PHYSICAL REVIEW VOLUME 100, NUMBER 6 DECEMBER 15, 1955

Theory of the Hyperfine Structure of the NO Molecule. II. Errata and Some Additional Discussion*

CHUN C. LIN,† *Harvard University, Cambridge, Massachusetts*

AND

MASATAKA MIZUSHIMA,‡ *Department of Physics, Duke University, Durham, North Carolina*

(Received August 4, 1955)

A theoretical formula for the magnetic hfs of diatomic molecules previously given by one of us (M.M.) is revised by including the Fermi term and correcting an error in the choice of phase. The new formula gives $eQq=-1.7$ Mc/sec and $eQq'=22$ Mc/sec for the $^2\Pi$ state of the NO molecule. It was found that these constants together with the values $a=23.14$ Mc/sec, $b=14.056$ Mc/sec, for the parameters of the magnetic hfs, defined in the first paper give theoretical frequencies which explain not only 1/2→3/2 spectra but also the 3/2→5/2 transitions of the $^2\Pi_{\frac{1}{2}}$ state. A discussion on the theory of the magnetic resonance spectrum of the $^2\Pi_{\frac{3}{2}}$ state is also given.

NOTE ON MAGNETIC HFS

ALTHOUGH the first-order theory of the magnetic interaction of NO has been given by several authors,[1–3] the second-order effects remain to be examined. The Hamiltonian for NO, exclusive of nuclear quadrupole and Λ-doubling effect, can be written as[4]

$$\begin{aligned} H&=H_0+H_1,\\ H_0&=D\Lambda S_z+B[(J_x-S_x)^2+(J_y-S_y)^2]\\ &\qquad\qquad+2B(J_xS_x+J_yS_y),\\ H_1&=-2B(J_xS_x+J_yS_y)\\ &\quad+\frac{2g_n\beta_n\beta}{r^3}\left[\mathbf{I}\cdot\mathbf{L}+\frac{3(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})}{r^2}-\mathbf{I}\cdot\mathbf{S}\right]\\ &\qquad+\frac{16\pi}{3}g_n\beta_n\beta|\psi(0)|^2(\mathbf{I}\cdot\mathbf{S}). \end{aligned}\tag{1}$$

Here D and B represent the spin-orbit coupling constant and the rotational constant, respectively, of NO. The other symbols have a fairly standard significance. We shall construct the Hamiltonian matrix in a Hund's case (a) representation, i.e., a representation where Ω, Σ, Λ, J, I, and F are diagonal. H_0 is completely diagonal in this scheme and will be taken as the unperturbed Hamiltonian. If we introduce the symbols a, b, c, and d as defined by Dousmanis[3] (also by Frosch and Foley[1]), the matrix elements of H_1 can be expressed as

$$\begin{aligned}(\Sigma,\Omega,J|H_1|\Sigma,\Omega,J)\\ =-\tfrac{1}{2}\Omega[a\Lambda+(b+c)\Sigma]R(J)[J(J+1)]^{-1},\end{aligned}\tag{2}$$

$$\begin{aligned}(\Sigma,\Omega,J|H_1|\Sigma,\Omega,J-1)=-\tfrac{1}{2}[a\Lambda+(b+c)\Sigma](J^2-\Omega^2)^{\frac{1}{2}}\\ \times f(J)[J(4J^2-1)^{\frac{1}{2}}]^{-1},\end{aligned}\tag{3}$$

$$\begin{aligned}(\Sigma,\Omega,J|H_1|\Sigma\pm1,\Omega\pm1,J-1)\\ =\mp\tfrac{1}{8}b[(J\mp\Omega)(J\mp\Omega-1)]^{\frac{1}{2}}[S(S+1)-\Sigma(\Sigma\pm1)]^{\frac{1}{2}}\\ \times f(J)[J(4J^2-1)^{\frac{1}{2}}]^{-1},\end{aligned}\tag{4}$$

$$\begin{aligned}(\Sigma,\Omega,J|H_1|\Sigma+1,\Omega+1,J)\\ =\tfrac{1}{8}b[J(J+1)-\Omega(\Omega+1)]^{\frac{1}{2}}[S(S+1)-\Sigma(\Sigma+1)]^{\frac{1}{2}}\\ \times R(J)[J(J+1)]^{-1}+B[J(J+1)-\Omega(\Omega+1)]^{\frac{1}{2}}\\ \times[S(S+1)-\Sigma(\Sigma+1)]^{\frac{1}{2}},\end{aligned}\tag{5}$$

