too close to the screening electrons, the agreement between the value of s derived from the two different formulas disappears. This is illustrated by the wide difference between the numbers in the fourth column of Table V of the preceding article and those in this third column of Table I. This is the same divergence as has long been noted in the x-ray field and which caused Sommerfeld² to introduce the two screening constants σ and s , and to write the total energy of an orbit in the form

$$\frac{\nu}{R} = \left(\frac{Z-\sigma}{n}\right)^2 + \left[\frac{1}{4} + \frac{n-k}{k}\right] \alpha^2 \left(\frac{Z-s}{n}\right)^4. \quad (3)$$

In this equation σ represents the screening[†] corresponding to the Moseley-Bohr formula and s the screening corresponding to the relativity-doublet formula. It is well known that the latter has the value 3.5 for the L_{II} L_{III} levels in the x-ray field, and that the former is always larger and varies through quite wide limits, Bohr and Coster³ making σ (their γ) change in the range between argon and niton from 9.5 to 21.7.

This divergence between the values of σ and s when the orbits approach too close to the screening electrons or even penetrate into the region between them and the nucleus, can scarcely be regarded as impairing the theoretical basis of either of the formulas, since a screening constant must cease to be a constant, i. e., it must be different in different parts of the orbit, when there is such close approach or interpenetration, so that any central force represented by a term of the form $(Z-s)$ can scarcely be expected to yield the same average value of s when obtained from an equation in $(Z-s)^4$ as when obtained from an equation in $(Z-s)^2$. In other words, we can scarcely expect to obtain any physical interpretation of s except when we are dealing with orbits which are quite remote

² Sommerfeld, p. 509. We have changed the notations slightly, n being in (3) the total, k the azimuthal, and $(n-k)$ the radial quantum numbers.

³ Bohr and Coster, *Zeits. f. Phys.* **12**, 366 (1923)

from the screening electrons. *For such orbits the two formulas yield results which are beautifully consistent with one another as well as with the known values of the number of electrons in the K and L levels as revealed by radioactive, chemical and x-ray data.*

It is worth while to note, in passing, that the agreement between these three methods in predicting the number of electrons in the K and L levels *constitutes unambiguous proof that the negative electrons have Coulomb fields*; for there is no possibility of neutralizing the Coulomb field which the α -ray-scattering experiments show exists about the positive nucleus except by similar Coulomb fields surrounding the electrons which do the neutralizing.

2. SIMPLIFICATION OF THE RULES GOVERNING SPECTROSCOPIC BEHAVIOR

From the experimental point of view the foregoing results introduce very beautiful simplifications in the rules which describe spectroscopic behavior.

(1) They require at once the extension of a well established optical rule into the whole of the x-ray field in definitely identifying the L_I , M_I , N_I x-ray levels with the s terms of optical series; also the L_{II} , L_{III} , M_{II} , M_{III} , N_{II} , N_{III} etc., with the p_2p_1 terms, and the M_{IV} , M_V , N_{IV} , N_V , etc. levels with the d_2d_1 terms, etc. This step had been previously suggested in a brief note by de Broglie and Dauvillier⁴ and also by Lande⁵, though the experimental evidence in favor of the step was then very meager and the full consequences of it not pointed out.

(2) They require conversely the extension of both the regular and irregular doublet laws from the x-ray field so as to cover the whole field of optics. Thus the irregular doublet law requires the frequency difference between the L_I and the L_{II} terms to progress linearly with atomic number for similar structures. In the field of optics this is the frequency difference, according to (1), between the s and the p_2 terms, which is shown very beautifully in Tables IV and VI of the preceding article to so progress, the slight differences being simply interpretable in terms of the changes in the relative distances between the radiating and the screening electrons. On the other hand, the regular, or relativity, doublet-law requires the fourth root of the difference between the L_{II} and L_{III} levels to progress linearly with the atomic number for similar structures. Such progression is shown in the separations in the p , d , and f terms in all of the foregoing tables.

⁴ L. de Broglie et A. Dauvillier, C. R. **175**, 755 (1922)

⁵ A. Lande, Zeits. f. Phys. **16**, 391 (1923)

(3) They require that, contrary to current usage, one and the same selection principle as to inner and azimuthal quantum numbers be used in both the field of optics and in that of x-rays. Thus if, following Bohr and Sommerfeld, the azimuthal quantum number is permitted to change in the field of optics only by plus or minus 1 while the inner quantum number may change by zero and plus or minus 1, then the same rule must apply to the x-ray field as well. Lande⁵ has previously pointed out the inconsistency in the usual assumptions in this matter, and has suggested the foregoing assignment to eliminate it, without, however, fully pointing out the difficulties involved in the change.

3. DIFFICULTIES

The foregoing definite identification of the p_2p_1 orbits in optics with the L_{II} L_{III} orbits in the x-ray field requires that if L_{II} L_{III} correspond to 2_12_2 orbits, then p_2p_1 must also correspond to 2_12_2 orbits. Now, as a matter of fact L_{II} L_{III} are taken by all writers as 2_12_2 orbits respectively, and must be so taken if their difference is to be explained on the relativity basis; i. e., if they really constitute a relativity doublet, as the foregoing data as well as all x-ray data appears abundantly to indicate. However, making p_2 a 2_1 orbit and p_1 a 2_2 orbit, instead of assigning them both to 2_2 orbits and letting a change in an inner quantum number take care of their slight difference in frequency, not only overthrows the validity of all of the interpenetration ideas with the aid of which Bohr explains so beautifully the experimental values of the series terms in optics, but it meets with the following very specific difficulties:

(1) The p_2p_1 orbits in spite of their widely different shapes actually do possess the same screening constant, since their two frequencies are so close together that in the formula (2) no appreciable difference in s can be found.

