

Interpretation of the Hydrogen and Helium Spectra

Author(s): J. C. Slater

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Circuit Figure	BREAK AND T PITCH, d'					
	I, T'		$I, T + T'$		$I + I', T'$	$I + I', T + T'$
	9		10		11	12
Crest at C m. f.	0.015	0.075	0.035	0.17	0.06	0.12 m. f.
L from C	1.9	1.55	0.83	0.69	1.9	1.0 hen.
L actual	1.5	1.5	0.89	0.83	1.9	1.2 hen.
Pitch taken	${}^b b''$	${}^b b'$	${}^b b''$	${}^b b'$	${}^b b'$	${}^b b'$

These rather crude relations could easily be improved; but they go as far as the flat crests warrant and they seem definitely to exclude any other pitch. Thus ${}^b b'$ occurs 6 times, ${}^b b''$ 4 times and d' not at all, even when this is the telephone pitch. Finally the double crests in figures 9 and 10 are the octaves ${}^b b''$, ${}^b b'$, stimulated by the d' (c.f. survey of pipe crests, l.c.).

Practically therefore a primary break of variable pitch does not seem to be needed, a spring mercury break of fixed pitch (d' for instance), sufficing. Finally the short pipes (15 cm.) harbor ${}^b b''$ and ${}^b b'$; but the multiresonance of the pipe survey below d' may be spurious.

* Advance note from a Report to the Carnegie Inst. of Washington, D. C.

¹ *Proc. Nat. Acad. Sci.*, **11**, pp. 581-584, 1925.

INTERPRETATION OF THE HYDROGEN AND HELIUM SPECTRA

BY J. C. SLATER

JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY

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The anomalous Zeeman effect and multiplicity of spectral terms have been generally supposed to result from magnetic interaction between the valence electrons and the core of the atom. The doublet and triplet separations appear, however, to arise from relatively rather than from magnetic action. Pauli¹ has accordingly suggested that the multiplicity and related effects all result from peculiarities inherent to the valence electrons themselves, and that there is no magnetic interaction between a closed shell of electrons and valence electrons outside it. In particular, he connects the double levels in atoms having one valence electron with an assumed duality (Zweideutigkeit) in the quantum laws. If this suggestion is correct, we should expect the spectra of hydrogen and helium to resemble those of the alkalis and alkaline earths, respectively, except for shielding. It is the purpose of the present paper to show that this resemblance exists. If the evidence presented be regarded as sufficient, Pauli's suggestion receives support; we can also conclude that even hydro-

gen demands a change in the conventional quantum principles for its proper description.

Helium.—Helium and the alkaline earths resemble each other in having two series of terms, one of multiplets (doublets in He, triplets in the alkaline earths), and the other of singlets, between which combinations are possible (Lyman² has recently found $1S-2p$ in He). The normal state both in He and in the alkaline earths is a singlet S level, and in neither case is there a multiple s level of the same total quantum number as that of the normal S state. For all higher quantum numbers, the triplet s levels in the alkaline earths, and the doublet s in He, are more tightly bound than the corresponding singlet levels. The p orbits are pene-

