A COMPLETE SECOND-ORDER PERTURBATION CALCULATION OF THE QUADRUPOLE HYPERFINE STRUCTURE OF THE ROTATIONAL SPECTRUM OF ETHYL BROMIDE

Thesis for the Degree of M. S.

MICHIGAN STATE UNIVERSITY

Paul Francis Dougher

1964

ABSTRACT

A COMPLETE SECOND-ORDER PERTURBATION CALCULATION OF THE QUADRUPOLE HYPERFINE STRUCTURE OF THE ROTATIONAL SPECTRUM OF ETHYL BROMIDE

by Paul Francis Dougher

A procedure is described for a complete second-order perturbation calculation of the quadrupole hyperfine structure in the pure-rotational spectrum of an asymmetric molecule. Characteristics are summarized and equations are given for the matrices of the products of direction cosines required in the theory. Short tables ($J \leq 6$) of the numerical values of the functions needed are also given.

The theory is applied to the spectra of the ^{79}Br and ^{81}Br isotopes of CH_3CH_2Br, $CH_3{}^{13}CH_2Br$, $^{13}CH_3CH_2Br$, CD_3CH_2Br and CH_3CD_2Br using the experimental data of Pierce and Flanagan (J. Chem. Phys. 38, 2963 (1963)). The quadrupole parameters were reevaluated and are reported. An extension to a partial third-order perturbation treatment was found necessary to predict the experimental spectra of the ^{79}Br and ^{81}Br species of CH_3CD_2Br.

The new quadrupole constants are used to show that the assumption of cylindrical charge distribution about the C-Br bond is most nearly the approximation to the experimental case.

A COMPLETE SECOND-ORDER PERTURBATION CALCULATION OF THE QUADRUPOLE HYPERFINE STRUCTURE OF THE ROTATIONAL SPECTRUM OF ETHYL BROMIDE

By

Paul Francis Dougher

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Master of Science

Department of Chemistry

1964

To my parents

and grandparents

ACKNOWLEDGMENTS

I wish to tender great appreciation to Professor R. H. Schwendeman for the kind and fruitful guidance in the assimilation of this thesis.

I also wish to thank Mr. James H. Hand for his discussions of the computer programs used.

I wish to thank the Petroleum Research Fund of the American Chemical Society for partial support of the research.

TABLE OF CONTENTS

		Page
I.	HISTORICAL BACKGROUND	1
II.	THEORY OF QUADRUPOLE INTERACTION	3
	2.1 Introduction	3
	2.2 Causality and Effect of Nuclear Quadrupole Interaction	4
	2.3 Rotational and Asymmetry Dependence of $\langle \partial^2 V/\partial z_J^2 \rangle_{AV}$	12
	2.4 First-order Quadrupole Perturbation	16
	2.5 Second-order Quadrupole Perturbation	19
	2.6 Summary	21
III.	APPLICATION OF NUCLEAR ELECTRIC QUADRUPOLE INTERACTION OF ETHYL BROMIDE	22
	3.1 Introduction	22
	3.2 Analysis of the Spectra in Terms of Rotational and Quadrupole Parameters	24
	3.3 Extension to Partial Third-order Perturbation.	28
	3.4 Summary	29
REFERENCES	. . . . .	40
APPENDIX	. . . . .	42

LIST OF TABLES

Table		Page
I.	Rotational Parameters of the Ethyl Bromide Species . .	31
II.	Quadrupole Coupling Constants	32
IIIa-e.	Observed and Calculated Frequencies (Mc) of Ethyl Bromide	33–> 36
IIIf.	Third-order Corrections to the Calculated Spectra of $CH_3CD_2{}^{79}Br$ and $CH_3CD_2{}^{81}Br$..	37
IV.	Experimental and Calculated Hypothetical Unsplit Frequencies of the Ehtyl Bromide Species	38
V.	Transformation Angles Derived from Quadrupole Theory and Experimentation	39

I. HISTORICAL BACKGROUND

Prior to 1945, nuclear quadrupole investigations were limited to the atomic level optical spectra (1) and to molecular beam radio-frequency spectra of diatomic molecules (2). Unfortunately, only the latter method provided the necessary precision to investigate, with accuracy, nuclear moments of atoms. The declassification and sale of governmental electronic systems after the Second World War led to a tremendous output of research literature in the fields of radio frequency atomic and molecular experimentation and theory. Microwave spectroscopy, a child of radar electronics, allowed unprecedented accuracy in the determinations of molecular structures and parameters. Because of the high resolution inherent in microwave spectroscopy, Good (3), in 1946, discovered a nuclear quadrupole effect in the inversion spectra of $^{14}NH_3$. The effect appeared as a group of weak symmetrical satellites bracketing a strong absorbtion line. This spectrum was studied more thoroughly in the same year by Dailey, Kyhl, Strandberg, Van Vleck and Wilson (4).

The initial theoretical discourse on quadrupole interaction was given in the classic work by Casimir (5). As the experimental techniques allowed the analysis of more complex systems, the theory was extended to cover linear molecules by Nordsieck (6) and by Feld and Lamb (7), symmetric-top molecules by Coles and Good (8) and by Van Vleck (9). It was this later extension of the theory which was used to account for the hyperfine spectra of $^{14}NH_3$.

In 1948, quadrupole interaction was extended to include asymmetric rotors by Bragg (10) and by Knight and Feld (11). The unsymmetrical nature of the systems which could now be investigated allowed for a greater extension into the theory of molecular structure and electronic cloud distributions.

II. THEORY OF QUADRUPOLE INTERACTION

2.1 Introduction

As the definition of a species further removes the multiplicity or degeneracy of a genus and allows a fuller exploration of the particular object under discussion, so the hyperfine structure perturbing the pure rotational levels yields more information concerning the nuclear and electronic composition of a molecule than pure rotational spectra. This thesis is particularly concerned with but one of the many forms of hyperfine structure, that arising from electric quadrupole interaction. It neglects those which do not generally contribute to molecules, as magnetic hyperfine structure; or those which are not easily measurable and are called "isotope effects".

Magnetic hyperfine interaction is usually neglected because most molecules have spin-paired electrons and are therefore in a $^1\Sigma$ ground state. A few molecules such as NO and ClO_2, which have large molecular megnetic movements due to unpaired electrons, do exhibit extensive magnetic hyperfine structure which greatly overshadows the nuclear quadrupole interactions. The "isotope effects", which are measured as small shifts of the spectra due to a finite nuclear mass and the discontinuity of the electron density within the nuclear radius, are extremely small and may be noticeable only by comparing various isotopic species, hence the name of this effect. This thesis is concerned uniquely with the removal of the $2I+1$ degeneracy by the nuclear quadrupole interaction and the aforementioned effects are neglected in the treatment.

2.2 Causality and Effect of Nuclear Quadrupole Interaction

Nuclear moment theory is based upon several experimentally provable, but not theoretically derivable statements. Nuclei with an odd mass number, (i.e. the sum of the number of protons and neutrons is odd), have half-integral spin values and obey Fermi statistics. Nuclei with an even mass number have integral units of $\hbar$* for their spin values and obey Bose statistical theory. The spin of the nucleus, I, is then defined as the maximum component of the quantum-mechanical vector $\vec{I}$, a dimensionless vector related proportionally to the spin angular momentum of the nucleus. It will be apparent below that nuclei with spins of zero or 1/2 do not exhibit nuclear quadrupole spectra. Hence the discussion will be restricted to nuclei of spin greater than 1/2.

