THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 73, NO. 2 JANUARY 15, 1948

Calculation of Nuclear Quadrupole Effects in Molecules

J. BARDEEN AND C. H. TOWNES
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received October 9, 1947)

Methods are given for the computation of nuclear quadrupole interactions in molecules. They apply primarily to the interpretation of microwave spectra of linear and symmetric top molecules in which either one or two nuclei on the molecular axis show quadrupole coupling to the molecular field. Tables are given of the energy values, based on Casimir's formula, for the quadrupole coupling of a single nucleus, and also of transformation coefficients for application to the case of intermediate coupling when two nuclei are involved. Spectral intensities are discussed briefly. Examples are given to illustrate various aspects of the theory. The molecules BrCN and ClCN show quadrupole effects resulting from the nitrogen nucleus as well as to the halogen. In the latter case, the intermediate coupling theory is required for a complete explanation of the observed microwave-absorption lines, as there are significant deviations from the first-order linear approximation.

NUCLEAR quadrupole effects in molecules were first discovered by Rabi[1] and his associates by the use of molecular beam spectroscopy. Recently the resolution afforded by microwave spectroscopy has made possible detection and measurement of these effects in microwave-absorption spectra of gases. It appears that nuclear quadrupole effects will be found in many spectra in the microwave region and will yield considerable nuclear and molecular information. Casimir's formula[2] for nuclear quadrupole-coupling energies in an isolated atom has previously been extended[1-5] to cases where a single atom shows quadrupole coupling in a linear or symmetric top molecule. There are also a number of interesting molecules containing two atoms with measurable quadrupole coupling; a comparison between experimental and theoretically expected spectra of some of these has already been published.[6] The theory applicable to these molecules, as well as to similar cases involving other types of coupling, is developed here. This theory, plus tables which are included, allow a fairly convenient method for interpreting quadrupole effects caused by either one or two nuclei on the axis of a linear or symmetric top molecule. Since experimental measurements of quadrupole effects in molecules and their theoretical explanation have developed together, a number of cases which test theoretical expectations are available, and these are briefly discussed.

The Hamiltonian for interaction between a nuclear quadrupole moment and molecular elec-

---

[1] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, and J. R. Zacharias, Phys. Rev. **57**, 677 (1940).

[2] H. B. G. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (Teyler's Tweede Genootschap, E. F. Bohn, Haarlem, 1936).

[3] A. Nordsieck, Phys. Rev. **58**, 310 (1940).

[4] D. K. Coles and W. E. Good, Phys. Rev. **70**, 979 (1946).

[5] J. H. Van Vleck, Phys. Rev. **71**, 468 (1947).

[6] C. H. Townes, A. N. Holden, J. Bardeen, and F. R. Merritt, Phys. Rev. **71**, 644 (1947); C. H. Townes, A. N. Holden, and F. R. Merritt, Phys. Rev. **72**, 513 (1947).

TABLE I. Values of $[\frac{3}{4}C(C+1)-I(I+1)J(J+1)]/2I(2I-1)(2J-1)(2J+3)$, where $C=F(F+1)-I(I+1)-J(J+1)$.

	I	1	3/2	2	5/2	3	7/2	4	9/2
J	F								
1	11/2								0.05000
	5							0.05000	
	9/2						0.05000		−0.13333
	4					0.05000		−0.13750	
	7/2				0.05000		−0.14286		0.09167
	3			0.05000		−0.15000		0.09821	
	5/2		0.05000		−0.16000		0.10714		
	2	0.05000		−0.17500		0.12000			
	3/2		−0.20000		0.14000				
	1	−0.25000		0.17500					
	1/2		0.25000						
	0	0.50000							
2	13/2								0.07143
	6							0.07143	
	11/2						0.07143		−0.08333
	5					0.07143		−0.08929	
	9/2				0.07143		−0.09694		−0.08333
	4			0.07143		−0.10714		−0.08291	
	7/2		0.07143		−0.12143		−0.08163		0.00595
	3	0.07143		−0.14286		−0.07857		0.01403	
	5/2		−0.17857		−0.07143		0.02551		0.13095
	2	−0.25000		−0.05357		0.04286		0.14031	
	3/2		0		0.07143		0.15306		
	1	0.25000		0.12500		0.17143			
	1/2		0.25000		0.20000				
	0			0.25000					
3	15/2								0.08333
	7							0.08333	
	13/2						0.08333		−0.05556
	6					0.08333		−0.06250	
	11/2				0.08333		−0.07143		−0.09167
	5			0.08333		−0.08333		−0.09464	
	9/2		0.08333		−0.10000		−0.09762		−0.06111
	4	0.08333		−0.12500		−0.10000		−0.05595	
	7/2		−0.16667		−0.10000		−0.04762		0.00556
	3	−0.25000		−0.09167		−0.03333		0.01786	
	5/2		−0.05000		−0.00667		0.03571		0.08333
	2	0.20000		0.05000		0.06333		0.09821	
	3/2		0.20000		0.11000		0.11905		0.15278
	1			0.20000		0.15000		0.16369	
	1/2				0.20000		0.17857		
	0					0.20000			

