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SODIUM AND MAGNESIUM SPARK LINES IN THE FAR
ULTRA-VIOLET, AND THE QUANTITATIVE APPLICA-
TION OF THE IRREGULAR DOUBLET LAW
TO ISOELECTRONIC SEQUENCES

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ABSTRACT

New levels in Na III, Mg IV, and Mg V are identified through the transition $2s \leftarrow 2p$. The value of the negative term $2s2p^5 \ ^3P$ of O I is predicted.

The relativistic screening number $\sigma_2(L_{21}L_{22})$, is 3.19 for $Z = 10, 11$ compared with the value 3.49 for heavier atoms, usually considered independent of Z . The difference is probably due to outer screening.

Wentzel's result $\sigma_1(n, l+1) - \sigma_1(n, l) = 0.58 \cdot 2^n$ for the first order screening number σ_1 in x-rays is applied instead of the usual qualitative form of the irregular doublet law to determine the rate of dependence of the transition energy $2s^22p^5 \leftarrow 2s2p^6$ upon Z in the fluorine-like isoelectronic sequence. The extremely high result, $49 \cdot 10^3 \text{cm}^{-1}$, is verified by the new Na III and Mg IV data. Certain regularities in the curves showing the rates of dependence of the irregular doublet transition frequencies upon the atomic number in isoelectronic sequences, as functions of the number of electrons present, may be used for interpolation of these rates.

SEVERAL new lines and some old ones, due to the transition $2s \leftarrow 2p$ in the spark spectra of sodium and magnesium, have been photographed with the University of Michigan's one meter vacuum spectrograph and classified.²

Due to the necessity of breaking down the rare gas shell $2p^6$, the several times ionized atoms in this part of the periodic table require more energy for excitation than any others of the same stage of ionization except those isoelectronic with helium and hydrogen. Attempts to obtain the lines of Na IV and Al IV and extend the scheme of Mg III have been thus far unsuccessful. The failure to obtain the PP^o group of Na IV expected at $244 \cdot 10^3 \text{cm}^{-1}$, in the face of the success with Mg V, may be attributed to the inconvenient physical properties of sodium. We had to insert the sodium as a

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² We are indebted to Messrs. R. F. Bacher and G. R. Miller for aid in the photographic work.

TABLE I. Lines and new levels in sodium and magnesium.

		SODIUM				
		Lines		New Levels ($\cdot 10 \text{ cm}^{-1}$)		
(Bowen)	Int λ	Int λ	ν ($\cdot 10 \text{ cm}^{-1}$)	Assignment	Na III	
	2 372.04	3	372.16	$2s^2 2p^6 \ ^1S_0 - 2s^2 2p^5 3s \ ^1P_1^o$	$2s^2 2p^5 \ ^2P_{3/2}^o$	0
	1 376.34	2	376.63	$^1S_0 - \ ^3P_1^o$	$2s^2 2p^5 \ ^2S_{1/2}$	138
		1	378.34	$2s^2 2p^5 \ ^2P_{1/2}^o - 2s^2 2p^5 \ ^2S_{3/2}$	$2s^2 2p^5 \ ^2S_{3/2}$	26431
		1	380.33	$^2P_{1/2}^o - \ ^2S_{3/2}$		
		1	380.33	$^2P_{3/2}^o - \ ^2S_{3/2}$		
		MAGNESIUM				
		Lines		New Levels ($\cdot 10 \text{ cm}^{-1}$)		
(Mil. Bow.)	Int λ	Int λ	ν ($\cdot 10 \text{ cm}^{-1}$)	Assignment	Mg IV	
	2 231.6	2	231.71	$2s^2 2p^6 \ ^1S_0 - 2s^2 2p^5 3s \ ^1P_1^o$	$2s^2 2p^5 \ ^2P_{3/2}^o$	0
		1	234.25	$^1S_0 - \ ^3P_1^o$	$2s^2 2p^5 \ ^2S_{3/2}$	221
		1	276.28	$^3P_1^o - \ ^2S_{3/2}$	$2s^2 2p^5 \ ^2S_{3/2}$	31162
	5 320.9	2	320.90	$2s^2 2p^5 \ ^2P_{1/2}^o - 2s^2 2p^5 \ ^2S_{3/2}$		
	4 323.2	2	323.20	$^2P_{3/2}^o - \ ^2S_{3/2}$		
		0	338.48	$^2P_{3/2}^o - \ ^2S_{3/2}$		
		1	349.07	$2s^2 2p^4 \ ^3P_2 - 2s^2 2p^5 \ ^3P_0^o$	$2s^2 2p^4 \ ^3P_2$	0
		1	351.03	$^3P_1 - \ ^3P_0^o$	$2s^2 2p^4 \ ^3P_2$	161
		1	352.13	$^3P_1 - \ ^3P_0^o$	$2s^2 2p^4 \ ^3P_2$	254
	0 352.9	2	353.03	$^3P_{1,2} - \ ^3P_0^o$	$2s^2 2p^5 \ ^3P_2^o$	28326
		1	354.19	$^3P_0 - \ ^3P_1^o$	$2s^2 2p^5 \ ^3P_2^o$	28507
		1	355.31	$^3P_1 - \ ^3P_2^o$	$2s^2 2p^5 \ ^3P_2^o$	28580

