

sequently, all the light absorbed in the bulb is contained in the parallel components of the four longer wave-length lines, which are the ones that have  $3/2$  normal triplet Zeeman patterns. This condition satisfies the requirements of the theory and the results of v. Keussler are in agreement with the prediction.

No doubt in the above case the fact that the intensity of the anomalous line is practically zero plays some part, but if a source giving narrower lines were used, for example, a resonance bulb instead of a water-cooled arc, 100 per cent polarization should be obtained in field strengths as low as 2000 gausses, at which field the intensity of the anomalous line is of considerable magnitude.

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<sup>1</sup> NATIONAL RESEARCH FELLOW.

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## THE DIELECTRIC CONSTANT OF ATOMIC HYDROGEN IN UNDULATORY MECHANICS

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1. In a recent paper J. H. Van Vleck<sup>1</sup> used the expressions for the energy of a hydrogen atom in an electric field, derived by I. Waller<sup>2</sup> and the writer,<sup>3</sup> for computing the dielectric constant. The interesting method he applies is analogous to that used by J. H. Jones<sup>4</sup> for the same purpose in Bohr's quantum theory, and is outlined in section 1 of the following paper by Evelyn F. Aylesworth.<sup>5</sup> It appears from this last paper that, in Bohr's theory, the atomic energy has a different expression for weak and for strong fields. If the strength of field is above a certain critical value, the atoms acquire an orientation with respect to it, if it is below this value, their orientation is arbitrary and not affected by the field. The critical value is particularly high for the normal state of the atom, so that here we have the largest deviation from the behavior of the gas in strong fields. On the other hand, Van Vleck shows by a very convincing argument that, from the point of view of undulatory mechanics, an atom in the normal state must change its energy in weak and in strong fields according to the same law.

It seemed, therefore, desirable to treat the problem of the energy change

in an electric field by a different method, in connection with the question of orientation with respect to the field, and to bring out the similarities and the differences between the old and the new theory. The result of this discussion is that, for the excited states of the atom, the conditions are much the same in undulatory mechanics as those found by E. F. Aylesworth; in weak fields the orientation is arbitrary, in strong ones it has a relation to the field. On the other hand, the question of orientation is without meaning for the normal state of the atom, owing to its complete spherical symmetry. For this state, the system can be quantized in any system of polar or parabolic coördinates leading always to the same type of pulsation and to the same energy expression.

2. *Statement of the Mathematical Problem.*—We consider an electron of the charge  $-e$  and mass  $\mu$  moving under the action of a fixed nucleus  $e$  and of a superposed homogeneous electric field of the strength  $D$ . If  $x$  is the coördinate in the direction of the field, the potential energy has the expression  $V = e^2/r - eDx$ . Though the influence of relativity will be of great importance to us, we may neglect it in this section and write Schroedinger's wave equation in the form

$$\nabla^2\psi + 2\mu(E + e^2/r - eDx)\psi/K^2 = 0. \quad (1)$$

We are going to express this equation in a system of polar coördinates  $r, \vartheta, \varphi$ , and our further treatment of it will be similar to that given for this same case by Schroedinger,<sup>6</sup> however, with one important difference. Schroedinger chose the direction of the field as the polar axis of his system. Now the polar axis is a principal direction of the atom, as it controls the arrangement of the partial oscillations. Its meaning in undulatory dynamics is much the same as in Bohr's theory for a system subject to a complete space quantization in polar coördinates. In our case, choosing the polar axis in the direction of the field would be begging the question we propose to investigate. Our problem is whether there will occur an orientation of the partial oscillations of the atom with respect to the electric field. Therefore, we shall choose the polar axis under an angle  $\gamma$  to the  $x$ -direction and shall write for  $x$

$$x = r \cos \vartheta \cos \gamma + r \sin \vartheta \sin \gamma \cos \varphi. \quad (2)$$

For solving equation (1) we use the standard method of successive approximations, putting

$$\begin{cases} E = E_0 + E_1D + E_2D^2, \\ \psi = \psi_0 + \psi_1D + \psi_2D^2. \end{cases} \quad (3)$$

Substituting into (1) and collecting terms of equal order of magnitude

$$\begin{aligned} K^2\nabla^2\psi_0/2\mu + (E_0 + e^2/r)\psi_0 &= 0, \\ K^2\nabla^2\psi_1/2\mu + (E_0 + e^2/r)\psi_1 &= (ex - E_1)\psi_0, \\ K^2\nabla^2\psi_2/2\mu + (E_0 + e^2/r)\psi_2 &= (ex - E_1)\psi_1 - E_2\psi_0. \end{aligned} \quad (4)$$