tric fields is given by Casimir's expression[2]

$$H(\mathbf{I},\mathbf{J})=2eQ\{\sum_k e_k(3\cos^2\theta_k-1)/R_k^3\}_{\text{Av}}F(\mathbf{I},\mathbf{J}),\quad(1)$$

where

$$F(\mathbf{I},\mathbf{J})=\frac{3(\mathbf{I}\cdot\mathbf{J})^2+\frac{3}{2}(\mathbf{I}\cdot\mathbf{J})-I(I+1)J(J+1)}{2J(2J-1)2I(2I-1)},$$

e = electronic charge,

Q = quadrupole moment of nucleus (defined below),

$\mathbf{R}_k$ = radius vector from nucleus to individual charge e_k in molecule,

θ_k = angle between $\mathbf{R}_k$ and an axis fixed in space,

$\mathbf{I}$ = nuclear spin in units of $h/2\pi$,

$\mathbf{J}$ = angular momentum caused by molecular rotation in units of $h/2\pi$.

The average is taken over the normal electronic state, the appropriate vibrational state, and the rotational state with $m_J=J$, that is, the one for which the projection of $\mathbf{J}$ along the fixed axis is a maximum.

When applied to a linear molecule, or to a symmetric top molecule with the nucleus on the axis of symmetry, Casimir's expression reduces to[3]

$$H(\mathbf{I},\mathbf{J})=eQq(3\cos^2\theta-1)_{\text{Av}}F(\mathbf{I},\mathbf{J}),\quad(2)$$

where θ is now the angle between the molecular axis and the axis fixed in space, and the average is over the rotational wave function with $m_J=J$.

TABLE I.—*Continued.*

	I	1	3/2	2	5/2	3	7/2	4	9/2
J	F								
	17/2								0.09091
	8							0.09091	
	15/2						0.09091		−0.03788
	7					0.09091		−0.04546	
	13/2				0.09091		−0.05520		−0.08658
	6			0.09091		−0.06818		−0.09172	
	11/2		0.09091		−0.08636		−0.09740		−0.07955
	5	0.09091		−0.11364		−0.10325		−0.07711	
	9/2		−0.15909		−0.10779		−0.07189		−0.03788
4	4	−0.25000		−0.10552		−0.06104		−0.02667	
	7/2		−0.07143		−0.03766		−0.00928		0.02056
	3	0.17857		0.01786		0.01948		0.03873	
	5/2		0.17857		0.07143		0.06540		0.08117
	2			0.17857		0.10714		0.10239	
	3/2				0.17857		0.13265		0.13258
	1					0.17857		0.15179	
	1/2						0.17857		0.16667
	0							0.17857	
	19/2								0.09615
	9							0.09615	
	17/2						0.09615		−0.02564
	8					0.09615		−0.03365	
	15/2				0.09615		−0.04396		−0.08013
	7			0.09615		−0.05769		−0.08677	
	13/2		0.09615		−0.07692		−0.09432		−0.08547
5	6	0.09615		−0.10577		−0.10256		−0.08517	
	11/2		−0.15385		−0.11026		−0.08242		−0.05769
	5	−0.25000		−0.11218		−0.07457		−0.04808	
	9/2		−0.08333		−0.05385		−0.03205		−0.01068
	4	0.16667		0		−0.00385		0.00801	
	7/2		0.16667		0.05000		0.03663		0.04380
	3			0.16667		0.08333		0.06937	
	5/2				0.16667		0.10714		0.09615
	2					0.16667		0.12500	
	3/2						0.16667		0.13889
	1							0.16667	
	1/2								0.16667

Our definition of q differs from previous usage, as will be discussed below. If we define

V = electrostatic potential produced by all charges except those inside a small sphere surrounding the nucleus,
z = coordinate along the molecular axis,

then our q is defined as

$$q \equiv \partial^2 V/\partial z^2.$$

Notation for the expression $eQ(\partial^2 V/\partial z^2)$ is in a rather confused state, a number of different forms having appeared in the literature. Kellogg *et al.*[1] and Nordsieck[3] define and use quantities q and q', where

$$q' = (1/2e)(\partial^2 V/\partial z^2) \quad \text{and} \quad q = (-2J/(2J+3))q'.$$

In addition, they use a quantity written as $\partial^2 V/\partial z^2$, which is our $\partial^2 V/\partial z^2$ divided by e. Coles and Good,[4] in an expression which will be discussed later, use Q for the quadrupole moment, which is our Q multiplied by $-(2I+3)/2I$. They also use a symbol q which is twice Kellogg and Nordsieck's q'. Van Vleck[7] has given an expression with a symbol Q differing from the usual Q by a factor of 4. The Q defined here appears to be that most widely used, and is

$$\frac{1}{e}[\rho r^2(3\cos^2\theta-1)]_{\text{Av}},$$

where the average is over the nuclear charge density ρ and θ is the angle between the spin vector and the radius r to the element of charge. Since there is already so much notational confusion, and notation used in the past does not

---

[7] B. P. Dailey, R. L. Kyhl, M. W. P. Strandberg, J. H. Van Vleck, and E. B. Wilson, Jr., Phys. Rev. **70**, 984 (1946).

seem to us particularly suited to our discussion, we have taken the liberty of redefining the symbol q as the fundamental molecular quantity $\partial^2 V/\partial z^2$.

