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The Zeeman Effect in Oxygen*

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This paper describes the calculation of the energy of magnetic sub-levels belonging to the $^3\Sigma$-state of O_2 in an external magnetic field. A general secular determinant is derived, the roots of which yield the desired energies. The results are particularly useful in the investigation of levels associated with a low value of the rotational quantum number. The perturbation representing the external magnetic field is introduced together with the perturbations leading to the rotational triplets; thus the distortion of the rotational triplets is considered from the beginning of the calculation. The work is performed in two stages to avoid the mathematical difficulties of treating a ninth-order secular determinant. Comparison between theory and experiment is satisfactory.

I. INTRODUCTION

As a result of the application of microwave techniques to the examination of molecular Zeeman patterns, a need has arisen for more exact theoretical expressions for the Zeeman energy levels of a diatomic molecule. Recently a method for computing these levels has been applied to the $^2\Pi_{3/2}$-state of $N^{14}O^{16}$;[1] the results of the calculation are in good agreement with experiment. In the present paper the same method is used to compute the energy values of the magnetic sub-levels of the rotational triplets in $O^{16}O^{16}$. The mathematical details are somewhat different, since O_2 is an example of Hund's case (*b*), whereas NO corresponds closely to Hund's case (*a*).

A general method of computing the Zeeman effect in O_2 has been discussed in a paper by Schmid, Budó, and Zemplén.[2] Their procedure is to suppose that the rotational spin triplets in O_2 are examples of Hund's case (*b*); then, employing eigenfunctions representing case (*b*), they introduce the external magnetic field as a perturbation on the three state functions corresponding to a rotational triplet. Essentially the result is that the effect of the external magnetic field is superimposed on the rotational triplets. Unfortunately, when applied to the most intense lines in the spectrum, their work agrees only approximately with the experimental results of Beringer and Castle.[3]

In this paper we start with a set of eigenfunctions corresponding to Hund's case (*a*). Certain perturbations (discussed below) treated in conjunction with this set lead to the rotational triplets in O_2. We introduce the operator representing the effect of the external magnetic field along with these perturbations and thereby take into account from the beginning of the calculation the distortion of the energy levels of the rotational triplets by the external magnetic field. The results of this calculation reduce to those of Schmid, Budó, and Zemplén for large values of the rotational quantum number, K; the approximation is increasingly good for all $K > 5$. Hence we are primarily interested in the magnetic sub-levels belonging to the rotational levels for which $K=1$ and 3. (States for which K is even are prohibited by the homonuclear character of O_2.)

II. THE VECTOR MODEL FOR O_2

The energy levels to be investigated belong to the $^3\Sigma$-state of the oxygen molecule. This state is a close approximation to Hund's ideal case (*b*). The quantum number Λ, which represents the projection along the internuclear axis of the total orbital angular momentum, is zero. The total electronic spin, **S**, has associated with it a quantum number, S, which has the value unity; we suppose that **S** is the result of the addition of the individual spins of two electrons. The sum of **S** and the rotational angular momentum vector, **K**, is represented by the vector **J**, the total angular momentum of the molecule; associated with **K** and **J** are the quantum numbers K and J. For a given value of K, there are three possible values of J; these depend on the three possible orientations of **S** relative to **K**. As a result, each rotational energy level of the $^3\Sigma$-state of O_2 (characterized by a particular value of the rotational quantum number, K) is divided into three sub-levels, the values of J associated with these sub-levels being $J=K$; $J=K\pm 1$. There is a magnetic moment associated with **J**, and this magnetic moment interacts with an external magnetic field, **H**. The result is that each member of a rotational triplet is further divided into $2J+1$ sub-levels which depend on the $2J+1$ possible orientations of **J** relative to **H**. The quantum number M_J is used to designate the projection of **J** in the direction of this field. The energy level diagram for the case $K=1$ is shown qualitatively in Fig. 1. We use the notation $W(J, K, M_J)$ to represent the energy of a magnetic sub-level. $W(J, K, M_J)$ will of course be a function of the strength of the external magnetic field, H. We shall compare the theory to be developed with experiment by finding those values of the magnetic field strength,

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** Assisted by the ONR.

