NUCLEAR QUADRUPOLE HYPERFINE STRUCTURE IN SLIGHTLY ASYMMETRIC ROTOR MOLECULES

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Preface

The following report contains excerpts from the doctoral thesis of Geoffrey Knight, Jr., "Interaction of Nuclear Electric Quadrupole Moments with Molecular Rotation in Slightly Asymmetric Rotor Molecules." It is concerned with the theory for the interpretation of the hyperfine structure patterns of rotational transitions in slightly asymmetric rotor molecules. The approach has been to approximate the molecular wave functions in terms of symmetric rotor wave functions, and to derive explicit expressions for the quadrupole interaction in terms of the quantum numbers appropriate to the molecular states and of a single asymmetry parameter which measures the departure of the molecule from a symmetric top.

The material is being prepared for publication in The Physical Review. This report is issued in order to make the results available to workers in the field as rapidly as possible.
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Introduction

We wish to determine the energy of a nuclear electric quadrupole in the field produced by the electrons and the other nuclei of a molecule. This problem has been solved for the atomic case by Casimir (1) in an investigation of the source of deviations from the interval rule in the hyperfine structure of atomic spectra. Nordsieck (2) has extended the solution to the linear molecules HD and D$_2$ and Jauch (3) and others have solved the problem for symmetric top type molecules. Recently Bragg (4), making use of previous investigations of the wave mechanical and matrix mechanical descriptions of a rotating asymmetric top (15), has obtained two solutions for the general case of asymmetric top type molecules; one formal, and the other involving interpolation in published tables of line strengths.

The objective of this paper is the evaluation of Bragg's formal solution for slightly asymmetric molecules so that the pattern of the interaction is made clear, and so that numerical results can be obtained more readily. The formulae obtained should be useful in the identification of the fine structure of rotational transitions observed in microwave spectroscopy (5), of the subsidiary minima observed in molecular beam measurements (6), and ultimately of the hyperfine structure of electronic transitions in molecular spectroscopy. Also they should simplify the evaluation of the products of certain molecular constants with the nuclear quadrupole moment, once identification has been made.

I. Formulation of the Problem

Classically the energy of a charge distribution \(\rho(\mathbf{r}')\) in a field \(\mathbf{E}_{\text{ext}}\) produced by other charge far away from the given distribution is (7):

\[
W = Z_e \Phi_{\mathbf{r}=0} + \mathbf{P}_{\mathbf{r}=0} \cdot \mathbf{E}_{\mathbf{r}=0} - \frac{1}{6} \mathbf{Q} \cdot \mathbf{E}_{\mathbf{r}=0} + \ldots
\]

where \(Z_e\) is the total charge, \(\mathbf{P}_{\mathbf{r}=0} = \int \mathbf{r}' \rho(\mathbf{r}') d\mathbf{r}'\) is the dipole moment, (which is zero for a nucleus), and \(\mathbf{Q} = \int (3\mathbf{r}' \mathbf{r}' - \mathbf{r}'^2) \cdot \rho(\mathbf{r}') d\mathbf{r}'\) is the quadrupole moment dyadic of the charge distribution. We will be concerned here only with the last term.

Classically the quadrupole moment dyadic is the charge-weighted average of the simple dyadic \((3\mathbf{r}' \mathbf{r}' - \mathbf{r}'^2)\). The corresponding quantum mechanical average for a nuclear quadrupole is:

\[
\langle \text{Im}_I | \mathbf{Q} | \text{Im}_I \rangle = \int \psi^* \psi \langle I, m_I | (r' \mathbf{r} - \mathbf{r}'^2) (3 \mathbf{U}_r \mathbf{U}_r - \mathbf{r}'^2) \rangle dr' d\theta' d\phi'
\]
where $\Psi_{I,m_I}$ is the wave function describing the state of the nucleus and $\hat{u}_{r'}$, is the unit vector in the $r'$ direction. $\Psi_{I,m_I}$ must have the form

$$g(r')Y_{I,m_I}^{(m_I)}(\theta',\phi')$$

if the nuclear spin $I$ and its component $m_I$ completely specify the state; the integral then becomes:

$$\langle Im_1 |Q| Im_1 \rangle = \int g^*(r')r'^4 g(r')dr'$$

$$\cdot \int Y_{I}^{(m_I)}(\theta',\phi') (3\hat{u}_{r'},\hat{u}_{r'} - \hat{I}) Y_{I}^{(m_I)}(\theta',\phi') sin\theta' d\theta' d\phi'$$

since $\hat{u}_{r'}$ depends only on $\theta'$ and $\phi'$.

We would like to replace $\hat{u}_{r'}$ in this expression by some operator with known eigenvalues belonging to $\Psi_{I,m_I}$. This can be done if we note that $3/2(\hat{I}_x + \hat{I}_y) - I^2$ has the same angular dependence as $(3\hat{u}_{r'},\hat{u}_{r'} - \hat{I})$ so that its substitution as the operator in the matrix element in place of $3\hat{r}'r' - r'^2$ will change only the integral over $r'$.

$$\langle Im_1 |Q| Im_1 \rangle = \text{const} \langle Im_1 |3(\hat{I}_x + \hat{I}_y) - I^2| Im_1 \rangle .$$

The symmetrized form $\hat{I}_x + \hat{I}_y$ (tilde = transposed) must be used to correspond to $Q_{ij} = Q_{ji}$ since $I_i I_j \neq I_j I_i$, $i \neq j$.

To evaluate the constant we may consider the expectation value of the ZZ component of $Q$ for the state $m_I = I$:

$$eQ = \langle II |Q_{zz}| II \rangle$$

$$= \text{const} \langle II |3Z^2 - I^2| II \rangle$$

$$= \text{const} I(2I - 1)$$

$$\therefore \quad Q_{op} = \frac{eQ}{I(2I - 1)} \left[ \frac{3}{2}(\hat{I}_x + \hat{I}_y) - I^2 \right]$$

where

$$eQ = \int \psi_{I,I}^* (3Z^2 - r'^2) \psi_{I,I} dr'$$

is called "the" quadrupole moment.

