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THE THEORY OF THE STARK EFFECT WITH HYPERFINE  
STRUCTURE FOR NEAR-DEGENERATE ENERGY  
LEVELS OF AN ASYMMETRIC ROTOR

A THESIS

Presented to  
the Faculty of the Graduate Division

By

Donald Frohlichstein Eagle

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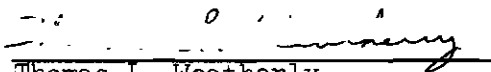
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THE THEORY OF THE STARK EFFECT WITH HYPERFINE  
STRUCTURE FOR NEAR-DEGENERATE ENERGY  
LEVELS OF AN ASYMMETRIC ROTOR

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## SUMMARY

The theory of the Stark effect in the rotational spectrum of an asymmetric rotor has been given by Golden and Wilson. These authors recognized that near-degeneracy of rotational levels is almost inevitable, and they included a discussion of the Stark effect for such cases. The Stark effect for rotational energy levels split by a nuclear quadrupole interaction has been worked out by Mizushima. However, Mizushima did not discuss the case of rotational near-degeneracy. The principal aim of this research has been to develop and test a method for calculating the Stark effect in the presence of nuclear quadrupole interaction for this condition. The secondary aim was to confirm previously reported values for the dipole moments of nitryl chloride and nitrosyl bromide.

The theoretical problem has been attacked along two lines. In the first approach, the Hamiltonian matrix  $H_r + H_Q + H_S$ , which contains rotational terms, nuclear quadrupole interaction terms, and Stark effect terms, was obtained and diagonalized. In the second approach, a method similar to that of Mizushima has been employed, in which the Stark and quadrupole effects are treated separately in the matrix formulation of the problem. In this second approach, the rotational plus Stark Hamiltonian,  $H_r + H_S$ , is obtained and diagonalized. The matrix elements of the quadrupole Hamiltonian,  $H_Q$ , are then added to the previously diagonalized matrix,  $(H_r + H_S)_{\text{diag}}$ , and the resultant matrix,  $(H_r + H_S)_{\text{diag}} + H_Q$ , is then diagonalized to obtain the perturbed rotational energies of the molecule.

The first approach has the more general validity, but the second is more simply calculated. The restriction on the use of the second approach, or a modified Mizushima method, is that the quadrupole matrix elements of the two closely spaced levels must be almost the same. Otherwise, the more difficult simultaneous treatment of the two perturbations is required. The two methods of solution have been evaluated by calculating absorption spectra of nitryl chloride and nitrosyl bromide, and comparing the calculated transitions with experimental observations.

The  $2_1 \rightarrow 3_0$  transition of nitryl chloride has been investigated. The  $2_1$  and  $2_2$  levels are the closely spaced ones, and their quadrupole matrix elements differ only by about one per cent. For this case, the results of applying the two theories are nearly the same, both agreeing with the experimental results.

In the case of nitrosyl bromide, the  $1_1 \rightarrow 2_0$  transition has been examined. The  $1_1$  and  $1_0$  levels lie very close together, and their quadrupole matrix elements differ by about fifty per cent. In this case, the modified Mizushima theory was inadequate and simultaneous treatment of the two perturbations was required for a good prediction of the absorption spectrum. Quantitative results of this comparison are given.

The investigation reported in this dissertation confirms the value of 0.53 debye for the dipole moment of  $\text{NO}_2\text{Cl}$ <sup>35</sup>, and for  $\text{NOBr}$ <sup>79</sup>, it gives a value of 1.80 debye for the component of the dipole moment along the axis of least inertia, rather than a previously reported value of 1.76 debye.

## CHAPTER I

## INTRODUCTION

The theory of the interaction between nuclear electric quadrupole moments and molecular rotation in asymmetric top molecules has been worked out by Bragg (1). The Stark effect for an asymmetric rotor was developed by Golden and Wilson (2) for both the non-degenerate case and the case of accidental near-degeneracy of pairs of rotational levels. Mizushima (3) has considered the combined problem of the Stark effect of an asymmetric top with hyperfine structure resulting from nuclear quadrupole interaction for the case of non-degeneracy. In the weak-field case, his method is an extension of the work of Low and Townes (4) to cover asymmetric tops. In the intermediate-field case, his method is to compute independently the Stark energy according to the theory of Golden and Wilson, and add this Stark energy correction to the rotational energy on the diagonal of the Hamiltonian matrix. He then adds the diagonal and off-diagonal matrix elements of the quadrupole Hamiltonian and solves the resulting secular equation for the perturbed rotational energies.

The present paper is an extension of Mizushima's work on the intermediate-field case to cover the case of accidental near-degeneracy of rotational levels. A straightforward matrix formulation of the problem is used in which the Stark and quadrupole interaction perturbations are simultaneously included. The contact transformation employed by Golden and Wilson is applied to the Hamiltonian to facilitate the diagonalization process. This approach is compared with the method of Mizushima

(independent treatment of the two perturbations) corrected by using the degenerate calculation of the Stark energies.

When hyperfine structure is present, it is convenient to discuss the Stark effect under three different conditions: weak field, strong field and intermediate field.

In the weak-field case, the applied electric field is so small that the Stark energy is considerably less than the quadrupole interaction energy. In this case the molecular wave functions and the hyperfine structure are only slightly perturbed by the electric field. This means that the precession of the molecule due to the applied field is slow enough that the interaction between the nucleus and the molecule is very little affected. In a weak field, the molecular state may be specified by the quantum numbers  $J$ ,  $I$ ,  $F$  and  $M_F$ ; where  $\underline{J}$  is the rotational angular momentum of the molecule,  $\underline{I}$  is the nuclear spin angular momentum,  $\underline{F}$  is the total angular momentum  $\underline{J} + \underline{I}$ , and  $M_F$  specifies the Z-component of the total angular momentum. The Stark effect splits each hyperfine line into a number of different components depending on the value of  $M_F$ ; this splitting is small compared to the quadrupole splitting. A more quantitative discussion of this case is given in Chapter III.

In the strong-field case, the Stark energy is very much greater than the quadrupole interaction energy. The molecule precesses so rapidly that  $\underline{J}$  and  $\underline{I}$  are decoupled, and therefore  $F$  loses its significance as a quantum number. In this case the molecular state may be specified by the quantum numbers,  $J$ ,  $I$ ,  $m_J$ , and  $m_I$ ; where  $J$  and  $I$  are the same as defined above,  $m_J$  specifies the component of  $\underline{J}$  in the direction of the applied field, and  $m_I$  specifies the component of  $\underline{I}$  in the direction

of the field. Under strong field conditions, the quadrupole interaction produces a splitting of each Stark energy level which is considerably smaller than the separation between Stark levels.

In the intermediate-field case, the Stark energy and the quadrupole interaction energy are of the same order of magnitude. Their combined effect is appreciably more difficult to treat than either of the previous two cases. The parameters  $m_J$ ,  $m_I$ , and  $F$  all lose their significance as quantum numbers, and the wave functions must be made up of linear combinations of the wave functions for either the weak-field case or the strong-field case. Calculation of the appropriate wave functions and energy levels is, in general, difficult. Line splittings of the two effects are comparable. Detailed treatment of this case will be found in Chapters III and IV. Notation will be chosen so that it corresponds with that found in the literature. Thus, the symbols  $E_i^0$  and  $W_i^0$  are both used to describe rotational energy levels.

## CHAPTER II

STARK EFFECT AND NUCLEAR QUADRUPOLE INTERACTION  
FOR AN ASYMMETRIC ROTOR

Theory of the Stark Effect.--The theory of the Stark effect for an asymmetric rotor has been developed by Golden and Wilson (5). It will be useful, however, to reproduce their work here with somewhat greater detail than is given in the original paper.

In the non-degenerate case, the expression for the Stark energy of an asymmetric top may be developed from conventional perturbation theory. The Hamiltonian is

$$H = H^0 + EH^S = H^0 + \sum_{g=1}^3 \mu_g E \cos \alpha_g ,$$

where  $H^0$  is the rotational energy Hamiltonian for an asymmetric rotor,  $E$  is the applied electric field,  $\mu_g$  is the component of the electric dipole moment along the  $g^{\text{th}}$  principal axis, and  $\alpha_g$  is the angle between  $\underline{E}$  and the  $g^{\text{th}}$  axis. In terms of asymmetric top wave functions, the rotational energy is

$$W^0 = (J\tau m_J | H^0 | J\tau m_J) .$$

The first order Stark correction is

$$W^1 = (J\tau m_J | EH^S | J\tau m_J) ,$$

and this correction is found to be zero. The second order term is

$$W^2 = \sum_{J'\tau'm'_J} \frac{(J\tau m_J | EH^S | J'\tau'm'_J)(J'\tau'm'_J | EH^S | J\tau m_J)}{W^0(J\tau m_J) - W^0(J'\tau'm'_J)} . \quad (1)$$

The symbol  $\sum'$  means the sum is taken only over elements for which

$$J'\tau'm'_J \neq J\tau m_J .$$

For a particular dipole moment component  $\mu_g$ , the contribution to the energy is

$$W_g^2 = \sum_{J'\tau'm'_J} \mu_g^2 E^2 \frac{(J\tau m_J | \cos \alpha_g | J'\tau'm'_J)(J'\tau'm'_J | \cos \alpha_g | J\tau m_J)}{W^0(J\tau m_J) - W^0(J'\tau'm'_J)} .$$

For an electric field in the space-fixed Z-direction, the matrix elements of  $\cos \alpha_g$  vanish except for  $\Delta J = 0, \pm 1$  and  $\Delta m_J = 0$ . Thus

$$W_g^2 = \mu_g^2 E^2 \left\{ \sum_{\tau'} \frac{(J\tau m_J | \cos \alpha_g | J-1\tau'm_J)(J-1\tau'm_J | \cos \alpha_g | J\tau m_J)}{W^0(J\tau m_J) - W^0(J-1\tau'm_J)} \right. \quad (2)$$

$$+ \sum_{\tau' \neq \tau} \frac{(J\tau m_J | \cos \alpha_g | J\tau'm_J)(J\tau'm_J | \cos \alpha_g | J\tau m_J)}{W^0(J\tau m_J) - W^0(J\tau'm_J)}$$

$$\left. \sum_{\tau'} \frac{(J\tau m_J | \cos \alpha_g | J+1\tau'm_J)(J+1\tau'm_J | \cos \alpha_g | J\tau m_J)}{W^0(J\tau m_J) - W^0(J+1\tau'm_J)} \right\} .$$

Using the notation  $(J\tau m_J | \cos \alpha_g | J'\tau'm'_J) = (\Phi_{FG})_{J\tau m_J; J'\tau'm'_J}$ , where

F denotes one of the space-fixed axes X, Y, Z, equation (2) becomes

$$\begin{aligned}
 W_g^2 = \mu_g^2 E^2 \left\{ \sum_{\tau'} \frac{|(\Phi_{Fg})_{J\tau m_J; J-1\tau' m_J}|^2}{W^0(J\tau m_J) - W^0(J-1\tau' m_J)} \right. \\
 \left. + \sum_{\tau' \neq \tau} \frac{|(\Phi_{Fg})_{J\tau m_J; J\tau' m_J}|^2}{W^0(J\tau m_J) - W^0(J\tau' m_J)} + \sum_{\tau'} \frac{|(\Phi_{Fg})_{J\tau m_J; J+1\tau' m_J}|^2}{W^0(J\tau m_J) - W^0(J+1\tau' m_J)} \right\}. \quad (3)
 \end{aligned}$$

The squares of the matrix elements appearing in the above equation can be obtained from the following expression given in a paper by Cross, Hainer and King (6):

$$\sum_{F m_J m_J'} |\Phi_{Fg}|_{J\tau m_J; J'\tau' m_J'}^2 = 3 |\Phi_{Zg}|_{JJ'}^2 |\Phi_{Zg}^A|_{J\tau; J'\tau'}^2 \sum_{m_J m_J'} |\Phi_{Zg}|_{Jm_J; J'm_J'}^2.$$

The factor 3 results from the sum over F, the three spacial directions X, Y, Z. In order to use this result in equation (3), the summations over F,  $m_J$  and  $m_J'$  must be removed. For F = Z and a particular  $m_J = m_J'$ , one obtains

$$|\Phi_{Zg}|_{J\tau m_J; J'\tau' m_J'}^2 = |\Phi_{Zg}|_{JJ'}^2 |\Phi_{Zg}^A|_{J\tau; J'\tau'}^2 |\Phi_{Zg}|_{Jm_J; J'm_J'}^2.$$

From Table I of Cross, Hainer, and King II(7),

$$\begin{aligned}
 |\Phi_{Zg}|_{J\tau m_J; J-1\tau' m_J'}^2 &= \left[ 16J^2(4J^2-1) \right]^{-1} |\Phi_{Zg}|_{J\tau; J-1\tau'}^2 4(J^2 - m_J^2), \\
 &= \frac{J^2 - m_J^2}{4J^2(4J^2-1)} |\Phi_{Zg}|_{J\tau; J-1\tau'}^2;
 \end{aligned}$$

$$\begin{aligned}
|\Phi_{Zg}|_{J\tau m_J; J\tau' m_J}^2 &= [16J^2(J+1)^2]^{-1} |\Phi_{Zg}|_{J\tau, J\tau', 4m_J}^2, \\
&= \frac{m_J^2}{4J^2(J+1)^2} |\Phi_{Zg}|_{J\tau, J\tau'}^2; \\
|\Phi_{Zg}|_{J\tau m_J; J+1\tau' m_J}^2 &= [16(J+1)^2(2J+1)(2J+3)]^{-1} |\Phi_{Zg}|_{J\tau; J+1\tau', 4(J+m_J+1)(J-m_J+1)}, \\
&= \frac{(J+1)^2 - m_J^2}{4(J+1)^2(2J+1)(2J+3)} |\Phi_{Zg}|_{J\tau, J+1\tau'}^2. \quad (4)
\end{aligned}$$

Substituting Equations (4) into Equation (3) gives

$$\begin{aligned}
W_g^2 &= \mu_g^2 E^2 \left\{ \frac{J^2 - m_J^2}{4J^2(4J^2 - 1)} \sum_{\tau'} \frac{|\Phi_{Zg}|_{J\tau, J-1\tau'}^2}{W^0(J\tau m_J) - W^0(J-1\tau' m_J)} \right. \\
&+ \frac{m_J^2}{4J^2(J+1)^2} \sum_{\tau' \neq \tau} \frac{|\Phi_{Zg}|_{J\tau, J\tau'}^2}{W^0(J\tau m_J) - W^0(J\tau' m_J)} \\
&\left. + \frac{(J+1)^2 - m_J^2}{4(J+1)^2(2J+1)(2J+3)} \sum_{\tau'} \frac{|\Phi_{Zg}|_{J\tau; J+1\tau'}^2}{W^0(J\tau m_J) - W^0(J+1\tau' m_J)} \right\}. \quad (5)
\end{aligned}$$

This is the expression for the Stark energy correction in the non-degenerate case derived by Golden and Wilson (8). From the definition of the line strength  $\lambda_g$  and Table I of Cross, Hainer and King II (9), it may be shown that

$$\begin{aligned}
|\Phi_{Zg}|_{J\tau; J+1\tau'}^2 &= 4(J+1) \lambda_g(J\tau; J+1\tau'); \\
|\Phi_{Zg}|_{J\tau; J-1\tau'}^2 &= 4J \lambda_g(J\tau; J-1\tau'); \\
|\Phi_{Zg}|_{J\tau; J\tau'}^2 &= \frac{4J(J+1)}{2J+1} \lambda_g(J\tau; J\tau').
\end{aligned}$$

Substituting these into Equation (5) gives

$$\begin{aligned}
 W_g^2 = \mu_g^2 E^2 \left\{ \frac{J^2 - m_J^2}{J(4J^2 - 1)} \sum_{\tau} \frac{\lambda_g(J\tau; J-1\tau')}{W^0(J\tau m_J) - W^0(J-1\tau' m_J)} \right. \\
 + \frac{m_J^2}{J(J+1)(2J+1)} \sum_{\tau \neq \tau'} \frac{\lambda_g(J\tau; J\tau')}{W^0(J\tau m_J) - W^0(J\tau' m_J)} \\
 \left. + \frac{(J+1)^2 - m_J^2}{(J+1)(2J+1)(2J+3)} \sum_{\tau} \frac{\lambda_g(J\tau; J+1\tau')}{W^0(J\tau m_J) - W^0(J+1\tau' m_J)} \right\}. \quad (6)
 \end{aligned}$$

The  $\lambda_g$  appearing in this equation have been tabulated by Cross, Hainer and King (10) and Schwendeman and Laurie (11).

In the degenerate case, the Stark energy is obtained from a modification of conventional perturbation theory. Again consider the Hamiltonian  $H = H^0 + EH^S$ . Now, however, apply to it a unitary transformation\*

$$U = e^{iES} = 1 + iES - \frac{1}{2} E^2 S^2 + \dots$$

The transformed Hamiltonian is

$$\begin{aligned}
 UHU^{-1} &= e^{iES} H e^{-iES} = (1 + iES - \frac{1}{2} E^2 S^2)(H^0 + EH^S)(1 - iES - \frac{1}{2} E^2 S^2) \\
 &= H^0 + E[H^S + i(SH^0 - H^0S)] \\
 &\quad + E^2[SH^0S - \frac{1}{2} S^2H^0 - \frac{1}{2} H^0S^2 + i(SH^S - H^SS)].
 \end{aligned}$$

---

\*This development also follows Golden and Wilson (12), with the exception of expressing the unitary transformation as an exponential. The resulting  $S_{ij}$  differ only in the appearance of the imaginary  $i$ .