$$\begin{aligned}(\Sigma=-\tfrac{1}{2},\Omega=\tfrac{1}{2},J|H_1|\Sigma=\tfrac{1}{2},\Omega=-\tfrac{1}{2},J)\\ =\tfrac{1}{4}d(J+\tfrac{1}{2})R(J)[J(J+1)]^{-1},\end{aligned}\tag{6}$$

$$\begin{aligned}(\Sigma=\mp\tfrac{1}{2},\Omega=\pm\tfrac{1}{2},J|H_1|\Sigma=\pm\tfrac{1}{2},\Omega=\mp\tfrac{1}{2},J-1)\\ =\pm\tfrac{1}{8}df(J)/J,\end{aligned}\tag{7}$$

where

$$\begin{aligned}f(J)&=[(F+J-I)(F+I-J+1)\\ &\qquad\times(F+I+J+1)(J+I-F)]^{\frac{1}{2}},\\ R(J)&=J(J+1)+I(I+1)-F(F+1).\end{aligned}\tag{8}$$

We have omitted the "high-frequency" matrix elements connecting Λ and Λ±1. The first-order magnetic interaction energy arises from the matrix elements (2) and (6). To obtain the second-order correction we apply a Van Vleck transformation[5] to remove the nondiagonality in J and Ω. It is then found that all the second-order terms are negligibly small except the one arising from the matrix elements of the type (5), where $\Sigma=-1/2$, $\Omega=1/2$. This is the one which comes from the mixture of $\Pi_{\frac{1}{2}}$ state and $\Pi_{\frac{3}{2}}$ state. Although the effect of this mixing was already taken into account in the formula (36) of Part I, the Fermi-type hfs effect was neglected there. The following formula is the

---

* This research was supported in part by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

† duPont Company predoctoral fellow (Chemistry), 1954–1955. Present address: Department of Physics, University of Oklahoma, Norman, Oklahoma.

‡ Present address: Department of Physics, University of Colorado, Boulder, Colorado.

[1] R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952).

[2] M. Mizushima, Phys. Rev. **94**, 569 (1954). It is called Part I or I in this paper.

[3] G. C. Dousmanis, Phys. Rev. **97**, 967 (1955).

[4] J. H. Van Vleck, Revs. Modern Phys. **23**, 213 (1951).

[5] See, for example, E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937), p. 394.

generalization of the formula (36) of I:

$$\Delta W_{c,\,d}=-(b\nu/8)[(2J+3)(2J-1)]^{\frac{1}{2}}[J(J+1)]^{-1} \times[F(F+1)-I(I+1)-J(J+1)] \quad (9)$$

where

$$b=-g_n\beta_n\beta\left\langle\frac{3\cos^2\theta-1}{r^3}\right\rangle_{\mathrm{Av}}+(16\pi/3)g_n\beta_n\beta|\psi(0)|^2.$$

This formula gives

$$\Delta P_{c,\,d}(J=3/2)=+0.20\ \mathrm{Mc/sec} \quad (10)$$

as a contribution to the value of P (formula (39) of Part I) of the $J=3/2$ state, instead of the former value +0.18 Mc/sec, and is closer to +0.23 Mc/sec required from the experimental result.

ERRATA ABOUT ELECTRIC QUADRUPOLE HFS

There was an error in the calculation published by one of the present authors[2] on the same title, and the formula for the electric quadrupole hfs obtained there was wrong. The error came from the formula (A6) of Part I:

$$({}^2\Pi_{\frac{1}{2}}Jm|=(4J+2)^{-\frac{1}{2}}[(2J-1)^{\frac{1}{2}}(KSJm| +(2J+3)^{\frac{1}{2}}(K+1SJm|].$$

In that paper the same formula for $(J_+m|$ and $(J_-m|$ states, where J_+ and J_- mean states where the component of J along the molecular axis is positive and negative, respectively, was used. The correct wave function should be

$$({}^2\Pi_{\frac{1}{2}}J_+m|=(4J+2)^{-\frac{1}{2}}[(2J-1)^{\frac{1}{2}}(K_+SJm| +(2J+3)^{\frac{1}{2}}(K+1_+SJm|], \quad (11a)$$

and

$$({}^2\Pi_{\frac{1}{2}}J_-m|=(4J+2)^{-\frac{1}{2}}[(2J-1)^{\frac{1}{2}}(K_-SJm| -(2J+3)^{\frac{1}{2}}(K+1_-SJm|]. \quad (11b)$$

