THE STARK EFFECT FROM THE POINT OF VIEW OF SCHROEDINGER'S QUANTUM THEORY

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Abstract

A theory of the Stark effect based on Schroedinger's ideas is presented. (1) *Positions of lines* practically coincide with those obtained in the writer's old theory which gave an excellent agreement with experiment. (2) *Intensity expressions* are obtained in a simple closed form: (a) Components which, in the old theory, had to be ruled out by a special postulate now drop out automatically. (b) The computed intensities of the remaining components check the observed within the limits of experimental error.

1. *Introductory.* In the rapid development of the quantum theory during the last year, Schroedinger's concept of characteristic oscillations in the atom[1] represents the most significant contribution. From the formal mathematical point of view it includes the whole of the Heisenberg-Born-Dirac matrix theory and gives, moreover, a simplified, practically convenient method of finding the matrices. Beyond this, it opens new avenues of thought and seems to afford our first glimpse of the true nature of the quanta.

It seemed highly desirable to carry through this ingenious method in as many special cases as possible. Accordingly, a complete theory of the radiation of a hydrogen-like atom in an electric field (Stark effect) has been worked out and is presented in the following sections. After a general mathematical exposition of the method (Sections 2,3), the positions of the components are determined to terms of the second order in the electrical field, (Sections 4, 5), while the rest of the paper is devoted to calculating the intensities. The positions of the lines turn out to be practically the same as in the writer's old theory.[2] The first order terms are identical with the old expressions, the second order terms show a very slight difference. The main interest of the paper lies, therefore, in the intensity formulas, which are remarkably simple in their structure and agree with the observed values better than Kramers'[3] intensity expressions derived from Bohr's correspondence principle.

2. *Outline of the mathematical problem.* We have to start from Schroedinger's equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{2\mu}{k^2}(E-U)\psi=0, \tag{1}$$

[1] Schroedinger, Ann. d. Physik. **79**, 361, 489, 734 (1926).

[2] P. S. Epstein, Ann. d. Physik. **50**, 489; **51**, p. 183 (1926).

[3] H. A. Kramers. Roy. Danish Academy, p. 287 (1919).

where μ and e denote the mass and charge of an electron and k is an abbreviation for $h/2\pi$. Moreover, U is the potential energy of the dynamical system, and E a constant corresponding to the total energy in Bohr's theory. In the case of the combined action of a nucleus $+Ze$ and a homogeneous field of the strength D, which we propose to treat in this paper,

$$U=-\frac{Ze^2}{r}+eDz \tag{2}$$

if the z-axis is taken in the direction of the field.

The first question that arises is to find a set of separation coordinates for Eq. (1). It is easy to see that this can be accomplished by using the same coordinates which brought the solution of the Stark effect in the old theory,[4] i. e. parabolical coordinates given by the representation

$$x=\sqrt{\xi\eta}\cos\varphi,\quad y=\sqrt{\xi\eta}\sin\varphi,\quad z=\frac{\xi-\eta}{2}, \tag{3}$$
$$0\leqq\xi\leqq\infty,\ 0\leqq\eta\leqq\infty,\ 0\leqq\varphi\leqq 2\pi$$

This gives

$$r=\frac{\xi+\eta}{2},$$

$$ds^2=\frac{1}{4}(\xi+\eta)\left(\frac{d\xi^2}{\xi}+\frac{d\eta^2}{\eta}\right)+\xi\eta d\varphi^2,$$

$$\Delta^2\psi=\frac{4}{\xi+\eta}\left\{\frac{\partial}{\partial\xi}\left(\xi\frac{\partial\psi}{\partial\xi}\right)+\frac{\partial}{\partial\eta}\left(\eta\frac{\partial\psi}{\partial\eta}\right)+\frac{1}{4}\left(\frac{1}{\xi}+\frac{1}{\eta}\right)\frac{\partial^2\psi}{\partial\varphi^2}\right\} \tag{4}$$

and Schroedinger's equation becomes

$$\frac{\partial}{\partial\xi}\left(\xi\frac{\partial\psi}{\partial\xi}\right)+\frac{\partial}{\partial\eta}\left(\eta\frac{\partial\psi}{\partial\eta}\right)+\frac{1}{4}\left(\frac{1}{\xi}+\frac{1}{\eta}\right)\frac{\partial^2\psi}{\partial\varphi^2}+\frac{\mu}{2k^2}\left[E(\xi+\eta)+2Ze^2-\frac{eD(\xi^2-\eta^2)}{2}\right]\psi=0 \tag{5}$$

We make the substitution

$$\psi=M(\xi)N(\eta)\begin{matrix}\cos\\ \sin\end{matrix}(s-1)\varphi, \tag{6}$$

and get for the functions M and N the two plain differential equations

$$\begin{aligned}\frac{d^2M}{d\xi^2}+\frac{1}{\xi}\frac{dM}{d\xi}+\left(\frac{\mu E}{2k^2}+\frac{\mathfrak{A}}{\xi}-\frac{(s-1)^2}{4}\frac{1}{\xi^2}-\frac{\mu eD}{4k^2}\xi\right)M=0,\\ \frac{d^2N}{d\eta^2}+\frac{1}{\eta}\frac{dN}{d\eta}+\left(\frac{\mu E}{2k^2}+\frac{\mathfrak{A}'}{\eta}-\frac{(s-1)^2}{4}\frac{1}{\eta^2}+\frac{\mu eD}{4k^2}\eta\right)N=0,\end{aligned} \tag{7}$$

[4] P. S. Epstein, Ann. d Physik. **50,** 495 (1916).