core in a hollow aluminum electrode, whereas whole electrodes were easily made of magnesium.

Table I shows all the lines, $\lambda < 380$ of Na, and $\lambda < 360$ of Mg, that have ever been detected. The already classified Na II and Mg III lines are included for completeness.³ The present assignment of Mg $\lambda\lambda 320, 323$ has been suggested among other possibilities by Turner.⁴ Now the quantitative applicability of the irregular doublet law (Part III, below), and the relative unlikelihood of the strong occurrence of such x-ray transitions as $s^2p^5s^2 \leftarrow sp^6s^2$ in magnesium alone, make this assignment certain. The intensity relations, especially when examined in connection with those given in Millikan and Bowen's first paper on far ultra-violet spectra, (Table I, Mg, first column) are most satisfactory.

Table II gives the relativistic screening numbers $\sigma_2(2s^22p^4$ or $2s2p^5)$ for oxygen-like systems and $\sigma_2(2s^22p^5)$ for fluorine-like systems, respectively, as functions of the atomic number Z . The number σ_2 is calculated from the Sommerfeld formula $\Delta\nu = \alpha^2 R(Z - \sigma_2)^4 / n^3 l(l+1)$, which applies in these cases if $\Delta\nu$ is the doublet separation or the overall separation of the triplet.⁵ The frequency of the transition $2s \leftarrow 2p$, is given in the next to last column, while the last column shows the differences in the frequency of the transitions $2s \leftarrow 2p$ for successive members of each isoelectronic sequence. The extraordinarily high values of these differences will be discussed below (Part III). The numbers in parentheses are interpolated. Backward extrapolation of the next to last column to the arc spectra shows that O I $sp^5 \ ^3P$ lies about $15 \cdot 10^3 \text{ cm}^{-1}$ above the lowest state $s^2p^3 \ ^4S$ of O II, and F I $sp^6 \ ^2S$ about $16 \cdot 10^3 \text{ cm}^{-1}$ above the lowest state $s^2p^4 \ ^3P$ of F II. Neither of these negative levels has been observed.

The mean error in wave-length separations is about 0.03A, which at 300A amounts to 30 cm^{-1} . Thus the screening numbers at the bottom of each sequence in Table II are uncertain by about 0.03, while those at the top are perhaps ten times as accurate. Only in F II is it possible to distinguish, with the available measurements, between the values of the s^2p^4 and the sp^5 screening.

³ Detailed references to sources of spectroscopic data are omitted. The x-ray references may be found in Handbuch der Physik **21**, 338; optical spectra, in the forthcoming University of Michigan term tables. Of special importance for this paper are the following:

F I: (the tentative assignment of $s^2p^6 \leftarrow sp^6$ is wrong). H. Dingle, Roy. Soc. Proc. A **117**, 40 (1928).

F I, F II: I. S. Bowen, Phys. Rev. **29**, 231 (1927).

Ne II: H. N. Russell, K. T. Compton, and J. C. Boyce, Nat. Acad. Sci. Proc. **14**, 280 (1928).

Ne III: J. C. Boyce and K. T. Compton, Nat. Acad. Sci. Proc. **15**, 656 (1929).

Na II: I. S. Bowen, Phys. Rev. **31**, 967 (1928).

Mg III: J. E. Mack and R. A. Sawyer, Science **68**, 1761 (1928).