These wave functions give the following result for the nuclear electric quadrupole effect:

$$W_{c,\,d}'=eQqY(F)[3(\tfrac{1}{2})^2(J^2+J)^{-1}-1], \quad (12)$$

where

$$Y(F)=[\tfrac{3}{4}C(C+1)-J(J+1)I(I+1)] \times[2(2J-1)(2J+3)I(2I-1)]^{-1},$$

instead of the formulas (30) of Part I.

Formula (12) is nothing but the usual formula for a symmetric top molecule and the anomaly reported in I was fallacious. Accordingly, the formulas (42) and (43) in I which gave the value of the coupling constant of the electric hfs should be changed. The correct value for them will be given below. The formulas (44) and (46) should be revised also.

NEW FORMULA FOR ELECTRIC QUADRUPOLE HFS

It was emphasized in Part I that a rotational state of the ground electronic state is not a pure ${}^2\Pi_{\frac{1}{2}}$ state, but a small amount of ${}^2\Pi_{\frac{3}{2}}$ state is mixed because of the end-over-end rotation (Zeeman effect showed ${}^2\Sigma$ is also mixed to a still smaller extent[6]). Thus, the wave functions $(J_+m|$ and $(J_-m|$ should be

$$(J_\pm m|=\mu({}^2\Pi_{\frac{1}{2}}J_\pm m|+\nu({}^2\Pi_{\frac{3}{2}}J_\pm m|, \quad (13)$$

where one should take upper or lower signs together. Each rotational state splits into two, because of the Λ-type doubling, and their wave functions are

$$(cJm|=2^{-\frac{1}{2}}\{(J_+m|+(J_-m|\}, \quad (14a)$$

$$(dJm|=2^{-\frac{1}{2}}\{(J_+m|-(J_-m|\}, \quad (14b)$$

where c designates the lower component and d the higher.

If we express the interaction between electrons and the nuclear electric quadrupole moment as

$$H_2=\mathbf{Q}\cdot\nabla E, \quad (15)$$

it is evident that H_2 is diagonal in Σ (component of spin along the molecular axis) since H_2 does not contain any spin coordinates. Thus, only

$$({}^2\Pi_{\frac{1}{2}}J_\pm m|H_2|{}^2\Pi_{\frac{1}{2}}J_\pm m), \quad ({}^2\Pi_{\frac{1}{2}}J_\pm m|H_2|{}^2\Pi_{\frac{3}{2}}J_\mp m)$$

and

$$({}^2\Pi_{\frac{3}{2}}J_\pm m|H_2|{}^2\Pi_{\frac{3}{2}}J_\pm m)$$

are finite while all the other matrix elements are zero. We obtain from the formulas (14a), (14b), and (15):

$$(cJm|H_2|cJm)=A'+B', \quad (16a)$$

$$(dJm|H_2|dJm)=A'-B', \quad (16b)$$

where

$$A'=\{({}^2\Pi_{\frac{1}{2}}J_+m|H_2|{}^2\Pi_{\frac{1}{2}}J_+m) +({}^2\Pi_{\frac{1}{2}}J_-m|H_2|{}^2\Pi_{\frac{1}{2}}J_-m)\}/2, \quad (16c)$$

$$B'=\nu\{({}^2\Pi_{\frac{1}{2}}J_+m|H_2|{}^2\Pi_{\frac{3}{2}}J_-m) +({}^2\Pi_{\frac{1}{2}}J_-m|H_2|{}^2\Pi_{\frac{3}{2}}J_+m)\}/2. \quad (16d)$$

We assumed $|\mu|\gg|\nu|$, $\mu\simeq1$.

It can be shown that (16c) reduces to the conventional formula,

$$A'=eQqY(F)[3(\tfrac{1}{2})^2(J^2+J)^{-1}-1]\sim W_{c,\,d}', \quad (17)$$

while the B' term will give something new. The calculation of this term can be performed by using Racah's method and the formulas obtained in I.[7] The wave functions one should use are shown in the formulas (11a) and (11b) and the similar formulas for $({}^2\Pi_{\frac{3}{2}}J_\pm m|$ can be obtained from the formula (A7) of I.

