It is very unfortunate that time did not permit of further experiments with a wider variety of elements and with devices for the detection of radiation of other kinds. The importance of a complete investigation arises from the fact that the tracing of the subsequent history of the atomic nucleus which has been disrupted by the collision of an α-particle is, at present, one of our few paths to a knowledge of the forces within the nucleus.

In conclusion, I wish to thank Sir Ernest Rutherford for giving me this very interesting problem; and Mr. Bieler for his assistance during observations.

Cavendish Laboratory,
Cambridge, 1921.

C. *On the Appearance of Unsymmetrical Components in the Stark Effect.* *By* A. M. Mosharrafa, *B.Sc.**

§ 1. *Preliminary.*

THE theory of spectral lines which has hitherto proved most successful in interpreting the results of experiment is based upon certain assumptions of a quantum type introduced by Bohr †, Sommerfeld ‡, and others. Such assumptions are only justifiable in so far as they give satisfactory interpretations of correlated phenomena. The effect of an electric field upon spectral lines emitted by substances subjected to the field was first investigated by J. Stark § in 1913; and an approximate theory was furnished by K. Schwarzschild ‖ and by P. Epstein ¶ independently in 1916: the two theories are similar and give satisfactory explanations of the phenomenon as investigated by Stark. *Now, according to their theory, the components into which any given spectral line is split up are symmetrically distributed about the original position of the line.* In the

* Communicated by Dr. J. W. Nicholson, F.R.S.

† See *e.g.* N. Bohr, "Constitution of Atoms and Molecules," Phil. Mag. July 1913.

‡ See Arnold Sommerfeld, 'Atombau und Spektrallinien,' II. Auf. (1921).

§ *Berliner Sitzungsber.*, November 1913; *Ann. d. Phys.* xliii. p. 983 (1914).

‖ K. Schwarzschild, "Zur Quantentheorie," *Berliner Sitzungsber.*, April 1916.

¶ P. S. Epstein, "Zur Theorie des Starkeffektes," *Ann. d. Phys.* l. p. 489 (1916).

present paper a closer approximation is worked out, and it is found [see § 4] that for stronger fields than those used by Stark this symmetry no longer follows from the theory: on the other hand, a pair of components which, for fields comparable with those that Stark used *, appear symmetrically situated, would for stronger fields be displaced *in the same direction*, so that the symmetry is destroyed. We, naturally, also find that the relation between the strength of the field and the displacements of the lines is no longer represented graphically by straight lines, but by parabolic curves whose curvatures change sign with the displacements (*i. e.* displacements of opposite signs correspond to parabolas of opposite curvatures).

It appears to the present writer that an experimental investigation of the Stark effect for fields stronger than those that have already been employed by Stark is highly desirable as a further test of the fundamental hypotheses of the quantum theory of spectra: if such an investigation result in the verification of the predictions already referred to, then this will add to our faith in the foundations of the quantum theory of spectral lines: whereas a negative experimental result would, unless the analysis here presented be at fault, lead us to a reconsideration of our assumptions, and perhaps to certain modifications thereof.

§ 2. *Previous Work.*

The equations restricting the motion of an electron moving under the influence of an attraction towards a nucleus as well as a fixed force F can be written in the form

$$\left.\begin{aligned} J_\xi=\int_0\sqrt{f_1(\xi)}\,d\xi=n_1h, \qquad J_\eta=\int_0\sqrt{f_2(\eta)}\,d\eta=n_2h, \\ \sqrt{m_0}\int_0^{2\pi}\alpha\,d\psi=n_3h, \end{aligned}\right\} \tag{1}$$

where h is Planck's quantum of action, $n_1\, n_2\, n_3$ are whole numbers, m_0 is the mass of the electron, and $f_1(\xi)\, f_2(\eta)$ are given by

$$\left.\begin{aligned} \frac{1}{m_0}f_1(\xi)&=2(e\mathrm{E}+\beta)+2\mathrm{W}\xi^2-e\mathrm{F}\xi^4-\frac{\alpha^2}{\xi^2}, \\ \frac{1}{m_0}f_2(\eta)&=2(e\mathrm{E}-\beta)+2\mathrm{W}\eta^2+e\mathrm{F}\eta^4-\frac{\alpha^2}{\eta^2}, \end{aligned}\right\} \quad . \tag{2}$$

* For the H lines, *e. g.*, Stark used a field of about 28,500 volt × cm.$^{-1}$ (=95 C.G.S. electrostatic units). We find that a field of about 10 times this strength would give quite measurable effects.