[1] H. Margenau and A. Henry, Phys. Rev. **78**, 587 (1950).

[2] Schmid, Budó, and Zemplén, Zeits. f. Physik **103**, 250 (1936).

[3] R. Beringer and J. G. Castle, Jr., Phys. Rev. **78**, 581 (1950).

H, for which

$$W(J,K,M_J)-W(J,K,M_J-1)=\nu_0 \qquad (1)$$

where ν_0 is the operating frequency.

III. THE QUANTUM-MECHANICAL CALCULATION

Oxygen is an example of Hund's case (*b*). Nevertheless we begin the calculation with a set of eigenfunctions corresponding to case (*a*). Such eigenfunctions are sharp with respect to the quantum numbers J, S, Σ, and M_J, where Σ is the quantum number representing the component of $\mathbf{S}$ along the internuclear axis. We use this set so that we may take advantage of the work of previous authors; we expect the final result to be independent of the particular basic set of eigenfunctions employed, provided we consider the interaction of a sufficient number of eigenfunctions from the basic set.

The symbol $|J,S,\Sigma,M_J)$ is to designate an eigenfunction of the basic set; explicit dependence on vibrational and electronic quantum numbers is not indicated.

The functions $|JS\Sigma M_J)$ which correspond to Hund's ideal case (*a*), are obtained as eigenfunctions of the Hamiltonian of the oxygen molecule in a magnetic field only when certain terms in that Hamiltonian are neglected. In order to obtain a more accurate state function for the molecule, these terms must be treated as perturbations.

In doing this we first consider the terms in the Hamiltonian neglected when the wave equation of the entire molecule is separated into electronic, vibrational, and rotational parts. We indicate these terms by the symbol H'. They are given explicitly by Van Vleck,[4] who computes the following matrix elements of H' between eigenfunctions, $|JS\Sigma M_J)$

$$(JS\Sigma M_J|H'|JS\Sigma\pm 1M_J)$$
$$=B[(S\pm\Sigma+1)(S\mp\Sigma)(J\pm\Sigma+1)(J\mp\Sigma)]^{\frac{1}{2}}, \qquad (2)$$
$$(JS\Sigma M_J|H'|JS\Sigma M_J)=B[S(S+1)-\Sigma^2],$$

$B\equiv\hbar^2/2m\rho^2$; $m\equiv$reduced mass of molecule; $\rho\equiv$internuclear distance.

Two other perturbations of importance in this calculation were first introduced by Kramers.[5] The first involves the interaction of the spins of the two outermost electrons; the sum of these spins gives the molecule a total spin of 1. The second perturbation takes into account the interaction of the magnetic moments associated with $\mathbf{K}$ and $\mathbf{S}$. Mathematically, the two are,

$$A[3S_{z'}^2-S^2] \quad\text{and}\quad \mu\mathbf{K}\cdot\mathbf{S},$$

where A and μ are proportionality constants; $S_{z'}$ is the operator representing the component of total electron spin along the internuclear axis. Kramers gives the matrix elements of the first as

$$(JS\Sigma M_J|A(3S_{z'}^2-S^2)|JS\Sigma M_J)$$
$$=A[3\Sigma^2-S(S+1)]. \qquad (3)$$

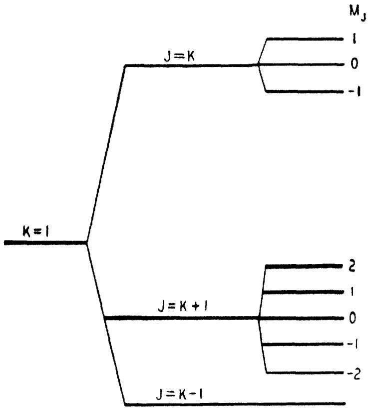

FIG. 1. Qualitative energy level diagram for the lowest rotational state of O_2 in a magnetic field.