Nuclear quadrupole energy arises out of the interaction of the spin property of the nucleus with all of the external charge distribution. This particular treatment is based on the premise that there is only one nucleus in the system which has a spin greater than 1/2, or as assumed in Section 3, the interaction with other nuclei with spins greater than 1/2 is so weak as to be neglected. Therefore the only extra-nuclear charge distribution is that of the electrons surrounding the nuclei, and point charges at the nuclear placement.

The theoretical discussion leading to nuclear quadrupole interaction is based on the well known theory of electrostatic interaction of a charge distribution with another surrounding charge distribution.

---

* $\hbar = h/2\pi$ where h = Planck's Constant, 6.6252×10^{-27} erg-sec.
$\hbar = 1.0544 \times 10^{-27}$ erg-sec.

This classical treatment of electrostatic interaction, discussed in terms of multipole expansion potential theory, is given below with the thought of deriving a "good" quantum-mechanical Hamiltonian for a nuclear quadrupole interaction. The discussion follows that given by Ramsey (13).

By fixing an axis system at the mass center of a nucleus of charge density $\rho_n(\vec{r}_n)$, the interaction between a volume element, $d\tau_n$ of the nuclear distribution at a distance, $\vec{r}_n$, from the axis center and a volume element, $d\tau_e$ of the external charge distribution at a distance, $\vec{r}_e$, from the axis center may be written as:

$$\mathcal{H}_{el} = \int_{\tau_e}\int_{\tau_n} \frac{\rho_e(\vec{r}_e)\,\rho_n(\vec{r}_n)\,d\tau_e\,d\tau_n}{R} \qquad (2\text{-}1)$$

where $\mathcal{H}_{el}$ is the contribution to the potential energy of a molecule from electrostatic interaction. It may be more easily viewed as the average of all the interactions between two points defined by the volume elements $d\tau_e$ and $d\tau_n$ separated by a distance R. To calculate $\mathcal{H}_{el}$ R is written as a function of the two measurable vectors $\vec{r}_e$ and $\vec{r}_n$. Therefore from the simple trigonometric cosine law:

$$\frac{1}{R} = \frac{1}{\sqrt{r_e^2 + r_n^2 - 2r_e r_n \cos\theta_{en}}} \qquad (2\text{-}2)$$

θ_{en} = angle between the two vectors $\vec{r}_e$ and $\vec{r}_n$.

The solution is, however, not soluble unless an assumption is made that r_e is always greater than r_n, that is, the electrons are never allowed to exist inside the nucleus. As mentioned before, this discontinuity of the wave functions at the nuclear position yields a very

small but measurable "isotopic effect". Assuming then that $r_n < r_e$, equation (2-2) may be rewritten and expanded in a power series in r_n/r_e (12) by the use of the MacLaurin series expansion,

$$(1 - 2xy + y^2)^{-1/2} = \sum_{\ell=0}^{\infty} P_\ell(x) y^\ell. \tag{2-3}$$

In this equation the $P_\ell(x)$ are Legendre polynomials of order ℓ. Rewriting equation (2-2) as:

$$\frac{1}{R} = \frac{1}{r_e}\left[1 + \left(\frac{r_n}{r_e}\right)^2 - 2\left(\frac{r_n}{r_e}\right)\cos\theta_{en}\right]^{-1/2}, \tag{2-4}$$

and expanding using equation (2-3)

$$\frac{1}{R} = \frac{1}{r_e} \sum_{\ell=0}^{\infty} P_\ell(\cos\theta_{en})\left(\frac{r_n}{r_e}\right)^\ell. \tag{2-5}$$

Equation (2-5) has meaning, however, only when the series expression converges to a finite value. Since $|\cos\theta_{en}| \leq 1$, $P_\ell(\cos\theta_{en})$ has extreme limits of ± 1 and therefore $|P_\ell(\cos\theta_{en})| < 1$. Therefore the coefficients of $(r_n/r_e)^\ell$ are in absolute value never greater than one, and convergence will be assured if the value of $(r_n/r_e)^\ell$ is always less than 1. This can only occur if $r_n < r_e$, that is, when the extra-nuclear charge distribution is never allowed to permeate the nuclear charge distribution.

Expansion of equation (2-5) and substitution into equation (2-1) will now yield

$$\mathcal{H}_{el} = \iint \frac{\rho_e(\vec{r}_e)\rho_n(\vec{r}_n)}{r_e}\left[P_0(\cos\theta_{en})\left(\frac{r_n}{r_e}\right)^0 + P_1(\cos\theta_{en})\left(\frac{r_n}{r_e}\right) + P_2(\cos\theta_{en})\left(\frac{r_n}{r_e}\right)^2 + \cdots\right] d\tau_e d\tau_n. \tag{2-6}$$

The first few Legendre Polynomials are

$$P_0 (\cos \theta_{en}) = 1, \tag{2-7a}$$

$$P_1 (\cos \theta_{en}) = \cos \theta_{en}, \tag{2-7b}$$

$$P_2 (\cos \theta_{en}) = 1/2(3 \cos^2 \theta_{en} - 1). \tag{2-7c}$$

Substitution of equations (2-7a,b,c) into equation (2-6) now yields the form

$$\mathcal{H}_{el} = \iint \frac{\rho_e(\vec{r_e})\,\rho_n(\vec{r_n})}{r_e}\left[1 + \left(\frac{r_n}{r_e}\right)\cos\theta_{en} + \left(\frac{r_n}{r_e}\right)^2\left(\tfrac{3}{2}\cos^2\theta_{en} - \tfrac{1}{2}\right) + \ldots\right] d\tau_e d\tau_n. \tag{2-8}$$

The expansion is generated only to the third order Legendre Polynomial for reasons which will be evident later. Equation (2-8) is now written as a sum of integrals, and the individual components are discussed separately.

The first component of the sum in equation (2-8) is referred to as the monopole moment, i.e. the electrostatic energy at r_e due to the action of a point nuclear charge, $\rho_n(0)d\tau_n$, situated at the origin of the axis system.

$$\mathcal{H}_{el}^{\text{monopole}} = \iint \frac{\rho_e(\vec{r_e})\,\rho_n(\vec{r_n})}{r_e}\, d\tau_e d\tau_n \tag{2-9}$$

This monopole contribution is included in the normal atomic theory to make up the molecular electronic states. Since it is the same in both rotational states it will be neglected in this discussion.

The second term of the series is the dipole expression and represents energy due to the nuclear electric dipole moment. This condition arises due to a consideration of the parity operator which commutes with

the Hamiltonian of the nuclear system. The parity operator, acting on the functions for which ℓ is odd in equation (2-5), yields an inversion of coordinates system of the Hamiltonian. This inversion of the coordinates of the Legendre Polynomial cancels the contribution from the nuclear charge distribution and the integral vanishes. A more complete theoretical discussion of the restrictions on the orders of electrical multipoles may be found in reference (13). This reference also contains the proof that the requirement for the non-vanishing of the integral containing ℓ is $I \geq \frac{1}{2}$, and therefore, as previously mentioned, spins of zero or 1/2 do not exhibit nuclear quadrupole interaction (i.e. $\ell = 2$). The proof has been experimentally verified in that no nuclear electric dipole interaction has been observed.