The next step is to attempt to specify  $S$  so as to remove off-diagonal first order elements. The effects of such terms will then appear as second order corrections on the diagonal. In other words, attempt to pick  $S$  so that  $SH^0 - H^0S = iH^S$ . Consideration of an explicit term makes it apparent that a good definition for  $S$  is

$$S_{ij} = \frac{-iH_{ij}^S}{W_i^0 - W_j^0} \quad \text{for } W_i^0 \text{ not near } W_j^0, \quad (7)$$

and  $S_{ij} = 0$  otherwise ;

where  $W_i^0$  is used to denote the non-zero elements of the diagonal matrix  $H^0$ . The  $ij^{\text{th}}$  element of the first order correction is

$$H_{ij}^1 = E \left[ H_{ij}^S + i \sum_k (S_{ik} H_{kj}^0 - H_{ik}^0 S_{kj}) \right]$$

since  $H^0$  is diagonal, this reduces to

$$\begin{aligned} H_{ij}^1 &= E \left[ H_{ij}^S + i(S_{ij} W_j^0 - W_i^0 S_{ij}) \right] \\ &= E \left[ H_{ij}^S + iS_{ij} (W_j^0 - W_i^0) \right] \end{aligned}$$

With the definition of  $S_{i,j}$  given above, this expression becomes, for non-degenerate levels ( $W_j^0$  not near  $W_i^0$ ):

$$\begin{aligned}
H_{ij}^1 &= E \left[ H_{ij}^S + \frac{H_{ij}^S}{W_i^0 - W_j^0} (W_j^0 - W_i^0) \right] \\
&= E \left[ H_{ij}^S - H_{ij}^S \right] \\
&= 0 .
\end{aligned} \tag{8}$$

For near-degenerate pairs of levels  $W_i^0$  and  $W_j^0$ ,  $S_{ij} = 0$ , and therefore

$$H_{ij}^1 = E H_{ij}^S . \tag{9}$$

The  $ij^{\text{th}}$  element of the second order correction is

$$\begin{aligned}
H_{ij}^2 &= E^2 \left\{ \sum_{k,m} \left[ S_{ik} H_{km}^0 S_{mj} - \frac{1}{2} S_{ik} S_{km} H_{mj}^0 - \frac{1}{2} H_{ik}^0 S_{km} S_{mj} \right] \right. \\
&\quad \left. + i \sum_k (S_{ik} H_{kj}^S - H_{ik}^S S_{kj}) \right\} \\
&= E^2 \left\{ \sum_k \left[ S_{ik} W_k^0 S_{kj} - \frac{1}{2} S_{ik} S_{kj} W_j^0 - \frac{1}{2} W_i^0 S_{ik} S_{kj} + i(S_{ik} H_{kj}^S - H_{ik}^S S_{kj}) \right] \right\} .
\end{aligned}$$

Using the definition of  $S_{ij}$  given in (5), this expression becomes

$$\begin{aligned}
H_{ij}^2 &= E^2 \left\{ \sum_k' \left[ \frac{-H_{ik}^S W_k^0 H_{kj}^S}{(W_i^0 - W_k^0)(W_k^0 - W_j^0)} + \frac{1}{2} \frac{H_{ik}^S H_{kj}^S (W_j^0 + W_i^0)}{(W_i^0 - W_k^0)(W_k^0 - W_j^0)} \right. \right. \\
&\quad \left. \left. + \frac{H_{ik}^S H_{kj}^S}{W_i^0 - W_k^0} - \frac{H_{ik}^S H_{kj}^S}{W_k^0 - W_j^0} \right] \right\} .
\end{aligned}$$

The symbol  $\sum'$  indicates that the sum is taken over all terms for which the denominator is not near zero. Should any denominator approach zero,

the corresponding element of the transformation matrix  $S$  would be zero and the entire term would vanish. Further simplification gives

$$\begin{aligned}
 H_{ij}^2 &= E^2 \sum_k' \frac{H_{ik}^S H_{kj}^S}{(W_i^0 - W_k^0)(W_k^0 - W_j^0)} \left[ -W_k^0 + \frac{1}{2}W_j^0 + \frac{1}{2}W_i^0 + W_k^0 - W_j^0 - W_i^0 + W_k^0 \right] \\
 &= E^2 \sum_k' \frac{H_{ik}^S H_{kj}^S}{(W_i^0 - W_k^0)(W_k^0 - W_j^0)} \left[ W_k^0 - \frac{1}{2}W_j^0 - \frac{1}{2}W_i^0 \right] \\
 &= \frac{1}{2} E^2 \sum_k' \left[ \frac{H_{ik}^S H_{kj}^S}{W_i^0 - W_k^0} + \frac{H_{ik}^S H_{kj}^S}{W_j^0 - W_k^0} \right].
 \end{aligned}$$

Since second order off-diagonal elements contribute nothing below fourth order to the energy, only diagonal terms ( $H_{ii}^2$ ) of the above form need be considered. These terms are

$$H_{ii}^2 = E^2 \sum_k' \frac{H_{ik}^S H_{ki}^S}{W_i^0 - W_k^0}. \quad (10)$$

This expression has the same form as Equation (1).

Thus, with the definition (7), Equations (8) and (10) show that the application of the transformation does not affect the contributions of the non-degenerate levels to the perturbation energy; the previously quoted results are still valid. However, Equation (9) shows that first order off-diagonal terms linking near-degenerate pairs of rotational levels do appear in the Hamiltonian matrix. For these near-degenerate pairs of levels, a two by two secular determinant must be solved to obtain

the corrected energy levels. The diagonal elements of these two by two matrices have the form of Equation (6) with terms linking the near-degenerate pair of levels omitted from the sum. The off-diagonal terms are obtained from Equation (6) by multiplying  $[W^0(J\tau m_J) - W^0(J'\tau' m_J)]$  by the proper omitted term, and extracting the square root of the product. For both nitryl chloride and nitrosyl bromide, diagonal terms are of the form

$$\mu_g^2 E^2 \left\{ \frac{J^2 - m_J^2}{J(4J^2 - 1)} \sum_{\tau'} \frac{\lambda_g(J\tau; J-1\tau')}{W^0(J\tau m_J) - W^0(J-1\tau' m_J)} + \frac{(J+1)^2 - m_J^2}{(J+1)(2J+1)(2J+3)} \sum_{\tau'} \frac{\lambda_g(J\tau; J+1\tau')}{W^0(J\tau m_J) - W^0(J+1\tau' m_J)} \right\},$$

and off-diagonal terms are of the form

$$\mu_g E m_J \left[ \frac{\lambda_g(J\tau; J\tau')}{J(J+1)(2J+1)} \right]^{\frac{1}{2}}.$$

Theory of the Nuclear Quadrupole Interaction.--Although the development of the theory leading to Equation (17) may be found in Ramsey (13), for example, it is desirable to reproduce it here with some additional detail. The electrostatic interaction between a nucleus and its electrons may be written as follows:

$$H_{el} = \int_{\tau_e} \int_{\tau_n} \frac{\rho_e(\underline{r}_e) \rho_n(\underline{r}_n)}{r} d\tau_n d\tau_e,$$

where  $\rho_e(\underline{r}_e)$  is the electron charge density in the volume element  $d\tau_e$  at position  $\underline{r}_e$  relative to the center of the nucleus,  $\rho_n(\underline{r}_n)$  is the nuclear charge density in the volume element  $d\tau_n$  at position  $\underline{r}_n$  relative to the center of the nucleus, and  $r$  is the magnitude of the radius vector joining  $d\tau_e$  and  $d\tau_n$ .

If  $\theta_{en}$  is the angle between  $\underline{r}_e$  and  $\underline{r}_n$ , then one obtains

$$r^2 = r_e^2 + r_n^2 - 2r_e r_n \cos \theta_{en},$$

and

$$\begin{aligned} \frac{1}{r} &= \frac{1}{(r_e^2 + r_n^2 - 2r_e r_n \cos \theta_{en})^{1/2}} \\ &= \frac{1}{r_e} + \frac{r_n}{r_e^2} \cos \theta_{en} + \frac{1}{2} \frac{r_n^2}{r_e^3} (3 \cos^2 \theta_{en} - 1) + \dots, \end{aligned}$$

after a power series expansion in  $\frac{r_n}{r_e}$  is made.

The first term in this expansion has the form of the radial dependence of the potential of an electric monopole, the second that of an electric dipole, and the third that of an electric quadrupole.

The quadrupole interaction then has the form

$$\begin{aligned} H^Q &= \int_{\tau_e} \int_{\tau_n} \frac{\rho_e(\underline{r}_e) \rho_n(\underline{r}_n) r_n^2 (3 \cos^2 \theta_{en} - 1)}{2r_e^3} d\tau_n d\tau_e \\ &= \int_{\tau_e} \int_{\tau_n} \frac{\rho_e(\underline{r}_e) \rho_n(\underline{r}_n)}{2r_e^5} (3r_n^2 r_e^2 \cos^2 \theta_{en} - r_n^2 r_e^2) d\tau_n d\tau_e. \end{aligned}$$

Expanding in Cartesian coordinates by using the relation

$$r_n r_e \cos \theta_{en} = \sum_i X_{ni} X_{ei}, \text{ one obtains}$$

$$\begin{aligned} H^Q &= \int_{\tau_e} \int_{\tau_n} \frac{\rho_e(\underline{r}_e) \rho_n(\underline{r}_n)}{2r_e^5} \left[ 3 \sum_{ij} X_{ni} X_{nj} X_{ei} X_{ej} - r_n^2 r_e^2 \right] d\tau_n d\tau_e \\ &= \int_{\tau_e} \int_{\tau_n} \frac{\rho_e(\underline{r}_e) \rho_n(\underline{r}_n)}{2r_e^5} \frac{1}{3} \sum_{ij} (3X_{ni} X_{nj} - r_n^2 \delta_{ij}) (3X_{ei} X_{ej} - r_e^2 \delta_{ij}) d\tau_n d\tau_e \\ &= \frac{1}{6} \sum_{ij} \int_{\tau_n} \rho_n(\underline{r}_n) (3X_{ni} X_{nj} - r_n^2 \delta_{ij}) d\tau_n \int_{\tau_e} \frac{\rho_e(\underline{r}_e)}{r_e^5} (3X_{ei} X_{ej} - r_e^2 \delta_{ij}) d\tau_e \\ &= -\frac{1}{6} \sum_{ij} Q_{ij} (\underline{\nabla E})_{ij} = -\frac{1}{6} \underline{Q} : \underline{\nabla E}, \end{aligned} \quad (11)$$

where

$$\begin{aligned} Q_{ij} &= \int_{\tau_n} \rho_n(\underline{r}_n) (3X_{ni} X_{nj} - r_n^2 \delta_{ij}) d\tau_n, \\ (\underline{\nabla E})_{ij} &= - \int_{\tau_e} \frac{\rho_e(\underline{r}_e)}{r_e^5} (3X_{ei} X_{ej} - r_e^2 \delta_{ij}) d\tau_e, \end{aligned}$$

and the symbol  $:$  indicates the inner product of two tensors defined by the summation.

To exhibit explicitly the symmetric character of these tensors, they may be written in the form

$$Q_{ij} = \int_{\tau_n} \rho_n(\underline{r}_n) \left[ 3 \frac{X_{ni}X_{nj} + X_{nj}X_{ni}}{2} - r_n^2 \delta_{ij} \right] d\tau_n ,$$

$$(\nabla \underline{E})_{ij} = - \int_{\tau_e} \frac{\rho_e(\underline{r}_e)}{r_e^5} \left[ 3 \frac{X_{ei}X_{ej} + X_{ej}X_{ei}}{2} - r_e^2 \delta_{ij} \right] d\tau_e .$$

From a tedious matrix multiplication (14) or from a group theoretic argument (15) applying to symmetric tensors of the second rank with zero trace which are constructed in the same manner from vectors satisfying the same commutation relationships with respect to  $I$ , it may be shown that the quantum mechanical matrix elements diagonal in  $I$  of all such tensors have the same dependence on  $m_I$ . It then follows that

$$Q_{ij} = C \left[ 3 \frac{(\underline{I})_i (\underline{I})_j + (\underline{I})_j (\underline{I})_i}{2} - \delta_{ij} \underline{I}^2 \right] . \quad (12)$$

The arbitrary constant  $C$  can be expressed as follows in terms of the conventional nuclear quadrupole moment  $Q$ , which is the  $ZZ$  component of the above with  $m_I = I$ .

$$\begin{aligned} Q &= \frac{1}{e} \int \rho_n, m_I=I (3Z_n^2 - r_n^2) d\tau_n = \frac{1}{e} (II | Q_{33} | II) \\ &= \frac{1}{e} C (II | 3(\underline{I})_Z^2 - \underline{I}^2 | II) \\ &= \frac{1}{e} C [3I^2 - I(I+1)] \\ &= \frac{1}{e} C I(2I-1) . \end{aligned}$$

Thus 
$$C = \frac{eQ}{I(2I-1)} .$$

Substituting for  $C$  in Equation (12) gives

$$Q_{ij} = \frac{eQ}{I(2I-1)} \left[ 3 \frac{(\underline{I})_i(\underline{I})_j + (\underline{I})_j(\underline{I})_i}{2} - \delta_{ij} \underline{I}^2 \right]. \quad (13)$$

Similarly, when  $J$  is a good quantum number, the same reasoning applies, and it follows that

$$(\underline{\nabla E})_{ij} = -C' \left[ 3 \frac{(\underline{J})_i(\underline{J})_j + (\underline{J})_j(\underline{J})_i}{2} - \delta_{ij} \underline{J}^2 \right]. \quad (14)$$

The arbitrary constant  $C'$  can be expressed in terms of the average field gradient at the quadrupole nucleus for  $m_J = J$ ,  $\left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av}$ .

The potential  $V$  at the nucleus due to an electronic charge distribution  $\rho_e$  is given by

$$V = \int \rho_e \left( \frac{1}{r_e} \right) d\tau_e .$$

Thus

$$\frac{\partial V}{\partial Z} = \int \rho_e \frac{\partial}{\partial Z} \left( \frac{1}{r_e} \right) d\tau_e = \int \rho_e \frac{-Z_e}{r_e^3} d\tau_e ,$$

and

$$\begin{aligned} \frac{\partial^2 V}{\partial Z^2} &= \int \rho_e \frac{\partial}{\partial Z} \left( \frac{-Z_e}{r_e^3} \right) d\tau_e \\ &= \int \rho_e \left[ \frac{3Z_e^2}{r_e^5} - \frac{1}{r_e^3} \right] d\tau_e \\ &= \int \rho_e \left[ \frac{3Z_e^2 - r_e^2}{r_e^5} \right] d\tau_e . \end{aligned}$$

Then proceeding as above:

$$\begin{aligned}
 \left\langle \frac{\partial^2 v}{\partial z^2} \right\rangle_{Av} &= \int \rho_{e, m_e = J} \left[ \frac{z_e^2 - r_e^2}{r_e^5} \right] d^3 e = (JJ | (\nabla E)_{33} | JJ) \\
 &= C^2 (JJ | 3(\underline{J})_z^2 - \underline{J}^2 | JJ) \\
 &= C^2 [3J^2 - J(2J+1)] \\
 &= C^2 J(2J-1) .
 \end{aligned}$$

Thus 
$$C^2 = \frac{1}{J(2J-1)} \left\langle \frac{\partial^2 v}{\partial z^2} \right\rangle_A .$$

Substituting for  $C^2$  in Equation (14) gives

$$(\nabla E)_{ij} = - \frac{\left\langle \frac{\partial^2 v}{\partial z^2} \right\rangle_{Av}}{J(2J-1)} \left[ 3 \frac{(\underline{J})_i (\underline{J})_j + (\underline{J})_j (\underline{J})_i}{2} - \delta_{ij} J^2 \right] . \quad (15)$$

If expressions (13) and (15) are put back into Equation (11), one obtains:

$$\begin{aligned}
 eQ &= \frac{1}{6} \frac{eQ \left\langle \frac{\partial^2 v}{\partial z^2} \right\rangle_{Av}}{I(2I-1)J(2J-1)} \sum_{i,j} \left[ 3 \frac{(\underline{I})_i (\underline{I})_j + (\underline{I})_j (\underline{I})_i}{2} - \delta_{ij} I^2 \right] \\
 &\quad \times \left[ 3 \frac{(\underline{J})_i (\underline{J})_j + (\underline{J})_j (\underline{J})_i}{2} - \delta_{ij} J^2 \right] \\
 &= \frac{1}{6} \frac{eQ \left\langle \frac{\partial^2 v}{\partial z^2} \right\rangle_{Av}}{I(2I-1)J(2J-1)} \sum_{i,j} \left[ \frac{9}{2} (\underline{I})_i (\underline{I})_j (\underline{J})_i (\underline{J})_j + \frac{9}{2} (\underline{I})_i (\underline{I})_j (\underline{I})_j (\underline{J})_i \right. \\
 &\quad \left. - 3(\underline{I})_i (\underline{I})_j \delta_{ij} J^2 - 3(\underline{I})_i (\underline{I})_j \delta_{ij} I^2 + I^2 J^2 \delta_{ij} \right] . \quad (16)
 \end{aligned}$$

It is shown in Appendix A that Equation (16) is equivalent to the following expression for  $H^Q$ :

$$\begin{aligned}
 H^Q &= \frac{1}{6} \frac{eQ \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av}}{I(2I-1)J(2J-1)} \left\{ \frac{9}{2}(\underline{I} \cdot \underline{J})^2 + \frac{9}{2}(\underline{I} \cdot \underline{J})^2 + \frac{9}{2}(\underline{I} \cdot \underline{J}) - 3\underline{I}^2 \underline{J}^2 - 3\underline{I}^2 \underline{J}^2 + 3\underline{I}^2 \underline{J}^2 \right\} \\
 &= \frac{eQ \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av}}{2I(2I-1)J(2J-1)} \left\{ 3(\underline{I} \cdot \underline{J})^2 + \frac{3}{2} (\underline{I} \cdot \underline{J}) - I(I+1) J(J+1) \right\} \quad (17)
 \end{aligned}$$

This is the form of the Hamiltonian usually used in evaluating the nuclear quadrupole contribution to the energy of a molecule.

The evaluation has two parts: one is the computation of  $\left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av}$ , and the other is the solution of the secular determinant obtained from Equation (17). Bragg (16) has obtained the following expression for

$$\left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av} :$$

$$\left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av} = \frac{2J}{(2J+1)(2J+3)} \sum_{\tau, \tau'} \left[ \frac{\partial^2 V}{\partial x^2} \lambda_x (J_\tau, J_{\tau'}) + \frac{\partial^2 V}{\partial y^2} \lambda_y (J_\tau, J_{\tau'}) + \frac{\partial^2 V}{\partial z^2} \lambda_z (J_\tau, J_{\tau'}) \right];$$

where  $x, y, z$  are molecule-fixed axes and  $\lambda_x, \lambda_y, \lambda_z$  are the line strengths tabulated by Cross, Hainer, and King (17). The matrix elements of  $\left\{ 3(\underline{I} \cdot \underline{J})^2 + \frac{3}{2} (\underline{I} \cdot \underline{J}) - I(I+1) J(J+1) \right\}$  are given by Kellogg, Rabi, Ramsey and Zacharias (18). Using these matrix elements and Bragg's expression for

$\left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av}$ , the problem of computing the quadrupole correction is a straight-

forward one.

