The Paschen-Back Effect

VII. Configuration Interaction

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The spectrum of krypton furnishes a very fine example of the effect of configuration interaction. The levels $3s_5$ and $4d_2$, belonging to configurations of the same parity are less than 1 cm^{-1} apart, and the Zeeman patterns of lines arising from them show large perturbations, both as regards positions and relative intensities of the components. A semiempirical theory is discussed which leads to excellent agreement with experiment.

The problem of determining the positions and relative intensities of the components of a Paschen-Back pattern when the perturbing levels belong to the same configuration has been discussed in V.[1] It was possible, in those cases, to calculate the problem accurately, because the wave functions of the energy levels could be completely specified in terms of LS wave functions. When two configurations of the same parity lie close together, this is no longer possible. Each of the levels of each configuration partakes of the nature of the other configuration. This means that the transformation matrix given in V, Eq. (2a), contains nondiagonal elements between terms of the two different configurations. The calculation of this matrix for particular cases, while it may be possible, would be exceedingly laborious. It is the purpose of this paper to present a semiempirical method of carrying out these calculations and to apply it to the particular case of the interaction between $3s_5$ (configuration $4p^57s$) and $4d_2$ (configuration $4p^55d$) of krypton. Both of these configurations being odd, they are capable of perturbing each other.

In the general case, in the absence of a magnetic field, the energy matrix is diagonal in J; in the presence of a magnetic field, it is diagonal in M. If we confine our attention to these two quantum numbers, we see that the nondiagonal elements in V, Eq. (4a), can be divided into two classes: (1) those for which $\Delta J=0$, when the element is proportional to M; and (2) those for which $\Delta J=1$, when the element is proportional to $(J^2-M^2)^{\frac{1}{2}}$, where J is the larger of the two J's. The diagonal elements contain terms proportional to Mg', where g' is the weak-field g factor. The important thing to notice is that the factor of proportionality is the same[2] for all values of M.

The portion of the energy matrix for two perturbing levels for a given value of M would therefore be

$$\begin{array}{c|cc|} & J-1 & J \\ \hline J-1 & A+Mg_1\omega & K\omega(J^2-M^2)^{\frac{1}{2}} \\ J & K\omega(J^2-M\ )^{\frac{1}{2}} & B+Mg_2\omega \\ \hline \end{array} \qquad (1)$$

where g_1 and g_2 are the weak-field g factors of $(J-1)$ and J, respectively; A and B their respective field-free positions; ω the normal Lorentz separation; and K a constant depending on the LS parameters of the two levels. Setting each of the determinants of this matrix equal to zero for each value of M enables us to determine the positions of the two levels in the magnetic field in terms of the constant K. K is then determined from the experimentally determined energy levels. Having determined K, we may then proceed to find the transformation matrix in V, Eq. (8a), which is necessary for the calculation of the intensities of the components. It is not possible, however, to determine the sign of K definitively from the experimentally determined energy levels. K appears in these calculations only as K^2. A similar uncertainty with respect to sign therefore occurs also in the transformation matrix of V, Eq. (8a), and we must resort to the

[1] J. B. Green and J. F. Eichelberger, Phys. Rev. **56**, 51 (1939).

[2] This fact is not clearly brought out by Roberson and Mack, Phys. Rev. **57**, 1074 (1940), who find the result experimentally. The problem has also been discussed for a simpler case by Mack and Laporte, Phys. Rev. **51**, 291 (1937), who, however, have not considered the problem of calculating the intensities.

TABLE I. *Data for the pattern of* $\lambda 7493$.

	$2p_8-3s_5$			$2p_8-4d_2$		
TRANSITION	POSITION	INTENSITY $K>0$ $\gamma>0$	INT. $K<0$ $\gamma=0.8$	POSITION	INTENSITY $K>0$ $\gamma>0$	INT. $K<0$ $\gamma=0.8$
$2\rightarrow 1$	3.20	2	2			
$1\rightarrow 0$	2.26	$(0.74\sqrt{3}+0.67\gamma)^2$	0.50	2.83	$(0.67\sqrt{3}-0.74\gamma)^2$	3.10
$0\rightarrow -1$	1.77	$(0.96\sqrt{3}+0.29\gamma\sqrt{3})^2$	1.54	2.94	$(0.29\sqrt{3}-0.96\gamma\sqrt{3})^2$	3.42
$-1\rightarrow -2$	1.15	$(0.99\sqrt{2}+0.14\gamma\sqrt{6})^2$	1.19	3.17	$(0.14\sqrt{2}-0.99\gamma\sqrt{6})^2$	4.76
$-2\rightarrow -1$	-3.20	2	2			
$-1\rightarrow 0$	-2.57	$(0.99\sqrt{3}-0.14\gamma)^2$	3.38	-0.55	$(0.14\sqrt{3}+0.99\gamma)^2$	0.25
$0\rightarrow 1$	-1.95	$(0.96\sqrt{3}-0.29\gamma\sqrt{3})^2$	4.32	-0.78	$(0.29\sqrt{3}+0.96\gamma\sqrt{3})^2$	0.66
$1\rightarrow 2$	-1.46	$(0.74\sqrt{2}-0.67\gamma\sqrt{6})^2$	5.57	-0.89	$(0.67\sqrt{2}+0.74\gamma\sqrt{6})^2$	0.22
$2\rightarrow 2$	1.34	8	8			
$1\rightarrow 1$	0.40	$(0.74\sqrt{2}+0.67\gamma\sqrt{6})^2$	0.08	0.97	$(0.67\gamma\sqrt{2}-0.74\gamma\sqrt{6})^2$	5.72
$0\rightarrow 0$	-0.09	$(0.29\gamma\sqrt{8})^2$	0.46	1.08	$(\quad -0.96\gamma\sqrt{8})^2$	4.70
$-1\rightarrow -1$	-0.71	$(-0.99\sqrt{2}+0.14\gamma\sqrt{6})^2$	2.92	1.31	$(-0.14\sqrt{2}-0.99\gamma\sqrt{6})^2$	2.92
$-2\rightarrow -2$	-1.34	8	8			

