THEORY OF THE FINE STRUCTURE
OF THE MOLECULAR OXYGEN GROUND STATE
WITH AN EXPERIMENTAL STUDY
OF ITS MICROWAVE PARAMAGNETIC SPECTRUM

by
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ABSTRACT

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Submitted to the Department of Physics on May 17, 1954, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

A rather complete solution for the fine-structure problem of \( \text{O}_2 \) 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 \( \lambda \) and \( \mu \) 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 \( \lambda' \) and \( \mu' \), are evaluated using an expression for the electronic wave function as a superposition of configurations. In the calculation of \( \lambda' \), exchange effects, inclusion of ionic states, and the rapid change of configuration mixing coefficients with internuclear distance \( R \) play leading roles; \( \mu' \) is relatively insensitive to details. It turns out that \( \lambda' \) gives almost all of \( \lambda \), whereas \( \mu' \) gives only \( \frac{1}{4} \) per cent of \( \mu \). The second order contributions of the spin-orbit coupling to \( \lambda \) and \( \mu \) and the electronic contribution to the effective moment of inertia are related to each other and to certain magnetic effects to be mentioned later. This interrelation enables them all to be essentially evaluated experimentally.

The effective Hamiltonian is diagonalized through terms in \( \frac{(B/\hbar)\omega}{2} \) and the eigenvalues compared with the experimental 5 mm spectrum. The fitting establishes the constants \( \mu = 252.67 \pm 0.05 \text{ Mc/sec} \); \( \lambda = 59,386 \pm 20 \text{ Mc/sec} \);

\[ \lambda_1 = (R d\lambda/dR)_e = 16,896 \pm 150 \text{ Mc/sec}; \quad \lambda_2 = (\frac{d^2}{dR^2}(\lambda / dR)^2)_e = (5\pm2) \times 10^{14} \text{ Mc/sec}; \]

and \( \lambda_{\text{eff}}(v = 0) = 59,501.57 \pm 15 \text{ Mc/sec} \).

The transformations which diagonalize the field-free Hamiltonian are given with respect to both Hund case (a) and case (b) bases. These transformations are applied to matrix elements of \( S_2 \). 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 sizable intensities for the "forbidden" \( \Delta K = \pm 2 \) lines.

The dominant interaction of \( \text{O}_2 \) 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 is
removed by introducing two corrections. The larger ($\approx 0.1$ per cent 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 $\mu''$ in the spin-rotation coupling constant. The smaller ($\approx 1$ 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 magnetic moment to 60 ppm and also confirms the validity of the Zeeman effect theory.

A new result is the rotational magnetic moment of $-0.25\pm0.05$ nuclear magnetons per quantum of rotational angular momentum. Knowledge of this moment allows the electronic contributions 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 magnitude of $\lambda''$, the second order spin-orbit contribution to the coupling of the spin to the figure axis, is $165\pm50$ Mc/sec, or less than one per cent of the total coupling constant.

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 $\Delta M = \pm 1$ 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 $\Delta M^J = \pm 2$ transitions to comprise roughly half of all lines observed.

The results of line breadth measurements at 300°K. and 78°K. on lines with a representative selection of $K$, $J$, and $M$ values are given. These results show a slight ($\approx 7$ per cent) decrease in breadth with increasing $K$ but no significant ($<\pm 2$ per cent) $M$ dependence. The mean temperature dependence is $\Delta v = T^p$, where $n = 0.75\pm0.04$. Line widths in air indicate that the $N_2-O_2$ collision cross section equals or exceeds the $O_2-O_2$ cross section for the Zeeman-split levels which concern us here.

A final chapter is devoted to a discussion of the microwave, magnetic, and electronic apparatus developed to carry out this research.

Thesis Supervisor: M. W. P. Strandberg

Title: Associate Professor of Physics.
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CHAPTER I

INTRODUCTION

It is a familiar fact that a large share of our understanding of physical phenomena is based upon detailed studies of a few relatively simple examples. The methods developed in these studies may subsequently be applied to more complex examples, or perhaps adequate understanding can be deduced by more qualitative generalizations. The hydrogen atom and molecule are particularly well-known examples. A great deal of effort has been expended in experimentally determining finer and finer details of the structures of these two substances and in theoretically interpreting these structures. In the process, a great deal of generally significant information about the structure of matter has been uncovered.

In keeping with these observations, it is the purpose of this thesis to present a rather complete treatment of a somewhat more complicated example, the oxygen molecule. The additional complication over the hydrogen molecule stems both from the eight-fold increase in the number of electrons and from the fact that the ground electronic state of $O_2$ has a resultant electronic spin of unity, as opposed to zero for $H_2$. The latter fact is often indicated by saying that $O_2$ is the simplest ferromagnetic substance found free in nature. Since it is this magnetic property which most uniquely characterizes our example, it is natural that a detailed study of the interaction of the molecule with an external magnetic field should form an important part of this research. However, the coupling of the spins in internal magnetic fields produced by rotation and by other spins is also important. These interactions are present even in the absence of an external field, and they must be understood before we have a sufficiently secure base on which to build a theory of the interaction with an external field. Accordingly, Part I of the thesis is devoted to a thorough study of the molecule in field-free space.

In the first part we draw upon the results of infrared spectroscopy to determine certain basic constants of the molecule. We also use the results of Meckler's^1 recent study of the electronic wave function of the ground state of $O_2$ to evaluate the scale factors in certain spin-dependent
interactions. This application shows the inadequacy of more naive pictures of the electronic motion. Finally, we use the methods of microwave spectroscopy and of matrix algebra to measure and explain some of the more detailed aspects of the spin multiplet structure and spectrum, such as centrifugal distortion. The agreement of theory and experiment which is obtained is quite satisfactory, and our theory lacks the flaws found in the several previous treatments.

In Part II of the thesis, we develop a comprehensive theory of the effect of an external magnetic field on the eigenfunctions of the field-free problem. The dominant interaction is of course with the electronic spin magnetic moment. However, our precise experiments require the inclusion of two corrections to get satisfactory agreement. The first is the interaction of the external field with the magnetic moment of the small amount of electronic orbital angular momentum coupled into the ground state by spin-orbit coupling. The second is the interaction of the rotational magnetic moment with the external field. With these corrections, the agreement of the theoretical and experimental microwave paramagnetic resonance spectra is to within the estimated errors, namely + 50 parts per million. By accurately fitting this spectrum, we are enabled to evaluate parameters which provide valuable insight into the internal interactions giving rise to the field-free energy levels. For example, two physical interaction mechanisms (spin-spin and spin-orbit coupling) which give rise to indistinguishable results in the field-free problem give distinct results in the interaction with a magnetic field. This example illustrates the sort of advantage which is gained by an intensive "vertically integrated" study in which a variety of methods on many levels are applied to study a single substance.

To complete the magnetic resonance study, relative intensities were measured for all of the 120 lines observed at X-band. The agreement with theoretical predictions is roughly as good as the expected accuracy of the data, or + 10 per cent. Absolute intensities and line breadths were also determined for representative transitions at both 78°K and 300°K. The line breadth data are of course useful in gaining an understanding of the interaction between molecules in the gas. However, only rather qualitative conclusions could be reached in this regard.
A. History of the Field-Free Problem

With this general view of the scope of the thesis in mind, let us review the history of the field-free problem before proceeding to the direct unified treatment which is the bulk of the thesis.

The most carefully studied electronic transitions of the oxygen molecule are those between $^3\Sigma^+_u$, $^3\Pi_u$, and $^1\Delta_g$ states and the ground state. These occur in the ultra-violet at 49,802 cm$^{-1}$, in the visible red at 13,195 cm$^{-1}$, and in the infrared at 7918 cm$^{-1}$, respectively. These identifications of states are due to Mulliken (1928). Van Vleck (1934) pointed out that the observed intensities were consistent with those calculated for magnetic dipole transitions for the red and infrared transitions, which are forbidden as electric dipole transitions. The vibration-rotation band structure of the $^3\Sigma^+_u - ^3\Sigma^+_g$ transition has been studied by Dieke and Babcock (1927) and recently by Babcock and Herzberg (1948). The $^3\Pi_u - ^3\Sigma^+_g$ bands have been studied by Curry and Herzberg (1934). As a result of these studies, the moment of inertia and vibrational potential parameters of the molecule in its ground state are known to very good accuracy.

In these spectra it is found that each rotational level of the ground state is further split into a triplet, with $|\vec{J}| = |\vec{K} + \vec{S}| = K, K+1$. Since the ground state is a $\Sigma$ state, this splitting can not be of the usual spin-orbit multiplet type. The coupling of spin to the rotational angular momentum $K$ was treated in general by Van Vleck (1929) as part of his classic paper, which has served as the basis for a large share of the interpretation of molecular fine structure ever since. This coupling is not large enough to account for the observed splittings. An explanation for the splittings was provided by Kramers (1929). He noted that the magnetic spin-spin interaction of two unpaired electronic spin moments averaged over a spatial distribution with the axial symmetry of a diatomic molecule gives a contribution to the energy proportional to $(3 \cos^2 \alpha - 1)$, where $\alpha$ is the angle between $\vec{S}$ and the figure axis of the molecule. Kramers then combined this effective coupling of spin to figure axis with a spin-rotation coupling, based on only terms diagonal in electronic quantum numbers, in a first order perturbation calculation.
His results agreed moderately well with experiment. The agreement was made completely satisfactory by Schlapp\textsuperscript{11} (1937), who solved the perturbation problem exactly including deviations from pure Hund\textsuperscript{12} case (b) coupling. (In Hund's case (b), J, K, S, and M are rigorous good quantum members.)

In the meantime, Hebb\textsuperscript{13} had shown that energy terms, having exactly the same dependence on the angular momentum vectors as the mechanisms given by Kramers, resulted from consideration of the second order effects of the (unquantized) electronic orbital angular momentum perpendicular to the figure axis. The separation of these two sets of interactions is impossible on the basis of the field-free spectrum alone, and the relative importance of the two sets has been a subject of speculation and estimation first clearly resolved by the research reported in this thesis.

With the postwar advent of microwave spectroscopy, it has become possible to measure directly the separation of the $J = K+1$ terms from the $J = K$ terms within each rotational triplet. With only one exception, these energy differences lie in the vicinity of 60,000 Mc/sec or at a wavelength of 5 mm. Early work on the unresolved spectrum at roughly atmospheric pressure was carried out by Beringer\textsuperscript{14} (1946), Lamont\textsuperscript{15} (1948), and by Strandberg, Meng, and Ingersoll\textsuperscript{16} (1949). More recently, the spectrum at pressures low enough to give resolved lines has been measured by Burkhalter, Anderson, Smith, and Gordy\textsuperscript{17} (1950) and by Gokhale and Strandberg\textsuperscript{18} (1951). These measurements revealed systematic discrepancies from the predictions of the Schlapp formulae. Burkhalter, et al, forced a reasonable fit by introducing empirical correction terms which have not found theoretical basis. Gokhale\textsuperscript{19} considered the effects of centrifugal distortion on the moment of inertia, with no significant improvement in the fit. Still more recently, Miller and Townes\textsuperscript{20} (1953) reviewed the problem and obtained a satisfactory fit by adding phenomenological centrifugal distortion correction terms proportional to $K(K+1)$ to both the reciprocal moment of inertia $B$ and the spin-spin coupling parameter $\lambda$ in formulae for the frequencies of the transitions resembling those of Schlapp. This procedure is not rigorous and fails to provide a value for $d\lambda/dR$. Finally, while this thesis research was
being completed, Mizushima and Hill (1954) have remeasured the spectrum and given a theory accounting for centrifugal distortion under the adiabatic approximation. The exact eigenfunctions, which we require as a basis for considering the magnetic perturbations treated in Part II of this thesis, are not provided by their treatment. Also, there are several errors in their calculation which are pointed out later in this thesis.

Since the shortcomings of these previous works are eliminated in the treatment which we will give in this thesis, let us now turn directly to our systematic study of the oxygen molecule in field-free space. 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.

B. Outline of the Solution for the Field-Free Problem given in this Thesis

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

\[ H = H_{el} + V_{nuc} + T_{nuc} + H_{so} + H_{ss} + H_{hfs} \]  

by carrying the Born-Oppenheimer approximation to sufficiently high orders of refinement. In this equation, \( H_{el} \) 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; \( H_{so} \) is the spin orbit energy, and \( H_{ss} \) is the spin-spin energy resulting from the magnetic dipole interaction between the electronic spins; \( H_{hfs} \) 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 $^{16}$ nuclei. The essence of the Born-Oppenheimer approximation is that we can express the total state function to a good approximation as

$$\Psi = \Psi_{el} \Psi_{vb} \Psi_{rot} \Psi_{nuc} \Psi_{spin} \Psi_{trans}$$

(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 $\Psi_i$ by considering the $\Psi_i$, corresponding to other energy terms and coordinates to be fixed, or at least reduced to parameters. Thus Meckler solved for $\Psi_{el}$ by considering the nuclei fixed and neglecting the terms $\mathcal{H}_{nuc}$, $\mathcal{H}_{so}$, $\mathcal{H}_{ss}$, and $\mathcal{H}_{hfs}$. His result is and energy $E_{el}(R)$ and an electronic wave function $\Psi_{el}(r_j, s_j | R)$, 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 $E_{el}(R)$ as the effective potential for vibration and use this $\Psi_{el}$ 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.) Thus our vibrational Hamiltonian is taken to be

$$\mathcal{H}_{vb} = \frac{P_v^2}{2M} + \frac{1}{2} M \omega_e^2 R_e^2 \xi^2 + b \xi^3$$

(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

$$\mathcal{H}_{rot} = \frac{\pi^2}{2MR^2} = \beta_e (1 - 2\xi + 3\xi^3) \bar{N}^2$$

(4)

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

The effect of $\mathcal{H}_{so} + \mathcal{H}_{ss}$ in determining the fine structure can be reduced (see Chapter II) to an effective Hamiltonian
\[ \mathcal{H}_{\text{spin}} = \frac{3}{2} \left( \lambda_0 + \lambda_x \mathbf{s}_x + \lambda_z \mathbf{s}_z \right) \left( 3 \mathbf{s}_y^2 - \mathbf{s}_z^2 \right) + \mu \mathbf{K} \cdot \mathbf{S} \]  

(5)

where \( \mathbf{S} \) is the resultant electronic spin vector, and \( \lambda \) and \( \mu \) are spin coupling constants to be determined from \( \psi_{e1}(\mathbf{R}, \mathbf{\hat{s}}_i | \mathbf{R}) \). The term in \( \mu \) 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 \( \lambda \) comes from the diagonal spin-spin energy in the electronic ground state. It is noteworthy that if one tried to estimate \( \lambda \) from the simple model of two interacting spins with one concentrated at each center the values obtained for \( \lambda_0 \) and \( \lambda_1/\lambda_0 \) would even have the wrong \textit{sign}. Thus it is clear that our more accurate calculation is necessary to explain the observed behavior of \( \lambda \). In this calculation, exchange effects, inclusion of ionic states, and the rapid change of configuration mixing coefficients with \( \mathbf{R} \) play the leading roles.

In \( \text{O}_2 \) we have \( I = 0 \), allowing only the one state, \( \psi_{\text{nuc spin}} = 1 \). Thus there can be no \textit{hyperfine} effects. The translational motion of the center of mass is of no interest to us here, but \( \psi_{\text{trans}} \) 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

\[ (\mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{rot}} + \mathcal{H}_{\text{spin}} - E) \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{spin}} = 0 \]  

(6)

is by purely matrix methods. (Here, \( \psi_{\text{spin}} \) describes the state of the resultant electronic spin that enters into \( \mathcal{H}_{\text{spin}} \). The matrix components of the Hamiltonian are readily obtained (see Chapter III) in a Hund case (a) basis \( ^1 \text{D}_2 \) characterized by the quantum numbers \( v, J, M, S, \) and \( \Sigma \), where \( J \) is the total angular momentum of all kinds, and \( \Sigma = S + J \). 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 \( 10^5 \)), eliminating the discrepancy with the Schlapp formula mentioned above. This fitting establishes the constants \( \lambda_0 \), \( \lambda_1 \), and \( \lambda_2 \) 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) eigenfunction, in which $\vec{\mathbf{\Sigma}}^2$ rather than $S_z$ is diagonal.

Using these eigenvectors, the intensities of both allowed and "forbidden" transitions are calculated in 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 in the presence of the spin-spin coupling energy.
CHAPTER 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. 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 \( \vec{N} \) for the true instantaneous nuclear orbital angular momentum. \( \vec{\chi} = \vec{N} + \vec{L} = \vec{J} - \vec{S} \) differs from \( \vec{N} \) only by "high-frequency" off-diagonal elements of the electronic orbital angular momentum. We shall introduce \( K \) in section III as the conventional label for the final eigenfunctions; it has the magnitude of \( \chi \) 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 \( \Psi_{el}(r_j, s_j | R) \) 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 \( r_j \) are referred to the axes fixed in the molecule, but the wave function still describes the system with respect to a fixed frame. The \( \Psi_{vib} \) are harmonic oscillator eigenfunctions of the internuclear distance \( R \) for the angular frequency of oscillation \( \omega_e \); the \( \Psi_{rot} \) are symmetrical top eigenfunctions for a linear rotor with internal spin angular momentum. As stated above, \( \Psi_{nuc spin} \) is trivial for \( I = 0 \), and \( \Psi_{trans} \) 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 \( E^0_n \), reasonable approximations to the vibrational and rotational energy, the diagonal spin-spin energy in \( \lambda \), and the small diagonal contribution to \( \mu \) 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,* 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 \( \lambda \), defined in (5), which measures the effective coupling of the spin to the z (internuclear) axis.

Spin-Spin Contribution to \( \lambda \)

Since Van Vleck gives no formulas for the coefficient \( \lambda \) and since Kramers's \(^{9,10}\) 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

\[ \mathcal{H}_{ss} = J^2 \beta^2 \sum_{k>l} \left[ (\hat{s}_l \cdot \hat{r}_{lk}) \hat{r}_{lk}^2 - \hat{3} (\hat{s}_l \cdot \hat{r}_{lk}) (\hat{s}_k \cdot \hat{r}_{jk}) \right] \hat{r}_{lk}^2 \]  

(7)

where \( \hat{r}_{jk} = \hat{r}_j - \hat{r}_k \). By simply expanding into components and regrouping, this can be written as shown on the next page.

---

*Of course, one could start with electronic eigenfunctions for the problem including spin-orbit interaction. These, however, could not have \( \Lambda \) and \( \Sigma \) as good quantum numbers and would thus be less convenient. As usual, all magnetic spin-coupling effects are neglected in Meckler's solution.
\[
\mathcal{H}_{ss} = -g^2 \beta^2 \sum_{j>i} \left\{
\frac{3 \chi_{ij} y_{ij}}{r_{ij}^5} \left( s_{ij} s_k y + s_{ij} s_k x \right)
+ \frac{3 \chi_{ij} \beta_{ij}}{r_{ij}^5} \left( s_{ij} s_k x + s_{ij} s_k y \right)
+ \frac{3}{2} \frac{\chi_{ij}^2 - y_{ij}^2}{r_{ij}^5} \left( s_{ij} s_k x - s_{ij} s_k y \right)
+ \frac{1}{2} \frac{\chi_{ij}^2 - y_{ij}^2}{r_{ij}^5} \left( 3 s_{ij} s_k z - \vec{s}_j \cdot \vec{s}_k \right)
\right\}
\]

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\(^{24}\) points out, have matrix components proportional with the same constant of proportionality to corresponding elements of \(\vec{S}\). (This can be proved by direct multiplication of the matrix elements of a vector of the type \(\vec{\Lambda}\). See Condon and Shortley\(^{27}\), Theory of Atomic Spectra, hereafter referred to as TAS.) Thus all elements of \((3s_{ij} s_k z - \vec{s}_j \cdot s_k^2)\) are proportional to those of \((3s_z^2 - s_z^2)\), and the proper dependence of the interaction on \(S\) is shown. To evaluate \(\lambda\), it is convenient to compute the diagonal element of \(\mathcal{H}_{ss}\) for the state \(S_z = \Sigma = 1\), and to note that the diagonal part \(\lambda'\) of \(\lambda\) is given by

\[
\lambda'(\vec{S}) = \lambda'_e + \lambda'_1 \frac{\vec{S}}{S} + \lambda'_2 \frac{\vec{S}^2}{S^2} = \frac{3}{2} E_{ss} |_{S=1}
\]

The \(\vec{S}\) dependence enters because \(\Psi_{el}\) depends parametrically on \(R(\text{or } \vec{S})\).
The electronic wave function given by Meckler is expressed as a superposition of configurations

\[ \psi_{e \xi} = \sum_{\mu} C_\mu \phi_\mu \]  

(10)

where each \( \phi \) 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 \( \frac{S z}{\sqrt{2}} \) to Meckler's eigenfunctions, have been given by Kleiner. They are more convenient here because the dominant configuration is then a single determinant. The coefficients \( C_\mu \) 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 \( C_\mu \) of the order 0.1. Since the \( C \)'s are real, the diagonal energy is simply

\[ E_{e \xi} = \sum_{\mu \mu'} C_\mu C_{\mu'} H_{\mu \mu'} \]  

(11)

It is clear that we make an error of the order of only one per cent 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

\[ H_{ij} = -\frac{3}{2} \frac{3^2}{2} \sum_{j \neq k} \frac{3^2}{2} \frac{3^2}{2} \left[ 2 s_{i j}^z s_{k z}^z - s_{i j} s_{k z} - s_{i z} s_{k z} + s_{i z} s_{k z} \right] \]  

(12)

(where \( s_{i j} = s_{j x} + is_{j y} \)) 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. The spin part of (12) gives a factor of \( \pm 1/2 \) 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 example, this leaves just

\[ (H_{ii})_{cc} = H_{cc} = -\frac{3}{4} \frac{3^2}{2} \frac{3^2}{2} \left\{ \int \chi_{+}^*(1) \chi_{+}^*(2) \frac{3^2}{2} \frac{3^2}{2} \chi_{+}^*(1) \chi_{+}(2) d\tau_1 d\tau_2 \right\} \]

\[ -\int \chi_{-}^*(1) \chi_{-}^*(2) \frac{3^2}{2} \frac{3^2}{2} \chi_{-}^*(1) \chi_{+}(2) d\tau_1 d\tau_2 \]  

(13)
where $\chi_{\pi}$ is Meckler's notation for the $2p_{\pi}^{\pm}$ 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

$$H_{cc} = \frac{-64g^2 \hbar^2 S^2 K^4}{\pi a^3} \int \left[ \tau_1 \sin \theta_1 \ e^{-\frac{b \tau_1^2}{2}} \sinh b \tilde{r}_{12} \right]^2 \left[ \tau_2 \sin \theta_2 \ e^{-\frac{b \tau_2^2}{2}} \sinh b \tilde{r}_{12} \right]^2 \sinh^2 (\varphi_2 - \varphi_1) \frac{2 y_1^2 y_2}{r_{12}^5} \ d\tau_1 \ d\tau_2$$

(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 $p_{\pi}$ nature of these $\chi_{\pi}$ 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 non-ionic 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 $\lambda$ 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

\[ \xi = \chi_1 - \chi_2 \quad \xi' = \chi_1 + \chi_2 \]

\[ \eta = \gamma_1 - \gamma_2 \quad \eta' = \gamma_1 + \gamma_2 \]

\[ \zeta = \frac{\xi}{\eta} \quad \zeta' = \frac{\xi'}{\eta'} \]

\[ \rho^2 = \xi^2 + \eta^2 + \zeta^2 = r^2 \]

The integral then becomes

\[ H_{cc} = -\frac{2\alpha^2\beta^2}{\pi^{3/2}} e^{-bR^2} \int \prod \frac{e^{-bR^2}}{(\frac{3\pi^2}{4})^3} \left[ \cosh bR - \cosh bR' \right]^2 \, d\tau \, dt' \]  

Replacing 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

\[ H_{cc} = \frac{2\alpha^2\beta^2}{\pi^{3/2}} \frac{2}{\pi^{3/2}} \left( \frac{1}{30} + e^{-\frac{bR^2}{4}} - \frac{e^{-2bR^2}}{2} \right) \sum_{n=0}^{\infty} \frac{2n^2 - 1}{(2n+1)(2n+3)} \left( \frac{bR^2}{2} \right)^n \]

where

\[ K^2 = \left( 1 - e^{-bR^2} \right)^{-1} \]

We note that this is the product of a characteristic energy \( e^{-bR^2} \) 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 \( e^{-bR^2} \) 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 per cent; 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 \( b^{3/2} \sim \langle 1/r^3 \rangle \).
This result should be independent of the detailed choice of wave function. Kleiner \(^{28}\) 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 \(^{30}\) with the aid of Lowdin's analytic fitting. \(^{31}\) 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 with this higher value of \(b\) used in the \(b^{3/2}\) factors, but in the overlap factors, \(bR^2\) has Meckler's value. This procedure can be seen to preserve a consistent orthonormalization.

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 \(C_{ij}\) 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.

<table>
<thead>
<tr>
<th>(H_{\mu\nu})</th>
<th>Combined Coefficient</th>
<th>Contribution to Energy (kMc/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(bR^2 \rightarrow 4.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H_{cc} = H_{ee})</td>
<td>27.656</td>
<td>27.286</td>
</tr>
<tr>
<td>(H_{dd} = H_{ff})</td>
<td>20.370</td>
<td>20.148</td>
</tr>
<tr>
<td>(H_{cd} = H_{ef})</td>
<td>39.434</td>
<td>38.998</td>
</tr>
<tr>
<td>(H_{cg} = -H_{ch} = -H_{ci})</td>
<td>186.22</td>
<td>191.10</td>
</tr>
</tbody>
</table>

From these energies, the spin-spin contribution \(\chi\) to \(\lambda\) was computed, and the results are compared with the experimental values (obtained in section III) in Table II.
Table II

Comparison of Calculated and Experimental Values of $\lambda$ (Mc/sec)

<table>
<thead>
<tr>
<th></th>
<th>calc.</th>
<th>exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_e$</td>
<td>35.0</td>
<td>59.386</td>
</tr>
<tr>
<td>$\lambda_1 = (d\lambda/d\xi)_e$</td>
<td>19.6</td>
<td>16.90</td>
</tr>
</tbody>
</table>

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 per cent less than the "experimental value" obtained from the magnetic hyperfine structure in $1\text{6}_D^{17}$ by Miller, Townes, and Kotani.\textsuperscript{32} 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 $\lambda$. This conclusion is supported by the determination of the contribution of second-order spin-orbit effects given later in the thesis.

Inspection of Table I reveals that the $R$ dependence of $\lambda$, which determines $\lambda_1$, comes almost entirely from the change in the configuration mixing coefficients $C_{\mu}$, 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 unpublished treatment now in progress using better orbitals. This mechanism for the change in $\lambda$ again shows that a rather detailed examination of the electronic wave function is necessary for explaining the observed values of $\lambda$.

Nuclear Contribution to $\mu$

Van Vleck's\textsuperscript{24} equation (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 $\Sigma$ 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 (correcting the trivial omission of \( r_{jk}^{-3} \) in his more general equation (39))

\[
\mathcal{H} = \frac{-2\beta}{c} \sum_{j,k} \frac{Z_{jk}}{r_{jk}^3} \left( \vec{r}_{jk} \times \vec{v}_k \right) \cdot \vec{s}_j
\]

(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 \( \vec{v}_k \) by \( \vec{\omega} \times \vec{r}_k \) or \( (\vec{\omega}/MR^2) \times \vec{R} \), since the difference between the true nuclear angular momentum \( \vec{R} \) and \( \vec{R} \) is only oscillatory electronic angular momentum which averages to zero in this sort of an interaction. We assume a rigid nuclear frame, so the \( \vec{r}_k \) are constant vectors of \( + \frac{1}{2} R \vec{k} \), where \( \vec{k} \) is a unit vector in the z direction. Also \( \kappa_z = 0 \), 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 \( \mathcal{H} \) in components reduces to

\[
\mathcal{H} = \frac{4}{A} \frac{2\beta \mu}{R} \left[ \sum_j \frac{3r_{jk} - R/2}{r_{jk}^3} s_j \right] \cdot \vec{R}
\]

(20)

In this, \( Z \) is the atomic number, \( A \) is the atomic weight, \( \beta_n \) is the nuclear magneton, and \( r_{jk} \) is \( |\vec{r}_j - (R/2)\vec{k}| \).

