Physics. — *Series of alkaline atoms in an electric field* *). By E. SEGRÈ and G. C. WICK (Rome). (Communicated by Prof. P. ZEEMAN.)

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In this paper we investigate the behaviour in an electric field of the potassium series $4S$—nP, $4S$—nS, $4S$—nD. We calculate the intensities of the lines in both permitted and forbidden series. We explain the disappearence of the last members of the permitted series and we compare the theoretical results with experiment.

§ 1. *Introductory.*

KUHN [1]) has studied the absorption spectrum of potassium near the limit of the series $4S$—nP in an electric field. He has pointed out some remarkable features of this spectrum. His experiments have been improved by C. J. BAKKER [2]), working in Professor ZEEMAN's Laboratory in Amsterdam, and who has kindly sent us some photometries of his plates.

Their outstanding features are: with zero field one may follow the series $4S$—nP up to about its 31st term; in the electric field the intensity of the lines diminishes progressively and the series breaks down. The effect of the electric field is greater on the π-components than on the σ ones. For instance with a field of 1600 volt/cm the parallel polarized series breaks down at about the 19th term whereas one may observe about two more terms of the σ series.

Whilst the permitted series becomes weaker and shorter, the occurrence of forbidden lines belonging to the $4S$—nD and $4S$—nS series is clearly to be seen. The two series are not resolved. These lines begin to be detectable at a certain n, their intensity increases with n, until they are stronger than the permitted ones of the same frequency; then they become weaker and fade away.

It was believed at first that these rather complicated effects ought to be explained by a theory similar to that of LANCZOS [3]) for the ionization of hydrogen atoms in an electric field (forced ionization). However KUHN has pointed out some discrepancies between theory and experiment which are even more prominent in BAKKER's plates and which show that this interpretation is not the correct one.

The aim of the present paper is a thorough examination of the whole question; we will consider the breaking down of the series together with

*) See also: C. J. BAKKER. These Proceedings, p. 589.

[1]) H. KUHN, ZS. f. Phys. **61**, 805, 1930.

[2]) C. J. BAKKER, Proc. Amst. **36**, 589.

[3]) C. LANCZOS, ZS. f. Phys. **68**, 204, 1931.

the occurrence of the forbidden lines. The essential point is the existence of a sum rule, according to which the intensity of the permitted lines is transferred to the forbidden ones. This gives an explanation of the phenomenon in qualitative agreement with experiment and this effect is far more important than forced ionization (when the field is not too great) and is mainly responsible for the fading of the S—P series. On the other hand the effect of ionization begins abruptly for a certain n and produces the total extinction of the following lines.

In § 2 we evaluate the probability of ionization and show that it is not sufficient to explain the observed effect; in § 3 we will establish the sum rule and calculate the intensity of the forbidden lines for K_α by means of the perturbation theory. § 4 is devoted to the comparison of theoretical and experimental results. In § 5 we give the asymptotic values of some matrix elements which occur in the former sections.

§ 2. *Forced ionization.*

According to classical theory the higher quantum states of the valence electron become unstable in an electric field F. This happens because the surfaces $V=E$ (where V is the potential energy) are not closed for $E>-2\sqrt{e^3F}$; therefore there are no discrete quantum levels above this limit. This energy corresponds to an effective quantum number $n_{eff}=21$ for $F=1600$ volt/cm and to $n_{eff}=25$ for $F=800$ volt/cm. Accordingly no lines corresponding to transitions from $4S$ to levels above $-2\sqrt{e^3F}$ are observed.

However, also lines well under this limit are noticeably weakened. According to quantum mechanics there is also a finite ionisation probability for levels under $-2\sqrt{e^3F}$. As a matter of fact the electron may get out of the atom *through* the potential barrier, by a process similar to that which is responsible for α-particle disintegration according to GAMOW's theory. One could think that this could provide an explanation of the effects described above.

However KUHN has pointed out that the broadening of the lines produced by ionization is not sufficient to explain the weakening of the lines in the case of high terms and rather weak fields.