## CHAPTER III

MIZUSHIMA'S THEORY OF THE STARK EFFECT IN THE  
PRESENCE OF HYPERFINE STRUCTURE

In connection with Mizushima's approach, it is helpful to develop a few results from perturbation theory. Consider the Hamiltonian

$$H = H^0 + \epsilon H^1 + \epsilon^2 H^2 + \dots ,$$

the wave function  $\psi(n) = \psi_0(n) + \epsilon \psi_1(n) + \epsilon^2 \psi_2(n) + \dots$ , and the energy  $E(n) = E_0(n) + \epsilon E_1(n) + \epsilon^2 E_2(n) + \dots$ , where  $n$  stands for all the quantum numbers characterizing the unperturbed wave function. Substituting the above three expressions into Schrodinger's equation,  $H\psi = E\psi$ , and equating coefficients of equal powers of  $\epsilon$  gives the following:

$$0^{\text{th}} \text{ order} - H^0 \psi_0(n) = E_0(n) \psi_0(n) ;$$

$$1^{\text{st}} \text{ order} - H^1 \psi_0(n) + H^0 \psi_1(n) = E_0(n) \psi_1(n) + E_1(n) \psi_0(n) ;$$

$$2^{\text{nd}} \text{ order} - H^2 \psi_0(n) + H^1 \psi_1(n) + H^0 \psi_2(n) = E_0(n) \psi_2(n) + E_1(n) \psi_1(n) + E_2(n) \psi_0(n).$$

The first order wave functions may be expressed as a combination of the zeroth order wave functions as follows:

$$\psi_1(n) = \sum_{n'}^{\infty} a_{nn'} \psi_0(n') ,$$

where

$$a_{nn'} = \frac{H_{n'n}^1}{E_0(n) - E_0(n')}, \quad n' \neq n,$$

and

$$a_{nn} = 0.$$

The results obtained for the energies are

$$E_0(n) = H_{nn}^0; \quad (18)$$

$$E_1(n) = H_{nn}^1;$$

$$E_2(n) = H_{nn}^2 + \sum_{n' \neq n} \frac{H_{nn'}^1 H_{n'n}^1}{E_0(n) - E_0(n')}.$$

Weak Field Case.--In Mizushima's weak-field approximation, the Stark effect is considered as a perturbation on the rotational plus hyperfine energy and is calculated using zero-order wave functions specified by  $J$ ,  $\tau$ ,  $I$ ,  $F$ , and  $M$ . These wave functions diagonalize the rotational plus quadrupole Hamiltonian. The Hamiltonian to be considered is

$$H = (H^r + H^Q) + H^S = H^0 + \epsilon H^1,$$

where  $H^r$  is the rotational energy Hamiltonian,  $H^Q$  is the quadrupole interaction term, and  $H^S$  is the Stark energy Hamiltonian. As before

$H^S = \sum_g \mu_g E \cos \alpha_g$ , where  $\mu_g$  is the component of the electric dipole moment along the  $g^{\text{th}}$  principal axis,  $E$  is the external applied field,

and  $\alpha_g$  is the angle between the applied field and the  $g^{\text{th}}$  axis. From Equation (18) above

$$\begin{aligned} E_1(n) &= H_{nn}^1 = (J\tau IFM | H^S | J\tau IFM) \\ &= (J\tau IFM | \sum_g \mu_g E \cos \alpha_g | J\tau IFM) \\ &= \sum_g \mu_g E (J\tau IFM | \cos \alpha_g | J\tau IFM) ; \end{aligned}$$

$$\begin{aligned} E_2(n) &= \sum_{n' \neq n} \frac{H_{nn'}^1 H_{n'n}^1}{E_0(n) - E_0(n')} \\ &= \sum_{J'\tau'F'} \frac{(J\tau IFM | \sum_g \mu_g E \cos \alpha_g | J'\tau'IF'M)(J'\tau'IF'M | \sum_g \mu_g E \cos \alpha_g | J\tau IFM)}{E_0(J\tau F) - E_0(J'\tau'F')} \\ &= \sum_g \sum_{J'\tau'F'} \mu_g^2 E^2 \frac{(J\tau IFM | \cos \alpha_g | J'\tau'IF'M)(J'\tau'IF'M | \cos \alpha_g | J\tau IFM)}{E_0(J\tau F) - E_0(J'\tau'F')} . \end{aligned}$$

Since the matrix is diagonal in I and M, summation over I' and M' was omitted in the above expression. The matrix elements of  $\cos \alpha_g$  can be evaluated by using Racah's method. Mizushima has solved the problem (19), and his result for the Stark energy due to the  $g^{\text{th}}$  component of the dipole moment is

$$E_1(n) = \sum_g \mu_g E (J\tau IFM | \cos \alpha_g | J\tau IFM) = 0 ;$$

$$E_2(n) = W_{J\tau IFM} = \sum_g (W_g)_{J\tau IFM},$$

$$(W_g)_{J\tau IFM} = \mu_g^2 E^2 \left\{ \begin{aligned} & f_1(JIFM) \sum_{\tau'} \frac{\lambda_g(J\tau; J+1 \tau')}{E_0(J\tau F) - E_0(J+1 \tau' F)} \\ & + f_2(JIFM) \sum_{\tau'} \frac{\lambda_g(J\tau; J+1 \tau')}{E_0(J\tau F) - E_0(J+1 \tau' F+1)} \\ & + f_3(JIFM) \sum_{\tau'} \frac{\lambda_g(J\tau; J+1 \tau')}{E_0(J\tau F) - E_0(J+1 \tau' F-1)} \\ & + f_4(JIFM) \sum_{\tau'} \frac{\lambda_g(J\tau; J\tau')}{E_0(J\tau F) - E_0(J\tau' F+1)} \\ & + f_5(JIFM) \sum_{\tau' \neq \tau} \frac{\lambda_g(J\tau; J\tau')}{E_0(J\tau F) - E_0(J\tau' F)} \\ & + f_4(JIF-1M) \sum_{\tau'} \frac{\lambda_g(J\tau; J\tau')}{E_0(J\tau F) - E_0(J\tau' F-1)} \\ & + f_1(J-1IFM) \sum_{\tau'} \frac{\lambda_g(J\tau; J-1\tau')}{E_0(J\tau F) - E_0(J-1\tau' F)} \\ & + f_2(J-1IF-1M) \sum_{\tau'} \frac{\lambda_g(J\tau; J-1\tau')}{E_0(J\tau F) - E_0(J-1\tau' F-1)} \\ & + f_3(J-1IF+1M) \sum_{\tau'} \frac{\lambda_g(J\tau; J-1\tau')}{E_0(J\tau F) - E_0(J-1\tau' F+1)} \end{aligned} \right\};$$

where the  $\lambda_g$  are the line strengths defined by Golden and Wilson (20) and tabulated by Cross, Hainer and King (21), and the  $f$ 's are given by

$$f_1(\text{JIFM}) = \frac{M^2 (J+I+F+2)(I+F-J)(I+J+1-F)(F+J+1-I)}{4F^2 (F+1)^2 (2J+3)(2J+1)(J+1)} ;$$

$$f_2(\text{JIFM}) = \frac{(J+I+F+3)(J+I+F+2)(J-I+F+2)(J-I+F+1) [(F+1)^2 - M^2]}{4(F+1)^2 (2F+3)(2F+1)(2J+3)(2J+1)(J+1)} ;$$

$$f_3(\text{JIFM}) = \frac{(I+F-J)(I+F-J-1)(I+J-F+2)(I+J-F+1) [F^2 - M^2]}{4F^2 (2F-1)(2F+1)(2J+3)(2J+1)(J+1)} ;$$

$$f_4(\text{JIFM}) = \frac{(I+J+F+2)(I+J-F)(I+F-J+1)(J+F-I+1) [(F+1)^2 - M^2]}{4J(J+1)(2J+1)(F+1)^2 (2F+3)(2F+1)} ;$$

$$f_5(\text{JIFM}) = \frac{M^2 [J(J+1) + F(F+1) - I(I+1)]^2}{4J(J+1)(2J+1) F^2 (F+1)^2} .$$

Intermediate Field Case.--When the applied electric field is sufficiently strong that the Stark and quadrupole energies are of the same order of magnitude, the assumptions under which the above results were derived no longer hold, and therefore the theory is inadequate and perturbation theory must be further considered. The development given below was reported previously, in the author's master's thesis (22). Mizushima (23) originally solved the problem in the non-degenerate case, but his paper gives only the resulting secular determinant from which the actual calculations are made.

According to the matrix formulation of quantum mechanics, the perturbed energies of a system can be obtained by computing the Hamiltonian matrix  $H$  in terms of the unperturbed wave functions  $\psi_0$  and diagonalizing this matrix. The allowed energies then appear as the diagonal elements.

The elements of H are of the form

$$\begin{aligned} & \int \bar{\psi}_0(n) [H^0 + \epsilon H^1 + \dots] \psi_0(n') d\tau \\ &= \int \bar{\psi}_0(n) H^0 \psi_0(n') d\tau + \epsilon \int \bar{\psi}_0(n) H^1 \psi_0(n') d\tau + \dots \\ &= E_0(n) \delta_{nn'} + \epsilon H_{nn'}^1 + \dots \end{aligned}$$

The diagonal elements of this matrix are

$$H_{nn} = E_0(n) + \epsilon H_{nn}^1 + \dots ,$$

and the off-diagonal elements are

$$H_{nn'} = \epsilon H_{nn'}^1 + \dots .$$

When the Hamiltonian matrix is diagonalized, it is found that the off-diagonal elements  $\epsilon H_{nn'}^1$ , contribute to the energy only in the next higher order: that is, in terms of order  $\epsilon^2$ . Thus, when the matrix elements of H are computed using zero-order wave functions, it is found that the off-diagonal elements are zero to zero order in  $\epsilon$ , and the diagonal elements are the perturbed energies correct to first order in  $\epsilon$ . This suggests that if wave functions correct to first order in  $\epsilon$  are used, the off-diagonal elements of H would be zero to first order and the diagonal elements would be the perturbed energies correct to second order.

To show that this is true, define

$$\psi_I(n) = \psi_0(n) + \epsilon \psi_1(n) = \sum_{n'} b_{nn'} \psi_0(n') ,$$

where

$$b_{nn'} = \frac{\epsilon H_{n'n}^1}{E_0(n) - E_0(n')} \quad , \quad n' \neq n ;$$

and

$$|b_{nn}|^2 = 1 - \sum_{n' \neq n} |b_{nn'}|^2 = 1 - \epsilon^2 \sum_{n' \neq n} \frac{|H_{n'n}^1|^2}{[E_0(n) - E_0(n')]^2} .$$

The diagonal elements of H are:

$$\begin{aligned} W_2(n) &= \int \bar{\psi}_I(n) H \psi_I(n) d\tau \\ &= \int \sum_{n'} \bar{b}_{nn'} \bar{\psi}_0(n') (H^0 + \epsilon H^1) \sum_{n''} b_{nn''} \psi_0(n'') d\tau \\ &= \sum_{n'} \sum_{n''} \bar{b}_{nn'} b_{nn''} \int \bar{\psi}_0(n') H^0 \psi_0(n'') d\tau \\ &\quad + \epsilon \sum_{n'} \sum_{n''} \bar{b}_{nn'} b_{nn''} \int \bar{\psi}_0(n') H^1 \psi_0(n'') d\tau . \end{aligned}$$

Denoting  $\int \bar{\psi}_0(n') H^1 \psi_0(n'') d\tau$  by  $H_{n'n}^1$  and making use of the relation

$H^0 \psi_0 = E_0 \psi_0$ , the above expression for  $W_2(n)$  becomes

$$\begin{aligned}
W_2(n) &= \sum_{n'} \sum_{n''} \bar{b}_{nn'} b_{nn''} E_0(n'') \int \bar{\psi}_0(n') \psi_0(n'') d\tau + \epsilon \sum_{n'} \sum_{n''} \bar{b}_{nn'} b_{nn''} H_{n'n''}^1 \\
&= \sum_{n'} \sum_{n''} \bar{b}_{nn'} b_{nn''} E_0(n'') \delta_{n'n''} + \epsilon \sum_{n'} \sum_{n''} \bar{b}_{nn'} b_{nn''} H_{n'n''}^1 \\
&= \sum_{n'} |b_{nn'}|^2 E_0(n') + \epsilon \sum_{n'} \sum_{n''} \bar{b}_{nn'} b_{nn''} H_{n'n''}^1 \\
&= |b_{nn}|^2 E_0(n) + \sum_{n' \neq n} |b_{nn'}|^2 E_0(n') + \epsilon |b_{nn}|^2 H_{nn}^1 \\
&\quad + \epsilon \sum_{n' \neq n} \bar{b}_{nn'} b_{nn} H_{n'n}^1 + \epsilon \sum_{n'' \neq n} \bar{b}_{nn} b_{nn''} H_{nn''}^1 + \epsilon \sum_{n' \neq n} \sum_{n'' \neq n} \bar{b}_{nn'} b_{nn''} H_{n'n''}^1.
\end{aligned}$$

Substituting for  $|b_{nn}|^2$ , and then for  $b_{nn'}$ ,

$$\begin{aligned}
W_2(n) &= E_0(n) - E_0(n) \sum_{n' \neq n} |b_{nn'}|^2 + \sum_{n' \neq n} |b_{nn'}|^2 E_0(n') + \epsilon H_{nn}^1 \\
&\quad - \epsilon \sum_{n' \neq n} |b_{nn'}|^2 H_{nn}^1 + \epsilon \sum_{n' \neq n} \bar{b}_{nn'} b_{nn} H_{n'n}^1 + \epsilon \sum_{n'' \neq n} \bar{b}_{nn} b_{nn''} H_{nn''}^1 \\
&\quad + \epsilon \sum_{n' \neq n} \sum_{n'' \neq n} \bar{b}_{nn'} b_{nn''} H_{n'n''}^1 \\
&= E_0(n) - \epsilon^2 \sum_{n' \neq n} \frac{|H_{n'n}^1|^2}{[E_0(n) - E_0(n')]^2} [E_0(n) - E_0(n')] + \epsilon H_{nn}^1
\end{aligned}$$

$$\begin{aligned}
& - \epsilon^3 \sum_{n' \neq n} \frac{|H_{n',n}^1|^2 H_{nn}^1}{[E_0(n) - E_0(n')]^2} + \epsilon^2 \sum_{n' \neq n} \frac{\bar{H}_{n',n}^1 H_{n',n}^1}{E_0(n) - E_0(n')} \left\{ 1 - \epsilon^2 \sum_{n' \neq n} \frac{|H_{n',n}^1|^2}{[E_0(n) - E_0(n')]^2} \right\}^{\frac{1}{2}} \\
& + \epsilon^2 \sum_{n'' \neq n} \frac{H_{n''n}^1 H_{nn''}^1}{E_0(n) - E_0(n'')} \left\{ 1 - \epsilon^2 \sum_{n' \neq n} \frac{|H_{n',n}^1|^2}{[E_0(n) - E_0(n')]^2} \right\}^{\frac{1}{2}} \\
& + \epsilon^3 \sum_{n' \neq n} \sum_{n'' \neq n} \frac{H_{nn}^1 H_{n''n}^1 H_{n',n''}^1}{[E_0(n) - E_0(n')] [E_0(n) - E_0(n'')]}.
\end{aligned}$$

Neglecting all terms of order higher than  $\epsilon^2$ , and noting that  $\bar{H}_{n',n}^1 = H_{nn'}^1$ , this reduces to

$$\begin{aligned}
W_2(n) &= E_0(n) + \epsilon H_{nn}^1 + \epsilon^2 \left\{ \sum_{n' \neq n} \frac{H_{nn}^1 H_{n',n}^1}{E_0(n) - E_0(n')} + \sum_{n'' \neq n} \frac{H_{n''n}^1 H_{nn''}^1}{E_0(n) - E_0(n'')} - \sum_{n' \neq n} \frac{|H_{n',n}^1|^2}{E_0(n) - E_0(n')} \right\} \\
&= E_0(n) + \epsilon H_{nn}^1 + \epsilon^2 \sum_{n' \neq n} \left[ \frac{2|H_{n',n}^1|^2}{E_0(n) - E_0(n')} - \frac{|H_{n',n}^1|^2}{E_0(n) - E_0(n')} \right] \\
&= E_0(n) + \epsilon H_{nn}^1 + \epsilon^2 \sum_{n' \neq n} \frac{|H_{n',n}^1|^2}{E_0(n) - E_0(n')}.
\end{aligned}$$

These are the perturbed energies correct to second order in  $\epsilon$  as given by non-degenerate perturbation theory.

The off-diagonal terms are of the form:

$$\begin{aligned}
\int \bar{\Psi}_I H \Psi_I' d\tau &= \int \sum_{n'} \bar{b}_{nn'} \bar{\psi}_0(n') (H^0 + \epsilon H^1) \sum_{m'} b_{mm'} \psi_0(m') d\tau, \quad n \neq m, \\
&= \sum_{n'} \bar{b}_{nn'} \sum_{m'} b_{mm'} \int \bar{\psi}_0(n') H^0 \psi_0(m') d\tau + \epsilon \sum_{n'} \sum_{m'} \bar{b}_{nn'} b_{mm'} H_{n'm}^1, \\
&= \sum_{n'} \bar{b}_{nn'} \sum_{m'} b_{mm'} E_0(m') \delta_{n'm'} + \epsilon \sum_{n'} \sum_{m'} \bar{b}_{nn'} b_{mm'} H_{n'm}^1, \\
&= \epsilon^2 \sum_{n' \neq n} \frac{\bar{H}_{n'n}^1}{E_0(n) - E_0(n')} \sum_{n' \neq m} \frac{H_{n'm}^1}{E_0(m) - E_0(n')} E_0(n') \\
&\quad + \epsilon \frac{H_{mm}^1}{E_0(n) - E_0(m)} \left\{ 1 - \epsilon^2 \sum_{n' \neq m} \frac{|H_{n'm}^1|^2}{[E_0(m) - E_0(n')]^2} \right\}^{\frac{1}{2}} E_0(m) \\
&\quad + \epsilon \left\{ 1 - \epsilon^2 \sum_{n' \neq n} \frac{|\bar{H}_{n'n}^1|^2}{[E_0(n) - E_0(n')]^2} \right\}^{\frac{1}{2}} \frac{H_{nm}^1}{E_0(m) - E_0(n)} E_0(n) \\
&\quad + \epsilon^3 \sum_{n' \neq n} \frac{\bar{H}_{n'n}^1}{E_0(n) - E_0(n')} \sum_{m' \neq m} \frac{H_{m'm}^1}{E_0(m) - E_0(m')} H_{n'm'}^1 \\
&\quad + \epsilon^2 \sum_{n' \neq n} \frac{\bar{H}_{n'n}^1}{E_0(n) - E_0(n')} \left\{ 1 - \epsilon^2 \sum_{m' \neq m} \frac{|H_{m'm}^1|^2}{[E_0(m) - E_0(m')]^2} \right\}^{\frac{1}{2}} H_{n'm}^1 \\
&\quad + \epsilon^2 \left\{ 1 - \epsilon^2 \sum_{n' \neq n} \frac{|\bar{H}_{n'n}^1|^2}{[E_0(n) - E_0(n')]^2} \right\}^{\frac{1}{2}} \sum_{m' \neq m} \frac{H_{m'm}^1}{E_0(m) - E_0(m')} H_{nm'}^1 \\
&\quad + \epsilon \left\{ 1 - \epsilon^2 \sum_{n' \neq n} \frac{|\bar{H}_{n'n}^1|^2}{[E_0(n) - E_0(n')]^2} \right\}^{\frac{1}{2}} \left\{ 1 - \epsilon^2 \sum_{m' \neq m} \frac{|H_{m'm}^1|^2}{[E_0(m) - E_0(m')]^2} \right\}^{\frac{1}{2}} H_{nm}^1.
\end{aligned}$$

Neglecting all terms of order higher than  $\epsilon$ , this simplifies to

$$\int \bar{\psi}_I H \psi_I' d\tau = \epsilon \frac{\bar{H}_{mn}^1}{E_0(n) - E_0(m)} E_0(m) + \epsilon \frac{H_{nm}^1}{E_0(m) - E_0(n)} E_0(n) + \epsilon H_{nm}^1, n \neq m.$$

Noting that  $\bar{H}_{mn}^1 = H_{nm}^1$  and collecting terms:

$$\begin{aligned} \int \bar{\psi}_I' H \psi_I d\tau &= \epsilon \frac{H_{nm}^1}{E_0(m) - E_0(n)} [E_0(n) - E_0(m)] + \epsilon H_{nm}^1, n \neq m, \\ &= -\epsilon H_{nm}^1 + \epsilon H_{nm}^1, n \neq m, \\ &= 0. \end{aligned}$$

Thus the perturbed wave functions diagonalize  $H$  to first order in  $\epsilon$ , and the diagonal elements are the perturbed energies correct to second order.