Matrix components of the bracketed operator are reduced to single electron integrals by the method of Slater.\(^{19}\) (TAS p. 169.) Since \( \chi_z = 0 \), we have only terms in \( s_x \) and \( s_y \), which are both nondiagonal in \( \Sigma \). Thus we seek elements that are diagonal in orbital quantum numbers but off-diagonal in \( \Sigma \). Using Meckler's dominant configuration \( c \), namely, \((1 + i_3)/\sqrt{2}\) in his notation, for \( \Sigma = 0 \), and Kleiner's derived configuration \( \phi_c \) for \( \Sigma = 1 \), application of the general methods yields

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

$$
(\sum c \sum |\mathcal{H}| c \sum z = 1) = \frac{-4\pi}{\mathcal{A}} \frac{3 \bar{\beta} \bar{v}}{R} \left( \frac{\chi_+}{\sqrt{\sum z}} \right)^{\frac{\bar{v}}{2}} \left( \frac{\bar{v}}{\sqrt{\sum z}} \right)^{\frac{\bar{v}}{2}} \hat{K} \cdot \hat{s} \equiv \mu' \hat{K} \cdot \hat{s}
$$

(21)

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

The final problem is to actually evaluate the coefficient $\mu'$ by integration over the electronic $\chi_+$ 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

$$
\mu' = \frac{-4\pi}{\mathcal{A}} \frac{3 \bar{\beta} \bar{v}}{R} \left( \frac{2}{\pi b R^2} \right)^{\frac{\bar{v}}{2}} \exp \left[ -\frac{b R^2}{2} \left( \bar{K} \cdot \bar{S} \right) \right]
$$

(22)

where

$$
S_r(\chi) = \sum_{n=1}^{\infty} \frac{(2n+1)}{1 \cdot 3 \cdot 5 \cdots (2n+1)} \left( \frac{\chi}{2} \right)^n
$$

(23)

Noting that this depends on $b$ only through the overlap parameter $b R^2$ and not on the atomic scale factor separately, this should be evaluated by using Meckler's $b = 0.8$ atomic units, not the value obtained above by fitting $\left< 1/r^3 \right>$. If this is done, the result is $\mu' = \pm 10.0$ Mc/sec. This shows that the magnitude of the first-order contribution is only $\frac{1}{4}$ per cent 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 $2(Z/A) \left( \bar{\beta} \bar{P}_N / R^3 \right)$ 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 \( \langle (z - R/2)/r^3_{jk} \rangle \). From this picture, we see that the dependence of \( \mu' \) on the detailed electronic wave function is of secondary importance. Further, \( \mu' \) makes only a small contribution to \( \mu \). Finally, there are no off-diagonal elements of \( \mathcal{H}_1 \) between the dominant \( \phi_c \) 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 per cent of \( \mu' \) or 0.1 per cent of \( \mu \).

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 \( \mathbf{A} \mathbf{L} \cdot \mathbf{S} \) 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.* The rotation-electronic coupling is through the term \( 2BL \mathbf{L} \cdot \mathbf{H} \) in the rotational energy.**

*This rather phenomenological replacement is supported by the considerable success it has had in application to molecular spectra by Van Vleck (ref. 8) 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 \( \sum a_i \mathbf{L}_i \cdot \mathbf{S}_i \) 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.

**The \( B \) in this expression is the half reciprocal moment \( B_{10} \) 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 \( B_0 \) without any \( S \) dependence.
\[ \mathcal{H}_{\text{rot}} = B \bar{N}^2 = B (\bar{\mathbf{K}} - \bar{\mathbf{L}})^2 = B \bar{\mathbf{K}}^2 - 2B \bar{\mathbf{K}} \cdot \bar{\mathbf{L}} + B (\mathbf{L}_x^2 + L_y^2) \]  

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.\(^{33***}\)

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

\[ \psi_n = \psi_0 - \sum_n \frac{\langle n | \bar{\mathbf{K}} \cdot \bar{\mathbf{S}} - 2B \bar{\mathbf{K}} \cdot \bar{\mathbf{L}} | \phi \rangle}{E_n - E_0} \psi_n \]  

The indicated matrix elements are quadratures over orbital functions.

Since the operators \( \bar{\mathbf{S}} \) and \( \bar{\mathbf{K}} \) are independent of the orbital wave functions, they may be simply taken out and treated as numbers at this state. We note that elements of \( \mathbf{L}_z \) are diagonal in \( \Lambda \) and proportional to \( \Lambda \) and thus vanish for the \( \Sigma \) state with which we are dealing. Further, in a field of axial symmetry, we have the relation (see reference 24)

\***A Highly illuminating example of this type of problem is that of determining the wave function of an electron bound in a one dimensional potential which is moving classically with velocity \( \mathbf{v} \) with respect to the reference frame. In this case the effective perturbative term introduced in reducing the time-dependent problem to a stationary one is easily shown to be \(-v \mathbf{p}_x\), in complete analogy to \(-2B \bar{\mathbf{K}} \cdot \bar{\mathbf{L}} = -\bar{\mathbf{J}} \cdot \bar{\mathbf{L}}\) in our rotational case. It might appear surprising that uniform translational motion of the force center should have any effect at all. In fact, there is no change in the motion relative to the force center, but the motion relative to the fixed frame (which is what concerns us) and only referred to the moving one must be modified by the addition of some linear momentum. Since there is an \( i \) in the \( \mathbf{p}_x \) operator and since our unperturbed wave functions may be chosen to be \( \bar{\mathbf{J}} \) real, the change in \( |\Psi|^2 \) is only second order in \( \mathbf{v} \). Thus although we have first order currents we have only second order charge distortions. For the particularly simple case of a harmonic oscillator potential, one can readily show that the electronic energy evaluated with the true Hamiltonian (just \( p^2/2m + \mu \mathbf{r}^2 \)) over the wave function perturbed by \(-v \mathbf{p}_x\) is increased by \( \frac{1}{2}mv^2 \) over the unperturbed energy. This is a highly reasonable result. Our general conclusion then is that this type of perturbation is a kinematic one, not depending for its existence on the acceleration characteristic of rotation.
\[(\Lambda | L_y | \Lambda \pm i) = \pm i (\Lambda | L_x | \Lambda \pm i)\] (26)

all other elements vanishing. Thus the perturbed \(3\Sigma\) wave function has only \(\pi\) states mixed in, and the mixing is proportional to the matrix elements of electronic orbital angular momentum perpendicular to the axis.

\[\psi_{\Sigma} = \psi^{o}_{\Sigma} - \sum_{n=\pi} \sum_{g=x,y} \left( \frac{\langle n|AL_{g}|0\rangle S_{g} - \langle n|2BL_{g}|0\rangle K_{g}}{E_{n} - E_{o}} \right) \psi^{o}_{n}\] (27)

**Effect on Energy**

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

\[E'' = -\sum_{n} \sum_{g=x,y} \left( \frac{\langle n|AL_{g}|0\rangle S_{g} - \langle n|2BL_{g}|0\rangle K_{g}}{E_{n} - E_{o}} \right) \left( \langle n|AL_{g}|0\rangle S_{g} - \langle n|2BL_{g}|0\rangle K_{g} \right)\] (28)

Using the property (26) of the matrix elements of \(I_{z}\), we see that \(xy\) terms drop out, and this reduces to the form

\[E'' = \frac{2}{3} \lambda' \left[ 3 S_{x}^{2} - 3 (S^{2} + i) \right] + \mu'' \bar{\mathbf{K}} \cdot \mathbf{S} - B'' \bar{\mathbf{K}}^{2} + \text{const},\] (29)

where

\[\lambda'' = \frac{1}{2} \sum_{n} \left( \frac{\langle n|AL_{x}|0\rangle}{E_{n} - E_{o}} \right)^{2}\]
\[B'' = 4 \sum_{n} \left( \frac{\langle n|BL_{x}|0\rangle}{E_{n} - E_{o}} \right)^{2}\]
\[\mu'' = 4 \mathcal{R}_{o} \sum_{n} \left( \frac{\langle n|AL_{x}|0\rangle \langle n|BL_{x}|0\rangle}{E_{n} - E_{o}} \right)\] (30)

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

Since the actual matrix elements required cannot be calculated in the absence of wave functions for the $W$ 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 and vibrational ground-state and the order of magnitude of $A$ can be estimated from the multiplet separation of the $W$ states. With $A$ and $B$ removed, all the sums become the same, namely,

$$
\sum_n \frac{|\langle n | L_1 | 0 \rangle|^2}{E_n - E_0} = \frac{L(L+1)}{\hbar \nu}
$$

(31)

The right member is merely symbolic, but if we use Van Vleck's "hypothesis of pure precession" (ref. 8, p. 483) it could be used to infer the characteristic energy separation $\hbar \nu$. This sum then is 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 (given in Part II of this thesis) 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. Conclusions from This Chapter

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

*It is interesting to note that the diagonal value of $H_2$ itself is raised by precisely $B' \mathcal{R}^2$ due to the increased momentum of the electrons with respect to the fixed frame. The nuclear energy is lowered by $2B \mathcal{R}^2$ because the added mass reduces its share of the quantized total angular momentum. The net effect is the lowering of energy quoted above.
\[ H_{\text{eff}} = P_e^2 / 2 \hbar + \frac{1}{2} M \omega_e^2 r_e^2 \vec{S}^2 + B \vec{S}^2 + \frac{2}{3} \lambda (3 S_z^2 - S^2) + \mu \vec{B} \cdot \vec{S} \]  

(32)

where

\[ B = B' - B'' \]
\[ \lambda = \lambda' + \lambda'' \]
\[ \mu = \mu' + \mu'' \]

(33)

In this, \( \lambda', \lambda'', \mu', \mu'', B', \text{ and } B'' \) have been defined earlier in the chapter. Because they enter in exactly the same form, \( \lambda', \lambda''; \mu', \mu''; \text{ and } B', B'' \) 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 to be described in Part II. Although these interrelations are discussed more fully in Part II, let us anticipate enough of the results to complete this present picture.

With the known experimental value of \( \mu = \mu' + \mu'' \) (see section III), and the value of \( \mu' \) calculated in the previous section, we can determine \( \mu'' \) to be -262.7 Mc/sec. Taking \( B = 43.1 \) kMc/sec, this implies that \( AL(L + 1)/h \nu \) is \(-1.52 \times 10^{-3}\) which is consistent with reasonable values of \( A, L(L + 1), \text{ and } h \nu \). In particular, the minus sign checks with the plus sign for \( A \) in the \( \Pi \) states of \( \sigma^+ \) according to Van Vleck's general theory (ref. 8, p. 499). Using the value \( A = 21 \text{ cm}^{-1} \) indicated by the Zeeman-effect studies, we find \( \lambda'' \) 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 uncertainty in the correct value for the spin-spin part. Therefore \( \lambda \) serves as a reliable check on the quality of the wave function. The facts are that the calculated value was 40 per cent low even after adjusting \( b \) to give a better approximation to the Hartree-Fock atomic orbital near the nucleus, and it was 80 per cent 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)hν, we compute B" = 17.3 Mc/sec, which is a correction of 400 ppm. 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 ppm⁶), it is clear that this rather sizable correction should be applied in inferring the internuclear distance from Bₑₑ and the atomic masses. This correction decreases the computed R by 65 ppm. Recalculation, using Herzberg's value for (Bₑₑ)ₑₑ and the newly adjusted atomic constants, yields Rₑₑ = 1.20741 Å. It is significant to note that the recommended least-squares fitted value of (Nh/e)¹/², which enters in the conversion, has increased by 76 ppm between 1947 and 1952 (Dumond and Cohen⁴). 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 Rₑₑ 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.
CHAPTER III.

SOLUTION OF THE FINE-STRUCTURE PROBLEM

A. Energy Levels and Spectrum

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

$$\hat{H} = \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \nu^2} + \frac{1}{2} M \omega^2 \nu^2 + b \nu^3 + B J^2 + 2 \lambda S^2 + (\mu - 2 \lambda) J \cdot \hat{S} + (\delta - \mu J^2) \hat{S}^2 \tag{34}$$

where

$$\beta = \beta_c (1 - 2 \xi + 3 \xi^2)$$

$$\lambda = \lambda_c + \lambda_1 \xi + \lambda_2 \xi^2 \tag{35}$$

The expansion of $B$ to allow for the nonrigidity of the molecule is well known. The first two coefficients in the expansion of $\lambda$ have been estimated theoretically in section II but all three are treated as parameters to be evaluated by fitting the experimental data. No $\xi$ dependence has been given $\mu$ because the same value sufficed for both $\nu = 0$ and $\nu = 1$ states as observed in the infrared spectra, whereas a change in $\lambda$ was required. In some excited states, such as the $^3\Sigma_u^-$ state, $\mu$ is an order of magnitude larger than it is in the ground state, and its $\xi$ dependence can no longer be overlooked. Inclusion of this dependence would involve no difficulty. However, for the high vibrational states observed in the $^3\Pi_u^-$ 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.

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

$$(J \mid \hat{J}^2 \mid J) = J(J+1)$$

$$(S \Xi \mid S_\Xi \mid S \Xi) = \Xi$$
\[ (J \Sigma | \tilde{J} \cdot \tilde{z} | J \Sigma') = \frac{1}{2} [J(J+1) - \Sigma(\Sigma + 1)]^{1/2} \delta_{\Sigma', \Sigma} + \Sigma^2 \delta_{\Sigma', \Sigma} \]

\[ (\nu | x^2 | \nu') = \epsilon^{1/2} \left[ (\nu + 1)^{1/2} \delta_{\nu', \nu+1} + \nu^{1/2} \delta_{\nu', \nu-1} \right] \]

\[ (\nu | x^2 | \nu') = \epsilon \left[ (\nu + 1)^{1/2} (\nu + 2)^{1/2} \delta_{\nu', \nu+2} + (2 \nu + 1) \delta_{\nu', \nu} \right] \]

\[ + \nu^{1/2} (\nu - 1)^{1/2} \delta_{\nu', \nu-2} \]

\[ (\nu | x^3 | \nu') = \epsilon^{3/2} \left[ (\nu + 1)^{1/2} (\nu + 2)^{1/2} (\nu + 3)^{1/2} \delta_{\nu', \nu+3} \right] \]

\[ + 3 \nu^{3/2} \delta_{\nu', \nu+1} \]

\[ + 3 \nu^{3/2} \delta_{\nu', \nu-1} \]

\[ + \nu^{1/2} (\nu - 1)^{1/2} (\nu - 2)^{1/2} \delta_{\nu', \nu-3} \]

(36)

where \( \epsilon = B_e / h \omega \) and \( \delta_{\nu', \nu} \) is the Kronecker symbol. The elements of \( \tilde{J} \cdot \tilde{S} \) are obtained by noting that \( \tilde{S} \) satisfies the "reversed" commutation relation (see ref. 24) in the gyrating frame and that \( J_z = \Sigma \) since \( N_z = 0 \). Since \( \tilde{S} \) obeys ordinary commutation relations, we have the result given above. The elements of \( x^2 \) and \( x^3 \) are obtained by matrix multiplication of the familiar matrix elements of \( \tilde{S} \) 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 \( (\nu \Sigma | \mathcal{H} | \nu' \Sigma') \). 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. Using
\[ (v^\pm | H_{\text{eff}} | v' \pm') = -\sum_{E_{v'}, \pm} \frac{(v^\pm | \mathcal{H} | v' \pm')(v' \pm' | \mathcal{H} | v^\pm')}{E_{v'} - E_{v'}} \]  

(37)

we obtain a 3 x 3 matrix between the \( \pm 1,0 \) states for a given vibrational (and total angular momentum) state. Including terms of order \( \epsilon^2 \), these reduced elements are*

\[ \omega \equiv (v \pm 1 | H_{\text{eff}} | v \pm 1) = B_v J(J+1) - \epsilon^2 \left[ \frac{8B}{3} \lambda_1 J(J+1) + 4B \lambda^2 (J+1)^2 \right] \]

\[ \chi \equiv (v \pm 0 | H_{\text{eff}} | v \pm 0) = - (2 \lambda_v + \lambda) + B_v (J^2 + J + 2) \]

\[ -\epsilon^2 \left[ 4B (J^2 + J + 2) \lambda^2_1 + 16B J(J+1) \right] \]

\[ + \frac{16}{3} \lambda_1 J(J+2) + 4 \lambda^2 / 3B \]  

(38)

\[ y \equiv (v \pm 0 | H_{\text{eff}} | v \pm i) = \left[ \frac{J(J+1)}{2} \right] \left[ \frac{\lambda}{2} \right] - 2B_v - \epsilon^2 [16B (J^2 + J + 4 + \lambda_1/3)] \]

\[ \tilde{y} \equiv (v \pm 1 | H_{\text{eff}} | v \pm 0) = - \epsilon^2 B B J(J+1) \]

where

\[ B_v = B_o \left[ 1 + (2v+1)(3 \epsilon + 12B^2 \epsilon^2) \right] \]

\[ \lambda_v = \lambda_0 + (2v+1)(6\epsilon \lambda_0 - 6B^2 \epsilon \lambda_0) \]  

(39)

We note that large vibration-dependent terms can be taken out by defining \( v \)-dependent constants \( \lambda_v \) 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 \( B_o \) and \( B_v \) is unnecessary and the subscripts are dropped. (Numerical evaluation was actually made with the use of \( B_v \)).

*Detailed consideration shows that a somewhat more accurate treatment in this case of the anharmonic oscillator is obtained by replacing \( \epsilon = B_o / \omega_o \) by \( \epsilon' = B(o) / \hbar \omega_{01} \), where \( \omega_{01} = E_o (v = 1) - E_o (v = 0) \).

This has been done in the numerical evaluations.
The diagonal elements given here are such that the zero of energy is

\[ E_0(v) = (v + \frac{\lambda}{2}) \hbar \omega + 30 \beta \varepsilon^2 (\hbar \omega \lambda)^4 (v^2 + v + \frac{\lambda}{3 \beta}) + \frac{2}{3} \lambda v - \mu \]  

(40)

Application of the Wang\textsuperscript{37,38} 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

\[ E - E_0(v) = \omega - \frac{v}{2} + \frac{(\omega + v + \lambda)}{2} + \left\{ \frac{(\omega^2 + v^2)}{2} + 2 v \right\}^{1/2} \]  

(41)

The results can be stated concisely as

\[ E(J+K) - E(J) = \omega - \frac{v}{2} + (8 \varepsilon + 8 \varepsilon^2 \lambda_1 \beta) K(K+1) - 4 \varepsilon^2 K^2(K+1)^2 \]  

(42)

\[ \mu_-(K) = E(J=K) - E(J=K-1) = \lambda v + \frac{\lambda v}{2} + B v (2K-1) \]

\[ + 4 \varepsilon^2 \left\{ B(-4K^2 + 6K - 6K + 2) + \frac{\lambda v}{2} \left( 3K^2 + K + 4 + \frac{2K}{B} \right) \right\} \]

\[ - \left[ \sum_{n=0}^{3} \frac{3}{A_n} K^{3n} (K-1)^n \right]^{1/2} \]  

(43)

\[ \mu_+(K) = E(J=K) - E(J=K+1) = \lambda v + \frac{\lambda v}{2} - B v (2K+3) \]

\[ + 4 \varepsilon^2 \left\{ B(4K^2 + 18K^2 + 30K + 18) + \frac{\lambda v}{2} \left( 3K^2 + 5K + 6 + \frac{2K}{B} \right) \right\} \]

\[ + \left[ \sum_{n=0}^{3} \frac{3}{A_n} K^{3n} (K+2)^n \right]^{1/2} \]  

(44)

where

\[ A_0 = \left[ (\lambda v + \frac{\lambda v}{2} - B v) + \varepsilon^2 (8B + 16 \lambda_1 \beta + 2 \lambda_1^2 \beta B) \right] \]

\[ A_1 = \left[ \mu - 2B v + \varepsilon^2 (16B + 8 \lambda_1 \beta) \right]^2 + \varepsilon^2 (16B + 8 \lambda_1 \beta) \left[ \lambda + \frac{\lambda v}{2} - B \right] \]

\[ + \varepsilon^2 (8B + 16 \lambda_1 \beta + 2 \lambda_1^2 \beta B) \]  

(45)

\[ A_2 = \varepsilon^2 \left\{ 32B \left[ (\mu - 2B) + \varepsilon^2 (16B + 2 \lambda_1 \beta) \right] + \varepsilon^2 (8B + 4 \lambda_1 \beta) \right\} \]

\[ A_3 = \varepsilon^4 256 B^2 \]

\[ J = 0 \text{ is a special case in which the secular equation reduces to a linear one. The results are} \]
\[ E(J=0, K=1) - E_0(v) = -(2\lambda v + \mu) + 2Bv - 4\varepsilon^2(4B + 8\lambda_1/3 + \lambda_1^2/38) \]

and

\[ \nu_-(1) = 2\lambda v + \mu + 16\varepsilon^2\lambda_1(1 + \lambda_1/12B) \quad (43') \]

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

In fitting the spectrum it is useful to note that

\[ \nu_-(K) + \nu_+(K-2) = 2\lambda v + \mu + 8\varepsilon^2\lambda_1(2K^2 - K + 2 + \lambda_1/6B) \quad (46) \]

The precision with which this parabolic form fits the experimental data is shown in Fig. 1.

---

**Fig. 1** -- Comparison of theoretical and experimental dependence of the sum \( \nu_-(K) + \nu_+(K-2) \) on the rotational quantum number \( K \). This dependence is due to centrifugal distortion.
By considering sums of this sort, on readily determines \( (2\lambda_{\nu} + \mu) \) and \( \lambda_1 \). With these constraints, \( \mu \) and \( \lambda_{\nu} \) are separately fixed by considering individual frequencies, using (43) and (44). Because the results are so insensitive to \( B, b, \) and \( \omega_e \), 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 \( 2.99790 \times 10^{10} \) cm/sec. Some of the derived constants are \( B(0) = 43.1029 \) kMc/sec, \( b = -32.012 \) kMc/sec, and \( \epsilon = B(0)/\kappa \omega_0 = 0.92384 \times 10^{-3} \).

To determine \( \lambda_2 \) it is necessary to use data from an excited vibrational state. For this purpose the infrared data of Babcock and Herzberg\(^6\) for the \( v = 1 \) state of \( O_2 \) 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\(^7\) formula.

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

**Table III. Experimental Spin Coupling Constants (Mc/sec)**

\[
\begin{align*}
\lambda_e &= 59,386 \pm 20 & \lambda(0) &= 59,501.57 \pm 0.15 \\
\lambda_1 &= 16,896 \pm 150 & \lambda(1) &= 59,730.00 \pm 40 \\
\lambda_2 &= (5 \pm 2) \times 10^4 & \mu &= 252.67 \pm 0.05
\end{align*}
\]

Table IV lists all of the microwave experimental data 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\(^{17}\) and of Gokhale,\(^{18}\) neglecting the apparently erroneous \( \nu(25) \) and the wavelmeter measurements. Since then the data of Mizushima and Hill\(^{21}\) 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 wavelmeter accuracy. If \( \lambda(0) \) and \( \lambda_1 \) 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).
Table IV. Comparison of Experimental and Calculated Frequencies in Mc/sec for $^{16}O_2$ Fine-Structure Transitions

<table>
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<th>K</th>
<th>Experimental</th>
<th>Calculated</th>
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<td></td>
<td>Burkhalter</td>
<td>Gokhale</td>
<td>Hill</td>
</tr>
<tr>
<td>1</td>
<td>56,265.1</td>
<td>56,265.2 ± .5</td>
<td>56,265.6 ± .6</td>
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<tr>
<td>3</td>
<td>56,446.2</td>
<td>56,446.3 ± .4</td>
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</tr>
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<td>5</td>
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<tr>
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<td>60,433.4 ± .2</td>
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<tr>
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</table>

* Wavemeter reading.
At this point, let us review the relation of this solution with previous ones mentioned in I-A. In the works of Kramers,9,10 of Hebb,13 and of Schlapp11 the nonrigidity of the nuclear framework is neglected. Thus $\varepsilon = B/k\omega = 0$. 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 $\lambda/B$, but Hebb indicates the manner in which the more exact solution using the radical is obtained from the work of Hill and Van Vleck.40 Schlapp gives the form with the radical. His solution gave satisfactory agreement with the infrared data, provided that different values of $B$ and $\lambda$ were chosen for excited vibrational states.

The precise microwave measurements of Burkhalter et al.17 revealed substantial deviations from the Schlapp formulae. In particular, the sum $\nu(K) + \nu(K-2)$ was not constant as predicated by the Schlapp formula (our (46) with $\varepsilon = 0$), but increased with $K$. Burkhalter obtained a reasonable fit by empirically adding $\delta K + \alpha(K+1)^{-1/2}$ to Schlapp's $\nu(K)$, leaving $\nu(K)$ unchanged. Gokhale19 considered the effect of centrifugal distortion on $B$, but assumed $\lambda$ and $\mu$ 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 Townes20 reviewed the problem, and fitted the spectrum satisfactorily by making both $B$ and $\lambda$ in their formulas depend on $K$ through centrifugal distortion correction terms proportional to $K(K+1)$. Their formulas are

$$\nu_-(K) = \lambda + \mu K + (2K-1)(B-\mu/2) - \left[\lambda^2 - 2\lambda(B-\mu/2) + (2K-1)^2(B-\mu/2)^2\right]^{1/2} \quad (47)$$

$$\nu_+(K) = \lambda - \mu(K+1) - (2K+3)(B-\mu/2) + \left[\lambda^2 - 2\lambda(B-\mu/2) + (2K+3)^2(B-\mu/2)^2\right]^{1/2} \quad (48)$$

Since these formulae are derived from a secular equation connecting several $K$ states, the values of $B$ and $\lambda$ are not well defined and this procedure is not rigorous. Further, it fails to give a value for d$\nu$/d$R$, 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, Mizushima21
has 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 $\lambda_e$ or $\lambda_2^*$ and does not give the diagonalizing transformation. Thus the present treatment verifies Mizushima'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 $3 \times 3$ 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:

$$\left\{ H_{eff} - [E + E_c(n)] \right\} \psi = 0$$

where

$$H_{eff} = \begin{pmatrix} w & y & z \\ y & x & z \\ z & y & w \end{pmatrix}$$

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

$$T_J = (\Psi_{K=J-1}, \Psi_{K=J}, \Psi_{K=J+1}) = \begin{pmatrix} \alpha_J & -1/\sqrt{2} & c_J \\ a_J & c_J & 0 \\ a_J & 1/\sqrt{2} & c_J \end{pmatrix}$$

where

$$c_J = 2^{-1/4} \Gamma a_J = 2^{-1/4} \Gamma (2 + r^2)^{-1/4}$$

$$\Gamma = \left[ E - E_0(n) - \frac{1}{2} \lambda_0 \right] x^1_{J=K+1}$$

These coefficients are listed in Table V for the states occurring in $\Sigma$.  

*Note that his $\lambda_c$, is related to ours by $(\lambda_c)_M = 4 \epsilon^2 (\lambda_c)_T$. Also note that he has apparently omitted a numerical factor of 2\pi in going from his equation (17b) to (18). As a result, his value for $(\lambda/d\lambda)_c$ is inconsistent with ours.
Table V. Transformation Coefficients of Eigenvectors

<table>
<thead>
<tr>
<th>J</th>
<th>$a_J$</th>
<th>$c_J$</th>
<th>$a'_J$</th>
<th>$c'_J$</th>
<th>$b_J$</th>
<th>$d_J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.480462</td>
<td>0.518303</td>
<td>0.547723</td>
<td>0.447214</td>
<td>0.990351</td>
<td>0.138562</td>
</tr>
<tr>
<td>4</td>
<td>0.489369</td>
<td>0.510410</td>
<td>0.527046</td>
<td>0.471404</td>
<td>0.997059</td>
<td>0.076638</td>
</tr>
<tr>
<td>6</td>
<td>0.492680</td>
<td>0.507214</td>
<td>0.518874</td>
<td>0.480384</td>
<td>0.998694</td>
<td>0.053009</td>
</tr>
<tr>
<td>8</td>
<td>0.494413</td>
<td>0.505526</td>
<td>0.514496</td>
<td>0.485071</td>
<td>0.999178</td>
<td>0.040530</td>
</tr>
<tr>
<td>10</td>
<td>0.495480</td>
<td>0.504480</td>
<td>0.511766</td>
<td>0.487950</td>
<td>0.999462</td>
<td>0.032813</td>
</tr>
<tr>
<td>12</td>
<td>0.496202</td>
<td>0.503769</td>
<td>0.509902</td>
<td>0.489898</td>
<td>0.999620</td>
<td>0.027569</td>
</tr>
<tr>
<td>14</td>
<td>0.496723</td>
<td>0.503256</td>
<td>0.508548</td>
<td>0.491304</td>
<td>0.999717</td>
<td>0.023776</td>
</tr>
<tr>
<td>16</td>
<td>0.497117</td>
<td>0.502867</td>
<td>0.507519</td>
<td>0.492366</td>
<td>0.999782</td>
<td>0.020902</td>
</tr>
<tr>
<td>18</td>
<td>0.497424</td>
<td>0.502562</td>
<td>0.506712</td>
<td>0.493197</td>
<td>0.999825</td>
<td>0.018652</td>
</tr>
<tr>
<td>20</td>
<td>0.497571</td>
<td>0.502318</td>
<td>0.506061</td>
<td>0.493865</td>
<td>0.999858</td>
<td>0.016842</td>
</tr>
<tr>
<td>22</td>
<td>0.497873</td>
<td>0.502117</td>
<td>0.505525</td>
<td>0.494413</td>
<td>0.999881</td>
<td>0.015355</td>
</tr>
<tr>
<td>24</td>
<td>0.498042</td>
<td>0.501950</td>
<td>0.505076</td>
<td>0.494872</td>
<td>0.999900</td>
<td>0.014112</td>
</tr>
<tr>
<td>26</td>
<td>0.498185</td>
<td>0.501808</td>
<td>0.504695</td>
<td>0.495261</td>
<td>0.999914</td>
<td>0.013057</td>
</tr>
</tbody>
</table>

$a_J$ 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 equation (49). $b_J$ and $d_J$ express $O_2$ Eigenfunctions with respect to Hund (b) basis by equation (54).