Mg lines: R. A. Millikan and I. S. Bowen, Phys. Rev. **23**, 1 (1924).

⁴ L. A. Turner, Phys. Rev. **32**, 727 (1928).

⁵ S. Goudsmit, Phys. Rev. **31**, 946 (1928).

TABLE II. Application of the doublet laws to oxygen- and fluorine-like spectra.

Oxygen-like isoelectronic sequence.					
Z	$s^2p^4 \ ^3P$ $\Delta\nu(\text{cm}^{-1})$	$sp^5 \ ^3P$ $\Delta\nu(\text{cm}^{-1})$	$\sigma_2(s^2p^4)$	$\sigma_2(sp^5)$	$s^2p^4 \ ^3P_2 - sp^5 \ ^3P_2$ $\nu(\cdot 10 \text{ cm}^{-1})$ diff.
8 O I	226	486	3.010	2.957	16480
9 F II	492		2.976		20430 (24378) mean 28326
10 Ne III		904		2.94	
11 Na IV		(1560)		(2.90)	
12 Mg V		2540		2.85	
Flourine-like isoelectronic sequence.					
Z	$s^2p^5 \ ^2P$ $\Delta\nu(\text{cm}^{-1})$		$\sigma_2(s^2p^5)$		$s^2p^5 \ ^2P_{3/2} - sp^6 \ ^2S_{1/2}$ $\nu(\cdot 10 \text{ cm}^{-1})$ diff.
9 F I	408		3.216		21627
10 Ne II	782		3.194		4804
11 Na III	1380		3.15		26431
12 Mg IV	2210		3.17		31162

II. ON THE REGULAR DOUBLET LAW

Fig. 1 shows the screening numbers from Table II, with the other relativistic $2p$ -screening numbers, calculated with the aid of the Goudsmit separation factors.⁵ The assumption of normal coupling, where necessary for calculating the screening, is well justified.⁶ The fourth power formula is applied throughout, for it is a good approximation to call the $2p$ -electrons non-penetrating. All principal quantum numbers omitted in the notation are 2. The $1s^2$ shell is present in each configuration. Within the limits of experimental error, all the values decrease smoothly toward horizontal asymptotes.⁷ The p^2 and sp^2 curves are considerably flatter than their neighbors.

The addition of an s -electron to s^2p^5 makes a change only on the order of 0.01 in the $2p$ -screening, quite in contrast with the case where less than five $2p$ -electrons are present, as in N I, for instance, where the presence of a $3s$ -electron alters the screening by half a unit. This often-noted constancy

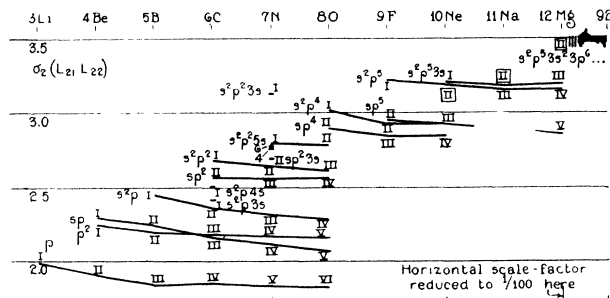


Fig. 1. Values of $\sigma_2(2p)$.

now extends from neon to magnesium. The study of the neon spectrum has been exceedingly fruitful, but this sharp distinction between five and less than five equivalent p -electrons seems still to need a special explanation.

The square boxed II's in Fig. 1 mark the real x-ray screening numbers. The difference of 0.30 in the value of σ_2 between the lower and the higher atomic numbers is probably due to the influence of the outer electrons $3s^23p^6 \dots$, which is also noticeable⁸ in the slopes of the first order screening number curves. In some cases among the σ_2 's for electrons of higher principal quantum number, the difference is in the other direction: e.g., for Ni II $3d^9$, $\sigma_2 = 13.70$, whereas for the x-rays of the heavier elements, $\sigma_2(M_{32}M_{33}) = 13.0$; but in these cases disturbances arising from interaction with the fields

⁵ This is not true for He I, Li II ($1s$) p , which are consequently omitted from the figure. For the hydrogen-like sequence, which is also omitted, of course $\sigma_2 = 0$ for all Z .