The third and last term of the truncated expansion under the integral is the nuclear electric quadrupole addition to the energy of the molecule and is expressed as

$$\mathcal{H}_{\substack{\text{quadrupole} \\ \text{el}}} = \iint \frac{\rho_e(\vec{r}_e)\rho_n(\vec{r}_n)}{r_e} \left(\frac{r_n}{r_e}\right)^2 \left(\frac{3}{2}\cos^2\theta_{en} - \frac{1}{2}\right) d\tau_e d\tau_n. \quad (2\text{-}11)$$

All other terms of the expansion are deleted for one of two reasons:

1) The order of the expansion is odd, i.e. ℓ is odd, and for reasons mentioned above, they do not contribute to the nuclear electric interaction, or:

2) The even power terms have weak components as measured experimentally. Only the hexadecapole term, $\ell = 4$, has ever been measured. As mentioned before, I must be ≥ 2 to allow the hexadecapole term to enter into the Hamiltonian of the system.

The nuclear electric quadrupole term may now be rewritten in the

form given by Strandberg (16) in which the physical significance may be more easily seen. Noting that the vector product $(\vec{r}_n \cdot \vec{r}_e)^2 = r_n^2 r_e^2 \cos^2\theta_{en}$, the inner part of equation (2-11) is written:

$$\left(\frac{r_n}{r_e}\right)^2\left(\frac{3}{2}\cos^2\theta_{en} - \frac{1}{2}\right) = \frac{3(\vec{r}_n \cdot \vec{r}_e)^2 - r_n^2 r_e^2}{2r_e^5}$$

$$= \sum_F \sum_{F'} \frac{3F_n F_n' F_e F_e' - (F_n F_e)^2}{2r_e^5} \qquad (2\text{-}12)$$

where F_n = x,y,z components of $\vec{r}_n$

F_e = x,y,z components of $\vec{r}_e$.

Equation (2-12) may be further factored into two terms, one dependent on the nuclear coordinates and one dependent on the electronic coordinates:

$$(2\text{-}12) = \frac{1}{6r_e^5} \sum_F \sum_F (3F_n F_n' - \delta_{FF'} r_n^2)(3F_e F_e' - \delta_{FF'} r_e^2). \qquad (2\text{-}13)$$

$$\delta_{FF'} = 0, \; F \neq F'$$
$$= 1, \; F = F'.$$

The nuclear quadrupole Hamiltonian may now be written

$$\mathcal{H}_Q = \frac{1}{6} \sum_F \sum_{F'} V_{FF'} Q_{FF'} , \qquad (2\text{-}14)$$

where using a tensor definition,

$$V_{FF'} = \int_e \rho_e(\vec{r}_e) \frac{(3F_e F_e' - \delta_{FF'} r_e^2)}{r_e^5} d\tau_e, \qquad (2\text{-}15)$$

$$Q_{FF'} = \int_n \rho_n(\vec{r}_n)(3F_n F_n' - \delta_{FF'} r_n^2) d\tau_n. \qquad (2\text{-}16)$$

The tensor elements are simply the charge weighted quadrupole moments

of the nucleus. The term $V_{FF'}$ may be further simplified by noting that the values of the tensor are simply the second derivatives of the potential of all the extranuclear charges evaluated at the nucleus. Also utilizing a classical mechanical expression relating the potential to a force, equation (2-14) may be rewritten as

$$\mathcal{H}_Q = -\frac{1}{6} \sum_F \sum_{F'} Q_{FF'} (\nabla \vec{E})_{FF'}, \qquad (2\text{-}17)$$

where $(\nabla \vec{E})_{FF'}$ = electric field gradient tensor of the field evaluated at the nucleus.

A further appraisal of equations (2-15) and (2-16) will yield two very important properties of both $V_{FF'}$ and $Q_{FF'}$;

1) Since the components of a vector, either $\vec{r}_e$ or $\vec{r}_n$, commute among themselves, that is

$$FF' = F'F, \qquad (2\text{-}18)$$

both tensors are symmetric about the diagonal.

2) The traces of both tensors are equal to zero.

The most useful form of $\mathcal{H}_Q$ was first derived by Kellogg, Rabi, Ramsey, and Zacharias (2) using the methods of Casimir (5). This form was extended to include asymmetric tops by Bragg and Golden (10,14). It is derived by a lengthy procedure by first noting that $Q_{FF'}$ is a function of the nuclear spin-operator alone and that $(\overline{\nabla E})_{FF'}$ is a function of the rotational operator, only.

Thus the operator form of $Q_{FF'}$ is

$$Q_{FF'} = \frac{eQ}{I(2I-1)} \left[3 \frac{(\vec{I})_F (\vec{I})_{F'} + (\vec{I})_{F'} (\vec{I})_F}{2} - \delta_{FF'} \vec{I}^2\right], \qquad (2\text{-}19)$$

where

$$Q = \frac{1}{e} \int \rho_{n(m_I=I)} [3z_n^2 - r_n^2] d\tau_n = \langle 3z_n^2 - r_n^2 \rangle_{AV}$$

= nuclear quadrupole moment.

The operator form of $(\overrightarrow{\nabla E})_{FF'}$ is

$$(\overrightarrow{\nabla E})_{FF'} = - \frac{eq_J}{J(2J-1)} \left[3 \frac{(\vec{J})_F(\vec{J})_{F'} + (\vec{J})_{F'}(\vec{J})_F}{2} - \delta_{FF'}\vec{J}^2\right], \quad (2\text{-}20)$$

where

$$q_J = \frac{1}{e}\int \rho_{e(m_J=J)} \left[\frac{3z_e^2 - r_e^2}{r_e^5}\right] d\tau_e. \quad (2\text{-}22)$$

By rewriting equation (2-17) using the new forms written in equations (2-19) and 2-20) and using the usual commutation relations for angular momentum operators, an equation vividly showing the concept of $\vec{I}\cdot\vec{J}$ coupling may be written as

$$\mathcal{H}_Q = \frac{eq_JQ}{2I(2I-1)J(2J-1)}\left[3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}\vec{I}\cdot\vec{J} - \vec{I}^2\vec{J}^2\right]. \quad (2\text{-}22)$$

The quantity q_J may also be written as

$$q_J = \int \rho_{e(m_J=J)} \frac{(3\cos^2\theta - 1)}{r^3} d\tau_e = \langle \partial^2 V/\partial z_J^2 \rangle_{AV}. \quad (2\text{-}23)$$

Therefore the Hamiltonian for nuclear electric quadrupole interaction for a one-quadrupole system, (i.e. atom or molecule) may be written

$$\mathcal{H}_Q = \frac{eQ\langle \partial^2 V/\partial z^2 J\rangle_{AV}}{2I(2I-1)J(2J-1)}\left[3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - \vec{I}^2\vec{J}^2\right]. \quad (2\text{-}24)$$

The Hamiltonian of (2-24) is still not in the most useful form because the average value of $\partial^2 V/\partial z_J^2$ is with respect to an arbitrary space-fixed axis system. Because q_J changes with molecular rotation it is more convenient to express q_J with respect to a molecule-fixed axis system. This is discussed in Section 2.3 with relation to direction cosine matrix elements.