The Hamiltonian for an asymmetric rotor containing a nucleus with an electric quadrupole moment and subjected to an external electric field is

$$H = H^0 + \epsilon_S H^S + \epsilon_Q H^Q,$$

where  $H^0$  is the rotational energy Hamiltonian,  $\epsilon_S H^S$  is the Stark energy term, and  $\epsilon_Q H^Q$  is the quadrupole interaction term. The energy eigenvalues are obtained by computation of the Hamiltonian matrix in terms of a complete set of orthogonal functions, and subsequent diagonalization of that matrix. In this particular case, it is desirable to use a complete set of wave functions of the type  $\psi_I$  which diagonalize  $H^0 + \epsilon_S H^S$  to first order in  $\epsilon_S$ . The only first-order off-diagonal elements of  $H$  will then be those of  $\epsilon_Q H^Q$ . These wave functions will be designated  $\psi_n^S$  and are defined by

$$\psi_n^S = \psi_n^0 + \epsilon_S \psi_n^1 = \sum_n b_{nn} \psi_n^0;$$

where

$$b_{nn'} = \frac{\epsilon_S^{H^S}{}_{n'n}}{E_0(n) - E_0(n')} , \quad n' \neq n ,$$

and

$$|b_{nn}|^2 = 1 - \sum_{n' \neq n} |b_{nn'}|^2 = 1 - \epsilon_S^2 \sum_{n' \neq n} \frac{|H_{n'n}^S|^2}{[E_0(n) - E_0(n')]^2} .$$

Now  $\psi_n^0 = \psi(J\tau, I m_J, m_I) = \psi(J\tau, m_J) \phi(I m_I)$  where  $\psi(J\tau, m_J)$  is an asymmetric rotor wave function, and  $\phi(I m_I)$  is the nuclear spin wave function. The matrix elements of  $H$  are  $(\psi_n^S | H | \psi_{n'}^S) = \int \bar{\psi}_n^S H \psi_{n'}^S d\tau$ . Diagonalization of  $H$  requires the solution of the following secular equation for the allowed energies:

$$|(\psi_n^S | H | \psi_{n'}^S) - E \delta_{nn'}| = 0 . \quad (19)$$

In this equation

$$\begin{aligned} (\psi_n^S | H | \psi_{n'}^S) &= (\psi_n^S | H^0 + \epsilon_S H^S + \epsilon_Q H^Q | \psi_{n'}^S) \\ &= (\psi_n^S | H^0 + \epsilon_S H^S | \psi_{n'}^S) + (\psi_n^S | \epsilon_Q H^Q | \psi_{n'}^S) . \end{aligned} \quad (20)$$

The off-diagonal elements of the first term in this equation are zero to first order in  $\epsilon$ , as shown above, and the diagonal elements are

$$(\psi_n^S | H^0 + \epsilon_S H^S | \psi_n^S) = E_n^0 + \epsilon_S^{H^S}{}_{nn} + \epsilon_S^2 \sum_{n' \neq n} \frac{|H_{n'n}^S|^2}{E_0(n) - E_0(n')}$$

where the matrix elements on the right, designated by subscripts, are evaluated using zero order wave functions. As stated in Chapter II, the diagonal matrix elements  $\epsilon_{S_{nn}}^{\text{H}^{\text{S}}}$  vanish. Therefore

$$(\psi_n^{\text{S}} | \text{H}^{\text{O}} + \epsilon_{\text{S}}^{\text{H}^{\text{S}}} | \psi_n^{\text{S}}) = E_n^{\text{O}} + \epsilon_{\text{S}}^2 \sum_{n' \neq n} \frac{|\text{H}_{n'n}^{\text{S}}|^2}{E_n^{\text{O}} - E_{n'}^{\text{O}}} = E_n^{\text{O}} + W_n^{\text{S}}, \quad (21)$$

where  $W_n^{\text{S}}$ , which has been substituted for the term involving the sum, is the Stark energy in the absence of quadrupole interaction. As shown in Chapter II, it is given by

$$\begin{aligned} W_n^{\text{S}} = \sum_{g=1}^3 (W_g)_{J\tau m_J} &= \sum_{g=1}^3 \mu_g^2 E^2 \left\{ \frac{J^2 - m_J^2}{4J^2(4J^2 - 1)} \sum_{\tau'} \frac{|\Phi_{Zg}|_{J\tau; J-1\tau'}^2}{W^{\text{O}}(J\tau m_J) - W^{\text{O}}(J-1\tau' m_J)} \right. \\ &+ \frac{m_J^2}{4J^2(J+1)^2} \sum_{\tau' \neq \tau} \frac{|\Phi_{Zg}|_{J\tau; J\tau'}^2}{W^{\text{O}}(J\tau m_J) - W^{\text{O}}(J\tau' m_J)} \\ &\left. + \frac{(J+1)^2 - m_J^2}{4(J+1)^2(2J+1)(2J+3)} \sum_{\tau'} \frac{|\Phi_{Zg}|_{J\tau; J+1\tau'}^2}{W^{\text{O}}(J\tau m_J) - W^{\text{O}}(J+1\tau' m_J)} \right\}. \end{aligned}$$

In terms of the line strengths  $\lambda_g$ :

$$\begin{aligned} W_n^{\text{S}} = \sum_{g=1}^3 (W_g)_{J\tau m_J} &= \sum_{g=1}^3 \mu_g^2 E^2 \left\{ \frac{J^2 - m_J^2}{J(4J^2 - 1)} \sum_{\tau'} \frac{\lambda_g(J\tau; J\tau')}{W^{\text{O}}(J\tau m_J) - W^{\text{O}}(J-1\tau' m_J)} \right. \\ &+ \frac{m_J^2}{J(J+1)(2J+1)} \sum_{\tau' \neq \tau} \frac{\lambda_g(J\tau; J\tau')}{W^{\text{O}}(J\tau m_J) - W^{\text{O}}(J\tau' m_J)} \\ &\left. + \frac{(J+1)^2 - m_J^2}{(J+1)(2J+1)(2J+3)} \sum_{\tau'} \frac{\lambda_g(J\tau; J+1\tau')}{W^{\text{O}}(J\tau m_J) - W^{\text{O}}(J+1\tau' m_J)} \right\}. \end{aligned}$$

Substituting Equation (21) back into Equation (20) and then putting the results into Equation (19) gives

$$|(\mathbb{E}_n^0 + W_n^S)\delta_{nn'} + (\psi_n^S | \epsilon_Q^{H^Q} | \psi_{n'}^S) - \mathbb{E}_n \delta_{nn'}| = 0.$$

Now consider the matrix elements

$$\begin{aligned} (\psi_n^S | \epsilon_Q^{H^Q} | \psi_{n'}^S) &= (\psi_n^0 + \epsilon_S \psi_n^1 | \epsilon_Q^{H^Q} | \psi_{n'}^0 + \epsilon_S \psi_{n'}^1) \\ &= (\psi_n^0 | \epsilon_Q^{H^Q} | \psi_{n'}^0) + \epsilon_S^2 \epsilon_Q (\psi_n^1 | H^Q | \psi_{n'}^1) \\ &\quad + \epsilon_S \epsilon_Q (\psi_n^0 | H^Q | \psi_{n'}^1) + \epsilon_S \epsilon_Q (\psi_n^1 | H^Q | \psi_{n'}^0). \end{aligned}$$

The Stark splitting is a second order effect and the hyperfine splitting is a first order effect, but in the intermediate-field case under discussion the magnitudes of the two splittings are comparable. Therefore  $\epsilon_Q$  is of order  $\epsilon_S^2$ . Thus

$$\begin{aligned} (\psi_n^S | \epsilon_Q^{H^Q} | \psi_{n'}^S) &\approx (\psi_n^0 | \epsilon_Q^{H^Q} | \psi_{n'}^0) + \epsilon_S^4 (\psi_n^1 | H^Q | \psi_{n'}^1) \\ &\quad + \epsilon_S^3 (\psi_n^0 | H^Q | \psi_{n'}^1) + \epsilon_S^3 (\psi_n^1 | H^Q | \psi_{n'}^0). \end{aligned}$$

Neglecting terms of order higher than  $\epsilon_S^2$ , there remains

$$(\psi_n^S | \epsilon_Q^{H^Q} | \psi_{n'}^S) \approx (\psi_n^0 | \epsilon_Q^{H^Q} | \psi_{n'}^0) = \epsilon_Q^{H^Q}_{nn'}.$$

Therefore, to a second approximation for the energy, the secular equation may be written

$$|\epsilon_Q^{H^Q}_{nn'} + (W_n^S + \mathbb{E}_n^0 - \mathbb{E}_n)\delta_{nn'}| = 0, \quad (22)$$

where the matrix elements  $\epsilon_Q^{H^Q}_{nn'}$  are calculated using zero-order wave functions. In this expression  $n$  stands for all the quantum numbers  $J$ ,

$I$ ,  $m_J$ , and  $m_I$ . The explicit form of the quadrupole interaction Hamiltonian, as derived in Chapter II, is

$$\epsilon_Q H^Q = \frac{eQ \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av}}{2J(2J-1)I(2I-1)} \left\{ 3(\underline{I} \cdot \underline{J})^2 + \frac{3}{2} (\underline{I} \cdot \underline{J}) - I(I+1) J(J+1) \right\}.$$

The matrix elements of  $\epsilon_Q H^Q$  are diagonal in  $J$ ,  $I$ , and  $M = m_J + m_I$ . This means that the secular determinant can be separated into blocks for each particular value of  $J$  and  $M$ . Within each block  $E_n^0$  will be constant and we may set  $E_n^1 - E_n^0 = E^1$ , the perturbation energy. Thus Equation (22) can be rewritten in the form

$$\left| \frac{eQ \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av}}{2J(2J-1)I(2I-1)} (J I m_J m_I \left| 3(\underline{I} \cdot \underline{J})^2 + \frac{3}{2} \underline{I} \cdot \underline{J} - I(I+1)J(J+1) \right| J I m'_J m'_I) \right. \quad (23)$$

$$\left. + (W_{J+1 m_J}^S - E^1) \delta_{m_J m'_J} \delta_{m_I m'_I} \right| = 0.$$

This is Mizushima's result for the non-degenerate case giving the secular equation used to compute the energy splitting when both the Stark effect and hyperfine structure are present and are of the same order of magnitude.

CHAPTER IV  
SIMULTANEOUS PERTURBATION TREATMENT  
OF THE STARK EFFECT AND QUADRUPOLE INTERACTION

This chapter extends the related work of other investigators, which has been discussed in the previous chapters, to cover the case of the Stark effect and quadrupole interaction in the presence of rotational near-degeneracy. In this treatment the Hamiltonian which is considered is the sum of the rotational, the Stark interaction, and the quadrupole interaction Hamiltonians. To this Hamiltonian is applied a unitary transformation which removes off-diagonal elements of the Stark effect linking non-degenerate energy levels and introduces the proper correction on the diagonal. The transformed Hamiltonian is then simplified as much as possible while retaining all terms necessary to give the perturbed energy correct to second order.

Consider the Hamiltonian  $H' = W^0 + H^Q + EH^S$ . Apply to it the unitary transformation  $U = e^{iES}$ . The transformed Hamiltonian is then

$$H = UH'U^{-1} = e^{iES}H'e^{-iES}.$$

Expanding the exponential functions gives

$$\begin{aligned} H &= (1 + iES - \frac{1}{2} E^2 S^2)(W^0 + H^Q + EH^S)(1 - iES - \frac{1}{2} E^2 S^2) \quad (24) \\ &= W^0 + H^Q + E \left[ iS(W^0 + H^Q) - (W^0 + H^Q)iS + H^S \right] \\ &\quad + E^2 \left[ -\frac{1}{2} S^2(W^0 + H^Q) - (W^0 + H^Q) \frac{1}{2} S^2 + S(W^0 + H^Q)S + iSH^S - H^SiS \right], \end{aligned}$$

correct to second order.

The next step is to specify the form of  $S$ . It proves convenient to use the same definition that appears in Chapter II. Although another transformation was examined which removed more of the off-diagonal elements it resulted in diagonal terms that consisted of infinite series, the convergence of which could not be established. Thus, the definition of  $S$  is again chosen to be as follows:

$$S_{ij} = \frac{-iH_{ij}^S}{W_i^O - W_j^O} \quad \text{for } W_i^O \text{ not near } W_j^O,$$

and  $S_{ij} = 0$ , otherwise.

The  $ij^{\text{th}}$  zero order term of expression (24) is then

$$H_{ij}^O = W_{ij}^O \delta_{ij} + H_{ij}^Q = W_i^O \delta_{ij} + H_{ij}^Q.$$

The first order term from (24) is given by

$$H_{ij}^1 = E \left[ \sum_k i S_{ik} (W_{kj}^O + H_{kj}^Q) - \sum_k (W_{ik}^O + H_{ik}^Q) i S_{kj} + H_{ij}^S \right].$$

Since all off-diagonal terms of the rotational energy are zero, the above reduces to

$$H_{ij}^1 = E \left[ i S_{ij} W_j^O - W_i^O i S_{ij} + \sum_k i (S_{ik} H_{kj}^Q - H_{ik}^Q S_{kj}) + H_{ij}^S \right]. \quad (25)$$

From the definition of  $S_{ij}$ , one obtains for (25) when  $W_i^O$  is not near  $W_j^O$ :

$$\begin{aligned}
H_{ij}^1 &= E \left\{ \frac{H_{ij}^S W_j^O}{W_i^O - W_j^O} - \frac{W_i^O H_{ij}^S}{W_i^O - W_j^O} + \sum_k \left[ \frac{H_{ik}^S H_{kj}^Q}{W_i^O - W_k^O} - \frac{H_{ik}^Q H_{kj}^S}{W_k^O - W_j^O} \right] + H_{ij}^S \right\} \\
&= E \left\{ \frac{(W_j^O - W_i^O) H_{ij}^S}{W_i^O - W_j^O} + \sum_k \left[ \frac{H_{ik}^S H_{kj}^Q}{W_i^O - W_k^O} - \frac{H_{ik}^Q H_{kj}^S}{W_k^O - W_j^O} \right] + H_{ij}^S \right\} ;
\end{aligned}$$

or, since the first and third terms cancel each other,

$$H_{ij}^1 = E \sum_k \left[ \frac{H_{ik}^S H_{kj}^Q}{W_i^O - W_k^O} - \frac{H_{ik}^Q H_{kj}^S}{W_k^O - W_j^O} \right] . \quad (26)$$

For  $W_i^O$  near  $W_j^O$ ,  $S_{ij} = 0$  and Equation (25) becomes

$$H_{ij}^1 = E H_{ij}^S + E \sum_k i (S_{ik} H_{kj}^Q - H_{ik}^Q S_{kj}) .$$

Again using the definition of  $S$  given above, one obtains

$$H_{ij}^1 = E H_{ij}^S + E \sum_k \left[ \frac{H_{ik}^S H_{kj}^Q}{W_i^O - W_k^O} - \frac{H_{ik}^Q H_{kj}^S}{W_k^O - W_j^O} \right] . \quad (27)$$

The symbol  $\sum'$  appearing above indicates that the sum is taken over all terms for which the denominators are not near zero. For any term whose denominator approaches zero, the corresponding  $S_{ik}$  would be zero, and the entire term would vanish.