QUADRUPOLE COUPLING FOR A SINGLE NUCLEUS

If only one nucleus of a linear molecule shows appreciable coupling, and if no vibrational bending modes are excited, the energy caused by nuclear quadrupole effects may be expressed in terms of the quantum number F for the total angular momentum, $\mathbf{F}=\mathbf{I}+\mathbf{J}$. The energy is[1–3]

$$E=-eQq\frac{\frac{3}{4}C(C+1)-I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)}, \quad (3)$$

where

$$C=F(F+1)-I(I+1)-J(J+1).$$

Table I gives the values of the factor multiplying $-eQq$ in Eq. (3) for all possible values of F, for $0<J\leq 5$, and for $1\leq I\leq 9/2$. If $J=0$ or $I<1$, the quadrupole-coupling energy is identically zero. This table for energy levels plus published tables for relative intensities of different transitions[8] allows a rapid calculation of the quadrupole splitting of molecular rotational lines involving low values of J. It may be noted from the table that when $F=J+I$ or $F=J-I$, the interaction energy is independent of I. The tabulated function becomes, indeed, $J/4(2J+3)$ when $F=J+I$ and $(J+1)/4(2J-1)$ when $F=J-I$. If $I=1$ and $F=J$, it becomes -0.25. The table also shows that for any I and J, positive quantities are obtained for extreme values of F, and negative quantities for intermediate F's. This is because the interaction varies approximately as the square of the cosine between $\mathbf{I}$ and $\mathbf{J}$.

Van Vleck[5] and Coles and Good[4] showed that for a single nucleus in a symmetric top molecule, expression (3) should be multiplied by $(1-3K^2/J(J+1))$, where K is the quantum number for angular momentum about the symmetry axis. Their result follows from the fact that $(3\cos^2\theta-1)$ averaged over the symmetric top wave function, with the magnetic quantum number m_J equal to the total angular momentum J, is $(-2J/(2J+3))(1-3K^2/J(J+1))$. The linear molecule is a special case of the symmetric top in which $K=0$, and in this case $(3\cos^2\theta-1)_{\text{Av}}$ is $-2J/(2J+3)$. Good examples of quadrupole effects in a symmetric top molecule are afforded by the now famous ammonia inversion spectrum,[4, 7] and by the rotational spectra of CH_3I, CH_3Br, and CH_3Cl.[9] Table I may be used for energy levels of symmetric top molecules if the correction factor $(1-3K^2/J(J+1))$ is applied.

The expression for quadrupole energy levels in a symmetric top molecule also applies to linear molecules excited to bending vibrational states. Because of the degeneracy of the bending modes of a linear molecule, excitation of one of these modes produces an angular momentum around the molecular axis. Under this condition the molecule is almost a symmetric top, its two larger moments of inertia generally differing by about one part in a thousand. It should, therefore, be expected that the symmetric top formula for quadrupole splitting holds to a high degree of accuracy if K is replaced by l, the quantum number for angular momentum produced by this type of vibration. The result may be more rigorously demonstrated by calculating $(3\cos^2\theta-1)_{\text{Av}}$. The wave functions for each of the two states of a molecule undergoing a bending vibration involve a combination of symmetric top functions with l positive and l negative.[10] The quantity $(3\cos^2\theta-1)_{\text{Av}}$ is, however, independent of the sign of l and becomes

$$\frac{-2J}{2J+3}\left(1-\frac{3l^2}{J(J+1)}\right).$$

Examples of quadrupole splitting in linear molecules with excited bending modes are afforded by BrCN and ClCN. Spectra of their excited molecules agree well with the above theory.[6]

QUADRUPOLE COUPLING FOR TWO NUCLEI

In case there are two nuclei with angular momenta I_1 and I_2 contributing to the interaction, the Hamiltonian is a combination of functions such as expression (2):

$$H=H_1(\mathbf{I}_1, \mathbf{J})+H_2(\mathbf{I}_2, \mathbf{J}). \quad (4)$$

---

[8] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York 1935).

[9] W. Gordy, A. G. Smith, and J. W. Simmons, Phys. Rev. **71**, 917 (1947); **72**, 249 (1947); **72**, 344 (1947).

[10] See, for example, G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 377.

