Theory of the Fine Structure of the Molecular Oxygen Ground State*

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A rather complete solution for the fine-structure problem in the oxygen molecule is given in the framework of the Born-Oppenheimer approximation. The reduction of the effect of the electronic state on the fine structure to an effective Hamiltonian, involving only the resultant electronic spin in addition to rotational and vibrational quantum numbers, is demonstrated. In this Hamiltonian the parameters λ and μ measure the effective coupling of the spin to the figure axis and the rotational angular momentum, respectively. The contributions to these parameters which are diagonal in electronic quantum numbers, namely λ' and μ', are evaluated by using an expression for the electronic wave function as a superposition of configurations. It turns out that λ' gives almost all of λ, whereas μ' gives only 4 percent of μ. The second-order contributions of spin-orbit coupling and rotation-induced electronic angular momentum to λ and μ, and the electronic contribution to the effective moment of inertia are related to each other and to certain magnetic effects to be given later. This interrelation enables them all to be essentially evaluated experimentally.

The effective Hamiltonian is diagonalized through terms in $(B/\hbar\omega)^2$ and the eigenvalues compared with the experimental spectra. The fitting establishes the constants: $\mu=252.67\pm0.05$ Mc/sec; $\lambda_e=59\,386\pm20$ Mc/sec; $\lambda_1=[Rd\lambda/dR]_e=16\,896\pm150$ Mc/sec; $\lambda_2=[(R^2/2)(d^2\lambda/dR^2)]_e=(5\pm2)\times10^4$ Mc/sec; $\lambda_{\text{eff}}(v=0)=19\,501.57\pm0.15$ Mc/sec. The transformation that diagonalizes the Hamiltonian is given with respect to both Hund case (*a*) and case (*b*) bases. These transformations are applied to matrix elements of S_Z. The results are tabulated and applied to calculate the exact intensity factors for spectral lines. This calculation shows slight deviations from the usual case (*b*) results for allowed lines and predicts quite sizeable intensities for the "forbidden" $\Delta K=2$ lines.

I. INTRODUCTION

ALTHOUGH the general principles are well established, there exist few cases in which the Born-Oppenheimer[1] approximation has been carried through to give a complete solution for the eigenfunctions and eigenvalues of a molecule. The recent publication of a reasonably good and analytically convenient solution for the $^3\Sigma$ electronic ground state of O_2 by Meckler[2] and the existence of precise microwave[3] and infrared[4] data on the energy levels make the oxygen molecule a particularly attractive one for study. Interest was increased by the presence of a spin-dependent fine structure which showed some discrepancies from earlier theoretical predictions. To develop certain internal theoretical relations between parameters, and because of the great diversity of existing treatments, we shall give a unified systematic treatment that incorporates the new results and indicates their connection with previous work. It is hoped that this treatment will serve as an example that shows the relation between the wave mechanical electronic theory and the traditionally matrix mechanical fine structure theory. It will also show how far the calculation can be carried in an actual case.

The over-all problem can be stated as that of determining the eigenvalues and eigenfunctions of the Hamiltonian operator

$$\mathcal{H}=\mathcal{H}_{\text{el}}+V_{\text{nuc}}+T_{\text{nuc}}+\mathcal{H}_{\text{so}}+\mathcal{H}_{\text{ss}}+\mathcal{H}_{\text{hfs}}. \quad (1)$$

In this $\mathcal{H}_{\text{el}}$ is the electronic energy operator used by Meckler which includes the electronic kinetic energy, mutual repulsion energy, and the attraction to the nuclei; V_{nuc} is the Coulomb repulsion of the nuclei, and T_{nuc} is the kinetic energy of the nuclei that can be decomposed into vibration, rotation, and center-of-mass motion; $\mathcal{H}_{\text{so}}$ is the spin-orbit energy, and $\mathcal{H}_{\text{ss}}$ is the spin-spin energy resulting from the magnetic dipole interaction between the electronic spins; $\mathcal{H}_{\text{hfs}}$ is the interaction of nuclear magnetic dipole and electric quadrupole moments with their environment.

The eigenfunctions will be functions of space and spin coordinates of the electrons, separation and angles of orientation of the nuclei, and center-of-mass coordinates of the molecule. In general, we would also have nuclear spin coordinates entering, but since O^{16} has no spin these terms do not concern us here. Those eigenfunctions must be antisymmetric on interchange of electrons and symmetric on interchange of the O^{16} nuclei. The essence of the Born-Oppenheimer approximation is that we can express the total state function to a good approximation as

$$\Psi=\psi_{\text{el}}\psi_{\text{vib}}\psi_{\text{rot}}\psi_{\text{nuc spin}}\psi_{\text{trans}}, \quad (2)$$

and that this approximation can be improved by use of perturbation theory between functions of this sort. In determining these functions, we can approximately compute each ψ_i by considering the ψ_j corresponding to other energy terms and coordinates to be fixed, or at least reduced to parameters. Thus Meckler solved for ψ_{el} by considering the nuclei fixed and neglecting the terms T_{nuc}, $\mathcal{H}_{\text{so}}$, $\mathcal{H}_{\text{ss}}$, and $\mathcal{H}_{\text{hfs}}$. His result is an energy $E_{\text{el}}(R)$ and an electronic wave function $\psi_{\text{el}}(\mathbf{r}_j,\mathbf{s}_j|R)$, with the internuclear distance R entering as a parameter and with no dependence at all on the other "lower-energy" coordinates.

In solving the rest of the problem, we should take this $E_{\text{el}}(R)$ as the effective potential for vibration and

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[1] M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

[2] A. Meckler, J. Chem. Phys. **21**, 1750 (1953).

[3] Burkhalter, Anderson, Smith, and Gordy, Phys. Rev. **79**, 651 (1950).

[4] H. Babcock and L. Herzberg, Astrophys. J. **108**, 167 (1948).

use this ψ_{el} to evaluate such things as the spin-spin coupling constants. In practice, we shall approximate $E_{el}(R)$ by a two-term power-series expansion about the minimum. This is justified, since we are only concerned with the two lowest vibrational levels. (For study of the higher vibrational levels, more terms would have to be taken or else recourse be made to a Morse curve or other analytic approximation.[5]) Thus our vibrational Hamiltonian is taken to be

$$\mathcal{H}_{\mathrm{vib}}=P_R^2/2M+\tfrac{1}{2}M\omega_e^2R_e^2\xi^2+b\xi^3, \qquad (3)$$

where $\xi=(R-R_e)/R_e$, R_e is the equilibrium internuclear distance, and M is the reduced mass. The rotational Hamiltonian is

$$\mathcal{H}_{\mathrm{rot}}=\mathbf{N}^2/2MR^2=B_e(1-2\xi+3\xi^2)\mathbf{N}^2, \qquad (4)$$

where $\mathbf{N}$ is the angular momentum of nuclear rotation and B_e is the reciprocal moment of inertia of the nuclei at R_e. The expansion in ξ allows for the change in moment of inertia with centrifugal stretching and vibration.

The effect of $\mathcal{H}_{\mathrm{so}}+\mathcal{H}_{\mathrm{ss}}$ in determining the fine structure can be reduced (see Sec. II) to an effective Hamiltonian,

$$\mathcal{H}_{\mathrm{spin}}=\tfrac{2}{3}(\lambda_e+\lambda_1\xi+\lambda_2\xi^2)(3S_z^2-\mathbf{S}^2)+\mu\mathbf{\mathfrak{K}}\cdot\mathbf{S}, \qquad (5)$$

where $\mathbf{S}$ is the resultant electronic spin vector, and λ and μ are spin coupling constants to be determined from $\psi_{el}(\mathbf{r}_j,\mathbf{s}_j|R)$. The term in μ will be seen to come largely from the interaction of rotation-induced electronic angular momentum with the spin through the spin-orbit coupling. We shall also see that the principal part of the term in λ comes from the diagonal spin-spin energy in the electronic ground state. It is noteworthy that if one tried to estimate λ from the simple model of two interacting spins with one concentrated at each center the values obtained for λ_e and (λ_1/λ_e) would even have the wrong *sign*. Thus it is clear that our more accurate calculation is necessary to explain the observed behavior of λ. In this calculation, exchange effects, inclusion of ionic states, and the rapid change of configuration mixing coefficients with R play the leading roles.

In $(O^{16})_2$ we have $I=0$, allowing only the one state, $\psi_{\mathrm{nuc\ spin}}=1$. Thus there can be no hyperfine effects. The translational motion of the center-of-mass is of no interest to us here, but ψ_{trans} would be simply a plane wave satisfying appropriate boundary conditions. This motion will be neglected throughout the rest of the paper.

Our solution of the fine structure problem,

$$(\mathcal{H}_{\mathrm{vib}}+\mathcal{H}_{\mathrm{rot}}+\mathcal{H}_{\mathrm{spin}}-E)\psi_{\mathrm{vib}}\psi_{\mathrm{rot}}\psi_{\mathrm{spin}}=0, \qquad (6)$$

is by purely matrix methods. (Here, ψ_{spin} describes the state of the resultant electronic spin that enters into $\mathcal{H}_{\mathrm{spin}}$.) The matrix components of the Hamiltonian are readily obtained (see Sec. III) in a Hund case (a) basis[6] characterized by the quantum numbers v, J, M, S, and Σ, where J is the total angular momentum of all kinds, and $\Sigma=S_z$. This matrix is then diagonalized to high approximation, yielding $E(v,K,J)$ and the corresponding eigenvectors. These eigenvalues E fit the microwave results satisfactorily to their limit of accuracy (approximately 1 in 10^5), explaining the discrepancy mentioned above. This fitting establishes the constants λ_e, λ_1, and λ_2 for comparison with the calculated values found in II. The eigenvectors are listed with respect to Hund case (a) eigenfunctions and also with respect to Hund case (b) eigenfunctions, in which $\mathfrak{K}^2$ rather than S_z is diagonal.

With these eigenvectors, the intensities of both allowed and "forbidden" transitions are calculated in Sec. IV. This reveals small corrections to the usual Hund case (b) values for the allowed transitions, and quite appreciable intensities for $\Delta K=2$ transitions. The latter are made possible by the breakdown of the rotational quantum number $\mathfrak{K}$ in the presence of the spin-spin coupling energy.

II. DEDUCTION OF THE EFFECTIVE HAMILTONIAN

The coupling of angular momenta in molecules and the general methods of establishing an effective fine structure Hamiltonian have recently been reviewed by Van Vleck.[7] The calculations of this section are an application of those general methods to a specific case which can be carried particularly far. Our choice of angular momentum notation generally follows that given by Van Vleck. One slight extension is the use of $\mathbf{N}$ for the true instantaneous nuclear orbital angular momentum. $\mathbf{\mathfrak{K}}=\mathbf{N}+\mathbf{L}=\mathbf{J}-\mathbf{S}$ differs from $\mathbf{N}$ only by "high-frequency" off-diagonal elements of the electronic orbital angular momentum. We shall introduce K in Sec. III as the conventional label for the final eigenfunctions; it has the magnitude of $\mathfrak{K}$ for the pure Hund (b) state which is dominant in the eigenfunction.

The basis functions in terms of which we shall describe the state of the molecule are products of the form (2). In this form the $\psi_{el}(\mathbf{r}_j,\mathbf{s}_j|R)$ are solutions to $\mathcal{H}_{el}$ for the case in which the nuclei are not rotating and are "clamped" a distance R apart. When the molecule rotates, the coordinates $\mathbf{r}_j$ are referred to the axes fixed in the molecule, but the wave function still describes the system with respect to a fixed frame. The ψ_{vib} are harmonic oscillator eigenfunctions of the internuclear distance R for the angular frequency of oscillation ω_e; the ψ_{rot} are symmetrical top eigenfunctions for a linear rotor with internal spin angular momentum.[8]

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[5] For details, see G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Publishing Company, Inc., New York, 1950), Chap. III.

[6] F. Hund, Z. Physik **36**, 657 (1926). These coupling cases are also discussed in reference 5, Chap. V.