⁷ Except for N I sp^4 $^4P_{3/2}$ = 63.5, $\sigma_2 = 3.37$, which has been omitted from the figure. This anomaly is well verified experimentally (S. B. Ingram, Phys. Rev. **34**, 421 (1929)).

⁸ J. E. Mack, O. Laporte and R. J. Lang, Phys. Rev. **31**, 748 (1928).

of the many closed shells, are probably sufficient to account for the discrepancy.⁹

III. ON THE IRREGULAR DOUBLET LAW

Heretofore the irregular doublet law has been applied to optical spectra only in the following qualitative rule: In an isoelectronic sequence, the transition frequency $\nu(n, l) - \nu(n, l+1)$ is approximately a linear function of the atomic number Z .

The irregular doublet law for x-rays can be stated, following Wentzel, in a refined form¹⁰ as

$$\sigma_1(n, l+1) - \sigma_1(n, l) = 0.58 \cdot 2^l n \quad (1)$$

for inner electrons; where n and l have their usual spectroscopic meaning, R is Rydberg's energy constant, and $\sigma_1 = Z - n (\nu_{\text{red}}/R)^{1/2}$. If $5 \cdot 10^{-5}(Z - \sigma_2)^4$ may be neglected compared with ν/R , as it may be for our purposes among the light elements with which we are concerned,¹¹ then ν_{red} is the same as ν , the energy required to remove the electron.

From Eq. (1) and the definition of σ_1 , we have

$$\nu_{\text{red}}(n, l) - \nu_{\text{red}}(n, l+1) = 0.58 \cdot 2^l R [0.58 \cdot 2^l + 2(Z - \sigma_1(n, l+1))/n] \quad (2)$$

$$\frac{\Delta}{\Delta Z} [\nu_{\text{red}}(n, l) - \nu_{\text{red}}(n, l+1)] = \frac{0.58 \cdot 2^{l+1} R}{n} \left[1 - \frac{\Delta}{\Delta Z} \sigma_1(n, l+1) \right] \quad (3)$$

for inner electrons.

With the aid of the newly found data we can study (Table III and Fig. 2) the frequency of the irregular doublet transition $2s \leftarrow 2p$ as a function of the atomic number (Z) and the net charge (indicated by a roman numeral), for systems of one to nine electrons. The rows labeled "upper config." and "lower config." in Table III show the electron configurations between which the transition takes place. All omitted principal quantum numbers are 2. The $1s^2$ shell is present except in the configurations marked () or (1s). The row $(Z+1)$ II gives the transition frequency¹² (in terms of the Rydberg constant) for the first spark spectrum isoelectronic with the arc spectrum of atomic number Z . The row $(Z+1)$ II - Z II (row *A*) gives the rate at which the transition frequency for first spark spectra depends upon Z , while the row $(Z+1)$ II - Z I (row *B*) gives the rate at which the transition frequency depends upon Z in each isoelectronic sequence. The organization

⁹ The importance of such disturbances is shown, for instance, by the fact that the separations for some of the one-electron doublets among the heavier atoms actually have negative values. The case of Hg II $5f^2 F \Delta \nu = -257$ (F. Paschen, Preus, Akad. Sitzungsber. p. 536 (1928)) is especially striking.

¹⁰ G. Wentzel, Zeits. f. Physik **16**, 41 (1926); A. Sommerfeld, "Atombau" 4th ed. p. 459.

¹¹ At $Z=10$, Ne II, "reduction" decreases the $-2s$ term (L_{11}) from $3.563R$ to $3.509R$, and the $-2p$ term (L_{21}) from $1.592R$ to $1.585R$.

¹² In the optical part, the frequency given is the difference between the lowest level in the lower configuration and the lowest level of the same multiplicity in the upper configuration.

TABLE III. Transition frequencies $2s \leftarrow 2p$. (Unit-Rydberg constant).

