THE SIGNIFICANCE OF THE $\frac{1}{2}$ TERMS IN SPECTRAL SERIES FORMULÆ

BY

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Sommerfeld¹ from his mathematical derivation of the empirical Ritz equation concluded that the ratio of the constant a^* for the enhanced spectrum of an alkali earth to the constant a for the arc spectrum of the alkali of next lower atomic number should be $a^*/a = 2$.

Fues² showed that this relation was approximately true only when to m were assigned the values 1.5, 2.5 etc. in the ms and $m\text{ } \mathfrak{S}$ terms. The ratios thereby obtained for the elements Mg/Na , Ca/K , Sr/Rb , Ba/Cs , are 2.9, 2.2, 2.6, 2.1 respectively. The mean value is $2.45 \pm 12\%$ average deviation, or a positive average deviation from 2 of 22% .

In spite of these large variations Sommerfeld³ later affirms that the "atomic field constant s gives the deviation from half numbers rather than from whole numbers."

The constant a by Sommerfeld's derivation takes the following form, to terms of the first order.

$$a = \frac{(2\pi)^4 m^2 e^2 k c_1}{n^3 h^4} \dots \dots \dots (1)$$

$$c_1 = \frac{1}{4} (Z - k) e^2 a_1^2 \dots \dots \dots (2)$$

where $k = 1$ for arc spectra, $k = 2$ for spark spectra, a_1 is the diameter of the ring of electrons surrounding the nucleus, and n the azimuthal quantum number. Sommerfeld assumed that c_1 remained constant for any pair of elements. However, with the same number of electrons in a ring, the diameter of the ring decreases when the charge on the nucleus is increased. If this

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¹ Sommerfeld *Atombau*, 2nd Ed. p. 506. $(m, a) = \frac{Nk^2}{[m + a + a(m, a)]^2}$

² Ann. d. Phys. **63**, p. 1, 1920.

³ Ann. d. Phys. **63**, p. 238, 1920.

factor is considered we no longer obtain $a^* = 2a$, although the approximation is closer when a large number of electrons are assumed in the same ring. For 50 electrons in a ring $a^* = 1.8a$.

As a little better representation, however, of actual atomic conditions we shall consider two coplanar rings, the inner ring containing p electrons, the outer ring q electrons and around the whole the quantized coplanar orbit of the single remaining valence electron. The azimuthal quantum number for the inner ring is 1 and for the outer ring 2. On carrying through the derivation for the case of two rings, exactly as Sommerfeld's except that we consider the effect of the nuclear charge on the radii a_1 and a_2 of the rings, as follows:⁴

$$a_1 = \frac{1^2 a_h}{Z - s_p} \quad a_2 = \frac{2^2 a_h}{(Z - p - s_q)}$$

we obtain eq (3) for the general relation between a^* and a .

$$\frac{a^*}{a} = 2 \frac{\frac{p}{(Z^* - s_p)^2} + \frac{16q}{(q+2-s_q)^2}}{\frac{p}{(Z - s_p)^2} + \frac{16q}{(q+1-s_q)^2}} \dots\dots\dots (3)$$

Here Z^* and Z are the atomic numbers of the alkali earth and alkali respectively and s_p and s_q are the nuclear defects of the rings.

The following table gives the values $a^* = \mathfrak{S}$ and $a = s$, as far as known, for the alkali earths and the alkalis, empirically deter-

$\mathfrak{S}$ and s terms for integral m

q	Element	$a^* = \mathfrak{S}$	Element	$a = s$	a^*/a	
					obs.	comp.
8	Mg	.93	Na	.65	1.43	1.48
8	Ca	1.20	K	.82	1.46	1.49
18	Sr	1.32	Rb	.81	1.63	1.66
18	Ba	1.43	Cs	.95	1.50	1.66
					Av. dev. = 4%	

⁴ Sommerfeld Atombau, p. 258. a_h = radius of hydrogen atom.

mined for integral values of m . They accordingly contain the quantity $\frac{1}{2}$ ordinarily considered as belonging to m . Column 6 gives the ratio a^*/a obtained from these data and column 7 the ratio computed by eq (3).

The average deviation of the computed values of this ratio from the observed is only 4% in contrast with 22% found by Fues. This fact would seem to indicate that to m should be assigned integers for the ms and $m\mathfrak{S}$ terms, as is the case with the mp , md and mb terms. To an approximation (3) may be written

$$\frac{a^*}{a} = 2 \frac{(q+1-s_q)^2}{(q+2-s_q)^2} \dots\dots\dots (4)$$

It may be noted that by assigning various integers to q and in some cases by using more rings, these equations may be manipulated to give fairly close values of a and a^* as well as of their ratio. In the above, however, we have employed the generally accepted numbers for q , and the distribution of inner rings does not materially affect the ratio a^*/a .

Conclusion: The frequently expressed opinion that the half integral values of m in the ms terms have some mysterious significance is not founded upon sufficient reason. The simple physical conceptions of the quantum theory suggest that m should be an integer and in the present note as good evidence is offered confirming this viewpoint as has been advocated to the contrary.

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