The same results can be obtained by another pro-

---

[6] Mizushima, Cox, and Gordy, Phys. Rev. **98**, 1034 (1955).

[7] There were some misprints in those formulas in Sec. 4 of I: in (15b), $I(2I-1)$ should be $/I(2I-1)$; in (18), the right-hand side should be $(-1)^{-K-J+\frac{1}{2}}6\{A(A+1)-(4/3)J(J+1)K(K+1)\cdots$; in (19) the last factor in the right-hand side should be $[4K(K+1)\cdots]^{-\frac{1}{2}}$; in (20), the right-hand side $\cdots K(K+1)\times(2K+3)(2K-1)]^{-\frac{1}{2}}\cdots$; in (23), the right-hand side should start as $-\frac{1}{4}\{K(K+1)\cdots$; in (24), $\frac{1}{2}$ should be taken off. Formula (A7) should be $-(\Pi_{\frac{3}{2}}J|=\cdots$.

TABLE I. Observed and calculated frequencies (Mc/sec).

J		F	ν(obs.)	ν(calc.)
1/2→3/2	c	3/2→5/2	150 176.54	150 176.29
		1/2→3/2	150 198.85	150 198.86
		3/2→3/2	150 218.89	150 218.84
		1/2→1/2	150 225.75	150 225.83
		3/2→1/2	150 245.69	150 245.81
	d	3/2→1/2	150 375.48	150 375.62
		3/2→3/2	150 439.22	150 439.19
		3/2→5/2	150 546.50	150 546.34
		1/2→1/2	150 580.70	150 580.73
		1/2→3/2	150 644.37	150 644.40
3/2→5/2	c	5/2→7/2	250 435.60	250 435.26
		3/2→5/2	250 439.20	250 439.19
		1/2→3/2	250 447.16	250 447.41
		3/2→3/2	250 474.42	250 474.24
		5/2→5/2	250 481.52	250 481.82
	d	5/2→7/2	250 794.98	250 795.47
		3/2→5/2	250 814.64	250 814.81
		1/2→3/2	250 816.24	250 816.02
		3/2→3/2	250 752.61	250 752.45
		5/2→5/2	250 707.92	250 707.66

cedure, namely, using Van Vleck's method.[4] The result of them is

$$({}^2\Pi_{\frac{1}{2}}J_+IF|H_2|{}^2\Pi_{\frac{3}{2}}J_-IF) = -\tfrac{1}{8}eQq'(2J+1) \times[(2J-1)(2J+3)]^{\frac{1}{2}}(J^2+J)^{-1}Y(F), \quad (18)$$

where

$$q' = -\left(e_+\left|\frac{\partial^2 V}{\partial x^2}+2i\frac{\partial^2 V}{\partial x\partial y}-\frac{\partial^2 V}{\partial y^2}\right|e_-\right) = 3e\left\langle\frac{x^2+y^2}{r^5}\right\rangle_{\pi\text{ odd}} n. \quad (19)$$

The symbol $\langle\ \rangle_{\pi\text{ odd}}$ means the average value over the odd π electron and n is the effective number of such electrons. From the above formula, we obtain

$$B' = -\tfrac{1}{4}\nu eQq'(2J+1)[(2J-1)(2J+3)]^{\frac{1}{2}} \times(J^2+J)^{-1}Y(F), \quad (20)$$

$$R = eQ\{-q\mp\nu q'(2J+1)[(2J+3)(2J-1)]^{-\frac{1}{2}}\}/ 8J(J+1)I(2I-1), \quad (21)$$

where the double sign means − for c and + for d states, respectively. Since we know that $\nu=-0.0247$ in the $J=3/2$ state, we can obtain the value of the coupling constants by comparing the formulas (16a), (16b), (18), and (21) with the value of R shown in Table I of I as follows:

$$eQq = -1.7 \text{ Mc/sec}, \quad (22)$$

$$eQq' = 22 \text{ Mc/sec}. \quad (23)$$

eQq' is a quantity which has never been observed for any molecule previously. At first sight it appears rather surprising that q' be so large compared to q. The following rough theoretical estimates, however, make the magnitude found for q' appear reasonable. As is shown in the definition (19), only the odd $p\pi$ electron contributes to this quantity. If we assume that there is exactly one odd electron which is in the pure $p\pi$-orbital, we can estimate q'. Using the Slater wave function $(\alpha^5/2\pi)^{\frac{1}{2}}r\sin\theta e^{i\varphi}e^{-\alpha r}$, one can easily obtain

$$q' = (8/5)e\alpha^3 = 3.82\times10^{16} \text{ cgs esu}, \quad (24)$$

where the numerical value is obtained with $\alpha=1.95$ a.u. (atomic units). Somewhat more accurate value can be obtained by using the Hartree wave function. Dousmanis[3] calculated $\langle(x^2+y^2)/r^5\rangle_\pi$ by employing the Hartree wave function and modifying the result. From his result, we obtain

$$q' = 2.58\times10^{16} \text{ cgs esu}. \quad (25)$$

Using the observed value shown in (23), we obtain

$$\begin{aligned} Q &= 0.008\times10^{-24} \text{ cm}^2 \text{ from (24)}, \\ Q &= 0.012\times10^{-24} \text{ cm}^2 \text{ from (25)}. \end{aligned} \quad (26)$$

Both of these estimates agree with the value 0.01×10^{-24} cm^2 obtained by Sheridan and Gordy,[8] but is smaller than the value 0.02×10^{-24} cm^2 obtained by Townes and Dailey.[9] This value, however, is based on the assumption that exactly one electron contributes to eQq', which is not necessarily true as will be shown in the third paper of this series.[10] The more detailed discussion on this point and accordingly a more reliable value of Q will be given there.

ANALYSIS OF $J=3/2\rightarrow5/2$ TRANSITIONS

Johnson and Gallagher[11] observed the next rotational transition $J=3/2\rightarrow J=5/2$ of the NO molecule at ${}^2\Pi_{\frac{1}{2}}$ state. Their experimental data are cited in Table I.

The hfs of $J=5/2$ state must be expressed by formula (39) of Part I:

$$W = P\{F(F+1)-I(I+1)-J(J+1)\} +R[\tfrac{3}{4}C(C+1)-J(J+1)I(I+1)].$$

The theoretical formula with the values of the parameters given by formula (40) of I yields

$$P_c = -7.00 \text{ Mc/sec}, \quad P_d = 12.29 \text{ Mc/sec}. \quad (27)$$

The contribution due to the mixing of the ${}^2\Pi_{\frac{3}{2}}$ state is by formula (9)

$$\Delta P_{c,d} = -\frac{\sqrt{8}}{35}b\nu, \quad (28)$$

and ν, the parameter which gives the extent of mixing of the ${}^2\Pi_{\frac{3}{2}}$ state, is calculated in the same way as was done in the appendix of I, to be

$$\nu(J=5/2) = -0.0404; \quad (29)$$

---

[8] J. Sheridan and W. Gordy, Phys. Rev. **79**, 513 (1950).

[9] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

[10] M. Mizushima, Phys. Rev. (to be published).

[11] C. M. Johnson and J. J. Gallagher, post-deadline paper, American Physical Society meeting, Columbia University, New York, New York (January, 1954).

thus

$$\Delta P_{c,\,d}=+0.23\ \text{Mc/sec}. \tag{30}$$

The theoretical values of R can be calculated by the formulas (21), (22) and (23). The results are given in Table II.

Although in Part I one of the authors tried to adjust the numerical values of the parameters P and R so as to reproduce the observed frequencies of $J=1/2\rightarrow J=3/2$ transition[12] as far as possible, we were not concerned about the theoretically predicted relations between them. In this paper, we have tried to reduce everything into eight parameters, whose numerical values are shown in Table III. In Table III, the ν_0's are the frequencies which are obtained by subtracting the effect of hfs, while a and b are quantities which were defined in the formulas (11a) and (11b) of Part I and which are related to Dousmanis' parameters[3] as follows:

$$\begin{aligned} 4a&=a-(b+c)/2\ \text{of Dousmanis},\\ 8b&=d\ \text{of Dousmanis}. \end{aligned} \tag{31}$$

As the correction in P due to the mixing of $^2\Pi_{\frac{3}{2}}$ state, the theoretical values cited in (10) and (30) are used. The calculated frequencies agree with the observed values with the average deviation of 0 08 Mc/sec for the $J=1/2\rightarrow 3/2$ transition, and 0.24 Mc/sec for the $J=3/2\rightarrow 5/2$ transition. See Table I. Most of the deviations are within the experimental error which is assumed to be about 0.10 Mc/sec for $J=1/2\rightarrow 3/2$ and 0.25 Mc/sec for $J=3/2\rightarrow 5/2$.