The two constants $\mathfrak{A}$ and $\mathfrak{A}'$ must satisfy the relation

$$\mathfrak{A}+\mathfrak{A}'=\frac{\mu Ze^2}{k^2} \tag{8}$$

The main mathematical problem is to pick the constants E and $\mathfrak{A}$ in such a way that one of the integrals of either equation becomes finite in the point $\xi=0$ (resp. $\eta=0$) and vanishes for $\xi=\infty$ (resp. $\eta=\infty$).

3. *Conditions in a vanishing field.* If the homogeneous field vanishes, it is not hard to satisfy the above condition. Let us simplify our expressions by substituting

$$\left\{\begin{aligned} &M=\xi^{(s-1)/2}e^{\alpha\xi}X(\xi), \quad N=\eta^{(s-1)/2}e^{\alpha\eta}Y(\eta), \\ &\alpha=\sqrt{-\frac{\mu E}{2k^2}}\,. \end{aligned}\right. \tag{9}$$

Eqs. (7) then are reduced to

$$\left\{\begin{aligned} &\frac{d^2X}{d\xi^2}+\left(2\alpha+\frac{s}{\xi}\right)\frac{dX}{d\xi}+\left(\frac{\mathfrak{A}+s\alpha}{\xi}-\frac{\mu eD}{4k^2}\xi\right)X=0, \\ &\frac{d^2Y}{d\eta^2}+\left(2\alpha+\frac{s}{\eta}\right)\frac{dY}{d\eta}+\left(\frac{\mathfrak{A}'+s\alpha}{\eta}+\frac{\mu eD}{4k^2}\eta\right)Y=0 \end{aligned}\right. \tag{10}$$

In the special case $D=0$ these equations are obviously of the hypergeometric type and the functions $\overline{X}$ and $\overline{Y}$ can be readily represented by power series. We shall write in this case X_0, Y_0, $\mathfrak{A}_0$, α_0. If we denote for short

$$\mathfrak{A}_0+s\alpha_0=-2\alpha_0 m, \quad \mathfrak{A}_0'+s\alpha_0=-2\alpha_0 n, \tag{11}$$

the exponents of the first terms of the ascending series are 0 and $-(s-1)$. We can, therefore, use only the series with the exponent 0, since the second will give values infinite in the point $\xi=0$ (s being a positive integer):

$$\left\{\begin{aligned} &X_0=1+\frac{m}{1\cdot s}\,2\alpha_0\xi+\frac{m(m-1)}{2!s(s+1)}\,(2\alpha_0\xi)^2+\cdots \\ &Y_0=1+\frac{n}{1\cdot s}\,2\alpha_0\eta+\frac{n(n-1)}{2!s(s+1)}\,(2\alpha_0\eta)^2+\cdots \end{aligned}\right. \tag{12}$$

These expansions show that our functions can be reduced to ordinary hypergeometric functions by the following process:

$$X_0=\lim_{\substack{\beta=\infty,\,x=0\\ \beta x=\xi}} F(-m,\beta,s,-2\alpha_0 x).$$

That is, we let x decrease and β increase indefinitely keeping, however, the product βx finite. We could, therefore, starting from the representation of the hypergeometric function by a definite integral give a similar representation for our function $\overline{X}_0$.

The behavior of our functions in the point ∞ follows in the simplest way from the original Eqs. (7) with $D=0$. We may neglect $\mathfrak{A}/\xi$ compared with the preceding constant term and the remaining equation is a cylindrical one which has for $\xi=\infty$ the two asymptotic solutions $e^{\alpha\xi}/\sqrt{\xi}$ and $e^{-\alpha\xi}/\sqrt{\xi}$. It is easy to show that the particular solution (12), multiplied by $\xi^{(s-1)/2}e^{\alpha\xi}$, is equal ton either of these two integrals separately but to a linear aggregate of both, so that, in general, it does not vanish for $\xi=\infty$ and does not satisfy the requirements of last section. The only exception is formed by integral values of m. From our expansion (12) it is clear that for

$$m,\ n=0,\ 1,\ 2,\ 3,\ 4,\cdots$$

the series for $\overline{X}_0$ and Y_0 are finite and that the corresponding values (9) of M_0 and N_0 vanish for $\xi=\infty$ if α_0 is negative. The integral values of m and n are, therefore, the only ones we may use in our theory. The values of $\mathfrak{A}_0$ and α_0 follow, from (11), adding the two equations and taking into account relation (8)

$$\alpha_0=-\frac{\mu Ze^2}{2k^2}\frac{1}{m+n+s}=-\frac{\mu Ze^2}{2k^2}\cdot\frac{1}{l} \tag{16}$$

$$\mathfrak{A}_0=\frac{\mu Ze^2}{2k^2}\frac{s+2m}{m+n+s} \tag{17}$$

Whence

$$E_0=-\frac{2k^2}{\mu}\alpha_0{}^2=-\frac{\mu Z^2e^4}{2k^2}\frac{1}{l^2}\cdot \tag{18}$$