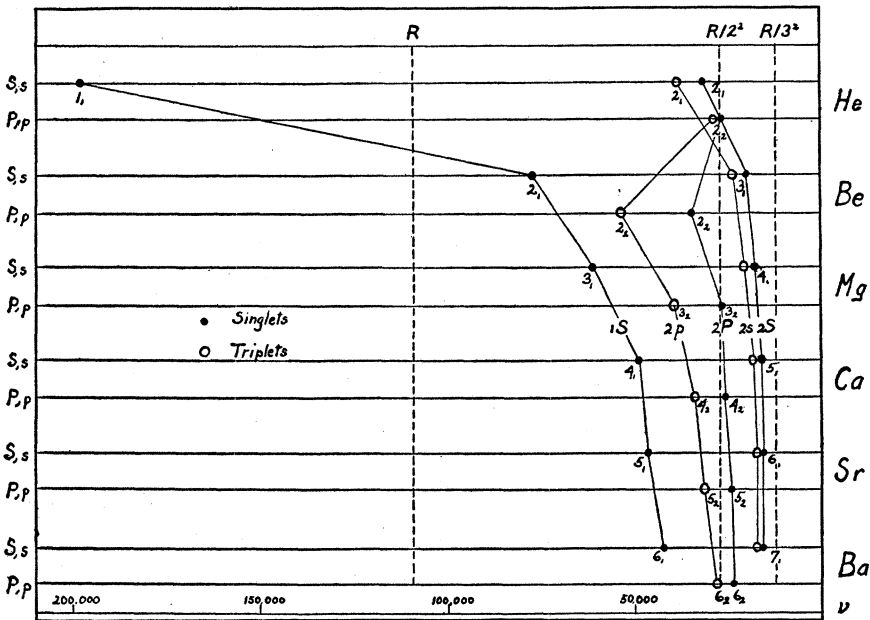


FIGURE 1

trating for all alkaline earths, non-penetrating in He. This would be expected from the reduced shielding in He, but prevents smooth extrapolation of the p levels to He. We give in figure 1 the terms of the sharp and principal series for the alkaline earths and He. (The terms for Be are estimated from the known lines of the spectrum, and should not be enough in error to affect the curves appreciably.) It is seen that the extrapolation to He is very reasonable, not only as regards the larger features but also in such details as the separation between the singlet and multiplet s levels. There are, however, two points in which He does not obviously resemble the alkaline earths: the multiplicity of the double levels, and the Zeeman effect.

Multiplicity. The first term in the principal series of multiplets in He, the only resolved fine structure, is an inverted doublet instead of an ordinary triplet. This indicates that if He is really similar to the alkaline earths, the triplet must have degenerated into a doublet, and must also have become inverted. It is remarkable that the corresponding triplet of Be shows abnormalities which seem to be the beginning of such a process. In figure 2 the triplets are plotted for the alkaline earths, the magnitudes being divided by Z^2 , the square of the atomic number. The division by Z^2 is used simply because it reduces all the values to the same order of magnitude (see Sommerfeld, "Atombau und Spektrallinien," 4th ed., p. 666). It is seen that the Be triplet³ is abnormally small, and that the levels p_1 and p_0 are abnormally close together, suggesting that between Be and He these two levels coalesce, and also cross p_2 and rise above it. The possible extrapolation to He is indicated in figure 2.

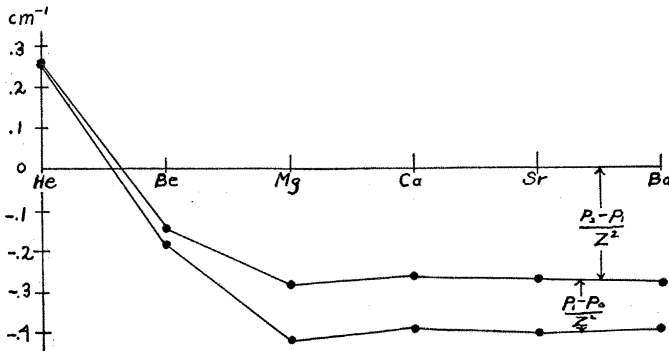


FIGURE 2

Zeeman effect. The Zeeman effect in He⁴ is rather complicated. The first line of the sharp series is double in the absence of a field. At low fields the strong component splits into an approximately normal triplet, the weak component into a triplet with about twice normal separation. At higher fields, the weak line shows interaction with the strong one, one component being lost, another remaining, until the final effect is not greatly different from a single normal triplet. For the corresponding line in an alkaline earth the weak field pattern is that of an ordinary (sp) triplet. For the strong line this is $\frac{(0) (1) 2 3 4}{2}$ with $(0)/2$ and $2/2$ as the strong components; for the next line, it is $\frac{(1) 2 3}{2}$; for the final one, $(0)/2$. This shows a resemblance to what is found in He. The principal components of the resolution of the strong line form in fact a normal Zeeman triplet. It might be supposed that the weaker lines would obscure this; but in Be, Back³ finds that the intensities are anomalous, the component $3/2$ of the strongest line having an intensity only $1/10$ of that

of $2/2$, and the $4/2$ being still fainter. This suggests that a tendency is present in Be which leads to the complete suppression of all but the normal triplet in He. For the parallel components, the agreement is not so good: in Be, the component $(O)/2$ is abnormally weak, that at $(I)/2$ being strengthened, whereas in He the $(O)/2$ is the only one visible. This discrepancy, however, does not seem serious when one considers the profound change the Be triplet must undergo in degenerating into the He doublet. For the weakest line, there is in He as in Be a Zeeman triplet of twice normal separation. For strong fields, the analogy does not hold so well; both show Paschen-Back effects, but a closer resemblance can hardly be traced. Thus the evidence from Zeeman effect for our hypothesis of the similarity of He to the alkaline earths, although not particularly favorable, seems at least not adverse.