He also provides matrix elements of the second between eigenfunctions corresponding to Hund's case (*b*) in which J, K, S, M_J are "good" quantum numbers. Following his work, we shall not introduce this perturbation until the stage at which we are dealing with state functions which correspond closely to case (*b*) eigenfunctions. The matrix elements then are

$$(JKSM_J|\mu\mathbf{K}\cdot\mathbf{S}|JKSM_J)$$
$$=\tfrac{1}{2}\mu[J(J+1)-K(K+1)-S(S+1)]. \qquad (4)$$

Finally we consider the effect of the external magnetic field. Since Λ is 0, and O_2 has no nuclear spin, the only interaction with the external field is that involving S, the total electronic spin. This interaction may be written

$$H_m=2\mu_0\mathbf{H}\cdot\mathbf{S};\quad \mu_0\equiv\text{the Bohr magneton.}$$

For the basic set of eigenfunctions $|JS\Sigma M_J)$, the total spin is quantized along the internuclear axis the projection being designated by the quantum number Σ. The arguments of the rotational part of $|JS\Sigma M_J)$ are the Eulerian angles θ and ψ. (See Kronig.[6] Without losing any generality we may let the Eulerian angle ϕ be zero.) These angles specify the position of an axis system, $X'Y'Z'$, with origin at the center of mass of the two nuclei and Z' lying along the internuclear axis of the molecule, relative to XYZ, another axis system having the same origin but with the X, Y, and Z directions fixed in space. We suppose that the external magnetic field of magnitude H is in the Z direction. Then, if we let $H_{x'}$, $H_{y'}$, and $H_{z'}$ be the components of $\mathbf{H}$ in the X', Y', and Z' directions, we obtain

$$H_{x'}=0;\quad H_{y'}=H\sin\theta;\quad H_{z'}=H\cos\theta.$$

Therefore

$$\begin{aligned}H_m&=2\mu_0\mathbf{H}\cdot\mathbf{S}=2\mu_0[H_{x'}S_{x'}+H_{y'}S_{y'}+H_{z'}S_{z'}],\\ H_m&=\mu_0H[2\cos\theta S_{z'}-i\sin\theta(S'^{+}-S'^{-})],\end{aligned} \qquad (5)$$

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[4] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

[5] H. A. Kramers, Zeits. f. Physik **53**, 422 (1929).

[6] R. Kronig, *Band Spectra and Molecular Structure* (Cambridge University Press, London, 1930).

where

$$S'^{+}\equiv S_{x'}+iS_{y'};\quad S'^{-}\equiv S_{x'}-iS_{y'}.$$

We obtain matrix elements of H_m by employing the matrix elements between symmetric-top eigenfunctions given by Rademacher and Reiche[7] and by use of the relations

$$S'^{+}|S\Sigma)=[(S-\Sigma)(S+\Sigma+1)]^{\frac{1}{2}}|S,\Sigma+1),$$
$$S'^{-}|S\Sigma)=[(S+\Sigma)(S-\Sigma+1)]^{\frac{1}{2}}|S,\Sigma-1),$$

$|S\Sigma)$ being the spin part of $|JS\Sigma M_J)$. The matrix elements which we require are

