The Interaction of Nuclear Electric Quadrupole Moments with Molecular Rotation in Asymmetric Top Molecules. II. Approximate Methods for First-Order Coupling

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An expression is developed for the rotational dependence of $\langle \partial^2 V/\partial z^2 \rangle_{Av}$ for asymmetric top molecules. The expression is valid for all rotational energy levels, and requires only a knowledge of the reduced energy spectrum as a function of asymmetry of the rotor.

The application of three distinct methods of approximating the energy of the asymmetric rotor to the expression for $\langle \partial^2 V/\partial z^2 \rangle_{Av}$ is described. This permits the calculation of quadrupolar interactions for certain rotational states (in particular, those of high J) for which energies have not yet been tabulated.

The expressions which are derived will usually prove to be at least as accurate as the first-order approximation to the quadrupolar interaction, in which $\langle \partial^2 V/\partial z^2 \rangle_{Av}$ is involved.

I. INTRODUCTION

IN the first paper of this series,[1] hereinafter referred to as I, the general theory of nuclear quadrupole coupling in asymmetric top molecules was outlined. The only part of the first-order problem which differs significantly from previous treatments for linear molecules[2] and symmetric top molecules[3] is the evaluation of the rotational dependence of $\langle \partial^2 V/\partial z^2 \rangle_{Av}$. In this quantity V is the electrostatic potential at the quadrupolar nucleus, z is a space-fixed axis, and the average is taken in the representation which diagonalizes the rotational energy of the molecule in question. In I, two expressions were given for $\langle \partial^2 V/\partial z^2 \rangle_{Av}$ in asymmetric top problems; one, Eq. (8), makes use of published line strengths of pure rotation transitions[4] of the asymmetric rotor for $J \leq 12$, and the other, Eq. (10), involves explicity the coefficients of the transformation from a symmetric rotor basis to one which diagonalizes the energy of the rotor in question.

It is the purpose of the present work to provide an expression which is applicable for all J, the use of which involves little labor.* The method is based on a suggestion of J. H. Van Vleck, and its essential result is that the dependence upon rotational state of the quadrupole coupling can, to first order, be obtained from a knowledge of the reduced energy spectrum of the asymmetric rotor as a function of the asymmetry of the rotor.

Tables of the reduced energies for $J \leq 10$ have been published:[5] the method is extended to all J in the regions of asymmetry for which certain approximations to the reduced energies have been developed.[6-8]

II. GENERAL DEVELOPMENT OF THE METHOD

It may be verified by reference to Eq. (10) of I that $\langle \partial^2 V/\partial z^2 \rangle_{Av}$ may be expressed in terms of the average values of the angular momentum operators $\mathbf{P}_a$, $\mathbf{P}_b$, and $\mathbf{P}_c$ about the principal axis of inertia, a, b, and c. As is customary, a, b, and c are chosen so that the moments of inertia satisfy $I_a \leq I_b \leq I_c$. Matrices of these operators are given, for example, in reference 5 (see Eq. (6)).

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[2] J. M. P. Kellogg, I. I. Rabi, N. F. Ramsey, Jr., and J. R. Zacharias, Phys. Rev. **57**, 677 (1940); J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).
[3] B. P. Dailey, R. L. Kyhl, M. W. P. Strandberg, J. H. Van Vleck, and E. B. Wilson, Jr., Phys. Rev. **70**, 984 (1946); D. K. Coles and W. E. Good, Phys. Rev. **70**, 979 (1946).
[4] P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. **12**, 219 (1944).

* A method applicable to slightly asymmetric tops has been described by Knight and Feld, Phys. Rev. **74**, 354 (1948).

[5] G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. **11**, 27 (1943).
[6] G. W. King, J. Chem. Phys. **15**, 820 (1947).
[7] S. Golden, J. Chem. Phys. **16**, 78 (1948).
[8] S. Golden and J. K. Bragg, to be published.

TABLE I.*

quantity \ representation	I^r	I^l	III^r	III^l
F	$\frac{1}{2}(\kappa-1)$	$\frac{1}{2}(\kappa-1)$	$\frac{1}{2}(\kappa+1)$	$\frac{1}{2}(\kappa+1)$
$G-F$	$-\frac{1}{2}(\kappa-3)$	$-\frac{1}{2}(\kappa-3)$	$-\frac{1}{2}(\kappa+3)$	$-\frac{1}{2}(\kappa+3)$
$H/(G-F)$	$(\kappa+1)/(\kappa-3)$	$(\kappa+1)/(3-\kappa)$	$(1-\kappa)/(\kappa+3)$	$(\kappa-1)/(\kappa+3)$
$(d/d\kappa)[H/(G-F)]$	$-4/(\kappa-3)^2$	$4/(\kappa-3)^2$	$-4/(\kappa+3)^2$	$4/(\kappa+3)^2$

* This table has been derived from Table III of reference 5. The various representations are identified in Table II of that paper.