The other factor appearing in the quadrupole term of the energy is $VE$. If it is noted that classically $VE$ is the charge weighted average of the simple dyadic $-1/r^5[3\hat{r} \hat{r} - r^2]$, we find by the argument just applied to $Q$ that

$$E_{op} = \frac{-eQ}{J^2(2J^2 - 1)} \left[ \frac{3}{2}(\hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x) - J^2 \right]$$

is called "the" quadrupole moment.
where
\[ eq = \int \psi^*_{J',J'} \left( \frac{3 \cos^2(zr) - 1}{r^3} \right) \psi_{J',J'} \, d\tau \]

and \( \vec{J}' \) is the total angular momentum of the molecule exclusive of \( \vec{I} \).

The operator for the quadrupole term of the energy is \((-1/6)\) times the dyadic dot product of these two operators:
\[ W_{op} = -\frac{1}{6} Q_{op} \cdot \nabla E_{op} \]
\[ = \frac{1}{2} \frac{e^2 Q}{I(2I - 1) J'(2J' - 1)} \left[ 3(\vec{I} \cdot \vec{J}')^2 + \frac{3}{2} (\vec{I} \cdot \vec{J}') - I^2 J'^2 \right] \]

and the energy of a nuclear quadrupole in the electric field in the interior of a molecule, when the nucleus has spin \( \vec{I} \) and the rest of the molecule as a whole has angular momentum \( \vec{J}' \), is the expectation value of this \( W_{op} \) in the state \( F = I + J' \), assuming this quadrupole interaction is small compared with the fine structure so that \( F \) remains a good quantum number. This expectation value is
\[ W = \frac{1}{2} \frac{e^2 Q}{I(2I - 1) J'(2J' - 1)} \left[ \frac{3}{4} C(C + 1) - I(I + 1) J'(J' + 1) \right] \]

where
\[ C \equiv F(F + 1) - I(I + 1) - J'(J' + 1) \]

\( I, J', \) and \( C \) are numbers that specify nuclear and molecular states. The constant \( Q \) is the quadrupole moment of the nucleus, since it depends only on the nuclear spin, \( I \), it can have only one value for a given nucleus in its ground state. Therefore it is a number also; a number that we hope to be able to determine by measuring \( W \). Thus of the various quantities that appear in this formula only \( eq \) requires further investigation.

II. Evaluation of \( eq \) by Wave Mechanics

By definition \( eq \) is the charge-weighted average of the function \( (3 \cos^2(zr) - 1)/r^3 \) for the rotational state \( J', J' \cdot \vec{u}_z = J' \); i.e.
\[ eq = \int \psi^*_{J',J'} \left( \frac{3 \cos^2(zr) - 1}{r^3} \right) \psi_{J',J'} \, d\tau \]

where \( \vec{r} \) is the radius vector from the quadrupolar nucleus to the volume element \( d\tau \) which contains an amount of charge \( \psi^* \psi \, d\tau \). In so far as the molecule approximates a rigid body, the charge density \( \psi^* \psi \) can be split into two factors, one depending on the position of \( d\tau \) in a molecule fixed system with coordinates \( r, \theta'', \phi'' \) and the other depending on the orientation of
the molecule in space. This orientation is most simply described in terms of Euler's angles (8):

Here A, B, and C are the principal axes of the molecule. (ON is the intersection of the AB and XY planes so it is perpendicular to both C and Z.) Then

\[ (\psi^*\psi)_{JJ} = (\psi^*\psi)(r, \theta'', \phi'') \cdot (\psi^*\psi)_{JJ}(\theta, \phi, \psi) \]

where \( \vec{J} \) is the rotational angular momentum of the molecule.

Likewise the function \( 3\cos^2(z, \vec{r}) - 1/\vec{r}^3 \) can be expressed in terms of the polar coordinates of \( \vec{r} \) and \( z \) in the molecule fixed coordinate system by the addition theorem of spherical harmonics (9).

The combination of these two expansions gives:

\[
eq \left( \psi^* \frac{3}{2} \cos^2 \theta'' - \frac{1}{2} \psi_p \right) \cdot \left( \psi^* \frac{3}{2} \cos^2 \theta - \frac{1}{2} \psi_{JJ} \right) \cdot \psi^* \psi_J \psi_{JJ} d\psi d\theta d\psi_{rot}
\]

\[
+ \left( \psi^* \psi_{JJ} \left[ - \frac{3}{2} \sin 2\theta'' \sin 2\theta \sin(\phi + \phi'') \right] \right) \cdot \psi_p \psi_{JJ} d\psi d\theta d\psi_{rot}
\]

\[
+ \left( \psi^* \psi_{JJ} \left[ - \frac{3}{2} \sin 2\theta'' \sin 2\theta \cos(\phi + \phi'') \right] \right) \cdot \psi_p \psi_{JJ} d\psi d\theta d\psi_{rot} \quad (a)
\]

The averages over the molecular charge are characteristic constants of each molecule in a given electronic and vibrational state; we will not consider them further.

The evaluation of the rotational integrals for slightly asymmetric molecules is the actual contribution of this paper.

Polar angles of \( \vec{r} \) and \( z \) in the molecule-fixed coordinate system. Note that the polar coordinates of \( z \) in the ABC system are \( \theta \) and \( \pi/2 - \phi \) where \( \theta \) and \( \phi \) are the Euler's angles of ABC in the space-fixed system.
The wave functions $\psi_{JJ}$ that we require are solutions of the following wave equation which describes the rotation of a rigid asymmetric body (10) (11):

$$(A_0 + b \cos 2\theta) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial \psi}{\partial \theta})$$

$$+ (A_0 - b \cos 2\theta) \frac{1}{\sin^2 \theta} \left[ \frac{\partial^2 \psi}{\partial \theta^2} - 2 \cot \theta \frac{\partial \psi}{\partial \theta} + \frac{\partial^2 \psi}{\partial \phi^2} \right] + (1 + b \cos 2\theta) \frac{\partial^2 \psi}{\partial \phi^2}$$

$$+ 2b \frac{\sin 2\phi}{\sin \theta} \left[ \frac{\partial^2 \psi}{\partial \theta \partial \phi} - \cot \theta \frac{\partial \psi}{\partial \phi} \right] - 2b \cos 2\theta \cot \theta \frac{\partial \psi}{\partial \phi} + b \sin 2\theta (1 + 2\cot^2 \theta) \frac{\partial \psi}{\partial \phi}$$

$$- 2b \sin 2\theta \cot \theta \csc \phi \frac{\partial \psi}{\partial \phi} + \lambda \psi = 0$$

where

$$A_0 = \frac{1}{2C} \left[ \frac{1}{A} + \frac{1}{B} \right]; \quad b = \frac{1}{2C} \left[ \frac{1}{A} - \frac{1}{B} \right]; \quad \lambda = \frac{2}{B} \frac{E}{h^2}; \quad C_0 = \frac{1}{C} - \frac{1}{2} \left[ \frac{1}{A} + \frac{1}{B} \right].$$