$$\left.\begin{aligned}
(JS\Sigma M_J|H_m|JS\Sigma M_J)&=\frac{2\Sigma^2 M_J}{J(J+1)}\mu_0 H,\\
(JS\Sigma M_J|H_m|J+1,S\Sigma M_J)&=\frac{2\Sigma}{J+1}\left[\frac{[(J+1)^2-\Sigma^2][(J+1)^2-M_J{}^2]}{(2J+1)(2J+3)}\right]^{\frac{1}{2}}\mu_0 H,\\
(JS\Sigma M_J|H_m|JS,\Sigma+1,M_J)&=-\frac{\mu_0 H M_J}{J(J+1)}[(J-\Sigma)(J+\Sigma+1)(S-\Sigma)(S+\Sigma+1)]^{\frac{1}{2}},\\
(JS\Sigma M_J|H_m|J+1,S,\Sigma+1,M_J)&=\mu_0 H\left[\frac{(J+\Sigma+2)(J+\Sigma+1)(S+\Sigma+1)(S-\Sigma)[(J+1)^2-M_J{}^2]}{(J+1)^2(2J+1)(2J+3)}\right]^{\frac{1}{2}},\\
(JS\Sigma M_J|H_m|J-1,S,\Sigma+1,M_J)&=-\mu_0 H\left[\frac{(J-\Sigma)(J-\Sigma-1)(S+\Sigma+1)(S-\Sigma)(J^2-M_J{}^2)}{J^2(2J-1)(2J+1)}\right]^{\frac{1}{2}}.
\end{aligned}\right\}\quad(6)$$

In computing them we suppose $|JS\Sigma M_J)$ to be multiplied by a phase factor, $\exp[-i|\Sigma-M_J|\pi/2]$, so that the results given in the table of Rademacher and Reiche have a consistent sign.

Since we are interested in energy changes within a particular rotational level, we neglect the constant electronic and vibrational energies associated with that level. The total Hamiltonian of the molecule may then be written

$$H_0=H_T+H'+A[3S_{z'}{}^2-S^2]+\mu\mathbf{K}\cdot\mathbf{S}+H_m,\qquad(7)$$

where H_T is the operator representing the rotational energy of the molecule in case (a); it is the Hamiltonian of the symmetric top for case (a) and has a matrix element which is the energy of the symmetric top. Thus

$$(JS\Sigma M_J|H_T|JS\Sigma M_J)=B[J(J+1)-\Sigma^2].\qquad(8)$$

In order to describe adequately the energy level belonging to a rotational triplet, it is necessary to use nine functions from the basic set in conjunction with the Hamiltonian (8). We avoid the ninth-order secular determinant which arises from such a procedure by performing the calculations in two stages. These stages are best described with the help of Fig. 2.

We begin with the nine eigenfunctions the energy levels of which are represented under the column "start" in Fig. 2; the values of the quantum numbers J and Σ which distinguish them are indicated on the figure; the energies associated with them are $B[J(J+1)-\Sigma^2]$. Since they are case (a) eigenfunctions, they have no correspondence to states of the O_2 molecule.

Next, we form a linear combination of

$$|J_1S,1,M_J),\quad |J_1S,0,M_J)\quad\text{and}\quad |J_1S,-1,M_J)$$

and diagonalize the Hamiltonian (8) with respect to it, omitting the term $\mu\mathbf{K}\cdot\mathbf{S}$ at this stage. This procedure gives rise to a secular determinant the roots of which are

$$\left.\begin{aligned}
E(J_1,J_1+1)&=B[J_1(J_1+1)+1]-\frac{\lambda}{3}+\frac{\mu_0 H M_J}{J_1(J_1+1)}\\
&\quad+\left\{(2J_1+1)^2\left[B-\frac{\mu_0 H M_J}{J_1(J_1+1)}\right]^2+\lambda^2-2B\lambda+\frac{2\lambda\mu_0 H M_J}{J_1(J_1+1)}\right\}^{\frac{1}{2}},\\
E(J_1,J_1)&=BJ_1(J_1+1)+\frac{2}{3}\lambda+\frac{2\mu_0 H M_J}{J_1(J_1+1)},\\
E(J_1,J_1-1)&=B[J_1(J_1+1)+1]-\frac{\lambda}{3}+\frac{\mu_0 H M_J}{J_1(J_1+1)}\\
&\quad-\left\{(2J_1+1)^2\left[B-\frac{\mu_0 H M_J}{J_1(J_1+1)}\right]^2+\lambda^2-2B\lambda+\frac{2\lambda\mu_0 H M_J}{J_1(J_1+1)}\right\}^{\frac{1}{2}},
\end{aligned}\right\}\quad(9)$$

where $\lambda\equiv\frac{3}{2}A$.