This effect might be evaluated by a three dimensional extension of GAMOW's method; this would involve rather elaborate calculations, therefore we will content ourselves, like KUHN, with a rather rough approximation which consists in evaluating the transparency of the barrier along a line parallel to the electric field, i.e. in the most favourable direction. The transparency is given by

$$exp\left(-\frac{4\pi}{h}\int_{z_1}^{z_2}\sqrt{2m\,(V-E)}\,dz\right).$$

The integral is limited between the roots of $V-E=0$.

One finds that the transparency is practically nil for all discrete levels, except perhaps the highest one. E.g. for 800 volt/cm the limit of the series lies at $n_{eff} = 25$; for $n_{eff} = 24$ the transparency has already sunken to $e^{-38} = 3{,}2\ 10^{-17}$. It is now clear that it is useless to take into account the GAMOW effect as it affects at most only one term. Above this one the series breaks down abruptly even classically.

§ 3. *Perturbation theory of forbidden and permitted lines.*

The behaviour of intensities in the $4S$—nP series is essentially connected, as we shall see, with the occurrence of forbidden lines. Let us briefly recollect the well known theory [1]) of forbidden transitions in an electric field with special reference to the case of potassium with which the experiments have been performed.

Consider two levels a and b that do not combine with each other, and a series of levels i that combine with both a and b. An electric field parallel to the z axis perturbes the eigenfunctions which become in first approximation:

$$\psi_b = \psi_b^0 + \sum_i{}' \frac{e F z_{bi}}{E_b - E_i} \psi_i^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the present case a is the $4S$ level, b is an nS or nD level, i is any level of the P series.

The influence of spin is not essential and will be neglected; the eigenfunction ψ_a is practically unperturbed.

In sum (1) only such terms are important for which $E_b - E_i$ is small; this happens for the highest terms of the series.

The perturbed ψ_b combines with ψ_a and the intensity which is emitted with π-polarisation (parallel to the electric field) is proportional to

$$I_\pi = F^2 \left| \sum_i{}' \frac{z_{ai}\, z_{ib}}{E_i - E_b} \right|^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the intensity of σ polarized light is

$$I_\sigma = F^2 \left| \sum_i{}' \frac{x_{ai}\, z_{ib}}{E_i - E_b} \right|^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This first approximation is valid as long as the forbidden lines are weak compared with the permitted ones. In this case the intensity of the latter ones does not change. This is not true when the intensities of both sort of lines are comparable. There is indeed a sum rule, according to which the sum of the intensities of all lines having a common initial term, which is practically unperturbed, is independent from the field.

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[1]) See for instance C. J. BAKKER and E. SEGRÈ, ZS. f. Phys. **79**, 655, 1932.

This is most clearly seen in the following example; consider only one perturbed state b and only one perturbing state i. The perturbed eigenfunctions are (exactly):

$$\psi_b = \frac{\psi_b^0 + \alpha\,\psi_i^0}{\sqrt{1+\alpha^2}} \qquad \psi_i = \frac{\psi_i^0 - \alpha\,\psi_b^0}{\sqrt{1+\alpha^2}}$$

where

$$\alpha = \frac{2\,e\,F\,z_{b\,i}}{E_b - E_i + \sqrt{(E_b - E_i)^2 + 4\,e^2\,F^2\,z_{ib}^2}}$$

which reduces to (1) if

$$|\,E_b - E_i\,| \rangle\rangle 2\,e\,F\,z_{i\,b}$$

On the other hand the intensities of the a—b and a—i combinations are proportional to

$$\frac{\alpha^2}{1+\alpha^2} \quad \text{and} \quad \frac{1}{1+\alpha^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

whose sum is constant. If there are several i and b states entangled with each other, as in the present case, a similar result is obtained; the intensity of a forbidden line increases at the expense of the nearest permitted transitions.

Even a summary examination of the plates shows that the intensity of the forbidden lines is of sufficient magnitude to explain the strong weakening of the permitted ones.