THEORY OF THE MAGNETIC RESONANCE SPECTRUM OF NO IN $^2\Pi_{\frac{3}{2}}$ STATE

The magnetic resonance spectrum of NO in $^2\Pi_{\frac{3}{2}}$ state has been observed by Beringer and Castle,[13] and a theoretical account has been given by Margenau and Henry[14] and also by Henry.[15] Recently Beringer, Rawson, and Henry[16] have made more accurate measurements on the spectrum. With the new data it is seen that the Margenau and Henry treatment, in which the secular equation is set up in the Hund's case (*b*) representation, does not provide very good agreement between the calculated and experimental results. Since NO is a good Hund's case (*a*) molecule, it should be more natural to solve this problem by starting from a case (*a*) representation and treating the Zeeman effect, rotational distortion terms, etc., as perturbations.

TABLE II. The values of hfs parameters derived by the values cited in Table I (Mc/sec).

J	1/2		3/2		5/2	
	c	d	c	d	c	d
P	−6.66	68.37	−8.63	21.37	−6.77	12.52
R	0	0	0.08	0.04	0.04	0.008

TABLE III. The adjusted values of hfs parameters (Mc/sec).

$a=$ 23.14	$\nu_{c,\,0}(J=1/2\rightarrow 3/2)=150\,195.40$
$b=$ 14.065	$\nu_{d,\,0}(J=1/2\rightarrow 3/2)=150\,550.54$
$eQq=-1.7$	$\nu_{c,\,0}(J=3/2\rightarrow 5/2)=250\,443.13$
$eQq'=$ 22	$\nu_{d,\,0}(J=3/2\rightarrow 5/2)=250\,797.00$

The Hamiltonian of NO in a magnetic field exclusive of the interactions due to the nuclear spin, can be written as

$$H=H_0+H',$$

where

$$H'=-2B(J_xS_x+J_yS_y)+\mu_0(\Lambda+2S)\cdot\mathcal{H} \tag{32}$$

and H_0 is given in (1). In a representation where Σ, Λ, Ω, J, and M_J are diagonal, the matrix elements of the first term in (32) are well-known, and the second term can be expressed as

$$(\Lambda+2S)_{z'}=2\lambda_{z'x}S_x+2\lambda_{z'y}S_y+\lambda_{z'z}(\Lambda+2\Sigma),$$

where x', y', z' and x, y, z represent coordinate axes systems fixed in space and in the molecule respectively, and the λ's are the directional cosines. The matrix elements of $(\Lambda+2S)_{z'}$ can therefore be calculated by taking the direct products of $\lambda_{z'x}$ and S_x, etc. We thus find

$$\begin{aligned}
&(J,\Omega,\Sigma,M_J|H'|J+1,\Omega-1,\Sigma-1,M_J)\\
&\quad=-(J+1)^{-1}[(2J+1)(2J+3)]^{-\frac{1}{2}}Q(J+1,M_J)\\
&\qquad\times[(J-\Omega+1)(J-\Omega+2)]^{\frac{1}{2}}P(S,\Sigma)\mu_0\mathcal{H},\\
&(J,\Omega,\Sigma,M_J|H'|J,\Omega-1,\Sigma-1,M_J)\\
&\quad=B[J(J+1)-\Omega(\Omega-1)]^{\frac{1}{2}}P(S,\Sigma)\\
&\qquad-[J(J+1)]^{-1}[(J+\Omega)(J-\Omega+1)]^{\frac{1}{2}}\\
&\qquad\times P(S,\Sigma)M_J\mu_0\mathcal{H},\\
&(J,\Omega,\Sigma,M_J|H'|J-1,\Omega-1,\Sigma-1,M_J)\\
&\quad=[J^2(4J^2-1)]^{-\frac{1}{2}}[(J+\Omega)(J+\Omega-1)]^{\frac{1}{2}}\\
&\qquad\times Q(J,M_J)P(S,\Sigma)\mu_0\mathcal{H},\\
&(J,\Omega,\Sigma,M_J|H'|J+1,\Omega,\Sigma,M_J)\\
&\quad=(J+1)^{-1}[(2J+1)(2J+3)]^{-\frac{1}{2}}\\
&\qquad\times[(J+\Omega+1)(J-\Omega+1)]^{\frac{1}{2}}\\
&\qquad\times Q(J+1,M_J)(\Lambda+2\Sigma)\mu_0\mathcal{H},\\
&(J,\Omega,\Sigma,M_J|H'|J,\Omega,\Sigma,M_J)\\
&\qquad\qquad=[J(J+1)]^{-1}\Omega(\Lambda+2\Sigma)M_J\mu_0\mathcal{H},
\end{aligned} \tag{33}$$