If we recall the relations from the theory of hypergeometric functions

$$(\gamma-\alpha-1)F(\alpha,\beta,\gamma,x)+\alpha F(\alpha+1,\beta,\gamma,x)=(\gamma-1)F(a,\beta,\gamma-1,x),$$

$$(\beta-\gamma+1)xF(\alpha,\beta,\gamma,x)=(\gamma-1)(1-x)F(\alpha,\beta,\gamma-1,x)-(\gamma-1)F(\alpha-1,\beta,\gamma-1,x),$$

$$\frac{dF(\alpha,\beta,\gamma,x)}{dx}=\frac{\alpha\beta}{\gamma}F(\alpha+1,\beta+1,\gamma+1)$$

we can by means of definition (13) derive from them

$$sX_0(m,s)=(s+m)X_0(m,s+1)-mX_0(m-1,s+1), \tag{19}$$

$$2\alpha_0\xi X_0(m,s)=(s+m)X_0(m+1,s)-(s+2m)X_0(m,s)+mX_0(m-1,s), \tag{20}$$

$$(2\alpha_0\xi)^2X_0(m,s)=(s+m)(s+m+1)X_0(m+2,s)$$
$$-2(s+m)(s+2m+1)X_0(m+1,s) \tag{21}$$
$$+[(s+m)(m+1)+(s+2m)^2+(s+m-1)m]X_0(m,s)$$
$$-2m(s+2m-1)X_0(m-1,s)+m(m-1)X_0(m-2,3),$$

$$\frac{dX_0}{d\xi}=\frac{m}{\xi}[X_0(m,s)-X_0(m-1,s)]. \tag{22}$$

These formulas will be used a great deal in the following sections.

4. *First order terms of the Stark effect.* If the field does not vanish the functions X, Y, as well as the constants α, $\mathfrak{A}$, $\mathfrak{A}'$ will depend on D. We solve the problem by the method of successive approximations putting

$$\left\{\begin{aligned} \alpha&=\alpha_0+D\alpha_1+D^2\alpha_2+\cdots\\ \mathfrak{A}&=\mathfrak{A}_0+D\mathfrak{A}_1+D^2\mathfrak{A}_2+\cdots\\ \mathfrak{A}'&=\mathfrak{A}_0'-D\mathfrak{A}_1-D^2\mathfrak{A}_2+\cdots\\ X&=X_0+DX_1+D^2X_2+\cdots\\ Y&=Y_0+DY_1+D^2Y_2+\cdots \end{aligned}\right. \tag{23}$$

Such a method was, to the author's knowledge, first applied in a similar case by Matthieu. Substituting (23) into Eqs. (10) we get the system

$$\frac{d^2X_0}{d\xi^2}+\left(2\alpha_0+\frac{s}{\xi}\right)\frac{dX_0}{d\xi}-\frac{2\alpha_0 m}{\xi}X_0=0, \tag{24a}$$

$$\frac{d^2X_1}{d\xi^2}+\left(2\alpha_0+\frac{s}{\xi}\right)\frac{dX_1}{d\xi}-\frac{2\alpha_0 m}{\xi}X_1=-2\alpha_1\frac{dX_0}{d\xi}-\frac{\mathfrak{A}_1+s\alpha_1}{\xi}X_0 +\frac{\mu e}{4k^2}\xi X_0, \tag{24b}$$

$$\frac{d^2X_2}{d\xi^2}+\left(2\alpha_0+\frac{s}{\xi}\right)\frac{dX^2}{d\xi}-\frac{2\alpha_0 m}{\xi}X_2=-2\alpha_1\frac{dX_1}{d\xi}-\frac{\mathfrak{A}_1+s\alpha_1}{\xi}X_1 +\frac{\mu e}{4k^2}\xi X_1-2\alpha_2\frac{dX_0}{d\xi}-\frac{\mathfrak{A}_2+s\alpha_2}{\xi}X_0 \tag{24c}$$

The equations for Y result from these if we substitute n for m and change the sign of $\mathfrak{A}_1$, $\mathfrak{A}_2$ and of the term with $\mu e/4k^2$.

The solution of the first equation has been discussed in the preceding section. Eqs. (24b, c) are inhomogeneous equations of the same type, the right side being known when the preceding equation is solved. To accomplish this solution, we will discuss the equation

$$\frac{d^2u}{d\xi^2}+\left(2\alpha_0+\frac{s}{\xi}\right)\frac{du}{d\xi}-\frac{2\alpha_0 m}{\xi}u=\frac{CX_0(m',s)}{\xi}. \tag{25}$$

We try to substitute $u=C'X_0(m',s)$. This function satisfies Eq. (24a) with m' replacing m. The substitution gives, therefore,

$$2\alpha_0(m'-m)C'=C$$

or

$$u=\frac{C}{2\alpha_0(m'-m)}X_0(m',s). \tag{26}$$

This solution obviously satisfies all the requirements of finiteness, but it applies only to the case $m'\neq m$. If $m'=m$, the solution can be found by the method of variation of constants and it turns out to be

$$u=CX_0\int e^{2\alpha_0\xi}\xi^{s-1}Z_0X_0d\xi-CZ_0\int e^{2\alpha_0\xi}\xi^{s-1}X_0^2d\xi.$$

where Z_0 is an abbreviation for the second integral of (24a) mentioned in Section 3. As this integral does not satisfy the conditions of finiteness and enters as a factor into the second term of our expression, it follows that *it is not possible to satisfy the conditions of finiteness, if in* (25) $m'=m$.