Here $(-e)$ is the charge on the electron, E that on the nucleus, and α, β, W are constants arising from the integration of the Jacobian Differential Equation *. W represents the energy of the electron. The coordinates ξ and η are parabolic coordinates in accordance with the equation

$$x+iy=\tfrac{1}{2}(\xi+i\eta)^2, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where x, y, z are Cartesian coordinates at the nucleus, Ox *being chosen parallel to the external field* F. The limits of integration for the two first integrals in (1) are the maxima and minima of ξ and η respectively. Now these two integrals are both of the same form; so that we can write:

$$\int_0 \sqrt{A+\frac{2B}{r}+\frac{C}{r^2}+Dr}\, dr=2nh, \quad . \quad . \quad . \quad (4)$$

thus denoting the two cases for ξ and η by the suffixes 1 and 2 respectively we have

$$\left.\begin{aligned} A_1=2m_0W, \quad & B_1=m_0(eE+\beta), \quad C_1=-\left(\frac{n_3h}{2\pi}\right)^2, \\ & D_1=-m_0eF; \end{aligned}\right\} \quad (5\,a)$$

$$\left.\begin{aligned} A_2=2m_0W, \quad & B_2=m_0(eE-\beta), \quad C_2=-\left(\frac{n_3h}{2\pi}\right)^2, \\ & D_2=+m_0eF. \end{aligned}\right\} \quad (5\,b)$$

Now Sommerfeld † works out the value of the contour integral on the left-hand side. The value he gives is

$$2\pi i\left\{\sqrt{C}+\frac{B}{\sqrt{A}}+\frac{D}{4A^{3/2}}\left(\frac{3B^2}{A}-C\right)\right\}. \quad . \quad . \quad (6)$$

From (4) and (6) we can write,

$$B=-\sqrt{A}\left(\sqrt{C}+\frac{nhi}{\pi}\right)+\frac{D}{4A}\left(C-\frac{3B^2}{A}\right). \quad . \quad (7)$$

Both Sommerfeld and Epstein have obtained the value of W [which Epstein denotes by $(-A)$] by slightly different methods to the first order in F [Epstein's $(-E)$]. We shall proceed to a second approximation.

* For a fuller treatment of this section, see Epstein's paper already referred to, also Sommerfeld's 'Atombau u.s.w.' II. Auf. p. 542, and p. 482. Jacobi's method of integrating the Hamiltonian transformed equations is also given by Appell, 'Mécanique rationelle,' ii. p. 400 (Paris, 1904).

† 'Atombau u.s.w.' Zusatz vii. p. 482, under f.; we, however, write $\sqrt{C}$ for his $(-\sqrt{C})$.

§ 3. *Calculations for Comparatively Large Fields.*

We shall treat the term in D in equation (7) as a corrective term. Let $\overset{0}{\beta}$, $\overset{0}{\beta}+\overset{0}{\Delta}\beta=\beta'$, $\beta'+\Delta'\beta=\beta''$, etc., denote the successive approximations to the value of β; similarly for A, B, and W. We see that to the first order of small quantities

$$\overset{1}{\mathrm{B}}_1{}^2=[\overset{0}{\mathrm{B}}_1+\overset{0}{\Delta}\mathrm{B}_1]^2=[\overset{0}{\mathrm{B}}_1+m_0\overset{0}{\Delta}\beta]^2 \quad \text{from (5}\,a)$$

$$\doteq \overset{0}{\mathrm{B}}_1{}^2+2m_0\overset{0}{\mathrm{B}}_1\overset{0}{\Delta}\beta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8\,a)$$

and similarly

$$\overset{1}{\mathrm{B}}_2{}^2\doteq \overset{0}{\mathrm{B}}_2{}^2-2m_0\overset{0}{\mathrm{B}}_2\overset{0}{\Delta}\beta \quad \text{from (5}\,b). \quad . \quad . \quad . \quad (8\,b)$$