This equation cannot be solved in closed form. However, the part of it that remains when $b$, the parameter of asymmetry, equals zero, can be solved by separation of variables. The result is the wave function for the symmetric top (12)(13)

$$\psi_{JJK}^0(\theta, \phi, \psi) = N_{JJK} e^{i(K \phi + M \psi)} \cdot \left[ \frac{1 + \cos \theta}{2} \right]^{\frac{1}{2} |K + M|} \left[ \frac{1 - \cos \theta}{2} \right]^{\frac{1}{2} |K - M|}$$

$$\cdot P(-J + \beta/2 - 1, J + \beta/2; 1 + |K - M|; \frac{1 - \cos \theta}{2})$$

where $P(a,b;c;x)$ is the hypergeometric function, $\beta = |K + M| + |K - M| + 2$, and $N_{JJK}$ is the normalization constant. $K$ and $M$ are separation constants that must be integer if $\psi$ is to be single-valued. The third quantum number, $J$, is a positive integer such that $|K| \leq J \geq |M|$.

$$L_z \psi_{JJK} = \hbar \frac{\partial}{\partial \psi} \psi_{JJK} = M \hbar \psi_{JJK}$$

and

$$L_\phi \psi_{JJK} = \hbar \frac{\partial}{\partial \phi} \psi_{JJK} = K \hbar \psi_{JJK}$$

so $M \hbar$ is the component of angular momentum along the Z axis; $K \hbar$ is the component along the symmetry axis. Therefore, since $J$ is the maximum value of each of these two components, $J(J + 1) + 2$ must be the square of the total angular momentum.

In our problem we need to deal only with the case $M = J$; the wave function then simplifies to:

$$\psi_{JJK} = \frac{(2J + 1)!}{4\pi^2 (2J)(J + K)!} \frac{1}{(J + K)!} \frac{1 + \cos \theta}{2} \left[ \frac{1 - \cos \theta}{2} \right]^{\frac{1}{2} |K - M|} e^{i(K \phi + J \psi)}.$$
If this solution is substituted into the asymmetric top Hamiltonian from which the wave equation was derived, we find that (14):

\[ H_a \psi_{JK}^o = \left[ A_0 J(J + 1) + K^2 \right] \psi_{JK}^o \\
- \frac{b}{2} \left[ (J + K + 1)(J + K + 2)(J - K - 1)(J - K) \right]^{1/2} \psi_{JK+2J}^o \\
- \frac{b}{2} \left[ (J - K + 1)(J - K + 2)(J + K - 1)(J + K) \right]^{1/2} \psi_{JK-2J}^o \\
\]

in units of \( \hbar^2 c^2/2 \).

The first term on the right is the energy of a symmetric top type body. If we write \( H_a = H_s + H' \), we see that the only non-vanishing matrix elements of \( H' \) for symmetric top states are:

\[ \langle J K + 2J | H' | JK \rangle = -bF(J,K + 1) \]

and

\[ \langle J K - 2J | H' | JK \rangle = -bF(J,K - 1) \]

where

\[ F^2(J,n) = \frac{1}{4} \left[ J(J + 1) - n(n + 1) \right] \left[ J(J + 1) - n(n - 1) \right] \]

Since the symmetric top wave functions form a complete set (13), we can expand the asymmetric top wave functions in terms of them. We have just seen that the Hamiltonian is diagonal in \( J \) and \( M \), so the expansion has the form:

\[ \psi_{JTJ} = \sum_K S_{K^T} \psi_{JKJ} \]

Then for any function \( P(\theta, \phi, \psi) \),

\[ \int \psi_{JTJ}^* P_{JTJ} \psi_{JTJ} d\tau = \sum_{K,K'} S_{K^T} S_{K'^T} \int \psi_{JKJ}^* P_{JKJ} \psi_{JKJ}^* d\tau \quad \text{(b)} \]

We will apply this equation to each of the terms of eq in turn.

1. \[ \int \psi_{JKJ}^* (3 \cos^2 \psi - 1) \psi_{JKJ} \sin \theta d\psi d\phi d\theta \]

The \( \phi \) dependent part is

\[ \int_0^{2\pi} e^{-iK\phi} e^{-iK'\phi} d\phi = 2\pi \delta_{K,K'} \]

The \( \theta \) dependent part is

\[ c^2(J,K) \int_0^\pi (1 + \cos \theta)^{J+K}(1 - \cos \theta)^{J-K}(3 \cos^2 \theta - 1) \sin \theta d\theta \]

The substitution \( X = 1/2(1 - \cos \theta) \) reduces this to:

\[ -6 - \]
\[ c^2(J,K) \int_0^1 [2(1 - x)]^J [2x]^K \cdot 2 \left[ 1 - 6x(1 - x) \right] \cdot 2dx \]

\[ = c^2(J,K) 2^{2J+2} \left[ \int_0^1 (1 - x)^J [2x]^K \cdot 6 \left[ 1 - 6x(1 - x) \right] \cdot (1 - x)^J [2x]^K \cdot 2dx \right] . \]

According to integral No. 482 in Pierce's Tables this is:

\[ \frac{2(2J + 1)!}{(J + K)! (J - K)!} \left[ 1 - 6 \frac{(J + K + 1)(J - K + 1)}{(2J + 2)(2J + 3)} \right] \]

\[ = \frac{2J}{2J + 3} \left[ \frac{3K^2}{J(J + 1) - 1} \right] . \]

The dependent part is:

\[ \psi_{J,K}^{\ast} \sin^2 \theta \sin(\phi + \phi') \psi_{J,K} \sin \theta \sin \phi \sin \phi' \]

The dependent part is:

\[ \int_0^{2\pi} e^{-iK^1} \sin(\phi + \phi') e^{iK^1} d\phi = 0 \]

for \( K' \neq K + 1 \). We will find that if \( S_K, t \neq 0, S_{K+1}, t = 0 \).