The notation $E(J_1,J_1+1)$, etc. will be explained below. By putting the roots (9) back into the three equations which led to the secular determinant, we evaluate the coefficients of the linear combination and obtain the

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[7] H. Rademacher and F. Reiche, Zeits. f. Physik **41**, 453 (1927).

eigenfunctions corresponding to the three roots. They are

$$\left.\begin{aligned} \psi(J_1, J_1+1) &= a(J_1, J_1+1)|J_1S1M_J) \\ &\quad +b(J_1, J_1+1)|J_1SOM_J) \\ &\quad +c(J_1, J_1+1)|J_1S-1M_J), \\ a(J_1, J_1+1) &= c(J_1, J_1+1) \\ &= \frac{E(J_1, J_1+1)-E(J_1, J_1)}{\{2f^2+[E(J_1, J_1+1)-E(J_1, J_1)]^2\}^{\frac{1}{2}}}, \\ b(J_1, J_1+1) &= \frac{f}{\{2f^2+[E(J_1, J_1+1)-E(J_1, J_1)]^2\}^{\frac{1}{2}}}, \\ f &\equiv B[2J_1(J_1+1)]^{\frac{1}{2}}-\frac{2\mu_0HM_J}{[2J_1(J_1+1)]^{\frac{1}{2}}}, \end{aligned}\right\} \quad (10)$$

$$\left.\begin{aligned} \psi(J_1, J_1) &= a(J_1, J_1)|J_1S1M_J) \\ &\quad +b(J_1, J_1)|J_1SOM_J) \\ &\quad +c(J_1, J_1)|J_1S-1M_J), \\ a(J_1, J_1) &= c(J_1, J_1)=1/\sqrt{2}; \quad b(J_1, J_1)=0, \end{aligned}\right\} \quad (11)$$

$$\left.\begin{aligned} \psi(J_1, J_1-1) &= a(J_1, J_1-1)|J_1S1M_J) \\ &\quad +b(J_1, J_1-1)|J_1SOM_J) \\ &\quad +c(J_1, J_1-1)|J_1S-1M_J), \\ a(J_1, J_1-1) &= c(J_1, J_1-1) \\ &= \frac{E(J_1, J_1-1)-E(J_1, J_1)}{\{2f^2+[E(J_1, J_1-1)-E(J_1, J_1)]^2\}^{\frac{1}{2}}}, \\ b(J_1, J_1-1) &= \frac{f}{\{2f^2+[E(J_1, J_1-1)-E(J_1, J_1)]^2\}^{\frac{1}{2}}}. \end{aligned}\right\} \quad (12)$$

If we let λ and H be zero, the energies (9) have the form $BK(K+1)$, where $K=J_1+1$ for $E(J_1, J_1+1)$, $K=J_1$ for $E(J_1, J_1)$ and $K=J_1-1$ for $E(J_1, J_1-1)$. Now $BK(K+1)$ is the form for the energy of a molecule in Hund's case (*b*) with $\Lambda=0$; hence the energies (9) are all associated with the same value of J but with the values of K: $K=J_1$; $K=J_1\pm1$. This accounts for the notation of Eq. (9). For instance, $E(J_1, J_1+1)$ signifies that the value of J associated with this energy level is J_1 and the value of K is J_1+1. It follows that the functions $\psi(J_1, J_1+1)$, $\psi(J_1, J_1)$ and $\psi(J_1, J_1-1)$ are eigenfunctions of the operators $\mathbf{K}$ as well as the operator $\mathbf{J}$; hence these functions correspond to Hund's case (*b*) and thus are a good representation for states in the O_2 molecule.