The expression is:

$$\langle \partial^2 V/\partial z^2\rangle_{Av} = A\langle \mathbf{P}_a^2\rangle + B\langle \mathbf{P}_b^2\rangle + C\langle \mathbf{P}_c^2\rangle. \quad (1)$$

The angular brackets indicate an average taken in the basis in which the energy of the rotor is diagonal. A, B, and C are the aa, bb, and cc components of the dyadic $\nabla\mathbf{E}$, multiplied by $2/(J+1)(2J+3)$.

Equation (1) makes possible the expression of $\langle \partial^2 V/\partial z^2\rangle_{Av}$ in terms of the energy and one of the quantities $\langle \mathbf{P}_i^2\rangle$ alone. The energy of the rotor is given by:

$$E = a\langle \mathbf{P}_a^2\rangle + b\langle \mathbf{P}_b^2\rangle + c\langle \mathbf{P}_c^2\rangle; \quad (2)$$

in this equation the averages are indicated only for comparison with (1). a, b, and c are the rotational constants $\hbar^2/2I_a$, $\hbar^2/2I_b$, and $\hbar^2/2I_c$.

Using the relation $\langle \mathbf{P}_a^2\rangle + \langle \mathbf{P}_b^2\rangle + \langle \mathbf{P}_c^2\rangle = J(J+1)$ and substituting Eq. (2), one may write for Eq. (1),

$$\begin{aligned}\langle \partial^2 V/\partial z^2\rangle_{Av} = {} & [(B-A)/(b-a)]E \\ & + [[A(b-a)-a(B-A)]/(b-a)] \\ & \times J(J+1) + [[(C-A)(b-a) \\ & - (c-a)(B-A)]/(b-a)]\langle \mathbf{P}_c^2\rangle. \quad (3)\end{aligned}$$

The quantity $\langle \mathbf{P}_c^2\rangle$ may be set equal to $(\partial E/\partial c)$;[9] this relation is justified in the appendix. The energy may be expressed as[5]

$$E = [(a+c)/2]J(J+1) + [(a-c)/2]E_\tau^J(\kappa), \quad (4)$$

leading to:

$$\begin{aligned}\langle \mathbf{P}_c^2\rangle = {} & (1/2)J(J+1) - (1/2)E(\kappa) \\ & + [(a-c)/2](\partial E(\kappa)/\partial c). \quad (5)\end{aligned}$$

$E(\kappa)$ is the reduced energy of the rotor; κ is Ray's asymmetry parameter, defined by

$$\kappa = (2b-a-c)/(a-c).$$

Equation (5) may thus be rewritten as

$$\begin{aligned}\langle \mathbf{P}_c^2\rangle = {} & (1/2)J(J+1) - (1/2)E(\kappa) \\ & + (1/2)(\kappa-1)(\partial E(\kappa)/\partial\kappa). \quad (6)\end{aligned}$$

Substitution of (4) and (6) into (3), and simplification, leads to:

$$\begin{aligned}\langle \partial^2 V/\partial z^2\rangle_{Av} = {} & (A/2)[J(J+1) + E(\kappa) \\ & - (\kappa+1)(\partial E(\kappa)/\partial\kappa)] + B(\partial E(\kappa)/\partial\kappa) \\ & + (C/2)[J(J+1) - E(\kappa) \\ & + (\kappa-1)(\partial E(\kappa)/\partial\kappa)]. \quad (7)\end{aligned}$$

Equation (7) may be obtained in a variety of forms by use of the relation $A+B+C=0$, stemming from $\nabla^2 V = 0$. In particular, one of the parameters A, B, C may be eliminated.

The problem thus reduces to that of determining $E(\kappa)$ and $(\partial E(\kappa)/\partial\kappa)$. The accuracy with which these quantities may be calculated by present methods determines, therefore, the accuracy with which $\langle \partial^2 V/\partial z^2\rangle_{Av}$ may be evaluated. For $J \leq 10$, Eq. (7), together with the reduced energy tables of reference (5), should prove more accurate, in most cases, than Eq. (8) of I.

In the following section the use of approximation methods will be discussed.

III. APPROXIMATION METHODS[10]

In this section equations for $E(\kappa)$ and $(\partial E(\kappa)/\partial\kappa)$ will be given, as derived from the approximation methods of references 6, 7, and 8. The range of applicability of each is indicated. The accuracy of the results is at least what is warranted by the first-order nature of the quadrupole calculation involving $\langle \partial^2 V/\partial z^2\rangle_{Av}$ and

[9] This substitution, suggested by J. H. Van Vleck, is also applicable to the determination of the proportionality factor arising in electron spin multiplets in polyatomic molecules. (R. S. Henderson and J. H. Van Vleck, Phys. Rev. 74, 106 (1948).) This application will be discussed by Henderson in a forthcoming publication.