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

$$a'_J = \frac{1}{2} \left( \frac{J+1}{J+\frac{1}{2}} \right)^{1/2} \quad c'_J = \frac{1}{2} \left( \frac{J}{J+\frac{1}{2}} \right)^{1/2}$$

(51)

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

$$\mathcal{K} = J-1 \begin{pmatrix} \kappa & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \gamma \end{pmatrix}$$

(52)

where

$$\alpha = B \lambda J(J-1) - 2 \lambda r \frac{J}{2J+1} + \mu J - \epsilon^2 \left[ 4 B \lambda^2 (J-1)^2 + \frac{3}{5} \gamma^2 \left( \frac{J(J-1)}{2J+1} \right)^2 \right]$$

$$+ \frac{1}{3} \mu \lambda \frac{J}{2J+1}$$
\[
\rho = B J(J+1) - \epsilon^2 J(J+1) \left[ 4BJ(J+1) - 8\lambda_1/3 \right]
\]

\[
\chi = B J(J+1)(J+2) - 2\lambda J(J+1)/3 - \mu (J+1)
- \epsilon^2 \left[ 4BJ(J+1)(J+2) - 8\lambda_1 (J+1)(J+2)/2J+1 + 4\lambda_1^2 (J+1) \right]
\]

\[
\delta = \left[ J(J+1) \right]^{1/2} \left\{ 2\lambda J + \epsilon^2 B\lambda_1 \left[ (J^2 + J + 1) + \lambda_1/6B \right] \right\}
\]

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). This has been verified with the use of the case (b) matrix elements given by Van Vleck (ref. 24, p. 222). The effective Hamiltonian matrix in Mizushima's paper gives somewhat different coefficients for \(\lambda_1\). His error seems to have arisen in subtracting a 2/3 \(\lambda\), treated as independent of \(K\), from the diagonal elements.

The transformation which gives the oxygen eigenvector, characterized by \(K\), with respect to the Hund (b) basis, characterized by \(K\), if found to be

\[
T_b = (T_\chi^{-1} T_\rho = \chi = J-1 \quad J \quad J+1
\]

\[
\begin{pmatrix}
 b_J & 0 & d_J \\
 0 & 1 & 0 \\
 -d_J & 0 & b_J
\end{pmatrix}
\]

where

\[
b_J = 2(\alpha_J a_J + c_J c_J') \approx 1
\]

\[
d_J = 2(c_J a_J' - a_J c_J') \approx \frac{4}{3(J+1/2)}
\]

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.
CHAPTER IV

LINE INTENSITIES IN THE MILLIMETER AND SUB-MILLIMETER SPECTRUM

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

\[ H' = -g_s \beta S \cdot H_{rf} = -\mu \cdot H_{rf} \]

A well-known analysis\(^{11}\) shows that for well-separated lines the absorption coefficient \( \alpha \) is given by

\[ \alpha_{ij} = \frac{4\pi \omega^2 N}{\epsilon k T} \sum_M |(\mu_{ij})|^2 \frac{e^{-\varepsilon_j/kT}}{\varepsilon_j} \frac{e^{-\varepsilon_i/kT}}{\varepsilon_i} \]

where \( N \) is the number of molecules per unit volume, \( \mu_{ij} \) is the matrix element of the magnetic dipole moment, \( \varepsilon_j^{-1} = 2\pi\Delta \nu \), \( E_j \) is the energy of the \( j \)-th state, and the sum over \( j \) is the usual partition sum. Since \( \alpha \) is proportional to \( |\mu_{ij}|^2 \), it is proportional to \( |(S_{ij})_{Z}|^2 \) 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 \( M \),

\[ \sum_M |(S_{X})_{ij}|^2 = \sum_M |(S_{Y})_{ij}|^2 = \sum_M |(S_{Z})_{ij}|^2 \]

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

\[ \sum_M |(S_{Z})_{ij}|^2 \]

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

A. Matrix Elements of \( S_{Z} \)

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

\[ S_{Z} = \sum_g \phi_{Zg} S_g \]
These direction cosine matrix elements are tabulated in Appendix B
with the phase conventions we have used. Noting that \( \Omega = \Xi \) for our
\( \Lambda = 0 \) state, we find the following elements for \( S_z \) in a Hund case (a)
representation.

\[
(J M S \Xi | S_z | J M S \Xi) = \frac{\Xi^2 M}{J(3J+1)}
\]

\[
(J M S \Xi | S_z | J M S \Xi \pm 1) = M \frac{(J(J+1)-\Xi(\Xi \pm 1))^{1/2}}{2J(J+1)} \frac{[S(S+1)-\Xi(\Xi \pm 1)]^{1/2}}{\Xi}
\]

\[
(J M S \Xi | S_z | J-1 M S \Xi \pm 1) = \frac{\Xi (J^2-\Xi^2)^{1/2}}{J(3J-1)^{1/2}} \frac{(J^2-M^2)^{1/2}}{\Xi}
\]

\[
(J M S \Xi | S'_z | J-1, M S \Xi \pm 1) = \pm \frac{[(J^2-M^2)(J+\Xi)(J-\Xi-1)]^{1/2}}{2J(4J-1)^{1/2}} \frac{[S(S+1)-\Xi(\Xi \pm 1)]^{1/2}}{\Xi}
\]

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.

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

\[
(59)
\]
\[
\begin{bmatrix}
T_0^{-1}S_{00}T_0 & T_1^{-1}S_{01}T_1 & 0 & 0 \\
T_1^{-1}S_{11}T_1 & T_1^{-1}S_{12}T_2 & 0 & 0 \\
0 & T_2^{-1}S_{22}T_2 & T_2^{-1}S_{23}T_3 & 0 \\
0 & 0 & T_3^{-1}S_{33}T_4 & T_3^{-1}S_{33}T_3 \\
0 & 0 & 0 & 0 \\
\end{bmatrix}
\]

(59)

In these expressions, \(T_J\) and \(S_{JJ}\) are 3 \times 3 matrices.

Carrying out the indicated matrix multiplication, we find the following matrix elements of the form \((K, J, M \mid S_Z \mid K', J', M)\).

\[
(K, K, M \mid S_Z \mid K, K, M) = \frac{M}{J(J+1)^{3/2}} \equiv \frac{g(K, J=K, M)}{\mathcal{F}_K} \cdot M
\]

\[
(K, K+1, M \mid S_Z \mid K, K+1, M) = \frac{2a_J^2 M}{J(J+1)^{3/2}} \left[ 2c_J + \frac{a_J^2}{J(J+1)^{1/2}} \right] \equiv \frac{g(K, J=K+1, M)}{\mathcal{F}_K} \cdot M
\]

\[
(K, K-1, M \mid S_Z \mid K, K-1, M) = \frac{-2a_J^2 M}{J(J+1)^{3/2}} \left[ 2a_J - \frac{c_J}{J(J+1)^{1/2}} \right] \equiv \frac{g(K, J=K-1, M)}{\mathcal{F}_K} \cdot M
\]

\[
(J-1, J, M \mid S_Z \mid J-1, J, M) = 2M \left[ \frac{a_J^2 + c_J}{J(J+1)^{1/2}} + \frac{a_J^2 - c_J}{J(J+1)^{1/2}} \right] \equiv \mathcal{F}_J \cdot M
\]

(60)

\[
(J-2, J-1, M \mid S_Z \mid J-2, J-1, M) = f(J, M) \left[ \frac{a_J^2 - c_J}{J^{1/2}} + \frac{c_J - a_J^2}{J^{1/2}} \right] \equiv \mathcal{F}_J \cdot (J^2 - M^2)^{1/2}
\]

\[
(J-1, J-1, M \mid S_Z \mid J-1, J-1, M) = f(J, M) \left[ \frac{a_J^2 + c_J}{J^{1/2}} + \frac{c_J + a_J^2}{J^{1/2}} \right] \equiv \mathcal{F}_J \cdot (J^2 - M^2)^{1/2}
\]

\[
(J, J-1, M \mid S_Z \mid J, J-1, M) = f(J, M) \left[ \frac{c_J^2 - a_J^2}{J^{1/2}} + \frac{a_J^2 - c_J^2}{J^{1/2}} \right] \equiv \mathcal{F}_J \cdot (J^2 - M^2)^{1/2}
\]

\[
(J-1, J-1, M \mid S_Z \mid J+1, J, M) = f(J, M) \left[ \frac{c_J}{J^{1/2}} - \frac{a_J}{J^{1/2}} \right] \equiv \mathcal{F}_J \cdot (J^2 - M^2)^{1/2}
\]
where
\[ f(J, M) = \left[ \frac{2(J^2 - 1)(J^2 - M^2)}{J(4J^2 - 1)} \right]^{1/2} \]

with the special case
\[ (1, 0, 0 \mid S_z \mid 1, 1, 0) = -\left[ \frac{2(1-M^2)}{3} \right]^{1/2} \equiv C_0 (1-M^2)^{1/2} \tag{60'} \]

If we insert the tabulated values of \( a_J \) and \( c_J \), we obtain the proper transformed matrix elements, whereas if we insert \( a_J^b \) and \( c_J^b \) 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 \( (K \mid K') \) 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 formulae for \( \Delta K = 0 \) transitions differ from Hund (b), especially for 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. The numerical values are tabulated in Appendix C, but further discussion will be deferred to Part II of this thesis which gives a complete treatment of the interaction with a magnetic field.

**B. Results**

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 spatial directions. This results in an intensity factor I defined by
\[ \Gamma(J'', M'' \mid K', J') = 3 \sum_M \left| (K'' M'' \mid S_z \mid K' M') \right|^2 \tag{61} \]

The sum is readily evaluated explicitly using the fact that
\[ \sum_{M^2} M^2 = \frac{J(J+1)(2J+1)}{3} \]

The results have been tabulated in Table VI for \( J \leq 16 \), and the Hund (b) result.
TABLE VI

Line Intensities: \( I(K',J'|K'',J'') = 3 \sum_{\text{M}} |S_{\text{M}}(K''J''\text{M})|^2 \)

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

We can write the frequency of a $K_{\perp} \rightarrow K_{\perp} + 2$ transition in terms of the frequency

$$\nu_{K_{\perp}, K_{\perp} + 2} = E(J=K=K_{\perp} + 2) - E(J=K=K_{\perp})$$

and the frequencies of the 5 mm lines as follows:

$$\nu_{J, J+1, J=K} = \nu_{K_{\perp}, K_{\perp} + 2} - \nu_{K_{\perp} + 2}(K+2)$$

$$\nu_{J, J+1, J=K+1} = \nu_{K_{\perp}, K_{\perp} + 2} - \nu_{K_{\perp} + 2}(K+2) + \nu_{J+1}(K)$$

$$\nu_{J, J+1, J=K+2} = \nu_{K_{\perp}, K_{\perp} + 2} + \nu_{J+1}(K)$$

(62)

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.

$$\alpha_{J, J+1, J=K} = 0.46 (J+1)^{-\frac{1}{2}} \nu^2 / 10^{-6} e^{-0.069 K(K+1)}$$

$$\alpha_{J, J+1, J=K+1} = 4.2 J^{-1} \nu^2 / 10^{-6} e^{-0.069 K(K+1)}$$

(63)

$$\alpha_{J, J+1, J=K+2} = 1.4 J^{-1} \nu^2 / 10^{-6} e^{-0.069 K(K+1)}$$

In these, $\alpha$ is the value when $\nu = \nu_{J, J}$ and $\nu$ is expressed in kHz/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 $0.44 \times 10^{-6}$, $38 \times 10^{-6}$, and $17 \times 10^{-6}$ cm$^{-1}$, respectively.
PART II
INTERACTION WITH A MAGNETIC FIELD

CHAPTER V
INTRODUCTION TO PART II

In part I we have given 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 perturbation produced by a magnetic field. This part differs from Part I in that here we also have carried out extensive experimental investigations as part of the thesis research, whereas in Part I the experimental work was all done by other workers. In this experimental work, 120 lines were resolved in the X-band spectrum and 78 lines in the S-band spectrum.

The dominant interaction is of course that between the electronic spin magnetic moment and the external field—namely

$$\mathcal{H}_{ms} = -\frac{\gamma_s}{h} \beta \mathbf{S} \cdot \mathbf{H}$$

(64)

Accordingly, the effect 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 magnetic moments as additional perturbations to fit the precise experimental data taken with our equipment. The determination of the two parameters characterizing these interactions is thus made possible by the combination of theory and experiment, both an order of magnitude more precise than those previously existing for $O_2$. These two parameters then determine certain sums of matrix elements which are important in interpreting the field-free parameters $\lambda$ and $\mu$. Indidentally, our good fit may also be considered to confirm the theoretical anomalous magnetic moment of the electron (Schwinger\textsuperscript{45} and Karplus and Kroll\textsuperscript{46}) to $\pm 60$ ppm. (parts per million)

To complete the study of the effect of a magnetic field, we calculate theoretical transition probabilities, which in some respects are a more critical test of the eigenvectors than the test provided by the energy. However, the experimental accuracy is so much less than in the measurement
of line positions that we must be content to observe that a satisfactory check is obtained. That is, theoretical and experimental relative intensities check to within roughly $\pm 10$ per cent while varying in magnitude over a range of 100 to 1. The absolute intensities check less well, but much better than any previous measurements. These experiments confirm the theoretical prediction that $\Delta J = \pm 2$ transitions should have sizeable intensities for fields of more than a few kilogauss. This is true since the magnitude of the total angular momentum $|\vec{J}|$ is not a constant of the motion in the presence of a field.

Finally, we present the results of our line width measurements. Since the line width is almost entirely the result of collision broadening, these data supply some information concerning interactions between molecules. Our measurements are on transitions between two $M$ sublevels of the same $J$ state. Thus we have the possibility of making more refined studies of the collision cross section of individual states than are possible in the work on the field-free millimeter spectrum. In that work, it is only possible to measure an average over the degenerate $M$ levels, which is averaged again over the initial and final state $J$ values.

Details of the apparatus and experimental method are collected in Chapter XII.

A. History of the Magnetic Perturbation Problem

In the case of very weak fields (less than 100 gauss) the simple vector model calculation of a Lande' g-factor for the combination of a non-magnetic rotating molecule and an electronic spin magnetic moment is quite satisfactory. Even at low fields, however, this neglects the small rotational moment, the spin-orbit effects, and the deviation of $O_2$ from exact Hund case (b) coupling which was discussed in Part I.

The first serious attempt to treat the strong field case was by Schmid, Budd, and Zemplén* (1936). In their calculation, they treated $O_2$ as an exact example of Hund case (b). They then made the further approximation of neglecting the difference in energy between the $J = K \pm 1$ levels, and of replacing all values of $\gamma_+(K)$ and $\gamma_-(K)$ by an average. By these means they obtained explicit results of sufficient accuracy to qualitatively explain the Zeeman effect on the optical absorption bands.
The only other published work directly applying to this problem is
the experimental microwave resonance work of Beringer and Castle\(^4\) (1951)
and the accompanying theoretical treatment of Henry\(^4\) (1950). Henry's
calculation is a much more accurate one than that of Schmid, et al.
However, he breaks the problem up into two stages in such a way as to
introduce errors as well as simplifications. Thus the theory is not
accurate enough to reveal the significant corrections which our treatment
gives. His treatment of line intensities is also sufficiently inadequate
that he doesn't consider the existence of the \(\Delta J = \pm 2\) transitions which
we find to give over half of all the observed lines.

The experimental work of Beringer and Castle is very similar to that
which we have done. However, it is restricted to only X-band and seems
less precise. Our experimental techniques are similar in that we both
use magnetic field modulation small compared to the line width and thus
get a derivative type of curve. However, we use a continuous sweep with
chart recorder whereas they used a galvanometer in a point-by-point
technique. The advantage of our system in the detection of weak signals
is evidenced by our ability to detect 120 X-band lines compared to their
40 lines. Since many of these extra lines are of the "forbidden" \(\Delta J = \pm 2\)
type, these additional lines contribute significantly to the fullness of
our understanding of the spectrum.

The subject of rotational magnetic moments of molecules (which enter
in one of our corrections) was opened by a rather naive treatment\(^3\) in
which the electronic charge was assigned a rigid distribution. Wick\(^3\) gave
the first treatment in which the electrons were treated quantum mechanically.
This refinement is necessary to avoid results having the wrong sign for the
g-factor of the hydrogen molecule, which was first measured by Estermann
and Stern\(^4\) and most accurately measured by Harrick and Ramsey\(^5\). Ramsey\(^5\)
has extended Wick's treatment to isotopic molecules, and Eshbach and
Strandberg\(^4\) have treated the general asymmetric rotor. It appears that
our example of a magnetic molecule is the first one complicated enough to
give a real possibility of an internal check on the theory.
B. History of the Line Breadth Problem

The first theory of pressure broadening is the classic work of Lorentz\textsuperscript{55} (1906). He simply considered the average Fourier intensity distribution for an ensemble of classical oscillators which are abruptly interrupted at each randomly occurring collision. General quantum mechanical theories have subsequently been given by Weisskopf\textsuperscript{56} (1933), Foley\textsuperscript{57} (1946), Mizushima\textsuperscript{58} (1951), and Anderson\textsuperscript{59} (1949). The first three of these are based purely on the Fourier integral phase shift method using the adiabatic approximation. Anderson has observed that diabatic (non-adiabatic) collisions are important in the microwave region. His theory, though more complicated to apply, treats both types of collisions and has good success where reliable tests have been possible.

Line breadths in the microwave spectrum of oxygen were first inferred from fitting the unresolved 5 mm spectrum observed at atmospheric pressures (Strandberg, Meng, and Ingersoll\textsuperscript{16} (1949). These measurements are superceded by measurements on the resolved spectrum at low pressures by Burkhalter, Anderson, Smith, and Gordy, (1950) by Gokhale and Strandberg (1951), and by Anderson, Smith, and Gordy\textsuperscript{60} (1952). There are very sizeable discrepancies between the data of Anderson, et al., and of Gokhale, the latter being generally 50 per cent lower. Also Anderson found a maximum in the breadth near $K = 9$ (where the rotational level occupation number is maximum) which he attributed to rotational resonance. These widths were subsequently remeasured by Artman\textsuperscript{61}, who inferred the width from the calculated integrated intensity and the measured maximum intensity. In general, his data checked that of Anderson, but he failed to find the rotational resonance behavior.

The most recent line breadth measurements of the 5 mm spectrum are those of Hill and Gordy\textsuperscript{42}. They repeated some of the measurements of Anderson, getting satisfactory agreement, and also measured line widths at liquid air temperatures. They interpret their results as confirming the rotational resonance hypothesis mentioned above.

The line breadths in the paramagnetic resonance spectrum reported by Beringer and Castle are invalidated by their use of $\nu/H$ rather than $d\nu/dH$ to infer the meaningful frequency width from the measured width in field units. Thus the apparent remarkable dependence of line width on quantum
numbers which they report is incorrect. Their data when correctly interpreted is in reasonable agreement with the results presented in this thesis. The temperature dependence of $T^{-0.87}$, which they found, is in moderate agreement with that found by Hill and Gordy in the millimeter spectrum. However, it differs from the $T^{-0.75}$ which we find in this thesis and the $T^{-0.627}$ calculated by Artman.
CHAPTER VI
INTERACTION OF ELECTRONIC SPIN WITH EXTERNAL FIELD

A. Eigenvalues

If we define the direction of the external field as the Z direction, then the matrix of our perturbed Hamiltonian is that of

\[ \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{ms} = \mathcal{H}_0 - g_s^e \beta H S_Z \]

where \( g_s^e = -2.00229 \), \( \beta \) is the Bohr magneton, \( H \) is the magnitude of the applied field, and \( \mathcal{H}_0 \) is the field free Hamiltonian treated in Part I. Matrix elements of \( S_z \) in the basis which diagonalizes the field free problem have been given previously (equation (60) and appendix C). Noting that there are \( \Delta K = \pm 2,0 \) as well as \( \Delta J = \pm 1,0 \) elements we find that \( \mathcal{H}_{ms} \) does not factor into smaller submatrices which can be diagonalized exactly. If \( \mathcal{H}_{ms} \) were a rigorous example of Hund's case (b) in which \( K \) is a good quantum number, there would be no \( \Delta K = \pm 2 \) elements and the problem would be factored into \( 3 \times 3 \) submatrices, one for each value of \( K \). This factored form is the starting point taken for further approximations in the treatment of Schmid, Rudó, and Zemplén\(^{47}\), but is completely inadequate for our purposes. Although it is a better approximation, Henry's\(^{49}\) method is also too inaccurate.

The matrix of the complete Hamiltonian has the form:

\[
\begin{pmatrix}
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\vdots & X & X & \cdots & X & \cdots & \cdots \\
\vdots & \cdots & X & \cdots & X & \cdots & \cdots \\
\vdots & \cdots & \cdots & X & \cdots & X & \cdots \\
\vdots & \cdots & \cdots & \cdots & X & \cdots & \cdots \\
\vdots & \cdots & \cdots & \cdots & \cdots & X & \cdots \\
\vdots & \cdots & \cdots & \cdots & \cdots & \cdots & \vdots \\
\end{pmatrix}
\]

(66)

* Our systematic notation is to use superscripts \( e \) and \( n \) to distinguish electronic and nuclear contributions, and we use subscripts \( s, l, r \) for spin, spin-orbit, and rotation. All \( g \)-factors have the appropriate sign so that \( \mathcal{H} = g \beta \mathcal{J} \); e.g., that of the electron is a negative number. To conform to conventional usage we denote the magnetic field by \( H \) but give numerical values in gauss, the units of magnetic induction.
Since the energy separation between rotational levels is large compared to the magnetic perturbation, the dominant effect will come from the elements diagonal in \( K \). The effects of elements which are off-diagonal in \( K \) may be reduced to the diagonal (in \( K \)) by the Van Vleck transformation. The resulting \((J|H|J')\) elements for the effective 3 x 3 Hamiltonian matrix for the \( k \)th rotational level are:

\[
H_{ii} = (K-1|\mathcal{H}|K-1) = -\nu_- (K) - g(k,K-1)M^2 \beta H
+ \left\{ \frac{\Delta_k}{(4K-2)B} - \frac{\Delta_{k-1}}{4K-2} \right\} \left( \frac{3S_5^2}{4K-2} \right)^2 \beta^2 H^2
\]

\[
H_{22} = (K|\mathcal{H}|K) = -g(k,K) \beta H + \frac{A_{k+1}^2 (k^2-M^2)}{(4K+6)B} \left( \frac{3S_5^2}{4K+6} \right)^2 \beta^2 H^2
- \frac{\Delta_k}{(4K+6)B} \left( \frac{3S_5^2}{4K+6} \right)^2 \beta^2 H^2
\]

\[
H_{33} = (K+1|\mathcal{H}|K+1) = -\nu_+ (K) - g(k,K+1)M^2 \beta H
- \left\{ \frac{\Delta_{k+1}}{4K+6} \right\} \left( \frac{3S_5^2}{4K+6} \right)^2 \beta^2 H^2
\]

(67)

\[
H_{i3} = (K|\mathcal{H}|K) = -B_{k+1} \left( \frac{3S_5^2}{4K+6} \right)^2 \beta H - \frac{A_{k+1}^2 (k^2-M^2)}{(4K+6)B} \left( \frac{3S_5^2}{4K+6} \right)^2 \beta^2 H^2
\]

(68)

\[
H_{13} = (K-1|\mathcal{H}|K+1) = 0
\]

The complicated dependence of the elements on parameters makes a straight numerical solution the most attractive procedure.

*To get sufficient accuracy here, we use some energy denominators corrected to first order. This procedure is readily justified if the elements are derived by the method of continued fraction reduction. The error remaining from the reduction is then definitely less than 1 Mc/sec for all cases of interest.
For this purpose, the continued fraction forms are most useful. They are

\[ E_1 = H_{11} - \frac{H_{22}^2}{H_{22} - E_1 - \frac{H_{33}^2}{H_{33} - E_1}} \]

and

\[ E_2 = H_{11} + \frac{H_{22}^2}{E_2 - H_{33}^2} + \frac{H_{33}^2}{E_2 - H_{11}} \]   \hspace{1cm} (69)

The expression for \( E_3 \) is obtained from that for \( E_1 \) by interchange of the subscripts 1 and 3. These equations are exact equivalents of (5) and not a perturbation approximation. If the roots are well-separated, convergence to the desired root on iteration is rapid. If two roots are close together, convergence is slow.

The roots \( E_1, E_2, \) and \( E_3 \) have been evaluated to \( \pm 10 \) Mc/sec at \( H = \frac{1}{2}, 8, \) and 12 kilogauss for most \( M \) states for \( K \leq 13. \) The results have been plotted against \( H \) using graphical interpolation.* Some examples are shown in the accompanying figures. The small \( g \)-factors for \( J = K \) states (roughly \( -2/K(K + 1) \)) make their splittings very small, only three cases being as wide as 9400 Mc/sec for fields under 12 kilogauss. Thus most attention can be concentrated on the \( J = K \pm 1 \) levels. For \( K \geq 3 \) the families of curves are all quite similar. (The \( K = 1 \) curves are simpler since the \( J = 0 \) and \( J = 2 \) levels are widely separated.) For \( H \) less than a few hundred gauss, the splittings closely resemble the linear Zeeman splitting predicted by the field-free \( g \)-factors. (Appendix C) At very high fields the Paschen-Back effect sets in and we approach the limiting case of a completely decoupled spin. Then there must be \( (2K + 1) \) levels corresponding to each of \( M_S = \pm 1, 0. \) That this tendency is observed becomes clear if we note by inspection of the graphs that all the \( (2K + 1) \) levels from \( J = K \) are asymptotically going to \( M_S = 1 \) except the \( M = -K \) level, which goes to \( M_S = 0. \) Similarly the \( (4K + 2) \) sublevels from \( J = K \pm 1 \) provide \( (2K + 1) \) of \( M_S = -1, 2K \) of \( M_S = 0, \) and the single \( M = K + 1 \) sublevel of \( M_S = 1. \) These numbers check the proper limiting behavior.

* The numerical results are tabulated in Appendix D.
Fig. 2: Magnetic splitting of the K+1 energy levels
FIG. 3—MAGNETIC SPLITTING OF THE K+3 ENERGY LEVELS
Fig. 4-- Magnetic splitting of the $K=5$, $J=4,6$ energy levels.
Fig. 5—Magnetic splitting of the K=7; J=6,8 energy levels. Several typical transitions are indicated.
Fig. 6--Magnetic splitting of the K=9; J=8, 10 energy levels.
Even at fields as low as 8 kg. there is a marked tendency for the set of \(N_s = -1\) levels to split off into a bundle of nearly parallel lines of slope equal to \(s_s\theta_s\). In the intermediate region, which is of most interest, we find that characteristic repulsion of levels of the same \(M_s\) and the accompanying strong curvature.

From these curves the approximate values of \(\nu\) for a given resonant frequency \(\nu\) (energy level separation) may be found to an accuracy of about \(\pm 100\) gauss. This is close enough to identify many lines of the spectrum if full use is made of experimental information on \(K\) and \(\Delta M_s\). However, to give a secure identification and to check the theory in detail, each line must be calculated individually.

This was done by computing the position (to \(\pm 0.5\) Mc/sec) of both levels involved in the transition for two values of \(\nu\) separated by 200 gauss and centered about the approximately correct field, determined graphically. If the transition frequency is then expressed as

\[
\nu(\nu) = \nu(\nu_o) + (d\nu/d\nu)(\nu - \nu_o)
\]

(70)

the two calculated points fix \(\nu(\nu_o)\) and \(d\nu/d\nu\). This formula allows the calculated resonant field for any given experimental frequency to be determined to within about \(\pm 0.5\) gauss, since the curvature can be shown to be small over a region of a hundred gauss. The value of \(d\nu/d\nu\) is also necessary to interpret line width measurements at constant frequency and to make corrections for various perturbations to be considered later. The values of \(\nu\) for the experimental \(\nu\), and the value of \(d\nu/d\nu\) at that \(\nu\), are given for many lines of the spectrum in tables VII and IX. (Pages 68 and 71).

B. Eigenvectors

From the form of (66) it is evident that only \(M\) is a good quantum number in the presence of a magnetic field since, in principle, all \(J\)'s and \(K\)'s are mixed. However, the principal mixing is between the three \(J\) values corresponding to one \(K\). The admixture of other \(K\) states is small and could be treated by perturbation theory. In the worst case this amounts to only about a one per cent mixing amplitude even at 10 kg. Since this is too little to have any serious effect on any of our subsequent calculations, we neglect these effects and only compute the
transformation between the field-free and final eigenfunctions within a given $K$ rotational triplet.