Therefore, all terms of the second group in eq. vanish, either because of the vanishing of the integral or because of the vanishing of \( S_K, t S_{K+1}, t' \).

The dependent part is:

\[ \frac{1}{2} \int_0^{2\pi} e^{-iK^1} [e^{2i(\phi + \phi')} + e^{-2i(\phi + \phi')}] e^{iK^1} d\phi = \frac{1}{2} e^{2i(\phi + \phi')} \int_0^{2\pi} e^{i(K^1 - K + 2)\phi} d\phi \]

\[ + \frac{1}{2} e^{-2i(\phi + \phi')} \int_0^{2\pi} e^{i(K^1 - K - 2)\phi} d\phi = \pi e^{2i\phi'} \delta_{K, K-2} + \pi e^{-2i\phi'} \delta_{K, K+2} . \]

The dependent part of

\[ \int_0^{2\pi} \psi_{J,K}^{\ast} \sin^2 \phi \psi_{J,K+2} d\tau \]

is

\[ \int_0^{2\pi} C(J,K)C(J,K+2)(1 + \cos \phi)J^{K+1}(1 - \cos \phi)J-K \cdot \sin^2 \phi \sin \phi \]

\[ = C(J,K)C(J,K+2) \int_0^1 2^{2J}(1 - x)^J \cdot x^J \cdot 4x(1 - x)dx . \]

In the \( K + 2 \) case this is:
\[ 8 \cdot 2^{2J} C(J,K + 2) \int_0^1 (1 - x)^{J+K+2} x^{J-K} \, dx \]

\[ = \frac{2^J (2J + 1)!}{(J + K)! (J - K)!} \sqrt{\frac{(J - K - 1) (J - K)}{(J + K + 1) (J + K + 2)}} \left[ \frac{(J + K + 2)!(J - 1)!}{(2J + 3)!} \right] \]

\[ = \frac{2^J (2J + 1)!}{(2J + 2) (2J + 3)} \cdot \]

In the \( K - 2 \) case it is:

\[ 8 \cdot 2^{2J} C(J,K)C(J,K - 2) \int_0^1 (1 - x)^{J+K} x^{J-K+2} \, dx \]

\[ = \frac{2^J (2J + 1)!}{(J + K)! (J - K)!} \sqrt{\frac{(J + K - 1) (J + K)}{(J - K + 1) (J - K + 2)}} \left[ \frac{(J + K)!(J - K + 2)!}{(2J + 3)!} \right] \]

\[ = \frac{2^J (2J + 1)!}{(2J + 2) (2J + 3)} \cdot \]

Combining these results with Eq. (a), page 4, and with Eq. (b), page 6, and noting that

\[ \sum_K S_{K,\tau} S_{K-2,\tau} = \frac{F(J,K - 1)}{(J + 1)(2J + 3)} \sum_K S_{K+2,\tau} \frac{F(J,K + 1)}{(J + 1)(2J + 3)} \cdot S_{K,\tau} \]

we finally find that

\[ \text{eq} = \frac{1}{(J + 1)(2J + 3)} \sum_K \left\{ S_{K,\tau}^2 \left[ 3K^2 - J(J + 1) \right] \cdot \left\{ \psi^*_\rho \frac{3 \cos^2 \theta - 1}{r^3} \psi_\rho \, d\tau_\rho \right. \right. \]

\[ \left. \left. - 2S_{K,\tau} S_{K+2,\tau} F(J,K + 1) \cdot \left\{ \psi^*_\rho \frac{3 \sin^2 \theta \cos 2\phi}{r^3} \psi_\rho \, d\tau_\rho \right\} \right\} \cdot \]

This is identical with Bragg's formula (4).

Only the \( S_{K,\tau} \)'s, which depend on the degree of molecular asymmetry, remain to be evaluated. They cannot be obtained in a closed form in the general case, but if the molecule is nearly symmetrical we can find an approximate solution by means of perturbation theory.

We wish to find the eigenfunctions of the Hamiltonian \( H = H^0 + H' \) where \( H' \) is small, of the order \( b \). We know that \( H^0 \psi_{n,\alpha} = E_{n,\alpha}^0 \psi_{n,\alpha}^0 \), \( E_{n}^0 = A_0 J(J + 1) + K^2 \) where \( n \) represents \( J, K, J \) and \( \alpha = K / |K| \) is the quantum number of degeneracy. Let \( H \psi = E \psi \) and expand \( \psi \) in terms of the symmetric top wave functions:

\[ \psi = \sum_{n,\alpha} a_{n,\alpha} \psi_{n,\alpha}^0 \]

(These \( a_{n,\alpha} \) will become the \( S_{K,\tau} \)'s when they are properly normalized.) Then
\((H - H^O)\psi = H'\psi\) gives

\[
\sum_{n,\alpha} (E - E^O_n) a_{n,\alpha} \psi^O_{n,\alpha} = \sum_{n,\alpha} \left[ \sum_{m,\beta} a_{m,\beta} \langle n | H'| m \beta \rangle \right] \psi^O_{n,\alpha}
\]

\[
\therefore (E - E^O_n) a_{n,\alpha} = \sum_{m,\beta} a_{m,\beta} \langle n | H'| m \beta \rangle . \tag{1}
\]

If \(b,\) and therefore \(H',\) is small, we expect the energy values and the eigenfunctions to differ very little from those of the symmetric top. Therefore, as a first approximation we will assume that \(a_{m,\beta} \ll a_{p,\alpha}\) if \(E \simeq E^O_p.\) Then Eq. (1) becomes

\[
a_{n,\alpha}^p \simeq \sum_{p,\beta} a_{p,\beta}^p \frac{\langle n | H'| p \beta \rangle}{E_p - E^O_n} .
\]