In potassium the $(n+1)S$ and $(n-1)D$ terms fall almost exactly together whilst the nP term lies at midway between the nS and $(n+1)S$ terms. We have calculated the intensity of forbidden lines by means of formulae (2), (3). It is found that for the perturbation of S and D terms only the two nearest P terms are of importance. Therefore every S or D term with an effective quantum number n_{eff} is perturbed by two P terms with effective quantum number $n_{eff} \pm {}^1/_2$. For these terms the energy differences in the denominators of (2) and (3) are:

$$E_b - E_i = Rhc\left(\frac{1}{n_{eff}^2} - \frac{1}{(n_{eff} \pm \frac{1}{2})^2}\right) \backsimeq \pm \frac{Rhc}{n_{eff}^3}$$

with these values of $\triangle E$ and with the matrix elements evaluated in § 5 one gets

$$I_\pi = I_\pi\,(4S{-}nS) + I_\pi\,(4S{-}(n{-}2)\,D) = 4{,}47.10^{-19}\,F^2\,n_{eff}^{10}\,I_\pi^{S,P} \quad . \quad (5)$$

$$I_\tau = I_\tau\,(4S{-}(n{-}2)\,D) = 1{,}49.10^{-19}\,F^2\,n_{eff}^{10}\,I_\tau^{S,P} . \quad . \quad . \quad . \quad (6)$$

where $I^{S,P}$ is the mean value of the intensities of the two neighbouring permitted lines. F is the electric field in volt/cm. Notice that $I_\tau(4S—nS)$ vanishes. These formulae are valid if

$$\gamma_\pi = 4{,}47.10^{-19} F^2 n_{eff}^{10} \ll 1 \qquad \gamma_\tau = 1{,}49.10^{-19} F^2 n_{eff}^{10} \ll 1.$$

In order to evaluate the intensity also when γ is near one, i.e. when the intensity of permitted and forbidden lines are comparable, we have divided formulae (5) and (6) as well as the intensity of the permitted lines by $1+\gamma_\pi$ or $1+\gamma_\tau$ respectively. This proceeding is suggested by the analogy with formulae (4), which we have found for three states. In this way the calculated intensities satisfy the sum rule. However it must be borne in mind that this normalization is rather conventional, as it would be necessary to take into account higher approximations. Any way it reproduces the main features of the effect and spares the laborious calculations that would be necessary otherwise.

The quadratic STARK effect does not practically affect the term values, because every term lies between two terms which repel it with nearly the same strength, so that the resulting effect vanishes. The same two terms exert instead a concordant action on the intensity of the forbidden lines, as one can see by considering the signs of the matrix elements of § 5.

In the other alkali metals the terms lie differently and hence there are several modifications in the phenomena. E. g. the P and D terms of lithium and sodium are nearly degenerate, whilst the S terms lie midway between. Hence there should be a stronger STARK effect; moreover $S—S$ and $S—D$ forbidden lines should be resolved, and a relevant complication is caused by the degeneration of D, F, G ..... levels.

§ 4. *Comparison with experiment and conclusions.*

In fig. 1 we have plotted the intensities and frequencies of permitted and forbidden lines previously calculated. We have assumed that the intensity of permitted lines varies as $1/n_{eff}^3$ according to what happens in hydrogen and to observations on sodium [1]).

Fig. 1*a* corresponds to $F=0$; fig. 1*b* to $F=800$ volt/cm in π and σ polarization; fig. 1*c* to $F=1600$ volt/cm. The thick lines belong to the permitted series, the thin ones to the $4S—nS$ and $4S—nD$ series, which are not resolved. The length of a line is proportional to its intensity. The interruption of the series is produced rather abruptly by forced ionization according to § 2. Our diagrams are in good qualitative agreement (except perhaps for some little details) with BAKKER's photograms; this confirms the main features of our interpretation of the extinction of the series.

§ 5. *Computation of some matrix elements.*

In the preceeding sections use has been made of the matrix elements of

[1]) A. FILIPPOV und W. PROKOFJEW, ZS. f. Phys. **56**, 458, 1929.