This transformation matrix is made up of the eigenvectors of the matrix equation corresponding to (68), and it is written

$$\tau = \begin{pmatrix} \tau \end{pmatrix} = \begin{pmatrix} \tau_1 & \tau_2 & \tau_3 \\ \tau_4 & \tau_5 & \tau_6 \end{pmatrix}$$

$$U_{\tau} = \begin{pmatrix} U_{\tau_1} & U_{\tau_2} & U_{\tau_3} \\ U_{\tau_4} & U_{\tau_5} & U_{\tau_6} \end{pmatrix}$$

(71)

In this, $\tau$ denotes the new eigenfunctions but signifies no constant of the motion except the energy. The elements $U_{\tau \tau'}$ are defined by

$$\frac{U_{\tau \tau'}}{U_{\tau \tau}} = \frac{E_{\tau} - H_{uu}}{H_{uu}} \quad \frac{U_{\tau \tau'}}{U_{\tau \tau}} = \frac{H_{uu}}{E_{\tau} - H_{uu}}$$

(72)

and normalization.

Examples are plotted in Figures 7a and 7b showing two typical cases.

In Figure 7a we see the distortion of the $K = 3$, $M = 0$ state which starts as $J = 2$ at zero field. At a field of 6 kg the amplitude of $J = 4$ has risen to 0.35 and that of $J = 3$ has risen to 0.24. These figures show the substantial breakdown of $J$ as a quantum number under a magnetic field. This makes all $\Delta M = \pm 1, 0$ transitions "allowed", regardless of the principal or original value of $J$, provided the field is moderately strong. We will later see that the majority of the observed X-band transitions are of this field-allowed type. Figure 7b shows the more unusual case of two levels which attempt to cross each other, but instead repel. At the point of closest approach the J's are completely mixed, and as the levels move apart again, the dominant J's are found to have interchanged. Since the strong mixing dies out rapidly, there is seldom any doubt as to which $J$ is dominant in an eigenstate for a given field. We will use "$J$" in this sense throughout the paper rather than use the less suggestive $\tau$ notation introduced for the purpose of setting up the transformations $U$.

The correct sense of $J$ will always be clear from the content.

Numerical values for the transformation coefficients for a number of cases required in later parts of the calculation are tabulated in appendix E. Inspection of this table shows how universal is the large degree of mixing.
Fig. 7a-- Mixing coefficients of the J components in the lower K=3, M=0 state.

Fig. 7b-- Mixing coefficients of the J components in the lower K=3, M=-1 state.
CHAPTER VII

CORRECTIONS FOR ROTATIONAL MAGNETIC MOMENT AND ELECTRONIC ORBITAL MAGNETISM

When the results of the calculations of Chapter VI are compared with experiment (Tables VII and IX), a systematic discrepancy of the order 0.1 per cent is obvious. Since this was far beyond the expected error of either theory or experiment, it was assumed to be caused by neglect of these corrections. When the corrections treated in this section are made, the agreement is within the accuracy of the experiment and calculations, namely of the order ± 50 ppm.

The straightforward and universally sound method of handling perturbative terms of this sort is simply to write down all matrix components of the energy in a convenient basis and then to eliminate the elements which are off-diagonal in electronic quantum numbers by the Van Vleck transformation\(^{36}\). For a case as simple as the diatomic molecule which we treat, however, the same results can be obtained without complication by using a short cut method which gives a much clearer picture of the physical nature of the interactions. This second approach is followed here. Either method yields an effective Hamiltonian matrix only involving fine structure quantum numbers. The lowest order contributions to the energy are then found by application of the transformation (within the fine structure levels) which diagonalizes the Hamiltonian \( \mathcal{H}_0 + \mathcal{H}_{\text{ms}} \).

In Part I we noted that the spin-orbit coupling and the rotation-electronic interaction mixed \( \Pi \) states into the \( \Xi \) electronic orbital state as follows:

\[
\psi_{\xi} = \psi^0_{\xi} - \sum_{n=\pi} \sum_{q=x,y} \frac{(n|AL_{q'|0})S_{q'} - (n|2B_{q'|0})K_{q'} E_n - E_o}{E_n - E_o} \psi^0_{\eta} \tag{73}
\]

The first order electronic orbital angular momentum along the gth gyrating axis is then seen to be

\[
L_g = - \sum_{n,g'} \frac{(0|L_g|n)(n|AL_{q'|0})S_{q'} + \text{compl. conj.}}{E_n - E_o} + \sum_{n,g'} \frac{(0|L_g|n)(n|2B_{q'|0})K_{q'} + \text{compl. conj.}}{E_n - E_o}
\]
\[ L_g = - (g^e L^e_{12} + g^e \kappa_3)(1 - S_{12}^2) \]  

(74)

where

\[ g^e_{12} = 2 R^e \sum \frac{(0 \leftarrow \eta)(\eta \leftarrow AL_x \leftarrow 0)}{E^\eta - E^0} \]

and

\[ g^e_r = -4 R^e \sum \frac{(0 \leftarrow \eta)(\eta \leftarrow BL_x \leftarrow 0)}{E^\eta - E^0} \]  

(75)

In making this reduction we have used the facts that with axial symmetry the elements of \( L_x \) and \( L_y \) differ only by a phase of \( \pm i \) (equation (26)) and that elements of \( L_z \) vanish for a \( \Sigma \) state. In the general case of lower symmetry the \( g \)'s are not just diagonal tensors, but have the structure \( (g^e_{r,gg'}) \), for example. Then \( L_g \) would be a sum of terms over \( g' \).

The general case of rotation-induced moments has been treated in detail by Eshbach and Strandberg.\(^{54}\)

To obtain the interaction of this electronic orbital angular momentum with the external field, we project it onto the space-fixed \( Z \) axis by using the direction cosine matrix elements \( \Phi_{Zg} \). (See Appendix B.)

\[ L_Z = \sum_3 \Phi_{Zg} L_g \]  

(76)

For our case, the matrix elements of this product operator which are diagonal in electronic quantum numbers between total state functions whose electronic part is (73) may be shown (Appendix F) to be the same as those obtained by simply taking the product of the diagonal elements of \( L_g \) given in (74) and the elements of \( \Phi_{Zg} \) for the case \( \Lambda = 0 \). These \( \Phi_{Zg} \) elements are the same as those used in Part I to project \( S_g \) onto \( Z \). Combining (74) & (76),

\[ L_Z = -g^e_{12} \sum_{g=x,y} \Phi_{Zg} S_g - g^e_r \sum_{g=x,y} \Phi_{Zg} \kappa_g \]  

(77)

\[ = -g^e r \sum_{g=x,y} \Phi_{Zg} S_g - g^e r \kappa_Z \]

The second sum may be extended to include \( g = z \) because \( \kappa_z \) is zero. This is more convenient since it gives rise to the simple expression \( \kappa_z \). Noting
that \( S_\perp \) and \( S_\parallel \) are purely off-diagonal in \( \mathbf{z} \), whereas \( S_z \) is purely diagonal, we can write (77) as

\[
(\mathcal{J} M \mathbf{z} | L | \mathbf{z}' J' M \mathbf{z}') = -g^e_s (\mathcal{J} M \mathbf{z} | \mathbf{z} | J' M \mathbf{z}') - (1 - \delta_{z z'}) g^e_s (\mathcal{J} M \mathbf{z} | S_z | J' M \mathbf{z}')
\]

Before computing the effect of this electronic orbital angular momentum on the magnetic energy, let us note that the magnetic moment of the rotating nuclei in a homonuclear diatomic molecule is simply

\[
\mathbf{\mu}^n = g^r_s m \beta \mathbf{K} \equiv g^r_s \beta \mathbf{K}
\]

Again, the general asymmetric top has been treated by Eshbach and Strandberg\(^{54}\). If we combine this with the electronic rotation-induced moment \( g^e_s \beta \mathbf{K} \), we have a total rotational moment

\[
\mathbf{\mu}_r = \mathbf{\mu}^n + \mathbf{\mu}^e = (g^r_s + g^e_s) \beta \mathbf{K} = g_s \beta \mathbf{K}
\]

We now compute the energy contributed by the interaction of this total rotational moment with the external field. It is

\[
\mathcal{H}_{mr} = -g_s \beta H \mathbf{K} \mathbf{z} = -g_s \beta H (M - S_z)
\]

\( M \) is, of course, a known good quantum number. To get the diagonal value \( \langle S_z \rangle \) in the desired state, as perturbed by the interaction of the spin moment with the external field, we note that

\[
E_m = \langle \mathcal{H}_0 \rangle_m - g_s^z \beta H \langle S_z \rangle_m
\]

Thus to first order:

\[
\langle S_z \rangle_m = \frac{-1}{g_s^z \beta} (\partial E/\partial H)_m
\]

The total energy shift caused by the rotational moment is then

\[
\langle \mathcal{H}_{mr} \rangle_m = -g_s \beta H \left[ M + \frac{1}{g_s^z \beta} (\partial E/\partial H)_m \right]
\]

* It might appear anomalous that this argument does not also apply to eliminate \( (\mathbf{z} | \mathbf{z}') \) elements of \( \mathbf{K}_m \). The reason is that \( \mathbf{K} \) and \( \mathbf{K} \) both operate in the relative coordinate domain, making \( \mathbf{z} | \mathbf{z} \) a true matrix product in which \( (\mathbf{z} | \mathbf{z}') \) elements are generated from the \( (\mathbf{z} | \mathbf{z}') \) \( (\mathbf{z} | \mathbf{z}') \) elements. Since \( \mathbf{S} \) operates only on internal coordinates, in the case of \( \mathbf{S} \) we have a simple product and no such elements can be generated.
Accordingly, the change in frequency for a transition from $M'\rightarrow M + \Delta M$ is

$$
\Delta v_r = <\mathcal{H}_{m'r} >_{M + \Delta M} - <\mathcal{H}_{m'r} >_M = -3 \varepsilon \beta H \left( \Delta M + \frac{1}{3} \frac{d \nu}{d H} \right)
$$

(84)

where $d \nu/d H = d (E_M + \Delta M - E_{M'})/d H$ is known from previous calculations (equation 70). The corresponding change in $H$ required to maintain the fixed experimental resonance frequency is

$$
\Delta H_r = \frac{g_r}{g_s} \left( \frac{3 \varepsilon \beta \Delta M }{d \nu/d H} + 1 \right)
$$

(85)

Let us now take account of the energy of the spin-orbit induced orbital angular momentum in (78). From that equation

$$
(JM \Sigma | \mathcal{H}_{m'\Sigma} | J'M \Sigma \pm 1) = -g_s \beta H (JM \Sigma | S_z | J'M \Sigma \pm 1)
$$

(86)

All other elements vanish. This clearly has a different form from the rotational interaction (81) or from the principal spin interaction $\mathcal{H}_{ms}$. Thus all three will be experimentally separable. The first step in evaluating the contribution of (86) to the energy is to find the transformed elements in the basis which diagonalized the field-free Hamiltonian $\mathcal{H}_0$. This is done by using the transformation matrices $T_J$ in the method of equation (59). However, the results differ somewhat from equation (60) since the $(E|\mathcal{H}_{m'\Sigma}| E)$ elements vanish. This transformed matrix $(KWM | \tilde{\mathcal{H}}_{m'\Sigma} | K'J'M)$ has elements $K' = K, K \pm 2$ and $J' = J, J \pm 1$. For the reasons given in section VI-B, we may neglect all except $K' = K$ elements. These are written as $(J | \mathcal{H}_{m'\Sigma} | J')$ in the following:

$$
\mathcal{H}_0 = -(K-1 | \mathcal{H}_{m'\Sigma} | K-1) = -g_s \beta H (-4 \alpha_{K-1} c_{K-1} M)[K(K-1)]^{1/2}
$$

$$
\mathcal{H}_{0,0} = (K | \mathcal{H}_{m'\Sigma} | K) = 0
$$

$$
\mathcal{H}_{0,2} = (K+1 | \mathcal{H}_{m'\Sigma} | K+1) = -g_s \beta H (4 \alpha_{K+1} c_{K+1} M)[(K+1)(K+2)]^{1/2}
$$

$$
\mathcal{H}_{1,2} = (K-1 | \mathcal{H}_{m'\Sigma} | K) = -g_s \beta H \alpha_{K-1} \left[ \frac{2(K+1)(K^2-M^2)}{K(4K^2-1)} \right]^{1/2}
$$

$$
\mathcal{H}_{1,3} = (K-1 | \mathcal{H}_{m'\Sigma} | K+1) = 0
$$

$$
\mathcal{H}_{2,3} = (K | \mathcal{H}_{m'\Sigma} | K+1) = -g_s \beta H \left\{ \frac{2K}{(K+1)} \left[ \frac{(K+1)^2-M^2}{4(K+1)^2-1} \right] \right\}^{1/2} c_{K+1}
$$
with the special case

\[(1,0,0|H_{m^2}|1,1,0) = \frac{2}{3} \beta H \left[ \frac{2(1-m^2)}{3} \right]^{1/2} \]

In these, \(a_j\) and \(c_j\) are the transformation elements of \(T_j\) given in Table V of Part I. They are both approximately 1/2 for all \(j\).

From these elements we may note that the magnitude of the \(g\)-factors (diagonal elements) of the \(J = K + \frac{1}{2}\) levels are increased by roughly the fraction \(g_s^e/g_s^e\), whereas those of the \(J = K\) levels are unchanged. The off-diagonal elements are also increased, but in a different ratio. From these observations it is clear that if \(g_s^e/g_s^e\) is positive (as it turns out to be), this interaction will tend to shift the resonance to lower fields. However, to investigate the effect rigorously we must transform \((J|H_{m^2}|J')\) to the basis which diagonalizes \(H_{ms} + H_c\). This is done with the transformation \(U\) given in Chapter VI. The result is

\[
(\tau|H_{m^2}|\tau) = (U^* H_{m^2} U)_{\tau \tau}
\]

\[
= U_{1\tau}^2 H_{11} + 2 U_{1\tau} U_{2\tau} H_{12} + 2 U_{2\tau} U_{3\tau} H_{23} + U_{3\tau}^2 H_{33}
\]

(88)

The shift in the calculated magnetic field to maintain the same resonant frequency is then

\[
\Delta H = -\frac{d}{dH} \left[ (\tau'|H_{m^2}|\tau') - (\tau|H_{m^2}|\tau) \right]
\]

(89)

In view of the difficulty of making these corrections, they have only been computed for 27 examples. These results are tabulated in table VII and IX in the next Chapter. Clearly the agreement with experiment is excellent.
CHAPTER VIII

COMPARISON OF PREDICTED PARAMAGNETIC RESONANCE SPECTRUM WITH EXPERIMENT

A. Experimental Method

Since the apparatus used will be described more fully in Chapter XII, only a brief sketch is given here. The microwave arrangement uses a Pound-Zaffarano feedback circuit to stabilize the klystron frequency to the resonant frequency of the cavity containing the oxygen gas sample. This cavity is situated between the poles of a magnet, the field of which is monitored by a flip coil. This flip coil voltage is compared with a controllable fraction of the output of a small reference generator driven by the same shaft. The error signal is used in a feedback circuit to stabilize the field. The field is then slowly swept by using a geared down synchronous motor to vary the helipot which controls the comparison voltage. The stability is to within a fraction of a gauss.

Upon this slowly sweeping field is superposed a 50 cps modulation, adjustable from 0 to 80 gauss peak to peak. It also is feedback stabilized to eliminate phase and amplitude shifts with changing d-c fields and hence changing properties of the iron core. Provided the modulation amplitude is small compared to the line width, this will produce a 50 cps component proportional to \(d\chi'/dH\) (the derivative of the imaginary part of the susceptibility) in the power absorbed in the gas, and hence in the reflection or transmission coefficient of the cavity. This modulated microwave power is detected with a crystal (or bolometer). The resulting 50 cps signal is amplified in a low-noise amplifier and converted to d-c in a phase-sensitive detector which uses a Brown converter as the synchronous device. The output is recorded on a strip chart recorder. A block diagram of the apparatus is given in Fig. 8. The bolometer bridge is of course, absent when a crystal detector is used. This was the case for all measurements except those of absolute intensity.

All precise measurements of the magnetic field are made using proton resonance, the frequencies being measured with a BC-221 frequency meter accurate to \(\pm 40\) ppm by comparison with the M.I.T. frequency standard. The flip coil arrangement gives readings accurate to a few gauss under normal operating conditions. Precise frequency measurements were made by beating
Fig. 5—Block diagram of apparatus
the klystron frequency with harmonics of the M.I.T. frequency standard. Other frequency measurements were made using a calibrated wavemeter.

The X-band measurements were made using three different cavities. A $\text{TE}_{011}$ cylindrical cavity with a $Q$ of the order 35,000 was used for the highest sensitivity exploration. A much smaller $\text{TE}_{011}$ rectangular cavity was used for the precise measurements to minimize errors due to field inhomogeneity by allowing smaller pole separations. Finally, a $\text{TE}_{111}$ cylindrical cavity was used in conjunction with special microwave plumbing to produce a circularly polarized radiation field in the cavity. This field is set up by exciting the two degenerate orthogonal modes $90^\circ$ out of phase. This field configuration gives pure circularly polarized radiation only along the axis. (The fact that $\mathbf{\nabla} \cdot \mathbf{\mathbf{H}} = 0$ makes this true for any configuration. With $\text{TM}$ modes the energy would be equally divided between the two circular senses when averaged over the entire cavity.) Averaging $\mathbf{H}^2$ over the cavity, 52 per cent is circular in one sense, 4 per cent is circular in the other, and 44 per cent is axial. Comparison of the spectra observed with the two senses of rotation relative to the static magnetic field unambiguously separates $\Delta M = \pm 1,0$ transitions.

The rotational quantum number $K$ of the states involved in a transition can be determined by a comparison of the relative signal strengths of various lines at room temperature and at $78^\circ$K, if we note that the Boltzmann factor is given by $\exp(-\Delta K / K T)$, and if we assume that all line widths change in the same proportion. The well-known difficulty of making reproducible intensity measurements and the approximate nature of the above assumption limit the accuracy of this determination to a mean deviation in $K$ from the true value of roughly .8. Since only odd integral values of $K$ are allowed, this still gives a very useful restriction.

The S-band measurements were made using a $\text{TM}_{010}$ cylindrical transmission cavity fed through 7/32" coaxial line. In the Pound-Zaffarano circuit a hybrid ring ("rat race") was used in place of the magic Tee used with the X-band waveguide arrangement.

B. Experimental Results

Table VII shows the results of the precise measurements and calculations for 36 X-band lines. The experimental field values should be accurate to
roughly ± 60 ppm. (The last two readings at highest fields had to be made with the flip coil since the field exceeded the range of our proton probe.) In the second column are given the values of $H$ for resonance if only $\gamma_{ms}$ were effective. The next two columns give the corrections $\Delta H_x$ and $\Delta H_y$ calculated with (85) and (89). In making the corrections there are two parameters, $g_x$ and $g_y$. These were fitted by least squares (omitting the inaccurate high field line) with the results that $g_x = -(1.42 \pm .22) \times 10^{-4}$ and $g_y = -(2.94 \pm .05) \times 10^{-3}$. The residual errors are tabulated both in field and frequency units. These are of course related by the $\partial y/\partial H$ factor tabulated in a later column. The agreement is well within the accuracy of the calculation and measurement of $H$.

Since the accurate calculation of even the uncorrected $H$ is very tedious, it was desirable to try to identify as many of the other lines observed as possible by other means. In table VIII we list the positions of 24 additional lines (at X-band, but at 9430 Mc/sec rather than the 9476.75 Mc/sec of table VII). For each of them we list the $K$ determined from the temperature dependence of the relative intensity and the $\Delta M$ determined by use of circular polarization. When these data in conjunction with the graphical plots of $E(H)$ mentioned in Chapter VI permitted a reasonably secure identification, the complete specification of the transition is given. In this manner, an additional 37 lines were identified.

We note that a majority of the transitions are ones in which "J" changes. These are allowed in the presence of the magnetic field and theoretical intensities will be calculated in a subsequent section. Henry's failure to consider the possibility of transitions of this sort accounts for his ability to identify only 6 lines of the total of 41 observed by Beringer and Castle. The superior sensitivity of our sweep technique to the point-by-point technique of Beringer and Castle is demonstrated by our ability to measure 120 lines in the spectrum. The weakest observable lines are over a hundred fold weaker than the strongest lines of the spectrum at room temperature, and the range is 1000:1 at 78°K.

In table IX are listed the results of exact calculations for 34 S-band (2987 Mc/sec) lines and the corresponding experimental values. This table corresponds exactly to the X-band results in table VII. Because of the
uncertainty in the magnetic field over the large S-band cavity, these results are not as reliable as the X-band data. However, the magnitudes of the $\Delta H_x$ corrections are enough larger to provide some additional check on the choice of $g_r$. To give somewhat better agreement here, the value chosen was shifted from $-(1.42 \pm .22) \times 10^{-4}$ to $-(1.35 \pm .30) \times 10^{-4}$. This of course leaves the X-band agreement essentially unchanged.

Table IV lists the positions and signal amplitudes of 43 more S-band lines. Since neither $K$ nor $\Delta M$ was determined experimentally, it was impossible to identify any of these from the $E(H)$ curves.

Table VII. Results on Precisely Measured X-band Lines

(Table given on following page)

The first column gives the observed magnetic field for resonance at the experimental frequency 9476.75 Mc/sec. The second column gives the resonance field calculated on the assumption that only the electronic spin moment is present. The spin-orbit correction $\Delta H_x^e$ was made using the value $g_\perp^e = -.00294$ determined by a least squares fit. The correction for rotation-induced magnetic moment $\Delta H_x^r$ was made using $g_r = -0.25$ m/M. The values of $d\nu/dH$ give the rate of change of the resonance frequency with field in the vicinity of the observed values $H, \nu$. The calculated intensity factors listed in column 8 are the values of $4|\langle K|M|S_X|K'M'\rangle|^2 \exp -BK(K + 1)/kT$ at $T = 300^\circ K$. The experimental results are signal strengths at optimum modulation expressed in arbitrary units. Provided the frequency widths of all lines are essentially equal, the latter should be proportional to the calculated (integrated) intensities.
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<th>calc. H (gauss)</th>
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<th>δHᵣ</th>
<th>δH (gauss)</th>
<th>Jₚ</th>
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TABLE VIII

Survey of Other X-band Lines at 9430 Mc/sec

The accuracy of H is roughly ± .05 per cent unless stated to the contrary. K was determined from the temperature dependence of the intensity. ∆M was determined by use of circular polarization. Then an attempt was made to identify lines completely by using a graphical plot of E(H). If this failed, M was recorded as (+) or (−) accordingly as ∆M = +1 or −1. The signal strength has the same scale factor as in the table of precisely measured lines.

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<td>8+6 −1−2</td>
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</tr>
<tr>
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<td>(−)</td>
</tr>
<tr>
<td>H (exp.)</td>
<td>K</td>
<td>J</td>
</tr>
<tr>
<td>---------</td>
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<td>---</td>
</tr>
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</tr>
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<td>&lt;.06</td>
</tr>
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<td>8163</td>
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<td>8178</td>
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</tr>
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<td>8359</td>
<td>7-9</td>
<td>(-)</td>
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<tr>
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<td>8672</td>
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<td>8663</td>
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<td>(-)</td>
</tr>
<tr>
<td>8934</td>
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<td>10</td>
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<tr>
<td>9017</td>
<td>(+)</td>
<td>.11</td>
</tr>
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<td>(+)</td>
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<td>9150</td>
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<td>9200</td>
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<td>9238</td>
<td>15</td>
<td>(+)</td>
</tr>
<tr>
<td>11390±50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11990±50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12090±50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12870±50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE IX

Identified Lines of the S-band Spectrum

The first column gives the observed magnetic field for resonance at the experimental frequency of 2987.0 Mc/sec. Limits of error are estimated to be ±0.06 per cent. The other columns have the same significance as in the X-band table. The "signal amplitudes" are simply proportional to the deflections in a sweep made with constant amplitude magnetic field modulation.

<table>
<thead>
<tr>
<th>M</th>
<th>J</th>
<th>K</th>
<th>ΔH</th>
<th>ΔH_x</th>
<th>ΔH_y</th>
<th>ΔH_z</th>
<th>ΔH_0</th>
<th>ΔH_1</th>
<th>ΔH_2</th>
<th>ΔH_3</th>
<th>ΔH_4</th>
<th>ΔH_5</th>
<th>ΔH_6</th>
<th>ΔH_7</th>
<th>ΔH_8</th>
<th>ΔH_9</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>a</td>
<td>a</td>
<td>0.4</td>
<td>0.8</td>
<td>1.0</td>
<td>0.3</td>
<td>0.6</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
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<td>4</td>
<td>4</td>
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<td>1.0</td>
<td>1.0</td>
<td>0.3</td>
<td>0.6</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>6</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.3</td>
<td>0.6</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
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<td>8</td>
<td>8</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.3</td>
<td>0.6</td>
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<td>0.3</td>
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<td>1.0</td>
<td>1.0</td>
<td>0.3</td>
<td>0.6</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>
TABLE X

Survey of Other S-band Lines

The first column gives the observed magnetic field for resonance at the experimental frequency of 2987.0 Mc/sec. The limit of error is estimated to be \( \pm 0.06\% \). The signal amplitude column has the same significance as in the other S-band table.

<table>
<thead>
<tr>
<th>( H (\text{exp.}) ) (gauss)</th>
<th>Signal Amplitude</th>
<th>( H (\text{exp.}) ) (gauss)</th>
<th>Signal Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>2493</td>
<td>.1</td>
<td>6421</td>
<td>.15</td>
</tr>
<tr>
<td>2743</td>
<td>.1</td>
<td>6481</td>
<td>.2</td>
</tr>
<tr>
<td>2826</td>
<td>.05</td>
<td>6827</td>
<td>.3</td>
</tr>
<tr>
<td>3159</td>
<td>.2</td>
<td>6937</td>
<td>.2</td>
</tr>
<tr>
<td>3187</td>
<td>.08</td>
<td>7047</td>
<td>.15</td>
</tr>
<tr>
<td>3398</td>
<td>.2</td>
<td>7083</td>
<td>.15</td>
</tr>
<tr>
<td>3423</td>
<td>.3</td>
<td>7281</td>
<td>.3</td>
</tr>
<tr>
<td>3440</td>
<td>.3</td>
<td>7320</td>
<td>.15</td>
</tr>
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<td>3529</td>
<td>.2</td>
<td>7748</td>
<td>.1</td>
</tr>
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<td>3587</td>
<td>.1</td>
<td>7828</td>
<td>.3</td>
</tr>
<tr>
<td>3608</td>
<td>.15</td>
<td>7987</td>
<td>.1</td>
</tr>
<tr>
<td>3830</td>
<td>.2</td>
<td>8010</td>
<td>.2</td>
</tr>
<tr>
<td>4086</td>
<td>.08</td>
<td>8318</td>
<td>.1</td>
</tr>
<tr>
<td>4322</td>
<td>.06</td>
<td>8401</td>
<td>.2</td>
</tr>
<tr>
<td>4339</td>
<td>.06</td>
<td>8450</td>
<td>.1</td>
</tr>
<tr>
<td>4436</td>
<td>.2</td>
<td>8485</td>
<td>.1</td>
</tr>
<tr>
<td>4456</td>
<td>.08</td>
<td>8576</td>
<td>.15</td>
</tr>
<tr>
<td>4493</td>
<td>.2</td>
<td>8612</td>
<td>.15</td>
</tr>
<tr>
<td>4522</td>
<td>.35</td>
<td>8750</td>
<td>.15</td>
</tr>
<tr>
<td>4713</td>
<td>.3</td>
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<td>.15</td>
</tr>
<tr>
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<td>9090</td>
<td>.15</td>
</tr>
<tr>
<td>4819</td>
<td>.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER IX

DISCUSSION OF RESULTS

In table XI we collect parameters of the oxygen molecule which have become known or made more precise as a result of the work described in this thesis. The system of interrelations which enable these to be determined from the experimental data and compared with the theory are discussed in this section.

A. Source of Results

Direct Experimental Results

The spin coupling constants \( \lambda(0) \), \( \lambda(1) \), \( \lambda_1 \) and \( \mu \) were determined directly by fitting the field-free spectrum with the theoretical formulae derived in Part I. The quantities \( \phi_e \) and \( \phi_2 \) follow immediately from the theory presented there, and may be considered on firm ground. Similarly, \( g_\tau \) and \( g_e \) were determined by fitting the microwave spectrum in the presence of a magnetic field, under the assumption that \( g_e = -2.00229 \). On these quantities the quoted errors are the expected standard errors in a least-squares fit.