Hydrogen and Ionized Helium.—The alkalis have doublet spectra. The sharp series terms are single, all the others double. The doublet separation is thought to depend entirely on relativity,⁵ the difference between the s , p , d , . . . terms on the other hand coming from the different shielding of the nucleus by the electrons of the core, for the differently shaped orbits. To each term are assigned three quantum numbers, n , k and j , or, following Pauli, n , k_1 , k_2 , where k_1 and k_2 are used by analogy with Bohr and Coster's numbering of the X-ray levels. The sharp series terms have $k_1 = 1$, the principal series $k_1 = 2$, etc. One term of any doublet has $k_2 = k_1$, the other has $k_2 = k_1 - 1$, the term with $k_2 = k_1$ being the smaller except in inverted doublets. Then all terms with the same n and k_1 have the same shielding energy, all with the same n and k_2 the same relativity energy. Pauli's "duality" is seen in the fact that one quantum number is used to determine one kind of energy, another for the other kind. The selection principles for transitions are $k_1 \rightarrow k_1 \pm 1$, $k_2 \rightarrow k_2, k_2 \pm 1$. This scheme extrapolates to H simply by reducing the shielding to zero, so that all terms with given values of n and k_2 have exactly the same energy, regardless of k_1 . For example, the terms 3_{22} and 3_{32} (that is, terms with $n = 3$, $k_1 = 2$ and 3 , respectively, $k_2 = 2$) are equal; but they differ from terms 3_{33} by the relativity energy which, on the ordinary theory, would be the difference between 3_3 and 3_2 . We discuss the spectrum of such a system, first in the absence of a magnetic field, then in the presence of such a field.

Fine structure. Evidently the set of term values is exactly the same as on the usual theory; but the quantum numbers are different, making new transitions possible and changing the intensities of the fine structure. The hydrogen fine structure is so obscured by the natural breadth of the lines that no information can be obtained from it, and we must turn to the spectrum of ionized helium. For Paschen's data the reader is referred to Sommerfeld, figures 89-92. The only measurements of value for the

present purpose are those taken when no great field is present. The line λ 4686 ($4 \rightarrow 3$) is the most informing. It is represented schematically in figure 89b, and by an intensity curve in figure 90. The possible transitions on our scheme are shown in table 1, where we also give the transitions possible on the usual theory, and Sommerfeld's lettering of the corresponding lines. Forbidden transitions are enclosed in parentheses.