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

[8] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929); F. Reiche and H. Rademacher, Z. Physik **39**, 444 (1926); **41**, 453 (1927).

As stated above, $\psi_{\text{nuc spin}}$ is trivial for $I=0$, and ψ_{trans} is suppressed.

In the lowest order Born-Oppenheimer approximation, one takes a single product of these eigenfunctions as the total eigenfunction and takes the diagonal value of the complete Hamiltonian over it as the energy eigenvalue. This would give the sum of the unperturbed electronic energy E_n^0, reasonable approximations to the vibrational and rotational energy, the diagonal spin-spin energy in λ, and the small diagonal contribution to μ coming from the magnetic coupling of the electronic spins in the field of the rotating nuclei. However, it fails to include any electronic spin-orbit effects because the ${}^3\Sigma$ ground electronic state has no net orbital angular momentum,[9] and it fails to account for the coupling between electronic, vibrational, and rotational motions such as centrifugal distortion. These latter effects are found by going to a second-order approximation.

A. First-Order Contributions

These terms are to be evaluated by finding the diagonal values of the perturbative term over the electronic wave function. We start with the spin-spin contribution to the parameter λ, defined in (5), which measures the effective coupling of the spin to the z (internuclear) axis.

Spin-Spin Contribution to λ

Since Van Vleck gives no formulas for the coefficient λ and since Kramers'[10] treatment is in terms of permutation group theory rather than in the framework of the usual determinantal method, we must develop our result from the basic Hamiltonian,[11]

$$\mathcal{H}_{\text{ss}}=g^2\beta^2\sum_{k>j}[(\mathbf{s}_j\cdot\mathbf{s}_k)r_{jk}^2-3(\mathbf{s}_j\cdot\mathbf{r}_{jk})(\mathbf{s}_k\cdot\mathbf{r}_{jk})]r_{jk}^{-5},\quad(7)$$

where $\mathbf{r}_{jk}=\mathbf{r}_j-\mathbf{r}_k$. By simply expanding into components and regrouping, this can be written

$$\begin{aligned}\mathcal{H}_{\text{ss}}=-g^2\beta^2\sum_{k>j}\Bigg[&\frac{3x_{jk}y_{jk}}{r_{jk}^5}(s_{jx}s_{ky}+s_{jy}s_{kx})\\&+\frac{3y_{jk}z_{jk}}{r_{jk}^5}(s_{jy}s_{kz}+s_{jz}s_{ky})+\frac{3z_{jk}x_{jk}}{r_{jk}^5}(s_{jz}s_{kx}+s_{jx}s_{kz})\\&+\frac{3}{2}\frac{x_{jk}^2-y_{jk}^2}{r_{jk}^5}(s_{jx}s_{kx}-s_{jy}s_{ky})+\frac{1}{2}\frac{3z_{jk}^2-r_{jk}^2}{r_{jk}^5}\\&\times(3s_{jz}s_{kz}-\mathbf{s}_j\cdot\mathbf{s}_k)\Bigg].\end{aligned}\quad(8)$$

The symmetry of the molecule causes all except the last term to vanish when integrated over the electronic state. All of these spin functions are of the forms which, as Van Vleck points out, have matrix components proportional to corresponding elements of $\mathbf{S}$. (This can be proved by direct multiplication of the matrix elements of a vector of the type $\mathbf{T}$.[12]) Thus all elements of $(3s_{jz}s_{kz}-\mathbf{s}_j\cdot\mathbf{s}_k)$ are proportional to those of $(3S_z^2-\mathbf{S}^2)$, and the proper dependence of the interaction on $\mathbf{S}$ is shown. To evaluate λ, it is convenient to compute the diagonal element of $\mathcal{H}_{\text{ss}}$ for the state $S_z=\Sigma=1$, and to note that the diagonal part of λ is given by

$$\lambda'(\xi)=\lambda_e'+\lambda_1'\xi+\lambda_2'\xi^2=\tfrac{3}{2}E_{\text{ss}}|_{\Sigma=1}.\quad(9)$$

The ξ dependence enters because ψ_{el} depends parametrically on R (or ξ).

The electronic wave function given by Meckler[2] is expressed as a superposition of configurations,

$$\psi_{\text{el}}=\textstyle\sum_\mu C_\mu\phi_\mu,\quad(10)$$

where each ϕ_μ is a determinant or linear combination of determinants which is a spin eigenfunction with $S=1$ and $\Sigma=0$. The corresponding eigenfunctions for $\Sigma=1$, obtained by applying $S_+/\sqrt{2}$ to Meckler's eigenfunctions, have been given by Kleiner.[13] They are more convenient here because the dominant configuration is then a single determinant. The coefficients C_μ are given for several values of R. Near the equilibrium distance R_e, one configuration ($\mu=c$) is dominant, $|C_c|$ being of the order 0.97. The next largest has C_μ of the order 0.1. Since the C's are real, the diagonal energy is simply

$$E_{\text{ss}}=\textstyle\sum_{\mu\mu'}C_\mu C_{\mu'}H_{\mu\mu'}.\quad(11)$$

It is clear that we make an error of the order of only one percent if we neglect terms that do not involve the dominant configuration. Since other sources of error are larger, we shall make some simplifications of this kind. Our problem then is to compute the matrix components of

$$\mathcal{H}_{\text{ss}}=\frac{-g^2\beta^2}{2}\sum_{k>j}\frac{3z_{jk}^2-r_{jk}^2}{r_{jk}^5}\left[2s_{jz}s_{kz}-\frac{s_{j+}s_{k-}+s_{j-}s_{k+}}{2}\right]\quad(12)$$

(where $s_{j\pm}=s_{jx}\pm is_{jy}$) between these configurations.

These matrix components are reduced to sums of 2-electron integrals in terms of single electron orbitals by the usual methods developed by Slater.[14] The spin part of (12) gives a factor of $\pm\frac{1}{2}$ depending on whether the two spins involved are parallel or antiparallel. Thus, in summing to get the diagonal elements, all integrals involving paired spins cancel out. For the diagonal element over the dominant configuration, for

[9] Of course, one could start with electronic eigenfunctions for the problem including spin-orbit interaction. These, however, could not have Λ,Σ as good quantum numbers. As usual, all magnetic-spin-coupling effects are neglected in Meckler's solution.

[10] H. A. Kramers, Z. Physik **53**, 422 and 429 (1929).

[11] W. Heisenberg, Z. Physik **39**, 514 (1926).

[12] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1951), p. 59 ff.

[13] W. H. Kleiner, Quarterly Progress Report No. 9, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, July 15, 1953 (unpublished).

[14] Reference 12, p. 171; J. C. Slater, Phys. Rev. **34**, 1293 (1929).

example, this leaves just

$$(\mathcal{H}_{ss})_{cc}\equiv H_{cc}=\frac{-g^2\beta^2}{4}\biggl(\int\int\chi_+^*(1)\chi_-^*(2)\frac{3z_{12}^2-r_{12}^2}{r_{12}^5}\times\chi_+(1)\chi_-(2)d\tau_1d\tau_2-\int\int\chi_+^*(1)\chi_-^*(2)\times\frac{3z_{12}^2-r_{12}^2}{r_{12}^5}\chi_-(1)\chi_+(2)d\tau_1d\tau_2\biggr), \quad (13)$$

where $\chi_\pm$ is Meckler's notation for the $2p\pi_g{}^\pm$ symmetry orbitals. The subtracted term is, of course, the exchange integral. To evaluate the integrals, we insert Meckler's LCAO molecular orbital functions using Gaussian atomic orbitals. As we shall see, these Gaussians make it possible to evaluate the integral exactly. After some reduction, (13) becomes

$$H_{cc}=\frac{-64g^2\beta^2b^5K^4}{\pi^3}\int\int[r_1\sin\theta_1\exp(-br_1^2)\sinh bRz_1]^2\times[r_2\sin\theta_2\exp(-br_2^2)\sinh bRz_2]^2\times\sin^2(\varphi_2-\varphi_1)(3z_{12}^2-r_{12}^2)/r_{12}^5d\tau_1d\tau_2. \quad (14)$$

This resembles the classical average of the interaction between two identical electron clouds, each of which is concentrated in two toroids of charge encircling the axis of the molecule at the two nuclei. The axis is a nodal line and the perpendicularly bisecting plane is a nodal plane because of the $p\pi_g$ nature of these $\chi_\pm$ orbitals in which the unpaired spins are most apt to be found. However, the factor $\sin^2(\varphi_2-\varphi_1)$ gives a correlation in position tending to concentrate the two interacting electrons in perpendicular planes through the axis. This correlation is a direct result of the exchange integral and hence of the antisymmetry of the wave function. Also noteworthy is the fact that there is a large chance of both electrons being near the same center. This is the result of having ionic states given equal weight with nonionic states in a simple molecular orbital treatment. The principal contribution to the integral then comes when the two electrons are on the same center [because $(3z_{12}^2-r_{12}^2)/r_{12}^5$ is large then] and in perpendicular planes. Also, viewed in this way, the seemingly anomalous sign of λ is explained. Thus the characteristic distance of separation for the interaction is the *atomic* radius, not the internuclear distance.

Evaluation of (14) is made possible by changing variables to

$$\begin{aligned} \xi&=x_{12}=x_1-x_2, & \xi'&=x_1+x_2,\\ \eta&=y_{12}=y_1-y_2, & \eta'&=y_1+y_2,\\ \zeta&=z_{12}=z_1-z_2, & \zeta'&=z_1+z_2.\\ \rho^2&=\xi^2+\eta^2+\zeta^2=r_{12}^2, \end{aligned} \quad (15)$$

The integral then becomes

$$H_{cc}=\frac{-g^2\beta^2K^4b^5\exp(-bR^2)}{2\pi^3}\times\int\int\exp(-b\rho^2)\left(\frac{3\zeta^2-\rho^2}{\rho^5}\right)(\xi\eta'-\xi'\eta)^2\times\exp(-b\rho'^2)[\cosh bR\zeta'-\cosh bR\zeta]^2d\tau d\tau'. \quad (16)$$

If one replaces these Cartesian coordinates by cylindrical primed coordinates and spherical relative coordinates, the integration can be carried out analytically. Power-series expansion is required for the last integration. The result is[15]

$$H_{cc}=g^2\beta^2b^{\frac{3}{2}}2K^4\pi^{-\frac{1}{2}}\biggl\{\frac{1}{30}+\frac{\exp(-bR^2)}{15}+2\exp(-\tfrac{3}{4}bR^2)\times S_1(bR^2)-\frac{\exp(-bR^2)}{2}S_1(4bR^2)\biggr\}, \quad (17)$$

where

$$S_1(x)=\sum_{n=0}^{\infty}\frac{2n-1}{1\cdot3\cdot5\cdots(2n+5)}\left(\frac{x}{2}\right)^n \quad (18)$$

and

$$K^2=[1-\exp(-bR^2/2)]^{-1}.$$

We note that this is the product of a characteristic energy $g^2\beta^2b^{\frac{3}{2}}$ depending on the atomic scale factor b times a dimensionless factor which is a function only of bR^2, that is, of the degree of overlap of the two atomic orbitals. The latter is true, since $\exp(-bR^2)$ is the amplitude of one Gaussian orbital at the center of the other. Computation shows that the dependence on bR^2 is very weak. The total range R varying between zero and infinity, is only 30 percent; and since the region of interest is near a minimum, it is very nearly constant there. Thus the principal dependence of H_{cc} on the molecular wave function is on the degree of concentration of the *atomic* orbitals as measured by $b^{\frac{3}{2}}\sim\langle 1/r^3\rangle$. This result should be independent of the detailed choice of wave function.