TABLE II. Transformation coefficients $c(F_1, F_2)$ for $I_1=I_1$, $I_2=1$.
$\Sigma=I+J+F+1$

F_2 \ F_1	$F-1$	F	$F+1$
$J-1$	$\left(\frac{(\Sigma-2F-1)(\Sigma-2F)(\Sigma-2J-1)(\Sigma-2J)}{2J(2J+1)2F(2F+1)}\right)^{\frac{1}{2}}$	$\left(\frac{2(\Sigma-2F-1)(\Sigma-2I-1)\Sigma(\Sigma-2J)}{2J(2J+1)2F(2F+2)}\right)^{\frac{1}{2}}$	$\left(\frac{(\Sigma-2I-1)(\Sigma-2I)\Sigma(\Sigma+1)}{2J(2J+1)(2F+1)(2F+2)}\right)^{\frac{1}{2}}$
J	$\left(\frac{2(\Sigma-2F)(\Sigma-2I-1)\Sigma(\Sigma-2J-1)}{2J(2J+2)2F(2F+1)}\right)^{\frac{1}{2}}$	$\frac{2(F-I)(2F+2)+2(\Sigma-2F-1)(\Sigma-2I)}{(2J(2J+2)2F(2F+2))^{\frac{1}{2}}}$	$-\left(\frac{2(\Sigma-2F-1)(\Sigma-2I)(\Sigma-2J)(\Sigma+1)}{2J(2J+2)(2F+1)(2F+2)}\right)^{\frac{1}{2}}$
$J+1$	$\left(\frac{(\Sigma-2I-1)(\Sigma-2I)\Sigma(\Sigma+1)}{(2J+1)(2J+2)2F(2F+1)}\right)^{\frac{1}{2}}$	$-\left(\frac{2(\Sigma-2J-1)(\Sigma-2F)(\Sigma-2I)(\Sigma+1)}{(2J+1)(2J+2)2F(2F+2)}\right)^{\frac{1}{2}}$	$\left(\frac{(\Sigma-2J-1)(\Sigma-2J)(\Sigma-2F-1)(\Sigma-2F)}{(2J+1)(2J+2)(2F+1)(2F+2)}\right)^{\frac{1}{2}}$

We shall continue to represent the total angular momentum of the molecule by $\mathbf{F}$, and introduce, in addition, the quantity $\mathbf{F}_1$, which is the vector sum of $\mathbf{J}$ and the spin $\mathbf{I}_1$ of the first nucleus, and the quantity $\mathbf{F}_2$, which is the vector sum of $\mathbf{J}$ and the spin $\mathbf{I}_2$ of the second nucleus. Wave functions for the combined system may be obtained by first obtaining functions with F_1 fixed:

$$\mathbf{F}_1=\mathbf{J}+\mathbf{I}_1,\quad F_1=|I_1+J|,\ \cdots,\ |I_1-J|,$$

and then combining $\mathbf{I}_2$ with $\mathbf{F}_1$ to obtain the total angular momentum $\mathbf{F}$:

$$\mathbf{F}=\mathbf{F}_1+\mathbf{I}_2,\quad F=|F_1+I_2|,\ \cdots,\ |F_1-I_2|.$$

Let $\Psi_1(F, F_1)$ be the wave functions for states specified by the quantum numbers F and F_1. Different values of F_1, when combined with I_2, may lead to the same value of F. Thus there may be a number of wave functions, specified by different F_1, which all have the same total angular momentum, F. If the interaction H_2 is negligible, the states specified by different F, but with the same value of F_1, will all have the same energy. This degeneracy is removed if H_2 is appreciable.

Alternatively, it would be possible to first combine $\mathbf{I}_2$ with $\mathbf{J}$ to get states for fixed F_2, and then combine $\mathbf{F}_2$ with $\mathbf{I}_1$ to get states for fixed F. The number of different states with given F is just the same as before, and the two sets of wave functions are linearly related. Thus we may write

$$\Psi_1(F, F_1)=\sum_{F_2} c(F_1, F_2)\Psi_2(F, F_2). \qquad (5)$$

The matrix $c(F_1, F_2)$ is unitary, and the phases may be chosen so that the coefficients are real. The reverse transformation is then

$$\Psi_2(F, F_2)=\sum_{F_1} c(F_1, F_2)\Psi_1(F, F_1). \qquad (6)$$

As will be shown below, the secular determinant for the energy levels can be set up from the transformation matrix and the energy values for the individual interactions.

An expression for the matrix coefficients may be found by expanding both $\Psi_1(F, F_1)$ and $\Psi_2(F, F_2)$ in terms of a fundamental set of wave functions characterized by the quantum numbers (m_1, m_2, m_J) representing the components of I_1, I_2, and J. If these expansions are substituted into Eq. (5), and the coefficients of the wave functions of the fundamental set on the two sides are equated, a set of linear equations is obtained for $c(F_1, F_2)$. These may be solved simply in a formal way, but the resulting series expression is difficult to use for numerical calculations. Dr. G. H. Shortley has pointed out to us that Racah[11] recently obtained a closed formula for the coefficients, which, although still rather involved, is simpler to use than one which we had developed independently and used in our calculations. We shall accordingly refer to Racah's paper for the formula and its derivation. We will not reproduce it here because of its length. Our coefficient becomes in Racah's notation:

$$c(F_1, F_2)=(JI_1(F_1)I_2F|JI_2(F_2)I_1F). \qquad (7)$$

The closed formula of Racah[11] is his Eq. (5) of III, which refers back to his Eq. (36′) of II.