Derived Results

To separate the various physical mechanisms contributing to the parameters, we use the assumption (discussed in Part I) that the spin-orbit coupling parameter \( B \) and the reciprocal moment of inertia \( I \) can be treated as constants in the sums of matrix components which enter in the theory. Denoting the common factor \( \sum_{n=0}^{\infty} \left| \langle 0 | L_\parallel | n \rangle \right|^2 / E_n - E_0 \) by \( L(L+1)/\hbar \), and taking \( B = 1.44 \text{ cm}^{-1} \), one may readily deduce values for \( \lambda_0', \lambda_0'', \mu', \mu'', \lambda, L(L+1)/\hbar \), \( \chi_{H-F} \), and \( R_e \) (as corrected for electronic contributions to \( B \)) from the above direct experimental results. These results are also tabulated. The quoted errors reflect only the errors in the direct experimental results. No attempt has been made to allow for the error introduced by our theoretical assumption.

Calculated Results

Finally, we also list the values for \( \lambda_0', \lambda_1', \mu', \) and \( \chi_{\text{dia}} \) which were obtained by direct calculation using Meckler's expression for the molecular oxygen wave function. The method of calculation of \( \lambda' \) and \( \mu' \) was given in Chapter II. No limit of error was assigned to these quantities for lack of any sound manner of estimation.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Explanation</th>
<th>Experimental</th>
<th>calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_e$</td>
<td>$\lambda_{\text{eff}}(\nu = 0)$</td>
<td>59,501.57±.15 Mc/sec</td>
<td></td>
</tr>
<tr>
<td>$\lambda_{1}$</td>
<td>$\lambda_{\text{eff}}(\nu = 1)$</td>
<td>59,730±40 Mc/sec</td>
<td></td>
</tr>
<tr>
<td>$\lambda_{e}^{s}$</td>
<td>$\lambda_{e}^{s} + \lambda_{e}^{n}$</td>
<td>59,386±20 Mc/sec</td>
<td></td>
</tr>
<tr>
<td>$\lambda_{e}^{s}$</td>
<td>spin-spin part</td>
<td>58,920±60 Mc/sec</td>
<td></td>
</tr>
<tr>
<td>$\lambda_{1}$</td>
<td>$\left[ R(d\lambda/d\alpha) \right]_{e}$</td>
<td>465±50 Mc/sec</td>
<td></td>
</tr>
<tr>
<td>$\lambda_{1}^{s}$</td>
<td>$\left[ R(d\lambda/d\alpha) \right]_{e}$</td>
<td>16,896±150 Mc/sec</td>
<td></td>
</tr>
<tr>
<td>$\lambda_{2}$</td>
<td>$\frac{1}{2} \left[ R^2 d^2 \lambda / d\alpha^2 \right]_{e}$</td>
<td>(5±2)x10^4 Mc/sec</td>
<td></td>
</tr>
<tr>
<td>$\mu^{s}$</td>
<td>$\mu^{s} + \mu^{n}$</td>
<td>-252.67±.05 Mc/sec</td>
<td></td>
</tr>
<tr>
<td>$\mu^{n}$</td>
<td>spin-nuclear part</td>
<td>1±4 Mc/sec</td>
<td></td>
</tr>
<tr>
<td>$g_{x}^{e}$</td>
<td>$\frac{4}{3} \sum_{n} \frac{(C</td>
<td>AL_{x}</td>
<td>n)(n</td>
</tr>
<tr>
<td>$g_{s}^{e}$</td>
<td>$\frac{2}{3} \sum_{n} \frac{(0</td>
<td>L_{x}</td>
<td>n)(n</td>
</tr>
<tr>
<td>$g_{r}$</td>
<td>$g_{r}^{s} + g_{r}^{e}$</td>
<td>-(1.35±.30)x10⁻⁴ = -(2.5±.05)m/M</td>
<td></td>
</tr>
</tbody>
</table>

As explained in the text, the quoted errors are standard errors based on least squares fits of the experimental data. They include no estimates of the theoretical errors in assumed interrelations and thus are not necessarily limits of error.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Explanation</th>
<th>Numerical Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_r^n$</td>
<td>$(Z/A) (m/M)$</td>
<td>$2.72 \times 10^{-4} = 0.500m/M$</td>
</tr>
<tr>
<td>$g_r^e$</td>
<td>$-4 \text{ Re} \sum_n \frac{(0</td>
<td>L_x</td>
</tr>
<tr>
<td>$R_e$</td>
<td></td>
<td>$1.20741 \pm 0.00002$ A.</td>
</tr>
<tr>
<td>$\frac{L(L+1)}{h \nu}$</td>
<td>$\sum_n \frac{</td>
<td>(0</td>
</tr>
<tr>
<td>$\chi_{\text{dia}}$</td>
<td>Spin-orbit coupling parameter</td>
<td>$-(21 \pm 2)$ cm$^{-1}$</td>
</tr>
<tr>
<td>$\chi_{\text{dia}}$</td>
<td>$\frac{-N_0 e^2}{6mc^2} \sum_i \chi_i$</td>
<td>$-29.5 \times 10^{-6}$ cm$^3$/mole</td>
</tr>
<tr>
<td>$\chi_{\text{H-F}}$</td>
<td>$\frac{4N_0 \beta^2}{3} \sum_n \frac{</td>
<td>(0</td>
</tr>
<tr>
<td>$\chi_{\text{orb}}$</td>
<td>$\chi_{\text{dia}} + \chi_{\text{H-F}}$</td>
<td>$-(4.9 \pm 1.7) \times 10^{-6}$ cm$^3$/mole</td>
</tr>
<tr>
<td>$\chi_{\text{spin}}$</td>
<td>$2N_0 (g_r^e)^2 \beta^2/3kT$</td>
<td>$1.003/T$ cm$^3$/mole</td>
</tr>
</tbody>
</table>
B. Discussion of Individual Results

The Rotational Moment

A key to unraveling the entire problem experimentally was the fact that our precise Zeeman effect measurements and theory have allowed us to determine the rotational g-factor $g_r$ defined in equation (80). Admittedly, the measurement is not of high accuracy since it is based on small shifts superposed on the enormously larger splittings caused by the full Bohr magnetons of electron spin moment. Still, there is enough data to give reasonable assurance.

The magnitude and even the sign of $g_r$ are rather unexpected. It is well-known that in $H_2$ the electrons make almost no contribution to $g_r$, leaving $g_r^H = +0.883m/M = 0.883 \frac{g}{n}$. As another example, OCS has $g_r = -0.25m/M$. There appear to be no examples of so large a negative g-factor as the $-0.25m/M$ which we find in $O_2$ in any of the molecules previously studied.

It is of interest to compare the oxygen result with the resulting moment if the electronic charge cloud merely rotated rigidly with the nuclei. One can readily show that in this case, we have

$$g_r = \frac{g_r^n + g_r^e}{A} = \frac{3}{A} \left( \frac{x_i^2 + y_i^2}{(R/a)^2} \right)$$

where $z$ is the internuclear axis and $R$ is the internuclear distance. These one electron averages $\langle x_i^2 + y_i^2 \rangle$ are readily carried out using Meckler's molecular orbitals made up of Gaussian atomic orbitals. A simple integration shows that these Gaussian AO's have a value of $\langle r^2 \rangle$ which agrees with that of the Hartree-Fock atomic wave function within 10 per cent. This indicates that for a calculation of this type Meckler's MO's should give reasonably close approximations to the true values. The results are given in table XII for each orbital. If we assumed that the electrons in all orbitals moved rigidly with the molecule, the resultant $g_r^e$ would be $-0.75m/M$ and $g_r$ would be $-0.25m/M$. This only slightly exceeds the experimental value. The agreement would still be within the experimental error and the error due to the wave functions if one assumed that the 8 inner 1s and 2s electrons moved with unhindered precession about their nuclei, simply cancelling nuclear charge, while
TABLE XII

Integrals Over Oxygen Molecular Orbitals

The occupation numbers apply to the lowest energy configuration (Meckler's $\phi_c$). $R$ is the internuclear distance, $z$ is the internuclear axis, and $r$ is measured from the center of mass of the molecule.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Meckler Notation</th>
<th>occupation number</th>
<th>$\left\langle x^2 + z^2 \right\rangle / (R/2)^2$</th>
<th>$&lt;r^2&gt; \times 10^{-16}$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s $\sigma_g$</td>
<td>$\Phi_z$</td>
<td>2</td>
<td>1.02</td>
<td>.375</td>
</tr>
<tr>
<td>1s $\sigma_u$</td>
<td>$\chi_z$</td>
<td>2</td>
<td>1.02</td>
<td>.375</td>
</tr>
<tr>
<td>2s $\sigma_g$</td>
<td>$\Phi_\sigma$</td>
<td>2</td>
<td>1.36</td>
<td>.585</td>
</tr>
<tr>
<td>2s $\sigma_u$</td>
<td>$\chi_\sigma$</td>
<td>2</td>
<td>1.69</td>
<td>.710</td>
</tr>
<tr>
<td>2p $\sigma_g$</td>
<td>$\Phi_\pi$</td>
<td>2</td>
<td>1.96</td>
<td>.800</td>
</tr>
<tr>
<td>2p $\sigma_u$</td>
<td>$\chi_\pi$</td>
<td>0</td>
<td>2.62</td>
<td>1.038</td>
</tr>
<tr>
<td>2p $\pi_u^Z$</td>
<td>$\Phi_\pi$</td>
<td>4</td>
<td>1.61</td>
<td>.760</td>
</tr>
<tr>
<td>2p $\pi_g^Z$</td>
<td>$\chi_\pi$</td>
<td>2</td>
<td>1.87</td>
<td>.855</td>
</tr>
</tbody>
</table>
the 8 outer 2p electrons moved rigidly. This is a more reasonable semi-
classical model, since it is the asphericity of the charge distribution
which causes it to rotate with the molecule.

Viewed in terms of the rigorous quantum-mechanical picture, the
unusually large $g_e^R$ is probably a result of the fact that p orbitals,
which would tend to have larger angular momentum matrix elements than s
orbitals, are prominent in oxygen. This effect might be anticipated by
noting that the atomic correspondence at large $R$ is to atomic P states,
whereas in $H_2$ it is to S-states.

Spin-Orbit Coupling

The other key in the solution was the experimental measurement of $g_e^R$.
With $\frac{\mathbf{H} \cdot \langle 0 | \mathbf{l} \cdot \mathbf{n} | n \rangle}{E_n - E_0}$ evaluated from $g_e^R$, this gives us the spin-orbit
coupling parameter $A$, and hence the second-order spin-orbit contribution $\lambda''$ to the parameter $\lambda$. As is clear from the table, $\lambda''$ is less than 1 per cent
of $\lambda$. Thus even if this evaluation of $\lambda''$ has a serious fractional error,
we are still assured that the first order spin-spin contribution $\lambda'$ is the
overwhelming one. This makes $\lambda'_e$ and $\lambda'_i$ firmly known quantities, the
calculation of which would serve as a test for the quality of a proposed
electronic wave function. Since the calculation of Chapter II gave only
60 per cent of $\lambda'_e$, it is clear that the Gaussian MO's are not too good an
approximation (even when adjusted as described there.) On the other hand,
the calculated $\chi$ is roughly 16 per cent too high. This is really as good
agreement as one could expect.

From $g_e^R$ we directly find $\mu''$, using the relation $\mu'' = 2B_{\mu}$. This second-
order interaction of the rotation-induced orbital angular momentum with the
spin gives essentially the entire spin-rotation coupling constant $\mu$, leaving
1 ± 4 Mc/sec for the first order $\mu'$. Direct calculation of $\mu'$ (see Chapter
II) gave 10.0 Mc/sec, and appeared insensitive to detailed choice of wave
function. Since the experimentally deduced value is the difference of two
large numbers, this agreement is reasonably good. A more informative check is to compare $\mu''$ computed as above with the value obtained by subtracting
the reliably computed $\mu'$ from the experimental $\mu$. These results check to
within 3.5 per cent. Since the standard deviation in the least squares fit
is only 1.7 per cent, this indicates that an error of the order of 1 or 2
per cent may be introduced in removing B from the summation and giving
it its value in the ground electronic state. This is a reasonable
magnitude of error since a more detailed examination shows that the
expected error is of the same order of magnitude as the effect of zero-
point vibration, which is 0.6 per cent in O₂. It doesn't seem possible
to make any equally simple estimate of the error introduced by removing
A from the sum of matrix elements, nor can we check it experimentally
lacking a reliable calculated value for λ'. The error is no doubt greater
with A than with B, but our partial check is still encouraging.

Another viewpoint would be to assume from the start that \( g^e_\perp = (\mu - \mu')/2B \).
In this, B and \( \mu \) are known from the field-free spectrum and \( \mu' \) is
easily calculated to good accuracy. Thus \( g^e_\perp \) is determined a priori. Since the
contributions of \( g^e_\parallel \) to the spectrum are small and of a distinctive form,
they are easily eliminated. The only free parameter then left for the
Zeeman spectrum is \( g^e_\parallel \), the electron spin g-factor. Our excellent agreement
of theory and experiment then demonstrates that this has the theoretical
value -2.0023 with a precision of 60 ppm. This precision is two orders of
magnitude less than that obtained by Koenig, Prodell, and Kusch using
atomic hydrogen. It is also an order of magnitude less than that of Abragam
and Van Vleck in their interpretation of the data on the atomic oxygen
Zeeman effect taken by Rawson and Beringer. Nevertheless, it is a
reassuring check that there is no unexpected difficulty in treating the
case of two coupled spins in a molecular, as opposed to an atomic environ-
ment. The order of magnitude mentioned here are indices of the increasing
difficulty of the problem as one proceeds from the simplest atom to a more
complex atom, and finally to a molecule. For a molecular problem, our
agreement is quite satisfactory.

Susceptibilities

Starting with a general formula of Van Vleck, the molar suscepti-
bility of a diatomic molecule with electronic spin S but no diagonal orbital
angular momentum is seen to be

\[
\chi = \chi_{z \parallel} + \chi_{H-F} + \chi_{dia} \\
= \frac{N_o (g^e_\perp)^2 \beta^2 S(S+1)}{3K T} + \frac{4N_o \beta^2}{3} \sum_n \frac{|\langle 0|L_x|n\rangle|^2}{E_n - E_0} - \frac{N_o e^2}{6mc^2} \sum_i \langle \epsilon_i \rangle
\]  

\[ (91) \]
Evidently the first term is dominant since $kT \ll \left( E_{n} - E_{0} \right)$ in most cases and the diamagnetic term is always small. It is still of some interest to know the magnitudes of the temperature independent terms, however, in making detailed comparison of precise experimental data with the theory. The $\chi_{\text{dia}}$ is easily calculated from Meckler's wave function, and the expected accuracy is again moderately good because the function $r^2$ puts no particular weight on the detailed behavior near the nucleus. The results are given for each orbital in table VI. The high frequency paramagnetic contribution $\chi_{\text{H-F}}$ is evaluated using the value for $L(L + 1)/\hbar \nu$ determined from $g_{T}^2$. These two contributions nearly cancel, the diamagnetic term slightly exceeding the paramagnetic one. This remainder provides a correction of $5 \times 10^{-6}$ cm$^3$/mole to the spin susceptibility, which is $3.42 \times 10^{-3}$ cm$^3$/mole at $T = 20^\circ$C. This correction is small compared to the spread in the experimentally obtained values, but might be useful in explaining small departures from Curie's law. Since it is definitely too small a correction to explain the deviation found by Woltjer, Coppoolse, and Weisna (See ref. 64), that deviation must be ascribed to experimental error.
CHAPTER X
LINE INTENSITIES IN THE PARAMAGNETIC RESONANCE SPECTRUM

A. Theory

It is easily verified that the $1/Q$ increment due to absorption in a gas filled cavity is equal to $4\pi\mu^2$ or to $c/\omega$ times the absorption coefficient $\alpha$ of the gas for a plane wave of suitable polarization. Further, in these Zeeman effect studies all degeneracies are lifted, so there is no summation over $M$ states. The standard analysis then yields

$$ \left( \frac{l}{Q} \right)_{ij} = \frac{4\pi\omega N}{kT} \left| \langle \mu_r \rangle_{ij} \right|^2 \frac{e^{-E_j/kT}}{(\omega - \omega_{ij})^2 + \tau^{-2}} \sum_j e^{-E_j/kT} \tag{92} $$

where $\left| \langle \mu_r \rangle_{ij} \right|^2$ is the average squared matrix element of $\gamma_s \beta S_r$ or $\langle g_s \beta \hat{H}_{ij} \hat{S}_r \rangle / \langle \hat{H}_{ij}^2 \rangle$ being the component of $S$ along $\hat{H}_{\text{rf}}$. Also $\tau^{-1}$ is $2\Delta \nu$, $\Delta \nu$ being the frequency half-width at half-power absorption. Eliminating $N$ by using the ideal gas law, approximating the partition sum by its classical value $3kT/2B$, and setting $\omega = \omega_{ij}$, we find the maximum absorption to be

$$ \left( \frac{l}{Q} \right)_{ij} = \frac{32\pi^3 B^2 \nu}{(\Delta \nu/\beta)^3} \frac{e^{-B(K+1)/kT}}{(kT)^3} \left| \langle S_r \rangle_{ij} \right|^2 \tag{93} $$

Evidently lowering the temperature gives a rapid rise in intensity for the lower rotational levels. Since our experimental frequency $\nu$ is fixed by the cavity, $\nu$ is the same for all lines. Also it is an experimental fact that in oxygen the normalized line breadth parameter $(\Delta \nu/\beta)$ at a given temperature has the same value for all lines within roughly $\pm 10$ per cent. (Beringer and Castle's anomalous results were caused by their incorrect use of $\nu/H$ rather than $d\nu/dH$ to convert their field widths to frequency widths.) Thus at a given temperature, the variations of intensity from line to line comes almost entirely from the factor $e^{-B(K+1)/kT} \cdot \left| \langle S_r \rangle_{ij} \right|^2$. Since the Boltzmann factor is readily calculated, we are left with only the task of computing the matrix elements.
To handle the general case, it is convenient to expand $H_{rf}$ as

$$H = H^+ \vec{u}_+ + H^- \vec{u}_- + H^z \vec{u}_z$$

where

$$H^\pm = H_x \mp i H_y / \pi, \quad \vec{u}_\pm = \vec{u}_x \pm i \vec{u}_y$$

the $\vec{u}_x$ and $\vec{u}_y$ being unit vectors in the X and Y directions. Then

$$\vec{H} \cdot \vec{S}_{ij} = H^+(S^+)_{ij} / \pi + H^-(S^-)_{ij} / \pi + H^z (S_z)_{ij}$$

where $S^+$, $S^-$, and $S_z$ are all different, AM being +1, -1, and 0, respectively, only one term on the right will contribute to $(S_r)_{ij}$ for a given ij transition. The $S$ matrix elements will have coefficients $f$, depending on the rf field and sample configurations, which give the fraction of the stored energy active in inducing each particular type of transition.

For example,

$$| (S_r)_{ij} |^2 = \frac{\int_{\text{sample}} |H|^2 d\tau}{\int_{\text{cavity}} |H|^2 d\tau} \frac{|(S_r)_{ij}|^2}{a} = f_+ |(S_r)_{ij}|^2$$

Finally, we note that with cylindrical symmetry about the static field direction $Z$,

$$| (\tau M | S_{\pm} | \tau' M') |^2 = 4 | (\tau M | S_x | \tau' M') |^2$$

for elements which exist in the left member. This enables us to write in general

$$| (S_r)_{ij} |^2 = 2 | (S_x)_{ij} |^2 \left[ f_+ \delta_{M_i, M_j+1} + f_- \delta_{M_i, M_j-1} \right] + | (S_z)_{ij} |^2 f_0 \delta_{M_i, M_j}$$

For non-rotating radiation perpendicular to Z in a gas-filled cavity $f_+ = f_- = \frac{1}{2}$. For localized samples, these values would obviously be reduced by filling factors. With pure circularly polarized radiation, one of the $f$'s would be unity, all other $f$'s being zero. (Rotation is possible only when two degenerate modes are excited out of phase.)
The procedure for calculating the required matrix elements, starting from the simple elements of $S_Z$ referred to the gyrating coordinates $g$, can be symbolized as

$$(S^*_F)_{ij} = (U^*T^*S^*_F T U)_{ij} = \left[ U^*T^* \left( \sum_g \tilde{\Phi}^g \right) S^*_g T U \right]_{ij} \quad (99)$$

In this the $\tilde{\Phi}^g$ are the direction cosines between fixed and gyrating axes; $T$ is the transformation between the Hund case (a) basis (in which $S_Z = \Sigma$ is diagonal, and in which we express $\tilde{\Phi}^g$ and $S_g$) and the basis which diagonalizes the field-free Hamiltonian; $U$ is the transformation between the latter basis and the true eigenfunctions in the presence of the field. The transformations $T$ are derived and tabulated in Chapter III; $U$ is derived in Chapter VI and a number of specific cases are tabulated in Appendix E.

For $F = Z$, $(T^*S^*_F T)$ has been carried out in Chapter IV. As discussed in Chapter VI, we neglect the part of $U$ which is off diagonal in $K$. The resulting transformed matrix elements $(S^*_Z)_{ij}$ are of the type $(KJM|S^*_Z|K'J'M)$. For transitions possible below $50\text{kHz/sec}$, $J' = J \pm 2$. These would be forbidden in the absence of the magnetic field, but, as noted in Chapter VI, "T" breaks down as an angular momentum quantum number with increasing field, and is kept only as a convenient label. On the other hand, at high fields $\mathcal{H}_{ms} = -g_e S^*_Z \beta H S_Z$, is such an important part of the Hamiltonian that when the total Hamiltonian is diagonalized, $S_Z$ is nearly diagonal also. Thus the $(J|J \pm 2)$ elements of $S_Z$ never get very large. Detailed calculation verifies this conclusion, all $\Delta M = 0$ transitions having a calculated intensity less than one per cent of that of the strong $\Delta M = \pm 1$ transitions. The conclusion is further substantiated by the fact that $\Delta M = 0$ lines were not observed experimentally even when a cavity mode was used in which $f_0$ was $4.4$.

The transformations are carried out in exactly the same manner for $S_X$. We can carry them analytically to $2 (KJM|T^*(\sum_g \tilde{\Phi}^g S_g) T |KJ'M-1)$

$$J' = K-1 \quad J' = K \quad J' = K+1$$

$$J = K-1 \left[ \left( K(K-1)-M(M-1) \right)^{1/2} g(K,K-1)/g_s^2 \quad \begin{bmatrix} C_{K-1} \left[ (K-M)(K-M+1) \right]^{1/2} & 0 & B_{K+1} \left[ (K-M+1)(K-M+2) \right]^{1/2} \\ 0 & B_{K+1} \left[ (K+M)(K+M+1) \right]^{1/2} & g(K,K+1)/g_s^2 \end{bmatrix} \right]$$

$$K \quad \left[ C_{K-1} \left[ (K+M)(K+M-1) \right]^{1/2} \quad \begin{bmatrix} 0 & B_{K+1} \left[ (K+M)(K+M+1) \right]^{1/2} \\ B_{K+1} \left[ (K+M+2)(K+M+1) \right]^{1/2} & g(K,K+1)/g_s^2 \end{bmatrix} \right]$$

$$K+1 \left[ \left( K+1(K+2)-M(M-1) \right)^{1/2} \quad \begin{bmatrix} 0 & B_{K+1} \left[ (K+M)(K+M+1) \right]^{1/2} \\ B_{K+1} \left[ (K+M+2)(K+M+1) \right]^{1/2} & g(K,K+1)/g_s^2 \end{bmatrix} \right]$$

(100)
In this, the $c_{K-1}'$, $B_{K+1}$, and $g(K,J)$ are defined in equation (60) and tabulated in appendix C. We note that since we are dealing with $(M|M-1)$ elements, there is no symmetry of this matrix about the diagonal. Thus one must take extra care to read off the correct element. Inspection of this matrix shows that $\Delta J = \pm 2$ transitions are forbidden between the field-free eigenfunctions which form the basis for (100). The $\Delta J = \pm 1$ transitions contribute to the millimeter spectrum treated in Part I. The $\Delta J = 0$ elements are all proportional to $[J(J+1) - M(M-1)]^{\frac{1}{2}}$, and their squares will give the allowed transition probabilities for the paramagnetic spectrum very weak fields.

For the fields of interest in this experiment, however, the departure of $U$ from a diagonal (unit) matrix are so large (i.e., the $J$'s are so mixed) that it is essential that the transformation $U$ be applied. When this is done, it turns out that $\Delta"J" = \pm 2$ transitions have appreciable intensities even at a thousand gauss, and that their intensity is of the same order as that of the "allowed" lines for fields above roughly 6 kg. Of course, the intensities of the "allowed" lines is also strongly modified by $U$.

B. Comparison with Experiment

In table VII we list the values of $4|\langle S_X \rangle_{ij}|^2 \exp -B(K+1)/kT$ evaluated at $T = 300^\circ K$. for those lines for which the entire calculation indicated above was carried through. As remarked in connection with equation (93), these factors should be nearly proportional to the experimental signal strength. ("Signal strength" is defined as proportional to $(1/q)^{1/2}$. It differs from the (integrated) intensity by a factor of $(1/\nu)$. Inspection of the last two columns of table VII shows that the proportionality holds to an average of roughly $\pm 10$ per cent over a range of almost $100:1$ in absolute value. This agreement is highly satisfactory in view of the difficulty of the measurement and in view of the approximation that $\Delta \nu$ is the same for all lines.

An attempt was made to check (30) more completely by measuring the absolute intensity. Inserting the numerical values for $T = 300^\circ K$ with $\nu = 9400$ Mc/sec and $(\Delta \nu/P) = 2$ Mc/sec-mm Hg, one finds

$$(1/q)^{1/2} = 1.46 \times 10^{-7} |\langle S_X \rangle_{ij}|^2 e^{0.0069 K(K+1)} \left[ f_+ S_{M_i,M_{j+1}} + f_- S_{M_i,M_{j-1}} \right]$$

(101)
For linear polarization and the strong $K = J = 1$, $M = -1\cdot 0$ line, this gives $1.36 \times 10^{-8}$. This conveniently establishes the scale factor for the table VII, and any other cases can be computed by proportionality.

To relate these predictions to experimental data, we note that the power reflection coefficient of a cavity at its resonant frequency is

$$|r|^2 = \left(\frac{\xi - 1}{\xi + 1}\right)^2$$  \hspace{1cm} (102)

where $\xi = Q_e/Q_0$, $Q_e$ being the external $Q$ and $Q_0$ the unloaded cavity $Q$. Thus

$$\Delta|r|^2 = 4\xi(\xi - 1)(\xi + 1)^2 Q_e \left(\frac{1}{Q}\right)_{i,j}$$  \hspace{1cm} (103)

The coefficient in this equation has a broad maximum at the optimum operating point $\xi = 2 + 3$ where $|r|^2 = 1/3$. At that point

$$\Delta|r|^2 = 0.385 Q_e \left(\frac{1}{Q}\right)_{i,j}$$  \hspace{1cm} (104)

This change in reflection coefficient gives a proportional change in power at the bolometer detector which gives rise to a proportional unbalance voltage in the bolometer bridge (See Fig. 8). Collecting all coefficients of proportionality for our apparatus, we find the open circuit bridge output to be

$$E_{\text{rms}} = 6.0 \times 10^{-3} Q_e P_o \left(\frac{1}{Q}\right)_{i,j}$$  \hspace{1cm} (105)

where $P_o$ is the power (in mw.) reflected to the bolometer by a total reflection at the cavity under the operating conditions. This formula presumes optimum sinusoidal modulation of the field, in which case the 50 cps modulation component of $|r|^2$ has a peak amplitude of roughly 0.46 of the total change given by (104). The $E_{\text{rms}}$ is measured by comparison with a GR microvoltmeter which is substituted with appropriate attention to impedance considerations.

*Beringer and Castle quote a calculated $1/Q$ of $0.46 \times 10^{-8}$ under these same conditions. The discrepancy apparently comes from their value of $U^2$, which is defined as $g^2(S_X^2 + S_Y^2) = 8|\mathbf{s}_X|_{i,j}^2$. They use $U^2 = \frac{1}{1.45}$, which is the value of $|\mathbf{s}_X|_{i,j}^2$ or $4|\mathbf{s}_X|_{ij}^2$ evaluated before the transformation $U$ is applied. The transformation $U$ increased the result by a factor of 1.48 and if we also supply the factor of 2 which they omit, agreement with our value is obtained.
Using this method the absolute intensities of several lines were measured at both room temperature and 78^oK. In all cases the experimental values of $(1/Q)_{ij}$ were approximately a factor of two too low. In view of the difficulty in measuring all of the parameters accurately, it is possible that this represents only an accumulation of small errors. This seems rather unlikely, however, because of the high stability of the results with respect to changed conditions. It is worth noting that Beringer and Castle found a measured $(1/Q)_{ij}$ for the $K = J = 1, M = -1-0$ line, mentioned above, of $1.39 \times 10^{-9}$, a factor of ten less than our calculated value. Thus our factor of two is tantalizing, but not too surprising.
CHAPTER XI
LINE BREADTHS

A. Sketch of the Theory

In the experimental work which interests us here the only effective source of spectral line breadth is pressure broadening (neglecting the instrumental effect of magnetic field inhomogeneities over the sample volume). Thus we can neglect such effects as the Doppler broadening caused by the thermal motion of the molecules through the radiation field, and the effect of collisions with the walls. Care was also taken to keep the microwave power level low enough to avoid saturation effects which would increase the apparent line breadth.