Kleiner[13] has noted that the Gaussians used by Meckler give a very poor value for $\langle 1/r^3\rangle$ because of their failure to rise rapidly near $r=0$. In view of these remarks, it seemed best to fit the b in the Gaussian to give $\langle 1/r^3\rangle$ for the atomic orbital equal to that computed from the Hartree-Fock wave function of the oxygen atom.[16] This gave $b=1.696$, as opposed to the value $b=0.8$ (atomic units) chosen by Meckler from consideration of overlap. Numerical results are given

[15] Following Meckler's notation we use J, K, L, and M to denote normalization constants in electronic wave functions. No confusion with the usual angular momentum quantum numbers should result.

[16] Hartree, Hartree, and Swirles, Trans. Roy. Soc. (London) **A238**, 229 (1939). A very useful analytic fitting as the sum of three exponentials is given by P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

with this higher value of b used in the $b^{\frac{3}{2}}$ factors, but in the overlap factors, bR^2 has Meckler's value.

Other matrix elements computed in a similar way are given in Appendix A. Using these results, the numerical values of the matrix components were evaluated for $R=2.236$ and $R=2.372$ atomic units, corresponding to $bR^2=4.0$ and 4.5. These values bracket the equilibrium distance $R_e=2.28$. The coefficients C_μ were determined for these same values of R by interpolating between Meckler's given values. The nonvanishing results are given in Table I, with energies expressed in kMc/sec. From these energies, the spin-spin contribution to λ was computed, and the results are compared with the experimental values (obtained in Sec. III) in Table II.

In view of the crudeness of the Gaussian approximation, these calculated results must be considered unreliable despite the adjustment made in b. This is illustrated by the fact that even for the Hartree-Fock function $\langle 1/r^3\rangle$ is 29 percent less than the "experimental value" obtained from the magnetic hyperfine structure in $O^{16}O^{17}$ by Miller, Townes, and Kotani.[17] Although the uncertainty of interpretation of the latter makes it unwise to make a further adjustment of b, it does indicate that our calculation is apt to *underestimate* the true magnitude.

We thus conclude that the spin-spin interaction provides the major part of the coupling constant λ. This conclusion is supported by the estimation of the contribution of second-order spin-orbit effects given later in the paper.

Inspection of Table I reveals that the R dependence of λ, which determines λ_1, comes almost entirely from the change in the configuration mixing coefficients C_μ, the values of the matrix components being relatively constant. Presumably this behavior would also hold if a wave function constructed from better atomic orbitals were used. This presumption is strengthened by the fact that Ishiguro has obtained similar configuration mixing coefficients in a treatment now in progress using better orbitals.[18] This mechanism for the change in λ again shows that a rather detailed examination of the electronic wave function is necessary for explaining the observed values of λ.

TABLE I. Contributions to the spin-spin energy as given in Eq. (11).

bR^2	$H_{\mu\mu}'$ 4.0	$H_{\mu\mu}'$ 4.5	Combined coefficient 4.0	Combined coefficient 4.5	Contribution to energy kMc/sec 4.0	Contribution to energy kMc/sec 4.5
$H_{cc}=H_{ee}$	27.656	27.286	0.9620	0.9526	26.606	25.992
$H_{dd}=H_{ff}$	20.370	20.148	0.0165	0.0210	0.335	0.423
$H_{cd}=H_{ef}$	39.434	38.998	−0.2494	−0.2788	−9.820	−10.866
$H_{cg}=-H_{ch}=-H_{ci}$	186.22	191.10	0.0321	0.0436	5.974	8.324
					23.095	23.873

[17] Miller, Townes, and Kotani, Phys. Rev. **90**, 542 (1953).
[18] E. Ishiguro (unpublished).

TABLE II. Comparison of calculated and experimental values of λ (kMc/sec).

	Calc.	Exp.
λ_e	35.0	59.386
$\lambda_1=(d\lambda/d\xi)_e$	19.6	16.90

Nuclear Contribution to μ

Van Vleck's[7] Eq. (37) gives the magnetic interaction energy of an assembly of electron spins with each other and with the electronic and nuclear orbital motions. The only terms giving diagonal contributions in a Σ state are the spin-spin energy evaluated above and the terms having nuclear rather than electronic velocities as factors. Separating out the latter, we have[19]

$$\mathcal{H}_1=\frac{-g\beta}{c}\sum_{K,j}\frac{Z_K e}{r_{jK}^3}[\mathbf{r}_{jK}\times\mathbf{v}_K]\cdot\mathbf{s}_j. \tag{19}$$

The velocities and coordinates are measured in a fixed frame but referred to gyrating axes. As Van Vleck points out, it is permissible to replace $\mathbf{v}_K$ by $\boldsymbol{\omega}\times\mathbf{r}_K$ or $(\mathfrak{K}/MR^2)\times\mathbf{r}_K$, since the difference between the true nuclear angular momentum $\mathbf{N}$ and $\mathfrak{K}$ is only the oscillatory electronic orbital angular momentum which averages to zero in this sort of an interaction. We assume a rigid nuclear frame, so the $\mathbf{r}_K$ are constant vectors of $\pm\frac{1}{2}R\mathbf{k}$, where k is a unit vector in the z-direction. Also $\mathfrak{K}_z=0$, since we have a diatomic molecule. Finally, symmetry causes terms which are odd in x_j or y_j to vanish. By using these facts, expansion of H_1 in components reduces to

$$\mathcal{H}_1=\frac{-4Z}{A}\frac{g\beta\beta_N}{R}\left[\sum_j\frac{z_j-R/2}{r_{jK}^3}\mathbf{s}_j\right]\cdot\mathfrak{K}. \tag{20}$$

Here, Z is the atomic number, A is the atomic weight, β_N is the nuclear magneton, and r_{jK} is $|\mathbf{r}_j-\frac{1}{2}R\mathbf{k}|$.

Matrix components of the bracketed operator are reduced to single electron integrals by the method of Slater.[20] Since $\mathfrak{K}_z=0$, we have only terms in s_x and s_y, which are both nondiagonal in Σ. Thus we seek elements that are diagonal in orbital quantum numbers but off-diagonal in Σ. Using Meckler's[2] dominant configuration c, namely, $(I+I_s)/\sqrt{2}$, for $\Sigma=0$, and Kleiner's[13] derived configuration ϕ_c for $\Sigma=1$, application of the general methods yields

$$(c\Sigma=0|\mathcal{H}_1|c\Sigma=1)=\frac{1}{\sqrt{2}}[(\chi_-\beta|\mathcal{H}_1|\chi_-\alpha)+(\chi_+\beta|\mathcal{H}_1|\chi_+\alpha)].$$

The single electron spin operators s_{jx} and s_{jy} in $\mathcal{H}_1$ yield contributions which are just $1/\sqrt{2}$ times the matrix

[19] Correcting the trivial omission of r_{jK}^{-3} in his more general Eq. (39).
[20] Reference 12, p. 169.

elements of S_x and S_y. Also, $|\chi_-|^2=|\chi_+|^2$, so that the two orbital integrals can be combined. This reduces the element to

$$(c\Sigma=0|\mathcal{H}_1|c\Sigma=1)$$
$$=\frac{-4Z}{A}\frac{g\beta\beta_N}{R}\left(\chi_+\left|\frac{z-R/2}{r_{jK}^3}\right|\chi_+\right)\mathfrak{K}\cdot\mathbf{S}\equiv\mu'\mathfrak{K}\cdot\mathbf{S}. \quad (21)$$

This effective Hamiltonian form shows that this term gives a cosine-like coupling of the spin in the magnetic field of the rotating nuclei.

The final problem is to actually evaluate the coefficient μ' by integration over the electronic χ_+ orbitals. To carry this out, we transform to spherical coordinates about the nucleus at $z=R/2$. The integration then proceeds just as in the evaluation of the spin-spin energy and leads to

$$\mu'=\frac{-4Z}{A}\frac{g\beta\beta_N}{R^3}K^2\left(\frac{2}{\pi bR^2}\right)^{\frac{1}{2}}\exp(-bR^2)$$
$$\times[S_5(2bR^2)-\tfrac{1}{8}\exp(-bR^2)S_5(8bR^2)], \quad (22)$$

where

$$S_5(x)=\sum_{n=1}^{\infty}\frac{(8n+1)}{1\cdot3\cdot5\cdots(2n+1)}\left(\frac{x}{2}\right)^n. \quad (23)$$

Noting that this depends on b only through the overlap parameter bR^2 and not on the atomic scale factor b separately, this should be evaluated by using Meckler's $b=0.8$ atomic unit, not the value obtained above by fitting $\langle 1/r^3\rangle$. If this is done, the result is $\mu'=+10.0$ Mc/sec, compared to a total experimental value of $\mu=-252.7$ Mc/sec. This shows that the magnitude of the first-order contribution is only 4 percent of the total value, the rest being from the second-order effects of spin-orbit coupling discussed in the next section.

To make the physical nature of this first-order term clear, we note that simply calculating the energy of the electron spin in the magnetic field at one nucleus due to the rotation of the other about it would give a coupling constant of $2(Z/A)(g\beta\beta_N/R^3)$ or about $+8$ Mc/sec. The increase in magnitude from 8 to 10 Mc/sec is the result of distributing the electron over a region of radius $\sim R/2$, giving an increase in $\langle(z-R/2)/r_{jK}^3\rangle$. From this picture, we see that the dependence of μ' on the detailed electronic wave function is of secondary importance. Further, μ' makes only a small contribution to μ. Finally, there are no off-diagonal elements of $\mathcal{H}_1$ between the dominant ϕ_c configuration and the others in Meckler's wave function. Thus any contributions from the other configurations would be second-order effects of the order of one percent of μ' or 0.1 percent of μ. In view of the other more serious sources of error, it was not considered worth carrying this calculation further in order to evaluate these corrections.

B. Second-Order Contributions

Perturbation of the Electronic State

As our first step in improving the zeroth-order eigenfunction and first-order energy, we find the modification of the $^3\Sigma$ ground state by spin-orbit and rotational effects. We assume the conventional approximate form $A\mathbf{L}\cdot\mathbf{S}$ for the spin-orbit coupling energy rather than try to handle the rigorous microscopic Hamiltonian in terms of coordinates, velocities, and spins of the individual electrons.[21] The rotation-electronic coupling is through the term $-2B\mathbf{L}\cdot\mathfrak{K}$ in the rotational energy:[22]

$$\mathcal{H}_{\mathrm{rot}}=B\mathbf{N}^2=B(\mathfrak{K}-\mathbf{L})^2$$
$$=B\mathfrak{K}^2-2B\mathfrak{K}\cdot\mathbf{L}+B(L_x^2+L_y^2). \quad (24)$$

This cross term is precisely the effective perturbing term that appears in the electronic problem if the time-dependent problem of motion with respect to a classically rotating set of force centers is reduced to finding a wave function that is stationary with respect to the rotating frame.[23] If we assume that electronic excited states lie reasonably high, we can take account of these effects by first-order perturbation theory with the result that

$$\psi_0=\psi_0{}^0-\sum_n\frac{(n|A\mathbf{L}\cdot\mathbf{S}-2B\mathbf{L}\cdot\mathfrak{K}|0)}{E_n-E_0}\psi_n{}^0. \quad (25)$$

The indicated matrix elements are quadratures over orbital functions. Since the operators $\mathbf{S}$ and $\mathfrak{K}$ are independent of the orbital wave functions, they may be simply taken out and treated as numbers at this stage. We note that elements of L_z are diagonal in Λ and proportional to Λ and thus vanish for the Σ state with which we are dealing. Further, in a field of axial symmetry, we have the relation[24]

$$(\Lambda|L_y|\Lambda\pm1)=\pm i(\Lambda|L_x|\Lambda\pm1), \quad (26)$$

all other elements vanishing. Thus the perturbed $^3\Sigma$ wave function has only π states mixed in, and the mixing is proportional to the matrix elements of elec-

[21] This rather phenomenological replacement is supported by the considerable success it has had in application to molecular spectra by Van Vleck [Phys. Rev. **33**, 467 (1929)] and others. It is theoretically insecure in that even for the one electron case the form $\mathbf{l}\cdot\mathbf{s}$ is rigorous only in a central field. For the case of many electrons, it is necessary to consider a form at least as general as $\Sigma_i a_i \mathbf{l}_i\cdot\mathbf{s}_i$ to get the possibility of matrix elements between states of different multiplicity [R. Schlapp, Phys. Rev. **39**, 806 (1932)]. Despite these objections, we adopt the assumption as the most reasonable one-parameter form, since more rigorous calculation with the exact interaction is precluded by computational difficulty and the lack of reliable wave functions for excited states.