Since the general expression is complicated, we have computed expressions for the coeffi-

---

[11] G. Racah, I Phys. Rev. **61**, 186 (1942); II **62**, 438 (1942); **63**, III 367 (1943).

TABLE III. Transformation coefficients $c(F_1, F_2)$ for $I_1=I$, $I_2=\frac{3}{2}$. $\Sigma=I+J+F+\frac{3}{2}$

F_2	$F_1=F-\frac{3}{2}$	$F_1=F-\frac{1}{2}$
$J-\frac{3}{2}$	$\left(\frac{(\Sigma-2F-2)(\Sigma-2F-1)(\Sigma-2F)(\Sigma-2J-2)(\Sigma-2J-1)(\Sigma-2J)}{(2F-1)2F(2F+1)(2J-1)2J(2J+1)}\right)^{\frac{1}{2}}$	$\left(\frac{3(\Sigma-1)(\Sigma-2F-2)(\Sigma-2F-1)(\Sigma-2J-1)(\Sigma-2J)(\Sigma-2I-2)}{(2F-1)(2F+1)(2F+2)(2J-1)2J(2J+1)}\right)^{\frac{1}{2}}$
$J-\frac{1}{2}$	$\left(\frac{3(\Sigma-1)(\Sigma-2F-1)(\Sigma-2F)(\Sigma-2J-2)(\Sigma-2J-1)(\Sigma-2I-2)}{(2F-1)2F(2F+1)(2J-1)(2J+1)(2J+2)}\right)^{\frac{1}{2}}$	$\frac{[2(2F-1)(\Sigma-2I-1)+(\Sigma-2F)(-3I+3J+F-\frac{1}{2})]((\Sigma-2F-1)(\Sigma-2J-1))^{\frac{1}{2}}}{((2F-1)(2F+1)(2F+2)(2J-1)(2J+1)(2J+2))^{\frac{1}{2}}}$
$J+\frac{1}{2}$	$\left(\frac{3(\Sigma-1)\Sigma(\Sigma-2F)(\Sigma-2J-2)(\Sigma-2I-2)(\Sigma-2I-1)}{(2F-1)2F(2F+1)2J(2J+1)(2J+3)}\right)^{\frac{1}{2}}$	$\frac{[(2F-1)(\Sigma-2I)+(\Sigma-2F)(-3I+3J-F+\frac{1}{2})]((\Sigma)(\Sigma-2I-1))^{\frac{1}{2}}}{((2F-1)(2F+1)(2F+2)2J(2J+1)(2J+3))^{\frac{1}{2}}}$
$J+\frac{3}{2}$	$\left(\frac{(\Sigma-1)\Sigma(\Sigma+1)(\Sigma-2I-2)(\Sigma-2I-1)(\Sigma-2I)}{(2F-1)2F(2F+1)(2J+1)(2J+2)(2J+3)}\right)^{\frac{1}{2}}$	$-\left(\frac{3\Sigma(\Sigma+1)(\Sigma-2F)(\Sigma-2J-2)(\Sigma-2I-1)(\Sigma-2I)}{(2F-1)(2F+1)(2F+2)(2J+1)(2J+2)(2J+3)}\right)^{\frac{1}{2}}$
	$F_1=F+\frac{1}{2}$	$F_1=F+\frac{3}{2}$
$J-\frac{3}{2}$	$\left(\frac{3(\Sigma-1)\Sigma(\Sigma-2F-2)(\Sigma-2J)(\Sigma-2I-2)(\Sigma-2I-1)}{2F(2F+1)(2F+3)(2J-1)2J(2J+1)}\right)^{\frac{1}{2}}$	$\left(\frac{(\Sigma-1)\Sigma(\Sigma+1)(\Sigma-2I-2)(\Sigma-2I-1)(\Sigma-2I)}{(2F+1)(2F+2)(2F+3)(2J-1)2J(2J+1)}\right)^{\frac{1}{2}}$
$J-\frac{1}{2}$	$\frac{[2F(-3I-J+3F+\frac{1}{2})+3(\Sigma-2F-1)(\Sigma-2I-2)](\Sigma(\Sigma-2I-1))^{\frac{1}{2}}}{(2F(2F+1)(2F+3)(2J-1)(2J+1)(2J+2))^{\frac{1}{2}}}$	$-\left(\frac{3\Sigma(\Sigma+1)(\Sigma-2F-2)(\Sigma-2J)(\Sigma-2I-1)(\Sigma-2I)}{(2F+1)(2F+2)(2F+3)(2J-1)(2J+1)(2J+2)}\right)^{\frac{1}{2}}$
$J+\frac{1}{2}$	$\frac{-[2F(-3I+J+3F+\frac{1}{2})+3(\Sigma-2F)(\Sigma-2I-1)]((\Sigma-2F-1)(\Sigma-2J-1))^{\frac{1}{2}}}{(2F(2F+1)(2F+3)2J(2J+1)(2J+3))^{\frac{1}{2}}}$	$\left(\frac{3(\Sigma+1)(\Sigma-2F-2)(\Sigma-2F-1)(\Sigma-2J-1)(\Sigma-2J)(\Sigma-2I)}{(2F+1)(2F+2)(2F+3)2J(2J+1)(2J+3)}\right)^{\frac{1}{2}}$
$J+\frac{3}{2}$	$\left(\frac{3(\Sigma+1)(\Sigma-2F-1)(\Sigma-2F)(\Sigma-2J-2)(\Sigma-2J-1)(\Sigma-2I)}{2F(2F+1)(2F+3)(2J+1)(2J+2)(2J+3)}\right)^{\frac{1}{2}}$	$-\left(\frac{(\Sigma-2F-2)(\Sigma-2F-1)(\Sigma-2F)(\Sigma-2J-2)(\Sigma-2J-1)(\Sigma-2J)}{(2F+1)(2F+2)(2F+3)(2J+1)(2J+2)(2J+3)}\right)^{\frac{1}{2}}$