[10] Since the space required to summarize the three distinct approximation methods to asymmetric rotor energies here used would be prohibitive, a familiarity with the notation and results of these methods will be assumed.

by present precision in measurements of quadrupole effects of asymmetric rotors.

A. The Mathieu Function Approximation

This method is applicable for those levels whose energies are lowest for a given J (near-prolate rotor) or highest (near-oblate rotor). The computation of $E(\kappa)$ is described in detail in reference (7). A first approximation to the reduced energies is given by

$$E(\kappa)=FJ(J+1)+(G-F)\alpha, \tag{8}$$

where α is the characteristic value of Mathieu's equation appropriate to the level and value of κ in question, and F and $G-F$ are constants which depend on κ in a manner determined by the way in which a, b, and c are identified with molecule-fixed cartesian axes x', y', z'. Then:

$$\partial E(\kappa)/\partial\kappa=(dF/d\kappa)J(J+1)+(d(G-F)/d\kappa)\alpha +(G-F)(\partial\alpha/\partial\kappa). \tag{9}$$

By reference to Table I, which gives H, $G-F$, $H/(G-F)$, and $(d/d\kappa)[H/(G-F)]$ for the pertinent ways of assigning a, b, c to x', y', z', it may be seen that $dF/d\kappa=\frac{1}{2}$ and $d(G-F)/d\kappa=-\frac{1}{2}$ regardless of axis choice. Furthermore, one has $(\partial\alpha/\partial\kappa)=(\partial\alpha/\partial\theta)(d\theta/d\kappa)$, where θ is the constant appearing in Mathieu's equation:

$$(d^2y/dx^2)+(\alpha-2\theta\cos 2x)y=0,$$

given, for this approximation method, closely enough by

$$\theta=[H/(G-F)][J(J+1)/2]. \tag{10}$$

Equation (9) becomes, finally,

$$\partial E(\kappa)/\partial\kappa=\tfrac{1}{2}[J(J+1)-\alpha+(G-F)J(J+1) \times(\partial\alpha/\partial\theta)(d/d\kappa)[H/(G-F)]]. \tag{11}$$

In order to use this method, one determines θ from Eq. (10) and Table I. From tables of characteristic values of Mathieu's equation,[11] α and an approximate value of $\partial\alpha/\partial\theta$ may be obtained. $E(\kappa)$ and $\partial E(\kappa)/\partial\kappa$ may then be computed, and inserted in Eq. (7).

It is wise, in using Eq. (8) for $E(\kappa)$, to investigate whether sufficient accuracy is attained. First- and second-order corrections are tabulated in reference (7), and may be used if necessary. The value of $\partial E(\kappa)/\partial\kappa$ given by Eq. (11) should be sufficiently accurate for the present purpose without inclusion of these corrections.

B. The "Harmonic Oscillator Approximation"

This method, and the one to follow, the "correspondence principle" approach, are valid for those energy levels which are essentially degenerate in the sign of the limiting symmetric rotor quantum number K; i.e., those levels which are highest for a given J (near-prolate rotor) or lowest (near-oblate rotor). The present method yields an explicit expression for both $E(\kappa)$ and $\partial E(\kappa)/\partial\kappa$, which is, however, rather cumbersome, whereas the correspondence principle approach involves tabulated quantities from which computations are easily made. Therefore, each method should prove useful in certain cases.

The reduced energy $E(\kappa)$ is, up to and including first-order terms (see reference 8),

$$E_\tau{}^J(\kappa)=FJ(J+1)+(G-F)E'_\tau{}^J(\kappa)$$

where

$$E'_\tau{}^J(\kappa)=(J+\tfrac{1}{2})^2+(m+\tfrac{1}{2})^2-2J(m+\tfrac{1}{2})W -(6\beta/W^2)[\beta-\beta'(1+(1/2J))] \times(m^2+m+\tfrac{1}{2}). \tag{12}$$

Here $m=J-K_{-1}$ for a type I representation, $m=J-K_1$ for a type III representation, and K_{-1} and K_1 refer to the limiting K of the prolate and oblate symmetric tops, respectively. Also

$$W=[(1+(1/2J))^2-4\beta^2]^{\frac{1}{2}};$$
$$\beta=(1/2)[H/(G-F)][1+(1/2J) -(1/32J^2)+(1/64J^3)];$$
$$\beta'=(1/2)[H/(G-F)][1+(1/32J^2)].$$