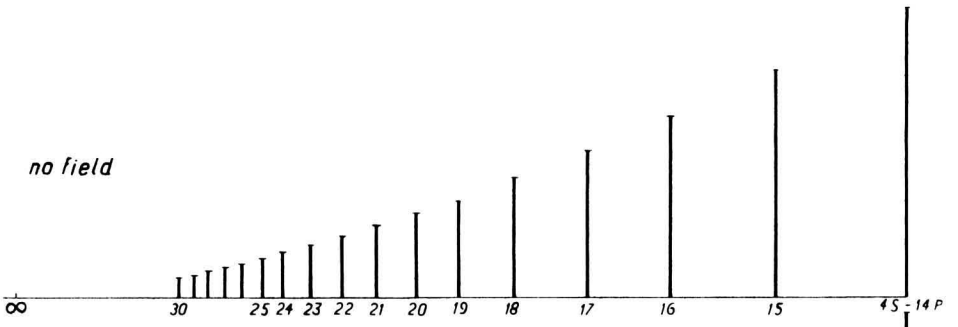
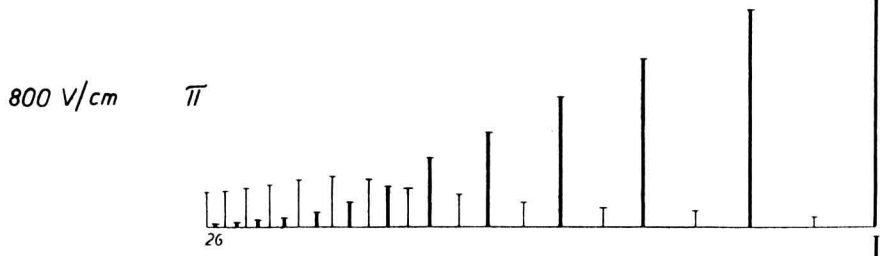


Fig. 1a



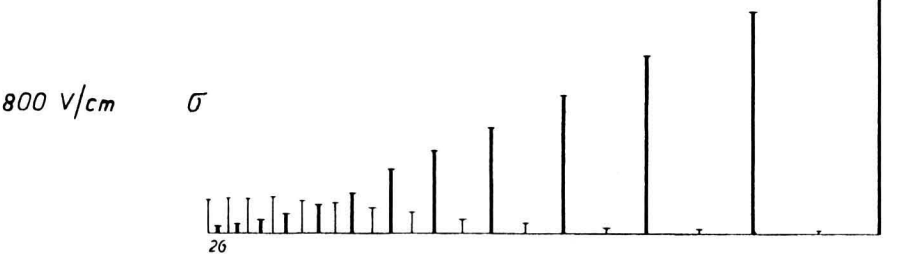
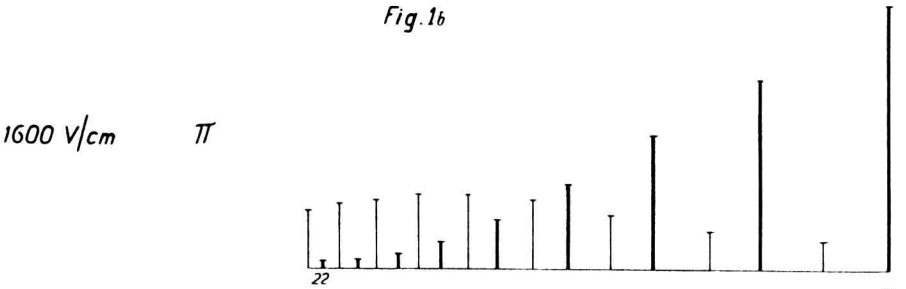