cients $c(F_1, F_2)$for two cases

(1) $I_1=1$; I_2, J arbitrary;
(2) $I_1=\frac{3}{2}$; I_2, J arbitrary.

The values are listed in Tables II and III. These should be sufficient for a large fraction of the molecules of practical interest.

We turn now to the calculation of the energy levels. In case both interactions, H_1 and H_2, are appreciable, the eigenfunctions are not given by either $\Psi_1(F, F_1)$ or $\Psi_2(F, F_2)$, but by an appropriate linear combination of either set. Let the correct wave function be given by the expansion

$$\Psi(F)=\sum_{F_1} a(F_1)\Psi_1(F, F_1). \tag{8}$$

The Hamiltonian equation $H\Psi=E\Psi$ becomes

$$\begin{aligned}\sum_{F_1} H_1(\mathbf{I}_1, \mathbf{J})a(F_1)\Psi_1(F, F_1) \\ +\sum_{F_1} H_2(\mathbf{I}_2, \mathbf{J})a(F_1)\sum_{F_2} c(F_1, F_2)\Psi_2(F, F_2) \\ =E\sum_{F_1} a(F_1)\Psi_1(F, F_1),\end{aligned} \tag{9}$$

in which use has been made of (5). By use of the relations

$$H_1(\mathbf{I}_1, \mathbf{J})\Psi_1(F, F_1)=E_1(F_1)\Psi_1(F, F_1), \tag{10}$$

$$H_2(\mathbf{I}_2, \mathbf{J})\Psi_2(F, F_2)=E_2(F_2)\Psi_2(F, F_2), \tag{11}$$

followed by replacement of Ψ_2 by (6), Eq. (9) reduces to

$$(A(F_1, F_1)+E(F_1)-E)a(F_1) + \sum_{F_1'\neq F_1} A(F_1, F_1')a(F_1')=0, \tag{12}$$

where

$$A(F_1, F_1')=\sum_{F_2} c(F_1, F_2)c(F_1', F_2)E_2(F_2). \tag{13}$$

The energies are determined by setting the determinant of the coefficients of the $a(F_1)$ equal to zero. If the interaction H_2 may be treated as a small perturbation and there is no degeneracy, energy values to the first order are

$$E=E(F_1)+A(F_1, F_1). \tag{14}$$

In general, the complete secular determinant must be solved.

It will be noted that this method for setting up the secular determinant makes no use of the specific form of the operator for the quadrupole interaction. The method can be used for any Hamiltonian of the general form of Eq. (4).

Another method for setting up the secular determinant is to calculate the elements of the determinant directly,

$$A(F_1, F_1') = \int \Psi_1(F, F_1')H_2(I_2, J)\Psi_1(F, F_1)d\tau,$$

making use of the form of $H_2(I_2, J)$. This method has recently been applied by Foley[12] to the case of a homonuclear diatomic molecule. It may be easier to use in some cases than the method described above, particularly if only first-order effects are desired. It is perhaps also the easiest method to use if more than two nuclei are involved in quadrupole interactions.

Because of the form of the interaction operator (Eq. (1)), the matrix elements of $(\mathbf{I}_2\cdot\mathbf{J})$ and of $(\mathbf{I}_2\cdot\mathbf{J})^2$ are required. Condon and Shortley (p. 71) give a general expression for the matrix elements of the scalar product of any two vectors **P** and **Q**. Use may be made of their results if we make the correlation

$$\begin{aligned} &j_1 = F_1, \quad j_2 = I_2, \\ &J = F, \\ &P = I_2, \quad Q = J. \end{aligned}$$