The expressions for F, $G-F$, etc., in terms of κ are those of Table I. With sufficient accuracy for the present purpose,

$$\beta[\beta-\beta'[1+(1/2J)]]\cong-[1/64J^2][H/(G-F)]^2,$$

and

$$W\cong[1+(1/2J)][1-\tfrac{1}{2}[H/(G-F)]^2].$$

[11] *Tables of Characteristic Values of Mathieu's Differential Equation*, a report prepared for the Applied Mathematics Panel, NDRC, by the Mathematical Tables Project, National Bureau of Standards, AMP report 165.1R. In these tables certain differences in notation occur: the characteristic values b are given in terms of a parameter s; these are related to α and θ by $\theta=\frac{1}{4}s$ and $\alpha=b-\frac{1}{2}s$. Therefore, $\partial\alpha/\partial\theta=4(\partial b/\partial s)-2$.

Then

$$\partial E(\kappa)/\partial\kappa \cong \tfrac{1}{2}[J(J+1)-E'(\kappa)] + (2J+1)(m+\tfrac{1}{2})H(d/d\kappa)(H/(G-F)) + \frac{3(m^2+m+(1/2))H[(d/d\kappa)(H/(G-F))]}{16J^2(1+(1/2J))^2(1-[H/(G-F)]^2)^2}. \quad (13)$$

The results of Eqs. (12) and (13) are to be substituted in Eq. (7).

C. The Correspondence Principle Approximation

The result of reference (6) of primary interest in the present work is the tabulation (Table I) of a "reduced energy ratio," η, as a function of a quantum number ratio λ, and κ. η and λ are defined by

$$\eta(\kappa)_{J,K}=E(\kappa)_{J,K}/J(J+1), \quad \lambda=K/[J(J+1)]^{\frac{1}{2}}.$$

K here is the limiting (prolate or oblate) symmetric top quantum number. $\eta(\kappa)$ and $\partial\eta(\kappa)/\partial\kappa$ can be taken from the table, and

$$\partial E(\kappa)/\partial\kappa = J(J+1)[\partial\eta(\kappa)/\partial\kappa]. \quad (14)$$

The derivative $\partial\eta(\kappa)/\partial\kappa$ is evaluated for constant λ, and must not be confused with the derivative $\partial\eta/\partial\lambda$ which is given, together with η, in the table.

APPENDIX

Let

$$\mathbf{H}_0 = a\mathbf{P}_a^2+b\mathbf{P}_b^2+c\mathbf{P}_c^2, \quad (15)$$

$$\mathbf{H}' = \delta c\mathbf{P}_c^2. \quad (16)$$

Then, if $E(a, b, c)$ is an eigenvalue of the unperturbed problem (15), and E' the first-order energy correction due to (16), $E'=\delta c\langle\mathbf{P}_c^2\rangle$, where the angular brackets denote an average over the (unperturbed) eigenstate corresponding to $E(a, b, c)$.

Let $E(a, b, c+\delta c)$ be the corresponding eigenvalue of the Hamiltonian,

$$\mathbf{H}=a\mathbf{P}_a^2+b\mathbf{P}_b^2+(c+\delta c)\mathbf{P}_c^2,$$

and define ϵ such that $E(a, b, c+\delta c)=E(a, b, c)+E'+\epsilon$. Then

$$\frac{\partial E(a, b, c)}{\partial c}=\lim_{\delta c\to 0}\frac{E'+\epsilon}{\delta c},$$

but $\epsilon=0(\delta c^2)$, so $\partial E(a, b, c)/\partial c=\langle\mathbf{P}_c^2\rangle$.

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On the Space Distribution of Slow Neutrons

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The behavior of the neutron density about a plane- or point-source of fast neutrons within a homogeneous slowing-down medium has been re-investigated. For the case of constant mean free path a known analytical expression for the neutron density has been reduced to a form, which is valid for slow neutrons and *for any distance* from the source. The feasibility of a numerical evaluation of the formula is demonstrated for $M=1$ (hydrogen). In particular, the asymptotic behavior at very large distances has been studied. For the more realistic example of a medium in which the mean free path decreases with decreasing energy of the neutrons, formulae are presented describing the asymptotic density and the asymptotic energy spectrum at large distances from the source.

1. INTRODUCTION

THE present paper is an extension, in two directions, of previous work[1] on the transport equation for the diffusion and slowing-down of neutrons about a point source in an infinite homogeneous medium. First, the formal solution for the case of constant mean free path has been reduced to a numerically manageable form for sufficiently slow neutrons at all distances from the source. Secondly, for the case of a mean free path that decreases as the energy of the neutrons decreases, an asymptotic formula valid at large distances from the source has been derived.

A partial result for the first case, namely the asymptotic form of the constant-mean-free-path solution at very large distances was communi-

[1] M. Verde and G. C. Wick, Phys. Rev. **71**, 852 (1947), henceforward referred to as "A."