TABLE 1
FINE STRUCTURE OF λ 4686, He II

LINE	SOMMERFELD'S THEORY	PRESENT THEORY			
<i>Ia</i>	$4_4 \rightarrow 3_3$	$4_{44} \rightarrow 3_{33}$			
<i>Ib</i>	$(4_3 \rightarrow 3_3)$	$(4_{33} \rightarrow 3_{33})$,	$4_{43} \rightarrow 3_{33}$		
<i>Ic</i>	$4_2 \rightarrow 3_3$	$4_{22} \rightarrow 3_{33}$,	$(4_{32} \rightarrow 3_{33})$		
<i>Id</i>	$(4_1 \rightarrow 3_3)$	$(4_{11} \rightarrow 3_{33})$,	$(4_{21} \rightarrow 3_{33})$		
<i>IIa</i>	$(4_4 \rightarrow 3_2)$	$(4_{44} \rightarrow 3_{22})$,	$(4_{44} \rightarrow 3_{32})$		
<i>IIb</i>	$4_3 \rightarrow 3_2$	$4_{33} \rightarrow 3_{22}$,	$(4_{43} \rightarrow 3_{22})$,	$(4_{33} \rightarrow 3_{32})$,	$4_{43} \rightarrow 3_{32}$
<i>IIc</i>	$(4_2 \rightarrow 3_2)$	$(4_{22} \rightarrow 3_{22})$,	$4_{32} \rightarrow 3_{22}$,	$4_{22} \rightarrow 3_{32}$,	$(4_{32} \rightarrow 3_{32})$
<i>IId</i>	$4_1 \rightarrow 3_2$	$4_{11} \rightarrow 3_{22}$,	$(4_{21} \rightarrow 3_{22})$,	$(4_{11} \rightarrow 3_{32})$,	$4_{21} \rightarrow 3_{32}$
<i>IIIa</i>	$(4_4 \rightarrow 3_1)$	$(4_{44} \rightarrow 3_{11})$,	$(4_{44} \rightarrow 3_{21})$		
<i>IIIb</i>	$(4_3 \rightarrow 3_1)$	$(4_{33} \rightarrow 3_{11})$,	$(4_{43} \rightarrow 3_{11})$,	$(4_{33} \rightarrow 3_{21})$,	$(4_{43} \rightarrow 3_{21})$
<i>IIIc</i>	$4_2 \rightarrow 3_1$	$4_{22} \rightarrow 3_{11}$,	$(4_{32} \rightarrow 3_{11})$,	$(4_{22} \rightarrow 3_{21})$,	$4_{32} \rightarrow 3_{21}$
<i>IIId</i>	$(4_1 \rightarrow 3_1)$	$(4_{11} \rightarrow 3_{11})$,	$4_{21} \rightarrow 3_{11}$,	$4_{11} \rightarrow 3_{21}$,	$(4_{21} \rightarrow 3_{21})$

The following differences are noted between the two theories: on the present theory, *Ib* is allowed, though previously forbidden; *IIc* and *IIId* are doubly allowed, though previously forbidden, *IIb*, *IId* and *IIIc* have each two possibilities of realization against one before. When we look at Sommerfeld's figure 90, we see that no check is possible in the case of *Ib*, *IIb*, *IIc* or *IId*, for they all lie in a complicated system whose principal members are *Ia* and *IIb*, and which is not well resolved. Not knowing the expected magnitude of *IIIc* exactly, this line also gives little information. The line *IIId* happens, however, to lie in a very suitable place for observation, and it is present with considerable intensity, contrary to the requirement of the conventional theory. Kramers explained its presence, with that of other forbidden lines, by assuming an external electric field. But its magnitude is very large for this; estimating its intensity by multiplying height and breadth from figure 90, we find *IIId* to be about 14 times as strong as *Id*, a forbidden line, and almost exactly half as strong as *IIIc*, an allowed line. It is interesting to note in connection with this that the principal components of *IIIc* and *IIId* are, respectively, $4_{22} \rightarrow 3_{11}$ and $4_{21} \rightarrow 3_{11}$, or simply the doublet of the principal series, whose intensities are known to be in the ratio 2 to 1. This apparent quantitative agreement between observation and theory should not be taken too seriously, however, both on account of the other lines $4_{32} \rightarrow 3_{21}$ of *IIIc* and $4_{11} \rightarrow 3_{21}$ of *IIId*, which might make the theoretical ratio different from 2 to 1, and because it is not stated whether the observations have

been corrected for the characteristic curve of the photographic plate, so that we cannot be sure that the observations represent true intensity. In the other lines measured by Paschen, $5 \rightarrow 3$ and $6 \rightarrow 3$, Sommerfeld gives no intensity curves, but only schematic diagrams. The lines corresponding to *III*d are again the only ones capable of giving information. In $5 \rightarrow 3$, figure 91, *III*e (analogue of *III*d) is present with considerable intensity, although it is not as large proportionally as before; the forbidden line *I*e (analogue of *I*d) is much weaker than *III*e. In $6 \rightarrow 3$, the resolution is not good enough to make it possible to draw conclusions.