where

$$P(S,\Sigma)=[S(S+1)-\Sigma(\Sigma-1)]^{\frac{1}{2}},\quad Q(x,y)=[x^2-y^2]^{\frac{1}{2}}.$$

To calculate the energy levels in a magnetic field, we apply the perturbation method to the third order. Taking 124.2 cm^{-1} as the value[17] of D and neglecting the uninteresting terms independent of M_J, we obtain

---

[12] C. A. Burrus and W. Gordy, Phys. Rev. **92**, 1437 (1953).
[13] R. Beringer and J. G. Castle, Jr., Phys. Rev. **78**, 581 (1950).
[14] H. Margenau and A. Henry, Phys. Rev. **78**, 587 (1950).
[15] A. Henry, Phys. Rev. **80**, 549 (1950).
[16] Beringer, Rawson, and Henry, Phys. Rev. **94**, 343 (1954).
[17] M. Guillery, Z. Physik **42**, 121 (1927); Jenkins, Barton, and Mulliken, Phys. Rev. **30**, 150 (1927).

TABLE IV. Experimental and calculated values of the microwave frequency for NO spectrum.

Line	Transitions		Resonance field (in gauss)	Microwave frequency observed (in Mc/sec)	Frequency calculated (neglecting Schwinger's spin-moment anomaly) (in Mc/sec)	Frequency calculated (including Schwinger's spin-moment anomaly) (in Mc/sec)
	M_J, M_I	M_J-1, M_I				
H_1	$3/2,\ 1\rightarrow$	$1/2,\ 1$	8398.61	9269.94	9270.5	9275.6
H_2	$3/2,\ 0\rightarrow$	$1/2,\ 0$	8425.71	9270.65	9270.7	9276.0
H_3	$3/2,\ -1\rightarrow$	$1/2,\ -1$	8453.44	9270.65	9270.7	9275.8
H_4	$1/2,\ 1\rightarrow$	$-1/2,\ 1$	8501.49	9270.65	9269.6	9274.7
H_5	$1/2,\ 0\rightarrow$	$-1/2,\ 0$	8528.28	9270.65	9269.2	9274.3
H_6	$1/2,\ -1\rightarrow$	$-1/2,\ -1$	8555.84	9270.65	9269.5	9274.7
H_7	$-1/2,\ 1\rightarrow$	$-3/2,\ 1$	8600.97	9269.81	9267.4	9272.5
H_8	$-1/2,\ 0\rightarrow$	$-3/2,\ 0$	8629.71	9270.65	9268.5	9273.7
H_9	$-1/2,\ -1\rightarrow$	$-3/2,\ -1$	8656.46	9270.65	9268.6	9274.2

for the energy levels:

$$\begin{aligned} E\ (\text{in Mc/sec}) &= 0.77713M_J\mu_0\mathcal{H}+3.917\times10^{-7}M_J^2\mu_0^2\mathcal{H}^2-4.4699 \\ &\quad\times10^{-12}M_J\mu_0^3\mathcal{H}^3+7.221\times10^{-13}M_J^3\mu_0^3\mathcal{H}^3. \end{aligned} \tag{34}$$