It is possible to discuss the eigenvalues of the operator

$[3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - \vec{I}^2\vec{J}^2]$, and hence the eigenvalues of $\mathcal{H}_Q$, without regard to either the rotational part of the problem or the form of the rest of the quadrupole Hamiltonian. This is possible because the operators in the brackets are dependent only on the magnitude of J and I. Casimir (5) determined the eigenvalues to be

$$\frac{3}{4}C(C + 1) - I(I + 1)J(J + 1), \qquad (2\text{-}25)$$

where $C = F(F + 1) - I(I + 1) - J(J + 1)$,

and $F = J + I, J + J - 1, \cdots, J - I$.

Here F is a new quantum number and is required because I is coupled to J and therefore only the total angular momentum is a constant of motion, i.e. a "good quantum number".

2.3 Rotational and Asymmetry Dependence of $\langle \partial^2 V/\partial z^2 J\rangle_{AV}$

Equation (2-24) is the general form used to describe the nuclear quadrupole interaction in one-quadrupole systems, but it is not the best form for describing rotating molecules because the term, q_J, is dependent upon the magnitude of J. It is possible to rewrite q_J in terms of a constant for all molecules times a function which is dependent on the asymmetry of the rotating molecule. This is accomplished by writing the $\langle \partial^2 V/\partial z^2 J\rangle_{AV}$ in terms of an axis system defined by the moments of inertia. The principal axes of inertia a,b,c, are defined in such a way that the moments of inertia are $I_a \leq I_b \leq I_c$. By writing $\langle \partial^2 V/\partial z_J^2\rangle$ in terms of the molecule-fixed axis system a transformation using direction cosines yields

$$\partial^2 V/\partial z_J^2 = \alpha_{za}^2(\partial^2 V/\partial a^2) + \alpha_{zb}^2(\partial^2 V/\partial b^2) + \alpha_{zc}^2(\partial^2 V/\partial c^2) +$$

$$2\alpha_{za}\alpha_{zb}(\partial^2 V/\partial a\partial b) + 2\alpha_{za}\alpha_{zc}(\partial^2 V/\partial a\partial c) + \qquad (2\text{-}26)$$

$$2\alpha_{zb}\alpha_{zc}(\partial^2 V/\partial b\,\partial c),$$

where α_{zi} = direction cosine between the z-space fixed axis and the "i" molecule fixed axis (i = a,b,c).

Before progressing further, a brief description of the rotational wave functions for asymmetric rigid rotators must be given. The Hamiltonian for the rigid asymmetric rotor may be written as

$$\mathcal{H}_r = h(AP_a^2 + BP_b^2 + CP_c^2) \qquad (2\text{-}27)$$

where

A, B, C = rotational constants, and

P_a, P_b, P_c = components of angular momentum in the inertial axis system of the molecule.

It is possible to introduce a basis set ψ_{JK} such that

$$P^2\psi_{JK} = (P_a^2 + P_b^2 + P_c^2)\,\psi_{JK} = J(J+1)\,\psi_{JK}$$

and

$$P_z\psi_{JK} = K\psi_{JK} \qquad K = J, J-1, \cdots, -J \qquad (2\text{-}28)$$

This basis set will yield the $\mathcal{H}_r$ matrix in diagonal block form, i.e., diagonal in J. Each of the diagonal blocks may be further factored into four independent submatrices by the Wang transformation (15). The Wang functions are symmetric and antisymmetric linear combinations of each $\psi_{J,|K|}$ and the corresponding $\psi_{J,-|K|}$. There now exists an orthogonal matrix which diagonalizes the energy matrix calculated using the Wang basis functions. That is, there exists a transforming matrix T such that

$$W_R = \tilde{T}\,\mathcal{H}_r\,T$$

where $\tilde{T}$ = transpose of T, and W_R = the diagonal matrix of the rigid rotor eigenvalues.

The transforming matrix T rotates the Wang linear combination of symmetric rotor functions into the asymmetric basis set in which the asymmetric rigid rotor Hamiltonian is diagonal. These transformed basis functions will be used and referred to throughout this thesis as the zeroth-order basis functions. Since I and J are coupled, requiring a new quantum number F to describe the state of a system, these basis functions must be combined with nuclear spin functions and the products transformed into a system which is an eigenfunction of an operator which is a function of F as well as J and I. This transformation leads to the matrix elements for $\mathcal{H}_Q$ given in equations (2-31 a,b,c). Only the elements diagonal in I are given since the extreme separation of nuclear energy states causes the elements off-diagonal in I to be negligible.

$$\langle F,J,\tau,M|\mathcal{H}_Q|F,J,\tau',M\rangle = \frac{eQ\,\langle J,\tau,M_J=J\,|\partial^2V/\partial Z_J^2|\,J,\tau',M_J=J\rangle}{8I(2I-1)J(2J-1)}$$

$$x[3C(C+1) - 4I(I+1)J(J+1)] \qquad (2\text{-}31a)$$

$$\langle F,J,\tau,M|\mathcal{H}_Q|F,J+1,\tau',M\rangle = \frac{eQ\,\langle J,\tau,M_J=J|\,\partial^2V/\partial Z_J^2|J+1,\tau',M_J=J\rangle}{8I(2I-1)J(2J+1)^{1/2}}$$

$$x[F(F+1) - I(I+1) - J(J+2)] \qquad (2\text{-}31b)$$

$$x[(I+J+F+2)(I-J+F)(J-I+F+1)(J+1-F+1)]^{1/2}$$

$$\langle F,J,\tau,M|\mathcal{H}_Q|F,J+2,\tau',M\rangle = \frac{eQ\,\langle J,\tau,M_J=J\,|\partial^2V/\partial Z_J^2|J+2,\tau',M_J=J\rangle}{16I(2I-1)[(2J+1)(J+1)]^{1/2}}$$

$$x[(I+J+F+2)(I+J+F+3)(I-J+F-1)(I-J+F)(J-I+F+1)$$

$$x(J-I+F+2)(I+J-F+1)(I+J-F+2)]^{1/2} \qquad (2\text{-}31c)$$

where

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

It is noted that the matrix elements of $\partial^2 V/\partial z_J^2$ need be evaluated only for $M_J = J$, since the matrix elements are diagonal in M_J. This is because the energy cannot depend on the projection of J(i.e. M_J) on an arbitrary direction in the space-fixed system.

As before, the problem reduces to the evaluation of $\partial^2 V/\partial z_J^2$ in terms of the inertial frame of reference, (i.e. the experimentally measureable axis system). The introduction of a new nomenclature allows the writing of equation (2-26) in the condensed form:

$$\partial^2 V/\partial z_J^2 = \sum_g \sum_{g'} \phi_{zg}\, \phi_{zg'}\, \partial^2 V/\partial g \partial g' \qquad (2\text{-}32)$$

where

g,g' = a,b,c, the inertial axis system.

Therefore, in the zeroth order representation, the transformed basis set in which the rotational energy is diagonal:

$$\partial^2 V/\partial z_J^2 = \sum_g \sum_{g'} \tilde{T}\ \phi_{zg}\, \phi_{zg'}\, T\, \partial^2 V/\partial g \partial g' \qquad (2\text{-}33)$$

It is known (17) that the direction cosines may be written as a product of three terms.

$$\phi_{Fg}(J,\tau,M_J;J',\tau',M_J') = \phi_{Fg}(J,J')\phi_{Fg}(J,M_J;J',M_J')\phi_{Fg}(J,\tau;J',\tau') \qquad (2\text{-}34)$$

F = x,y,z space-fixed axis.

g = a,b,c molecule fixed axis.