The procedure is now obvious. We transform the right side of (24b) with the help of relations (21) (22) into

$$-\frac{2\alpha_1 m}{\xi}[X_0(m,s)-X_0(m-1,s)]-\frac{\mathfrak{A}_1+s\alpha_1}{\xi}X_0(m,s)+\frac{1}{\xi}\frac{\mu e}{16k^2\alpha_0^2}\cdot$$
$$\cdot\{(s+m)(s+m+1)X_0(m+2,s)-2(s+m)(s+2m+1)X_0(m+1,s)$$
$$+[(s+m)(m+1)+(s+2m)^2+(s+m-1)m]X_0(m,s)$$
$$-2m(s+2m-1)X_0(m-1,s)+m(m-1)X_0(m-2,s)\}$$

From the preceding discussion we know that all terms will give a contribution of the required properties except those containing $\overline{X}_0(m,s)$. The condition which we have to impose on α_1 and $\mathfrak{A}_1$ is therefore, that the sum of the coefficients of this term must vanish:

$$\mathfrak{A}_1+(s+2m)\alpha_1=\frac{\mu e}{16k^2\alpha_0^2}[(s+m)(m+1)+(s+2m)^2+(s+m-1)m]. \tag{27}$$

Correspondingly, the solution of (24b) is, according to (26),

$$X_1=-\frac{\alpha_1}{\alpha_0}mX_0(m-1,s)+\frac{\mu e}{64k^2\alpha_0^3}\{(s+m)(s+m+1)X_0(m+2,s)$$
$$-4(s+m)(s+2m+1)X_0(m+1,s)+4m(s+2m-1)X_0(m-1,s)$$
$$-m(m-1)X_0(m-2,s)\}. \tag{28}$$

By analogy the formulas derived from the conditions to which Y is subject are:

$$-\mathfrak{A}_1+(s+2n)\alpha_1=-\frac{\mu e}{16k^2\alpha_0}[(s+n)(n+1)+(s+2n)^2+(s+n-1)n], \quad (27')$$

$$\begin{aligned}Y_1=&-\frac{\alpha_1}{\alpha_0}nY_0(n-1,s)-\frac{\mu e}{64k^2\alpha_0^3}\{(s+n)(s+n+1)Y_0(n+2,s)\\&-4(s+n)(s+2n+1)Y_0(n+1,s)+4n(s+2n-1)Y_0(n-1,s)\\&-n(n-1)\,Y_0(n-2,s)\}.\end{aligned} \quad (28')$$

Adding (27) and (27′) we have

$$\alpha_1=\frac{3}{16}\,\frac{\mu e}{k^2\alpha_0^2}(m-n), \quad (29)$$

which gives directly the Stark effect of the first order because of the connection (9) between α and the energy. However, we shall postpone the discussion of the results until Section 8.

5. *Second order terms of the Stark effect.* As in the computation of the first order terms, the condition which we have to impose upon $\mathfrak{A}_2$, α_2, is the vanishing of the term proportional to $\overline{X}_0(m,s)$ on the right side of (24c). All we have to do is to write down this part of that expression and make it equal to zero:

$$\begin{aligned}&-\alpha_1\frac{e\mu}{8k^2\alpha_0^3}(m+1)(s+m)(s+2m+1)+\frac{\mu e\alpha_1}{16k^2\alpha_0^3}2(s+m-1)(s+2m-1)m\\&+\frac{\mu^2e^2}{1024k^4\alpha_0^5}\{(s+m)(s+m+1)(m+1)(m+2)+8(s+m)(s+2m+1)^2(m+1)\\&-8m(s+2m-1)^2(s+m-1)-m(m-1)(s+m-2)(s+m-1)\}\\&-\mathfrak{A}_2-(s+2m)\alpha_2=0.\end{aligned}$$

This can be written in the simpler form

$$\begin{aligned}&-\frac{e\mu\alpha_1}{8k^2\alpha_0^3}[(m+1)(s+m)(s+m+1)-m(s+m-1)(s+2m-1)]\\&+\frac{\mu^2e^2}{512k^4\alpha_0^5}(s+2m)[4s^2+9s+5+34m(s+m)]=\mathfrak{A}_2+(s+2m)\alpha_2,\end{aligned}$$

and by analogy

$$\begin{aligned}&\frac{e\mu\alpha_1}{8k^2\alpha_0^3}[(n+1)(s+n)(s+n+1)-n(s+n-1)(s+2n-1)]\\&+\frac{\mu^2e^2}{512k^4\alpha_0^5}(s+2n)[4s^2+9s+5+34n(s+n)]=-\mathfrak{A}_2+(s+2n)a_2.\end{aligned}$$

Adding the two expressions

$$\alpha_2 = \frac{\mu^2 e^2}{1024 k^4 \alpha_0^5}\left[17(m+n+s)^2-21(m-n)^2-9s^2+18s+10\right] \qquad (30)$$

The consequences of this expression will be discussed in Section 8.

6. *Connection of the intensities with our expressions.* It has been shown by Schroedinger and independently by Eckart[3] that the components of Heisenberg's matrix are given by the expressions

$$q_x(m,n,s;m',n',s') = A(m,n,s)A(m',n',s') \cdot$$
$$\cdot \int\int\int x\psi(m,n,s)\psi(m',n',s')dxdydz, \qquad (31)$$

(with analogous expressions for y and z), the integration being extended over the whole space.