Zeeman effect: The Zeeman effect for hydrogen can hardly be resolved for weak fields. (See Sommerfeld, p. 669 for discussion and references.) For strong fields, however, an effect is observed in H_α and H_β which seems to resemble the ordinary Paschen-Back effect: the various components of the line grow together to give a single normal Zeeman triplet, the breadth of the lines being less than of the original fine structure. This phenomenon, quite inexplicable on the usual theory, is to be expected on the present interpretation. In strong magnetic fields, the level 2_{11} would split into magnetic energy levels with normal separation; 2_{22} and 2_{21} would combine into a single set of magnetic levels centering about the center of gravity of the term, or two-thirds of the distance from 2_{21} to 2_{22} . Similar phenomena would occur also for the 3 or 4 quantum levels, but on account of the smaller doublet separation the various sets of Zeeman components for these levels could be considered to coincide. Thus the structure of H_α would be a superposition of several normal triplets, the greatest spreading corresponding to approximately two-thirds of the original separation 2_{22} to 2_{21} , so that the lines would appear only about two-thirds as broad as the initial fine structure.

The ionized helium line $\lambda 4686$ has been measured accurately enough at weak fields⁶ to give some information about the ordinary Zeeman effect. Hansen and Jacobsen observed that the lines *I*a ($4_{44} \rightarrow 3_{33}$) and *II*b ($4_{33} \rightarrow 3_{22}$) each split up in fields of about 5000 gauss into a normal triplet of broadened line. We should expect that at these fields the 4 quantum levels would show the Paschen-Back effect, while the 3 quantum levels would still show ordinary Zeeman effect; that is, we should have a partial Paschen-Back effect. A sodium line analogous to *II*b is the line $3_{33} \rightarrow 3_{22}$. A photograph of the partial Paschen-Back effect for this line is given in Back and Landé's book on Zeeman effect, figure 31 in the plate at the end. (In the description of this figure on p. 208, the theoretical separations for the two lines of the doublet seem to have been interchanged.) While a number of components are present, the intensities are such that the effect is strikingly like that of a normal triplet with broadened lines. Back and Landé give no similar photograph for the other line, $4_{44} \rightarrow 3_{33}$; but in general the Zeeman effect

approaches the normal effect more and more closely as k_2 increases, so that this also would probably resemble a normal triplet. The patterns which we should expect for our helium line, at fields of the order of 5000 gauss, would thus be two normal triplets of broad lines, one at the position of each of the original lines, as Hansen and Jacobsen found. For higher fields, of the order of 20,000 gauss, we should expect the double level $3_{33} - 3_{32}$ to show Paschen-Back effect as in hydrogen. This again is in accordance with the observation of Hansen and Jacobsen that at these fields the parallel components of the two lines of $\lambda 4686$ coalesce. Thus the present hypothesis seems capable of explaining the magnetic behavior of both the hydrogen and the ionized helium lines.

¹ Pauli, W., Jr., *Zeit. Physik.*, **31**, 765 (1925).

² Lyman, T., *Astroph. J.*, **60**, 1 (1924).

³ Back, E., *Ann. Physik.*, **70**, 347 (1923).

⁴ Paschen and Back, *Ann. Physik.*, **39**, 897 (1912).

⁵ Bowen and Millikan, *Physic. Rev.*, **24**, 209 (1924).

⁶ Hansen and Jacobsen, *K. Danske. Vid. Sels., Mat.-Fys. Med.*, **3**, 11 (1921).

RADIATION EMITTED BY OPTICALLY EXCITED ZINC VAPOR

BY J. G. WINANS

UNIVERSITY OF WISCONSIN

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Studies of the radiation emitted by a metallic vapor when it is illuminated by radiation from a cooled arc of that metal have been made for mercury by Wood,¹ Fuchtbauer² and others; and for mercury, cadmium, lead, bismuth and thallium by Terenin.³ These results serve either as a verification of the Bohr energy level scheme of an atom or as a means for identification of certain energy levels in an atom whose series relations are unknown.

The apparatus used in the present work with zinc was similar to that used by Terenin³ though several important modifications have been made in the arc shown in figure 1. The anode is a molybdenum cylinder closed with a concave piece of molybdenum at one end and supported on a tungsten wire sealed into a pyrex tube. The cathode is an iron rod bored out to permit water cooling, the zinc being contained in a cup at the top. The anode and cathode are held in a quartz tube by sealing wax and the whole arc enclosed in a water-cooling jacket containing a hole through which the radiation is emitted. The arc is started by an induction coil and operated from 500 volt d. c. mains at a current of 3 to 4 amperes. A large inductance is connected in series and a weak magnetic field is used to con-