$J' = J,\ J \pm 1$

and as explained previously, when F = Z,M' = M = J. If now a function G(J',J") is defined as

$$G(J',J'') = \phi_{zg}(J',J'')\phi_{zg}(J',M=J;J'',M'=J), \qquad (2\text{-}35)$$

then

$$\phi_{zg}(J,\tau,M=J;J',\tau',M'=J) = G(J,J')\phi_{zg}(J,\tau;J'\tau') \qquad (2\text{-}36)$$

The possible values of G(J',J") required for later calculations are tabulated in Appendix A, as well as the products G(J,J')G(J',J") also required later.

The matrix elements of ϕ_{zg} are ordered according to the symmetry of the transformed rotational energy eigenfunctions, that is according to E^+, O^+, O^- and E^-, the indices corresponding to the symmetry of the Wang linear combinations. The arrangement of the matrices in this thesis is that used by Schwendeman (17,18) and is summarized in Table I and Figure 1 in the Appendix.

The matrix elements of $\partial^2 V/\partial z_J^2$ may now be written as

$$< J,\tau,M_J=J|\ \partial^2 V/\partial z_J^2|J',\tau',M_J'=J > = \sum_g \sum_{g'} \tilde{T} \sum_{J"} [G(J,J")G(J",J')$$

$$x \sum_{\tau"} \phi_{zg}(J,\tau;J",\tau")\phi_{zg'}(J",\tau";J',\tau')]T\ \partial^2 V/\partial g\,\partial g' \qquad (2\text{-}37)$$

Using the formulation of references 17 and 18, the direction cosine products will yield 108 individual products consisting of J|J, J|J+1, J|J+2 elements which are blocked by symmetry in terms of aa, bb, cc, ab, ac and bc products. Equations for the matrix elements of the 108 products and tables of the numbers required for their evaluation are given in Appendices A, B, C and D.

2.4 First-order Quadrupole Perturbation.

Using the equations defined in the previous section and the matrix elements given in the Appendix it is possible to evaluate the quadrupole interaction and its perturbing effect on the zeroth-order rigid rotor energy levels. This effect causes a small shift of the rigid

rotor energies and splits them into 2I+1 components. Since the quadrupole effect is very much smaller than the pure rotational effect, the Hamiltonian describing the quadrupole effect may be treated as a small perturbation and its expectation value taken over the zeroth-order wave functions, i.e. a first-order perturbation treatment may be used. Combining equations (2-31a) and the diagonal elements (i.e. g = g') of (2-37) the first-order quadrupole energy may be written:

$$W_Q^{(1)} = \langle F,J,\tau,M|\mathcal{H}_Q|F,J,\tau',M\rangle = eQ \times [f(I,J,J,F)]$$

$$\times \sum_g \langle J,\tau,M_J=J|\tilde{T}\,\phi_{zg}^{\,2}\,T|J,\tau,M_J=J\rangle\, \partial^2 V/\partial g^2 \qquad (2\text{-}38)$$

The f(I,J,J,F) are functions introduced by Casimir and are tabulated in Reference (19). They are related to the C(I,J,J',F) functions described in the Appendix. Bragg (14) makes use of the following expression for $\partial^2 V/\partial z_J^{\,2}$;

$$\langle J,\tau,M_J=J|\partial^2 V/\partial z_J^{\,2}|J,\tau,M_J=J\rangle = \frac{2}{(J+1)(2J+3)} \quad \frac{1}{2}\,\partial^2 V/\partial a^2[J(J+1)+E_\tau^J(\chi)$$

$$-(\chi+1)\frac{dE_\tau^J(\chi)}{d\chi}]+\frac{\partial^2 V}{\partial b^2}\frac{dE_\tau^J(\chi)}{d\chi}+\frac{1}{2}\frac{\partial^2 V}{\partial c^2}[J(J+1)-E_\tau^J(\chi)+(\chi-1)\frac{dE_\tau^J(\chi)}{d\chi}] \qquad (2\text{-}39)$$

where $E_\tau^J(\chi)$ = rigid asymmetric rotor energy levels, and

$\frac{dE_\tau^J(\chi)}{d\chi}$ = derivative of the energy with respect to the asymmetry parameter, χ.

Another useful form of writing equation (2-39) is written by first recognizing that

$$\frac{\partial W_r}{\partial A} = \frac{h}{2}[J(J+1)+E_\tau^J(\chi) - (\chi+1)\frac{dE_\tau^J(\chi)}{d\chi}]$$

$$\frac{\partial W_r}{\partial B} = h\frac{dE_\tau^J(\chi)}{d\chi} \qquad (2\text{-}40)$$

$$\frac{\partial W_r}{\partial C} = \frac{h}{2}[J(J+1) - E_\tau^J(\kappa) + (\kappa - 1)\frac{dE_\tau^J(\kappa)}{d\kappa}],$$

where W_r = rigid-rotor energy levels,

A,B,C = rotational constants.

Therefore

$$\langle J,\tau,M_J=J|\partial^2 V/\partial z_J^2|J,\tau,M_J=J\rangle = \frac{2}{h(2J+3)(J+1)}[\partial^2 W/\partial a^2 \frac{\partial W_r}{\partial A} + \partial^2 W/\partial b^2 \frac{\partial W_r}{\partial B} + \partial^2 W/\partial c^2 \frac{\partial W_r}{\partial C}] \quad (2\text{-}41)$$

By defining the quadrupole coupling constants

$$\chi_{gg} = eQ\ \partial^2 V/\partial g^2 = eQ\ q_{gg} \quad (2\text{-}42)$$

and the substituting (2-42) and (2-41) into (2-33), the first order quadrupole interaction energy expression in an easily computable form is given by

$$W_Q^{(1)} = [f(I,J,J,F)]\,[\chi_{aa} f_1(J,\kappa) + (\chi_{bb} - \chi_{cc})\, f_2(J,\kappa)] \quad (2\text{-}43)$$

where

$$f_1(J,\kappa) = \frac{2}{J(J+1)}\,(\partial W_r/\partial A - \tfrac{1}{2}\partial W_r/\partial B - \tfrac{1}{2}\,\partial W_r/\partial C)$$

$$f_2(J,\kappa) = \frac{2}{J(J+1)}\,(\partial W_r/\partial B - \partial W_r/\partial C)$$

Use has been made of the Laplace equation which is satisfied at the origin where the electronic charge is zero, such that

$$\sum_g \partial^2 V/\partial g^2 = 0.$$

At the present time it is also convenient to give another form of the first-order quadrupole energy which will be extremely useful in Section 3. By defining:

$$q_m = eQ\,\partial^2 V/\partial a^2 = \chi_{aa}$$

and (2-44)

$$\eta = (\partial^2 V/\partial b^2 - \partial^2 V/\partial c^2)/\partial^2 V/\partial a^2 = (\chi_{bb} - \chi_{cc})/\chi_{aa}$$

The first-order perturbation energy is written:

$$W_Q^{(1)} = \alpha q_m + \beta q_m \eta$$

where

$$\alpha = [f(I,J,J,F)]\, f_1(J,\chi)$$

and (2-46)

$$\beta = [f(I,J,J,F)]\, f_2(J,\chi)$$

2.5 Second-order Quadrupole Perturbation

Normally only the first-order quadrupole correction is needed to fit the observed spectra. However, under certain conditions it may be necessary to include higher-order perturbation to account for observed differences from the first-order predictions. The conditions listed below are given in terms of relative magnitudes, and therefore the real criterion for applying higher order perturbations is how well the lower order theory predicts the spectra. In general the second-order perturbation is applied under the conditions that

1) There must be a quadrupolar nucleus with spin $I \geq 1$.