We introduce our coordinates ξ, η, ϕ, by means of (3) and (4):

$$q_z = \frac{1}{8}A(m,n,s)A(m',n',s') \int\int\int(\xi^2-\eta^2)M(m,n,s,\xi)M(m',n',s',\xi) \cdot$$
$$\cdot N(m,n,s,\eta)N(m',n',s',\eta) \begin{matrix}\cos\\ \cdot\\ \sin\end{matrix}(s-1)\varphi \begin{matrix}\cos\\ \cdot\\ \sin\end{matrix}(s'-1)\varphi d\xi d\eta d\varphi.$$

We see that q_z is finite only when $s'=s$: *only oscillations corresponding to $s-s'=0$ are polarized in the direction z.*

$$q_z(m,n,s;m',n',s') = \frac{\pi}{8}A(m,n,s)A(m',n',s) \cdot$$
$$\cdot \int\int(\xi^2-\eta^2)M(m,\alpha,s,\xi)M(m',\alpha',s,\xi)N(n,\alpha,s,\eta)N(n',\alpha',s,\eta)d\xi d\eta \qquad (32)$$

In a similar way

$$q_{x,y} = \frac{1}{4}A(m,n,s)A(m',n',s') \cdot$$
$$\int\int\int\sqrt{\xi\eta}(\xi+\eta)M(m,n,s,\xi)M(m',n',s',\xi) \cdot$$
$$\cdot N(m,n,s,\eta)N(m',n',s',\eta) \begin{matrix}\cos\\ \cdot\\ \sin\end{matrix}(s-1)\varphi \begin{matrix}\cos\\ \cdot\\ \sin\end{matrix}(s'-1)\varphi \begin{matrix}\cos\\ \cdot\\ \sin\end{matrix}\varphi d\xi d\eta d\xi$$

The integration with respect to ϕ can be carried out immediately, giving a finite value ($\pm\pi/2$) only when $s'=s\pm 1$. *Oscillations polarized in the plane (x,y) correspond to quantum changes $s-s'=\pm 1$.*

[3] Carl Eckart, Phys. Rev. 28, 711 (1926).

$$|q_{x,y}| = \frac{\pi}{8}A(m,n,s)A(m',n',s') \cdot$$

$$\cdot \int\int \sqrt{\xi\eta}(\xi+\eta)M(m,\alpha,s,\xi)M(m',\alpha',s\pm 1,\xi) \cdot$$

$$\cdot N(n,\alpha,s,\eta)N(\eta',\alpha',s\pm 1,\eta)d\xi d\eta. \qquad (32')$$

As to the coefficients $A(m,n,s)$ they are defined by the requirement

$$\frac{\pi}{4}A^2(m,n,s)\int\int(\xi+\eta)M^2(m,\alpha,s,\xi)N^2(n,\alpha,s,\xi)d\xi d\eta = 1. \qquad (33)$$

It appears from this that the fundamental problem that must be solved, in order to find these expressions, is to calculate the integral

$$R(m,\alpha;m',\alpha' s) = \int_0^\infty\int_0^\infty M(m,\alpha,s,\xi)\, M'(m',\alpha',s,\xi)\, d\xi. \qquad (34)$$

7. *Auxiliary mathematical expressions.* In the developments of this section we shall keep m' and s constant. Therefore, we can abbreviate expression (34) by the symbol $R(m)$. For the computations of intensities it is a sufficient approximation to substitute for M and N the values M_0 and N_0 corresponding to a vanishing electric field ($D=0$) which differ from the exact values only by minute amounts. For convenience of writing, however, we shall drop the subscripts 0. We can obtain a recurrent relation for $R(m)$ directly from Eq. (7). If we multiply this equation by $M'=M(m',\alpha',s,\xi)$ and subtract from the product the equation obtained from (7) by the substitution of m',α' instead of m, α multiplied by $M=M(m,\alpha,s,\xi)$ the result is with the help of substitution (9) and (11)

$$M'\frac{d}{d\xi}\left(\xi\frac{dM}{d\xi}\right)-M\frac{d}{d\xi}\left(\xi\frac{dM'}{d\xi}\right)-[(\alpha^2-\alpha'^2)\xi+(s+2m)\alpha$$
$$-(s+2m')\alpha']MM'=O.$$

Integrating with respect to ξ from 0 to ∞

$$(\alpha^2-\alpha'^2)\int_0^\infty \xi MM'd\xi+[(s+2m)\alpha-(s+2m')\alpha']R(m)=0 \qquad (35)$$

We transform ξM with the help of formula (20) which applies to the functions M as well as to the functions $\overline{X}_0$.

$$(s+m)R(m+1)-\left[(s+m+m')u+(m-m')\frac{1}{u}\right]R(m)+mR(m-1)=0, \quad (36)$$

$$u = \frac{\alpha' - \alpha}{\alpha' + \alpha} = \frac{l - l'}{l + l'} \cdot \tag{37}$$

This result is in so far interesting as it shows that all the $R(m)$ can be computed from this formula if only $R(0,\alpha;\ 0,\alpha';\ s)$ is known. This last function, however, can be obtained directly from the definition (34), considering that $M(0,\ \alpha,\ s) = \xi^{(s-1)/2} e^{\alpha\xi}$.

$$R(0,0) = R(0,\alpha;0,\alpha';s) = (-1)^s \frac{(s-1)\,!}{(\alpha+\alpha')^s} \cdot \tag{40}$$

Apart from this factor the expressions $R(m)$ are, therefore, functions of the combination u only. It is natural to introduce new notations:

$$R(m) = \frac{1}{(\alpha+\alpha')^s} U(m). \tag{41}$$

For the $U(m)$ the same relation must hold

$$(s+m)\,U(m+1) - \left[(s+m+m')u + (m-m')\frac{1}{u}\right] U(m) + mU(m-1) = 0. \tag{42}$$