[22] The B in this expression is the half reciprocal moment B_N of the bare nuclei, the electronic contribution to the rotational energy being given explicitly by the cross terms. To simplify notation, we simply write B here. It is included in the quadrature because it is still an operator. We would only neglect the higher order effects of vibration on the electronic motion through the rotation by replacing B by the constant B_e without any ξ dependence.

[23] G. C. Wick, Z. Physik **85**, 25 (1933); Phys. Rev. **73**, 51 (1948).

[24] See reference 7, p. 219.

tronic orbital angular momentum perpendicular to the axis.

$$\psi_\Sigma = \psi_\Sigma{}^0 - \sum_{n=\pi}\sum_{g=x,y} \frac{(n|AL_g|0)S_g - (n|2BL_g|0)\mathfrak{R}_g}{E_n - E_0}\psi_n{}^0. \tag{27}$$

Effect on Energy

Next we find the contribution of these perturbation terms to the energy. This is

$$E'' = -\sum_n\sum_{gg'} \frac{[(n|AL_g|0)S_g - (n|2BL_g|0)\mathfrak{R}_g][(n|AL_{g'}|0)^*S_{g'}{}^* - (n|2BL_{g'}|0)^*\mathfrak{R}_{g'}{}^*]}{E_n - E_0}. \tag{28}$$

Using the property (26) of the matrix elements of L, we see that xy terms drop out, and this reduces to the form

$$E'' = \tfrac{2}{3}\lambda''[3S_z{}^2 - S(S+1)] + \mu''\mathfrak{R}\cdot\mathbf{S} - B''\mathfrak{R}^2 + \text{const}, \tag{29}$$

where

$$\lambda'' = \tfrac{1}{2}\sum_n \frac{|(n|AL_x|0)|^2}{E_n - E_0}, \quad B'' = 4\sum_n \frac{|(n|BL_x|0)|^2}{E_n - E_0},$$
$$\mu'' = 4\,\mathrm{Re}\sum_n \frac{(0|AL_x|n)(n|BL_x|0)}{E_n - E_0}. \tag{30}$$

These results are the same as those found by Hebb[25] except for a factor of two stemming from the fact that he counts each π state once whereas each appears twice (as $\Lambda = \pm 1$) in our expression. The term in λ'' is the second-order effect of the spin-orbit energy and turns out to be small. The term in μ'' gives the spin-orbit coupling energy to the electronic angular momentum of the π states admixed by the rotation. B'' lowers the effective reciprocal moment of inertia from the nuclear value, B_N, essentially by the addition of electronic mass to the rotating frame.[26]

Since the actual matrix elements required cannot be calculated in the absence of wave functions for the π states, these sums cannot be evaluated from first principles. However, to a reasonably good approximation these may be simplified by treating A and B as constants rather than as functions of the configuration. In particular, B can be considered to have the value observed in the electronic ground state and the order of magnitude of A can be estimated from the multiplet separation of the π states. With A and B removed, all the sums become the same, namely,

$$\sum_n \frac{(n|L_x|0)^2}{E_n - E_0} = \frac{L(L+1)}{h\nu}. \tag{31}$$

The right member is merely symbolic, but if we use Van Vleck's "hypothesis of pure precession"[27] it could be used to infer the characteristic energy separation $h\nu$. This sum then becomes a single disposable parameter, and theoretical relations between the various quantities become possible. This feature is greatly enhanced by the fact that the theory of the interaction of the molecule with a magnetic field (to be given in a subsequent paper) reveals two other experimentally accessible quantities of this same form. By combining all of these, a remarkably complete separation of effects, with some internal checks, becomes possible.

C. Analysis of Results

If we now collect the terms that depend on other than electronic coordinates, we have the effective Hamiltonian for vibration, rotation, and spin orientation. It is

$$\mathcal{H}_{\text{eff}} = P_R{}^2/2M + \tfrac{1}{2}M\omega_e{}^2R_e{}^2\xi^2 + b\xi^3 + B\mathfrak{R}^2 + \tfrac{2}{3}\lambda(3S_z{}^2 - \mathbf{S}^2) + \mu\mathfrak{R}\cdot\mathbf{S}, \tag{32}$$

where

$$B = B_N - B'', \quad \lambda = \lambda' + \lambda'', \quad \mu = \mu' + \mu''. \tag{33}$$

Because they enter in exactly the same form, λ', λ''; μ', μ''; and B, B'' will be indistinguishable in the eigenvalues of this operator. They can be separated, however, if one uses the results of the theoretical calculations and of the Zeeman-effect experiments.

With the known experimental value of $\mu = \mu' + \mu''$ (see Sec. III), and the value of μ' calculated in the previous section, we can determine μ'' to be -262.7 Mc/sec. Taking $B = 43.1$ kMc/sec, this implies that $AL(L+1)/h\nu$ is -1.52×10^{-3} which is consistent with reasonable values of A, $L(L+1)$, and $h\nu$. In particular, the minus sign checks with the plus sign for A in the π states of $O_2{}^+$ according to Van Vleck's general theory.[28] Using the value $A = -21$ cm^{-1} indicated by the Zeeman-effect studies, we find λ'' to be 465 Mc/sec, leaving 58 920 Mc/sec of the experimental value to the first-order spin-spin mechanism. This establishes the previous statement that the spin-spin contribution dominates. In fact, the second-order contribution is so small that errors in its estimation will not introduce much

[25] M. H. Hebb, Phys. Rev. **49**, 610 (1936).

[26] It is interesting to note that the diagonal value of H_{el} itself is *raised* by precisely $B''\mathfrak{R}^2$ due to the increased momentum of the electrons with respect to the fixed frame. The nuclear energy is lowered by $2B''\mathfrak{R}^2$ because the added mass reduces its share of the quantized total angular momentum. The net effect is the lowering of energy quoted above.

[27] See reference 8, p. 488.

[28] See reference 8, p. 499.

uncertainty in the correct value for the spin-spin part. Therefore λ serves as a reliable check on the quanity of the wave function. The facts are that the calculated value was 40 percent low even after adjusting b to give a better approximation to the Hartree-Fock atomic orbital near the nucleus, and it was 80 percent low with Meckler's choice of b. We must conclude that wave functions chosen to minimize the electronic energy cannot be expected to give good results for a quantity which has a dependence on coordinates that differs from that of the electronic energy. On the other hand, if a wave function did give a good result for λ as well as for the electronic energy, there would be grounds for believing that it is a superior approximation to the true eigenfunction.

Using the same values for B and $L(L+1)/h\nu$, we compute $B''=17.3$ Mc/sec, which is a correction of 400 ppm (parts per million). The usual procedure of using atomic rather than nuclear masses reduces this correction by 270 ppm, leaving 130 ppm. Since the experimentally quoted values for B from infrared data are presumed to be accurate to 10 ppm (being quoted to 1 ppm[4]), it is clear that this rather sizable correction should be applied in inferring the internuclear distance from B_{eff} and the atomic masses. This correction decreases the computed R by 65 ppm. Recalculation,[29] using Herzberg's value for $(B_{\text{eff}})_e$ and the newly adjusted atomic constants, yields $R_e=1.20741_5$ A.

III. SOLUTION OF THE FINE-STRUCTURE PROBLEM

A. Energy Levels and Spectrum

As outlined in Sec. I, our problem is to find eigenvalues and eigenvectors for the Hamiltonian operator $\mathcal{H}=\mathcal{H}_{\text{vib}}+\mathcal{H}_{\text{rot}}+\mathcal{H}_{\text{spin}}$. Since we will solve this in a Hund case (a) representation with v, J, M, S, and Σ diagonal, we eliminate $\mathfrak{K}$ from (32) by noting that $\mathfrak{K}=\mathbf{J}-\mathbf{S}$. This leads to

$$\mathcal{H}=P_R^2/2M+\tfrac{1}{2}M\omega_e^2R_e^2\xi^2+b\xi^3+B\mathbf{J}^2+2\lambda S_z^2 \\ +(\mu-2B)\mathbf{J}\cdot\mathbf{S}+(B-\mu-\tfrac{2}{3}\lambda)\mathbf{S}^2, \quad (34)$$

where

$$B=B_e(1-2\xi+3\xi^2), \\ \lambda=\lambda_e+\lambda_1\xi+\lambda_2\xi^2. \quad (35)$$

The expansion of B to allow for the nonrigidity of the molecule is well known. The first two coefficients in the expansion of λ have been estimated theoretically in Sec. II but all three are treated as parameters to be evaluated by fitting the experimental data. No ξ dependence has been given μ because the same value sufficed for both $v=0$ and $v=1$ states as observed in the infrared spectra[30] whereas a change in λ was required.

The required matrix components are (suppressing quantum numbers in which the element is diagonal and which have no effect on its value, and suppressing $\hbar$):

$$\begin{aligned}
&(J|\mathbf{J}^2|J)=J(J+1),\\
&(S\Sigma|S_z|S\Sigma)=\Sigma,\\
&(JS\Sigma|\mathbf{J}\cdot\mathbf{S}|JS\Sigma')=\tfrac{1}{2}[J(J+1)-\Sigma(\Sigma\pm1)]^{\frac{1}{2}}\\
&\qquad\times[S(S+1)-\Sigma(\Sigma\pm1)]^{\frac{1}{2}}\delta_{\Sigma',\Sigma\pm1}+\Sigma^2\delta_{\Sigma',\Sigma},\\
&(v|\xi|v')=\epsilon^{\frac{1}{2}}[(v+1)^{\frac{1}{2}}\delta_{v',v+1}+v^{\frac{1}{2}}\delta_{v',v-1}],\\
&(v|\xi^2|v')=\epsilon[(v+1)^{\frac{1}{2}}(v+2)^{\frac{1}{2}}\delta_{v',v+2}+(2v+1)\delta_{v',v}\\
&\qquad+v^{\frac{1}{2}}(v-1)^{\frac{1}{2}}\delta_{v',v-2}],\\
&(v|\xi^3|v')=\epsilon^{\frac{3}{2}}[(v+1)^{\frac{1}{2}}(v+2)^{\frac{1}{2}}(v+3)^{\frac{1}{2}}\delta_{v',v+3}\\
&\qquad+3(v+1)^{\frac{3}{2}}\delta_{v',v+1}+3v^{\frac{3}{2}}\delta_{v',v-1}\\
&\qquad+v^{\frac{1}{2}}(v-1)^{\frac{1}{2}}(v-2)^{\frac{1}{2}}\delta_{v',v-3}],
\end{aligned} \quad (36)$$

where $\epsilon=B_e/\hbar\omega_e=\hbar/2MR_e^2\omega_e$ and $\delta_{v',v}$ is the Kronecker symbol. The elements of $\mathbf{J}\cdot\mathbf{S}$ are obtained by noting that J satisfies the "reversed" commutation relation[7] in the gyrating frame and that $J_z=\Sigma$ since $N_z=0$. Since $\mathbf{S}$ obeys ordinary commutation relations, we have the result given above. The elements of ξ^2 and ξ^3 are obtained by matrix multiplication of the familiar matrix elements of ξ for the harmonic oscillator.