Along the diagonal of the Hamiltonian matrix ( $i = j$ ), Equations (26) and (27) both reduce to the following:

$$H_{ii}^1 = 2E \sum_k' \frac{H_{ik}^S H_{ki}^Q}{W_i^0 - W_k^0} . \quad (28)$$

The magnitude of this term actually corresponds to a second order correction. Off-diagonal, the summation terms in (26) and (27) may be neglected because their denominators are large, and they are therefore small. These terms are of the same order of magnitude as Equation (28), but because they are off-diagonal, their contribution to the perturbed energy is small compared to that of terms appearing in Equation (28), unless they link near-degenerate energy levels. The off diagonal first order correction then reduces to

$$H_{ij}^1 = 0, \quad W_i^0 \text{ not near } W_j^0 ;$$

$$H_{ij}^1 = EH_{ij}^S + E \sum_k' \left[ \frac{H_{ik}^S H_{kj}^Q}{W_i^0 - W_k^0} - \frac{H_{ik}^Q H_{kj}^S}{W_k^0 - W_j^0} \right], \quad W_i^0 \text{ near } W_j^0 .$$

Since the off-diagonal elements of the second order term in  $H$  contribute nothing below fourth order to the energy, they will be neglected; only diagonal elements will be considered to order  $E^2$ . The second order term from (24) is then given by

$$H_{ii}^2 = E^2 \left\{ -\frac{1}{2} \sum_{kl} S_{ik} S_{kl} (W_{li}^0 + H_{li}^Q) - \frac{1}{2} \sum_{kl} (W_{ik}^0 + H_{ik}^Q) S_{kl} S_{li} \right. \\ \left. + \sum_{kl} S_{ik} (W_{kl}^0 + H_{kl}^Q) S_{li} + i \sum_k S_{ik} H_{ki}^S - i \sum_k H_{ik}^S S_{ki} \right\} .$$

Since all off-diagonal terms of the rotational energy are zero, this reduces to

$$H_{ii}^2 = E^2 \left[ -\frac{1}{2} \sum_k S_{ik} S_{ki} W_i^0 - \frac{1}{2} \sum_\ell W_i^0 S_{i\ell} S_{\ell i} - \frac{1}{2} \sum_{k\ell} (S_{ik} S_{k\ell} H_{\ell i}^Q + H_{ik}^Q S_{k\ell} S_{\ell i}) \right. \\ \left. + \sum_k S_{ik} W_k^0 S_{ki} + \sum_{k\ell} S_{ik} H_{k\ell}^Q S_{\ell i} + i \sum_k (S_{ik} H_{ki}^S - H_{ik}^S S_{ki}) \right].$$

Replacing the dummy index  $\ell$  by  $k$  in the second term of this expression and collecting terms gives

$$H_{ii}^2 = E^2 \left[ \sum_k i (S_{ik} H_{ki}^S - H_{ik}^S S_{ki}) + \sum_k S_{ik} S_{ki} (W_k^0 - W_i^0) \right. \\ \left. + \sum_{k\ell} (S_{ik} H_{k\ell}^Q S_{\ell i} - \frac{1}{2} S_{ik} S_{k\ell} H_{\ell i}^Q - \frac{1}{2} H_{ik}^Q S_{k\ell} S_{\ell i}) \right].$$

Substituting in this relation for  $S$  from the definition given above results in the following:

$$H_{ii}^2 = E^2 \left[ \sum_k \left( \frac{H_{ik}^S H_{ki}^S}{W_i^0 - W_k^0} - \frac{H_{ik}^S H_{ki}^S}{W_k^0 - W_i^0} \right) - \sum_k \frac{H_{ik}^S H_{ki}^S}{(W_i^0 - W_k^0)(W_k^0 - W_i^0)} (W_k^0 - W_i^0) \right. \\ \left. + \sum_{k\ell} \left( \frac{1}{2} \frac{H_{ik}^S H_{k\ell}^S H_{\ell i}^Q}{(W_i^0 - W_k^0)(W_k^0 - W_\ell^0)} + \frac{1}{2} \frac{H_{ik}^Q H_{k\ell}^S H_{\ell i}^S}{(W_k^0 - W_\ell^0)(W_\ell^0 - W_i^0)} - \frac{H_{ik}^S H_{k\ell}^Q H_{\ell i}^S}{(W_i^0 - W_k^0)(W_\ell^0 - W_i^0)} \right) \right].$$

By combining the first three terms in this equation and factoring a  $\frac{1}{2}$  out of the double sum, one obtains

$$H_{ii}^2 = E^2 \left\{ \sum_k' \frac{H_{ik}^S H_{ki}^S}{W_i^0 - W_k^0} + \frac{1}{2} \sum_{kl} \left[ \frac{H_{ik}^S H_{kl}^S H_{li}^Q}{(W_i^0 - W_k^0)(W_k^0 - W_l^0)} + \frac{H_{ik}^Q H_{kl}^S H_{li}^S}{(W_k^0 - W_l^0)(W_l^0 - W_i^0)} - \frac{2H_{ik}^S H_{kl}^Q H_{li}^S}{(W_i^0 - W_k^0)(W_l^0 - W_i^0)} \right] \right\}. \quad (29)$$

where  $\sum'$  has the same meaning as before. Note that the denominators in the double sum are much greater than those in the single sum, since levels lying close to each other are excluded from consideration. Thus terms in the double sum are much smaller than terms in the single sum and will be neglected in comparison with the latter. Therefore, the second order correction now reduces to

$$H_{ii}^2 = E^2 \sum_k' \frac{H_{ik}^S H_{ki}^S}{W_i^0 - W_k^0}, \quad (30)$$

which is just the second order Stark energy correction obtained earlier.

The Hamiltonian which gives the perturbed energies correct to second order then has the following terms:

$$\text{Zeroth order: } H_{ij}^0 = W_i^0 \delta_{ij} + H_{ij}^Q;$$

$$\text{First order: } H_{ii}^1 = 2E \sum_k' \frac{H_{ik}^S H_{ki}^Q}{W_i^0 - W_k^0};$$

$$H_{ij}^1 = EH_{ij}^S + E \sum_k' \left[ \frac{H_{ik}^S H_{kj}^Q}{W_i^O - W_k^O} - \frac{H_{ik}^Q H_{kj}^S}{W_k^O - W_j^O} \right], \quad i \neq j, W_i^O \text{ near } W_j^O;$$

$$H_{ij}^1 = 0, \quad i \neq j, W_i^O \text{ not near } W_j^O;$$

$$\text{Second order: } H_{ii}^2 = E^2 \sum_k' \frac{H_{ik}^S H_{ki}^S}{W_i^O - W_k^O}. \quad (31)$$

For the nearly prolate asymmetric rotors nitryl chloride and nitrosyl bromide, two additional simplifications may be made:

1. Elements of  $H^Q$  off-diagonal in  $J$  and  $\tau$  linking near-degenerate pairs of levels are zero.

2. Terms of the form  $\frac{H_{ik}^Q H_{kj}^S}{W_j^O - W_k^O}$  are negligible.

Both of these simplifications follow from group theoretical arguments which are given in Appendix B. Off-diagonal elements of  $H^Q$  linking states which are not near-degenerate may be neglected since the pure quadrupole splitting for both molecules was accurately predicted without including these terms. Therefore, the Stark terms linking near-degenerate states are the only remaining matrix elements off-diagonal in  $J$  and  $\tau$ . For either nitryl chloride or nitrosyl bromide, then, a typical matrix to be diagonalized has the following form:

$$m_F = J + I - 2$$

		$J_\tau$			$J_{\tau'}$			
		$m_J=J$	$m_J=J-1$	$m_J=J-2$	$m_J=J$	$m_J=J-1$	$m_J=J-2$	
		$m_I=I-2$	$m_I=I-1$	$m_I=I$	$m_I=I-2$	$m_I=I-1$	$m_I=I$	
$J_\tau$	$m_J=J$	$m_I=I-2$	$W^0 + H^Q + H^2$	$H^Q$	$H^Q$	$EH^S$		
	$m_J=J-1$	$m_I=I-1$	$H^Q$	$W^0 + H^Q + H^2$	$H^Q$		$EH^S$	
	$m_J=J-2$	$m_I=I$	$H^Q$	$H^Q$	$W^0 + H^Q + H^2$			$EH^S$
$J_{\tau'}$	$m_J=J$	$m_I=I-2$	$EH^S$			$W^0 + H^Q + H^2$	$H^Q$	$H^Q$
	$m_J=J-1$	$m_I=I-1$		$EH^S$		$H^Q$	$W^0 + H^Q + H^2$	$H^Q$
	$m_J=J-2$	$m_I=I$			$EH^S$	$H^Q$	$H^Q$	$W^0 + H^Q + H^2$

Since  $I = 3/2$  for both nitryl chloride and nitrosyl bromide, these matrices may be as large as  $8 \times 8$  (for  $m_F = |J-I|$ ) or as small as  $2 \times 2$  (for  $m_F = J + I$ ). In general, of course, it may be necessary to include elements of  $H_{ij}^Q$  off-diagonal in  $J$  and  $\tau$ , elements of  $H_{ii}^1$ , and the complete expression for off-diagonal elements of  $H_{ij}^1$  linking near-degenerate states.

## CHAPTER V

## EXPERIMENTAL PROCEDURE

The experimental data were obtained from a Stark-modulated microwave spectrograph of the type first described by Hughes and Wilson (24). The absorption cell consists of a seventeen-foot section of X-band waveguide with a horizontal brass Stark electrode supported on Teflon strips running down the center. The plane of the Stark electrode is perpendicular to the E-field of the microwave energy. The Stark voltage is provided by an eighty-five kilocycle square wave generator (25) whose output is impressed on the brass center electrode. One side of the square wave is at ground potential, and its amplitude is variable from zero to -1000 volts. As a result of this 85-kc field applied to the molecules, the microwave energy is amplitude modulated when the klystron frequency is swept across an absorption line.

A reflex klystron supplies microwave energy to the absorption cell through a mica window. At the far end of the cell is a crystal diode which detects the 85-kc modulated signal. The output of the crystal is fed into a narrow band amplifier and a phase-sensitive detector whose reference voltage is supplied by the Stark-field generator. The output of the phase-sensitive detector may be displayed on an oscilloscope or on an Esterline Angus recording milliammeter. Greater sensitivity is obtained with the latter display because the klystron is slowly tuned by a mechanical drive, rather than being swept electrically, and this allows the use of filter circuits with long time constants.

Frequency measurements are obtained through a method similar to that described by Unterberger and Smith (26). The output of a 5-Mc crystal controlled oscillator is multiplied by vacuum tube circuitry until frequencies of 30, 90, 270, 540, 1080, and 2160 Mc are obtained. These frequencies are applied to a 1N26 crystal diode mounted in the waveguide, thus producing standard frequencies in the microwave region which are 30 Mc apart. Energy from the klystron is also fed to the crystal, so that the beat frequencies between the klystron output and the standard markers also appear across the crystal.

The frequency of beatnotes in the 15-to 30-Mc range is measured with a calibrated HRO Sixty communications receiver. An absorption wave-meter is used to determine which of the frequency markers is beating with the klystron. To aid further in identifying standard frequencies, it is possible to turn off the 30-Mc markers, leaving standard frequency markers 90 Mc apart in the microwave region. A block diagram of the experimental system and a more detailed description of its components have been given by Clayton (27).

To increase the population of the low-rotational levels involved in the transitions considered in this investigation, the absorption cell was cooled with dry ice. Since both  $\text{NO}_2\text{Cl}$  and  $\text{NOBr}$  decompose in the cell, they were continuously admitted at one end while an oil diffusion pump at the other end continuously pumped on the cell. Vapor pressure of the sample was controlled with the aid of liquid nitrogen. Initially, the sample holder was immersed in the nitrogen and the sample frozen. The liquid nitrogen level was then lowered until the temperature of the

sample rose to a point where the vapor pressure was suitable for spectrum measurements. Pressure control was maintained by slightly raising or lowering the nitrogen dewar during the course of the experiment. A second method of pressure control, which was used in the nitryl chloride investigation, is described by Weatherly, Williams, and Clayton (28).

## CHAPTER VI

## RESULTS OF THE INVESTIGATION

In calculating the spectra of the  $2_1 \rightarrow 3_0$  transition of  $\text{NO}_2\text{Cl}^{35}$  and the  $1_1 \rightarrow 2_0$  transition of  $\text{NOBr}^{79}$ , the following molecular parameters were used:

		$\text{NO}_2\text{Cl}^{35}$	$\text{NOBr}^{79}$
Rotational Constants	(Mc)		
	A	13250	83340
	B	5173.77	3747.24
	C	3721.13	3586.00
Quadrupole Coupling Constants	(Mc)		
	$\chi_{aa}$	-94.70	388.3
	$\chi_{bb}$	52.4	-239.5
	$\chi_{cc}$	42.3	-148.8
Dipole Moment (Debye)			
	$\mu$	$\mu = 0.53$	$\mu_a = 1.76$ and $1.80$
Asymmetry Parameter			
	$\kappa = \frac{2B-A-C}{A-C}$	-0.695	-0.996

Values for nitryl chloride are taken from Clayton (29), while those for nitrosyl bromide are taken from Eagle, Weatherly, and Williams (30).

To get the perturbed energies from which the spectra are calculated, rotational, quadrupole, and Stark matrix elements are needed for the Hamiltonian. Rotational energies may be obtained from the method given

by Gordy, Smith, and Trambarulo (31) or that given by Townes and Schawlow (32). In this work Gordy's procedure was used. Quadrupole terms were calculated from Equation (17) as indicated in Chapter II. Stark effect matrix elements for nitryl chloride and nitrosyl bromide have the form indicated on page 12, Chapter II. All matrix elements were evaluated in the  $J, I, m_J, m_I$  scheme.

For columns in the tables below labeled "Modified Mizushima Method," the degenerate Stark energies were calculated by the Golden and Wilson method and substituted for the non-degenerate Stark energies appearing on the diagonal of the Mizushima determinant. In other words, Equation (23) was used to obtain the perturbed energy levels, with the exception that  $W_{J, m_J}^S$  was calculated from degenerate theory rather than non-degenerate theory.

Columns headed "Simultaneous Perturbation Method" give the results of the simultaneous treatment of the Stark and quadrupole perturbations. Energy levels are obtained from matrices constructed of Equations (31), with the additional simplifications mentioned in Chapter IV. These matrices have forms similar to that depicted on page 41, Chapter IV.

The actual calculation of the perturbed rotational energy levels from which the spectra were derived was accomplished with the aid of a digital computer which obtained the eigenvalues of the Hamiltonian matrix. Energy levels involved in the computed spectra presented in Tables 1 and 2 were obtained from an IBM Type 650 Magnetic Drum Data-Processing Machine using the ML 08 eigenvalue routine, which was a part of the program library maintained by the Rich Electronic Computer Center at the Georgia Institute of Technology. Because of erratic operation of the 650 in the

running of the ML 08 program, an ALGOL routine for obtaining both eigenvalues and eigenvectors of any real, symmetric matrix was written and used with the Burroughs 220 Data-Processing System. With the aid of this program, the calculated spectrum and the relative intensities appearing in Table 3 were obtained. A copy of the ALGOL program is given in Appendix C.

Table 1 presents a comparison of the calculated and observed spectrum of the  $2_1 \rightarrow 3_0$  transition of nitryl chloride for a dipole moment of 0.53 debye and applied Stark fields between 214.6 and 1073 volts per centimeter. The value of 0.53 debye for the dipole moment of  $\text{NO}_2\text{Cl}^{35}$  was obtained by Clayton (33) from a consideration of the  $m_J = 2, m_I = 3/2$  component of the  $2_1 \rightarrow 3_0$  transition using the modified Mizushima method. This transition is rather unusual in that the upper state has no hyperfine structure and the lower state energy is obtained from a simple quadratic equation. Since Clayton deduced the value of 0.53 debye from a consideration of only this special case, and because Miller and Sinnott (34) have reported a dipole moment of 0.42 debye for  $\text{NO}_2\text{Cl}^{35}$ , it was decided to verify Clayton's result by applying the simultaneous perturbation method to all components of the  $2_1 \rightarrow 3_0$  transition. The near-degenerate levels are the  $2_2$  and the  $2_1$ ; their separation is 178.88 Mc. Transitions are identified by the dominant  $m_J$  and  $m_I$  values.

Table 1. Spectrum of the  $2_1 \rightarrow 3_0$   
Transition of  $\text{NO}_2\text{Cl}^{35}$

Dominant $m_J$	Character $m_I$	Applied Electric Field (volts/cm)	Modified Mizushima Method (Mc)	Simultaneous Perturbation Method (Mc)	Measured Frequency (Mc)
2	3/2	214.6	26698.81	26698.80	26699.0 ± 0.2
		321.9	26707.19	26707.18	26707.2 ± 0.5
		429.2	26717.81	26717.80	26718.0 ± 0.7
		557.9	26732.62	26732.60	26733.0 ± 1.0
		643.8	26743.37	26743.35	26744.0 ± 1.0
		751.1	26757.47	26757.44	26757.4 ± 1.5
		1073.0	26802.17	26802.13	26802.0 ± 1.5
2	1/2	214.6	26695.88	26695.83	26696.1 ± 0.2
		321.9	26701.77	26701.70	26702.0 ± 0.2
		429.2	26710.31	26710.21	26710.8 ± 1.0
		557.9	26723.39	26723.31	26723.0 ± 2.0
		643.8	26733.37	26733.30	26733.5 ± 1.0
		751.1	26746.79	26746.73	26747.0 ± 1.0
		1073.0	26790.40	26790.39	26791.0 ± 1.5
1	3/2	214.6	26672.63	26672.71	26672.7 ± 0.1
		321.9	26677.42	26677.56	26677.6 ± 0.2
		429.2	26682.69	26682.84	26683.0 ± 0.5
		557.9	26689.18	26689.32	26689.5 ± 0.2
		643.8	26690.64	26690.77	-
		751.1	26699.43	26699.55	26699.2 ± 0.5
		1073.0	26718.45	26718.53	26718.5 ± 1.0
2	-1/2	214.6	26693.85	26693.67	26694.0 ± 0.2
		321.9	26698.67	26698.40	26698.8 ± 0.5
		429.2	26707.41	26707.14	26707.3 ± 0.5
		557.9	26721.14	26720.90	-
		643.8	26731.47	26731.26	26731.5 ± 1.0
		751.1	26745.22	26745.05	26744.8 ± 1.0
		1073.0	26789.40	26789.30	26788.8 ± 1.5
1	1/2	214.6	26688.72	26687.97	26688.2 ± 0.2
		321.9	26692.63	26692.61	26692.8 ± 0.3
		429.2	26696.29	26696.31	26696.4 ± 0.1
		557.9	26701.06	26701.01	26701.2 ± 0.2
		643.8	26701.69	26701.64	26705.0 ± 0.5
		751.1	26709.71	26709.66	26710.0 ± 0.5
		1073.0	26727.42	26727.35	26727.8 ± 0.8

(Continued)

Table 1. (Continued)

Dominant Character	Applied Electric Field	Modified Mizushima Method	Simultaneous Perturbation Method	Measured Frequency	
$m_J$	$m_I$	(volts/cm)	(Mc)	(Mc)	
0	3/2	214.6	26670.66	26670.85	26670.8 ± 0.4
		321.9	26672.63	26672.95	26673.0 ± 0.2
		429.2	26674.06	26674.50	26674.6 ± 0.1
		557.9	26675.19	26675.64	26675.7 ± 0.1
		643.8	26675.71	26676.16	26676.2 ± 0.1
		751.1	26676.21	26676.62	26676.7 ± 0.1
		1073.0	26677.18	26677.58	26677.6 ± 0.1
2	-3/2	214.6	26712.22	26711.79	26712.5 ± 0.1
		321.9	26717.60	26717.42	26717.7 ± 0.5
		429.2	26725.63	26725.23	26726.0 ± 0.8
		557.9	26738.33	a	26738.5 ± 1.5
		643.8	26748.01	26747.70	26748.0 ± 1.0
		751.1	26761.30	26760.96	26760.5 ± 1.5
		1073.0	26804.57	26804.33	26804.2 ± 1.5
1	-1/2	214.6	26692.89	26692.71	26692.8 ± 0.1
		321.9	26695.77	26695.20	26695.5 ± 0.2
		429.2	26700.20	26699.93	26699.3 ± 0.2
		557.9	26706.21	26702.47	26705.5 ± 0.3
		643.8	26707.45	26706.55	26709.7 ± 0.2
		751.1	26716.06	26714.22	26714.4 ± 0.5
		1073.0	26734.73	26731.80	26731.3 ± 0.8
0	1/2	214.6	26670.43	26670.46	26670.8 ± 0.4
		321.9	26673.26	26673.69	26673.8 ± 0.1
		429.2	26676.77	26677.71	26677.7 ± 0.2
		557.9	26681.39	a	26682.7 ± 0.2
		643.8	26681.07	26686.92	26686.1 ± 0.2
		751.1	26687.18	26688.09	26688.0 ± 0.5
		1073.0	26690.24	26690.79	26690.8 ± 0.1
-1	3/2	214.6	26687.88	26688.08	26688.2 ± 0.2
		321.9	26689.79	26692.28	-
		429.2	26690.85	26692.25	-
		557.9	26691.99	26692.79	26693.3 ± 0.1
		643.8	26690.19	26691.82	26694.7 ± 0.5
		751.1	26695.93	26698.57	26698.2 ± 0.5
		1073.0	26711.71	26714.74	26716.0 ± 1.0

<sup>a</sup>Computer did not completely solve secular determinant.