Substitution of this approximation back into Eq. (1) gives as the second approximation:

\[
(E_p - E^O_n) a_{n,\alpha}^p \simeq \sum_{p,\beta} a_{p,\beta}^p \left[ \langle n | H'| p \beta \rangle + \sum_{\gamma, m \neq p} \frac{\langle n | H'| m \gamma \times m \gamma | H'| p \beta \rangle}{E_p - E^O_m} \right]. \tag{2}
\]

For the case \(n = p\) this is

\[
\sum_{p,\beta} a_{p,\beta}^p \left[ \langle p | H'| p \beta \rangle + \sum_{\gamma, m \neq p} \frac{\langle p | H'| m \gamma \times m \gamma | H'| p \beta \rangle - (E_p - E^O_p) a_{\beta}^p}{E_p - E^O_m} \right] \simeq 0 . \tag{3}
\]

The solution of Eq. (3) will give the ratio \(a_{p,1}^p / a_{p,2}^p\) as well as the energy \(E_p.\) Eq. (2) will then give \(a_{n,\alpha}^p, n \neq p\) in terms of one undetermined constant, say \(a_{p,1}^p,\) the value of which will be fixed by normalization.

In applying these results to our problem we must consider these equations for each value of \(p\) in turn, making use of the fact that

\[
\langle JK | H'| JK + 2J \rangle = -bF(J, K + 1)
\]

are the only non-vanishing matrix elements of \(H'.\)

For \(K = 0\) Eq. (3) gives

\[
E_0 = E^O_0 + \frac{\langle 0 | H'| 2 \rangle^2}{E^O_0 - E_2} + \frac{\langle 0 | H'| - 2 \rangle^2}{E^O_0 - E_2} .
\]

For \(K = 1\) the secular determinant is:
\[
\begin{vmatrix}
(E_1 - E_1^0) - \frac{\langle 1|H'|3\rangle^2}{E_1^0 - E_3^0} & -\langle 1|H'| - 1\rangle \\
-\langle 1|H'| - 1\rangle & (E_1 - E_1^0) + \frac{-\langle -1|H'| - 3\rangle^2}{E_1^0 - E_3^0}
\end{vmatrix} = 0.
\]

Now
\[\langle 1|H'|3\rangle = -bF(J,2) = -\langle 1|H'| - 3\rangle,\]
so
\[E_{1+} = E_1^0 + \langle 1|H'| - 1\rangle + \frac{\langle 1|H'|3\rangle^2}{E_1^0 - E_3^0}.\]

The first reduces Eq. (3) to \(a_{+1}^1 = a_{-1}^1\); the second gives \(a_{+1}^1 = -a_{-1}^1\).

For \(K = 2\) the elements \(T_{ii}\) of the secular determinant are:
\[
T_{11} = E_2 - E_2^0 - \frac{\langle 2|H'|0\rangle^2}{E_2^0 - E_0^0} - \frac{\langle 2|H'|4\rangle^2}{E_2^0 - E_4^0}
\]
\[
T_{12} = -\frac{\langle 2|H'|0\rangle\langle 0|H'| - 2\rangle}{E_2^0 - E_0^0} = T_{21}
\]
\[
T_{22} = E_2 - E_2^0 - \frac{\langle -2|H'|0\rangle^2}{E_2^0 - E_0^0} - \frac{\langle -2|H'| - 4\rangle^2}{E_2^0 - E_4^0}
\]

Now
\[\langle 2|H'|0\rangle = -bF(J,1) = \langle -2|H'|0\rangle\]
and
\[\langle 2|H'|4\rangle = -bF(J,3) = \langle -2|H'| - 4\rangle\]
so
\[E_{2+} = E_2^0 + \frac{\langle 2|H'|4\rangle^2}{E_2^0 - E_4^0} + \begin{cases} 
\frac{2\langle 2|H'|0\rangle^2}{E_2^0 - E_0^0} \\
0
\end{cases} \]
is the solution of the secular equation. The first reduces Eq. (3) to \(a_{-2}^2 = a_{+2}^2\); the second gives \(a_{-2}^2 = -a_{+2}^2\).

For \(K = 3\) the elements \(T_{ii}\) of the secular determinant are:
The substitution of this result into Eq. (3) does not give any relation between $a_{-3}^3$ and $a_{+3}^3$, but we note that if terms of the third order approximation, namely

$$
\langle 3|H'|1\rangle\langle 1|H'|-1\rangle\langle -1|H'|-3\rangle
\over (E_3 - E_1)(E_3 - E_1)
$$

had been included the result $a_{-3}^3 = \pm a_{+3}^3$ would have been obtained and $E_{3+}$ would no longer have been degenerate.

For $K > 3$ the solution of II is:

$$
E_K \approx E_K^0 + \langle K|H'|K - 2\rangle^2 + \langle K|H'|K + 2\rangle^2 \over E_K^0 - E_{K-2}^0 + E_K^0 - E_{K+2}^0
$$

$$
a_{-K}^K = \pm a_{+K}^K
$$

Thus

$$
E_0 = E_0^0 - b^2 {F^2(J,1)\over 2}
$$

$$
E_{1+} = E_1^0 + bF(J,0) - b^2 {F^2(J,2)\over 8}
$$

$$
E_{2+} = E_2^0 - b^2 {F^2(J,3)\over 12} + \left\{ b^2 {F^2(J,1)\over 2} \right\}
$$

$$
E_{3+} = E_3^0 + b^2 {F^2(J,2)\over 8} - b^2 {F^2(J,4)\over 16}
$$

$$
\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
$$

-11-
The $\pm$ subscript corresponds to the symmetric-antisymmetric combinations of degenerate symmetric top wave functions. Substitution of these values of $E$ into Eq. (2) and subsequent normalization give the $S_{K_T}$'s which can then be substituted into Bragg's formula. The resulting values of $\alpha\beta$ depend only on rotational quantum numbers and molecular constants. We obtained the following values of the $S_{K_T}$'s and formulae for $\alpha\beta$:

For $K = 0$

\[
S_{20} = b \frac{F(J,1)}{4} \\
S_{00} = 1 - b^2 \frac{F^2(J,1)}{16} \\
S_{-20} = b \frac{F(J,1)}{4}
\]

\[\therefore \ \alpha\beta = \frac{\partial^2 \psi}{\partial z^2} = \frac{1}{(J + 1)(2J + 3)} \cdot \left\{ \left[ -J(J + 1) + \frac{3}{2} b^2 F^2(J,1) \right] \frac{\partial^2 \psi}{\partial z^2} \\
- \left[ b F^2(J,1) \left( \frac{\partial^2 \psi}{\partial x^2} - \frac{\partial^2 \psi}{\partial y^2} \right) \right] \right\} \]

For $K = 1$

\[
S_{31} = -\frac{b}{\sqrt{2}} \frac{F(J,2)}{8} \left[ 1 \pm \frac{bF(J,0)}{8} \right] \\
S_{11} = \frac{1}{\sqrt{2}} - \frac{b^2 F^2(J,2)}{128} \\
S_{-11} = \pm \frac{1}{\sqrt{2}} + \frac{b^2 F^2(J,2)}{128} \\
S_{-31} = \pm \frac{b}{\sqrt{2}} \frac{F(J,2)}{8} \left[ 1 \pm \frac{bF(J,0)}{8} \right]
\]

\[\therefore \ \alpha\beta = \frac{\partial^2 \psi}{\partial z^2} = \frac{1}{(J + 1)(2J + 3)} \cdot \left\{ \left[ 3 - J(J + 1) + \frac{3}{8} b^2 F^2(J,2) \right] \frac{\partial^2 \psi}{\partial y^2} \\
- \left[ \pm F(J,0) \pm \frac{bF^2(J,2)}{8} \right] \left( \frac{\partial^2 \psi}{\partial x^2} - \frac{\partial^2 \psi}{\partial y^2} \right) \right\} \]

\[+ \left\{ b^2 \frac{F(J,0) F^2(J,2)}{32} \left[ \frac{\partial^2 \psi}{\partial x^2} - \frac{\partial^2 \psi}{\partial y^2} \right] \right\} \]

or $0$.
$K = 2$

\[ S_{4,2} = \frac{b}{\sqrt{2}} \frac{F(J, 3)}{12} \]

\[ S_{2,2} = \frac{1}{\sqrt{2}} - \frac{b^2}{\sqrt{2}} \left[ \frac{F^2(J, 3)}{288} + \frac{F^2(J, 1)}{16} \right] \]

\[ S_{0,2} = -\frac{b}{\sqrt{2}} \frac{F(J, 1)}{2} \]

\[ S_{-2,2} = \frac{1}{\sqrt{2}} - \frac{b^2}{\sqrt{2}} \left[ \frac{F^2(J, 3)}{288} + \frac{F^2(J, 1)}{16} \right] \]

\[ S_{-4,2} = \frac{b}{\sqrt{2}} \frac{F(J, 3)}{12} \]

\[ \therefore \text{eq} = \frac{\partial^2 v}{\partial z^2} = \frac{1}{(J + 1)(2J + 3)} \cdot \left\{ 12 - J(J + 1) + \frac{1}{3} b^2 F^2(J, 3) \left[ \frac{\partial^2 v}{\partial z^2} \right] \right\} \]

\[ - \left[ \frac{b}{6} F^2(J, 3) \right] \left[ \frac{\partial^2 v}{\partial x^2} - \frac{\partial^2 v}{\partial y^2} \right] \]
\[ S_{K+2K} = \frac{b}{\sqrt{2}} \frac{F(J,K + 1)}{4K + 1} \]

\[ S_{KK} = \frac{1}{\sqrt{2}} - \frac{b^2}{\sqrt{2}} \left[ \frac{F^2(J,K + 1)}{32(K + 1)^2} + \frac{F^2(J,K - 1)}{32(K - 1)^2} \right] \]

\[ S_{K-2K} = -\frac{b}{\sqrt{2}} \frac{F(J,K - 1)}{4(K - 1)} \]

\[ S_{-K+2K} = \mp \frac{b}{\sqrt{2}} \frac{F(J,K - 1)}{4(K - 1)} \]

\[ S_{-KK} = \mp \frac{1}{\sqrt{2}} \frac{b^2}{\sqrt{2}} \left[ \frac{F^2(J,K + 1)}{32(K + 1)^2} + \frac{F^2(J,K - 1)}{32(K - 1)^2} \right] \]

\[ S_{-K-2K} = \pm \frac{b}{\sqrt{2}} \frac{F(J,K + 1)}{4(K + 1)} \]

\[ \therefore eq = \frac{a^2V}{2z^2} = \frac{1}{(J + 1)(2J + 3)} \left\{ \begin{array}{c}
3K^2 - J(J + 1) + \frac{2b^2}{8} \left( \frac{(K + 2)F^2(J,K + 1)}{(K + 1)^2} - \frac{(K - 2)F^2(J,K - 1)}{(K - 1)^2} \right) \\
- b \frac{F^2(J,K - 1)}{2(K - 1)} \end{array} \right\} \]

These values of eq should be in error only by terms involving b to the third and higher powers.

The following table and graphs give the coefficients of

\[ -b \left( \frac{\partial^2V}{\partial x^2} - \frac{\partial^2V}{\partial y^2} \right) \]

in these formulae for eq. (It is important to note the term that is independent of b and which, therefore, does not appear in the expression for eq when K = 1.) Calculations are simplified by use of the identity

\[ F^2(J,n) = \frac{1}{4} \left\{ \begin{array}{c}
J^2 - n^2 \right\} (J + 1)^2 - n^2 \right\} \]

or by reference to Table I of King, Harner and Cross I (15).
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<td>0.856</td>
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<td>0.230</td>
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<td>0.674</td>
<td>0.964</td>
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<td>-1.551</td>
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Fig. 1 Magnitude of coefficient of $-b \left( \frac{\partial^2 v}{\partial x^2} - \frac{\partial^2 v}{\partial y^2} \right)$ vs. $K$ for different values of $J$. 