Fig. 1b



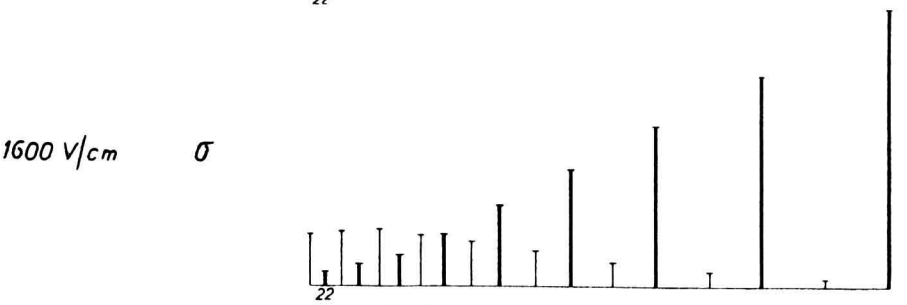


Fig. 1c

x and z for a transition $4S$—nP and of the elements of z for a transition nS—kP or nD—kP.

If we write the eigenfunctions in the following form:

$$\psi_{nlm}(r, \theta, \varphi) = f_{nl}(r) Y_l^m (\theta, \varphi)$$

where Y_l^m is a normalized spherical harmonic, then we find:
nS—kP:

$$z(0,0) = \frac{1}{\sqrt{3}} r_{n0,k1} \qquad x(0, \pm 1) = \frac{1}{\sqrt{6}} r_{n0,k1} \quad . \quad . \quad . \quad . \quad (7)$$

nD—kP

$$z(0, 0) = \frac{2}{\sqrt{15}} r_{n2,k1} \qquad z(1,1) = z(-1, -1) = \frac{1}{\sqrt{5}} r_{n2,k1} \quad . \quad . \quad (8)$$

all other elements vanish. The bracketted indices represent the initial and final values of m, and:

$$r_{nl,k1} = \int_0^\infty r f_{nl}(r) f_{k1}(r) r^2 dr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We will now evaluate these integrals by a method of approximation for high quantum numbers which is closely connected with BOHR's correspondence principle. As a preliminary remark notice that, if l is small ($l = 0, 1, 2$) and $n \gg 1$, the function $f_{nl}(r)$ behaves as follows: when r increases from 0 to ∞, $f_{nl}(r)$ oscillates about twice in the region where the field is not coulombian, then enters the region where the field may be practically regarded as a coulombian one and performs there many oscillations; the amplitude and length of the arcades increase until r reaches a value r_0 for which

$$E_{nl} + \frac{e^2}{r} - \frac{h^2}{8\pi^2 m} \frac{l(l+1)}{r^2} = 0$$

when $r > r_0$, f diminishes exponentially.

If $n \gg 1$ and $r < r_0$ and not too small, one may use the WENTZEL-BRILLOUIN approximation [1]):

$$r f_{nl}(r) = \frac{N}{\sqrt[4]{E_{nl} + \frac{e^2}{r}}} \cos \left\{ \frac{2\pi}{h} \int_r^{r_0} \sqrt{2m \left(E_{nl} + \frac{e^2}{r} \right)} dr - \frac{\pi}{4} \right\}. \quad (10)$$

For small values of r this formula can not be employed not only because WENTZEL-BRILLOUIN approximation is not sufficient, but also because the field is not a coulombian one and because (10) does not contain the term $\frac{l(l+1)}{r^2}$ which corresponds to centrifugal force. Moreover for $r > r_0$

[1]) See for instance H. A. KRAMERS. ZS. f. Phys. **39**, 828, 1926.

formula (10) ought to be replaced by a different one, and the two functions ought to be connected by KRAMERS' method [1]).

Anyway it is easily seen that (10) represents f sufficiently well, precisely in that region which gives most part of the contribution to the integrals (9) and to the normalization integrals. Therefore we will exclusively employ formula (10), limiting all integrals between 0 and r_0 i.e. to that part of the field where the electron moves, according to classical mechanics. In this approximation the effects of screening and of the quantum number l are only considered inasmuch as they affect the value of the RYDBERG correction and therefore E_{nl}.