Using these elements, the Hamiltonian matrix is readily written explicitly. Since all elements are diagonal in J, M, and S, we can write the elements simply as $(v\Sigma|\mathcal{H}|v'\Sigma')$. Since the vibrational level separation is so large, compared to rotational and spin energies, we can apply the Van Vleck transformation to reduce this matrix to an effective Hamiltonian matrix for the structure within each vibrational level.[31] Using

$$(v\Sigma|H_{\text{eff}}|v\Sigma')=-\sum_{\Sigma''v'}\frac{(v\Sigma|\mathcal{H}|v'\Sigma'')(v'\Sigma''|\mathcal{H}|v\Sigma')}{E_{v'}-E_v}, \quad (37)$$

we obtain a 3×3 matrix between the $\Sigma=\pm1,0$ states for a given vibrational (and total angular momentum) state. Including terms of order ϵ^2,[32] these reduced ele-

[29] It is significant to note that the recommended lease-squares fitted value of $(Nh/c)^{\frac{1}{2}}$, which enters in the conversion, has increased by 76 ppm between 1947 and 1952 [J. W. M. Dumond and E. R. Cohen, Revs. Modern Phys. **20**, 82 (1948) and **25**, 691 (1953)]. By chance, this almost exactly cancels this new theoretical correction for the electrons. Thus it is clear that the last decimal places of quoted values for R_e are significant only when a precise allowance can be made for the electronic contribution and even then only to the limit of our knowledge of the fundamental constants.

[30] In some excited states, such as the $^3\Sigma_u^-$ state, μ is an order of magnitude larger than it is in the ground state, and its ξ dependence can no longer be overlooked [P. Brix and G. Herzberg, Can. J. Phys. **32**, 110 (1954)]. Inclusion of this ξ dependence would involve no difficulty. However, for the high vibrational states observed in the $^3\Sigma_u^-$ state our simple approximation to the vibrational potential would have to be greatly extended. We avoid these accumulating complications by confining our treatment to the ground state.

[31] E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937).

[32] Detailed consideration shows that a somewhat more accurate treatment in this case of the anharmonic oscillator is obtained by replacing $\epsilon=B_e/\hbar\omega_e$ by $\epsilon'=B_{(0)}/\hbar\omega_{01}$, where $\hbar\omega_{01}=E_0(v=1)-E_0(v=0)$. This has been done in the numerical evaluations.

ments are

$$w=(vJ1|H_{\text{eff}}|vJ1)=B_vJ(J+1) -\epsilon^2[(8B-8\lambda_{\frac{1}{3}})J(J+1)+4BJ^2(J+1)]$$

$$x=(vJ0|H_{\text{eff}}|vJ0)=-(2\lambda_v+\mu)+B_v(J^2+J+2) -\epsilon^2[4B(J^2+J+2)^2+16BJ(J+1) +16\lambda_1(J^2+J+2)/3+4\lambda_1^2/3B], \tag{38}$$

$$y=(vJ0|H_{\text{eff}}|vJ1)=[J(J+1)/2]^{\frac{1}{2}} \times\{\mu-2B_v+\epsilon^2[16B(J^2+J+1)+8\lambda_1/3]\},$$

$$z=(vJ1|H_{\text{eff}}|vJ-1)=-\epsilon^2 8BJ(J+1),$$

where

$$B_v=B_e[1+(2v+1)(3\epsilon+12b\epsilon^3B^{-1})], \quad \lambda_v=\lambda_e+(2v+1)(\epsilon\lambda_2-6b\epsilon^3B^{-1}\lambda_1). \tag{39}$$

We note that large vibration-dependent terms can be taken out by defining v-dependent constants λ_v and B_v. This is the first-order Born-Oppenheimer approximation. However, there are higher-order centrifugal distortion terms that cannot be eliminated in this way. In these terms the distinction between B_e and B_v is unnecessary and the subscripts are dropped. (Numerical evaluation was actually made with the use of B_v.) The diagonal elements given here are such that the zero of energy is

$$E_0(v)=(v+\tfrac{1}{2})\hbar\omega_e -30b^2\epsilon^3(\hbar\omega_e)^{-1}(v^2+v+11/30)+\tfrac{2}{3}\lambda_v-\mu. \tag{40}$$

Application of the Wang[33] symmetrizing transformation to the Hamiltonian matrix with the elements (38) yields a factored secular equation by separating symmetric and antisymmetric states. This allows an exact solution, the eigenvalues being

$$E-E_v(v)=w-z, \quad \tfrac{1}{2}(w+x+z)\pm\{[(w-x+z)/2]^2+2y^2\}. \tag{41}$$

The results can be stated concisely as

$$E(J=K)-E_0(v)=w-z =(B_v+8\epsilon^2\lambda_1/3)K(K+1)-4B\epsilon^2K^2(K+1)^2, \tag{42}$$

$$\nu_-(K)=E(J=K)-E(J=K-1)=\lambda_v+\mu/2+B_v(2K-1) +4\epsilon^2[B(-4K^3+6K^2-6K+2) +(\lambda_1/3)(3K^2+K+4+\lambda_1/2B)] -[\sum_{n=0}^{3}A_nK^n(K-1)^n]^{\frac{1}{2}}, \tag{43}$$

$$\nu_+(K)=E(J=K)-E(J=K+1)=\lambda_v+\mu/2-B_v(2K+3) +4\epsilon^2[B(4K^3+18K^2+30K+18) +(\lambda_1/3)(3K^2+5K+6+\lambda_1/2B)] +[\sum_{n=0}^{3}A_n(K+1)^n(K+2)^n]^{\frac{1}{2}}, \tag{44}$$

[33] S. C. Wang, Phys. Rev. 34, 249 (1929); King, Hainer, and Cross, J. Chem. Phys. 11, 27 (1943).

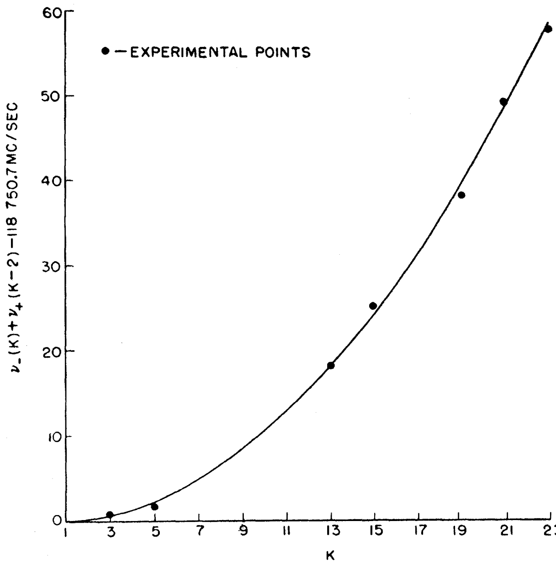

FIG. 1. Comparison of theoretical and experimental dependence of the sum $\nu_-(K)+\nu_+(K-2)$ on the rotational quantum number K.

where

$$A_0=[(\lambda_v+\mu/2-B_v)+\epsilon^2(8B+16\lambda_1/3+2\lambda_1^2/3B)]^2,$$

$$A_1=[\mu-2B_v+\epsilon^2(16B+8\lambda_1/3)]^2+\epsilon^2(16B+8\lambda_1) \times[\lambda+\mu/2-B+\epsilon^2(8B+16\lambda_1/3+2\lambda_1^2/3B],$$

$$A_2=\epsilon^2\{32B[(\mu-2B)+\epsilon^2(16B+2\lambda_1/3)] +\epsilon^2(8B+4\lambda_1)^2\},$$

$$A_3=\epsilon^4 256B^2. \tag{45}$$

$J=0$ is a special case in which the secular equation reduces to a linear one. The results are

$$E(J=0,K=1)-E_0(v)=-(2\lambda_v+\mu) +2B_v-4\epsilon^2(4B+8\lambda_1/3+\lambda_1^2/3B)$$

and

$$\nu_-(1)=2\lambda_v+\mu+16\epsilon^2[\lambda_1+\lambda_1^2/12B]. \tag{43'}$$

These results are labeled using K as the rotational quantum number to conform to the usual practice. Because of the spin coupling, $\mathfrak{K}^2$ is not a rigorous constant of the motion, but K describes the dominant value of $\mathfrak{K}$ when the eigenfunctions are expanded in a Hund case (b) representation. The fact that the state function of $(O^{16})_2$ must be totally symmetric on interchange of nuclei requires that only states with odd K exist. This restriction does not exist with $O^{16}O^{17}$ or $O^{16}O^{18}$.

In fitting the spectrum it is useful to note that

$$\nu_-(K)+\nu_+(K-2) =2\lambda_v+\mu+8\epsilon^2\lambda_1(K^2-K+2+\lambda_1/6B). \tag{46}$$

The precision with which this parabolic form fits the experimental data is shown in Fig. 1. By considering sums of this sort, one readily determines $(2\lambda_v+\mu)$ and

TABLE III. Experimental spin coupling constants (Mc/sec).

$\lambda_e = 59\,386 \pm 20$	$\lambda_{(0)} = 59\,501.57 \pm 0.15$
$\lambda_1 = 16\,896 \pm 150$	$\lambda_{(1)} = 59\,730.00 \pm 40$
$\lambda_2 = (5 \pm 2) \times 10^4$	$\mu = 252.67 \pm 0.05$

λ_1. With these constraints, μ and λ_v are separately fixed by considering individual frequencies, using (43) and (44). Because the results are so insensitive to B, b, and ω_e, the precise infrared values were used rather than attempting a fitting from the microwave data. In making the conversions, the velocity of light was taken to be 2.99790×10^{10} cm/sec. Some of the derived constants are $B_{(0)} = 43.1029$ kMc/sec, $b = -32.012$ kMc/sec, and $\epsilon = B_{(0)}/\hbar\omega_{01} = 0.92384 \times 10^{-3}$.

To determine λ_2 it is necessary to use data from an excited vibrational state. For this purpose, the infrared data of Babcock and Herzberg[4] for the $v=1$ state of $(O^{16})_2$ were fitted with (46) to determine $\lambda_{(v=1)}$. This fitting gave a result agreeing within its precision with the value obtained by Babcock and Herzberg by fitting the less accurate Schlapp[34] formula.

The results of all the fittings are tabulated in Table III. The indicated errors in λ are the statistically expected standard errors in the quoted mean values.

Table IV lists all of the microwave experimental data[3,35–37] and the theoretical frequencies computed by the use of these constants and formulas (43) and (44). The quoted fitting was made using the data of Burkhalter *et al.*[3] and of Gokhale and Strandberg,[35] neglecting the apparently erroneous $\nu_-(25)$ and the wave-meter measurements. Since then the data of Mizushima and Hill[36] has become available. It improves the previous values of $\nu_-(1)$ and $\nu_-(25)$ and fills in some gaps in the spectrum previously known only to wave-meter accuracy. If $\lambda_{(0)}$ and λ_1 are determined by fitting this new data with (46), the means agree with the above results well within the standard error, but the standard errors in the new data are twice as large as the old (which are quoted above).

At this point, let us relate this solution with previous ones. In the works of Kramers,[10] of Hebb,[25] and of Schlapp[34] the nonrigidity of the nuclear framework is neglected. Thus $\epsilon = B/\hbar\omega = 0$. Further, all their results are in error in that B must be replaced by $(B - \frac{1}{2}\mu)$. Kramers and Hebb both quote their results only to first order in λ/B, but Hebb indicates the manner in which the more exact solution using the radical is obtained from the work of Hill and Van Vleck.[38] Schlapp gives the form with the radical. His solution gave satisfactory agreement with the infrared data, provided that different values of B and λ were chosen for excited vibrational states.

[34] R. Schlapp, Phys. Rev. **51**, 342 (1937).
[35] B. V. Gokhale and M. W. P. Strandberg, Phys. Rev. **84**, 844 (1951).
[36] M. Mizushima and R. M. Hill, Phys. Rev. **93**, 745 (1954).
[37] Anderson, Johnson, and Gordy, Phys. Rev. **83**, 1061 (1951).
[38] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

The precise microwave measurements of Burkhalter *et al.*[3] revealed substantial deviations from the Schlapp formulas. In particular, the sum $\nu_-(K) + \nu_+(K-2)$ was not constant as predicted by the Schlapp formula (our (46) with $\epsilon = 0$), but increased with K. Burkhalter obtained a reasonable fit by empirically adding $\delta K + \alpha K(K+1)^{-\frac{1}{2}}$ to Schlapp's $\nu_-(K)$, leaving $\nu_+(K)$ unchanged. Gokhale[39] considered the effect of centrifugal distortion on B, but assumed λ and μ independent of R. Thus he failed to obtain a theoretical explanation for the deviations. He did, however, correct the confusion between B and $B - \frac{1}{2}\mu$, as did all succeeding workers.