The interaction arising from the nuclear spin in nitrogen consists of the nuclear spin-orbit, dipole-dipole, and Fermi $|\psi(0)|^2$ couplings as given in Eq. (1) and the nuclear quadrupole coupling. If we denote the operator for these interactions by H_N, it follows that[18]

$$\begin{aligned} (J,\Omega,M_J,M_I|H_N|J,\Omega,M_J,M_I) &= [J(J+1)]^{-1}[a\Lambda+(b+c)\Sigma]\Omega M_J M_I \\ &\quad -eQq[J(J+1)-3\Omega^2] \\ &\quad \times[4I(2I-1)(2J-1)(2J+3)J(J+1)]^{-1} \\ &\quad \times[J(J+1)-3M_J^2][I(I+1)-3M_I^2]. \end{aligned}$$

The nuclear quadrupole effect is small enough that a first-order perturbation treatment is sufficient. The off-diagonal matrix elements for the magnetic interaction terms in H_N can be calculated by the method described for H_1. Calculations show that the only second-order terms which amount to more than 0.1 Mc/sec are those from the cross-term between H' and H_N in

$$\frac{|(J,\Omega,\Sigma,M_J,M_I|H'+H_N|J,\Omega-1,\Sigma-1,M_J,M_I)|^2}{E_{J,\Omega,\Sigma}-E_{J,\Omega-1,\Sigma-1}}$$

and

$$\frac{|(J,\Omega,\Sigma,M_J,M_I|H'+H_N|J+1,\Omega,\Sigma,M_J,M_I)|^2}{E_{J,\Omega,\Sigma}-E_{J+1,\Omega,\Sigma}}.$$

For $J=3/2$ and $\Omega=3/2$, these two second-order terms become

$$-0.0120bM_IM_J+4.197\times10^{-7}[a+(b+c)/2]M_IM_J^2\mu_0\mathcal{H}.$$

The total energy including the nuclear effect is therefore

$$\begin{aligned} E &= 0.77713M_J\mu_0\mathcal{H}+3.915\times10^{-7}M_J^2\mu_0^2\mathcal{H}^2-4.4699 \\ &\quad\times10^{-12}M_J\mu_0^3\mathcal{H}^3+7.221\times10^{-13}M_J^3\mu_0^3\mathcal{H}^3 \\ &\quad+\{\tfrac{2}{5}[a+(b+c)/2]-0.0120b\}M_IM_J \\ &\quad+4.197\times10^{-7}[a+(b+c)/2]M_IM_J^2\mu_0\mathcal{H} \\ &\quad+eQq(20-4M_J^2)(2-3M_I^2)/80. \end{aligned} \tag{35}$$

If one takes the Schwinger spin moment anomaly[19] into consideration, the term $\mu_0(\Lambda+2S)\cdot\mathcal{H}$ in Eq. (32) should be replaced by $\mu_0(\Lambda+2.002290S)\cdot\mathcal{H}$ and the matrix elements in Eqs. (33) should be modified accordingly. The equation corresponding to Eq. (35) in this case is

$$\begin{aligned} E &= 0.77756M_J\mu_0\mathcal{H}+3.9020\times10^{-7}M_J^2\mu_0^2\mathcal{H}^2-4.4699 \\ &\quad\times10^{-12}M_J\mu_0^3\mathcal{H}^3+7.221\times10^{-13}M_J^3\mu_0^3\mathcal{H}^3 \\ &\quad+\{\tfrac{2}{5}[a+\tfrac{1}{2}(b+c)]-0.0120b\}M_IM_J \\ &\quad+4.197\times10^{-7}[a+\tfrac{1}{2}(b+c)]M_IM_J^2\mu_0\mathcal{H} \\ &\quad+eQq(20-4M_J^2)(2-3M_I^2)/80. \end{aligned}$$

Table IV shows a comparison between the experimental and calculated values of the frequencies corresponding to the transitions $\Delta M_J=1$ and $\Delta M_I=0$ at various magnetic field strengths. It is readily seen that when the Schwinger correction to the gyromagnetic ratio of the electronic spin is considered, all the theoretical frequencies are invariably higher than the experimental values. As an error of 1 cm^{-1} in the spin-orbit interaction constant would cause a difference of 2 Mc/sec in the microwave frequency, the uncertainty in D may be responsible for the discrepancies in Table IV.

One of us (C.C.L.) wishes to thank Professor J. H. Van Vleck for his constant help and encouragement during the course of this work.

---

[18] C. K. Jen, Phys. Rev. **76**, 1494 (1949).

[19] J. Schwinger, Phys. Rev. **73**, 416 (1947).