In view of these remarks, let us review the theory of pressure broadening to see what microscopic information can be inferred from the experimental results. To get our definitions clear and to separate the general dependences from the specific ones, we consider the simple kinetic theory model of a gas as an ensemble of hard spheres in thermal motion. Two spheres are said to collide if they approach within diameter b of each other. Then the volume swept out by an average molecule in time t is

\[ V = \pi b^2 \overline{v_{rel}} t \]

where \( \overline{v_{rel}} \) is the average relative velocity. If we let N be the number of molecules per unit volume, then the average number of collisions per unit time is

\[ \frac{1}{c} = \frac{N V}{c} = \pi b^2 \overline{v_{rel}} N \]

From the standard Lorentz theory\(^{55,70}\), we have the half width at half maximum intensity of the line given in terms of \( \tau \) by

\[ \Delta \omega = 2\pi \Delta v = \frac{1}{\tau} \]

Also

\[ \overline{v_{rel}} = \sqrt{v_1^2 + v_2^2} \]

if the particles are identical. Combining these relations, we find that the line breadth parameter is

\[ \Delta \nu = \frac{N \overline{v} b^3}{a} \quad (106) \]
Since it is an experimental fact that the line breadth is directly proportional to the pressure $P$ (at the pressures which concern us), it is more useful to consider a normalized line breadth parameter $\Delta \nu / P$. If we also make use of the results of Maxwell-Boltzmann statistics for an ideal gas, we may transform (106) to the following form.

$$\frac{\Delta \nu}{P} = \frac{2b^2}{(\pi m k T)^{1/2}}$$

(107)

The members of this equation are independent of pressure but depend on the temperature. The $T^{-1/3}$ dependence is a result for hard spheres. However, for actual gas molecules the effective collision diameter $b$ increases with the time which the molecules spend near each other at an encounter. Therefore $b$ decreases as $T$ increases, and $\Delta \nu / P$ is a stronger function of $T$ than $T^{-1/3}$ for these "softer" collisions. From this temperature dependence we can thus make inferences about the nature of the intermolecular potential. Of course, the collision diameter $b$ may also depend on the particular states involved. We then conclude that the theoretical problem is reduced to that of computing the effective collision cross section $\pi b^2$ for radiation interruption as a function of the states involved and of the thermal velocity of the colliding molecules.

The most suitable approximation to use in carrying out this computation depends on the relation of the duration of the collision encounter $\tau_c$ to the period $1/\nu$ of the radiation. If $\tau_c \gg 1/\nu$, then the energy levels of the radiating molecule are merely perturbed, giving rise to frequency-modulated emission or absorption as the molecule adiabatically adjusts to its changing environment. This is the situation at optical frequencies and the line breadth is treated by the Fourier integral phase shift method. In this method one obtains the frequency spectrum by making a Fourier integral analysis of the time dependent energy difference in the perturbed system. This time variation gives rise to phase shifts in the radiation. Weisskopf$^{56}$ simplified this by treating all collisions giving phase shifts greater than unity as equivalent to arbitrary phase shifts with complete interruption of radiation whereas all lesser phase shifts were ignored. This method then leads to a Lorentz line shape. The treatments of Foley$^{59}$ and Mizushima$^{58}$ take more rigorous account of the various phase shifts.
They then find the additional possibility that the center of the line may be displaced by an amount proportional to the width.

In the other limit, $\tau_c \ll 1/\nu$, and the collision occurs too rapidly for the molecule to follow adiabatically. As a result, transitions may be induced which break off the radiation wave train giving a line broadening. This type of collision is also the type required to maintain a thermal equilibrium distribution between states in the presence of an applied r-f field which is trying to equalize populations. Since it is an experimental fact (based on saturation studies) that almost all microwave "line broadening" collisions are also "relaxing" collisions, and since $\nu \tau_c < 1$ in the microwave region, we must conclude that the diatomic (non-adiabatic) collisions are the most important in microwave work. This conclusion is further strengthened by the experimental absence\textsuperscript{72} in microwave spectra of the frequency shifts predicted by the phase shift theory.

In Anderson's\textsuperscript{59} general theory both of these types of collisions are considered. For large values of the impact parameter, $\tau > 1/\nu$, and the adiabatic phase shift method is used. This formula for collision probability is then joined continuously to the constant value unity for values of the impact parameter less than that where the collision probability computed by the phase shift method reaches unity. For this inner region, it is presumed that every encounter brings complete interruption. This theory has been applied to a number of molecules by Anderson and by Smith and Howard\textsuperscript{73}, and to $O_2$ by Artman\textsuperscript{61b}.

Artman has given a careful survey of the various intermolecular interaction mechanisms. Of course, the homonuclear symmetry of $O_2$ precludes a long range electric dipole interaction. The strength of the magnetic dipole interaction is too small by two orders of magnitude. The electric quadrupole-quadrupole interaction seems an order of magnitude too small to explain the entire line width, but it may contribute noticeably. The principal interactions are the exchange repulsive forces, when the electronic charge clouds of the two molecules overlap, and the London dispersion forces. The latter may be described as an interaction between the fluctuating dipole moment of one molecule associated with the motion
of its electrons with the dipole moment which it induces in a second molecule. Artman selects polarizability and exchange parameters in accord with optical dispersion data and from data on the repulsion of closed shell atoms and ions. He also shows that rotational resonance interactions, in which the K's of the two colliding molecules change in opposite senses (conserving the total energy), should be unobservable for the case of O₂. If rotational resonance terms were noticeable, they should give a contribution to the line breadth proportional to the fraction of the molecules in adjacent rotational levels, i.e., to f(K-2) + f(K + 2). Naturally the resonance effects are completely lacking for O₂-N₂ broadening.

Considering exchange and polarizability interaction, he computes theoretical line widths for the 5 mm spectrum at 300°K and 223°K. His results predict a line width almost independent of K(1.94 Mc/mm Hg at 300°K) except for a slight rise at K = 1 (to 2.07 Mc/mm Hg). These values are in satisfactory agreement with his experimental data. The temperature dependence based on the two temperature he considered is T⁻⁰·⁶₂₇.

Artman also calculated the dependence of the quadrupole-quadrupole interaction according to Anderson's semi-diabatic method. He found that the normalized line breadth parameter should be proportional to T⁻¹·₇₅ and independent of K. Mizushima had previously given a treatment in the adiabatic approximation which also predicted a T⁻¹·₇₅ dependence, but which predicted a K⁻⁴⁻³ dependence.

No theoretical treatment is available for the line breadth in the case of our Zeeman-split energy levels. However, one would expect the general predictions given above to hold for the T and K dependences. There is no physical reason for there to be an M dependence of the mean collision cross section in field free space. However, at large field strengths the various possible orientations with respect to the field may really change the nature of the average interaction with other molecules. Also, our method of observation requires the various transitions to be observed at different values of H. Thus even if the cross section were independent of M at a given value of H, an apparent dependence on M might arise from an actual dependence on H.
Fig. 9 -- Recorder Trace of the Transition $K=1, J=2, K=-1\pm 0$. 
B. Experimental Data

Using the method sketched in chapter VIII, we obtain the derivative of the absorption curve $\chi''(H)$. An example curve directly from the chart recorder is shown in Fig. 9. To assure that we were getting a true derivative, inappreciably distorted by the finite modulation amplitude $H_m'$, we used a modulation amplitude not exceeding $1/10$ of $\Delta H$, the half width at half power of the line, and usually only half that great. Since this of course gives a proportionate decrease in signal strength, a further reduction in sweep would not have left a convenient signal-to-noise ratio on all of the lines studied. That this modulation amplitude is small enough was shown in two ways. First, experimental tests showed no noticeable difference in the apparent line width when the amplitude was changed from $1/20$ to $1/8$ of the half width. Second, Perlman and Bloom\textsuperscript{74} have shown by a simple argument that for ordinary line shapes the apparent second moment $(\Delta H)^2$ of the line is given by

$$
(\Delta H)^2_{a_{pp}} = (\Delta H)^2_{c_{pp}} + \frac{1}{3} H_m'^2
$$

(108)

The same qualitative result but with $1/4$ replacing $1/3$ was obtained more rigorously by Andrew\textsuperscript{75}. Using this formula, it is evident that an error of less than on per cent should be introduced even by our largest modulation amplitude.

It is clear that measuring the separation of the inflection points of $\chi''$ (the maxima of $d\chi''/dH$) gives a measure of the width of the absorption line. However, it is also apparent that since the deflection is stationary at these points, this is an inaccurate experimental quantity. More accurate determinations are possible of the points where $d\chi''/dH$ has fallen to $3/4$ or $1/2$ its maximum value, since at these points it is changing rapidly. To infer the half width of $\chi''$ from these data, we consider a Lorentz line

$$
\chi' = \frac{-\chi_0}{1 + \left(\frac{h}{\Delta H}\right)^2}
$$

(109)

where $h = H - H_0$ and $\Delta H$ is the half width at half intensity. Then

$$
\frac{d\chi''}{dH} = \frac{-\chi_0}{\left[1 + \left(\frac{h}{\Delta H}\right)^2\right]^2} \frac{2h}{(\Delta H)^2}
$$

(110)
\[ \frac{d^2 \chi''}{dH^2} = \frac{-2}{(\Delta H)^2 \left[ 1 + \left( \frac{\chi}{\Delta H} \right)^3 \right]^3} \left[ 1 - 3 \left( \frac{\chi}{\Delta H} \right)^3 \right] \]  
(111)

Thus the maximum derivative signal occurs where

\[ h_{max} = \frac{1}{\sqrt[3]{3}} \Delta H \]  
(112)

and this signal is proportional to

\[ \frac{d \chi''}{dH} \bigg|_{max} = \frac{3\sqrt{3}}{8} \frac{\chi}{\Delta H} \]  
(113)

To find the location of the 1/2 and 3/4 signal points, we simply equate (110) to 1/2 and 3/4 of \((d \chi''/dH)_{max}\) and solve for \(\Delta H\). This requires numerical solution of a quartic equation. The results are collected here.

\[ \Delta H = \sqrt{3} \ h_{max} = 0.977 \ h_{\frac{1}{2} max} = 0.722 \ h_{\frac{3}{4} max} \]  
(114)

The value of \( \Delta H \) was inferred by all three methods for each curve. The field scale factor was determined from marker pips on the trace. On lines strong enough to give excellent signal-to-noise and sufficiently pressure broadened that the field instability introduced no appreciable "horizontal noise", the three values of \( \Delta H \) so inferred normally agree within ± 2 per cent. Since there were no observable trends in these differences, one can conclude that the assumption of an undistorted Lorentz line shape is valid for our purposes. If for a given measurement the last two values in (114) were in reasonable agreement, the first value was dropped as too inaccurate to help. If the last two differed overly much due to a noisy signal, however, the first value was averaged in with a weight of \( \frac{1}{2} \) to help average out the errors. Each piece of raw data is the average of the widths obtained in this way by analyzing two charts of the given line at the same temperature and pressure.

The data obtained in this way were fitted to a dependence of the form

\[ \Delta H = A + B P = (\Delta H)_0 + (\Delta H/P) P \]  
(115)

by least squares. The values of \((\Delta H)_0\) increased from line to line as one went to lines at higher fields. This suggests that this residual width is
simply caused by the inhomogeneity of H over the cavity containing the sample gas. (Saturation was eliminated as a possible source of \( \Delta H \)_o by noting that data taken at another power level down by a factor of ten showed no significant change.) Since it seems evident that the residual width due to inhomogeneity should increase smoothly from zero, when \( H_o \) is zero, up through the region of interest, one can improve the raw fitting of (115) as follows: Plot the values of \( \Delta H \)_o (with their rather large least squares fitting errors) against \( H_o \). Draw a smooth curve, which passes through zero when \( H_o \) is zero, through these values. Assume the new values of \( \Delta H \)_o from this curve and fit the data again; this time only the slope \( \Delta H/P \) is a fitting parameter. By this new procedure we get part of the advantage of the data on all lines in fitting each line. The resulting second approximation should be closer to the true value of \( \Delta H/P \).

Two completely independent sets of data were taken and fitted in this way. They were made with different cavities and different pole pieces. In each set, data were taken at from 3 to 10 different pressures. Our adjustment procedure described above is supported by the fact that the largest adjustments occur with the same lines in both sets of data, but they were of opposite senses in the two cases, tending toward a common result. Thus we are assured that our procedure only averages out random errors and does not eliminate any actual effects.

The end results of our measurements are given in Table XIII after conversion of the field widths to frequency widths by the \( \Delta \nu/\Delta H \) factors from Table VII. The indicated errors are estimated standard errors based on the least squares errors of the individual fittings and on the differences between the results obtained with the two sets of data.

### Table XIII

<table>
<thead>
<tr>
<th>Transition</th>
<th>( \frac{\Delta \nu}{P} )</th>
<th>( \frac{\Delta \nu}{P} )</th>
<th>( \frac{\Delta \nu}{P} )</th>
<th>( \frac{\Delta \nu}{P} )</th>
<th>( \frac{\Delta \nu}{P} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>K J M</td>
<td>( \text{O}_2 \text{ at } 300^\circ \text{K} )</td>
<td>( \text{O}_2 \text{ at } 78^\circ \text{K} )</td>
<td>( \text{air at } 78^\circ \text{K} )</td>
<td>( \Delta \nu/12 \text{ air} )</td>
<td>( \Delta \nu/12 \text{ air} )</td>
</tr>
<tr>
<td>1 1 -1,0</td>
<td>2.35±.05</td>
<td>5.13±.14</td>
<td>6.13±.14</td>
<td>1.00±.03</td>
<td>.71±.02</td>
</tr>
<tr>
<td>1 2 1,2</td>
<td>2.20±.05</td>
<td>5.99±.07</td>
<td>6.02±.16</td>
<td>1.01±.03</td>
<td>.74±.02</td>
</tr>
<tr>
<td>1 2 0,1</td>
<td>5.92±.14</td>
<td>5.92±.14</td>
<td>5.92±.14</td>
<td>5.92±.14</td>
<td>5.92±.14</td>
</tr>
<tr>
<td>1 2 -1,0</td>
<td>2.23±.07</td>
<td>6.20±.05</td>
<td>6.21±.10</td>
<td>1.00±.02</td>
<td>.76±.03</td>
</tr>
<tr>
<td>3 2 0,1</td>
<td>5.93±.14</td>
<td>6.53±.11</td>
<td>6.53±.11</td>
<td>1.12±.03</td>
<td>.78±.03</td>
</tr>
<tr>
<td>3 4 -1,0</td>
<td>2.00±.05</td>
<td>5.70±.15</td>
<td>6.12±.13</td>
<td>1.07±.03</td>
<td>.78±.03</td>
</tr>
<tr>
<td>5 4 0,1</td>
<td>5.98±.23</td>
<td>5.98±.23</td>
<td>5.98±.23</td>
<td>5.98±.23</td>
<td>5.98±.23</td>
</tr>
<tr>
<td>5 6 -1,0</td>
<td>5.48±.16</td>
<td>5.48±.16</td>
<td>5.48±.16</td>
<td>5.48±.16</td>
<td>5.48±.16</td>
</tr>
</tbody>
</table>
For comparison let us consider the results of Beringer and Castle (Table XIV) which are more useful now that we have identified the transitions observed by them. As remarked above, their quoted results are incorrect because they used $\nu/H$ rather than $d\nu/dH$ to convert widths in gauss to widths in Mc/sec. This error is clearly corrected by a factor of $(H/\nu)(d\nu/dH)$. These corrected values are also given. The temperature dependence $T^{-n}$ based on their data is indicated in the last column. To simplify direct comparison with our data, their 85°K data has been converted to 78°K using an average $T$ dependence.

**TABLE XIV.** Line breadth data of Beringer and Castle (identified and reinterpreted)

<table>
<thead>
<tr>
<th>B.&amp;C. line number</th>
<th>Transition</th>
<th>B.&amp;C. $\Delta \nu/\rho$</th>
<th>$300^\circ$K</th>
<th>$85^\circ$K</th>
<th>corrected $\Delta \nu/\rho$</th>
<th>$300^\circ$K</th>
<th>$85^\circ$K</th>
<th>$78^\circ$K</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1 1  -1-0</td>
<td>1.93</td>
<td>5.62</td>
<td>2.24</td>
<td>6.52</td>
<td>6.98</td>
<td>.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1 2  -1-2</td>
<td>2.22</td>
<td>6.23</td>
<td>2.49</td>
<td>6.98</td>
<td>7.47</td>
<td>.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1 2  -0-1</td>
<td>6.17</td>
<td></td>
<td></td>
<td>6.26</td>
<td>6.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1 2  -1-0</td>
<td>2.04</td>
<td>6.27</td>
<td>2.08</td>
<td>6.38</td>
<td>6.84</td>
<td>.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>3 2  -0-1</td>
<td>4.13</td>
<td></td>
<td></td>
<td>5.83</td>
<td>6.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>3 4  -1-0</td>
<td>4.33</td>
<td></td>
<td></td>
<td>6.62</td>
<td>7.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3 2-4  -0-1</td>
<td>8.65</td>
<td></td>
<td></td>
<td>6.97</td>
<td>7.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3 4-2  -2-1</td>
<td>1.66</td>
<td>5.08</td>
<td>2.42</td>
<td>7.41</td>
<td>7.94</td>
<td>.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>5 4  -0-1</td>
<td>4.42</td>
<td></td>
<td></td>
<td>6.83</td>
<td>7.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>5 4-6  -0-1</td>
<td>4.75</td>
<td></td>
<td></td>
<td>7.02</td>
<td>7.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5 6-4  -2-1</td>
<td>1.82</td>
<td>5.14</td>
<td>2.18</td>
<td>6.16</td>
<td>6.60</td>
<td>.825</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>9 8-10  2-3</td>
<td>4.36</td>
<td></td>
<td></td>
<td>6.57</td>
<td>7.04</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Finally, let us tabulate for comparison the data given by Anderson, et al., by Gokhale and Strandberg, by Artman, and by Hill and Gordy for the 5 mm spectrum. Only Hill and Gordy give low temperature data which enables the temperature dependence to be determined. Their 90°K data is converted to 78°K using their quoted temperature dependence $T^{-n}$. 
TABLE XV. Line breadths in the 5 mm spectrum (Mc/mm Hg)

<table>
<thead>
<tr>
<th>Transition</th>
<th>Anderson (300°K)</th>
<th>Gokhale (300°K)</th>
<th>Artman (300°K)</th>
<th>Hill and Gordy 300°K</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1+</td>
<td>1.96</td>
<td>1.38±.28</td>
<td>2.20±.20</td>
<td>1.97 5.80 6.60</td>
<td>.90</td>
</tr>
<tr>
<td>1-</td>
<td>1.71</td>
<td>1.11±.12</td>
<td>2.23±.22</td>
<td>2.07 5.77 6.51</td>
<td>.85</td>
</tr>
<tr>
<td>3+</td>
<td>1.92</td>
<td>1.46±.12</td>
<td>1.96±.10</td>
<td>1.80 5.22 5.93</td>
<td>.90</td>
</tr>
<tr>
<td>3-</td>
<td>1.86</td>
<td>1.99±.10</td>
<td>1.93±.10</td>
<td>2.01 5.52 6.22</td>
<td>.84</td>
</tr>
<tr>
<td>5+</td>
<td>2.05</td>
<td>1.11±.20</td>
<td>1.82±.09</td>
<td>1.94 4.55 5.07</td>
<td>.76</td>
</tr>
<tr>
<td>7+</td>
<td>1.97</td>
<td>0.83±.12</td>
<td>2.00±.10</td>
<td>1.97±.20</td>
<td></td>
</tr>
<tr>
<td>9+</td>
<td>1.97</td>
<td>1.34±.24</td>
<td>1.97±.10</td>
<td>1.86±.10</td>
<td></td>
</tr>
<tr>
<td>11-</td>
<td>1.86</td>
<td>0.99±.12</td>
<td>1.90±.12</td>
<td>1.99±.10</td>
<td></td>
</tr>
<tr>
<td>13-</td>
<td>1.77</td>
<td>1.82±.18</td>
<td>1.62</td>
<td>1.91±.19</td>
<td></td>
</tr>
<tr>
<td>15-</td>
<td>1.76</td>
<td>1.58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17-</td>
<td>1.86</td>
<td>1.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19+</td>
<td>1.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19-</td>
<td>1.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C. Discussion

First let us compare our results (table XIII) with the analogous ones of Beringer and Castle (table XIV). Clearly our \((H/\nu)(d\nu/dH)\) correction has greatly reduced the scatter in their results. However, the agreement with our data is still rather poor. At 300°K., our results agree in the mean but differ by roughly 8 per cent. At 78°K, our means differ by 14 per cent but the mean deviation about that is only ± 5 per cent. This difference in behavior at the two temperatures is such that our values of the exponent \(n\) are in the vicinity of 0.75 whereas their values are near 0.85. Although they give no estimate of error, it seems clear that a systematic error is present somewhere. One possible source of error is in the measurement of the temperatures, particularly the low temperature. In our measurements, this was measured with a thermocouple soldered to the cavity wall. This thermocouple was calibrated at the boiling points of
and \( \text{O}_2 \), and temperatures were read to a fraction of a degree. It was found that this temperature was always within a degree of 78°K. with the commercial liquid nitrogen which we used. Since the data of Beringer and Castle is quoted at 85°K., presumably they used liquid air. The varying composition as the air boils away could cause an appreciable error if no allowance were made for it. However, even if we presumed that their temperature was 78°K., their normalized line width would still exceed ours. Perhaps a more promising explanation lies in the residual width \((\Delta H)_0\) at zero pressure. Beringer and Castle make no mention of this in their paper, but unless their field was exceptionally homogeneous, this would be a necessary correction. The fact that they used a different cavity at liquid air temperatures than at room temperatures would make the observed differential effect possible. In our work, of course, the same cavity and positioning were used for both temperatures and the residual width was carefully handled. Thus it would appear that our data should be the more reliable.

Considering only our data on \( \text{O}_2 \) self-broadening, there seems to be a trend toward lower line widths with increasing \( K \). However, the fall off in signal strength with increasing \( K \) has precluded carrying this far enough to establish whether it levels off or continues to drop slowly. In any case, the variation with quantum number is slight, the extremes being only ± 8 per cent. There also appears to be some variation in breadth with \( M \) in the group of three transitions of \( K = 1, J = 2 \) which we studied. The variation is only ± 2 per cent, however. In view of the fact that our standard errors are roughly ± 3 per cent, our limits of error (at 95 per cent confidence) should be ± 6 per cent. Thus it is clear that we can only hope for qualitative conclusions. These conclusions are that the \( M \) dependence of the line width is negligible and that there is a slight decrease in line width with increasing \( K \).

We find that the exponent \( n \) in the temperature dependence increases systematically with both \( J \) and \( K \), but the changes are within our limits of error. The mean value is 0.75. This is to be compared with the average of 0.86 found by Beringer and Castle, the average of 0.85 found by Hill and Gordy in the 5 mm spectrum, the value 0.627 calculated by Artman, the value
0.75 predicted for a quadrupole-quadrupole mechanism, and the value 1.0 for the polarizability and rotational resonance interactions considered by Anderson (and quoted by Hill and Gordy). Rotational resonance interactions would not be expected to be appreciable in the magnetic spectrum where the states are all non-degenerate and where hence there are few molecules in the appropriate states to give a resonant exchange of energy. This absence might account for the lower value of n which we find compared to that found by Hill and Gordy in the field-free 5 mm spectrum. This suggestion is strengthened by the fact that our widths are less than theirs at low temperatures where the resonance effect would be greatest because of the concentration of molecules in the lower rotational levels. Even if the experimental data were better, the interpretation would still not be clear until the apparent conflict, between Artman's prediction of 0.627 (from a calculation based on polarizability and exchange) and the value 1.0 quoted for the polarizability and resonance interactions, is resolved.

Lack of time has precluded a thorough investigation of those topics by the author.

The other type of data which we provide is the ratio of air broadening to pure O₂ self-broadening. We find that for the three different K = 1 transitions the ratio is 1.00±0.03, whereas for the two K = 3 transitions the ratio is 1.10±0.06. These results are rather surprising in view of the fact that both Anderson, et al., and Artman found N₂ only about 85 percent as effective a broadening agent as O₂. The difference again might be explained by rotational resonance. In the 5 mm spectrum this extra broadening is lost in going to air broadening, whereas in the paramagnetic spectrum it is never present. Thus if N₂ actually had a slightly larger non-resonant broadening effect (e.g., because of its larger molecular quadrupole moment), the discrepancy would be resolved.

Of course, any comparison of line widths in our paramagnetic spectrum with those of the field free spectrum is based on the fact that the line breadth is essentially the sum of the breadths of the initial and final energy levels and on the assumption that these states are not seriously modified by the presence of the magnetic perturbation. If these are true, then the width of a line of the 5 mm spectrum should be the average of the
width of a paramagnetic line for \( J = K \) and one for \( J = K + 1 \) (assuming the 
M dependence is negligible). Because of the inaccessibility of all except 
one \( J = K \) paramagnetic line, this hypothesis could not be given a real 
check. However, the line breadths which we find when we average over all 
transitions of a given \( K \) certainly are of the same order of magnitude as 
the corresponding widths in the 5 mm spectrum. This is consistent with 
the apparently weak dependence of line width on all quantum numbers.
CHAPTER XII
DETAILS OF APPARATUS AND EXPERIMENTAL METHOD

A. Linear Polarization Microwave Arrangement

X-band

Perhaps it would be appropriate here to trace the historical development of the microwave apparatus used at present. There is a description of the apparatus used by Kip and co-workers\textsuperscript{76,77} in their work at M.I.T. in the author's S. M. thesis\textsuperscript{78}. In this apparatus the klystron was manually tuned to the resonant frequency of the sample cavity and its power was supplied by batteries to eliminate ripple and to give short-term stability. Drift, however, was a serious problem. Another characteristic of the apparatus was that the entire microwave carrier was chopped at 50 kc/sec by a crystal modulator, and the absorption curve detected as a small modulation envelope on the resulting large 50 kc/sec steady signal.

To obtain the frequency stability necessary to allow the slow sweep (7 seconds) required for work with rather high sensitivity and high resolution, we modified this apparatus by introducing a Pound feedback frequency stabilizer, as described in the above-cited thesis.\textsuperscript{78,79} In this work we locked our oscillator frequency to an external high-Q wave meter cavity. The modulation scheme was also modified by changing our frequency to 6 kc/sec and by introducing audio balancing and linear detection. The latter enabled us to gain the narrow bandwidth associated with lock-in mixer operation. This apparatus performed satisfactorily for that work, but had certain drawbacks. First, if the wave meter reference cavity was not tuned exactly on the resonant frequency of the sample cavity, one can show\textsuperscript{78} that the signal obtained would contain a component of \( \chi' \), the real part of the susceptibility, proportional to the frequency error. The distortion and line asymmetry introduced in this way is highly objectionable. Second, the audio balancing arrangement is unstable and this results in extra noise.

These drawbacks are largely eliminated in the apparatus developed to carry out this thesis research. The first major modification is to lock the oscillator directly to the resonant frequency of the cavity containing the sample. If properly adjusted, this ensures that no frequency error
Fig. 10 -- General view of the apparatus.

Fig. 12 -- Microwave apparatus for linear polarization at S-band.

Fig. 11 -- Microwave apparatus for linear polarization at X-band.
occurs. For example, if the cavity frequency should change because of thermal expansion of the walls or because of the real part of the susceptibility of the sample near resonance, the feedback circuit forces the microwave oscillator frequency to change by the same amount. This prevents the mixing of $\chi'$ and $\chi''$. The other major change was to obtain our a-c signal by directly modulating the absorption with a small 50 cycle oscillating component in the applied magnetic field. This eliminated the need for modulating the microwave carrier and then balancing out the resulting large standing audio frequency voltage at the detector. As a result, the microwave arrangement was simplified and much superior long-term stability was obtained. With these modifications, the stability was such that continuous sweeps of one hour duration were feasible, and the sensitivity was also greatly enhanced.

A general view of the present apparatus is shown in Fig. 10. A better view of the microwave apparatus alone is shown in Fig. 11. The block diagram given as Fig. 8 in chapter VIII indicates the general arrangement, but more details of the microwave arrangement are sketched in Fig. 13. Central to the

![Diagram](image)

**Fig. 13** Sketch of microwave arrangements for linear polarization.
occurs. For example, if the cavity frequency should change because of thermal expansion of the walls or because of the real part of the susceptibility of the sample near resonance, the feedback circuit forces the microwave oscillator frequency to change by the same amount. This prevents the mixing of $\chi'$ and $\chi''$. The other major change was to obtain our a-c signal by directly modulating the absorption with a small 50 cycle oscillating component in the applied magnetic field. This eliminated the need for modulating the microwave carrier and then balancing out the resulting large standing audio frequency voltage at the detector. As a result, the microwave arrangement was simplified and much superior long-term stability was obtained. With these modifications, the stability was such that continuous sweeps of one hour duration were feasible, and the sensitivity was also greatly enhanced.