Miller and Townes[40] reviewed the problem, and fitted the spectrum satisfactorily by making both B and λ in their formulas depend on K through centrifugal distortion correction terms proportional to $K(K+1)$. Their formulas are

$$\begin{aligned} \nu_-(K) &= \lambda + \mu K + (2K-1)(B - \tfrac{1}{2}\mu) \\ &\quad - [\lambda^2 - 2\lambda(B - \tfrac{1}{2}\mu) + (2K-1)^2(B - \tfrac{1}{2}\mu)^2]^{\frac{1}{2}}, \\ \nu_+(K) &= \lambda - \mu(K+1) - (2K+3)(B - \tfrac{1}{2}\mu) \\ &\quad + [\lambda^2 - 2\lambda(B - \tfrac{1}{2}\mu) + (2K+3)^2(B - \tfrac{1}{2}\mu)^2]^{\frac{1}{2}}. \end{aligned} \tag{47}$$

TABLE IV. Comparison of experimental and calculated frequencies in Mc/sec for $(O^{16})_2$ fine-structure transitions.

K	Experimental: Burkhalter *et al.*[a]	Experimental: Gokhale and Strandberg[b]	Experimental: Mizushima and Hill[c]	Calculated
		$\nu_+(K)$		
1	56 265.1	56 265.2±0.5	56 265.6±0.6	56 264.7
3	58 446.2	58 446.3±0.4	58 446.2±0.2	56 446.9
5	59 610[d]		59 591.4±0.2	59 591.5
7	60 436[d]		60 433.4±0.2	60 435.5
9	61 120[d]		61 149.6±0.2	61 151.3
11	61 800.2		61 799.8±0.4	61 800.9
13	62 411.7	62 412.9±0.8	62 413.8±0.4	62 411.9
15	62 970[d]		62 996.6±0.2	62 998.5
17	63 568.3		63 567.2±0.2	63 568.7
19	64 127.6		64 128.0±0.8	64 127.6
21	64 678.9		64 678.2±0.2	64 678.2
23	65 220[d]		65 224.2±0.8	65 222.7
25	65 770[d]			65 762.6
		$\nu_-(K)$		
1	118 745.5[e]		118 750.5±0.5	118 750.7
3	62 486.1	62 486.2±0.4	62 487.2±0.4	62 486.7
5	60 306.4		60 308.0±0.2	60 306.1
7	59 163.4	59 164.2±0.2	59 163.4±0.2	59 164.0
9	58 324.0	58 324.9±0.3	58 323.2±0.1	58 323.6
11	57 612.0	57 612.3±0.4	57 611.4±0.2	57 612.1
13	56 968.7		56 970.8±0.4	56 967.8
15	56 362.8	56 364.2±0.5	56 364.0±0.4	56 363.1
17	55 784.1		55 784.6±0.4	55 783.6
19	55 220.8		55 221.6±0.4	55 221.5
21	54 672.5			54 671.6
23	54 130.0		54 129.4±0.4	54 130.9
25	53 592.2		53 599.4±0.8	53 597.3

[a] See reference 3.
[b] See reference 35.
[c] See reference 36.
[d] Wave-meter reading.
[e] See reference 37.

[39] B. V. Gokhale, Ph.D. thesis, Massachusetts Institute of Technology, 1951 (unpublished).
[40] S. L. Miller and C. H. Townes, Phys. Rev. **90**, 537 (1953).

Since these formulas are derived from a secular equation connecting several K states, the values of B and λ are not well defined and this procedure is not rigorous. Further, it fails to give a value for $d\lambda/dR$, and it fails to provide the single Hamiltonian (for all K) needed in deriving diagonalizing transformations preparatory to introducing other perturbations. Finally, while this work was being completed, Mizushima and Hill[36] have published a treatment that takes account of centrifugal distortion under the adiabatic approximation but assumes a harmonic vibrational potential. This treatment fails to provide a value for λ_e or λ_2,[41] and does not give the diagonalizing transformation. Thus the present treatment verifies Mizushima and Hill's general results and gives somewhat more information about the molecule. The closeness of fit to the experimental data is about equal to that of the methods of Miller and Townes and of Mizushima and Hill.

B. State Functions

We now obtain the 3×3 diagonalizing matrix which expresses the eigenvectors of the matrix (38) in the Hund case (a) representation. Our eigenvalues as given by (41) are inserted into the matrix equation

$$\{H_{\text{eff}}-[E+E_0(v)]\}\psi=0,$$

where

$$H_{\text{eff}}=\begin{bmatrix} w & y & z \\ y & x & y \\ z & y & w \end{bmatrix}. \tag{48}$$

The quantities w, x, y, and z are matrix elements defined in (38). The result of solving this equation is the transformation matrix:

$$T_J=(\psi_{K=J-1},\psi_{K=J},\psi_{K=J+1})$$

$$=\begin{array}{r} \Sigma=-1 \\ 0 \\ 1 \end{array}\begin{bmatrix} a_J & -1/\sqrt{2} & c_J \\ \sqrt{2}c_J & 0 & -\sqrt{2}a_J \\ a_J & 1/\sqrt{2} & c_J \end{bmatrix}, \tag{49}$$

where

$$c_J=2^{-\frac{1}{2}}ra_J=2^{-\frac{1}{2}}r(2+r^2)^{-\frac{1}{2}},$$
$$r=[E-E_v(v)-w-z]x^{-1}|_{J=K+1}. \tag{50}$$

These coefficients are listed in Table V for the states occurring in $(O^{16})_2$.

For comparison, we note that if oxygen were a rigorous example of Hund's case (b), in which $K=\mathfrak{K}$ is a good quantum number, the transformation could be obtained by simply diagonalizing the operator $\mathfrak{K}^2=\mathbf{J}^2+\mathbf{S}^2-2\mathbf{J}\cdot\mathbf{S}$. If this is done, the result is of the same form but with

$$a_{J'}=\frac{1}{2}\left(\frac{J+1}{J+\frac{1}{2}}\right)^{\frac{1}{2}},\quad c_J{}'=\frac{1}{2}\left(\frac{J}{J+\frac{1}{2}}\right)^{\frac{1}{2}}. \tag{51}$$

[41] Note that his λ_1 is related to ours by $(\lambda_1)_M=4\epsilon^2(\lambda_1)_T$. Also note that he has apparently omitted a numerical factor of 2π in going from his Eq. (17b) to (18). As a result, his value for $(d\lambda/dR)_e$ is inconsistent with ours.

TABLE V. Transformation coefficients of eigenvectors. a_J and c_J give O_2 eigenvectors with respect to Hund (a) basis, and $a_J{}'$ and $c_J{}'$ give Hund (b) eigenvectors with respect to Hund (a) basis, by use of Eq. (49). b_J and d_J express O_2 eigenfunctions with respect to Hund (b) basis by Eq. (54).

J	a_J	c_J	$a_J{}'$	$c_J{}'$	b_J	d_J
2	0.480462	0.518803	0.547723	0.447214	0.990351	0.138582
4	0.489369	0.510410	0.527046	0.471404	0.997059	0.076638
6	0.492680	0.507214	0.518874	0.480384	0.998594	0.053009
8	0.494413	0.505525	0.514496	0.485071	0.999178	0.040530
10	0.495480	0.504480	0.511766	0.487950	0.999462	0.032813
12	0.496202	0.503769	0.509902	0.489898	0.999620	0.027569
14	0.496723	0.503256	0.508548	0.491304	0.999717	0.023776
16	0.497117	0.502867	0.507519	0.492366	0.999782	0.020902
18	0.497424	0.502562	0.506712	0.493197	0.999825	0.018652
20	0.497671	0.502318	0.506061	0.493865	0.999858	0.016842
22	0.497873	0.502117	0.505525	0.494413	0.999881	0.015355
24	0.498042	0.501950	0.505076	0.494872	0.999900	0.014112
26	0.498185	0.501808	0.504695	0.495261	0.999914	0.013057

Using this latter transformation, we may transform (48) to a Hund case (b) basis. The result is

$$H_{\text{eff}}=\begin{array}{r} \mathfrak{K}=J-1 \\ J \\ J+1 \end{array}\begin{bmatrix} \alpha & 0 & \delta \\ 0 & \beta & 0 \\ \delta & 0 & \gamma \end{bmatrix}, \tag{52}$$

where

$$\alpha=B_vJ(J-1)-2\lambda_v\frac{J}{2J+1}+\mu J-\epsilon^2\left[4BJ^2(J-1)^2+\frac{8}{3}\lambda_1\frac{J(J-1)^2}{2J+1}+\frac{4}{3}\frac{\lambda_1{}^2}{B}\frac{J}{2J+1}\right],$$

$$\beta=B_vJ(J+1)-\epsilon^2J(J+1)[4BJ(J+1)-(8/3)\lambda_1],$$

$$\gamma=B_v(J+1)(J+2)-2\lambda_v\frac{J+1}{2J+1}-\mu(J+1)-\epsilon^2\left[4B(J+1)^2(J+2)^2+\frac{8}{3}\lambda_1\frac{(J+1)(J+2)^2}{2J+1}+\frac{4}{3}\frac{\lambda_1{}^2}{B}\frac{(J+1)}{(2J+1)}\right],$$

$$\delta=\frac{[J(J+1)]^{\frac{1}{2}}}{2J+1}\{2\lambda_v+\epsilon^2 8\lambda_1[(J^2+J+1)+\lambda_1/6B]\}. \tag{53}$$

This matrix is of course identical to that which would have been obtained if the entire problem had been set up in terms of Hund's case (b) instead of (a).[42]

The transformation which gives the oxygen eigenvector, characterized by K, with respect to the Hund (b) basis, characterized by $\mathfrak{K}$, is found to be

$$T_J{}^{(b)}=(T_J{}')^{-1}T_J=\begin{array}{r} \\ \mathfrak{K}=J-1 \\ J \\ J+1 \end{array}\begin{array}{c} \begin{array}{ccc} K=J-1 & J & J+1 \end{array} \\ \begin{bmatrix} b_J & 0 & d_J \\ 0 & 1 & 0 \\ -d_J & 0 & b_J \end{bmatrix} \end{array}, \tag{54}$$

[42] This has been verified with the use of the case (b) matrix elements given by J. H. Van Vleck [Revs. Modern Phys. **23**, 213 (1951), p. 222]. The effective Hamiltonian matrix in Mizushima and Hill's manuscript (reference 36) gives somewhat different coefficients for λ_1. His error seems to have arisen in subtracting a $\frac{2}{3}\lambda$, treated as independent of $\mathfrak{K}$, from the diagonal elements.