Upper config. Lower config. Z	$()p$ $()s$ 1	$(1s)p$ $(1s)s$ 2	p s 3	sp s^2 4	sp^2 s^2p 5	sp^3 s^2p^2 6	sp^4 s^2p^3 7	sp^5 s^2p^4 8	sp^6 s^2p^5 9	41	$1s^2sp^3s^2s^3p^6$ etc. (L_{11}) $1s^2s^2p^3s^2s^3p^6$ etc. (L_{21}) 73	91			
(Z+1)II	0	0.17	0.29	0.67	0.68	0.84	1.10	1.50	1.971	...	18.4	...	42.4	...	60.4
Same, reduced									1.924	mean	16.9	mean	32.5	mean	42
A (Z+1)II-ZII	0	0.17	0.12	0.38	0.01	0.16	0.26	0.40	.47	mean	.49	mean	.53		
B (Z+1)II-ZI	0	0.08	0.16	0.28	0.25	0.26	0.29	0.36 ^a	.44 ^a						
(Z+1)II $\sigma_1(2p)$ $\Delta\sigma_1/\Delta Z$								7.48		14.2	mean	19.9	mean	22.4	0.14
										mean	0.23	mean	0.16	mean	0.14

^a (Z+2)III - (Z+1)II is used here because the configurations sp^5 , sp^6 are unknown in the arc spectra.

of Table III will be made clear by a comparison of columns 8 and 9 with the last two columns of Table II (e.g. $216270 \text{ cm}^{-1} = 1.971R$, and $48040 \text{ cm}^{-1} = 0.44R$). Table III is divided by vertical lines into an optical part (left) and an x-ray part (right); column 9 must be included in both parts because of the double role of the L levels of Ne II. Elements 42 Mo, 74 W, and 92 U are chosen as samples for the x-ray part.

No modification of the meaning of any quantity is needed in putting the x-ray data in row $(Z+1)II$. But for clearness the "reduced" values are used in the rest of the x-ray part of the table, which means simply that the complicating effects of the relativity and spin corrections are eliminated.

There are no direct data on isoelectronic sequences of x-ray spectra, such as would be required to fill the spaces ditto-marked in the table. But all the difference between the quantity that belongs in such a space, and the quantity recorded just above it, is due to the influence of an outer electron. The presence of such an electron can have but little influence on an x-ray energy level, and clearly the subtraction of one L -level from another to determine the transition frequency, would tend to cancel out this little influence. So we can confidently conclude that the numbers in the spaces marked with ditto marks in row B should be very nearly the same as those above them in row A .

The ordinary $L_{21}L_{22}$ first order x-ray screening number, and its rate of dependence on Z (e.g. $(14.8 - 7.48)/(41 - 9) = 0.23$) are given in the last two rows.

We shall now show that the values of the numbers in italic type, column 9, are in quite close agreement with values that may be calculated for them simply by the use of the x-ray data to the right of the lines in Table III, the irregular doublet law, and the ionizing potential¹³ of Ne I.

The quantities appearing in the row $(Z+1)II$ reduced and row A of Table III are simply the $\nu_{\text{red}}(2, 0) - \nu_{\text{red}}(2, 1)$ in Eq. (2) and its derivative in Eq. (3), respectively. So as long as we confine ourselves to inner electrons (i.e. to x-ray levels) the quantities in row A are given by Eq. (3). And so are the quantities in row B , from our discussion of the ditto marks. Thus, using the average slope of σ_1 from the last row of the table, we have directly from Eq. (3):

$$\begin{aligned} (\text{italic numbers, Table III}) &= 0.58R (1 - 0.23) \\ &= 0.45R \\ &= 49 \cdot 10^3 \text{ cm}^{-1} \end{aligned}$$

an extraordinarily high value for the rate of dependence of an irregular doublet transition upon Z in an isoelectronic sequence, but in good agreement with the experimental data.

Fig. 2 shows the rate of dependence of the transition frequency $2s \leftarrow 2p$ upon the number of electrons present, for the cases we have been considering: Table III, row A , (first spark spectra)¹⁴ and row B (isoelectronic sequences)

¹³ Or any other data that gives the σ_1 's of Ne.

¹⁴ The abscissae for this curve are shifted by half a unit, since it is a first difference curve.

The change in scale factor masks the fact that the curve for the x-ray part of the figure, is almost horizontal. Three facts readable from Fig. 2 are worth pointing out here:

1). The extrapolability of the x-ray curve to $0.45R$ for the fluorine-like sequence, which has been discussed above.