A second relation can be obtained by differentiating $R(m)$ with respect to α:

$$\frac{dR(m)}{d\alpha} = \frac{d}{d\alpha}\int \xi^{\frac{s-1}{2}} e^{\alpha\xi} X(m,\alpha\xi)\, M' d\xi = \int \xi M M' d\xi + \frac{1}{\alpha}\int \xi^{\frac{s-1}{2}} e^{\alpha\xi} \frac{dX}{d\xi} d\xi.$$

On the other hand from (41)

$$\frac{dR(m)}{d\alpha} = -\left[sU(m) + (1+u)\frac{d\,U(m)}{du}\right] \cdot \frac{1}{(\alpha+\alpha')^{s+1}} \cdot$$

Comparing these two relations and using (20) and (22)

$$(1-u^2)\frac{dU(m)}{du} = -(s+m)\,U(m+1) + suU(m) + mU(m-1). \tag{43}$$

From (42) and (43) we obtain a differential equation determining $U(m)$. It is, however, convenient to make the substitution

$$U(m) = u^{m-m'} V(m) \tag{44}$$

and to use as independent variable the square $v = u^2$.
The equation then acquires the form

$$v(1-v)\frac{d^2V(m)}{dv^2} + [(m-m'+1) - (s+m-m'+1)v]\frac{dV(m)}{dv} + m'(s+m)\,V(m) = 0, \tag{45}$$

so that

$$V(m)=CF(s+m,-m',m-m'+1,v).$$

The third argument of the function must satisfy certain conditions to give a finite value and this gives for m' the restriction $m'\leqq m$.

It remains to determine the factor C. Its dependence on m can be obtained from the recursion (43) which shows that this part of the factor is $m!/(m-m')!$. The rest follows from the requirement of symmetry with respect to m and m' and the limiting value (40) for $m=m'=0$.

$$C=(-1)^s\frac{(s-1)!(s-1)!m!}{(s+m'-1)!(m-m')!} \tag{46}$$

It follows

$$R(m,\alpha,m',\alpha',s)=\frac{(-1)^s(s-1)!(s-1)!m!}{(s+m'-1)!(m-m')!}\frac{u^{m-m'}}{(\alpha+\alpha')^s}\cdot \tag{47}$$
$$\cdot F(s+m,-m',m-m'+1,u^2).$$

The symmetry of this expression becomes apparent when we rearrange it in falling powers of u^2:

$$R(m,\alpha;m',\alpha';s)=(-1)^{s+m'}\frac{(s+m+m'-1)!(s-1)!((s-1)!}{(s+m-1)!(s+m'-1)!}\frac{u^{m+m'}}{(\alpha+\alpha')^s} \tag{48}$$
$$F\left(-m,-m',-s-m-m'+1,\frac{1}{u^2}\right).$$

In the special case $m=m'$, $\alpha=\alpha'$

$$R(m,\alpha;m,\alpha;s)=(-1)^s\frac{(s-1)!(s-1)!m!}{(s+m-1)!}\frac{1}{(2\alpha)^s}\cdot \tag{49}$$

8. *Explicit expressions of the intensities.* To compute (32) we shall need another integral

$$T(m,\alpha;m',\alpha')=\int_0^\infty \xi^2MM'd\xi. \tag{50}$$

According to (20)

$$T(m,m')=\frac{1}{2\alpha}\int_0^\infty \xi\{(s+m)M(m+1)-(s+2m)M(m)+mM(m-1)\}M'd\xi.$$

On account of relations (35) and (36)

$$\int_0^\infty \xi MM'd\xi=\frac{(s+m+m')u-(m-m')}{(\alpha+\alpha')u}R(m), \tag{51}$$

and

$$T(m,m')=\frac{1}{(\alpha+\alpha')^2u}\left\{\left(\frac{1}{u}\left[(s+m+m')u-(m-m')\right]^2\right.\right. \qquad (52)$$

$$\left.+\left[(s+m+m')u+(m-m')\frac{1}{u}\right]R(m)-2mR(m-1)\right\}$$

According to expression (32)

$$q_z(m,m';n,n';s)=\frac{B}{u}\{T(m,m')R(n,n')-R(m,m')T(n,n')\}, \qquad (53)$$

where we use abbreviation

$$B=-\frac{\pi}{8}A(m,n,s)A(m',n',s)/(\alpha+\alpha')^2. \qquad (54)$$

This can be transformed into the form

$$q_z=\frac{B}{u^2}\{[-(m'-n')(1-u^2)$$

$$+(m-n)(1+u^2)]\cdot R(m,m')R(n,n')-2u[mR(m-1,m')R(n,n')$$

$$-nR(m,m')R(n-1,n')]\}.$$

A further reduction gives

$$q_z=\frac{Bu^{m+n-m'-n'-2}}{(\alpha+\alpha')^s}\{[(1+u^2)(m-n)-(1-u^2)(m'-n')]V(m,m')V(n,n')$$

$$-2[mV(m-1,m')V(n,n')-nV(m,m')V(n-1,n')]\}. \qquad (55)$$

It only remains to determine B which is defined by condition (33). Eq. (51) remains applicable in the case $m=m'$, $\alpha=\alpha'$, $u=0$ and gives

$$\int_0^\infty \xi M^2 d\xi=-\frac{s+2m}{2\alpha}R(m,\alpha;m,\alpha).$$

With the help of this relation (33) reduces to

$$-\frac{\pi A^2(m,n,s)}{4\alpha}(m+n+s)R(m,m)R(n,n)=1$$

and with the aid of (49) and (16) to

$$A(m,n,s)=\sqrt{\frac{2}{\pi\mu Z}}\,\frac{k}{e}\,\frac{(2\alpha)^{s+1}}{(s-1)!(s-1)!}\sqrt{\frac{(s+m-1)!\,(s+n-1)!}{m!\,n!}}.$$

$$B=\frac{k^2}{4\mu Ze^2}\frac{(\alpha+\alpha')^{2s}}{[(s-1)!]^4}(1-u^2)^{s+1}\cdot$$

$$\cdot\sqrt{\frac{(s+m-1)!(s+n-1)!(s+m'-1)!(s+n'-1)}{m!\,n!\,m'!\,n'!}}. \qquad (56)$$