-16-
Fig. 2 Magnitude of coefficient of \(-b\left(\frac{\partial^2 Y}{\partial x'^2} - \frac{\partial^2 Y}{\partial y'^2}\right)\) vs. J for different values of K.
III. Application of These Formulae to Experimental Measurements of Rotational Fine Structures

It was shown in Part I that the energy of a single nuclear quadrupole moment in the electric field in the interior of a rotating molecule is:

\[ W_Q = e^2 q(J, \tau) Q \frac{3}{5} C(C + 1) - I(I + 1)J(J + 1) \]

where

\[ C = F(J + 1) - I(I + 1) - J(J + 1) \]

so that in general each term for given J is split into a number of levels. Therefore, in any of the allowed transitions there will be fine structure. The magnitude of the separations of these fine-structure components will be simply:

\[ \Delta h v = W_Q(F_1, J_1, \tau_1) - W_Q(F_2, J_2, \tau_2) \]

As an example let us consider the J = 1 + J = 2 transition for I = 3/2. The rotational energies of the initial and final states are shown schematically (for a more complete diagram see Herzberg, "Infrared and Raman Spectra").

Here the first vertical group of levels refers to symmetric top energies; the second group to asymmetric top energies. In the next column the large numeral gives the J value and the small numerals give the K values of the limiting prolate and oblate symmetric tops. The numbers in the column labeled \( \tau \) give the order of the energy levels. \( \tau = K_{-1} - K_1 \).

Now each of these levels is split further by the quadrupole interaction. In our example these separations from the unperturbed rotational levels are:

\[ \Delta h v = \left( W_Q(F_1, J_1, \tau_1) - W_Q(F_2, J_2, \tau_2) \right) \]
\[
\begin{array}{cccc}
I & J & F & W_Q \\
3/2 & 1 & 5/2 & \frac{1}{8} e^{2q(1,\tau)}Q \\
3/2 & 3/2 & -e^{2q(1,\tau)}Q \\
1/2 & 5/2 & \frac{5}{8} e^{2q(1,\tau)}Q \\
2 & 7/2 & \frac{1}{8} e^{2q(2,\tau)}Q \\
5/2 & -\frac{5}{8} e^{2q(2,\tau)}Q \\
3/2 & 0 \\
1/2 & 7/2 & \frac{7}{8} e^{2q(2,\tau)}Q
\end{array}
\]

and the frequency fine structure is:
\[
\begin{align*}
\frac{1}{8} q(1,\tau_1) - \frac{1}{8} q(2,\tau_2) &= -A \frac{5}{2} + \frac{7}{2} \\
\frac{1}{8} q(1,\tau_1) + \frac{5}{8} q(2,\tau_2) &= -A \frac{5}{2} + \frac{5}{2} \\
-q(1,\tau_1) + \frac{5}{8} q(2,\tau_2) &= -A \frac{3}{2} + \frac{5}{2} \\
-q(1,\tau_1) &= -A \frac{3}{2} + \frac{3}{2} \\
\frac{5}{8} q(1,\tau_1) &= -A \frac{1}{2} + \frac{3}{2} \\
\frac{5}{8} q(1,\tau_1) - \frac{7}{8} q(2,\tau_2) &= -A \frac{1}{2} + \frac{1}{2}
\end{align*}
\]

where \( A \equiv h/e^2Q. \)

If we now subtract one of these lines, say the \( \frac{5}{2} + \frac{7}{2} \), from each of the others in turn, we obtain:
\[
\begin{align*}
\frac{7}{8} q(2,\tau_2) &= -A \left( \frac{5}{2} + \frac{5}{2} - \frac{5}{2} + \frac{7}{2} \right) = -A \frac{1}{2} \\
-\frac{5}{8} q(1,\tau_1) + \frac{7}{8} q(2,\tau_2) &= -A \left( \frac{3}{2} + \frac{5}{2} - \frac{5}{2} + \frac{7}{2} \right) = -A \frac{2}{2}
\end{align*}
\]
\[-\frac{5}{4} q(1, \tau_1) + \frac{1}{4} q(2, \tau_2) = -A\left(\frac{v_1}{2} + \frac{v_2}{2} - \frac{v_5}{2} + \frac{7}{2}\right) = -A^v_3\]

\[q(1, \tau_1) + \frac{1}{4} q(2, \tau_2) = -A\left(\frac{v_1}{2} + \frac{v_2}{2} - \frac{v_5}{2} + \frac{7}{2}\right) = -A^v_4\]

\[q(1, \tau_1) - \frac{5}{8} q(2, \tau_2) = -A\left(\frac{v_1}{2} + \frac{v_2}{2} + \frac{7}{2}\right) = -A^v_5\]

These correspond to the numbers obtained in the measurement of fine structure; that is, the separation of each line from a given line.

We have here the only possible pattern for \(J = 1 + J = 2\) fine structure, essentially in terms of the single parameter \(q(2, \tau_2)/q(1, \tau_1)\), as far as ratios of frequency differences are concerned. Similar patterns can be written for all specific cases of \(J_1 + J_2\).

In order to identify an experimentally determined set of fine lines for a slightly asymmetric molecule once the \(J_1\) and \(J_2\) values are known, we may need only the zero-order approximations to eq, i.e. those without \(b\) if \(b\) is sufficiently small. In that case the ratio \(q(J_2, \tau_2)/q(J_1, \tau_1)\) reduces to a set of numbers, one for each pair of values of \(\tau_1\) and \(\tau_2\) and the ratios of frequency differences are completely determined. There is one exception; if either \(\tau_1\) or \(\tau_2\) corresponds to \(K = 1\) the ratio of the \(q\)'s is not in general a pure number if

\[\frac{\partial^2 v}{\partial x^2} = \frac{\partial^2 v}{\partial y^2}\]

is comparable to \(\frac{\partial^2 v}{\partial z^2}\)

so there is nothing to be gained by substitution for the eq's.