TABLE VI. Matrix elements of the direction cosines.[a]

$J'=$	$J-1$	J	$J+1$
$(J\|\Phi\|J')$	$[J(4J^2-1)^{\frac{1}{2}}]^{-1}$	$[J(J+1)]^{-1}$	$\{(J+1)[(2J+1)(2J+3)]^{\frac{1}{2}}\}^{-1}$
$(J\Omega\|\Phi_{Fz}\|J'\Omega)$	$[J^2-\Omega^2]^{\frac{1}{2}}$	Ω	$[(J+1)^2-\Omega^2]^{\frac{1}{2}}$
$(J\Omega\|\Phi_{Fx}\|J'\Omega\pm 1)=\pm i(J\Omega\|\Phi_{Fy}\|J'\Omega\pm 1)$	$\pm\frac{1}{2}[(J\mp\Omega)(J\mp\Omega-1)]^{\frac{1}{2}}$	$\frac{1}{2}[J(J+1)-\Omega(\Omega\pm 1)]^{\frac{1}{2}}$	$\mp\frac{1}{2}[(J\pm\Omega+1)(J\pm\Omega+2)]^{\frac{1}{2}}$
$(JM\|\Phi_{Zg}\|J'M)$	$[J^2-M^2]^{\frac{1}{2}}$	M	$[(J+1)^2-M^2]^{\frac{1}{2}}$
$(JM\|\Phi_{Xg}\|J'M\pm 1)=\mp i(JM\|\Phi_{Yg}\|J'M\pm 1)$	$\pm\frac{1}{2}[(J\mp M)(J\mp M-1)]^{\frac{1}{2}}$	$\frac{1}{2}[J(J+1)-M(M\pm 1)]^{\frac{1}{2}}$	$\mp\frac{1}{2}[(J\pm M+1)(J\pm M+2)]^{\frac{1}{2}}$

[a] In wave mechanical language, these elements are simply integrals of the cosine of the angle between the space-fixed F axis and the gyrating g axis, over the symmetric top eigenfunctions specified by $(J\Omega M|J'\Omega'M')$. Since these angular eigenfunctions are completely determined by the angular momenta, these rather obscure integrals can be replaced by a matrix algebraic deduction from the commutation relations. In this deduction one finds that the elements of Φ_{Fg} may be factored in the form

$$(J\Omega M|\Phi_{F'g'}|J'\Omega'M')=(J|\Phi|J')(J\Omega|\phi_{Fg'}|J'\Omega')(JM|\phi_{F'g}|J'M'),$$

where Ω is J_z and M is J_Z. With our phase choice [which follows that of Condon and Shortley rather than that of Cross, Hainer, and King, J. Chem. Phys. **12**, 210 (1944), for example], the factors are as tabulated.

where

$$b_J=2(a_Ja_J'+c_Jc_J')\approx 1,$$
$$d_J=2(c_Ja_J'-a_Jc_J')\approx[3(J+\tfrac{1}{2})]^{-1}. \qquad (55)$$

These coefficients are also given in Table V. From these, it is clear that oxygen eigenvectors approach Hund case (b) eigenvectors as J becomes very large. This was to be expected since the rotational splittings increase as J, whereas the spin-spin energy which breaks down the case (b) coupling is constant.

IV. LINE INTENSITIES

Because of its homonuclear symmetry, no electric dipole transitions are possible in oxygen. The existence of a magnetic dipole moment of two Bohr magnetons makes magnetic dipole transitions allowed, and in fact quite intense. The perturbative Hamiltonian inducing transitions in an absorption experiment is

$$H'=-g_s{}^e\beta\mathbf{S}\cdot\mathbf{H}_{\mathrm{rf}}=-\boldsymbol{\mu}\cdot\mathbf{H}_{\mathrm{rf}}.$$

A well-known analysis[43] shows that for well-separated lines the absorption coefficient α is given by

$$\alpha_{ij}=\frac{4\pi\omega^2N}{ckT}\sum_M|(\mu_{ij})_M|^2\frac{\tau^{-1}}{(\omega-\omega_{ij})^2+\tau^{-2}}\frac{e^{-E_i/kT}}{\sum_n e^{-E_n/kT}}, \qquad (56)$$

where N is the number of molecules per unit volume, μ_{ij} is the matrix element of the magnetic dipole moment, $\tau^{-1}=2\pi\Delta\nu$, E_j is the energy of the jth state, and the sum over n is the usual partition sum. Since α is proportional to $|\mu_{ij}|^2$, it is proportional to $|(S_Z)_{ij}|^2$ if the magnetic vector of the incident rf radiation is polarized along Z. By the isotropy of field-free space we know that when summed over the orientational degeneracy quantum number M,

$$\textstyle\sum_M|(S_X)_{ij}|^2=\sum_M|(S_Y)_{ij}|^2=\sum_M|(S_Z)_{ij}|^2.$$

Thus all of the necessary information for the general case is obtained by evaluating the simplest of these, namely,

$$\textstyle\sum_M|(S_Z)_{ij}|^2.$$

In this, of course, i, j indicate the final and initial states, each characterized by quantum numbers J, K.

To compute the matrix elements of S_Z (where Z is a space-fixed coordinate) from the known elements of S in the gyrating (g) axes we use the known direction cosine matrix elements in the equation

$$S_Z=\textstyle\sum_g\Phi_{Zg}S_g. \qquad (57)$$

These direction cosine matrix elements are given in Table VI with the phase conventions we have used. Noting that $\Omega=\Sigma$ for our $\Lambda=0$ state, we find the following elements for S_Z in a Hund case (a) representation.

$$\begin{aligned}
(JMS\Sigma|S_Z|JMS\Sigma)&=\frac{\Sigma^2M}{J(J+1)},\\
(JMS\Sigma|S_Z|JMS\Sigma\pm 1)&=\frac{M[J(J+1)-\Sigma(\Sigma\pm 1)]^{\frac{1}{2}}[S(S+1)-\Sigma(\Sigma\pm 1)]^{\frac{1}{2}}}{2J(J+1)},\\
(JMS\Sigma|S_Z|J-1,MS\Sigma)&=\frac{\Sigma(J^2-\Sigma^2)^{\frac{1}{2}}(J^2-M^2)^{\frac{1}{2}}}{J(4J^2-1)^{\frac{1}{2}}},\\
(JMS\Sigma|S_Z|J-1,MS\Sigma\pm 1)&=\frac{\pm[(J^2-M^2)(J\mp\Sigma)(J\mp\Sigma-1)]^{\frac{1}{2}}[S(S+1)-\Sigma(\Sigma\pm 1)]^{\frac{1}{2}}}{2J(4J^2-1)^{\frac{1}{2}}}.
\end{aligned} \qquad (58)$$

[43] J. H. Van Vleck and V. F. Weisskopf, Revs. Modern Phys. **17**, 227 (1945).

The $(J|J+1)$ elements of S_Z are found by using the Hermiticity of the matrix. These elements must now be transformed to the basis which diagonalizes the unperturbed (field-free) Hamiltonian. Then the off-diagonal elements will give the transition probabilities between the actual eigenfunctions. Since these matrix elements are not diagonal in J, our transformation T_J must be extended as follows:

$$T^{-1}S_ZT=\begin{pmatrix} T_0^{-1} & & & 0 \\ & T_1^{-1} & & \\ & & T_2^{-1} & \\ 0 & & & \ddots \end{pmatrix}\begin{pmatrix} S_{00} & S_{01} & 0 & 0 & \cdot \\ S_{10} & S_{11} & S_{12} & 0 & \cdot \\ 0 & S_{21} & S_{22} & S_{23} & \cdot \\ 0 & 0 & S_{32} & S_{33} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}\begin{pmatrix} T_0 & & & 0 \\ & T_1 & & \\ & & T_2 & \\ 0 & & & T_3 \\ & & & & \ddots \end{pmatrix}$$

$$=\begin{pmatrix} T_0^{-1}S_{00}T_0 & T_0^{-1}S_{01}T_1 & 0 & 0 & \cdot \\ T_1^{-1}S_{10}T_0 & T_1^{-1}S_{11}T_1 & T_1^{-1}S_{12}T_2 & 0 & \cdot \\ 0 & T_2^{-1}S_{21}T_1 & T_2^{-1}S_{22}T_2 & \cdot & \cdot \\ 0 & 0 & T_3^{-1}S_{32}T_2 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}. \quad (59)$$

In these expressions, T_J and $S_{JJ'}$ are 3×3 matrices.

Carrying out the indicated matrix multiplication, we find the following matrix elements of the form $(K,J,M|S_Z|K',J',M)$:

$$(K,K,M|S_Z|K,K,M)=\frac{M}{J(J+1)}=\frac{g(K,\,J=K)}{g_s^e}M,$$

$$(K,\,K+1,\,M|S_Z|K,\,K+1,\,M)=\frac{2a_JM}{[J(J+1)]^{\frac{1}{2}}}\times\left[2c_J+\frac{a_J}{[J(J+1)]^{\frac{1}{2}}}\right]=\frac{g(K,\,J=K+1)}{g_s^e}M,$$

$$(K,\,K-1,\,M|S_Z|K,\,K-1,\,M)=\frac{-2c_JM}{[J(J+1)]^{\frac{1}{2}}}\times\left[2a_J-\frac{c_J}{[J(J+1)]^{\frac{1}{2}}}\right]=\frac{g(K,\,J=K-1)}{g_s^e}M,$$

$$(J-1,\,J,\,M|S_Z|J+1,\,J,\,M)=2M\left[\frac{a_Jc_J}{J(J+1)}+\frac{c_J^2-a_J^2}{[J(J+1)]^{\frac{1}{2}}}\right]=h_JM, \quad (60)$$

$$(J-2,\,J-1,\,M|S_Z|J,\,J,\,M)=f(J,M)\left[\frac{a_{J-1}}{(J)^{\frac{1}{2}}}-\frac{c_{J-1}}{(J-1)^{\frac{1}{2}}}\right]=A_{J-1}(J^2-M^2)^{\frac{1}{2}},$$

$$(J-1,\,J-1,\,M|S_Z|J-1,\,J,\,M)=f(J,M)\left[\frac{a_J}{(J)^{\frac{1}{2}}}+\frac{c_J}{(J+1)^{\frac{1}{2}}}\right]=B_J(J^2-M^2)^{\frac{1}{2}},$$

$$(J,\,J-1,\,M|S_Z|J,\,J,\,M)=f(J,M)\left[\frac{c_{J-1}}{(J)^{\frac{1}{2}}}+\frac{a_{J-1}}{(J-1)^{\frac{1}{2}}}\right]=C_{J-1}(J^2-M^2)^{\frac{1}{2}},$$

$$(J-1,\,J-1,\,M|S_Z|J+1,\,J,\,M)=f(J,M)\left[\frac{c_J}{(J)^{\frac{1}{2}}}-\frac{a_J}{(J+1)^{\frac{1}{2}}}\right]=D_J(J^2-M^2)^{\frac{1}{2}},$$

where

$$f(J,M)=\left[\frac{2(J^2-1)(J^2-M^2)}{J(4J^2-1)}\right]^{\frac{1}{2}},$$

with the special case

$$(1,0,0|S_Z|1,1,0)=-[\tfrac{2}{3}(1-M^2)]^{\frac{1}{2}}=C_0(1-M^2)^{\frac{1}{2}}. \quad (60')$$

If we insert the tabulated values of a_J and c_J, we obtain the proper transformed matrix elements, whereas if we insert a_J' and c_J' we get the matrix elements for S_Z in a pure Hund case (b) system. In the latter case, inspection of a' and c' shows that all $(K|K')$ elements of S_Z vanish if $K'\neq K$. This is not true using a and c. Thus our precise calculation has revealed the possibility of $\Delta K=2$ transitions. Also, the formulas for $\Delta K=0$ transitions differ from Hund (b), especially for

TABLE VII. Line intensities: $I(K',J'|K'',J'')=3\sum_M|(K'J'M|S_Z|K''J''M)|^2$.

K	$I(K, K+1\|K, K)$ Exact	$I(K, K+1\|K, K)$ Case (b)	$I(K, K-1\|K, K)$ Exact	$I(K, K-1\|K, K)$ Case (b)	$I(K, K\|K+2, K+1)$ Exact	$I(K, K+1\|K+2, K+1)$ Exact	$I(K, K+1\|K+2, K+2)$ Exact
1	2.452	2.500	2.000	2.000	0.006110	0.3924	0.1280
3	6.710	6.750	6.539	6.667	0.005045	0.2128	0.06343
5	10.80	10.833	10.736	10.800	0.003874	0.1466	0.04175
7	14.85	14.875	14.82	14.86	0.003109	0.1119	0.03103
9	18.88	18.90	18.86	18.89	0.002589	0.09043	0.02466
11	22.90	22.92	22.88	22.91	0.002216	0.07607	0.02046
13	26.91	26.93	26.90	26.92	0.001937	0.06561	0.01749
15	30.92	30.94	30.92	30.93	0.001720	0.05770	0.01527

low J. For precise work, as in inferring line breadths from calculated intensity and observed signal strength. these corrections should be made.