If we substitute into expression (55) the functions

$$\Phi(m,m')=F(s+m,-m',m-m'+1,u^2) \tag{57}$$

this expression can be reduced to its simplest form ($l=m+n+s$)

$$q_z=\frac{k^2}{4\mu Ze^2}\sqrt{\frac{(s+m-1)!\,(s+n-1)!\,m!\,n!}{(s+m'-1)!\,(s+n'-1)!\,m'!\,n'!}}\;\frac{(1-u^2)^{s+1}u^{l-l'-2}}{(m-m')!\,(n-n')!}\cdot$$

$$\cdot\left\{\left[(1+u^2)(m-n)-(1-u^2)(m'-n')\right]\Phi(m,m')\Phi(n,n')\right. \tag{58}$$

$$\left.-2\left[(m-m')\Phi(m-1,m')\Phi(n,n')-(n-n')\Phi(m,m')\Phi(n-1,n')\right]\right\}.$$

To handle expression (32′), we have to make use of formulas (19) and (51). In the case $s'=s+1$) we obtain

$$q_x=\frac{k^2}{4\mu Ze^2}\sqrt{\frac{(s+m-1)!\,(s+n-1)!\,m!\,n!}{(s+m')!\,(s+n')!\,m'!\,n'!}}\cdot\frac{u^{l-l'-2}(1-u^2)^{s+2}}{(m-n)!\,(m'-n')!}\cdot \tag{59}$$

$$.\left[(s+m)(s+n)u^2\Phi(m,m',s+1)\Phi(n,n',s+1)-(m-m')(n-n')\cdot\right.$$

$$\left.\cdot\,\Phi(m-1,m',s+1).\Phi(n-1,n',s+1)\right].$$

In the case $s'=s-1$

$$q_x=\frac{k^2}{4\mu Ze^2}\sqrt{\frac{(s+m-1)!\,(s+n-1)!\,m!\,n!}{(s+m'-2)!\,(s+n'-2)\,m'!\,n'!}}\;\frac{u^{l-l'-2}(1-u^2)^{s+1}}{(m-m'+1)!\,n-n'+1)!}\,\cdot$$

$$\cdot\left[(m-m'+1)(n-n'+1)\Phi(m,m',s)\Phi(n,n',s)-m'n'u^2\Phi(m,m'-1,s)\right.$$

$$\left.\cdot\,\Phi(n,n'-1,s)\right].$$

9. *Position of the components.* According to definition (9)

$$E=-\frac{2k^2}{\mu}\alpha^2$$

or expanding in powers of D and denoting the part of E proportional to D by Δ_1E, that proportional to D^2 by Δ_2E:

$$E_0+\Delta_1E+\Delta_2E=-\frac{2k^2}{\mu}(\alpha_0+\alpha_1D+\alpha_2D^2)^2$$

or

$$\Delta_1E=-\frac{4k^2}{\mu}\alpha_0\alpha_1D_1,$$

$$\Delta_2E=-\frac{2k^2}{\mu}(\alpha_1^2+2\alpha_0\alpha_2)D^2.$$

Substituting expressions (16), (29), and (30) and remembering that $k=h/2\pi$

$$\Delta_1E=\frac{3h^2D}{8\pi^2\mu Ze}(m+n+s)(m-n), \tag{60}$$

$$\Delta_2 E = -\frac{D^2}{16Z^4 m^3}\left(\frac{h}{2\pi e}\right)^6 (m+n+s)^4[17(m+n+s)^2 - 3(m-n)^2 - 9s^2 + 18s + 10]. \quad (61)$$

There can be hardly any doubt how to interpret these expressions. According to Sections 1 and 2

$$s = 1, 2, 3, 4, \cdots \qquad m, n = 0, 1, 2, 3, \cdots\cdot \quad (62)$$

In the old theory we had

$$n_3 = 1, 2, 3, 4, \cdots \qquad n_1, n_2 = 0, 1, 2, 3, \cdots\cdot$$

Therefore, m, n, s must be identified with the quantic numbers n_1, n_2, n_3, respectively. It will be remembered that the restriction for the azimuthal quantum number $n_3 > 0$ was an additional one, not following from the dynamical conditions. It was introduced by Bohr for the purpose of eliminating plane orbits, moving in which the electrons would sooner or later undergo a collusion with the nucleus. In our new theory an additional restriction is not necessary: only $(s-1)^2$ enters into Eq. (7). The case $s=0$ does not represent, therefore, a new oscillation, it is identical with the case $s=2$, so that by the assignment (62) all possible states are taken care of.

Formula (60) is, therefore, identical with the writer's old expression for the Stark effect whose agreement with the experimentally determined positions is all that can be desired. Formula (61) differs slightly from the expression of the second order effect given by the author[6] and by M. Mosharrafa[7] in that it contains the terms $18s+10$ which were absent in the old formula.