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![Diagram](image)

**Fig. 13** Sketch of microwave arrangements for linear polarization.
operation of this apparatus is the "magic tee". This is a four terminal
element characterized by equal transmission to the two arms adjacent to
any given input arm and no transmission to the fourth arm. In the line
connecting the source to the tee we have a ferrite one-way attenuator.
This eliminates klystron pulling effects by attenuating the reflected
power with very little loss of forward power transmission. There is also
an ordinary variable attenuator to control the power level.

The 30 Mc/sec modulator arm of the magic tee is made roughly equal in
length to the arm going to the cavity in order to give a cancellation of
the dispersive effects of a long length of guide. This procedure is
necessary if one is to obtain the most desirable discriminator action. An
attenuator may also be included in this arm as shown when it is desired to
minimize the power to the detector crystal which has not been reflected from
the cavity arm. This was done in the absolute intensity measurements. Of
course there is a variable phase shifter in this line to allow adjustment
for exact discriminator phasing at a given frequency. It is this phase
shifter which must be set correctly to ensure that the oscillator is locked
at the exact center of the cavity resonance curve. The proper setting is
indicated by minimum reflected power from the cavity as seen through the
directional coupler. For work with high-Q cavities, this adjustment is
usually not very delicate. This same monitoring point is used to check
the cavity coupling and to make approximate frequency measurements by
comparison with the calibrated wave meter. (A review of optimum cavity
coupling procedures is given in appendix G.) Precise frequency measurements
are made by beating harmonics of the quartz crystal in the M.I.T. frequency
standard with the microwave carrier in the crystal mixer. The beat
frequency is measured with an S-36 receiver which has been calibrated with
a BC-221 frequency meter. By this technique, frequencies are readily
measured to 1 part in $10^6$.

The signal power from the magic tee is split again in a second tee to
provide separate outputs for frequency control and for signal. This allows
a bolometer to be inserted for the signal detector without disturbing the
frequency stabilization. As remarked previously, a bolometer was used only
for the absolute intensity measurements. There seemed to be no marked
advantage in the actual signal-to-noise ratio in using the bolometer as opposed to a crystal at the power levels we were using. Since a crystal has a much higher conversion gain, it is more convenient to work with one of them, than with a bolometer. There was a very marked variation in the noise output at 50 cps over the dozen crystals tried. Of the dozen, two were found to be especially good, and these were used as the detector crystals in all of the work.

S-band

The microwave apparatus used in the S-band experiments (Fig. 12) is very similar to the X-band arrangement just described except that coaxial cable replaces waveguide and a hybrid ring ("rat race") replaces the magic tee. The 7076 klystron is locked to the $T_{010}$ cavity by the same Pound circuit. Since the cavity is used in transmission, the signal is obtained from a different point than in Fig. 13. The coupling into the cavity is by means of a loop which is adjusted for optimum and then soldered in place. The output is coupled by means of a probe to avoid presenting a closed loop in which a spurious 50 cps voltage would be induced by the modulation on the magnetic field.

B. Circular Polarization Microwave Arrangement

In Chapter X we showed that the experimentally observed signal strength should be proportional to the fraction $f_\pm$ of the energy stored in the cavity which has the appropriate polarization. In particular, $\Delta M = \pm 1$ transitions will give equal responses if the radiation is linearly polarized ($f_+ = f_-\). However, if we can provide a rotating magnetic field in the cavity, we can preferentially observe $\Delta M = +1$ or $-1$ transitions.

An apparatus which we developed to provide such a field is shown schematically in Fig. 14. Although the author developed and used a matrix method (Appendix B) of formally describing the operation of various elements in conjunction with a guide propagating in two modes, our final results can be discussed in simpler terms. The incident wave propagates down the square guide, polarized along a diagonal. At the far end the vertical and horizontal components are shorted a quarter wave apart by means of a vertical shorting vane. The reflected components combine to
Fig. 14-- Schematic diagram of special coupler for circular polarization.

Fig. 15-- Photograph of special coupler for circular polarization.

Fig. 16-- Microwave apparatus for circular polarization.
give a wave polarized along the other diagonal which leaves through the	herm arm. This output arm is oriented at exactly 90° to the input arm
to avoid direct cross coupling. (The choke plunger is adjusted for optimum
matching of the input and output arms. By symmetry, the same setting is
best for both.) The incident and reflected waves combine to set up a
standing wave pattern in which the vertically and horizontally polarized
waves are 90° out of phase (in space and time) because of the γ/4
difference in path lengths to the effective shorting position. The
coupling hole to the cavity is located on the center line of the wall of
the square guide at such a distance from the end that it is at the maximum
of both the longitudinal H of the horizontally polarized standing wave and
the transverse H of the vertically polarized standing wave. With 1" X 1"
square waveguide and a wavelength of 3.2 cm., the magnitude of these two
components are almost exactly equal. Thus we have succeeded in producing
a circularly polarized field at the window to the cavity.

The circular excitation will not give circular radiation in the cavity,
though, unless we have two degenerate orthogonal modes present. If there
are two such modes, they can be considered to be excited independently and
90° out of phase, with a circularly polarized radiation field as the result.
Along the axis, the field will rotate purely in one direction. However,
averaged over the cavity (which is full of the sample) this is not true.
In fact if we use TM modes, on the average the energy is shared equally
between the two senses. That this is so can be seen qualitatively by noting
that the lines of H are closed. In a plane field, this implies that as many
rotate in one direction as in the other. If we go to a TE mode, however,
longitudinal H is allowed, and the loops of H can close in the axial
direction. This enables us to get a net circular polarization over the
cavity at the expense of also acquiring some axial fields. The latter will
induce 4M = 0 transitions.

For the TE_{III} mode actually used, Lamont^80 quotes as one of the
possible configurations:

\[ H_\phi = \frac{\pi^2}{\ell} J_n(kp) \cos \phi \sin \frac{\pi z}{\ell} \]
\[ H_\rho = \frac{\pi}{\ell} J_n'(kp) \cos \phi \cos \frac{\pi z}{\ell} \]
\[ H_\zeta = -\frac{\pi}{kp} J_n(kp) \sin \phi \cos \frac{\pi z}{\ell} \]

(116)
The mode orthogonal to this is obtained by letting $\phi \to \phi - \frac{\pi}{2}$. In these equations, $k$ is defined as the first root of $J_1'(ka) = 0$, where $a$ is the radius of the cylinder. If we superpose these two modes with a phase factor of $i$, the result is (cf. chapter X, p. 82)

$$\tilde{H} = H^+_u u^+_x + H^-_u u^-_x + H^2_u u^2_x$$  \hspace{1cm} (117)

where the $\tilde{u}$'s are unit vectors and where

$$\sqrt{2} \ H^2 = \frac{(\pi/2\rho)}{\cos \frac{\pi}{2} \ e^{i\rho}} \ \left[ (k\rho) J_1'(k\rho) \pm J_1(k\rho) \right]$$  \hspace{1cm} (118)

and

$$H^2 = k^2 \ \sin \frac{\pi}{2} \ e^{i\rho} \ J_1(k\rho)$$

Since $x \ J_1'(x) \rightarrow J_1(x)$ as $x \to 0$, it is clear that near the axis ($\rho = 0$) we have $\tilde{H}^+ / H^+ \to 0$, and we have purely one sense of rotation, as remarked above. If the normalization integrals are performed and evaluated for the typical example $l = 1.5 a$, we obtain $f_+ = 0.52$, $f_- = 0.04$, and $f_0 = 0.44$ for the averages over the cavity which we quoted in a previous chapter. (For TM modes, these results are $f_+ = f_- = \frac{1}{2}$, $f_0 = 0$.)

A photograph of the actual apparatus is given in Fig. 15. Note the tuning screws in the cavity. They are required to balance out the effect of coupling into a guide which is not equivalent in the two orthogonal directions, and to compensate for any other imperfections which destroy the exact degeneracy of the two modes. An O-ring-mica vacuum seal is used. To reverse the sense of rotation, the assembly is unscrewed and turned through $180^\circ$ at the square flange joint visible in Fig. 15.

In Fig. 16 we show the complete microwave arrangement for use with circular polarization. The essentials of the apparatus are sketched in Fig. 17. It is basically the same as that for linear polarization, but the topology is modified by the presence of the special piece of plumbing to couple into the square guide. A piece of flexible guide was used to enable the figure to be closed without fabricating precisely dimensioned brass guide. This flexible guide is clearly visible in the photograph.

In operation, a chart is run showing the spectrum when one sense of rotation is dominant. Then the cavity assembly is rotated through $180^\circ$ and another chart is taken. The deflections of $\Delta M = \pm 1$ transitions change by factors of $2^4/4 = 13$ in opposite senses in going from one chart to the
other, whereas $\Delta M = 0$ transitions would have the same deflection on both. Thus a completely unambiguous experimental determination of $\Delta M$ is possible.

![Diagram](image)

**Fig. 17** Sketch of microwave arrangement for circular polarization

**C. The Magnetic Field**

It should probably be noted that the equipment described in this section was all designed and built during the last three years. None of it is a carry over from previous researches. In previous work here a less efficient smaller magnet was used. The field as swept by applying the shaped output of a multivibrator of sufficiently long period to the motor generator through a suitable d-c amplifier. There was no stabilization. The field was measured by rectifying the flip coil output. Because of the rectifier drift, this was unsatisfactory for accurate, reproducible results.

**Magnet Design**

As may be seen in the photographs of the apparatus, the magnet used in this research is of a novel yokeless design. The original suggestion was by Prof. Bitter, but the detailed design work was carried out in the paramagnetic resonance laboratory. This design has some advantages with
regard to aligning the pole faces exactly parallel and in arranging the windings. However, it has the disadvantage of producing large stray fields and requiring more power per gauss than a conventional magnet of equal size, especially at small gaps. The latter was not too serious a hindrance on our case, since we always used moderately large gaps. With a 5/8" gap and 8" diameter pole pieces we could obtain 7000 gauss at an input power of 5 kW and 11,000 gauss at a power of 12 kW. This power was supplied by two motor-generators connected to separate windings. One of the generators merely supplied a manually controlled bias field whereas the other was used for all feedback control purposes.

The pole pieces of the magnet were furnished with shims of rectangular cross section following the Rose prescription. 81  They were held apart by three dural blocks 3/4" x 1\(\frac{3}{8}\)" in cross section and differing in length by less than 0.0003". The homogeneity of the field was within roughly \(\pm 0.1\) per cent over a volume 3 inches in diameter. To eliminate a gradient in the field along the axis, it was necessary to divert a small part of the current from the windings on one half of the magnet by means of a shunt.

Field Control

The field is continuously monitored by a rotating flip coil driven by a synchronous motor. To avoid excessive loading of the motor and heating of the flip coil by eddy current dissipation, the flip coil shaft must be of non-conducting material over the length which is in the field. (With a brass shaft the loading is 1/75 HP at 10,000 gauss for typical dimensions.) The output of the flip coil is compared with a fraction of the output of a reference generator driven on the same shaft, the fraction being controlled by a helipot which can be swept by a geared-down synchronous motor. The difference signal is amplified in a 30 cps tuned amplifier and detected in a phase-sensitive manner by a Brown converter. This gives a d-c output, the sense and magnitude of which are proportional to those of the error in the field. This d-c output is applied to the grids of a bank of parallel 815 tubes through a d-c amplifier. (See R.L.E. Dwg. # A-1319-4) The plate current of these tubes (from a 3 phase rectifier supply) forms the excitation current for the field coils of the controlled motor generator supplying current to the magnet. In this manner we close the loop and stabilize the
magnetic field against the reference generator. As the helipot is swept linearly in time, the field is also swept linearly and at each instant is stabilized to within a gauss at the appropriate field.

Actually the servo loop would oscillate if it were operated exactly as described above. The basic reason is that there are long lags associated with both the generator and the magnet. These introduce such phase shifts that the feedback becomes regenerative at a frequency at which the loop gain still exceeds unity. To make the loop stable, we introduce an inner loop which applies amplified current feedback from the magnet winding current to the input of the d-c amplifier driving the 815's. This inner loop greatly accelerates the response of the elements it encloses, thereby reducing the lag and rendering the overall loop stable at a loop gain of the order of 80.

Even with this current feedback operating, the response is still slow and the field tends to wander over a region of roughly one gauss. The control can be greatly tightened by applying the output current of the 815's directly to the magnet through high resistance trimmer coils. This avoids the lag in the generator and in the massive length of the iron core by directly controlling the field in the gap. As a result the response time is reduced to a fraction of a second and the field is stable to within a few tenths of a gauss. When this type of feedback control is used, the generator must be put on manual control to avoid oscillation of the loop. This makes long sweeps difficult. However, since the trimmer coils will control over several hundred gauss, this engenders no difficulty on lines narrow enough to require high stability for satisfactory measurement.

Field Measurement

For most purposes one can measure the field accurately enough by simply comparing the flip coil output with a fraction of the output of the reference generator on a null basis. This is done with a mixer and 30 cps tuned amplifier chassis which has been named the "comparator". (See R.L.E. Dwg. # A-1283-4) This amplifier is also equipped with 60 cps and 150 cps rejection filters to eliminate specific interference and harmonics. To obtain the exact phase relation required for a sharp null, adjustable condensers are used. Simple circuit analysis shows that these condensers
introduce no noticeable amplitude changes when used to correct the small phase errors of only a fraction of a degree which are encountered. The division of the reference generator voltage is performed with two G.R. 4-dial decade resistance boxes. This arrangement is so calibrated that the field in gauss (from 0 to 11,110) is read directly off one of the boxes, the other box being set to hold the total resistance constant. This direct reading feature is, of course, very convenient. These boxes are visible between the two racks in Fig. 10. To the left of them is the motor driven helipot sweep control, and directly above them is the comparison oscilloscope on which the nulls are read.

When high accuracy magnetic field measurements are required, they are made with a proton probe. The circuit used is an adaptation of that given by Knoebel and Hahn. Since we operate with an oscillatory component in the magnetic field, no frequency modulation of the oscillator is required for oscillographic presentation. The frequency of oscillation is determined by observing beats with harmonics of a BC-221 frequency meter. To eliminate positioning errors, data was taken in one position and again with the positions of sample cavity and probe reversed. Even if these differed, the mean should be very near to the true value.

Field Modulation

As described earlier in this chapter, it is necessary to superimpose a 50 cps component on the static magnetic field. This is done with a modulator (R.L.E. Dwg. # A-1389) which supplies a maximum output power of 45 watts to a pair of modulation coils. This will provide sweeps of up to 90 gauss peak-to-peak. To ensure a constant modulation frequency, this unit is driven by a 50 cps signal derived from the quartz crystal of the M. I. T. frequency standard by frequency division. To avoid phase and amplitude changes when the static field is changed (thus changing the properties of the iron core), the modulation is feedback stabilized. A small pickup coil fastened to the center of one pole face provides an induced voltage proportional to the modulation. This is amplified and fed back degeneratively. Since the stable loop gain is about 7, we obtain a 7-fold reduction in the phase and amplitude changes. The modulation amplitude is controlled by a potentiometer across the reference voltage in
complete analogy to the static field control feedback arrangement. The linear dial on this potentiometer has been calibrated to read directly in gauss peak-to-peak.

D. Signal Circuit Instrumentation

Again, all the apparatus described in this section has been built up since the previous work in the laboratory was completed (1951). The interrelation of the equipment described here is shown in Fig. 8 in Chapter VIII.

Bolometer Bridge

If bolometer detection is used, circuitry is required to transform the resistance changes of the bolometer into an input voltage for the amplifier. This bridge performs that task. It also served to measure microwave power levels, if one notes how much series resistance must be removed from the bolometer arm to restore the bridge to balance. With the Sperry type 821A barreter (bolometer) used, the conversion factor $\alpha$ is 4.56 ohms/mw. Since in power measurements the device is operated at constant current, the increase in power dissipated in the bolometer comes partially from the increased $i^2R$ heating. Considering this effect, the relation between the resistance change and the microwave power can be shown to be

$$\Delta R = \frac{\alpha}{1 - \alpha \frac{\Delta I}{I}} \Delta P_{R+} = 6.45 \Delta P_{R+}$$  \hspace{1cm} (119)$$

If the bridge is not run at exactly constant current, e.g., in signal detection, the factor is between 4.56 and 6.45. For our circuit parameters it turns out to be 5.5 ohms/mw.

In considering the coupling of this bridge to an amplifier, it is convenient to replace the bridge (shown at the left) by the equivalent circuit.

![Diagram of equivalent circuit](image)

$$e = V \frac{\Delta R}{R + R_o}$$
(shown on the right). The equivalence is, of course, based on Thevenin’s theorem. In the circuit used, V = 45 volts, R = 5000 ohms, and R₀ = 180 ohms. For simplicity, various meters and switching arrangements have been omitted in the sketch. Also we should remark that the whole circuit is enclosed in a permalloy shield box to minimize the induction of noise voltages.

Amplifier
The amplifier designed for this work (R.L.E. Dwg. # A-1282-4) is a transformer-input high-gain low-noise amplifier tuned to 50 cps by RC feedback circuits. The gain is roughly 5 x 10⁶ and is controlled by a 30 db switch and by 10 db and 1 db step attenuators. The bandwidth is 5 cps. However, two twin-tee rejection filters tuned to 60 cps reduce the gain to the order of only 10 at 60 cps, effectively eliminating an obvious source of interference. The noise figure is roughly 2.

Demodulator (Lock-in Mixer)
This unit (R.L.E. Dwg. # A-1327-4) taken the output of the amplifier and rectifies it in a phase sensitive manner by means of a Brown converter. (The operation of this unit is closely analogous to that of the field stabilizer unit). This converter is driven synchronously from the same 50 cps source which drives the modulator. Because of the feedback in the modulator the phase relation between the signal and the converter is unchanged even at high static fields where the properties of the iron core change. This is necessary to avoid spurious signals and distortions of line shapes caused by a field-dependent phase relation. The reason for using the frequency standard (instead of an ordinary oscillator) as our 50 cps source is to avoid the phase shifts in the tuned amplifier resulting from frequency changes. With these precautions, the phase relation is very stable and an undistorted derivative signal is the result. This signal controls a balanced 6SN7 current amplifier which drives the front panel indicating meter and a chart recorder. The gain through the entire system is roughly such that 0.1 microvolts to the input of the amplifier gives full scale deflection on the demodulator meter.
Integrator

If it is important to have a plot of $\chi''$ itself rather than $d\chi''/dH$, a signal from the demodulator is applied to an electronic integrator unit. This integrator uses a chopper-type high-gain d-c amplifier to give a large effective time constant. On sweeps of many minutes duration, baseline drifts are a definite problem. Also it normally requires a trial run to establish an appropriate gain setting for any particular integration. For these reasons, it is usually more efficient to abstract the desired data directly from the derivative curve if that is possible.

Recorders

A great amount of exploratory work was done using the standard Esterline-Angus recording milliammeter. However, to avoid the inconvenience of working on curvilinear coordinates, a Bristol self-balancing potentiometric type of recorder was used in the line width studies.
CHAPTER XIII
CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

As a consequence of the structure of this thesis we have presented and discussed the conclusions from each part as they become clear. This was desirable because the scope of the material treated was sufficient that this compartmentation helped avoid confusion. Now, however, let us try to put the whole back into the general framework set up in the introduction. The numerical results of fitting the spectra and of the calculations referred to below have been collected in table XI on page 74, and will not be repeated here.

Starting with the basic Hamiltonian

\[ \hat{H} = \hat{H}_{el} + V_{nu} + T_{nuc} + \hat{H}_{SO} + \hat{H}_{SS} \]  

where \( \hat{H}_{SO} = A \hat{S} \cdot \hat{S} \) and \( \hat{H}_{ss} \) is the spin-spin dipolar interaction, we have essentially integrated out the electronic coordinates over the ground electronic state to obtain the effective Hamiltonian

\[ \hat{H}_{eff} = \frac{P_z^2}{2m} + \frac{1}{2} M \omega_0^2 R_e^2 S_z^2 + B \sum 3 \lambda(\xi)(3S_z^2 - S^2) + \mu \hat{S} \cdot \hat{S} \]  

where

\[ B(\xi) = B_n - B'' = B_0 (1 - 2 \xi + 3 \xi^2) \]

\[ \lambda(\xi) = \lambda(\xi) + \lambda''(\xi) = \lambda_0 + \lambda_1 \xi + \lambda_2 \xi^2 \]

\[ \mu = \mu' + \mu'' \]

The notation is as defined in Chapter II. For example, \( \lambda' \) and \( \lambda'' \) are contributions to the coupling of the spin to the figure axis which are, respectively, first order effects of \( \hat{H}_{SS} \) and second order effects of \( \hat{H}_{SO} \), and \( \xi = R - R_e / R_e \).

This sort of reduction had been indicated before in a formal manner, but in this thesis we have actually carried out an evaluation of the constants \( \lambda_0 \), \( \lambda'_0 \), and \( \mu' \) by using an adjusted form of Meckler's electronic wave function for \( \text{O}_2^+ \). This evaluation showed that \( \lambda' \gg \lambda'' \) and \( |\mu'| \ll |\mu''| \). This evaluation also showed how exchange effects and the presence of ionic states corrects the error in sign and magnitude of \( \lambda_0 \) as estimated with a naive picture of the electronic state. The rapid change of configuration mixing coefficients explain the sign of \( \lambda'_0 / \lambda_0 \), which is also incorrectly
given by the naive picture. A final general conclusion from the evaluation is that one can only expect accuracy to perhaps ± 50 per cent when evaluating an arbitrary molecular parameter (such as λ) with an approximate electronic wave function chosen by minimizing the electronic energy. If a wave function were found which gave good results for both calculations, then we would presume it to be much closer to the truth.

Matrix elements of (120) were computed in a convenient basis, and the eigenvalues and eigenvectors were calculated. Using the eigenvectors to compute transitions probabilities, we showed the existence of errors of the order one per cent in the values previously calculated with less exact eigenfunctions. This is significant when line breadths are inferred from measured peak absorption and calculated total absorption. More striking was the prediction of appreciable intensities for \( \Delta K = \pm 2, \pm 4, \ldots \) lines of submillimeter wavelengths. These were forbidden in the previous approximate theory. The eigenvalues of (120) were used to fit the 5 mm spectrum to roughly 1 part in 10^5, eliminating the discrepancies with previously existing theories which failed to include the centrifugal distortion effects resulting from the \( \xi \)-dependence of \( \lambda \). Fitting the 5 mm spectrum determines \( \mu^\prime, \lambda^\prime, \) and \( \lambda \), with excellent accuracy. By analysis of optical band data, \( \lambda \) is determined (in addition to the usual vibration-rotation constants \( \omega_v, R_e, b, \) and \( B_e \)). This gives an experimental determination of the total parameters \( \lambda (\xi) \) and \( \mu \), but no experimental separation of \( \lambda^\prime, \lambda^\prime, \mu^\prime, \mu \) to check the theoretical calculations mentioned above.

The desired experimental check is obtained by considering the effect of a magnetic field on the molecule. We show that the microwave paramagnetic resonance spectrum of O₂ can be fit to roughly 1 part in 20,000 (which is within the expected error in the calculation and in the experimental data) by the eigenvalues of the Hamiltonian

\[
H = H_{\text{eff}} + H_{\text{ms}} + H_{\text{mr}} + H_{\text{nr}}
\]

\[
= H_{\text{eff}} - 3 \xi \beta H S_z + \beta H \chi_z - 3 \xi \beta H (\hat{\Phi}_x S_x + \hat{\Phi}_y S_y)
\]  

In this equation \( H_{\text{eff}} \) is the field-free effective Hamiltonian, \( H_{\text{ms}} \) is the interaction of the electronic spin magnetic moment with the external field \( H \), \( H_{\text{mr}} \) is the interaction of the rotational moment of the molecule (nuclear
and electronic contributions) with $H$, and $\mathcal{Y}_{mil}$ is the interaction of spin-orbit induced electronic orbital angular momentum with $H$. The fitting confirms the anomalous moment of the electron to 6 parts in $10^5$ and evaluates $g_e$ to a few per cent and $g_r$ to 20 percent. Since $g_e$ and $g_r$ enter (121) only in small correction terms, they can only be evaluated as a result of our precise calculations based on our thorough understanding of the field-free problem.

With them evaluated experimentally, we can unravel the network of first and second order effects by using experimental data in conjunction with only the formal definitions of the second order terms as sums of products of matrix elements. The values of $\lambda'$, $\lambda''$, $\mu'$, and $\mu''$ separated in this way confirm the results of the wave function calculations mentioned above. Beyond this though, we can also determine the electronic contribution $B''$ to the effective reciprocal moment of inertia. This enables us to eliminate an error in the value of the internuclear distance $R_e$ inferred from $B_e$. We are also enabled to compute $\chi_{HF}$, the high frequency part of the static susceptibility. Another result of general interest is that the error introduced by the usual procedure of removing $B (=1/2I_g)$ from the sums of matrix elements is, as anticipated, of the same order of magnitude as the zero-point corrections—namely, a few per cent. It is believed that our example is one of the first in which there are enough parameters to establish this check on the theory by internal consistency. In fact the possibility of establishing a consistent picture of this much detail is one of our principal conclusions.

The calculated eigenvectors of the magnetically perturbed problem show a substantial breakdown of the total angular momentum quantum number $J$. This is confirmed experimentally by the fact that more than half of the observed transitions have been identified as ones in which the dominant value of $J$ changes by $\pm 2$. These would be forbidden if $J$ were a good quantum number. The experimental technique of circular polarization has proved to be of great utility in the identification of the spectrum since it unambiguously separates $M = +1, -1$, and 0 transitions.

On the subject of line breadths and intermolecular interactions we have less definite conclusions to offer. We can say, however, that the
striking dependence of the line breadth on all quantum numbers reported
by Beringer and Castle was the result of improper theoretical interpre-
tation of their experimental data. With the lines which they observed
identified by our work and with the correct interpretation of the widths,
their work is in fair agreement with ours. Our results show a slight
decrease in width with increasing K but no significant M dependence
(≤2 per cent). The temperature dependence is as \( T^{-n} \), where \( n = 0.75 \pm 0.04 \).
This indicates a "softer" interaction than that of hard spheres \( (n = 0.5) \)
or the combination of exchange and polarizability interactions considered
by Artman \( (n = 0.627) \). A quadrupole-quadrupole interaction would give
\( n = 0.75 \), but it seems likely that other interactions are more important.
A suggestion for further work is to review these interactions, especially
as they affect the non-degenerate states produced by the Zeeman splitting.
Another specific point to check is whether Artman's 0.627 result is
dependent on his choice of temperatures. This could be checked by
calculating the width predicted by his model at the 78°C temperature
actually used.

Our final line breadth result is that air broadening is as effective
or slightly more effective than pure \( O_2 \) self-broadening. This indicates
that for non-degenerate levels which concern us the \( O_2-N_2 \) collision cross
section equals or exceeds the \( O_2-O_2 \) cross section. This is contrary to
results of previous investigators on the field-free spectrum, which indicated
that \( \sigma_{O_2-N_2} \approx 0.85 \sigma_{O_2-O_2} \). This discrepancy is explained by the assumption
that rotational resonance interactions make an appreciable contribution to
the \( O_2 \) self-broadening in the field-free case.