Agreement between calculated and measured values in Table 1 is in general good. The root mean squared deviation of the calculated values in this table from the measured values is 1.28 Mc for the "Modified Mizushima Method" and 0.83 Mc for the "Simultaneous Perturbation Method." The average deviations are -0.43 Mc and -0.32 Mc, respectively. These average deviations could have been reduced (indicating a better fit) by using a value of 0.533 debye for the dipole moment of nitryl chloride rather than 0.53 debye. However, the uncertainty in determining the applied electric field leads to an uncertainty of  $\pm 0.01$  debye in the value of the dipole moment, and a third digit is therefore not significant.

Note that there is little difference between the results of the modified Mizushima computation and the simultaneous perturbation treatment. This is true because the quadrupole matrix elements of the two closely spaced levels are nearly identical for nitryl chloride. Thus, mixing of the wave-functions for these two states is not apparent. Whenever this condition is met, the simpler modified Mizushima method may be used, as long as the corrected Stark energies are put in on the diagonal of the Hamiltonian matrix.

For cases in which the quadrupole matrix elements of the near-degenerate levels are not nearly equal, the more complicated simultaneous treatment of the perturbations must be employed. This was verified by calculating the spectrum of the  $1_1 \rightarrow 2_0$  transition of NOBr<sup>79</sup> by both methods and comparing them with the observed spectrum. Table 2 presents these results for a value of  $\mu_a$  equal to 1.76 debye units. The transition is not sensitive to  $\mu_b$ . The value of 1.76 debye for  $\mu_a$  has been

reported previously (35). It was obtained from a consideration of the  $2_0 \rightarrow 3_{-1}$  transition of NOBr<sup>79</sup>. Non-degenerate theory was used in calculating the spectrum of that transition. The  $1_1$  and  $1_0$  rotational levels of nitrosyl bromide comprise the near-degenerate pair; their separation is 161.24 Mc. Lines are identified by the F and  $M_F$  values which would apply in the weak-field limiting case. Neither F nor  $M_F$  is a good quantum number for the Stark fields used, however.

Table 2. Spectrum of the  $1_1 \rightarrow 2_0$  Transition of NOBr<sup>79</sup>

(Calculations Made with  $\mu_a = 1.76$  Debye)

Weak Field Case Identification F $\rightarrow$ F'	$M_F$	Applied Electric Field (volts/cm)	Modified Mizushima Method (Mc)	Simultaneous Perturbation Method (Mc)	Measured Frequency (Mc)
5/2 $\rightarrow$ 7/2	5/2	107.3	14791.28	14790.96	-
		160.9	14778.78	14778.20	-
		214.6	14763.78	14762.96	-
		321.9	14731.71	14729.07	14727.2 $\pm$ 1.0
		429.2	14694.83	14693.44	-
		643.8	14623.00	14621.35	-
	3/2	107.3	14795.04	14795.58	-
		160.9	14784.58	14785.45	-
		214.6	14770.65	14771.68	14771.00 $\pm$ 0.7
		321.9	14738.09	14737.83	14736.27 $\pm$ 0.5 (a)
		429.2	14698.88	14700.12	-
		643.8	14619.68	14621.05	-
	1/2	107.3	14799.10	14799.61	-
		160.9	14794.95	14793.35	-
		214.6	14786.82	14778.41	14777.24 $\pm$ 0.5
		321.9	14756.13	14738.95	14736.27 $\pm$ 0.5 (a)
		429.2	14715.43	14697.44	-
		643.8	14633.51	14614.65	-

(Continued)

Table 2. (Continued)

Weak Field Case Identification $F \rightarrow F'$	$M_F$	Applied Electric Field (volts/cm)	Modified Mizushima Method (Mc)	Simultaneous Perturbation Method (Mc)	Measured Frequency (Mc)	
$3/2 \rightarrow 5/2$	$3/2$	107.3	14897.06	14896.36	14896.47 ± 0.5	
		160.9	14895.65	14894.57	14894.16 ± 0.5	
		214.6	14895.72	14894.35	14894.43 ± 0.5	
		321.9	14900.22	14898.92	-	
		429.2	14909.97	14908.87	14908.39 ± 0.6	
		643.8	14945.91	14945.04	-	
	$1/2$	107.3	14889.15	14881.78	14881.76 ± 0.5	
		160.9	14878.73	14869.24	14868.49 ± 0.5	
		214.6	14870.62	14864.70	14864.41 ± 0.5	
		321.9	14868.56	14866.22	-	
		429.2	14873.92	14872.45	14871.52 ± 1.0	
		643.8	14899.29	14898.32	-	
	$1/2 \rightarrow 3/2$	$1/2$	107.3	14781.85	14784.28	-
			160.9	14771.18	14776.15	14775.54 ± 0.5
214.6			14757.51	14764.99	14763.46 ± 0.7	
321.9			14727.22	14737.02	14736.27 ± 0.5 (a)	
429.2			14692.38	14705.77	-	
643.8			14625.62	14640.69	-	
$5/2 \rightarrow 5/2$	$5/2$	107.3	14851.44	14851.11	14849.85 ± 0.5	
		160.9	14839.10	14838.52	14837.35 ± 0.5	
		214.6	14824.67	14823.86	14822.74 ± 0.5	
		321.9	14794.80	14792.16	-	
		429.2	14762.29	14760.91	-	
		643.8	14708.96	14707.31	-	
	$3/2$	107.3	14855.17	14855.72	-	
		160.9	14845.27	14846.14	-	
		214.6	14832.27	14833.31	-	
		321.9	14803.24	14802.98	-	
		429.2	14770.75	14772.02	-	
		643.8	14718.11	14719.48	-	
	$1/2$	107.3	14859.29	14859.80	-	
		160.9	14855.72	14854.14	-	
		214.6	14848.46	14840.05	14839.00 ± 0.5	
		321.9	14820.58	14803.40	-	
		429.2	14784.61	14766.62	-	
		643.8	14721.38	14702.52	-	

(Continued)

Table 2. (Continued)

Weak Field Case Identification $F \rightarrow F'$	$M_F$	Applied Electric Field (volts/cm)	Modified Mizushima Method (Mc)	Simultaneous Perturbation Method (Mc)	Measured Frequency (Mc)	
$3/2 \rightarrow 3/2$	3/2	107.3	14854.42	14853.72	14854.13 $\pm$ 0.5	
		160.9	14852.97	14851.88	14852.23 $\pm$ 0.5	
		214.6	14852.79	14851.42	14851.95 $\pm$ 0.5	
		321.9	14855.40	14854.11	14854.44 $\pm$ 0.5	
		429.2	14859.87	14858.76	-	
		643.8	14870.56	14869.69	14869.41 $\pm$ 0.5	
	1/2	107.3	14846.77	14839.39	-	
		160.9	14836.73	14827.23	-	
		214.6	14829.15	14823.23	-	
		321.9	14828.62	14826.29	-	
		429.2	14835.63	14834.16	-	
		643.8	14857.52	14856.55	-	
	$1/2 \rightarrow 1/2$	1/2	107.3	14722.08	14724.51	14725.14 $\pm$ 0.7
			160.9	14711.33	14716.29	-
214.6			14697.44	14704.91	-	
321.9			14666.00	14675.80	14675.62 $\pm$ 1.0	
429.2			14628.62	14642.01	-	
643.8			14552.86	14567.92	-	

<sup>a</sup>One of three lines unresolved experimentally.

Examination of Table 2 shows differences as great as 10 or 15 Mc appearing in the predictions by the two methods of calculation. The root mean squared deviation of the calculated values from the observed values is 6.26 Mc for the "Modified Mizushima Method" and 0.97 Mc for the "Simultaneous Perturbation Method." The respective average deviations are +1.95 Mc and +0.59 Mc. These numbers are somewhat misleading because the two theories give approximately the same prediction for about half

the Stark components measured. When the results of the two methods of calculation differ appreciably, the simultaneous treatment of the two perturbations gives a much better prediction of the absorption spectrum of NOBr<sup>79</sup> than does the modified Mizushima method, even though the degenerate calculation of Stark corrections is used with the latter.

Agreement between theoretical and experimental frequency values may be improved by using a value of 1.80 debye units for  $\mu_a$ . The results of this calculation are given in Table 3.

Table 3. Spectrum of the  $1_1 \rightarrow 2_0$  Transition of NOBr<sup>79</sup>  
(Calculations Made with  $\mu_a = 1.80$  Debye)

Weak Field Case Identification $F \rightarrow F'$	$M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method) (Mc)	Measured Frequency (Mc)	Relative Intensity
5/2 → 7/2	5/2	42.9	14801.016	-	-
		64.4	14798.404	-	-
		85.8	14794.908	-	-
		107.3	14790.650	-	82.4
		128.8	14785.754	14786.17 ± 0.5	-
		150.2	14780.329	14781.15 ± 0.5	-
		171.7	14774.476	14775.08 ± 0.5	-
		193.1	14768.286	14769.30 ± 0.7 (b)	-
		214.6	14761.820	-	80.1
		268.2	14744.808	14745.29 ± 0.5	-
		321.9	14727.024	14727.2 ± 1.0	-
		429.2	14690.337	-	-
		536.5	14653.039	-	-
		643.8	14615.584	-	101.5

(Continued)

Table 3. (Continued)

Weak Field Case Identification $F \rightarrow F'$	$M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method) (Mc)	Measured Frequency (Mc)	Relative Intensity
$5/2 \rightarrow 7/2$	$3/2$	42.9	14802.005	-	-
		64.4	14800.464	-	-
		85.8	14798.250	-	-
		107.3	14795.294	14794.88 $\pm$ 1.0	135.9
		128.8	14791.626	-	-
		150.2	14787.235	14786.94 $\pm$ 0.5	-
		171.7	14782.237	14782.63 $\pm$ 0.5	-
		193.1	14776.663	14776.60 $\pm$ 0.5	-
		214.6	14770.622	14771.00 $\pm$ 0.7	113.6
		268.2	14753.978	-	-
		321.9	14735.835	14736.27 $\pm$ 0.5 (d)	-
		429.2	14697.176	-	-
		536.5	14656.999	-	-
		643.8	14616.099	-	52.6
		$5/2 \rightarrow 7/2$	$1/2$	42.9	14802.549
64.4	14801.788			-	-
85.8	14800.835			-	-
107.3	14799.461			-	164.4
128.8	14797.649			14796.96 $\pm$ 0.5	-
150.2	14794.825			-	-
171.7	14790.373			-	-
193.1	14784.291			14785.67 $\pm$ 0.5	-
214.6	14777.161			14777.24 $\pm$ 0.5	53.7
268.2	14757.471			-	-
321.9	14736.730			14736.27 $\pm$ 0.5 (d)	-
429.2	14694.351			-	-
536.5	14651.842			-	-
643.8	14609.972			-	55.3

(Continued)

Table 3. (Continued)

Weak Field Case Identification $F \rightarrow F'$	$M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method)	Measured Frequency (Mc)	Relative Intensity
			(Mc)		
$3/2 \rightarrow 5/2$	$3/2$	42.9	14899.380	-	-
		64.4	14898.431	$14898.30 \pm 0.5$	-
		85.8	14897.347	$14897.53 \pm 0.5$	-
		107.3	14896.272	$14896.47 \pm 0.5$	91.9
		128.8	14895.353	$14895.26 \pm 0.5$	-
		150.2	14894.671	$14894.70 \pm 0.5$	-
		171.7	14894.281	$14894.44 \pm 0.5$	-
		193.1	14894.165	$14894.43 \pm 0.5$	-
		214.6	14894.309	$14894.43 \pm 0.5$	88.3
		268.2	14895.743	$14895.61 \pm 0.5$	-
		321.9	14898.518	-	-
		429.2	14907.607	$14908.39 \pm 0.7$	-
		536.5	14921.026	$14923.7 \pm 2.0$	-
		643.8	14938.196	-	19.2
		$3/2 \rightarrow 5/2$	$1/2$	42.9	14896.483
64.4	14892.272			$14892.61 \pm 0.5$	-
85.8	14887.245			$14887.07 \pm 0.5$	-
107.3	14881.393			$14881.76 \pm 0.5$	109.6
128.8	14875.693			$14875.51 \pm 0.5$	-
150.2	14870.686			$14870.64 \pm 0.5$	-
171.7	14867.225			$14867.38 \pm 0.5$	-
193.1	14865.352			$14865.44 \pm 0.5$	-
214.6	14864.444			$14864.41 \pm 0.5$	42.7
268.2	14864.432			-	-
321.9	14865.898			-	-
429.2	14871.941			$14871.52 \pm 1.0$	-
536.5	14880.719			$14880.49 \pm 0.5$	-
643.8	14893.507			-	12.1

(Continued)

Table 3. (Continued)

Weak Field Case Identification $F \rightarrow F'$	Case $M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method) (Mc)	Measured Frequency (Mc)	Relative Intensity
$1/2 \rightarrow 3/2$	1/2	42.9	14789.555	-	-
		64.4	14788.293	-	-
		85.8	14786.500	$14786.26 \pm 0.5$	-
		107.3	14784.097	$14783.66 \pm 0.5$	75.9
		128.8	14781.120	$14780.74 \pm 0.5$	-
		150.2	14777.573	$14778.46 \pm 0.5$	-
		171.7	14773.510	-	-
		193.1	14768.959	$14769.30 \pm 0.7$ (b)	-
		214.6	14763.953	$14763.46 \pm 0.7$ (c)	63.7
		268.2	14750.195	$14750.92 \pm 1.0$	-
		321.9	14734.955	$14736.27 \pm 0.5$ (d)	-
		429.2	14702.718	-	-
		536.5	14668.330	-	-
		643.8	14633.430	-	72.2
$5/2 \rightarrow 5/2$	5/2	42.9	14860.913	$14860.21 \pm 1.0$	-
		64.4	14858.331	-	-
		85.8	14854.879	$14854.70 \pm 0.5$ (a)	-
		107.3	14850.682	$14849.85 \pm 0.5$	58.8
		128.8	14845.867	$14844.60 \pm 0.5$	-
		150.2	14840.547	$14840.07 \pm 0.5$	-
		171.7	14834.828	$14834.71 \pm 0.5$	-
		193.1	14828.804	-	-
		214.6	14822.542	$14822.74 \pm 0.5$	49.2
		268.2	14806.241	-	-
		321.9	14789.526	-	-
		429.2	14756.347	-	-
		536.5	14724.716	-	-
		643.8	14695.153	-	18.3

(Continued)

Table 3. (Continued)

Weak Field Case Identification $F \rightarrow F'$		$M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method) (Mc)	Measured Frequency (Mc)	Relative Intensity
$5/2 \rightarrow 5/2$	$3/2$	42.9	14861.925	-	-	
		64.4	14860.444	-	-	
		85.8	14858.318	-	-	
		107.3	14855.482	-	10.3	
		128.8	14851.969	-	-	
		150.2	14847.777	-	-	
		171.7	14843.024	-	-	
		193.1	14837.751	-	-	
		214.6	14832.075	-	0.9	
		268.2	14816.668	-	-	
		321.9	14800.326	-	-	
		429.2	14767.365	-	-	
		536.5	14736.009	-	-	
		643.8	14706.986	-	0.1	
$5/2 \rightarrow 5/2$	$1/2$	42.9	14862.481	-	-	
		64.4	14861.793	-	-	
		85.8	14860.941	-	-	
		107.3	14859.703	-	0.0	
		128.8	14858.061	-	-	
		150.2	14855.443	-	-	
		171.7	14851.235	-	-	
		193.1	14845.441	14846.05 $\pm$ 0.5	-	
		214.6	14838.620	14839.00 $\pm$ 0.5	52.9	
		268.2	14819.999	14821.80 $\pm$ 0.5	-	
		321.9	14800.647	-	-	
		429.2	14762.579	-	-	
		536.5	14725.701	-	-	
		643.8	14691.992	-	29.4	

(Continued)

Table 3. (Continued)

Weak Field Case Identification $F \rightarrow F'$	$M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method) (Mc)	Measured Frequency (Mc)	Relative Intensity
$3/2 \rightarrow 3/2$	3/2	42.9	14856.638	$14856.58 \pm 0.5$	-
		64.4	14855.716	$14856.21 \pm 0.5$	-
		85.8	14854.666	$14854.70 \pm 0.5$	(a) -
		107.3	14853.625	$14854.13 \pm 0.5$	87.9
		128.8	14852.737	$14853.00 \pm 0.5$	-
		150.2	14852.074	$14852.55 \pm 0.5$	-
		171.7	14851.684	$14851.75 \pm 0.5$	-
		193.1	14851.538	$14852.06 \pm 0.5$	-
		214.6	14851.608	$14851.95 \pm 0.5$	80.0
		268.2	14852.593	$14852.86 \pm 0.5$	-
		321.9	14854.371	$14854.44 \pm 0.5$	-
		429.2	14859.077	-	-
		536.5	14864.336	$14864.80 \pm 0.5$	-
		643.8	14869.912	$14869.41 \pm 0.5$	96.4
		$3/2 \rightarrow 3/2$	1/2	42.9	14853.771
64.4	14849.632			-	-
85.8	14844.705			-	-
107.3	14838.982			-	3.8
128.8	14833.440			-	-
150.2	14828.626			-	-
171.7	14825.386			-	-
193.1	14823.766			-	-
214.6	14823.119			-	6.1
268.2	14823.958			-	-
321.9	14826.389			-	-
429.2	14834.470			-	-
536.5	14844.016			-	-
643.8	14854.956			-	0.1

(Continued)

Table 3. (Continued)