The only observation on record of the second order effect is due to Takamine and Kokubu.[8] These authors found a displacement of the central perpendicular component of H_γ in the red direction by an amount which they estimate at 1A in a field of 130 kilovolts per cm. As we shall see in our next section, we have for this component the following quantic numbers of the first term $m=n=1$, $s=3$. Because of the factor $(m+n+s)^6$ the second term $(m'+n'+s'=2)$ is negligible compared with the first. The shift in wave-numbers is given by $\Delta_2 V = \Delta_2 E/h$, in wave-lengths by $\Delta_2\lambda = -\Delta_2 E \cdot \lambda^2/hc$. If we measure λ in Å, D in kilovolt/cm, the value of the numerical coefficient of the shift corresponding to formula (61) becomes $5.21 \times 10^{-1/}$ giving for the above conditions ($\lambda = 4340.5$A) $\Delta_2\lambda = 0.42$A. This theoretical value lies in the right direction and is of

[6] P. S. Epstein (l.c.). By an oversight the sign of the expression was there given as positive.

[7] A. M. Mosharrafa Phil. Mag. **44**, 371 (1922).

[8] Takamine and Kokubu, Proc. Tokyo Math. Phys. Soc. **9**, 396 (1919).

the right order of magnitude. However, one gets practically the same result with the old formula. The positions of the lines are represented equally well by both theories.

10. *Numerical values of intensities.* Formulas (58), (59), (59′) of Section 7 are very convenient for numerical computation. Owing to the fact that in the Balmer series m' and n' cannot be larger than one, the hypergeometric function (57) reduces to one or two terms, and our expressions can be evaluated in a few seconds for every combination of quantic numbers. In the following tables we abbreviate by Q the expression

$$Q=(m+n+s)(m-n)-(m'-n'-s')(m'-n')$$

giving the position of the component according to formula (60). We have seen in Section 6 that the electric vector of the emitted light is parallel to the applied field (p-components) when $s-s'=0$, and perpendicular to it (s-components) when $s-s'=\pm 1$.

Hα-line. p-components.

Q :	2	3	4	8
Calc. Ampl.:	0.8	1.0	1.3	0.03
Obs. Int. :	1	1.1	1.2	—

Hα line. s-components.

Q	0	1	5	6
Calc. Ampl.:	2.0	1.2	0.1	0.1
Obs. Int. :	2.6	1	—	—

Hβ line. p-components.

Q	0	2	6	8	10	12	14
Calc. Ampl.:	0	1.6	4.8	7.4	10.2	—	0.5
Obs. Int. :	1.4	1.2	4.8	9.1	11.5	1	—

Hβ line. s-components.

Q	0	2	4	6	8	10	12
Calc. Ampl.:	—	5.0	12.6	10.2	—	1.4	1.6
Obs. Int.	1.4	3.3	12.6	9.7	1.3	1.1	1

Hγ line. p-components.

Q	2	5	8	12	15	18	22
Calc. Ampl.:	3.4	2.6	1	3.5	6.5	9.8	0.7
Obs. Int. :	1.6	1.5	1	2.0	7.2	10.8	1

Hγ line. s-components.

Q	0	3	7	10	13	17	20
Calc. Ampl.:	5.4	3.1	1.1	4.3	4.2	0.7	0.9
Obs. Int. :	7.2	3.6	1.2	4.3	6.1	1.1	1

Hδ line. p-components.

Q	0	4	8	6	16	20	24	28	32
Calc. Ampl.:	0	1.0	1.5	1.6	1.2	1.2	2.5	4.2	0.4
Obs. Int. :	0	1	1.2	1.5	1.2	1.1	2.8	7.2	1

Hδ line. s-components.

Q	2	6	10	14	18	22	26	30
Calc. Ampl.:	1.4	3.2	2.2	0.3	2.5	2.5	0.5	0.7
Obs. Int. :	1.3	3.2	2.1	1.0	2.0	2.4	1.3	1

We have given only the positive values of Q. From the symmetry of our formulas it is evident that we shall have the same intensities for the negative Q. Special remarks must be made only with respect to the last columns of the p-components and the last but one of the s-components; here the second argument (m' or n') of R is larger than the first, so that our formulas cannot be used in the given form but must be slightly changed by inverting the hypergeometric functions as in Eq. (48).

Comparing the calculated values with those observed by Stark[9] we notice the phenomenon stated by H. N. Russel[10] in his work on the intensities of multiplets. The observed values, estimated by the experimental physicist from the blackening of the photographic plate, are not proportional to the intensities but to their square roots, i.e., to the amplitudes of the emitted waves. Therefore, we have tabulated alongside with Stark's observed data the calculated amplitudes. We see that the agreement is fair, and decidedly better than that obtained from Bohr's correspondence principle in Kramers' work.

On account of our discussion of the second order displacement of the central $H\gamma$ line ($Q=0$, s-component) in the preceding section, it will be well to state the following particulars. This component represents the superposition of two different transitions: from $m=1$, $n=1$, $s=3$ to $m'=n'=2$, $s'=2$ and from $m=n=2$, $s=1$ to $m'=n'=0$, $s'=2$. The first transition, however, contributes 85 percent of the total intensity and the second only 15 percent. Therefore, it is permissible for the purpose of the last section to neglect the second origin of this line altogether, as we have done.

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July 29, 1926.

[9] J. Stark, Ann. d. Phys. **48**, 193 (1915).
[10] H. N. Russel, Nature **115**, 835 (1925).