The non-vanishing matrix elements of $\mathbf{I}_2\cdot\mathbf{J}$, as obtained from the expressions of Condon and Shortley, are

$$\begin{aligned} (F_1, I_2, F|\mathbf{I}_2\cdot\mathbf{J}|F_1, I_2, F) &= \tfrac{1}{2}(F_1|J|F_1)(F(F+1)-F_1(F_1+1)-I_2(I_2+1)), \\ (F_1, I_2, F|\mathbf{I}_2\cdot\mathbf{J}|F_1-1, I_2, F)& \\ &= -\tfrac{1}{2}(F_1|J|F_1-1)\{(F+F_1-I_2)(F+I_2-F_1+1)(F+F_1+I_2+1)(F_1+I_2-F)\}^{\frac{1}{2}}, \\ (F_1, I_2, F|\mathbf{I}_2\cdot\mathbf{J}|F_1+1, I_2, F)& \\ &= -\tfrac{1}{2}(F_1|J|F_1+1)\{(F+F_1-I_2+1)(F+I_2-F_1)(F+F_1+I_2+2)(F_1+I_2-F+1)\}^{\frac{1}{2}}, \end{aligned} \tag{16}$$

in which

$$\begin{aligned} (F_1|J|F_1) &= \frac{J(J+1)-I_1(I_1+1)+F_1(F_1+1)}{2F_1(F_1+1)}, \\ (F_1|J|F_1-1) &= \left\{\frac{(F_1-J+I_1)(F_1+J-I_1)(F_1+J+I_1+1)(J+I_1-F_1+1)}{4F_1^2(2F_1-1)(2F_1+1)}\right\}^{\frac{1}{2}}, \\ (F_1|J|F_1+1) &= \left\{\frac{(F_1-J+I_1+1)(F_1+J-I_1+1)(F_1+J+I_1+2)(J+I_1-F_1)}{4(F_1+1)^2(2F_1+1)(2F_1+3)}\right\}^{\frac{1}{2}}. \end{aligned} \tag{17}$$

The matrix for $(\mathbf{I}_2\cdot\mathbf{J})^2$ can be obtained by squaring that for $\mathbf{I}_2\cdot\mathbf{J}$. The general expressions are rather complicated, but it might not be too difficult to carry out the numerical calculations for a particular case.

The methods described above, together with the tables, allow a fairly convenient determination of energy levels, although in some cases considerable computation is still required.

INTENSITIES

In addition to energy levels, intensities are generally required. Let us assume that the intensity of a molecular line can be calculated if no quadrupole effects are present, and call its intensity A. If the quadrupole interaction of one nucleus splits this line, relative intensities of each of the hyperfine components may be found from tables in Condon and Shortley,[8] as pointed out above. The intensity of each component is then

$$\frac{AS(I_1J|F_1|I_1J'F_1')}{\sum_{F_1}\sum_{F_1'} S(I_1JF_1|I_1J'F_1')}, \tag{33}$$

where $S(I_1JF_1|I_1J'F_1')$ can be obtained from the tables. If a second nucleus produces a quadrupole interaction, but its coupling is small compared with the coupling of the first nucleus, the tables may be again applied to find intensities of all components of the still more finely split hyperfine structure. They are proportional to

---

[12] H. M. Foley, Phys. Rev. **71**, 751 (1947).

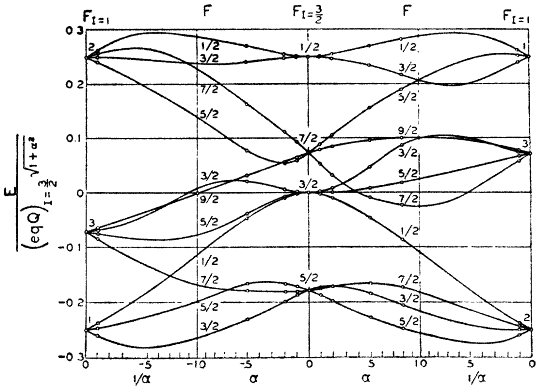

FIG. 1. Energies E resulting from quadrupole coupling of two nuclei of spin 1 and $\frac{3}{2}$, when $J=2$. Parameter $\alpha=(eqQ)_{I=1}/(eqQ)_{I=3/2}$. Minus sign should be placed in front of eqQ.

$S(I_1JF_1|I_1J'F_1')S(I_2F_1F|I_2F_1'F')$. If coupling of the two nuclei is not widely different, then true intensities cannot be found so directly, but a fair approximation to the intensities may be obtained by interpolating between the two extreme cases when coupling of the first nucleus is large compared to coupling of the second nucleus, and when it is small. Intensities for these extreme cases are thus proportional to

$$S(I_1JF_1|I_1J'F_1')S(I_2F_1F|I_2F_1'F')$$

and

$$S(I_2JF_2|I_2J'F_2')S(I_1F_2F|I_1F_2'F'),$$

respectively.