Summarizing, we conclude that the intensive "vertically integrated"
type of study, which characterizes this thesis research, has paid well in
terms of an understanding of the \( O_2 \) molecule. Such an approach might
fruitfully be applied to \( (e.g.) NO \), where we have the additional complications
of electronic orbital angular momentum and nuclear spin. Not only have the
discrepancies of earlier restricted approaches to the oxygen problem been
explained and eliminated, but also quite unexpected dividends, such as
the determination of the rotational magnetic moment and the spin-orbit
coupling parameter, have turned up. It seems unlikely that these dividends would ever have been found by any approach other than that actually used, namely, a persistent pursuit of an accurate theory which agrees with accurate experimental data. This pursuit is particularly swift if the theoretical and experimental work are done by the same person.
MATRICES ELEMENTS OF THE SPIN-SPIN HAMILTONIAN

By the same methods used in Chapter II, the following matrix elements
between configurations may be computed. We let $\hbar^2 = \Delta$, \(\frac{3}{12} = \gamma\), and \(\frac{\gamma}{12} = \rho\) for simplicity.

\[
H_{ee} = H_{cc} = -\frac{3}{4} \beta^2 \langle \sum \chi_+^*(i) \chi_-^*(j) \rangle \frac{3}{2} \langle \chi_+^*(i) \chi_-^*(j) - \chi_-^*(i) \chi_+^*(j) \rangle d\tau, d\tau.
\]

\[
= g^2 \beta^2 b^2 \kappa^2 \pi^{-1/2} \left\{ \frac{1}{30} + \frac{e^{-3\Delta}}{\Delta} \right\} S_1(\Delta) - \frac{e^{-3\Delta}}{\Delta} S_1(\Delta).
\]

\[
H_{dd} = H_{ff} = -\frac{3}{4} \beta^2 \langle \sum \Phi_+^*(i) \Phi_+^*(j) \rangle \frac{3}{2} \langle \Phi_+^*(i) \Phi_+^*(j) - \Phi_-^*(i) \Phi_-^*(j) \rangle d\tau, d\tau.
\]

\[
= g^2 \beta^2 b^2 \kappa^2 \pi^{-1/2} \left\{ \frac{1}{30} + \frac{e^{-3\Delta}}{\Delta} \right\} S_1(\Delta) - \frac{e^{-3\Delta}}{\Delta} S_1(\Delta).
\]

\[
H_{cd} = H_{ef} = -\frac{3}{4} \beta^2 \langle \sum \Phi_+^*(i) \Phi_-^*(j) \rangle \frac{3}{2} \langle \chi_+^*(i) \chi_-^*(j) - \chi_-^*(i) \chi_+^*(j) \rangle d\tau, d\tau.
\]

\[
= g^2 \beta^2 b^2 \kappa^2 \pi^{-1/2} \left\{ \frac{1}{30} + \frac{e^{-3\Delta}}{\Delta} \right\} S_1(\Delta).
\]

\[
H_{ce} = H_{cb} = H_{cc} = H_{cf} = 0.
\]

\[
H_{ad} = H_{bd} = H_{ae} = H_{be} = H_{af} = H_{bf} = H_{de} = H_{df} = 0
\]

\[
H_{eg} = -H_{eh} = -H_{ce} = 2 \gamma^2 R_{\alpha} H_{cE} = g^2 \beta^2 b^2 \kappa^2 \pi^{-1/2} \left\{ \frac{1}{30} + \frac{e^{-3\Delta}}{\Delta} \right\} S_1(\Delta).
\]

\[
\begin{align*}
&\left\{ e^{\Delta/\Delta} \left[ \Delta + \Delta^2 - B E + \gamma_\alpha - \frac{e^{-3\Delta}}{\Delta} \right] - (B + \Delta^2) (E + \Delta^2) S_1(\Delta) \\
&- 4 \left[ \Delta + \Delta^2 (2 B - E) \right] e^{\Delta^2} S_1(\Delta) - \frac{1}{2} S_1(\Delta) \\
&+ \frac{1}{4} \Delta^{3/2} (3 \Delta^2 + 2 B + E) S_3(\Delta) + 4 \Delta^{3/2} (\Delta^2 + 2 B - E) e^{\Delta^2} S_3(\Delta) \\
&+ \frac{1}{8} \Delta^{-3/2} S_4(\Delta) \right\}
\end{align*}
\]

In these

\[
S_1(\Delta) = \sum_{n=0}^{\infty} \frac{2 \gamma^{n-1}}{1 \cdot 3 \cdot 5 \cdots (2n + 1)} \left( \frac{\Delta}{\gamma} \right)^n
\]

\[
S_2(\Delta) = \sum_{n=0}^{\infty} \frac{2 \gamma^{n-1}}{1 \cdot 3 \cdot 5 \cdots (2n + 3)} \left( \frac{\Delta}{\gamma} \right)^n
\]

\[
S_3(\Delta) = \sum_{n=0}^{\infty} \frac{(2 \gamma)(2 \gamma - 1)}{1 \cdot 3 \cdot 5 \cdots (2n + 1)} \left( \frac{\Delta}{\gamma} \right)^{n+1}
\]

\[
S_4(\Delta) = \sum_{n=1}^{\infty} \frac{(2 \gamma)(2 \gamma - 1)}{1 \cdot 3 \cdot 5 \cdots (2n + 3)} \left( \frac{\Delta}{\gamma} \right)^{n+1}
\]
and the constants $B$, $E$, $J,K,L$, and $M$ and the functions $\phi$ and $\chi$ are as defined by Meckler. In evaluating $R_{eg}$, the terms in $\phi_O$ and $\chi_O$ 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 $b^{3/2}$ and $bR^2 = \Delta$, the $\Delta$ dependence turning out to be rather slight.

APPENDIX B

MATRIX ELEMENTS OF THE DIRECTION COSINES

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 $(JmM' \mid J'M')$. 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 $\Phi_{fg}$ may be factored in the form

$$(JmM \mid \Phi_{fg} \mid J'M') = (J \mid \Phi \mid J')(JmM - \Phi_{fg} \mid J'M')(JmM \mid \Phi_{fg} \mid J'M')$$

where $\Omega$ is $J_z$ and $M$ is $J_M$. With our phase choice (which follows that of Condon and Shortley rather than that of Cross, Hainer, and King, for example), the factors are as follows.

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<th>$J$</th>
<th>$J+1$</th>
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<td>$[T(J,J^2-1)^{1/2}]^{-1}$</td>
<td>$[T(J(J+1))^{-1}]$</td>
<td>$[T(J+1)(J+1)(J+2)]^{1/2}$</td>
</tr>
<tr>
<td>$(JmM \mid \Phi_{fg} \mid J'M')$</td>
<td>$(J^2-\Omega^2)^{1/2}$</td>
<td>$\Omega$</td>
<td>$[(J+1)^2-\Omega^2]^{1/2}$</td>
</tr>
<tr>
<td>$(JmM \mid \Phi_{fg} \mid J'M')$</td>
<td>$\pm \frac{1}{2}[J(J+1)-\Omega(J+1)]^{1/2}$</td>
<td>$\frac{1}{2}[J(J+1)-\Omega(J+1)]^{1/2}$</td>
<td>$\pm \frac{1}{2}[J(J+1)-\Omega(J+1)]^{1/2}$</td>
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<tr>
<td>$(JmM \mid \Phi_{fg} \mid J'M')$</td>
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<td>$M$</td>
<td>$[(J+1)^2-M^2]^{1/2}$</td>
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<tr>
<td>$(JmM \mid \Phi_{fg} \mid J'M')$</td>
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<td>$\frac{1}{2}[J(J+1)-M(M+1)]^{1/2}$</td>
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APPENDIX C

MATRIX ELEMENTS OF $S_z$ WITH RESPECT TO THE BASIS IN WHICH THE FIELD-FREE PROBLEM IS DIAGONAL

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.

\[
\begin{array}{cccc}
K & g(K,K-1)/g_s^e & g(K,K)/g_s^e & g(K,K+1)/g_s^e \\
- & & & \\
1 & -0.317330 & 0.5000000 & 0.483997 \\
3 & -0.197357 & 0.0833333 & 0.247357 \\
5 & -0.141070 & 0.0333333 & 0.165727 \\
7 & -0.110723 & 0.0178571 & 0.124612 \\
9 & -0.0907038 & 0.0111111 & 0.0997945 \\
11 & -0.0768013 & 0.00757576 & 0.0832115 \\
13 & -0.0665888 & 0.00549451 & 0.0713505 \\
15 & -0.0587707 & 0.00416666 & 0.0624471 \\
\end{array}
\]

APPENDIX D

TABLE OF CALCULATED ENERGIES IN THE PRESENCE OF A MAGNETIC FIELD

In this appendix we give the roots of equation (68) for the specific values 4, 8, and 12 kilogauss. The energies are expressed in $\text{kMc/sec}$ and the zero of energy is taken at the unperturbed position of the $J = K$ level.
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APPENDIX E

TABLE OF FIELD DEPENDENT TRANSFORMATIONS

$U_1$ is the coefficient of the $J=K-1$ state function, $U_2$ is that of $J=K$, and $U_3$ is that of $J=K+1$.

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APPENDIX F

VERIFICATION OF THE SHORT CUT METHOD OF HANDLING MATRIX ELEMENTS

To illustrate how these deductions may be carried through in more detail, let us consider the $L_2$ induced by a perturbation $\mathcal{H}$. Using the Van Vleck transformation, or simply evaluating the matrix element between first order
perturbed wave functions, we have

\[
(n \Lambda J M z \mid L_z \mid n \Lambda J' M' z') = \sum_{n' \Lambda J' M' z'} \frac{(n \Lambda J M z \mid \Phi_{L_g} L_g \mid n' \Lambda J' M' z') (n \Lambda J M z \mid \Phi_{L_g} L_g \mid n \Lambda J' M' z')}{E_{n'} - E_n}
\]

\[
- \sum_{n' \Lambda J' M' z'} \frac{(n \Lambda J M z \mid L_z \mid n' \Lambda J' M' z') (n \Lambda J M z \mid \Phi_{L_g} L_g \mid n \Lambda J' M' z')}{E_{n'} - E_n}
\]

where in our case \( n \Lambda \) is the ground \( \frac{3}{2} \) state, \( n' \) runs over \( \pi \) states, and \( \Lambda'' = \pm 1 \) within each \( \pi \) state. This is an expression for a matrix element diagonal in the high energy (\( n \)) quantum numbers, but general in the low energy (\( J M z \)) quantum numbers.

As a specific example, take the spin-orbit perturbation \( A L_g S = A L_g L_g S_g \).

Then

\[
(n \Lambda J M z \mid L_z \mid n \Lambda J' M' z')
\]

\[
= - \sum_{n', \Lambda J' M' z'} \frac{1}{E_{n'} - E_n} \sum_{\Lambda J' M' z'} (n \Lambda J M z \mid \Phi_{L_g} L_g \mid n' \Lambda J' M' z') (n \Lambda J M z \mid A L_g S_g \mid n \Lambda J' M' z')
\]

\[
- \sum_{n', \Lambda J' M' z'} \frac{1}{E_{n'} - E_n} \sum_{\Lambda J' M' z'} (n \Lambda J M z \mid A L_g S_g \mid n' \Lambda J' M' z') (n \Lambda J M z \mid \Phi_{L_g} L_g \mid n \Lambda J' M' z')
\]

The dependence of \( E_n \) on \( \Lambda J M z \) can be neglected, and the elements of the inner sum depend on \( n' \) only through a common scale factor in the \( A L_g \) and \( L_g \) elements. Indicating this dependence by writing \( A L_g (n') \), the inner sums are simply matrix products over the subspace restricted to a single \( n' \) state. Thus we have

\[
(n \Lambda J M z \mid L_z \mid n \Lambda J' M' z') = - \sum_{n', \Lambda J' M' z'} \frac{1}{E_{n'} - E_n} \left( n \Lambda J M z \mid \Phi_{L_g} L_g (n') \right) \left( A L_g (n') S_g \right) \left( n \Lambda J' M' z' \right)
\]

\[
- \sum_{n', \Lambda J' M' z'} \frac{1}{E_{n'} - E_n} \left( n \Lambda J M z \mid A L_g (n') S_g \right) \left( \Phi_{L_g} L_g (n') \right) \left( n \Lambda J' M' z' \right)
\]

The operators here operate in three distinct domains. The direction cosines \( \Phi_{L_g} \) obviously operate on the orientation angles of the molecule with respect to a space fixed frame. \( A \) and \( L_g \) operate on electronic orbital coordinates, and \( S_g \) operates on electron spin coordinates. Operators in different domains commute, and the matrix element of a product of two such operators is a simple factored product, not a matrix product summed on intermediate states. These observations allow us to convert the above equation to
$$(n \Lambda | J M | S \Lambda | n \Lambda J' M' \Xi')$$

$$= - \sum_{g g'} \left[ \sum_{\nu''} \frac{(n \Lambda | L_{g''} (nu''| n \Lambda)+ (n \Lambda | A L_{g''} (nu''| n \Lambda))}{E_{\nu''} - E_{\nu}} \right] \times (n \Lambda | J M | S_g | n \Lambda J' M' \Xi')( \Xi | S_g' | \Xi')$$

$$= - \sum_{g g'} (g^e_{g'} g_{g}) (J M \Xi | \Phi_{z g} S_{g'} | J' M' \Xi') (\Xi | S_g' | \Xi')$$

$$= - \sum_{g g'} (g^e_{g'} g_{g}) (J M \Xi | \Phi_{z g} S_{g'} | J' M' \Xi')$$

We have dropped the $\Lambda$ in $\Phi_{z g}$ since it is zero on both sides and thus does not affect the value of the matrix element (as given in appendix B). To get a form more closely resembling that given in the text, we re-expand the $L_{g_g}$ products, obtaining

$$(g^e_{g'}) g_{g} = \sum_{\nu''} \frac{(n \Lambda | L_{g''} (nu''| n \Lambda)+ (n \Lambda | A L_{g''} (nu''| n \Lambda))}{E_{\nu''} - E_{\nu}}$$

$$= \sum_{\nu''} \frac{(n \Lambda | L_{g''} (nu''| n \Lambda)+ (n \Lambda | A L_{g''} (nu''| n \Lambda))}{E_{\nu''} - E_{\nu}}$$

Given the symmetry of a diatomic molecule, we have equation (26) and therefore the cross terms are imaginary and drop out. Also, when $g=z$, the elements vanish for our $\Lambda=0$ state. Then we have simply

$$(n \Lambda | J M | S \Lambda | n \Lambda J' M' \Xi') = - \sum_{g} (g^e_{g}) g_{g} (J M \Xi | \Phi_{z g} S_{g} | J' M' \Xi')$$

Suppressing the $(n \Lambda | n \Lambda)$ as understood, and omitting the vanishing term in $(g^e_{g})_{zz'}$, we have

$$(J M \Xi | L_{z} | J' M' \Xi') = - \sum_{g=x,y} g^e_{g} (J M \Xi | \Phi_{z g} S_{g} | J' M' \Xi')$$

Since $g^e_{g}$ is just a number, this is an operator identity, which can be written

$$L_{z} = - g^e_{g} \sum_{g=x,y} \Phi_{z g} S_{g}$$

This confirms the result (77) of our short cut method in which $\Phi_{z g}$ and $S_{g}$ were carried through as operators completely independent of electronic coordinates throughout.
APPENDIX G

REVIEW OF CAVITY COUPLING

In chapter X we noted that the power reflection coefficient of a cavity at resonance is

$$|r|^2 = \left(\frac{\xi - 1}{\xi + 1}\right)^2$$  (1)

where $\xi = Q_e/Q_o$, $Q_e$ being the external $Q$ (which measures the coupling) and $Q_o$ being the unloaded cavity $Q$. From this we found

$$4|r|^4 = 4 \xi (\xi - 1)(\xi + 1)^3 Q_o (1/Q)_{ij}$$  (2)

to be the change produced by an absorption $(1/Q)_{ij}$. Differentiation of this coefficient with respect to the coupling parameter $Q_e$ shows that the maximum change is

$$4|r|^2_{max} = 385 Q_o (1/Q)_{ij}$$  (3)

which occurs when the coupling is adjusted to give $\xi = 2\sqrt{3}$ or $|r|^2 = 1/3$.

One might also ask what size solid sample should be used to give the largest signal in the application of paramagnetic resonance to solid-state problems. The competing effects are the increasing filling factor $f_x$, and the decreasing $Q_o$ due to the electric losses. Since one normally puts the sample at a point where $H_{rf}$ is maximum and $E_{rf}$ passes through zero, we treat $H_{rf}$ as a constant over the sample and $E_{rf}$ as passing linearly through zero at the center of the sample (e.g., sample located in the central plane in a rectangular TE$_{012}$ mode cavity). If we consider a cylindrical sample (such as the capillaries used in much work in our laboratory), then as we increase the radius, a simple integration shows that the electric losses increase as $V^2$, where $V$ is the sample volume. If we consider a sample in the form of a flat plate covering the entire cross section of the guide, we can insert more sample close to the $E = 0$ plane, but the loss rises as $V^3$ as the thickness is increased. Quite generally, then, we assume

$$1/Q_o = 1/Q_c + \gamma V^n$$

where $1/Q_c$ is the loss in the cavity walls alone. Using this relation and the assumption that $(1/Q)_{ij}$ is proportional to $V$, we find the maximum signal when $V$ is chosen to give a $Q_o$ satisfying

$$1/Q_o = \frac{n}{n-1} (1/Q_c)$$
If we convert these Q's to values of $|r|^2$, the easily observed quantity, by means of (1), we obtain the following rule for maximum signal: Choose the window size ($Q_e$) and sample size ($V$) so that $|r|^2$ rises from .09 for cylindrical samples or .15 for flat samples to .33 when the sample is inserted. Since the treatment quoted here assumed an unperturbed field distribution, it should be considered only a first approximation in case the samples have high dielectric constants or conductivities.

In adjusting the coupling window, it is convenient to remember that for small windows $1/Q_e$ is proportional to the cube of the area of the window, to the square of the amplitude of the incident field at the window, and to the square of the amplitude of the normalized field in the cavity at the window. (H. A. Bethe, Phys. Rev. 66, (1944) and Rad. Lab. Report #43-30 (1943). The fact that the cavity field is normalized over the entire cavity volume causes the required window size to increase with cavity volume despite the fact that the $Q_o$ of the cavity is increasing.

For loop coupling, we have the approximate result (in M.K.S. units)

$$\frac{1}{Q_e} = \frac{\omega \mu \varepsilon}{Z_0 V} \frac{H^2}{H^2 A_n^2}$$

where $Z_0$ is the impedance of the coaxial line feeding the cavity, $V$ is the cavity volume, $H$ is the value of $H$ at the loop, $H^2$ is the average of $H^2$ over the cavity, and $A_n$ is the projected area of the loop normal to $H$. The analogous result for probe coupling is

$$\frac{1}{Q_e} = \frac{1}{\varepsilon \varepsilon_0} \frac{F_T}{\varepsilon_0 \omega} \frac{E_T^2}{E_T^2} \mathcal{L}^2$$

where $E_T$ is the tangential $E$ field along the probe and $\mathcal{L}$ is the probe length. These formulae gave reasonable agreement with the experimentally observed coupling into the TM010 S-band cavity.

Finally, if one uses a transmission cavity, the power transmission factor at resonance is

$$T = \frac{4Q_L^2}{Q_1 Q_2} \quad (4)$$

where $Q_1$ = $(Q_e)$ input, $Q_2$ = $(Q_e)$ output, $Q_L$ is the loaded $Q$, defined by

$$\frac{1}{Q_L} = \frac{1}{Q_e} + \frac{1}{Q_1} + \frac{1}{Q_2} \quad (5)$$
If we have an absorption \((1/Q)_{ij}\), the change in \(T\) is

\[
\Delta T' = \frac{-S Q^3}{Q_0 Q_1} \left( \frac{1}{Q} \right)_{ij}
\]  

(6)

The condition for maximum signal is \(Q_0 = Q_1 = Q_2\). In this case, \(\mathbf{T} = 4/9\), \(|r|^2 = 1/9\), and

\[
\Delta T_{\text{max}} = -0.296 \; Q_0 \left( \frac{1}{Q} \right)_{ij}
\]  

(7)

The fact that the maximum signal in transmission is somewhat less than that in reflection can be understood by noting that some of the information is wasted as modulation of the reflected signal present even in a transmission cavity.

**APPENDIX II**

**MATRIX METHOD FOR BIMODAL GUIDE AND CIRCULAR POLARIZATION**

In formally handling wave propagation and mode conversion in a waveguide which can propagate in two orthogonal degenerate modes, it is convenient to introduce a matrix operational method. In this method we follow the scattering matrix approach (J. Schwinger-Lecture Notes on Discontinuities in Waveguides; See also Radiation Laboratory Series). The fields are expanded in terms of waves traveling along the guide (\(Z\) direction) and polarized along \(X\) and \(Y\), respectively. Suppressing the universal transverse spacial dependence and the \(e^{i\omega t}\) time dependence, we have

\[
E_x^I = e^{-i\phi} y \; u_y \\
E_x^I = e^{-i\phi} x \; u_x
\]

The wave propagating in the reverse (left) direction would then be given by \(E_x^I, E_y^I\). Thus the field in any region of undistorted guide may be expressed by 4 complex numbers giving the amplitude and phase of these 4 waves. These numbers are conveniently collected in a column vector.

\[
\begin{pmatrix}
C_x^I \\
C_y^I \\
C_x^II \\
C_y^II
\end{pmatrix}
\]
The vectors in the various regions of guide will be related by matrix operators which represent the various types of elements introduced. These matrices are defined to have the property that they yield the coefficients of the 4 outgoing waves when the matrix is multiplied into a column vector composed of the coefficients of the incoming waves from both sides. To illustrate, if the situation is as shown in the sketch,

$$\begin{pmatrix}
\alpha
\beta
\gamma
\delta
\end{pmatrix}
\begin{pmatrix}
B
\end{pmatrix}
$$

then the matrix of $B$ must satisfy the equation

$$B \begin{pmatrix}
\alpha
\beta
\gamma
\delta
\end{pmatrix} = \begin{pmatrix}
\epsilon
\zeta
\gamma
\delta
\end{pmatrix}$$

The matrices of various devices are readily tabulated by considering simple cases. To handle a complicated system, one then sets up a group of these equations, eliminates the undesired unknowns which describe the waves inside the unit, and one is left with a new matrix which describes the more complex system.

Let us now list a few typical examples. If we introduce an element which produces a phase shift $\phi$ and a transmission factor $\alpha$ (depending on the mode), but no reflection or mode conversion, the matrix is simply

$$\Phi = \begin{pmatrix}
\alpha e^{i\phi} & 0 & 0 & 0 \\
0 & \alpha e^{i\phi} & 0 & 0 \\
0 & 0 & \alpha e^{i\phi} & 0 \\
0 & 0 & 0 & \alpha e^{i\phi}
\end{pmatrix}$$

A short converts waves propagating to the right to ones propagating to the left with a phase dependent on the location of the short. The matrix is

$$\Omega = \begin{pmatrix}
0 & 0 & -e^{i2\beta 3x} & 0 \\
0 & 0 & 0 & -e^{i2\beta 3x} \\
-e^{i2\beta 3x} & 0 & 0 & 0 \\
e^{-i2\beta 3x} & 0 & -e^{-i2\beta 3x} & 0
\end{pmatrix}$$
If we introduce a "Babinet compensator" B (in the form of a section of guide squeezed along the diagonal), we may consider the wave expanded in terms of \( \hat{x} \) and \( \hat{y} \) components at \( 45^\circ \) to the original I,II waves. These now propagate at different speeds because of the distortion. At the end of the squeezed section, we re-expand in the original basic waves. Neglecting reflection, the matrix is

\[
B = \begin{pmatrix}
\cos \delta & i \sin \delta & 0 & 0 \\
i \sin \delta & \cos \delta & 0 & 0 \\
0 & 0 & \cos \delta & i \sin \delta \\
0 & 0 & i \sin \delta & \cos \delta
\end{pmatrix}
\]

where \( \delta \) is half the relative phase shift; e.g., \( \delta = \pi/4 \) for a quarter wave plate.

If we consider an ideal transition piece which couples between two pieces of guide with axes turned at an angle \( \theta \), the matrix is

\[
T = \begin{pmatrix}
\cos \theta & \sin \theta & 0 & 0 \\
-\sin \theta & \cos \theta & 0 & 0 \\
0 & 0 & \cos \theta & -\sin \theta \\
0 & 0 & \sin \theta & \cos \theta
\end{pmatrix}
\]

where again we neglect reflection. The special coupler shown in Fig. 14 (p. 105) may be considered a particular form of such a device, with \( \theta = 45^\circ \), respectively, for the two side arms.

It turns out that the proper phase and amplitude relations to excite circularly polarized radiation in a cavity coupled through a hole in a side wall may be obtained in at least three ways with the components described above. If we take

\[
\begin{pmatrix}
1 \\
0 \\
\alpha \\
\beta \\
\gamma \\
\delta
\end{pmatrix}
\]

where the \( \begin{pmatrix} 1 \\ 0 \end{pmatrix} \) indicates that only vertically polarized radiation (I) is incident, where B is set to act as a quarter wave plate, and where \( Z_I = Z_{II} \).
in the short, then at an odd number of $1/8$ wavelengths from the short we have the proper relations. However, the magnitudes of the coupling fields are only $1/\sqrt{2}$ of their maximum values, and they are changing with position, making the positioning critical.

Better performance results if we insert a differential phase shifter.

$$
\begin{pmatrix}
1 \\
\chi \\
y
\end{pmatrix}
\rightarrow
\begin{pmatrix}
\phi \\
\phi' \\
\phi''
\end{pmatrix}
\rightarrow
\begin{pmatrix}
\alpha \\
\beta \\
\gamma \\
\delta
\end{pmatrix}
$$

The result of the matrix operation and algebraic reduction is

$$
\begin{pmatrix}
\alpha \\
\beta \\
\gamma \\
\delta
\end{pmatrix} =
\begin{pmatrix}
\cos \delta & e^{i\phi} \\
\cos \delta & e^{i\phi'} \\
\cos \delta & e^{i\phi''} \\
\cos \delta & e^{i\phi'''}
\end{pmatrix}
$$

From these coefficients, we may construct the $E$ field. From $E$, we may obtain the following dependence for $H$, using the fact that the amplitudes of transverse and longitudinal $H$ are equal for our choice of guide dimensions. (The general case introduces some factors which shift the correct settings slightly).

$$
\vec{H} \sim e^{i\omega t} \left\{ \sin \delta \cos (\beta z - \beta_3 x) \sin \beta (z - z_3) \frac{\overline{U}_z}{\sin \beta (z - z_3)} \right\}
$$

The conditions for circularity are

$$
\phi = \beta z = \phi - \beta_3 x
$$

and

$$
\sin \delta \sin \beta (z - z_3) = \cos \delta \cos \beta (z - z_3)
$$

These are satisfied by choosing $\delta = \eta + \phi$, $\phi = \pm \pi/4$, $z_3 - z = \pm \lambda/4$. This choice locates the window at maxima of both the coupling fields, where positioning is not critical. With this choice, we also have $x = 0$, $|y| = 1$.

Thus the returning wave is completely in the horizontally polarized (II) mode, if the incident wave is vertically polarized (I). An apparatus of this type
was built and successfully tested. However, the problem of coupling out the II mode and the adjustment of B and \( \Phi \) are troublesome.

These difficulties are removed in the final model, described in the text, which may be symbolized as follows.

\[
\begin{pmatrix}
1 \\
0
\end{pmatrix}
\quad T
\quad \begin{pmatrix}
(a^*) \\
0
\end{pmatrix}
\quad Cavity \quad S
\]

This gives

\[
\mathcal{H} \sim e^{i\omega t} \left\{ -\cos \Theta e^{-i\frac{\beta_3}{2}x} \cos \theta \left( e^{i\frac{\beta_3}{2}x} - e^{-i\frac{\beta_3}{2}x} \right) \mathbf{u}_x + \sin \Theta e^{-i\frac{\beta_3}{2}x} \sin \beta \left( e^{i\frac{\beta_3}{2}x} - e^{-i\frac{\beta_3}{2}x} \right) \mathbf{u}_y \right\}
\]

For circular polarization, we choose \( \Theta = 45^\circ \) and \( z_{II} - z_{II} = \pm \frac{\lambda g}{h} \), as described in section XII-B. This again results in \( x = 0 \), \( |y| = 1 \), but the special coupler eliminates the awkwardness in coupling out the second mode. Since the setting of \( \Theta \) and \( z_{II} - z_{II} \) are permanent mechanical properties of the unit, there is no positioning or adjustment problem.
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BIOGRAPHICAL NOTE

The author was born in Green Lake County, Wisconsin, on Feb. 23, 1928. He attended elementary school there and high school in Ripon, Wisconsin, after his family moved to that city. In his senior year in high school he was honored by winning a Westinghouse Science Talent Search Scholarship, and he graduated in 1945 as valedictorian.

The next year was spent in the U.S.N.R. as an electronic technician trainee. In the fall of 1946 he entered Ripon College, where he majored in mathematics and physics for three years. Two summers during this period were spent on instrumentation development at the Republic Steel Corporation, Canton, O. As part of this work he developed an "electronic pilot light" which was patented and is used widely in the plants of that company. His junior year brought election to Phi Alpha, the Ripon College scholastic honor society. After transferring to M.I.T. for completion of his undergraduate work, he was awarded the A.B. (Summa cum laude) from Ripon College in June of 1951. During that summer he completed a thesis entitled "A Study of Paramagnetic Resonance Absorption in Liquids", and received the S.M. degree from M.I.T. in September of that year.

In the fall of 1951 the author began his doctoral study at M.I.T., continuing to be supported by a half-time research assistantship for work in the Research Laboratory of Electronics under Prof. Strandberg. During these years he also taught sections in freshman physics and in thermodynamics and statistical mechanics. His final year's work was supported by a National Science Foundation Predoctoral Fellowship, and the same agency has awarded him a Postdoctoral Fellowship which he plans to use for study and research at Oxford, England, during the next academic year.

His publications are: Paramagnetic Resonance Absorption in Crystals Containing Color Centers, (with A.F. Kip), Phys. Rev. 83, 657(L), (1951); Paramagnetic Resonance in Liquids, (with R. Weinstein and A.F. Kip), Phys. Rev. 84, 848(L), (1951).

He is a member of the society of the Sigma Xi and of the American Physical Society.