By repeating the above process for the cases $J=J_1+1$ and $J=J_1-1$, we obtain the energy level scheme shown in stage (1) of Fig. 2; if we were to include all possible levels arising from different values of J, stage (1) would be a series of triplets, each set being associated with a different value of K. Except for the presence in the Hamiltonian of the operator representing the magnetic field and the temporary omission of the term $\mu\mathbf{K}\cdot\mathbf{S}$, the calculation and results at stage (1) are identical with those of Schlapp.[8] Since the state functions for O_2 must be antisymmetric in the exchange of the identical oxygen nuclei, states associated with even values of K do not exist; this result would appear automatically if we were to start with a basic set having the correct symmetry properties.

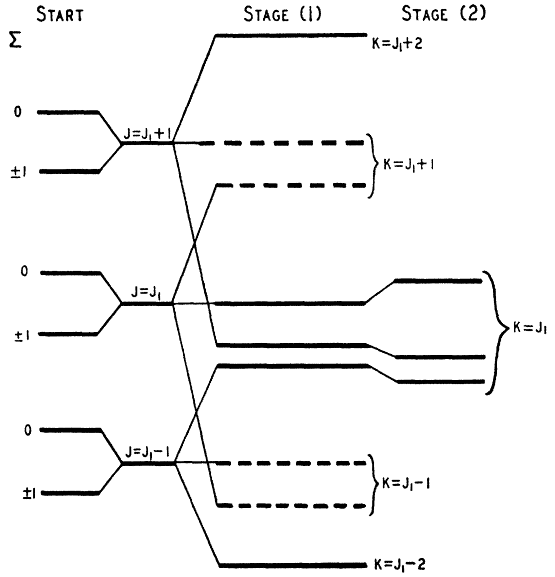

FIG. 2. Rotational energy levels at different stages of the calculation.

When $J=0$, Eq. (9) are not valid, since $[01, \pm1, M_J)$ does not exist. For this special case

$$\begin{aligned} E(0, 1) &= -(4/3)\lambda+2B, \\ \psi(0, 1) &= a(0, 1)|011M_J)+b(0, 1)|010M_J) \\ &\quad +c(0, 1)|01-1M_J), \end{aligned} \quad (13)$$

$$a(0, 1)=c(0, 1)=0; \quad b(0, 1)=1.$$

TABLE I. Theoretical and experimental field strengths and line intensities for transitions between Zeeman components of first two rotational levels in O_2.

K	J	Transition $M_J \rightarrow M_J-1$	H (oersted) Calc.	H (oersted) Obs.	Relative intensity Calc.	Relative intensity Obs.
1	1	$0\rightarrow-1$	5524.2	5527	0.35	0.60
1	1	$1\rightarrow0$	~10,000.0	——	0.35	—
1	2	$-1\rightarrow-2$	8703.6	8657	0.68	0.40
1	2	$0\rightarrow-1$	7169.5	7149	1.00	1.00
1	2	$1\rightarrow0$	6633.7	6620	0.99	1.00
1	2	$2\rightarrow1$	6023.0	6014	0.66	0.60
3	2	$0\rightarrow-1$	7447.5	7445	0.34	0.25
3	4	$0\rightarrow-1$	8528.8	8500	0.68	0.80

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[8] R. Schlapp, Phys. Rev. **39**, 806 (1932).