(2) If the p_2p_1 orbits have the form 2_12_2 then the s (or L_I) orbit must also have the form 2_1 , the difference between it and p_2 residing only in an inner quantum number. One would expect from such an equality in orbits of s and p_2 that the screening constants for s and p_2 would be very nearly the same, while as a matter of fact since s has a much higher frequency than p_1 the value of its screening constant as computed by Eq. (2) is much less than that of p_1 .

To avoid these two difficulties it is necessary to make the very unnatural assumption that the inner quantum number, i. e., the orientation of the orbit with respect to the atom body, has a much more powerful effect upon the screening constant s than has the wide difference in the shape of the orbit represented by the difference between 2_1 and 2_2 . In a word, the behavior

of the s , p , d , f , etc. terms shown in Paschen's tables,⁶ for example, speaks for the retention of the assignment of the azimuthal quantum numbers 1, 2, 3, 4, etc. to the s , p , d , f , etc. terms, respectively.

(3) In the spectra of Be_I, B_{II}, C_{III}, etc., as in the case of all the alkali earths, there are three p orbits designated as p_1 p_2 p_3 , while, since such orbits have a total quantum number of 2, the relativity theory permits but 2 different shapes, i. e., but one relativity doublet. In other words, in this case the additional p level *must be* in any case assigned to a change in an inner quantum number instead of to a change in an azimuthal quantum number. If, then, such a change in orientation is responsible for the difference between p_2 and p_3 it is at least altogether natural to assume, as has always been done heretofore, that the difference in energy between p_2 and p_1 is also due to such a change in orientation. In other words, the existence of these three levels is a strong argument in favor of explaining all of these fine structure differences by differences in orientation (inner quantum numbers) and leaving the differences in the shapes of orbits (azimuthal quantum numbers) to explain the large differences between the s and p terms. This is one of the strongest arguments for the usual assignment in the optical region of azimuthal and inner quantum numbers. If the relativity-doublet-conception is to be retained at all it is in any case necessary to let a change in orientation with respect, perhaps, to the atom body, produce the very large difference in energy between the s and p_2 terms, while a change in orientation, perhaps with respect to the second valence electron, provides the very small difference in energy between p_2 and p_3 .

The only way in which it appears to be possible to avoid the foregoing serious difficulties is to throw overboard altogether the relativity explanation of the "relativity-doublet" and to assume that the amazing success of this relativity formula in predicting the correct numerical values of s , as shown in Table I of the preceding article and the lower half of Table V, is not due at all to differences in the shapes of elliptical and circular orbits, as postulated by the relativity theory of doublet separations, but that there is some other cause which by mere chance leads exactly to this relativity formula without actually necessitating relativity conceptions.

In view of the fact, however, that this relativity formula was deduced from purely theoretical considerations involving no arbitrary constants whatever and that it nevertheless predicts quantitatively and very exactly not only the whole fine-line structure of the spectra of monatomic hydrogen and ionized helium, which are definitely known to be simple

⁶ Paschen, Ann. der Phys. **71**, 158 (1923)

nucleus-electron systems, but also the correct screening constants 2 and 10 as shown above, it is almost unbelievable that the fundamental conception underlying the development of the formula has no basis whatever in reality.

Again, if we discard the relativity explanation of the $p_2 p_1$ terms and with it of the L_{II} L_{III} terms, making, with Bohr and Sommerfeld, these two orbits of like shape and letting them differ only in inner quantum number and consequently assigning different shapes (different azimuthal number) to the s and p_2 terms (or to the L_I and L_{II} terms) there must still be a relativity effect separating the values of the s and p_2 terms, since the first is elliptical and the second circular. When, now, atomic numbers are high, this necessitates a relativity separation between the s and p (L_I and L_{II}) terms which is much larger than the observed separation. Indeed, for high atomic numbers L_{II} L_{III} are actually separated four or five times as far as are L_I L_{II} , so that it becomes altogether impossible to assign L_I L_{II} (or s and p_2) to different azimuthal quantum numbers, *unless we deny that electrons in these orbits are subject to the laws of relativity at all.*

This same argument may be stated in slightly different form, thus: The formula for the frequency (energy) of a given orbit is pushed up by the relativity correction (see Eq. (3) or Sommerfeld, p. 476) and of course pushed down by any electronic screening. The table on page 352 of the Bohr and Coster article³ shows that $\sqrt{v/R}$ actually rises above Z in the case of the uranium K level. *Without relativity there would be no possibility of this value getting quite as high as to 92, so that the relativity effect or something like it cannot possibly be assumed to be non-existent.*

The results in this and the foregoing article then force a choice between one or the other of the two horns of a dilemma, which may be stated thus: (1) The abandonment of relativity causes and effects altogether in electronic orbits, or (2) the abandonment of Bohr's interpenetration ideas and with them the practice of assigning azimuthal quantum numbers 1, 2, 3, 4, etc. to s , p , d , f , etc. terms, respectively. In this case some way must be found to permit two orbits which have the same shape (azimuthal quantum numbers) but different orientations (inner quantum number) to possess widely different screening constants, i. e. widely different energies. This would seem to require the introduction of a dissymmetry not heretofore contemplated into atomic models.*

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* The only escape from one or other of these conclusions is to discredit the foregoing evidence for the correspondence between the s and the L_I levels and between the p_2 p_1 and the L_{II} L_{III} levels.