experimentally determined intensity pattern to resolve this difficulty. The (strength)$^{\frac{1}{2}}$ of a particular component could be expressed as in V, Eq. (9a),

$$(A''jm|S^{\frac{1}{2}}|H''j'm')=[a_1'S_1^{\frac{1}{2}}+\gamma a_2'S_2^{\frac{1}{2}}],$$

where $S_1^{\frac{1}{2}}$ and $S_2^{\frac{1}{2}}$ are the (strengths)$^{\frac{1}{2}}$ of the individual transitions of the two components without perturbation, but reduced to the same scale so that the sum of the strengths of the components for each of the lines is the same; and γ^2 is the relative strength of the two lines in the absence of a magnetic field. A theoretical calculation of γ would be an almost hopeless task, involving, as it would, the relative transition probabilities of two different configurations, which, moreover, perturb each other.* The relative signs of a_1' and a_2' depend on the sign of K and on the selection rules given by Condon and Shortley.[3]

With respect to the particular case of the interaction between $3s_5$ and $4d_2$ of krypton, three lines were available for study:

$\lambda\lambda 6904$–5	$2p_{10}-4d_2$, $3s_5$
$\lambda\lambda 7486$–7	$2p_9-(4d_2)$, $3s_5$
$\lambda\lambda 7493$–4	$2p_8-4d_2$, $3s_5$.

* While it might be possible to determine the sign of γ by assuming that the radial functions of the configurations are nearly hydrogenic, and that the angular functions can be determined by assuming that the configurations are separate, we are still faced with the problem of determining the sign of K. The nondiagonal terms in the matrix (1) arise only because the configurations *are* mixed and this spoils our first assumption.

[3] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge, 1935), 9[3](11).

Careful measurements were made of the positions of the components, and having previously determined the g factors of $2p_{10}$, $2p_9$, and $2p_8$ from other lines, the relative positions of the levels of $3s_5(J=2)$ and $4d_2(J=1)$ were calculated. Since the levels corresponding to $M=2$ and $M=-2$ for $3s_5$ are unperturbed, their midpoint was called the zero position and all levels were referred to it. In a field for which $\omega=1.69$ cm^{-1}, the following levels were determined:

	$M=-2$	-1	0	1	2
$3s_5$	-5.06	-2.57	-0.09	2.26	5.06
$4d_2$		-0.55	1.08	2.84	

Knowing the unperturbed positions of

$3s_5$	-5.06	-2.53	0	2.53	5.06

we find that the levels of $3s_5$ have been shifted

$$-0.04 \qquad -0.09 \qquad -0.27$$

so that the levels of $4d_2$ must have been shifted

$$+0.04 \qquad +0.09 \qquad +0.27$$

making their unperturbed positions

$$-0.59 \qquad 0.99 \qquad 2.57$$

which yields a g value of 0.935. Putting these values back into (1) we find $K=0.098$ for all values of M with an accuracy of 0.01 cm^{-1}. This value of K substituted in (1) yields the following results:

	$M=-2$	-1	0	1	2
$3s_5$	-5.06	-2.57	-0.10	2.27	5.06
$4d_2$		-0.55	1.09	2.83	

These values determine the following transformation matrices (the upper sign for $K>0$, the lower for $K<0$)

$$
\begin{array}{ccccc}
M=-2 & M=-1 & M=0 & M=1 & M=2 \\
\begin{array}{cc} & s_5 \\ s_5' & \boxed{1.00} \end{array} &
\multicolumn{2}{c}{\begin{array}{c|cc|} & s_5 & d_2 \\ \cline{2-3} s_5' & 0.99 & \pm 0.14 \\ d_2' & 0.14 & \mp 0.99 \\ \cline{2-3} \end{array}} &
\multicolumn{2}{c}{\begin{array}{c|cc|} & s_5 & d_2 \\ \cline{2-3} s_5' & 0.96 & \pm 0.29 \\ d_2' & 0.29 & \mp 0.96 \\ \cline{2-3} \end{array}}
\end{array}
$$

$$
\begin{array}{c|cc|}
 & s_5 & d_2 \\ \cline{2-3}
s_5' & 0.74 & \pm 0.67 \\
d_2' & 0.67 & \mp 0.74 \\ \cline{2-3}
\end{array}
\qquad
\begin{array}{cc}
 & s_5 \\
s_5' & \boxed{1.00}
\end{array}
$$