Let us now calculate the normalisation factor N. We have

$$\frac{1}{N^2} = \int_0^{r_0} \frac{1}{\sqrt{E + \frac{e^2}{r}}} \cos^2 \varphi \, dr$$

if we denote with φ the phase in (10). The factor $\sqrt{E + \frac{e^2}{r}}$ varies slowly whilst $\cos^2 \varphi$ oscillates rapidly. Hence we can substitute $\cos^2 \varphi$ with its mean value $1/2$, and then

$$\frac{1}{N^2} = \frac{1}{2} \int_0^{r_0} \frac{dr}{\sqrt{E + \frac{e^2}{r}}} = \frac{1}{\sqrt{2m}} \int_0^{T/2} dt = \frac{T}{2\sqrt{2m}}$$

where T is the classical period of the orbit of energy E.

From (9) and (10), we get for neighbouring terms i.e.; for $|n-k| \ll n$:

$$r_{nl,\,k1} = N^2 \int_0^{r_0} \frac{r \, dr}{\sqrt{E + \frac{e^2}{r}}} \cos \varphi_n \cos \varphi_k \, dr$$

In

$$2 \cos \varphi_n \cos \varphi_k = \cos (\varphi_n + \varphi_k) + \cos (\varphi_n - \varphi_k)$$

we will neglect the rapidly oscillating $\cos (\varphi_n + \varphi_k)$ that gives a small contribution compared with $\cos (\varphi_k - \varphi_n)$. Moreover we may put:

$$\varphi_n - \varphi_k = \frac{2\pi m}{h} \int_r^{r_0} \frac{E_{nl} - E_{k1}}{\sqrt{2m\left(E + \frac{e^2}{r}\right)}} dr = \frac{2\pi}{h} \tau \frac{dE}{dn} \int_0^t dt$$

[1]) H. A. KRAMERS. l. c.

where t is the time employed by the electron to go from r to r_0 according to classical theory, and $\tau = n_{eff} - k_{eff}$. Then:

$$r_{nl,kl} = \frac{4}{T} \left\{ \int_0^{r_0} \frac{m\, r\, dr}{\sqrt{2m\left(E + \frac{e^2}{r}\right)}} \cos\left(\frac{2\pi}{h} \frac{dE}{dn} \tau t\right) = \right. \left. \int_0^{T/2} r(t) \cos\left(\frac{2\pi}{h} \frac{dE}{dn} \tau t\right) dt \right\} \quad . \quad . \quad (11)$$

For two states with the same l, τ is an integer and we find the result required by the correspondence principle, i.e. the coefficient of $e^{2\pi i \nu \tau t}$ in the FOURIER expansion of $r(t)$.

The integral (11) can be simplified through introduction of the excentric anomaly u by means of the formulae:

$$r = -\frac{e^2}{2E}(1 + \cos u) \qquad \frac{2\pi}{h} \frac{dE}{dn} t = u + sen u$$

hence finally

$$r_{nl,kl} = \frac{h^2}{4\pi^2 me^2} n_{eff}^2 \frac{1}{\pi} \int_0^{\pi} (1 + \cos u)^2 \cos\left[\tau\,(u + sen u)\right] du.$$

The last integral, K, involves BESSEL functions when τ is an integer. For $\tau = {}^1/_2$ or ${}^3/_2$ it has been calculated numerically with the following result

$\tau = 0$	$\frac{1}{2}$	1	$\frac{3}{2}$
$K = \frac{3\pi}{2}$	3,47	2,04	0,45$_6$

The former calculations do not apply to the elements $r_{4S,nP}$. It is well known [1]) that for $n \gg 1$:

$$r_{4S,nP} = \pm \frac{c}{\sqrt{n^3_{eff}}}$$

where c is a constant whose value is inessential. The sign depends on the conventions on the sign of the eigenfunctions. If $f > 0$ for $r \to \infty$ like in formula (10), the matrix elements $r_{4S,nP}$ are alternatively positive and negative.

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Roma, May 1933.

[1]) D. R. HARTREE. Proc. Cambr. Phil. Soc. **24**, 426, 1928, see also [5]).