Weak Field Case Identification $F \rightarrow F'$	$M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method) (Mc)	Measured Frequency (Mc)	Relative Intensity
$1/2 \rightarrow 1/2$	1/2	42.9	14729.699	-	-
		64.4	14728.456	$14728.25 \pm 0.5$	-
		85.8	14726.689	$14727.10 \pm 0.5$	-
		107.3	14724.313	$14725.14 \pm 0.7$	78.2
		128.8	14721.360	$14721.50 \pm 0.5$	-
		150.2	14717.828	$14717.75 \pm 0.5$	-
		171.7	14713.770	$14715.32 \pm 0.5$	-
		193.1	14709.205	-	-
		214.6	14704.154	-	63.3
		268.2	14690.170	-	-
		321.9	14674.444	$14675.62 \pm 1.0$	-
		429.2	14640.104	-	-
		536.5	14602.746	-	-
		643.8	14563.780	-	25.0
		$5/2 \rightarrow 3/2$	3/2	42.9	14819.183
64.4	14817.729			-	-
85.8	14815.637			-	-
107.3	14812.835			-	10.2
128.8	14809.353			-	-
150.2	14805.180			-	-
171.7	14800.427			-	-
193.1	14795.124			-	-
214.6	14789.374			-	21.5
268.2	14773.518			-	-
321.9	14756.179			-	-
429.2	14718.835			-	-
536.5	14679.319			-	-
643.8	14638.702			-	49.6

(Continued)

Table 3. (Continued)

Weak Field Case Identification $F \rightarrow F'$		$M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method) (Mc)	Measured Frequency (Mc)	Relative Intensity
$5/2 \rightarrow 3/2$	1/2	42.9	14819.769	-	-	
		64.4	14819.153	-	-	
		85.8	14818.401	-	-	
		107.3	14817.292	-	13.0	
		128.8	14815.808	-	-	
		150.2	14813.383	-	-	
		171.7	14809.396	-	-	
		193.1	14803.855	-	-	
		214.6	14797.295	-	12.8	
		268.2	14779.525	-	-	
		321.9	14761.138	-	-	
		429.2	14725.108	-	-	
		536.5	14688.998	-	-	
		643.8	14653.441	-	10.6	
$3/2 \rightarrow 1/2$	1/2	42.9	14793.915	-	-	
		64.4	14789.795	-	-	
		85.8	14784.894	-	-	
		107.3	14779.198	-	21.4	
		128.8	14773.680	-	-	
		150.2	14768.831	-	-	
		171.7	14765.646	-	-	
		193.1	14764.012	14764.98 $\pm$ 0.5	-	
		214.6	14763.320	14763.46 $\pm$ 0.7 (c)	31.6	
		268.2	14763.933	-	-	
		321.9	14765.878	14766.54 $\pm$ 0.5	-	
		429.2	14771.856	14772.52 $\pm$ 0.5	-	
		536.5	14778.432	14778.02 $\pm$ 0.5	-	
		643.8	14785.306	14785.56 $\pm$ 1.0	101.3	

(Continued)

Table 3. (Continued)

Weak Field Case Identification $F \rightarrow F'$	$M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method) (Mc)	Measured Frequency (Mc)	Relative Intensity
$3/2 \rightarrow 7/2$	$3/2$	42.9	14839.460	-	-
		64.4	14838.451	-	-
		85.8	14837.279	-	-
		107.3	14836.084	-	4.6
		128.8	14835.010	-	-
		150.2	14834.129	-	-
		171.7	14833.494	-	-
		193.1	14833.077	-	-
		214.6	14832.856	-	24.9
		268.2	14833.053	-	-
		321.9	14834.027	$14834.62 \pm 0.5$	-
		429.2	14837.418	$14837.86 \pm 0.5$	-
		536.5	14842.016	$14842.43 \pm 0.5$	-
		643.8	14847.309	$14847.28 \pm 0.7$	83.5
		$3/2 \rightarrow 7/2$	$1/2$	42.9	14836.551
64.4	14832.267			-	-
85.8	14827.139			-	-
107.3	14821.151			-	3.5
128.8	14815.281			-	-
150.2	14810.068			-	-
171.7	14806.363			-	-
193.1	14804.202			-	-
214.6	14802.985			-	106.5
268.2	14801.904			-	-
321.9	14801.981			-	-
429.2	14803.713			-	-
536.5	14806.860			$14807.21 \pm 0.5$	-
643.8	14811.487			$14811.74 \pm 0.5$	85.6

(Continued)

Table 3. (Continued)

Weak Field Case Identification $F \rightarrow F'$	$M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method) (Mc)	Measured Frequency (Mc)	Relative Intensity
$1/2 \rightarrow 7/2$	1/2	42.9	14772.335	-	-
		64.4	14770.928	-	-
		85.8	14768.934	-	-
		107.3	14766.266	-	2.0
		128.8	14762.961	-	-
		150.2	14759.015	-	-
		171.7	14754.487	-	-
		193.1	14749.395	-	-
		214.6	14743.819	-	9.6
		268.2	14728.141	-	-
		321.9	14710.547	-	-
		429.2	14671.961	-	-
		536.5	14631.174	-	-
		643.8	14589.961	-	13.7
$5/2 \rightarrow 1/2$	1/2	42.9	14759.913	-	-
		64.4	14759.316	-	-
		85.8	14758.590	-	-
		107.3	14757.508	-	0.7
		128.8	14756.048	-	-
		150.2	14753.638	-	-
		171.7	14749.656	-	-
		193.1	14744.101	-	-
		214.6	14737.496	-	7.9
		268.2	14719.500	-	-
		321.9	14700.627	-	-
		429.2	14662.494	-	-
		536.5	14623.414	-	-
		643.8	14583.791	-	24.2

(Continued)

Table 3. (Continued)

Weak Field Case Identification $F \rightarrow F'$	$M_F$	Applied Electric Field (volts/cm)	Calculated Frequency (Simultaneous Perturbation Method) (Mc)	Measured Frequency (Mc)	Relative Intensity
$1/2 \rightarrow 5/2$	1/2	42.9	14832.267	-	-
		64.4	14830.933	-	-
		85.8	14829.040	-	-
		107.3	14826.508	-	0.5
		128.8	14823.373	-	-
		150.2	14819.633	-	-
		171.7	14815.349	-	-
		193.1	14810.545	-	-
		214.6	14805.278	-	3.7
		268.2	14790.669	-	-
		321.9	14774.464	-	-
		429.2	14740.189	-	-
		536.5	14705.033	-	-
		643.8	14671.981	-	9.3

<sup>a</sup>One of two lines unresolved experimentally.

<sup>b</sup>One of two lines unresolved experimentally.

<sup>c</sup>One of two lines unresolved experimentally.

<sup>d</sup>One of three lines unresolved experimentally.

The rms deviation of the calculated values in Table 3 from the measured values is 0.63 Mc; the average deviation is -0.22 Mc. If this average deviation is compared with the corresponding value from Table 2 (+0.59 Mc), it would appear that a better fit could be obtained for a value of  $\mu_a$  slightly less than 1.80 debye. However, if the frequency of the pure rotation line is calculated from the same rotational constants

used in the Stark effect calculation and compared with the "measured" average rotation line obtained from the six observed quadrupole hyperfine lines, it is found that a discrepancy of  $-0.16$  Mc exists. Thus only  $-0.06$  Mc of the  $-0.22$  Mc deviation is due to the assignment of a  $1.80$  debye value for  $\mu_a$ . The rest (i.e.,  $-0.16$  Mc) is due either to centrifugal distortion or to errors in the frequency measurements.

There are many gaps in the measurement of the nitrosyl bromide spectrum. The reasons for this are:

1. The intensity of some of the lines was too low to measure.
2. The spectrum in the region investigated is complex, and the Stark components could not always be identified.
3. Stark components were sometimes masked by other absorption lines.

Since microwave measurements are frequently made to an accuracy of  $0.01$  or  $0.02$  Mc, the deviations quoted in this work may appear large. However, the accuracy of the reported measurements is affected by non-uniformity of the Stark field in the waveguide absorption cell and the fact that for nitrosyl bromide there are so many absorption lines that overlapping may shift observed peaks. It is also true for both nitryl chloride and nitrosyl bromide that displacements of Stark components from their parent lines are sufficiently great that a one megacycle deviation is not a large percentage of the displacement.

## CHAPTER VII

## CONCLUSIONS

The aims of this dissertation have been (1) to extend the theory of the Stark effect in the presence of nuclear quadrupole hyperfine structure for an asymmetric rotor to cover the case of near-degeneracy in the rotational energy levels of a molecule, and (2) to confirm the dipole moments of  $\text{NO}_2\text{Cl}$  and  $\text{NOBr}$ . It is believed that the theory presented in Chapter IV of this dissertation, culminating in Equations (31) and the associated secular determinant, accomplishes the first of the stated aims. Because this theory is very tedious to apply to specific calculations, an alternative procedure was also examined. This second procedure is based directly on Mizushima's work (36). In this approach, the Mizushima secular determinant, Equation (23), is used to obtain the perturbed rotational energy levels. However, instead of calculating the Stark correction which appears on the diagonal of the Hamiltonian matrix by non-degenerate theory (as Mizushima does), degenerate theory is used. The restriction on the use of the simpler second approach, or a modified Mizushima method, is that corresponding quadrupole matrix elements of the nearly degenerate rotational levels must be almost identical. Otherwise the more difficult simultaneous treatment of the two perturbations is required. Comparison of theoretical calculations with experimental results on nitryl chloride and nitrosyl bromide, as tabulated in Chapter VI, verifies this conclusion.

Table 1 presents a comparison of both methods of computation with the experimentally observed spectrum of the  $2_1 \rightarrow 3_0$  transition of nitryl chloride. The  $2_1$  and  $2_2$  levels of  $\text{NO}_2\text{Cl}$ , which are separated by 178.38 Mc, are the closely spaced pair, and their corresponding quadrupole matrix elements differ only by about one per cent. As Table 1 shows, the results of applying the two theories are nearly the same, both agreeing with the experimental results.

Table 2 presents a comparison of both methods of calculation with the experimentally observed spectrum of the  $1_1 \rightarrow 2_0$  transition of nitrosyl bromide. The near-degenerate levels are the  $1_1$  and  $1_0$  levels, which are separated by 161.24 Mc, and their corresponding quadrupole matrix elements differ by about fifty per cent. As Table 2 shows, the modified Mizushima method failed to give an accurate prediction of all the transitions in this case, whereas the more complicated simultaneous perturbation treatment did predict results for all lines in good agreement with experimental observation. The comparison of the calculated and observed spectra of the  $1_1 \rightarrow 2_0$  transition of  $\text{NOBr}$ <sup>79</sup> appearing in Table 3 gives additional evidence of the validity of the theory presented in Chapter IV. The slightly better agreement between theoretical and experimental values was brought about by changing the assumed value of the dipole moment for  $\text{NOBr}$ <sup>79</sup> used in the calculations from 1.76 to 1.80 debye.

When applying the theory that appears in Chapter IV to other molecules, it must be remembered that the additional simplifications to Equations (31) possible for nitrosyl bromide may not be acceptable. In particular, matrix elements of the quadrupole Hamiltonian linking near-degenerate energy levels may not be zero. In cases where it is necessary

to obtain a somewhat better approximation than was used in the investigation covered by this report, one would retain elements of the form

$$\frac{H_{ik}^S H_{kj}^Q}{W_i^O - W_k^O} \text{ which appear in the terms listed in Equations (31).}$$

This investigation confirms the dipole moment 0.53 debye reported by Clayton (37) for  $\text{NO}_2\text{Cl}^{35}$ . For  $\text{NOBr}^{79}$ , the inclusion of the effects of rotational near-degeneracy gives a value of 1.80 debye for the component of the dipole moment along the axis of least inertia, rather than the previously obtained value of 1.76 debye. For the transition analysed in the present work, it was necessary to take rotational near-degeneracy into account in order to obtain agreement between the calculated and the measured Stark effect. There are, however, cases in which an observed Stark spectrum, or a portion of one, can be satisfactorily fitted by a calculated spectrum without considering near-degeneracy of rotational energy levels. An example of this is the  $2_0 \rightarrow 3_{-1}$  transition of  $\text{NOBr}^{79}$  from which the value 1.76 debye was obtained. In such cases, the dipole moment giving the best agreement between calculated and observed spectrum components will not be the correct value for the molecule. It is hoped that the present investigation will emphasize the importance of rotational near-degeneracy in dipole moment measurements.

A P P E N D I C E S

## APPENDIX A

## DERIVATION OF EQUATION (17) FROM EQUATION (16)

In the development of the quadrupole Hamiltonian given in Chapter II, the following steps were omitted to preserve continuity of thought. They are included here for completeness.

Equation (16) is

$$H^Q = \frac{1}{6} \frac{eQ \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av}}{I(2I-1) J(2J-1)} \sum_{i,j} \left\{ \frac{9}{2} (\underline{I})_i (\underline{I})_j (\underline{J})_i (\underline{J})_j + \frac{9}{2} (\underline{I})_i (\underline{I})_j (\underline{J})_i (\underline{J})_j \right. \\ \left. - 3(\underline{I})_i (\underline{I})_j \delta_{ij} J^2 - 3(\underline{J})_i (\underline{J})_j \delta_{ij} I^2 + \underline{I}^2 \underline{J}^2 \delta_{ij} \right\}$$

Consider the expression inside the brackets term by term:

Because  $\underline{I}$  and  $\underline{J}$  commute

$$\begin{aligned} \sum_{i,j} (\underline{I})_i (\underline{I})_j (\underline{J})_i (\underline{J})_j &= \sum_{i,j} (\underline{I})_i (\underline{J})_i (\underline{I})_j (\underline{J})_j \\ &= \sum_i (\underline{I})_i (\underline{J})_i \left[ \sum_j (\underline{I})_j (\underline{J})_j \right] \\ &= \sum_i (\underline{I} \cdot \underline{J}) (\underline{I} \cdot \underline{J}) \\ &= \sum_i (\underline{I} \cdot \underline{J})^2 . \end{aligned} \tag{A-1}$$

$$\begin{aligned}
\sum_{i,j}^{\mathcal{O}} (\underline{I})_i (\underline{I})_j (\underline{J})_j (\underline{J})_i &= \sum_{i,j}^{\mathcal{O}} (\underline{I})_j (\underline{I})_i (\underline{J})_j (\underline{J})_i + \frac{\mathcal{O}}{2} i \sum_{i,j} (\underline{I})_{ixj} (\underline{J})_j (\underline{J})_i \\
&= \sum_{i,j}^{\mathcal{O}} (\underline{I})_j (\underline{J})_j (\underline{I})_i (\underline{J})_i + \frac{\mathcal{O}}{4} i \sum_{i,j} (\underline{I})_{ixj} \left[ (\underline{J})_j (\underline{J})_i \right. \\
&\quad \left. + (\underline{J})_j (\underline{J})_i \right] \\
&= \sum_{i,j}^{\mathcal{O}} \left[ \sum_j (\underline{I})_j (\underline{J})_j \right] \left[ \sum_i (\underline{I})_i (\underline{J})_i \right] + \frac{\mathcal{O}}{4} i \sum_{i,j} (\underline{I})_{ixj} \left[ (\underline{J})_j (\underline{J})_i \right. \\
&\quad \left. + (\underline{J})_i (\underline{J})_j + i (\underline{J})_{jxi} \right] \\
&= \frac{\mathcal{O}}{2} (\underline{I} \cdot \underline{J})^2 + \frac{\mathcal{O}}{4} i \sum_{i,j} (\underline{I})_{ixj} \left[ (\underline{J})_j (\underline{J})_i + (\underline{J})_i (\underline{J})_j \right] \\
&\quad - \frac{\mathcal{O}}{4} \sum_{i,j} (\underline{I})_{ixj} (\underline{J})_{jxi} .
\end{aligned}$$

In the middle term above, note that the expression in square brackets is symmetric in  $i$  and  $j$ , while the  $\underline{I}$  part is antisymmetric, that is,  $(\underline{I})_{ixj} = -(\underline{I})_{jxi}$ . Thus the entire term is antisymmetric in  $i$  and  $j$ , and when the summation is taken, the term vanishes. Therefore

$$\begin{aligned}
\sum_{i,j}^{\mathcal{O}} (\underline{I})_i (\underline{I})_j (\underline{J})_j (\underline{J})_i &= \frac{\mathcal{O}}{2} (\underline{I} \cdot \underline{J})^2 - \frac{\mathcal{O}}{4} \sum_{i,j} (\underline{I})_{ixj} (\underline{J})_{jxi} \\
&= \frac{\mathcal{O}}{2} (\underline{I} \cdot \underline{J})^2 + \frac{\mathcal{O}}{4} \sum_{i,j} (\underline{I})_{ixj} (\underline{J})_{ixj} \\
&= \frac{\mathcal{O}}{2} (\underline{I} \cdot \underline{J})^2 + \frac{\mathcal{O}}{2} \sum_k (\underline{I})_k (\underline{J})_k \\
&= \frac{\mathcal{O}}{2} (\underline{I} \cdot \underline{J})^2 + \frac{\mathcal{O}}{2} (\underline{I} \cdot \underline{J}) . \tag{A-2}
\end{aligned}$$

$$\begin{aligned}
 -3 \sum_{i,j} (\underline{I})_i (\underline{I})_j \delta_{ij} \underline{J}^2 &= -3 \left[ \sum_i (\underline{I})_i (\underline{I})_i \right] \underline{J}^2 \\
 &= -3 \underline{I}^2 \underline{J}^2 = -3 I(I+1) J(J+1) . \quad (\text{A-3})
 \end{aligned}$$

$$\begin{aligned}
 -3 \sum_{i,j} (\underline{J})_i (\underline{J})_j \delta_{ij} \underline{I}^2 &= -3 \left[ \sum_i (\underline{J})_i (\underline{J})_i \right] \underline{I}^2 \\
 &= -3 \underline{J}^2 \underline{I}^2 \\
 &= -3 \underline{I}^2 \underline{J}^2 = -3 I(I+1) J(J+1) . \quad (\text{A-4})
 \end{aligned}$$

$$\sum_{i,j} \underline{I}^2 \underline{J}^2 \delta_{ij} = 3 \underline{I}^2 \underline{J}^2 = 3I(I+1) J(J+1) . \quad (\text{A-5})$$

The substitution of Equations (A-1), (A-2), (A-3), (A-4), and (A-5) back into Equation (16) results in the first line of expression (17):

$$\begin{aligned}
 H^Q &= \frac{1}{6} \frac{eQ \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av}}{2I(2I-1)J(2J-1)} \left\{ \frac{9}{2} (\underline{I} \cdot \underline{J})^2 + \frac{9}{2} (\underline{I} \cdot \underline{J})^2 + \frac{9}{2} (\underline{I} \cdot \underline{J}) - 3 \underline{I}^2 \underline{J}^2 \right. \\
 &\quad \left. - 3 \underline{I}^2 \underline{J}^2 + 3 \underline{I}^2 \underline{J}^2 \right\} .
 \end{aligned}$$

## APPENDIX B

SOME CONSIDERATIONS OF GROUP THEORY AS  
APPLIED TO ASYMMETRIC ROTORS

In the rotational Hamiltonian, a molecule is represented only by the three principal moments of inertia  $I_a$ ,  $I_b$ , and  $I_c$ . Therefore, as far as its rotation is concerned, a molecule may be considered purely as an ellipsoid with principal moments of inertia  $I_a$ ,  $I_b$ , and  $I_c$ . The symmetry operations  $E$ ,  $C_2^a$ ,  $C_2^b$ , and  $C_2^c$  (representing the identity and rotation of  $180^\circ$  about each of the three axes) leave the ellipsoid unchanged. These operations form a group called the four-group, which is frequently designated  $D_2$ . Since the four-group is abelian, each of its elements belongs to a different class. Therefore, this group has four different irreducible representations (denoted by  $A$ ,  $B_a$ ,  $B_b$ , and  $B_c$ ), all of which are one-dimensional. The rotational wave functions of an asymmetric top  $\psi(J\tau m_J)$  and the direction cosines  $\alpha$  belong to these representations of the four-group. Table 4 gives the character table for the four-group and indicates the symmetries of the direction cosines and their products.