Now the equations for determining $\overset{0}{\Delta}\beta$ could easily be solved, but as we are assuming Epstein's work we shall merely give here the value obtained on solving his equations (61) *. We have

$$\overset{0}{\Delta}\beta=\frac{\mathrm{N}\,.\,\mathrm{F}\,.\,h^4(n_1+n_2+n_3)}{64m_0{}^2e\mathrm{E}^2\pi^4} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where

$$\mathrm{N}\equiv(6n_2{}^2+6n_2n_3+n_3{}^2)(2n_1+n_3)$$
$$+(6n_1{}^2+6n_1n_2+n_3{}^2)(2n_2+n_3), \quad (10)$$

so that we have from (8) and (9)

$$\overset{1}{\mathrm{B}}_1{}^2=\overset{0}{\mathrm{B}}_1{}^2+2m_0\overset{0}{\mathrm{B}}_1\times\frac{h^4(n_1+n_2+n_3)\mathrm{N}}{64m_0{}^2e\mathrm{E}^2\pi^4}\mathrm{F}, \quad . \quad (11\,a)$$

similarly

$$\overset{1}{\mathrm{B}}_2{}^2=\overset{0}{\mathrm{B}}_2{}^2-2m_0\overset{0}{\mathrm{B}}_2\times\frac{h^4\,.\,(n_1+n_2+n_3)\,.\,\mathrm{N}}{64m_0{}^2e\mathrm{E}^2\pi^4}\,.\,\mathrm{F}; \quad (11\,b)$$

also, $\overset{0}{\mathrm{B}}{}^2$ is obtained from (7) on neglecting the term in D, thus:

$$\overset{0}{\mathrm{B}}{}^2=\mathrm{A}\left(\sqrt{\mathrm{C}}+\frac{nhi}{\pi}\right)^2. \quad . \quad . \quad . \quad . \quad (12)$$

* *Ann. d. Phys.* l. p. 508 (1916); our $\overset{0}{\Delta}\beta$ corresponds to Epstein's $(e^2\Delta\beta)$.

From (11) and (12) we have

$$B^{\frac{1}{2}}=A\left(\sqrt{C}+\frac{nhi}{\pi}\right)^2 \mp \frac{h^4(n_1+n_2+n_3)\sqrt{A}N}{32m_0eE^2\pi^4}\left(\sqrt{C}+\frac{nhi}{\pi}\right)F. \quad . \quad . \quad . \quad (13)$$

Substituting this value for B^2 in the term involving D on the right-hand side of (7), we have

$$B=-\sqrt{A}\left(\sqrt{C}+\frac{nhi}{\pi}\right)+\frac{D}{4A}\left\{C-3\left(\sqrt{C}+\frac{nhi}{\pi}\right)^2 \pm F\times\frac{3h^4(n_1+n_2+n_3)N\left(\sqrt{C}+\frac{nhi}{\pi}\right)}{32m_0eE^2\sqrt{A}\,\pi^4}\right\},$$

or, substituting the values of D from (5), we have

$$B=-\sqrt{A}\left(\sqrt{C}+\frac{nhi}{\pi}\right)\mp\frac{m_0e}{4A}\left\{C-3\left(\sqrt{C}+\frac{nhi}{\pi}\right)^2\right\}F - \frac{3h^4(n_1+n_2+n_3)N\left(\sqrt{C}+\frac{nhi}{\pi}\right)}{128E^2\pi^4A^{3/2}}F^2; \quad . \quad (14)$$

writing the two equations embodied in (14) in full and adding, we obtain

$$m_0eE=-\sqrt{A}\left(\sqrt{C}+\frac{(n_1+n_2)hi}{2\pi}\right) + \frac{m_0eF}{4A}\left(\frac{3}{2}\frac{(n_2{}^2-n_1{}^2)h^2}{\pi^2}-\frac{3(n_2-n_1)hi\sqrt{C}}{\pi}\right) - \frac{3h^4(n_1+n_2+n_3)N}{128A^{3/2}\pi^4E^2}\left[\sqrt{C}+\frac{(n_1+n_2)hi}{2\pi}\right]F^2. \quad . \quad (15)$$