2a) The quadrupole coupling constant is "large", and/or

2b) There exist near-degenerate rigid-rotor energy levels such that the denominator of the second-order expression, equation (2-47), becomes sufficiently small.

The general form of the second-order quadrupole contribution to a given level is given as

$$W_Q^{(2)}(F,J,\tau) = \sum_{J',\tau'} \frac{\langle F,J,\tau|\mathcal{H}_Q|F,J',\tau'\rangle^2}{W^0(F,J,\tau) - W^0(F,J',\tau')} \qquad (2\text{-}47)$$

where

$W^0(F,J,\tau)$ = the zeroth-order rotational energy levels, and

$\mathcal{H}_Q$ = Quadrupole Hamiltonian after it has been properly transformed by the same transformation which diagonalized the zeroth-order problem.

A convenient form for $\mathcal{H}_Q$ is

$$\mathcal{H}_Q = [C(I,J,J',F)]^{1/2}\left\{\mathcal{H}_{aa}\chi_{aa} + \mathcal{H}_{ab}\chi_{ab} + \mathcal{H}_{ac}\chi_{ac} + \mathcal{H}_{bc}\chi_{bc}\right\} \qquad (2\text{-}48)$$

where

$$\mathcal{H}_{aa} = \mathcal{H}_q + \eta\,\mathcal{H}_\eta,$$

$$\mathcal{H}_q = \phi_{za}^2 - (\phi_{zb}^2 + \phi_{zc}^2)/2,$$

$$\mathcal{H}_\eta = (\phi_{zb}^2 - \phi_{zc}^2)/2$$

$$\eta = (\chi_{bb} - \chi_{cc})/\chi_{aa}, \text{ and}$$

$$\mathcal{H}_{gg'} = 2\phi_{zg}\phi_{zg'} \quad (g \neq g')$$

Equations for the C(I,J,J',F) and tables of their numerical values are given in the Appendix.

Of primary importance, it is to be noted that the second-order contribution to a given level is calculated by summing over all possible J's and τ's for a given F value, as shown by equation (2-47). Since for the representation used (17,18), the various blocks -- aa, ab, ac, and bc -- are independent of each other they may be transformed separately and evaluated in any order desired.

Using the equations derived in Sections 2.3, 2.4 and 2.5 and the tabulated matrix elements given in the Appendix, a complete second-

order perturbation calculation may be made for any one-quadrupole molecular system.

2.6 Summary

The rotational energy of a one-quadrupole molecular system may be treated as a zeroth-order problem perturbed by a higher order quadrupole interaction term. The addition (or subtraction) of the extra energy due to the interaction of a spinning nucleus with the electrostatic potential of an unsymmetrical charge distribution splits the asymmetric rigid rotor energy into 2I+1 levels, or 2J+1 whichever is the smaller.

$$W_{total} = W_R + W_Q^{(1)} + W_Q^{(2)} \tag{2-49}$$

The orders of magnitude of the various energies are such that

$$W_R >>> W_Q^{(1)} >> W_Q^{(2)}$$

However, within the limit of accuracy of microwave spectroscopy, terms as high as the second-order terms are of great importance in the analysis of the experimental spectra. In the next section it will be shown that in fact a partial third-order analysis is required to account for descrepancies not accounted for by the second-order terms.

III. APPLICATION OF NUCLEAR ELECTRIC QUADRUPOLE INTERACTION TO ETHYL BROMIDE

3.1 Introduction

Ethyl bromide is an important example to utilize in the application of quadrupole analysis for many reasons.

1) Both ^{79}Br and ^{81}Br have large nuclear quadrupole moments, 0.33×10^{24} cm^2 and 0.28×10^{24} cm^2 respectively (19), thus insuring a rather large first and second-order quadrupole effect if other requirements are satisfied.

2) ^{79}Br and ^{81}Br have nuclear spins of 3/2 therefore allowing the quadrupole effect as mentioned in the discussion of the existence of multipole expansion in terms of nuclear spin included in Section II.

3) Accidental near degeneracy of rotational levels of $CH_3CD_2{}^{79}Br$ and $CH_3CD_2{}^{81}Br$ is the predominate reason for the large second-order splittings.

4) The primary purpose of using ethyl bromide is to evaluate the angle required to diagonalize the experimental quadrupole tensor and to compare this angle to those calculated using the two predominate methods of estimating the off-diagonal element. The two approximations are

a) By simply calculating the angle between the "a" inertial axis and the C-Br bond and using this angle to evaluate the χ_{ab} trial term, or

b) By assuming a cylindrical charge distribution about the C-Br bond and using the relations of cylindrical symmetry,

$$\left(\frac{\partial^2 V}{\partial x^2}\right)_{AV} = \left(\frac{\partial^2 V}{\partial y^2}\right)_{AV} = -\left(\frac{1}{2}\frac{\partial^2 V}{\partial z^2}\right)_{AV}$$

where by the symmetry of the system,

$$\left(\frac{\partial^2 V}{\partial z^2}\right)_{AV} = 2\left(\frac{\partial^2 V}{\partial c^2}\right)_{AV}$$

and since

$$\left(\frac{\partial^2 V}{\partial a^2}\right) = \left(\frac{\partial^2 V}{\partial z^2}\right)_{AV} \left(\frac{3\cos^2\theta - 1}{2}\right)_{AV}$$

then

$$\frac{\chi_{aa}}{\chi_{zz}} = -\frac{\chi_{aa}}{2\chi_{cc}} = \left(\frac{3\cos^2\theta - 1}{2}\right).$$

The predominant near degenerate pairs occur between the 1_{10} and 2_{02} levels, the 2_{11} and 3_{03} levels and the 3_{12} and 4_{04} levels. Therefore, as shown by equation (2-47), as the running sum is carried over the J states and connects any pair of these near degenerate levels; the denominator of the second-order correction becomes quite small yielding a large second-order term to both connected levels. This effect is so large in the $CH_3CD_2{}^{79}Br$ and $CH_3CD_2{}^{81}Br$ species that it becomes necessary to use a partial third-order perturbation correction to predict the experimental spectra. This is discussed more fully in the following section.

A microwave analysis of the parent species $CH_3CH_2{}^{79}Br$ and $CH_3CH_2{}^{81}Br$ had been attempted in 1957 by Wagner, Dailey and Solimene (20). They assigned several "a"-type (R-branch) transitions for the two species and were able to evaluate the B and C rotational constants, as well as the diagonal components of the quadrupole tensor in the principal inertial axis system. Certain transitions, however, were indicated as being poorly fit, and the discrepancies could not be removed by including second-order quadrupole corrections. This was later disproved by

Flanagan and Pierce (21), who showed the χ_{ab} terms connect states which are extremely dependent on the rotational constant A. Flanagan and Pierce succeeded not only in determining the A rotational constant but were also able to establish the off diagonal element, χ_{ab} of the quadrupole tensor for the ten independent isotopes of ethyl bromide, i.e. the ^{79}Br and ^{81}Br species of CH_3CH_2Br, CH_3CD_2Br, CD_3CH_2Br, $CH_3{}^{13}CH_2Br$, and $^{13}CH_3CH_2Br$. They performed a partial second-order analysis of the quadrupole coupling using a symmetric rotor basis.