As in previous papers, we use the abbreviations

$$\alpha^2 = -2\mu E_0/K^2, \quad l = \mu e^2/K^2\alpha, \quad (5)$$

and, moreover, we introduce a new dependent variable by the substitution

$$\psi = e^{\alpha r}\Phi. \quad (6)$$

Equation (4) assumes the form

$$\begin{aligned} \nabla^2\Phi_0 + 2\alpha\partial\Phi_0/\partial r - 2\alpha(l-1)\Phi_0/r &= 0, \\ \nabla^2\Phi_1 + 2\alpha\partial\Phi_1/\partial r - 2\alpha(l-1)\Phi_1/r &= 2\mu(ex - E_1)\Phi_0/K^2, \\ \nabla^2\Phi_2 + 2\alpha\partial\Phi_2/\partial r - 2\alpha(l-1)\Phi_2/r &= 2\mu[(ex - E_1)\Phi_1 - E_2\Phi_2]/K^2. \end{aligned} \quad (7)$$

In order to treat these equations mathematically, we use the artifice of generalizing them and solving them for any value of  $\alpha$  and for an integral value of  $l$ . After such a solution is found, we can specialize it by reintroducing relation (5) between  $\alpha$  and  $l$ . Only solutions satisfying Schroedinger's conditions of finiteness will be considered.

3. *Auxiliary Formulae.*—The first of the equations (7) represents the wave motion in the atom not subjected to an external field. This problem has been exhaustively treated by Schroedinger and its solution is known to be

$$A_{nm}N(l,n)P_n^m(\cos\vartheta) \frac{\cos m\varphi}{\sin m\varphi}. \quad (8)$$

$A_{nm}$  is a constant,  $P_n^m(\cos\vartheta)$  the associated spherical harmonic, and  $N(l, n)$  is related to the functions  $\chi$  and  $M$ , defined in one of our previous papers,<sup>7</sup> in the following way

$$N(l, n) = e^{-\alpha r}\chi(l, n) = r^n M(l, n). \quad (9)$$

Accordingly, this function satisfies the equation

$$\frac{d^2N}{dr^2} + 2\left(\alpha + \frac{1}{r}\right)\frac{dN}{dr} - \left[\frac{2\alpha(l-1)}{r} + \frac{n(n+1)}{r^2}\right]N = 0. \quad (10)$$

The integers  $n, m$  can have any value consistent with the inequality  $m \leq n \leq l-1$ .

Let us now consider the inhomogeneous equation

$$\nabla^2u + 2\alpha\partial u/\partial r - 2\alpha(l-1)u/r = AN(l', n)P_n^m \cos m\varphi/r. \quad (11)$$

A solution of it is

$$u = \frac{A}{2\alpha(l' - l)} N(l', n)P_n^m \cos m\varphi, \quad (12)$$

provided that  $l' \neq l$ . If  $l' = l$ , there is no solution satisfying the requirements of finiteness.

In order to apply this result to equations (7), we shall have to reduce

the right sides. From formulae (8), (9), (10) of paper,<sup>7</sup> we easily deduce the following relations:

$$\begin{aligned}
 2\alpha rN(l,n) &= (l+n+1)N(l+1,n) - 2lN(l,n) + (l-n-1)N(l-1,n) \\
 &= \frac{2n(2n+1)}{2\alpha} [N(l+1,n-1) - 2N(l,n-1) + N(l-1,n-1)] \\
 &= \frac{2\alpha}{(2n+2)(2n+3)} [(l+n+1)(l+n+2)N(l+1,n+1) - \\
 &\quad - 2(l+n+1)(l-n-1)N(l,n+1) + (l-n-1)(l-n-2)N(l-1,n+1)].
 \end{aligned}
 \tag{13}$$

The parameter  $\alpha$  is supposed to be the same in all the terms of these relations. In addition to these formulae, we shall have to use the well-known relations of the theory of spherical harmonics

$$\begin{aligned}
 (2n+1) \cos \vartheta P_n^m &= (n-m+1)P_{n+1}^m + (n+m)P_{n-1}^m, \tag{14} \\
 (2n+1) \sin \vartheta P_n^m &= -(n-m+1)(n-m)P_{n+1}^{m-1} \\
 &\quad + (n+m-1)(n+m)P_{n-1}^{m-1} = P_{n+1}^{m+1} - P_{n-1}^{m+1}.
 \end{aligned}$$

4. *Conditions in Strong Fields.*—If the field is so strong that the relativistic correction term is negligible compared with the electric, the equations of section 2 are strictly applicable. The general solution of the first equation (7) can be written in the form

$$\Phi_0 = \sum_{n,m} A_{nm} N(l,n) P_n^m(\cos \vartheta) \cos m \varphi, \tag{15}$$

(if we omit for short the terms with  $\sin m\varphi$ ). To obtain  $\Phi_1$ , we have to represent the right side of the second equation as a sum of terms of the type (11). This can be easily done by means of relations (13) and (14). The terms of this expansion, proportional to one of the products of the sum (15), would prevent  $\Phi_1$  from satisfying Schroedinger's conditions of finiteness. We must, therefore, choose the value of  $E_1$ , in such a way as to make these terms vanish.