We proceed to solve for A by putting

$$A=-(K+LF+MF^2). \quad . \quad . \quad . \quad . \quad (16)$$

We have

$$\left.\begin{aligned}\sqrt{A} &= i\sqrt{K}\left(1+\frac{1}{2}\frac{L}{K}F+\frac{1}{8}\frac{4MK-L^2}{K^2}F^2\right) \quad \text{approximately,}\\ \text{and}\quad \frac{1}{A} &= -\frac{1}{K}\left(1-\frac{L}{K}F\right) \quad \text{,,}\\ \text{and}\quad \frac{1}{A^{3/2}} &= \frac{i}{K^{3/2}} \quad \text{,,}\end{aligned}\right\} \quad (17)$$

Thus, substituting in (15) and putting

$$\sqrt{C} = \frac{n_3 hi}{2\pi},$$

we have, on equating the coefficients of powers of F,

$$K = +\frac{4\pi^2(m_0 e E)^2}{(n_1+n_2+n_3)^2 h^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$L = \frac{3h^2}{4\pi^2 E}(n_2-n_1)(n_1+n_2+n_3), \quad . \quad . \quad . \quad (19)$$

$$M = \frac{L^2}{4K} - \frac{3m_0 e h L}{2\pi K^{3/2}}(n_2-n_1) - \frac{3h^4(n_1+n_2+n_3)N}{64\pi^4 E^2 K}. \quad . \quad . \quad . \quad (20)$$

On substituting from (18) and (19) in (20), we finally obtain

$$M = \frac{-27h^6(n_1+n_2+n_3)^3}{256\pi^6 E^4 m_0^2 e^2} N', \quad . \quad . \quad . \quad . \quad (21)$$

where $$N' = (n_1+n_2+n_3)(n_2-n_1)^2 + N. \quad . \quad . \quad . \quad (22)$$

We thus finally have the full expression for the energy:

$$W = -\frac{2\pi^2 m_0 e^2 E^2}{(n_1+n_2+n_3)^2 h^2} - \frac{3Fh^2}{8\pi^2 m_0 E}(n_2-n_1)(n_1+n_2+n_3) + \frac{27h^6(n_1+n_2+n_3)^3}{512\pi^6 E^4 m_0^3 e^2} N'F^2. \quad . \quad . \quad (23)$$

Thus if ΔW represent the change in W due to the introduction of the external field F, we have

$$-\Delta W = \frac{3Fh^2}{8\pi^2 m_0 E}(n_2-n_1)(n_1+n_2+n_3) - \frac{27h^6(n_1+n_2+n_3)^3}{512\pi^6 E^4 m_0^3 e^2} N'F^2. \quad . \quad (24)$$

Thus $\Delta\nu$ [the corresponding change in frequency] is given, according to Bohr's assumption

$$h\Delta\nu = \Delta W_m - \Delta W_n,$$

where W_m denotes the energy for motion in a path [characterized by the quantum numbers $m_1 m_2 m_3$] from which the electron starts to move towards the n-path, by the formula

$$\Delta\nu = \frac{3hF}{8\pi^2 m_0 E}\{(n_2-n_1)(n_1+n_2+n_3) - (m_2-m_1)(m_1+m_2+m_3)\} + \frac{27h^5F^2}{512\pi^6 E^4 m_0^3 e^2}\{-(n_1+n_2+n_3)^3 N'(n) + (m_1+m_2+m_3)N'(m)\}, \quad . \quad (25)$$

where $N'(m)$ and $N'(n)$ are identical functions of m and n respectively.