In stage (2) of the calculation, we form a linear combination of $\psi(J_1-1, J_1)$ from (10), (or 13, if $J_1=1$), $\psi(J_1, J_1)$ from (11), and $\psi(J_1+1, J_1)$ from (12). We diagonalize the Hamiltonian (7) with respect to this combination, including now the term $\mu\mathbf{K}\cdot\mathbf{S}$. This leads to the secular determinant

$$\begin{vmatrix}
E(K-1,K)-\mu(K+1)-W & \begin{array}{c} 2\mu_0H\left[\frac{(K+1)(K^2-M_J{}^2)}{K^2(2K+1)}\right]^{\frac{1}{2}} \\ \times\left[\frac{2a(K-1,K)}{\sqrt{2}}\left(\frac{K-1}{2K-1}\right)^{\frac{1}{2}} \right. \\ \left. +b(K-1,K)\left(\frac{K}{2K-1}\right)^{\frac{1}{2}}\right] \end{array} & 0 \\
\begin{array}{c} 2\mu_0H\left[\frac{(K+1)(K^2-M_J{}^2)}{K^2(2K+1)}\right]^{\frac{1}{2}} \\ \times\left[\frac{2a(K-1,K)}{\sqrt{2}}\left(\frac{K-1}{2K-1}\right)^{\frac{1}{2}} \right. \\ \left. +b(K-1,K)\left(\frac{K}{2K-1}\right)^{\frac{1}{2}}\right] \end{array} & E(K,K,-\mu-W & \begin{array}{c} 2\mu_0H\left[\frac{K[(K+1)^2-M_J{}^2]}{(K+1)^2(2K+1)}\right]^{\frac{1}{2}} \\ \times\left[\frac{2a(K+1,K)}{\sqrt{2}}\left(\frac{K+2}{2K+3}\right)^{\frac{1}{2}} \right. \\ \left. -b(K+1,K)\left(\frac{K+1}{2K+3}\right)^{\frac{1}{2}}\right] \end{array} \\
0 & \begin{array}{c} 2\mu_0H\left[\frac{K[(K+1)^2-M_J{}^2]}{(K+1)^2(2K+1)}\right]^{\frac{1}{2}} \\ \times\left[\frac{2a(K+1,K)}{\sqrt{2}}\left(\frac{K+2}{2K+3}\right)^{\frac{1}{2}} \right. \\ \left. -b(K+1,K)\left(\frac{K+1}{2K+3}\right)^{\frac{1}{2}}\right] \end{array} & E(K+1,K)+\mu K-W
\end{vmatrix}=0, \quad (14)$$

where quantities are labeled by the value of K; i.e., $E(K-1,K)$ is the energy for which $J=K-1$ and $K=K$. The roots of this determinant are the energy values required for the solution of Eq. (1). For large K or small H, (9) reduces to the analogous result in the paper of Schmid and Budó. Under the method of calculation used here it is necessary to consider the perturbation of neighboring rotational states in order to obtain for the energy a value which reduces to the Paschen-Back energy at very high fields.

We compute relative intensities by calculating for the transitions the numerical expression for the quantity

$$\begin{aligned}
&\langle\psi(JKM_J)|S_x+iSy|\psi(JKM_J-1)\rangle^2 \\
&\quad\times\exp\left[-\frac{W(JKM_J)}{kT}\right] \\
&=[-2a^2(J,K)+2a(J,K)b(J,K)(2J(J+1))^{\frac{1}{2}}]^2 \\
&\quad\times\frac{1}{J^2(J+1)^2}(J+M_J)(J-M_J+1) \\
&\qquad\times\exp\left[-\frac{W(JKM_J)}{kT}\right], \quad (15)
\end{aligned}$$

where the dependence of the eigenfunctions (10), (11) and (12) on the quantum number, M_J, is indicated in the notation $\psi(JKM_J)$. T stands for the absolute temperature of the oxygen in which the transition is taking place; k is the Boltzman constant.