Exact intensities may, of course, be obtained in cases of intermediate coupling by making use of the energy values obtained by the method described above and solving equations of the type (12) for the $a(F_1)$. Relative intensity for a transition from state i to state j may then be written as

$$\Big|\sum_{F_1'}\sum_{F_1} a_i(F_1)a_j(F_1')\times S^{\frac{1}{2}}(I_1JF_1|I_1J'F_1')S^{\frac{1}{2}}(I_2F_1F|I_2F_1'F')\Big|^2.$$

Careful attention must be paid to the phases (see Condon and Shortley,[8] p. 277). This procedure would, however, be tedious and could in most cases be replaced by the more rapid method of the preceding paragraph.

EXAMPLES

As an illustration of the above theory for quadrupole coupling of two nuclei, the energy levels for the case $J=2$, $I_1=\frac{3}{2}$, $I_2=1$ are plotted in Fig. 1 as a function of the ratio of the quadrupole couplings of the two nuclei. This ratio,

$$\alpha=\left\{eQ\frac{\partial^2 V}{\partial z^2}\right\}_{I=1}\Big/\left\{eQ\frac{\partial^2 V}{\partial z^2}\right\}_{I=3/2}$$
$$=(eqQ)_{I=1}/(eqQ)_{I=3/2},$$

is plotted along the axis of abscissae, the function $(1+\alpha)/(1+\alpha^2)^{\frac{1}{2}}$ being plotted linearly for positive α and $(1-\alpha)/(1+\alpha^2)^{\frac{1}{2}}$ linearly for negative α. Energy is plotted along the ordinate axis, $E/[(-eqQ)_{I=3/2}(1+\alpha^2)^{\frac{1}{2}}]$ being plotted linearly. Such a plot produces smooth curves and allows α a range from $-\infty$ to $+\infty$. Values for $1/\alpha$ rather than α are marked off in the region where $|\alpha|>1$. The curves are very similar to those for electronic energy levels showing coupling type ranging from pure LS to pure JJ. Points at which energy values were computed are shown by small circles; the solid curves were drawn to pass smoothly through all computed points. In the center of the figure the energy levels converge to those that would be obtained for the coupling of a single nucleus of spin $\frac{3}{2}$ to a rotational momentum 2, giving the various values of the sum of these two indicated by $F_{I=3/2}$. On the two edges, the levels converge to the proper values for positive and negative coupling of the nucleus of spin 1 with the rotational momentum

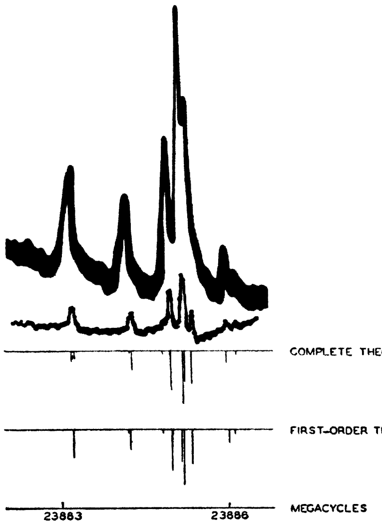

FIG. 2. Comparison of portion of observed spectrum of $Cl^{35}CN$ with first-order and complete theories.

2 to give a sum $F_{I=1}$. Between these three points, the levels split and are designated by the total angular-momentum quantum number F resulting from the sum of J and the spins of both nuclei. It may be seen that the first-order approximation to the complete theory, giving the initial slope of each energy level, is fairly accurate for $|\alpha| < 0.1$ or $|1/\alpha| < 0.1$, but that in intermediate ranges the first-order approximation gives little indication of the behavior of the energy levels.

Rotational transitions for BrCN ($J=2\rightarrow3$) and ClCN ($J=1\rightarrow2$) have been observed in the microwave region[6] and show in each case quadrupole effects resulting from two nuclei, N^{14} and the halogen. The above theory is found to fit the observed spectra well, with a value for $\alpha = (eqQ)_{N^{14}}/(eqQ)_{\text{Halogen}}$ about equal to 0.005 for BrCN and 0.05 for ClCN. In these cases the first-order approximation to the theory is rather good, although in the case of ClCN a deviation from the first-order theory can be seen which is explained by the complete theory. The rotational line $J=1\rightarrow2$ for ClCN lies at about 23,885 megacycles, and the line is split by the Cl quadrupole into a number of components with separations between 2 and 30 megacycles. Each of these lines is further split into several components separated by one megacycle or less because of the N^{14} quadrupole. Figure 2 shows the comparison between theoretically expected splitting and plots of a portion of the $Cl^{35}CN$ spectrum as produced on the oscilloscope of the detecting apparatus. The upper experimental spectrum is at a pressure of about 10^{-3} mm Hg, while the lower one is at a somewhat lower pressure. In the latter case this produced narrower lines, but with considerably reduced intensity because of saturation effects.[13] As may be seen, the first-order effects account for the main features of the spectrum, but deviations of about 50 kilocycles from the first-order theory can be observed which are explained by the complete theory. These deviations are best seen in the separations of the three strong lines in the center of the spectrum, and in the distance between the two weak lines at the high frequency end of the spectrum.

Experimental details and further experimental results will be presented in a later paper.

---

[13] C. H. Townes, Phys. Rev. **70**, 665 (1946).