§ 4. *Application to the* H_α *line.*

We proceed to apply equation (25) to specific lines of the elements. Let us take as an example the H_α line of the Balmer Series. Here $n_1+n_2+n_3=2$, $m_1+m_2+m_3=3$, $\nu=4{\cdot}571\times10^{14}$, $\lambda={\cdot}65628\times10^{-4}$; let us also write (25) in the form

$$\Delta\nu=(P_1-Q_1)\times K_1F+(Q_2-P_2)K_2F^2\,; \qquad (26)$$

then

$$\left.\begin{aligned}
P_1&=(n_2-n_1)(n_1+n_2+n_3),\quad Q_1=(m_2-m_1)(m_1+m_2+m_3),\\
K_1&=\frac{3h}{8\pi^2m_0E},\\
P_2&=(n_1+n_2+n_3)^4(n_2-n_1)^2+(n_1+n_2+n_3)^3N(n),\\
Q_2&=(m_1+m_2+m_3)^4(m_2-m_1)^2+(m_1+m_2+m_3)^3N(m),\\
K_2&=\frac{27h^5}{512\pi^6E^4m_0{}^3e^2},
\end{aligned}\right\} \qquad (27)$$

Then writing down in a tabular form the possible values of $n_1\,n_2\,n_3$ and $m_1\,m_2\,m_3$, we have, on availing ourselves of Sommerfeld's "Auswahlprinzip" for the definition of the plane of polarization and the restrictions on the possible combinations of the quantum numbers:

TABLE A.

	n_3.	n_2.	n_1.	P_1.	P_2.		m_3.	m_2.	m_1.	Q_1.	Q_2.
I.	2	0	0	0	128	*a.*	3	0	0	0	1458
II.	1	1	0	2	144	*b.*	2	1	0	3	2025
III.	1	0	1	−2	144	*c.*	2	0	1	−3	2025
IV.	0	1	1	0	192	*d.*	1	1	1	0	2106
V.	0	2	0	4	64	*e.*	1	2	0	6	1458
VI.	0	0	2	−4	64	*f.*	1	0	2	−6	1458
						g.	0	2	1	3	2025
						h.	0	1	2	−3	2025
						i.	0	3	0	9	729
						j.	0	0	3	−9	729

TABLE B.

First Group. $m_3-n_3=0$; p-component.

	P_1-Q_1.	Q_2-P_2.		P_1-Q_1.	Q_2-P_2.
(I. *b*)	-3	1897	(I. *c*)	$+3$	1897
(II. *d*)	$+2$	1962	(III. *d*) ...	-2	1962
(II. *e*)	-4	1314	(III. *f*) ...	$+4$	1314
(II. *f*)	$+8$	1314	(III. *e*)......	-8	1314
(IV. *g*)......	-3	1833	(IV. *h*) ...	$+3$	1833
(IV. *i*)	-9	537	(IV. *j*) ..	$+9$	537
(V. *g*)	$+1$	1951	(VI. *h*) ...	-1	1951
(V. *h*)	$+7$	1951	(VI. *g*) ...	-7	1951
(V. *i*)	-5	665	(VI. *g*) ...	$+5$	665
(V. *j*)	$+13$	665	(VI. *i*) ...	-13	665

TABLE C.

Second Group. $m_3-n_3=\pm 1$; n-component.

	P_1-Q_1.	Q_2-P_2.		P_1-Q_1.	Q_2-P_2.
(I. *a*)	0	1330	(I. *d*)	0	1978
(I. *e*)	-6	1330	(I. *f*)	$+6$	1330
(II. *b*)	-1	1881	(III. *c*) ...	$+1$	1881
(II. *c*)	$+5$	1881	(III. *b*) ...	-5	1881
(II. *g*)	-1	1881	(III. *h*) ...	$+1$	1881
(II. *h*)	$+5$	1881	(III. *g*) ...	-5	1881
(II. *i*)	-7	589	(III. *j*) ...	$+7$	589
(II. *j*)	$+11$	589	(III. *i*) ...	-11	589
(IV. *e*)......	-6	1266	(IV. *f*) ...	$+6$	1266
(V. *e*)	-2	1394	(VI. *f*) ...	$+2$	1394
(V. *f*)	$+10$	1394	(VI. *e*) ...	-10	1394
(V. *d*)	$+4$	2042	(VI. *d*) ...	-4	2042
(IV. *d*)......	0	1914			

The arrangement of the tables is very simple. In Table A we put down all the possible values for the n's and the m's separately for the line H_α. Then in Tables B and C we choose such combinations as give rise to $m_3-n_3=0$ or $m_3-n_3=\pm 1$ respectively. The group in Table A corresponds to lines where the plane of polarization is perpendicular to the impressed field F [*i. e.* the electric force parallel to F], and that of Table B to lines where the light is polarized in a plane parallel to F [*i. e.* the electric force perpendicular to F].