Agreement with experimental results was quite good except for the ^{79}Br and ^{81}Br isotopic species of CH_3CD_2Br which, as will be shown in Section 3.2, requires an extension to a third-order perturbation treatment of the quadrupole Hamiltonian.

3.2 Analysis of the Spectra in Terms of Rotational and Quadrupole Parameters

The experimental "a" and "b" - type transitions observed and reported by Pierce and Flanagan for the ethyl bromide series are used as the basis for establishing the molecular parameters. The experimental values of Pierce and Flanagan as well as the calculated values are entered in Tables IIIa,b,c,d,e.

A simple but extremely effective method was used to evaluate the parameters. The method discussed below was used for all species except the ^{79}Br and ^{81}Br isotopes of CH_3CD_2Br which required a modification to include a partial third-order perturbation analysis. The parameters, A, B, C, χ_{aa}, $\eta\chi_{aa}$ and χ_{ab} evaluated by Pierce and Flanagan were used as a first estimate to the problem. A FORTRAN language program developed at the Chemistry Department of Michigan State University, using only these parameters, was run on a Control Data Corporation 3600

Computer for each of the ten species of ethyl bromide. The program generates the Wang symmetric rotor basis set and transforms them to the correct asymmetry. It also generates the direction cosine matrix elements and their appropriate multiplicative factors used in evaluating the quadrupole interaction terms. All constants mentioned in the following discussion are calculated and generated as part of the output of this program.

It is possible to write the transition frequency as a simple sum of differences between levels;

$$\nu_t = W^0_{up} - W^0_{low} + W^{(1)}_{up} - W^{(1)}_{low} + W^{(2)}_{up} - W^{(2)}_{low} \qquad (3\text{-}1)$$

where

ν_t = experimental frequency,

W^0 = rigid rotor energy (upper and lower levels of a given transition),

$W^{(1)}$ = first-order quadrupole interaction energy, and

$W^{(2)}$ = second-order quadrupole interaction energy.

By using equation (3-1) it is possible to isolate the energy contribution from either the zeroth, first or second-order problem.

The procedure used to evaluate the final parameters listed is given below and was used for all species except the ^{79}Br and ^{81}Br isotopes of CH_3CD_2Br which will be discussed separately.

1. Since the contribution from the second-order perturbation is the smallest of the components a small error in evaluating this part would not greatly disturb any further evaluation of the other parameters. Several programs were run with variable values of χ_{ab} to give several sets of calculated spectra. Use of equations (3-1) and (2-48) allowed

the derivation of equation (3-2).

$$\chi_{ab}^{2} = \frac{(\underline{\chi_{ab}}^{2})[\nu_4^{exp} - \nu_3^{exp} - \nu_2^{exp} + \nu_1^{exp} - \nu_{4aa}^{2} + \nu_{3aa}^{2} + \nu_{2aa}^{2} - \nu_{1aa}^{2}]}{[\nu_{4ab}^{2} - \nu_{3ab}^{2} - \nu_{2ab}^{2} + \nu_{1ab}^{2}]} \quad (3\text{-}2)$$

where

$\underline{\chi_{ab}}^{2}$ = is a trial value of the square of the off diagonal quadrupole elements,

and where for example

$$\nu_{1ab}^{2} = \mathcal{H}_{ab}^{1\ up} - \mathcal{H}_{ab}^{1\ low}$$

The subscript integers, 1,2,3, and 4 label the four experimental components of a given transition in order of decreasing frequency.

By using several values of $\underline{\chi_{ab}}$, it is possible to evaluate many $\chi_{ab's}$ from which a value of χ_{ab} may be obtained for the rest of the calculations. It is interesting to note that the first-order terms do not occur in equation (3-2). This is because of the symmetrical nature of first-order theory which predicts that:

$$\nu_4^{exp} - \nu_3^{exp} \equiv \nu_2^{exp} - \nu_1^{exp}$$

that is, first-order theory predicts that four transitions will appear near the hypothetical unsplit frequency as two doublets, each of the same splitting.

2. The second step in the quadrupole analysis utilizes equations (3-1), (2-44) and 2-45):

$$\nu_t(F) - \nu^{(2)}(F) - \nu_t(F') + \nu^{(2)}(F') = \nu^{(1)}(F) - \nu^{(1)}(F') \quad (3\text{-}4)$$

where

$$\nu^{(1)}(f) = \Delta\alpha(F)\,\chi_{aa} + \Delta\beta(F)(\chi_{bb} - \chi_{cc}),$$

$$\nu^{(1)}(F') = \Delta\alpha(F')\,\chi_{aa} + \Delta\beta(F')(\chi_{bb} - \chi_{cc})$$

and F, F' indicate the various F components of a given transition.

Using a least squares program, the parameters χ_{aa} and $(\chi_{bb} - \chi_{cc})$ may be evaluated from a set of linear equations calculated using the experimental spectra. The individual diagonal χ's are evaluated using the relation

$$\chi_{aa} + \chi_{bb} + \chi_{cc} = 0. \qquad (3\text{-}5)$$

3. The last set of parameters to be fitted to the experimental spectra are the rotational constants A, B and C. Use may be made of another least squares calculation using a set of equations written in three variables of the form

$$\nu^{0}_{obs} - \nu^{0}_{calc} = (A_{obs} - A_{calc})\frac{\partial W_r}{\partial A} + (B_{obs} - B_{calc})\frac{\partial W_r}{\partial B} + (C_{obs} - C_{calc})\frac{\partial W_r}{\partial C}. \qquad (3\text{-}6)$$

where

ν^{0}_{obs} = experimental frequency - $\nu^{(1)}$ calculated - $\nu^{(2)}$ calculated.

ν^{0}_{calc} = calculated rigid-rotor frequency.

$(A,B,C)_{obs}$ = A, B and C rotational constants which will give the best possible fit to the ν^{0}_{obs} spectra.

$(A,B,C)_{calc}$ = A, B and C rotational constants used to evaluate ν^{0}_{calc}.

$\partial W_r/\partial i$ = The change of rotational energy with respect to the i = A, B, C rotational constants.

A second iteration of the three steps above did not appreciably change the values of the constants. As a check on the quadrupole

constants, a term known as the hypothetical unsplit frequency, defined as:

$$\nu_{exp} - \nu^{(1)}_{calc} - \nu^{(2)}_{calc} = \nu^{0}_{exp} = \text{hypothetical unsplit frequency} \qquad (3\text{-}7)$$

was calculated for all experimental frequencies listed and are tabulated with the calculated zeroth-order transitions in Table IV.

3.3 Extension to Partial Third-Order Perturbation

A noticeable discrepancy was noted when the procedures of Section 3.2 were applied to the ^{79}Br and ^{81}Br species of CH_3CD_2Br. This becomes immediately apparent when a fitting of χ_{ab} using equation (3-2) on the $2_{02} - 3_{03}$ and $2_{11} - 3_{12}$ transitions yielded values of χ_{ab} differing by 30-40 Mc. It was impossible to use the other reported transitions to calculate further $\chi_{ab's}$ because they were too insensitive to the changes in χ_{ab}. A simple average of the two $\chi_{ab's}$ yielded values similar to those reported by Pierce and Flanagan (21).