Once identification has been made the last set of equations can be solved for \(eq(J_1, \tau_1)/A\) and \(eq(J_2, \tau_2)/A\) and our formulae can then be used to obtain values of

\[eq \frac{\partial^2 v}{\partial x^2}, eq \frac{\partial^2 v}{\partial y^2}, \text{ and } eq \frac{\partial^2 v}{\partial z^2}\]

Very recently Mr. J. H. Goldstein (16) at Harvard has measured the separations of the components of two of the rotational lines of vinyl chloride, \(C_2\text{H}_2\text{Cl}^{35}\), which he has identified as \(1_{10} \rightarrow 2_{11}\) and \(1_{11} \rightarrow 2_{12}\) transitions, and very kindly permitted us to use his data.
$$C_2H_2Cl^35$$

| Transition  | Component  | Separation from Principal Component
|-------------|------------|-------------------------------------|
| $^{2}_{10} \rightarrow ^{2}_{11}$ | $5/2 - 7/2$ | 0
|            | $5/2 - 5/2$ | - 6.35* $v_1$
|            | $3/2 - 5/2$ | - 14.31 $v_2$
|            | $3/2 - 3/2$ | - 9.79 $v_3$
|            | $1/2 - 3/2$ | 4.51 $v_4$
|            | $1/2 - 1/2$ | 10.89 $v_5$

| $^{2}_{11} \rightarrow ^{2}_{12}$ | $5/2 - 7/2$ | 0
|            | $5/2 - 5/2$ | - 7.79 $v_1$
|            | $3/2 - 5/2$ | - 14.37* $v_2$
|            | $3/2 - 3/2$ | - 8.82 $v_3$
|            | $1/2 - 3/2$ | 3.10 $v_4$
|            | $1/2 - 1/2$ | 10.85 $v_5$

*The frequency of one line in each group has been altered slightly; 6.65 → 6.35 and 14.17 → 14.37.

When these frequencies are substituted into the last set of equations, we obtain

$$q(1,0)/A = -5.28 \pm 0.03 \text{ ergs}$$
$$q(1,1)/A = -6.36 \pm 0.03$$
$$q(2,0)/A = +7.32 \pm 0.05$$
$$q(2,-1)/A = +8.88 \pm 0.04$$

where the root mean square deviations of the various determinations of the $q$'s are given.

Our formulae are

$$eq(1,0) = + \frac{1}{10} \left[ \frac{\partial^2 v}{\partial z'^2} - \left( \frac{\partial^2 v}{\partial x'^2} - \frac{\partial^2 v}{\partial y'^2} \right) \right]$$
$$eq(1,1) = + \frac{1}{10} \left[ \frac{\partial^2 v}{\partial z'^2} + \left( \frac{\partial^2 v}{\partial x'^2} - \frac{\partial^2 v}{\partial y'^2} \right) \right]$$
$$eq(2,-1) = - \frac{1}{7} \left[ \frac{\partial^2 v}{\partial z'^2} + \left( \frac{\partial^2 v}{\partial x'^2} - \frac{\partial^2 v}{\partial y'^2} \right) \right]$$
$$eq(2,0) = - \frac{1}{7} \left[ \frac{\partial^2 v}{\partial z'^2} - \left( \frac{\partial^2 v}{\partial x'^2} - \frac{\partial^2 v}{\partial y'^2} \right) \right]$$
Substituting the experimental results gives

\[
e^Q \frac{\partial^2 v}{\partial z^2} = -58.2 \pm 0.3 \text{ Mc/sec}
\]
\[
e^Q \frac{\partial^2 v}{\partial y^2} = -56.7 \pm 0.5 \text{ Mc/sec}
\]
\[
e^Q \left( \frac{\partial^2 v}{\partial x^2} - \frac{\partial^2 v}{\partial y^2} \right) = -5.4 \pm 0.6 \text{ Mc/sec}
\]
\[
e^Q \frac{\partial^2 v}{\partial x^2} = -5.5 \pm 1.0 \text{ Mc/sec} \quad \text{(average)}
\]

Applying Laplace's equations, \( \nabla^2 v = 0 \), we find that

\[
e^Q \frac{\partial^2 v}{\partial x^2} = +26.0 \text{ Mc/sec}
\]
\[
e^Q \frac{\partial^2 v}{\partial y^2} = +31.5 \text{ Mc/sec} \quad .
\]

These average values agree perfectly with Goldstein's evaluation using one of Bragg's formulae and interpolation in the CHK tables. However, the 3-percent difference between the two values of \( e^Q \frac{\partial^2 v}{\partial z^2} \) may be significant, possibly indicating a second order effect.

Using the value \( Q = -0.079 \times 10^{-2}\text{ cm}^2 \) we find (17)(18):

\[
e^Q \frac{\partial^2 v}{\partial z^2} = +4.8 \times 10^6 \text{ ergs/cm}^2
\]
\[
e^Q \frac{\partial^2 v}{\partial x^2} = -2.2 \times 10^6
\]
\[
e^Q \frac{\partial^2 v}{\partial y^2} = -2.6 \times 10^6 \quad .
\]

Appendix

Relation between the Parameters of Asymmetry \( K \) and \( b \)

Label the moments of inertia so that \( A < B < C \). Let \( a = 1/A \), \( b = 1/B \), and \( c = 1/C \).

Then

\[
K = g - \frac{a(s+c)}{(a+c)} = \frac{2(b-c) + (c-s)}{(a-c)} \cdot \frac{2(b-c)}{(a-c)} - 1
\]

If \( A = B \),

\[
b_1 = g_0 - \frac{a(s+c)}{(a+c)} = \frac{b-c}{(a-c)} + \frac{b-c}{(a-c)} = \frac{b-c}{(a-c)} + \frac{b-c}{(a-c)} = \frac{b-c}{(a-c)} + \frac{b-c}{(a-c)}
\]

If \( B = C \),

\[
b_2 = g_0 - \frac{a(s+c)}{(a+c)} = \frac{b-c}{(a-c)} + \frac{b-c}{(a-c)} = \frac{b-c}{(a-c)} + \frac{b-c}{(a-c)} = \frac{b-c}{(a-c)} + \frac{b-c}{(a-c)}
\]

Note that \( |b| \leq 1/7 \) over half the range of \( K \) and \( |b| \leq 1/3 \) for any degree of asymmetry.
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