We observe that whereas (P_1-Q_1) has a negative value numerically equal to every one of its possible positive values, (Q_2-P_2) *on the other hand has an invariable positive sign and a roughly constant order of magnitude, viz.* 10^3.

If we avail ourselves of the most recent values * for the constants involved in the formula (25), viz.

$$h=6\cdot547\times10^{-27},\quad e=4\cdot774\times10^{-10},\quad \frac{e}{m_0}=5\cdot301\times10^{17},$$

and if we put $E=e$ for hydrogen, we have

$$K_1=5\cdot784\times10^8.\quad K_2=7\cdot677\times10\,; \quad . \quad . \quad (28)$$

so that (26) can now be written

$$\Delta\nu=5\cdot784\times10^8\times Z\times F+7\cdot677\times R_z\times10^4\times F^2, \qquad (29)$$

where

$$Z\equiv(P_1-Q_1),\quad R_z=\frac{Q_2-P_2}{1000},$$

or on the scale of wave-lengths, since $\Delta\nu=-\frac{c}{\lambda^2}d\lambda$,

$$-\Delta\lambda=\cdot8304\times10^{-10}\times F\times Z+1\cdot102\times10^{-14}\times R_zF^2. \quad (30)$$

Here it must be remembered that F is measured in absolute C.G.S. electrostatic units. In (30) we observe that Z is a whole number, positive or negative, between 0 and 13 and that R_z varies from about $\frac{1}{2}$ to about 2.

If we assume a value for $F=10^3$ [$=300{,}000$ volt $\times$ cm.$^{-1}$], then if λ' be written for $\lambda\times10^8$ [*i. e.* if we measure λ', the wave-length, in Ångström units] we write :

$$-\Delta\lambda'=8\cdot304Z+1\cdot102\times R_z. \quad . \quad . \quad . \quad . \quad (31)$$

We thus see that for small values of Z, the second term on the right-hand side of (31) is quite appreciable compared with the first term [*e. g.* for $Z=1$ the ratio is about $\frac{1}{4}$] ; *and*

* These are quoted from R. A. Millikan's 'The Electron,' The University of Chicago Press, Third Impression 1918, pp. 238 and 251.

since this term has an invariable value for equal and opposite values of Z, it follows that the symmetry of the lines is destroyed. Also the parabolic relation between $\Delta\nu$ and F [or $\Delta\lambda$ and F] is furnished by (29) and (30) respectively. We give here a table of the displacements of the nine lines observed by Stark for a hypothetical field of 300,000 volt $\times$ cm.$^{-1}$ as predicted by our theory.

	p-component.						*n*-component.				
Z	+2	−2	+3	−3	+4	−4	0			+1	−1
R_z ...	1·962	1·962	1·833	1·833	1·314	1·314	1·978	1·914	1·330	1·881	1·881
$\Delta\lambda'$ ...	−18·8	−14·4	−26·9	+22·9	−34·7	+31·8	−2·2	−2·1	−1·5	−10·3	+6·4

The *n*-component line which occupies the original position of the H_α line is seen to split into three components—two of which are, however, very close together—for higher fields. The position of these lines may, however, be appreciably affected by higher terms in equation (30) than the last term we have taken account of (*i. e.* terms in F^3 etc.). It is to be observed that the functions of the quantum numbers involved seem to become more and more important in determining the order of magnitude of the respective terms as we proceed to consider higher powers of F. However, the above calculations ought to furnish a fairly accurate theory for fields of the magnitude we have considered; and, in our opinion, it would be highly desirable to make exact measurements for such fields. Whether the above predictions will or will not be verified, remains to be seen.

In conclusion, I wish to express my thanks to Prof. J. W. Nicholson for useful suggestions.

King's College, London,
May 1921.