Table 4. Character Table of Four-Group and  
Symmetries of Direction Cosines

		$E$	$C_2^a$	$C_2^b$	$C_2^c$
$\alpha_{Za}^2, \alpha_{Zb}^2, \alpha_{Zc}^2$	$A$	1	1	1	1
$\alpha_{Zb}\alpha_{Zc}, \alpha_{Za}$	$B_a$	1	1	-1	-1
$\alpha_{Za}\alpha_{Zc}, \alpha_{Zb}$	$B_b$	1	-1	1	-1
$\alpha_{Za}\alpha_{Zb}, \alpha_{Zc}$	$B_c$	1	-1	-1	1

The quadrupole Hamiltonian  $H^Q$  contains the following factor:

$$\left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{Av} = \int \bar{\psi}(J\tau m_J=J) \frac{\partial^2 V}{\partial Z^2} \psi(J'\tau' m_J'=J') dv, \quad (B-1)$$

where Z is a space-fixed axis, and

$$\begin{aligned} \frac{\partial^2 V}{\partial Z^2} &= \alpha_{Za}^2 \frac{\partial^2 V}{\partial a^2} + \alpha_{Zb}^2 \frac{\partial^2 V}{\partial b^2} + \alpha_{Zc}^2 \frac{\partial^2 V}{\partial c^2} \\ &+ 2\alpha_{Za}\alpha_{Zb} \frac{\partial^2 V}{\partial a\partial b} + 2\alpha_{Zb}\alpha_{Zc} \frac{\partial^2 V}{\partial b\partial c} + 2\alpha_{Za}\alpha_{Zc} \frac{\partial^2 V}{\partial a\partial c}. \end{aligned} \quad (B-2)$$

For planar molecules such as nitryl chloride and nitrosyl bromide

$$\frac{\partial^2 V}{\partial a\partial c} = \frac{\partial^2 V}{\partial b\partial c} = 0,$$

and Equation (B-2) reduces to the following:

$$\frac{\partial^2 V}{\partial Z^2} = \alpha_{Za}^2 \frac{\partial^2 V}{\partial a^2} + \alpha_{Zb}^2 \frac{\partial^2 V}{\partial b^2} + \alpha_{Zc}^2 \frac{\partial^2 V}{\partial c^2} + 2\alpha_{Za}\alpha_{Zb} \frac{\partial^2 V}{\partial a\partial b}. \quad (B-3)$$

Since the integral of Equation (B-1) will vanish if its integrand is an odd function of any coordinate, the integrand of Equation (B-1) must belong to representation A of the four-group. Because  $\alpha_{Za}^2$ ,  $\alpha_{Zb}^2$ , and  $\alpha_{Zc}^2$  all belong to representation A, terms involving these elements will contribute to the quadrupole energy only when the product of  $\psi(J\tau m_J=J)$  and  $\psi(J'\tau' m_J'=J')$  belongs to A. This means that  $\psi(J\tau m_J=J)$  and  $\psi(J'\tau' m_J'=J')$  have the same symmetry. The remaining term involves the product  $\alpha_{Za}\alpha_{Zb}$ , which belongs to representation  $B_c$ . For this term to contribute to the quadrupole energy,

the product of  $\psi(J\tau m_J=J)$  and  $\psi(J'\tau' m_J'=J')$  must also belong to  $B_c$ . This means that the two wave functions either have symmetries A and  $B_c$  or have symmetries  $B_a$  and  $B_b$ .

For a near-prolate asymmetric rotor, the near-degenerate pairs of rotational energy levels have  $J'=J$  and  $\tau'=\tau+1$  (where the symbol ' is used to denote the upper state). The wave functions specifying these levels either have symmetries A and  $B_a$  or have symmetries  $B_b$  and  $B_c$ . In either case, the product of the wave functions  $\psi(J\tau m_J=J)$  and  $\psi(J'\tau' m_J'=J')$  belongs to representation  $B_a$  of the four-group. Therefore, elements of the quadrupole Hamiltonian linking near-degenerate levels of planar, near-prolate asymmetric rotors (such as nitryl chloride and nitrosyl bromide) are zero.

With the aid of this conclusion, it may be shown that terms of the

form  $\frac{H_{ik}^S H_{kj}^Q}{W_i^O - W_k^O}$  may be neglected in a second order approximation. Consider

such elements in terms of the parameters represented by the subscripts:

$$\frac{H_{ik}^S H_{kj}^Q}{W_i^O - W_k^O} = \frac{H_{J\tau m_J m_I}^S; J''\tau'' m_J'' m_I'' H_{J'\tau' m_J' m_I'}^Q}{W_{J\tau}^O - W_{J'\tau'}^O}. \quad (B-4)$$

Because first order theory is adequate for predicting the quadrupole spectrum, it may be assumed that elements of  $H^Q$  off-diagonal in  $J\tau$  are zero, except for those linking near-degenerate rotational states. It has been shown above that elements of  $H^Q$  off-diagonal in  $J\tau$  linking near-degenerate states are zero for planar, near-prolate asymmetric top molecules. Therefore, expression (B-4) simplifies to the following:

$$\frac{H_{ik}^S H_{kj}^Q}{W_i^O - W_k^O} = \frac{H_{J\tau m_J m_I}^S; J'\tau' m_J' m_I' H_{J'\tau' m_J' m_I'}^Q}{W_{J\tau}^O - W_{J'\tau'}^O}.$$

For  $W_{J\tau}^O$  near  $W_{J'\tau'}^O$ , the corresponding element of the transformation matrix  $S$  which produced the term is zero and the term vanishes. For  $W_{J\tau}^O$  not near  $W_{J'\tau'}^O$ , the term is off-diagonal and small. Such terms have magnitudes corresponding to second order off-diagonal corrections; their contributions to the energy would then be fourth order. It has thus been shown that

terms of the form  $\frac{H_{ik}^S H_{kj}^Q}{W_i^O - W_k^O}$  are negligible in a second order computation

of the perturbed energy for planar, near-prolate asymmetric rotors.

## APPENDIX C

ALGOL ROUTINE FOR OBTAINING EIGENVALUES AND EIGENVECTORS  
OF A REAL, SYMMETRIC MATRIX

The ALGOL program which appears below was used with the Burroughs 220 Data-Processing System to obtain the perturbed energy levels of nitrosyl bromide from which the spectrum presented in Table 3 was derived. The threshold Jacobi procedure for diagonalizing a matrix that appears in this program was developed by Mr. F. E. Schlaepfer of the Rich Electronic Computer Center at the Georgia Institute of Technology. The Jordan procedure for solving a linear system of equations and the Matrixprint procedure are standard items. The routine listed in this appendix will diagonalize any number of real, symmetric matrices of order 10 or less. It will produce correct eigenvectors as long as the coefficient of the  $n^{\text{th}}$  component of the vector is not zero (to ten decimal places). If the  $n^{\text{th}}$  component is zero, there is a contradiction in Step 95 of the program. However, such errors will be apparent in the homogeneity checks included in the routine.

The printed output of this program contains the following items:

1. The original matrix  $||a_{ij}||$ ;
2. The diagonalized matrix;
3. The trace of the original matrix (TRA), the trace of the diagonalized matrix (TRD), and their difference;
4. For each eigenvalue,  $\lambda_k$ , a four-column matrix which contains the eigenvalue at the head of column one and zeroes in the

rest of the column, the coefficients of the components of the corresponding eigenvector  $\psi(\lambda_k)$  in column two, one plus each coefficient (i.e.,  $1 + \psi_i(\lambda_k)$ ) in column three, and one plus each element of column one in column four;

5. The quantity  $\sum_{j=1}^N (a_{ij} - \lambda_k \delta_{ij}) \psi_j(\lambda_k)$  for each row,  $i$ , of the matrix, which serves to check that the eigenvector is in fact a solution of the set of  $N$  homogeneous equations.

The purpose of columns three and four in the matrix of Item 4 above is to indicate if and when the printer has failed to list a minus sign associated with the eigenvalue or any component of the eigenvector. This difficulty was sometimes encountered with the equipment in the Rich Electronic Computer Center.

All data cards must be identified by entering the number 5 into the first column (the digit 2 in column one denotes a program card). Data cards are prepared by entering the order of the matrix and then its elements row by row. In other words, for an  $N \times N$  matrix, punch the number  $N$  in column 3, say, of the first card, skip one space, and then begin entering the elements  $a_{11}$ ,  $a_{12}$ , etc. in decimal form, skipping at least one space between elements. The elements  $a_{ij}$  may extend over any number of cards. Only the first card needs the number  $N$  which specifies the order of the matrix. The only restrictions on format for data cards are: (1) column one must contain the number five, and (2) there must be at least one blank space between successive entries. To run the program, merely place the data cards behind the program deck in the input hopper. The program will successively call in and solve matrices until the hopper is empty.

## BURROUGHS ALGEBRAIC COMPILER - STANDARD VERSION 7/25/61

2	COMMENT EIGENVALUES AND EIGENVECTORS OF REAL SYMMETRIC MATRIX	\$ 1
2	INTEGER N,I,J,K	\$ 2
2	ARRAY A(10,10),REF(10,10),USE(10,10),X(10),Y(10,4),ID(10,10)	\$ 3
2	ARRAY GOOF (10),USO(10,10)	\$ 4
2	OUTPUT SNAFU (TRA,TRD,TRA-TRD)	\$ 5
2	FORMAT CHECK (*TRA =*,X13.4,B9,*TRD =*,X13.4,B9,*DIFF =*, X7.4,B13,W2)	\$ 6
2	OUTPUT GOOFO (I,GOOF (I))	\$ 7
2	FORMAT GOOFF(*VECTOR CHECK BY SUM OF PRODUCTS FOR ROW *,I2,X8.4,W0)	\$ 8
2	PROCEDURE MATRIXPRINT (N,M,A(,))	\$ 9 P1
2	BEGIN INTEGER I,J,K,M,N	\$ 10
2	FOR I = (1,1,N)	\$ 11
2	BEGIN J=1	\$ 12
2	UNTIL J GTR M	\$ 13
2	BEGIN WRITE (\$\$ROW,FMT)	\$ 14
2	J=K END END	\$ 15
2	RETURN	\$ 16
2	OUTPUT ROW (I,J,FOR K=(J,1,MIN(J+4,M)) \$ A(I,K))	\$ 17
2	FORMAT FMT (W0,( *ROW*,I3,B2,*COL*,I3,5X20.4,W0)) END MATRIXPRINT (.)	\$ 18
2	PROCEDURE TJACOBI (N,A(,),EPS)	\$ 19 P2
2	BEGIN INTEGER U,I,J,K,N	\$ 20
2	D=0.0	\$ 21

```

2   FOR I=(2,1,N)                                $ 22
2   FOR J=(1,1,I-1)                              $ 23
2   BEGIN IF ABS(A(I,J)) GTR D                   $ 24
2   D=ABS(A(I,J)) END                            $ 25
2   ETA=D/4.0                                     $ 26
2   START.. U=0                                   $ 27
2   FOR I=(2,1,N)                                $ 28
2   FOR J=(1,1,I-1)                              $ 29
2   BEGIN IF ABS(A(I,J)) GTR ETA                 $ 30
2   BEGIN U=1                                     $ 31
2   D=A(I,I)-A(J,J)                              $ 32
2   IF D EQL 0.0                                  $ 33
2   BEGIN C=0.7071068 $ S=0.7071068             $ 34
2   GO TO DIAG END                               $ 35
2   E = 0.5*ARCTAN(2.0*A(I,J)/D)                 $ 36
2   C=COS(E) $ S=SIN(E)                          $ 37
2   DIAG.. FOR K=(1,1,J-1),(J+1,1,I-1),(I+1,1,N) $ 38
2   BEGIN T=C.A(I,K)+S.A(J,K)                    $ 39
2   A(J,K)=A(K,J)=-S.A(I,K)+C.A(J,K)             $ 40
2   A(I,K)=A(K,I)=T END                          $ 41
2   T=C.C.A(I,I)+2.C.S.A(I,J)+S.S.A(J,J)        $ 42
2   A(J,J)=S.S.A(I,I)-2.C.S.A(I,J)+C.C.A(J,J)   $ 43
2   A(I,I)=T                                       $ 44
2   A(I,J)=A(J,I)=0.0 END                        $ 45
2   N=N END                                       $ 46
2   IF U EQL 1                                    $ 47

```

2	GO TO START	\$	48
2	IF ETA LSS EPS	\$	49
2	RETURN	\$	50
2	ETA = ETA/4.0	\$	51
2	GO TO START END TJACOBI ()	\$	52
2	PROCEDURE JORDAN (N,A(,)\$X())	\$	53 P3
2	BEGIN INTEGER I,J,K,L,N	\$	54
2	FOR K=(N+1,-1,1)	\$	55
2	BEGIN D=0	\$	56
2	FOR I=(2,1,K)	\$	57
2	IF ABS(A(I-1,1)) GTR D	\$	58
2	BEGIN L=I-1	\$	59
2	D=ABS(A(L,1)) END	\$	60
2	IF L NEQ 0	\$	61
2	FOR J=(1,1,K)	\$	62
2	BEGIN D=A(L,J)	\$	63
2	A(L,J)=A(1,J) \$ A(1,J)=D END	\$	64
2	FOR I=(1,1,N)	\$	65
2	X(I)=A(I,1)	\$	66
2	FOR J=(2,1,K)	\$	67
2	BEGIN D=A(1,J)/X(1)	\$	68
2	FOR I=(2,1,N)	\$	69
2	A(I-1,J-1)=A(I,J)-X(I).D	\$	70
2	A(N,J-1) = D END END	\$	71
2	RETURN END JORDAN ()	\$	72
2	WORK.. READ (\$\$DATA)	\$	73 CALC

```

2   FOR I=(1,1,N)                                     $   74
2   FOR J=(1,1,N)                                     $   75
2   BEGIN REF(I,J)=A(I,J)                             $   76
2   IF I EQL J $ ID(I,J)=1                             $   77
2   IF I NEQ J $ ID(I,J)=0  END                       $   78
2   MATRIXPRINT (N,N,A(,)) $ COMMENT PRINTS INPUT MATRIX $   79
2   TRA = 0                                           $   80
2   FOR I = (1,1,N)                                    $   81
2   TRA = TRA + A(I,I) $ COMMENT FORMS TRACE OF INPUT MATRIX $   82
2   TJACOBI (N,A(,),1.0**-6) $ COMMENT DIAGONALIZES MATRIX $   83
2   MATRIXPRINT (N,N,A(,)) $ COMMENT PRINTS DIAGONAL MATRIX $   84
2   TRD = 0                                           $   85
2   FOR I = (1,1,N)                                    $   86
2   TRD = TRD + A(I,I) $ COMMENT FORMS TRACE OF DIAGONAL MATRIX $   87
2   WRITE ($$SNAFU,CHECK) $ COMMENT PRINTS TRACES AND THEIR DIFF $   88
2   FOR K=(1,1,N)                                     $   89
2   BEGIN FOR I=(1,1,N)                               $   90
2   FOR J=(1,1,N)                                     $   91
2   BEGIN USE(I,J) = REF(I,J) - A(K,K).ID(I,J)       $   92
2   USO(I,J) = USE(I,J)  END                         $   93
2   JORDAN (N-1,USE(,)$X()) $ COMMENT SOLVES LINEAR SYSTEM
      OF N-1 EQNS                                     $   94
2   X(N)=-1 $ SUMX2 = 0                               $   95
2   FOR I=(1,1,N)                                     $   96
2   SUMX2 = SUMX2 + X(I).X(I)                         $   97
2   FOR I=(1,1,N)                                     $   98

```

```

2   Y(I,2) = X(I)/SQRT(SUMX2)           $   99
2   Y(1,1) = A(K,K)                   $  100
2   FOR I=(2,1,N) $ Y(I,1)=0          $  101
2   FOR I = (1,1,N)                   $  102
2   BEGIN Y(I,3) = Y(I,2) + 1.0       $  103
2   Y(I,4) = Y(I,1) + 1.0  END        $  104
2   MATRIXPRINT (N,4,Y(,))           $  105
2   COMMENT THIS PRINTS EIGENVECTOR AND ITS ASSOCIATED EIGENVALUE $ 106
2   FOR I = (1,1,N)                   $  107
2   BEGIN GOOF (I) = 0                 $  108
2   FOR J = (1,1,N)                   $  109
2   GOOF (I) = GOOF (I) + USO(I,J).Y(J,2) $ 110
2   COMMENT GOOF CHECKS HOMOGENEITY OF EIGENVECTOR SOLUTION $ 111
2   WRITE($$GOOFO,GOOFF)  END  END    $  112
2   GO TO WORK                         $  113
2   INPUT DATA(N,FOR I=(1,1,N)$FOR J=(1,1,N)$A(I,J)) $ 114
2   FINISH                              $  115

```

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36. Mizushima, op. cit.

37. Clayton, op. cit., p. 63.

## VITA

Donald Frohlichstein Eagle was born on January 30, 1933 in St. Louis, Missouri, the son of Samson Dewey Frohlichstein (now deceased) and Virginia Davis Frohlichstein. His elementary school education was completed in the St. Louis County public school system in 1946. In August, 1946, his mother married Mr. Leon Eagle of New Orleans, Louisiana, and the family established residence in that city.

Donald F. Eagle attended secondary school in New Orleans and was graduated from the Newman High School in that city in 1950. In 1950 he matriculated at Yale University in New Haven, Connecticut, from which he received his B. S. degree in physics in 1954. Mr. Eagle pursued his graduate studies at the Georgia Institute of Technology in Atlanta, Georgia. He received his M. S. degree in physics in 1956 and completed his work for the Ph. D. in 1962.

From June, 1956, until January, 1962, Mr. Eagle was employed by the Engineering Experiment Station of the Georgia Institute of Technology as an Assistant Research Physicist. On December 28, 1961, he married the former Miss Carol Victoria High, daughter of Mr. and Mrs. Harlem John High of Altamonte Springs, Florida. Mr. Eagle is a member of Sigma Xi, Sigma Pi Sigma, and the American Physical Society.