2). The uselessness of attempts to apply Wentzel's regularity to outer electrons.¹⁵

3). The smoothness of the isoelectronic sequences curve, compared with the successive first spark spectra curve, from $Z = 1$ to $Z = 9$. Wide irregularities occur in the optical part of row *A* curve, superimposed upon the general upward trend with increasing Z that might be expected due to the increasing differences in screening between $2s$ and $2p$, as the *K* and *L* shells are being added. It is often pointed out that such irregularities can be explained

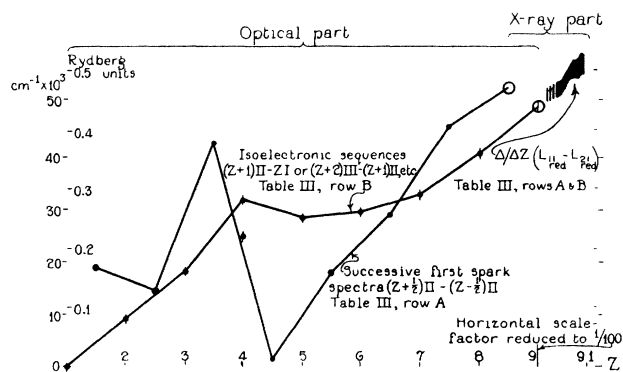


Fig. 2. Rates of dependence of the transition frequency $2s \leftarrow 2p$ upon the atomic number, in successive first spark spectra (*A*) and in isoelectronic sequences (*B*).

qualitatively by considerations based on the discrete changes in the number of electrons present: such as the formation of stable configurations at 2 and 4 and the neglect of higher multiplicities at 4, 5, and 6. To the first degree of approximation these irregularities are absent in the row *B* curve, because the differences in an isoelectronic sequence involve identical electron structures. Quite generally it appears that isoelectronic sequence irregular doublet transition curves such as the row *B* curve, depart from linearity only by a slight upward curvature, with a peak wherever the lower configuration is a Pauli shell.¹⁶ (See the $4s \leftarrow 4p$ data, below).

The irregular doublet we have been considering ($2s, 2p$) is uniquely favored for the quantitative application of the law to isoelectronic sequences,

¹⁵ E.g., B. C. Mukherjee and B. B. Ray, *Zeits. f. Physik* **57**, 345 (1929).

¹⁶ If we used $sp \leftarrow p^2$ in the beryllium-like sequence (the isolated point at 4, $0.22R$ in Fig. 2) we would eliminate the peak at 4. (Such a choice would also make the row *A* curve smoother, lowering the ordinate at 3.5 and raising that at 4.5 by 0.11*R*). Similarly in the $4s \leftarrow 4p$ list below, the choice of $3d4s \leftarrow 3d4p$ instead of $4s^2 \leftarrow 4s4p$ would lower the ordinate for the 20-electron sequence to 0.110.

for only here is it possible to excite an electron from a normally closed shell (here $2s^2$) in increasingly heavy atoms even up to those wherein the next shell with the same principal quantum number (here $2p^6$) is normally closed. But we can apply the regularities we have found for $2s \leftarrow 2p$, somewhat more crudely in other sequences. For instance, the following shows (in part) the rate of dependence upon Z in isoelectronic sequences, of the frequency $4s \leftarrow 4p$, analogous to Table III, row B :

lower config.					$3p^5s$	s	s^2	$3d^2s$	$3d^3s$	$3d^4s$	$3d^{10}s$	s^2			
No. electrons	1	...	11	12	13	...	18	19	20	21	...	27	28	29	30
rate	0		.059	.069	.074		.089	.111	.185 ¹⁶	.116		.133	.147	.161	.219

At 30 the experimental data stops, the $4s^2$ shell being so stable that there is no data on optical transitions involving $4s$ electrons for $Z > 30$; whereas the $4p$ electrons do not become inner electrons until $Z = 36$. It is not possible to calculate the rate in the sequence joining x-ray and "semi-optical" spectra (the bromine-like sequence in the case $4s \leftarrow 4p$) from Eq. (3) with the same accuracy as in the $2s \leftarrow 2p$ case, for the curvature and uncertainty in the x-ray, σ_1 curves increases with increasing principal quantum number.¹⁷ The rate for $4s \leftarrow 4p$ in the bromine-like sequence from Eq. (3) is about $0.58 \cdot 2(1 - .4)/4 = .17$.

Interpolations in such tables as this, allowing for the peaked but otherwise smooth character of the curves, should be quite reliable.

¹⁷ A. Sommerfeld, "Atombau" p. 460.