It will be sufficient to carry this through for the simple case  $l = 2$ , as all conclusions will be applicable to the general case. If  $l = 2$ ,

$$\Phi_0 = A_{11}N(2,1)P_1^1(\cos \vartheta) \cos \varphi + A_{10}N(2,0)P_1(\cos \vartheta) + A_{00}N(1,0)P_0. \tag{16}$$

The terms of  $\alpha r(ex - E_1)\Phi_0$ , proportional to these, are

$$\begin{aligned}
 (2A_{11}E_1 + 3A_{00} \sin \gamma)N(2,1)P_1^1 \cos \varphi + (2A_{10}E_1 + 3A_{00} \cos \gamma)N(2,0)P_1 \\
 + [2A_{00}E_1 + 3(A_{10} \cos \gamma + A_{11} \sin \gamma)/\alpha^2]N(2,0)P_0.
 \end{aligned}$$

This leads to the three conditions

$$\begin{aligned}
 2A_{11}E_1 + 3A_{00} \sin \gamma = 0, \quad 2A_{10}E_1 + 3A_{00} \cos \gamma = 0, \\
 2\alpha^2 A_{00}E_1 + 3(A_{10} \cos \gamma + A_{11} \sin \gamma) = 0.
 \end{aligned}
 \tag{17}$$

Corresponding to the three partial oscillations, we have to expect three values of  $E_1$ . The quantization coördinates are chosen in the right way, when each of these three values can be associated with one of the three possible combination of quantic numbers  $n, m$ : (1, 1), (1, 0), (0, 0). However, our purpose is to answer the simpler question, whether it is permissible to choose the axis of the system in the arbitrary direction we have given it. Since  $\varphi$  is the azimuth around the axis, the quantic number referring to the axis is  $m$ . The axis is chosen in a correct way, if we can associate one value of  $E_1$ , with  $m = 1$ , and two with  $m = 0$ . Tested by this criterion, our axis is not well chosen, as our equations (17) are mixed with respect to the second indices of  $A_{nm}$ . If we try to remedy this situation by a linear substitution, the only substitution that can be found is

$$\begin{aligned} A_{11} &= B_{10} \sin \gamma + B_{11} \cos \gamma, & A_{10} &= B_{10} \cos \gamma - B_{11} \sin \gamma, \\ A_{00} &= B_{00}, \end{aligned} \quad (18)$$

which brings equations (17) into the form

$$\begin{aligned} 2\alpha^2 B_{00} E_1 + 3B_{10} &= 0, & 3B_{00} + 3B_{10} E_1 &= 0, \\ B_{11} E_1 &= 0. \end{aligned} \quad (19)$$

The coördinates corresponding to the coefficients  $B_{nm}$  satisfy our requirements. The geometrical meaning of this transformation becomes apparent, when we substitute (18) into expression (15) for  $\Phi_0$ . Denoting by  $\vartheta'$ ,  $\varphi'$  the polar angle and azimuth referred to the direction  $x$  and the  $x, y$  plane, we obtain, with the aid of well-known trigonometrical relations,

$$\Phi_0 = B_{11} N(2, 1) P_1^1(\cos \vartheta') \cos \varphi' + B_{10} N(2, 1) P_1(\cos \vartheta') + B_{00} N(2, 0) P_0.$$

Our substitution (18) represents, therefore, a rotation of the polar axis into the direction  $x$ . In other words, the axis of the atom has the direction of the electric field.

5. *Conditions in Weak Fields.*—If the relativistic term is more important than the electric, we have to take it into account first. The motion without electric field is then the relativistic motion, and, instead of the first equation (7), we should take the equation corresponding to this case. The main feature of the relativistic motion is that in it the characteristic value  $E_0$  is a function, not only of the quantic number  $l$ , but also of  $n$ . This is, in fact, the only point of any importance for our purpose: if we bear it in mind, we may neglect relativity in every other respect and use the same analysis as in the previous case. Instead of (15), we shall have for the total quantic number  $l = 2$  two possible expressions of  $\Phi_0$ , corresponding to  $n = 1$  and  $n = 0$ ,

$$\begin{aligned}\Phi_0^{(1)} &= A_{11}N(2, 1)P_1^1 \cos \varphi + A_{10}N(2, 1)P_1, \\ \Phi_0^{(0)} &= A_{00}N(2, 0)P_0.\end{aligned}\tag{20}$$

Therefore, the equations analogous to (17) will be

$$A_{11}E_1 = 0, \quad A_{10}E_1 = 0, \quad A_{00}E_1 = 0.\tag{21}$$

We see that the requirement discussed in last section is satisfied: we can associate one of the three values of  $E_1$  with each of the existing combinations  $nm$ . (Incidentally  $E_1 = 0$ , in every case.) This shows that our system of polar coördinates with an arbitrary orientation of the axis is an adequate system for the quantization or, in other words, the atomic axis may have any direction.