The diagonal elements give the weak field g factors for the Zeeman effect. These also differ appreciably from the vector model results calculated with the assumption of pure case (b) coupling.[44] The numerical values are given in Table VII, but further discussion will be deferred to a subsequent paper giving a complete treatment of the interaction with a magnetic field.

To calculate the total intensity, we sum the squared matrix elements over the degenerate M states and multiply by 3 to include the 3 equivalent spacial directions. This results in an intensity factor I defined by

$$I(K''J''|K'J')=3\sum_M|(K''J''M|S_Z|K'J'M)|^2. \quad (61)$$

The sum is readily evaluated explicitly using the fact that

$$\sum_{M=-J}^{J} M^2=\frac{J(J+1)(2J+1)}{3}.$$

The results have been tabulated in Table VIII for $J\leq 16$, and the Hund (b) result[45] has been given for comparison when it is not zero. Evidently the differences are at most a few percent for the transitions allowed in Hund case (b). However, the predicted intensities for the "forbidden" $\Delta K=2$ lines is a completely new result, which can be checked when radiation of sufficiently high frequency is available. The skirts of these lines will give some effects at lower frequencies if the transmission is through oxygen (or air) at atmosphere pressure.

TABLE VIII. Matrix elements of S_Z with respect to the basis in which the field-free problem is diagonal.[a]

K	$g(K, K-1)/g_s^e$	$g(K,K)/g_s^e$	$g(K, K+1)/g_s^e$
1		0.5000000	0.483997
3	−0.317330	0.0833333	0.247357
5	−0.197357	0.0333333	0.165797
7	−0.141987	0.0178571	0.124612
9	−0.110723	0.0111111	0.0997945
11	−0.0907038	0.00757576	0.0832115
13	−0.0768013	0.00549451	0.0713505
15	−0.0665888	0.00416666	0.0624471
17	−0.0587707		

J	h_J	A_J	B_J	C_J	D_J
2	0.114371	−0.0349195	0.285889	0.249546	0.04000515
4	0.0343857	−0.0113202	0.163182	0.147276	0.01254283
6	0.0163845	−0.00553032	0.112209	0.1041814	0.00595644
8	0.0095616	−0.00326702	0.0853207	0.0805423	0.00346085
10	0.0062568	−0.00215461	0.0687875	0.0656293	0.00225829
12	0.0044164	−0.00152705	0.0576082	0.0553697	0.00158879
14	0.0032823	−0.00113872	0.0495493	0.0478813	0.00117839
16	0.0025354	−0.00088177	0.0434660	0.0421754	0.00090875

[a] These elements are given in Eq. (60) as the product of a J-dependent factor and a simple factor depending on both J and M. The J-dependent factors are tabulated here. In these, g_s^e is the algebraic electronic spin g factor, −2.00229, and $g(K,J)$ is the algebraic g factor of the K,J energy level.

We can write the frequency of a $K_1\rightarrow K_1+2$ transition in terms of the frequency difference

$$\nu(K_1, K_1+2)=E(J=K=K_1+2)-E(J=K=K_1)$$

and the frequencies of the 5-mm lines as follows:

$$\begin{aligned}\nu_{J,\,J+1;\,J=K}&=\nu_{K,\,K+2}-\nu_-(K+2).\\ \nu_{J,\,J;\,J=K+1}&=\nu_{K,\,K+2}-\nu_-(K+2)+\nu_+(K). \quad (62)\\ \nu_{J,\,J+1;\,J=K+1}&=\nu_{K,\,K+2}+\nu_+(K).\end{aligned}$$

Making an analytic approximation to the $I(K''J''|K'J')$ and using Eq. (56), one finds the following approximate results at 300°K, assuming the same line breadth parameter as in the millimeter spectrum:

$$\begin{aligned}\alpha_{J,\,J+1;\,J=K}&=0.046(J+1)^{-\frac{1}{2}}\nu^2 10^{-10}e^{-0.0069K(K+1)},\\ \alpha_{J,\,J;\,J=K+1}&=4.2J^{-1}\nu^2 10^{-10}e^{-0.0069K(K+1)}, \quad (63)\\ \alpha_{J,\,J+1;\,J=K+1}&=1.4J^{-1}\nu^2 10^{-10}e^{-0.0069K(K+1)}.\end{aligned}$$

In these, α is the value when $\nu=\nu_{ij}$ and ν is expressed in kMc/sec. As particular examples, the three lowest frequency lines are $K=1\rightarrow 3$ lines predicted to lie at 368 522 Mc/sec, 424 787 Mc/sec, and 487 274 Mc/sec. The absorption coefficients are calculated to be 0.44×10^{-6}, 38×10^{-6}, and 17×10^{-6} cm^{-1}, respectively.

APPENDIX A. MATRIX ELEMENTS OF SPIN-SPIN HAMILTONIAN

By the same methods used in Sec. II, the following matrix elements between configurations may be computed. We let $bR^2=\Delta$, for simplicity.

$$H_{ee}=H_{cc}=g^2\beta^2 b^{\frac{3}{2}}2K^4\pi^{-\frac{1}{2}} \times\{1/30+e^{-\Delta}/15+2e^{-3\Delta/4}S_1(\Delta)-\tfrac{1}{2}e^{-\Delta}S_1(4\Delta)\},$$

$$H_{dd}=H_{ff}=g^2\beta^2 b^{\frac{3}{2}}2L^4\pi^{-\frac{1}{2}} \times\{1/30+e^{-\Delta}/15-2e^{-3\Delta/4}S_1(\Delta)-\tfrac{1}{2}e^{-\Delta}S_1(4\Delta)\},$$

[44] R. M. Hill and W. Gordy, Phys. Rev. **93**, 1019 (1954).
[45] J. H. Van Vleck, Phys. Rev. **71**, 413 (1947).

$$H_{cd}=H_{ef}=g^2\beta^2b^{\frac{3}{2}}L^2K^2\pi^{-\frac{1}{2}}\{1/15+e^{-\Delta}S_1(4\Delta)\},$$

$$H_{ca}=H_{cb}=H_{ce}=H_{cf}=0,$$

$$H_{ad}=H_{bd}=H_{ae}=H_{be}=H_{af}=H_{bf}=H_{de}=H_{df}=0,$$

$$\begin{aligned}H_{cg}=-H_{ch}=-H_{ci}=2^{-\frac{1}{2}}ReH_{cE}=g^2\beta^2b^{\frac{3}{2}}JKLM(2\pi)^{-\frac{1}{2}}e^{-\Delta}\\ \times\{(e^{\Delta}/15)[\Delta+B\Delta^{\frac{1}{2}}-BE+\tfrac{1}{2}-5e^{-\Delta}/14]\\ -(B+\Delta^{\frac{1}{2}})(E+\Delta^{\frac{1}{2}})S_1(4\Delta)\\ -4[\Delta+\Delta^{\frac{1}{2}}(2B-E)]e^{\Delta/4}S_1(\Delta)-\tfrac{1}{2}S_2(4\Delta)\\ +\tfrac{1}{4}\Delta^{-\frac{3}{2}}(3\Delta^{\frac{1}{2}}+2B+E)S_3(4\Delta)\\ +4\Delta^{-\frac{3}{2}}(\Delta^{\frac{1}{2}}+2B-E)e^{\Delta/4}S_3(\Delta)+\tfrac{1}{8}\Delta^{-2}S_4(4\Delta)\}.\end{aligned}$$

In these,

$$S_2(x)=\sum_{n=1}^{\infty}\frac{1}{1\cdot3\cdot5\cdots(2n+3)}\left(\frac{x}{2}\right)^n,$$

$$S_3(x)=\left(\frac{x}{2}\right)\sum_{n=1}^{\infty}\frac{(2n)(2n-1)}{1\cdot3\cdot5\cdots(2n+5)}\left(\frac{x}{2}\right)^n,$$

$$S_4(x)=\left(\frac{x}{2}\right)\sum_{n=1}^{\infty}\frac{2n(2n-1)^2}{1\cdot3\cdot5\cdots(2n+5)}\left(\frac{x}{2}\right)^n,$$

and the constants B, E, J, L, and M are as defined by Meckler.[2] In evaluating H_{cg}, the terms in ϕ_0 and χ_0 giving orthogonality to the $1s$ orbitals have been dropped as negligible to allow integration by our artifice (which requires a common Gaussian factor for all orbitals). We note that all of the elements have the same sort of dependence on $b^{\frac{3}{2}}$ and $bR^2=\Delta$, the Δ dependence turning out to be rather slight.

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Interaction of Molecular Oxygen with a Magnetic Field*

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The dominant interaction of O_2 with a magnetic field is through the electronic spin magnetic moment. However, a precise comparison with experiment of the results of calculating the microwave paramagnetic spectrum, assuming only this interaction, shows a systematic discrepancy. This discrepancy is removed by introducing two corrections. The larger (approximately 0.1 percent, or 7 gauss) is a correction for the second-order electronic orbital moment coupled in by the spin-orbit energy. Its magnitude is proportional to the second-order term μ'' in the spin-rotation coupling constant. The smaller (approximately 1 gauss) is a correction for the rotation-induced magnetic moment of the molecule. Since the dependence of this contribution on quantum numbers is quite unique, this coefficient can also be determined by fitting the magnetic spectrum. A total of 120 X-band and 78 S-band lines were observed. The complete corrections have been made on 26 lines with a mean residual error of roughly 0.5 Mc/sec. This excellent agreement confirms the anomalous electronic moment to 60 parts per million (ppm) and also confirms the validity of the Zeeman-effect theory.

A new result is the rotational magnetic moment of -0.25 ± 0.05 nuclear magnetons per quantum of rotation. Knowledge of this moment allows the electronic contribution to the effective moment of inertia to be determined. Making this correction of 65 ppm, and using the latest fitting of the universal atomic constants, the equilibrium internuclear distance is recomputed to be $R_e=1.20741\pm0.00002$ A. We can also deduce that the magnitude of λ'', the second-order spin-orbit contribution to the coupling of the spin to the figure axis, is 465 ± 50 Mc/sec, or less than one percent of the total coupling constant λ.

Theoretical intensities of a number of the microwave transitions are calculated and successfully compared with experiment over a range of 100 to 1 in magnitude. It turns out that $\Delta M=0$ transitions are over a hundred times weaker than the $\Delta M=\pm1$ transitions and thus are too weak to observe. Also, J breaks down as a quantum number in the presence of a magnetic field. This allows $\Delta J=\pm2$ transitions to comprise roughly half of all lines observed.

IN a previous paper[1] (referred to as TSI), we gave a rather complete and precise treatment of the eigenvalues, eigenvectors, and transition intensities of the oxygen molecule in field-free space. Using this work as a foundation, we now give a similarly complete and precise treatment of the perturbations produced by a magnetic field. The dominant interaction will, of course, be that between the electronic spin magnetic moment and the external field; namely,

$$\mathcal{H}_{ms}=-g_s{}^e\beta\mathbf{S}\cdot\mathbf{H}. \tag{1}$$

Accordingly, the effects of this perturbation on the eigenvalues and eigenvectors is first determined to high accuracy. It is then found necessary to introduce the small effects of spin-orbit coupling and rotation-induced moments as additional perturbations to fit the precise experimental data. The fitting evaluates certain sums of matrix elements which are important in interpreting the field-free parameters λ and μ. Incidentally, the fit may also be considered to confirm the theoretical anomalous moment of the electron to ±60 parts per million (ppm). Selection rules and intensities will also be discussed and compared with experiment. It turns out that $\Delta M=\pm1$, 0 transitions are allowed, but the $\Delta M=0$ lines are at least 100 times weaker than the $\Delta M=\pm1$.

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† National Science Foundation Predoctoral Fellow.

[1] M. Tinkham and M. W. P. Strandberg, preceding paper [Phys. Rev. 97, 937 (1955)].