IV. RESULTS

The values of H which are solutions of (1) and which lie in the experimental range of Beringer and Castle's apparatus are given in in Table I along with the intensities computed by use of (15). The expressions for the constants needed in the calculation are as follows: $B=1.4377$ cm^{-1}, $\mu=0.008$ cm^{-1}, $\lambda=1.985$ cm^{-1}, $\nu_0=0.31163$ cm^{-1}, $T=78°$ Kelvin, $\mu_0=4.66846\times10^{-5}$ cm^{-1}/oersted. The first three are taken from the article of Schlapp;[7] the third and fourth are experimental values. Results are given only for the energy levels for which K equals (1 or 3). For $K=3$, all values of the field strength other than the two given lie outside the experimental range (9200 oersted). All of the intense lines arise from transitions within these two levels. The principal cause of the discrepancies between theoretical and experimental results is probably the proceedure of solving the problem in two stages. This proceedure neglects part of the distortion of the internal coupling by the magnetic field. Because the coupling in O_2 is quite small and is therefore easily broken down, this neglect may be significant. It is of no importance in NO (see reference 1) which has a large coupling energy.

Two more lines have been found in a preliminary investigation of the level for which $K=5$. The method of Schmid and Budó (which leads to results differing from experiment by about 200 oersteds for $K=1$) should be sufficient for the investigation of transitions within levels associated with values of K greater than 5. Even when this simpler formula is employed, the arithmetical work involved in identifying the entire spectrum resolved by Beringer and Castle is very laborious and has not been attempted.

I wish to thank Professor Henry Margenau for suggesting this problem and the method of solution and for helpful criticism and advice throughout the course of the calculation.

To Professor Robert Beringer and Mr. J. G. Castle, Jr. I am indebted for prepublication use of a part of their data on oxygen.

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The Influence of a Transverse Magnetic Field on the Conductivity of Thin Metallic Films

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The influence of a transverse magnetic field on the conduction properties of thin metallic films, of thickness comparable with the free path of the conduction electrons, is investigated. It is shown that, owing to scattering of electrons at the boundaries of the film, the Hall coefficient is increased, and the electrical resistance oscillates with the strength of the applied magnetic field.

I. INTRODUCTION

IN the theory of metals it is usual to assume that the conduction electrons may be treated as if they were free, the energy being proportional to the square of the wave vector. This assumption is sufficient to explain most of the conduction phenomena, but it leads to a zero change of resistance in a magnetic field, and to explain the usual type of magneto-resistance effect[1] it is necessary to employ more complicated models which take into account the departure of the energy surfaces from spherical symmetry.[2] However, in proving that there is no magneto-resistance effect for the free electron model it is tacitly assumed that all the dimensions of the specimen considered are large compared with the free path of the conduction electrons. This requirement is fulfilled under ordinary conditions, but it may break down in the case of thin films or wires at very low temperatures; under such conditions, where boundary scattering of electrons plays an essential part in determining the resistance, the alteration of the free electron trajectories in a magnetic field may lead to a finite magneto-resistance effect. This is a "geometrical" effect which is of a totally different type from the ordinary increase in resistance observed in the bulk metal, and, being essentially classical in nature, it is much simpler to understand. The details of the phenomena observed in any particular case depend, of course, upon the shape of the specimen and upon the relative configurations of specimen, electric current and magnetic field.

An effect of this type was first observed by MacDonald,[3] who found that the resistance of a thin sodium wire at low temperatures *decreased* when a longitudinal magnetic field was applied. In the present paper, however, we discuss only the case of a thin film placed in a magnetic field which is perpendicular to the plane of the film. Although this is perhaps not the simplest case to visualize, it is the easiest to analyze mathematically, and an exact solution can be obtained assuming only that the conduction electrons are quasi-free and that a time of relaxation can be defined for their collisions with the ionic lattice of the metal. These assumptions are sufficient to bring out all the essential features of the phenomena; a more general model, which leads also to a finite magneto-resistance effect in the bulk metal, will be examined in a later paper.

The increase in resistance of a thin metallic film in the absence of a magnetic field has been discussed by Fuchs,[4] and the present theory is a simple generalization of Fuchs' analysis. General formulas for the electrical conductivity and the Hall coefficient in a magnetic field of arbitrary magnitude are derived in Section II, both for the case in which the electrons suffer diffuse reflec-

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