Whether a given field is to be considered as strong or weak depends on the ratio of the corresponding electric perturbation to the relativistic. As the expressions for the relativistic doublet and for the Stark effect are almost the same in the old and the new theory, we have, roughly speaking, the same criterion in both of them.<sup>5</sup>

6. *Normal State of the Atom.*—In the normal state  $l = 1, n = m = 0$ . The solution of the unperturbed motion is

$$\Phi_0 = A_{00}N(1, 0)P_0.\tag{22}$$

By the same method as in section (4) we find for  $E_1$  the condition  $A_{00}E_1 = 0$ . There is only one value of  $E_1$  and one combination of the quantic numbers: (0, 0). The requirement of section 4 is, therefore, always satisfied. For strong, as for weak fields, we can choose any system of polar coördinates as the coördinates of quantization. We obtain for  $\Phi_1$

$$\Phi_1 = \mu A_{00}[N(3, 1) - 2N(2, 1)](P_1 \cos \gamma + P_1^1 \cos \varphi \sin \gamma)/K^2\alpha^2.\tag{23}$$

Substituting this into the third equation (7) we can compute the part of the right side which is proportional to  $N(1, 0)P_0$  and must vanish:

$$A(9\mu/2K^2\alpha^4 + 2E_2)N(1, 0)P_0.\tag{24}$$

The angle  $\gamma$  has dropped out of this expression and it gives always the same value for the coefficient:

$$E_2 = -9K^6/4\mu^3e^6,\tag{25}$$

which is, moreover, identical with the value resulting for the normal state in our theory of the Stark effect.

The physical cause of this particularity of the normal state becomes apparent if we notice that  $N(1, 0) = P_0 = 1$ . Therefore,  $\Phi_0 = A_{00} = \text{const.}$ , and the amplitude  $\psi$  of the oscillation becomes, according to equation (6),  $\psi = A_{00} \exp(\alpha r)$ . The normal state represents a radial pulsation of complete central symmetry. It is the same in every system of co-

ordinates and, therefore, is always affected in the same way by an electric field. If we describe the atom by parabolical coördinates,<sup>3</sup> we get for the normal state  $\psi = A_{00} \exp [\alpha(\xi + \eta)/2]$ , where  $(\xi + \eta)/2 = r$ , so that here again we get the same radial pulsation.

The numerical value of  $E_2$ , according to formula (25), is  $E_2 = -3,29.10^{-25}$  cm.<sup>3</sup> The dielectric constant<sup>1</sup> is connected with  $E_2$  by the relation  $\epsilon - 1 = 8\pi N E_2$  ( $N$ , number of atoms in unit volume), leading to the value  $\epsilon - 1 = 0,000224$ .

The spin of the electron has not been considered in this theory, but it hardly can introduce any appreciable change. We completely agree with Van Vleck's opinion that this theoretical value is more reliable than the result of the extremely difficult experimental determination of the index of refraction. The fact that for helium the experimental value  $\epsilon - 1 = 0,000074$  is very different from the above value, is not consistent with a model in which one electron is close to the nucleus, the other farther away. It can be regarded as a further confirmation of Heisenberg's theory assuming equivalent orbits for the two electrons.

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<sup>6</sup> Schroedinger, E., *Ann. Physik*, **80**, 478 (1926).

<sup>7</sup> Epstein, P. S., *Proc. Nat. Acad. Sci.*, **12**, 629 (1926).

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## THE DIELECTRIC CONSTANT OF ATOMIC HYDROGEN FROM THE POINT OF VIEW OF BOHR'S QUANTUM THEORY

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1. The following lines represent an abridgment of my thesis presented a year ago to the University of California. Their main purport is in relation to the question *whether a hydrogen atom in an electric field acquires a definite orientation or not*, and this question is answered from the point of view of Bohr's theory. Since this investigation was begun, the quantum theory has undergone a rapid development owing to the brilliant work of Heisenberg, Born, Schroedinger and others. The numerical part of our work is superseded by this new point of view, but our general results and the whole approach of the problem remain of practical value even in the new quantum theory, as will appear from the preceding paper by Professor