Let us now consider the calculation of a particular pattern. The line λ7493 has been chosen, for it affords several opportunities for the determination of the sign of K. The average g value of $2p_8$ had already been fixed as 1.10, so that the pattern for $\omega=1.69$ cm^{-1} may be calculated from

	$M=-2$	-1	0	1	2
$2p_8$	-3.72	-1.86	0	1.86	$3.72.$

Within a given Zeeman pattern, the relative intensities depend only on J, and we find that for $J=2\rightarrow J=2$ they are

$$2,\ 3,\ 3,\ 2;\ (8),\ (2),\ (0),\ (2),\ (8);\ 2,\ 3,\ 3,\ 2;$$

while for $J=1\rightarrow J=2$ they are

$$1,\ 3,\ 6;\ (6),\ (8),\ (6);\ 6,\ 3,\ 1$$

the intensity 6 belonging to the transitions $M=\pm 1\rightarrow M=\pm 2$. Each of these groups yield a total sum of 40, so that they are already reduced to the same scale. If we now assume that

$$\frac{\text{Int. }(p_8d_2)}{\text{Int. }(p_8s_5)}=\gamma^2,$$

the data for the pattern of λ7493 are given in the third and sixth columns of Table I for positive γ and K.

It is to be noted that reversing the sign of K produces the same effect as reversing the sign of γ in Table I. Really, only the relative sign of γ and K is of importance.

From estimates on the field-free intensities of the lines above, we come to the conclusion that $\gamma\doteq 0.8$. Comparing then the intensities of components $1\rightarrow 0$ and $1\rightarrow 2$ of $2p_8-3s_5$ we find that if γ(or K) is taken with the positive sign, $1\rightarrow 0$ will be greater in intensity than $1\rightarrow 2$ whereas $1\rightarrow 0$ is missing, and $1\rightarrow 2$ is very strong. Again, comparing $1\rightarrow 0$ and $1\rightarrow 2$ of $2p_8-4d_2$ we find a similar result. We therefore use γ with the sign reversed and arrive at columns 4 and 7. The results are plotted in Fig. 1.

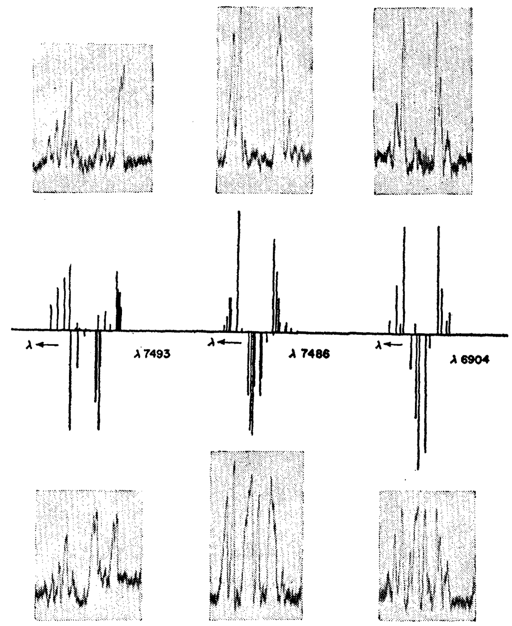

FIG. 1. Comparison of calculated and observed patterns for λ7493, λ7486, λ6904. At the top are the microphotometer traces for the perpendicular polarization. In the middle are the calculated patterns with the perpendicular polarization above and parallel polarization below. At the bottom are the microphotometer traces of the lines including both polarizations.

Proceeding in the same way with λ6904 we find that $\gamma=0.2$ fits the experimentally determined pattern quite accurately. In the case of λ7486, the procedure is much simpler, for $2p_9-4d_2$ is a "forbidden" transition. The calculated and observed patterns of these three lines are depicted in Fig. 1. The agreement is seen to be excellent.

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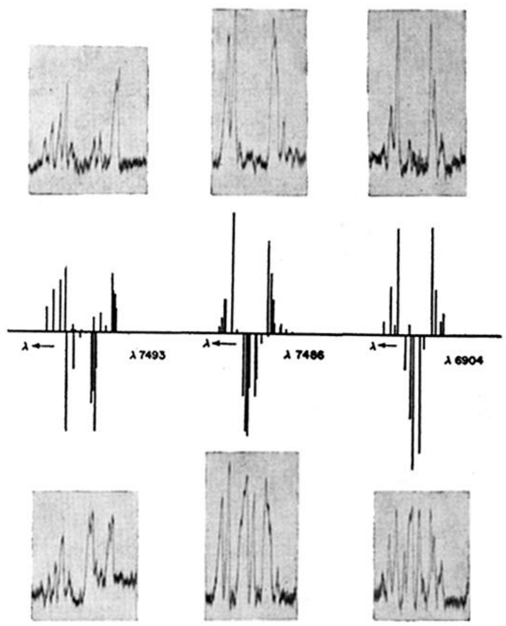

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