Since the most nearly degenerate pair of energy levels, $2_{11} - 3_{03}$, contributes to both transitions, it was thought that a partial third-order perturbation calculation would account for the discrepancy. This reasoning may more easily be seen by writing the partial third-order term.

$$W_1^{(3)}(F) = -W_2^{(3)}(F) = \left[\frac{\mathcal{H}_{12}\mathcal{H}_{12}}{W_1^0 - W_2^0}\right]\left[\frac{\mathcal{H}_{22} - \mathcal{H}_{11}}{W_1^0 - W_2^0}\right] \qquad (3\text{-}8)$$

where

$W_1^{(3)}(F)$, $W_2^{(3)}(F)$ = third-order energy of levels (1) and (2), the near degenerate pairs.

$\mathcal{H}_{22}$, $\mathcal{H}_{11}$ = the diagonal components of the first-order quadrupole Hamiltonian of the respective levels.

W^0_1 , W^0_2 = zeroth-order rigid rotor energy levels.

Equation (3-8) may be written more explicitly by noting that the first term in brackets is simply the second-order term connecting the two states in question, and that the numerator of the second bracketed term is simply the difference of the first-order quadrupole energies of the two states.

$$W^{(3)}_{2_{11}}(F) = - W^{(3)}_{3_{03}}(F) = W^{(2)}_{2_{11}-3_{03}}(F) \left[\frac{W^{(1)}_{3_{03}}(F) - W^{(1)}_{2_{11}}(F)}{W_{R2_{11}} - W_{R3_{03}}} \right] \quad (3\text{-}9)$$

The significant partial third-order terms evaluated are tabulated in Table IIIf where they are added as perturbations to the frequencies calculated to second-order. It is to be noted that the $5/2 \longrightarrow 7/2$ and $3/2 \longrightarrow 5/2$ assignments for the transition $2_{11} \longrightarrow 3_{12}$ must be inverted from that reported by Pierce and Flanagan for both the $CH_3CD_2{}^{79}Br$ and $CH_3CD_2{}^{81}Br$ species. The lack of more low J transitions hindered a more precise evaluation of the quadrupole constants.

3.4 Summary

The application of second-order perturbation to systems defined by the conditions discussed in Section 3.1 will allow for excellent correlation between observed and calculated spectra. And, as shown, when conditions are such that near degenerate levels are connected by the quadrupole off-diagonal elements then it becomes necessary to extend the theory to include a third-order correction.

Primarily, however, the most useful information derived from the accurate evaluation of the off-diagonal element of the quadrupole tensor is that it allows a further insight into the electronic structure of

the C-Br bond. The primary purpose of this thesis is to show from a complete second-order analysis which of the two commonly used methods is the more accurate for estimation of the off-diagonal element of the quadrupole tensor.

Table V lists in columns I and III the results of the two most used methods of estimation, and in column II, the experimental results from the second-order analysis. As can be seen from the angles tabulated, the approximation of assuming cylindrical charge distribution about the C-Br bond seems to be the more accurate. The uncertainty in the listed values of χ_{ab} is ± 10 Mc; therefore the values of Θ in column II are accurate to within ± 30'. This would account for the inversions in the orders of magnitudes of some of the angles listed, and also brings the values in column I close enough to the experimental limits of the values in column II to prohibit any positive statements concerning the existence of slightly bent bonds.

Table I. Rotational parameters of the ethyl bromide species.

Species	A (Mc)	B (Mc)	C (Mc)	χ
$CH_3CH_2{}^{79}Br$	29 955.82	3 803.95	3 522.89	-0.978735
$CH_3CH_2{}^{81}Br$	29 947.80	3 781.07	3 503.17	-0.978982
$CH_3{}^{13}CH_2{}^{79}Br$	29 147.70	3 765.49	3 478.75	-0.977659
$CH_3{}^{13}CH_2{}^{81}Br$	29 120.93	3 742.42	3 458.85	-0.977899
$^{13}CH_3CH_2{}^{79}Br$	29 665.00	3 669.87	3 404.02	-0.979754
$^{13}CH_3CH_2{}^{81}Br$	29 659.10	3 647.50	3 384.38	-0.979971
$CD_3CH_2{}^{79}Br$	24 663.62	3 297.91	3 076.20	-0.979460
$CD_3CH_2{}^{81}Br$	24 657.79	3 276.99	3 057.95	-0.979718
$CH_3CD_2{}^{79}Br$	23 213.13	3 675.70	3 373.55	-0.969541
$CH_3CD_2{}^{81}Br$	23 206.64	3 652.78	3 354.06	-0.969906

Table II. Quadrupole coupling constants (Mc).

Species	χ_{aa}	χ_{bb}	χ_{cc}	χ_{ab}	$\eta\chi_{aa}$	$\frac{\chi_{aa}^{79}}{\chi_{aa}^{81}}$ [a]
$CH_3CH_2{}^{79}Br$	417.2	-143.7	-273.5	299.8	129.9	1.1959
$CH_3CH_2{}^{81}Br$	348.9	-120.5	-228.4	247.7	107.9	
$CH_3{}^{13}CH_2{}^{79}Br$	421.0	-146.9	-274.1	289.6	127.2	1.2010
$CH_3{}^{13}CH_2{}^{81}Br$	350.6	-123.0	-227.6	240.6	104.6	
$^{13}CH_3CH_2{}^{79}Br$	411.4	-137.7	-273.7	298.3	136.0	1.1918
$^{13}CH_3CH_2{}^{81}Br$	345.2	-117.4	-227.8	259.7	110.3	
$CD_3CH_2{}^{79}Br$	397.1	-123.8	-273.3	312.4	149.4	1.1933
$CD_3CH_2{}^{81}Br$	332.8	-104.6	-228.2	259.3	123.6	
$CH_3CD_2{}^{79}Br$	436.4	-162.2	-274.2	272.0	112.1	1.1963
$CH_3CD_2{}^{81}Br$	364.8	-135.2	-229.6	226.0	94.4	

[a] The ratio of quadrupole moments of ^{79}Br and ^{81}Br is 1.19707 (Appendix VII, Reference (19)).

Table IIIa. Observed and calculated frequencies (Mc) of ethyl bromide.

Transition	$CH_3CH_2{}^{79}Br$		$CH_3CH_2{}^{81}Br$	
	Observed[a]	Calculated	Observed[a]	Calculated
$2_{02} - 3_{03}$				
7/2 - 9/2	21 966.25	21 966.51	21 839.67	21 839.74
5/2 - 7/2	21 966.25	21 966.30	21 839.67	21 839.63
3/2 - 5/2	21 992.44	21 992.51	21 861.55	21 861.47
1/2 - 3/2	21 991.60	21 991.66	21 860.97	21 860.89
$2_{12} - 3_{13}$				
7/2 - 9/2	21 545.67	21 545.71	21 424.66	21 424.60
5/2 - 7/2	21 571.56	21 571.61	21 446.41	21 446.29
3/2 - 5/2	21 576.45	21 576.36	21 450.30	21 450.24
1/2 - 3/2	21 550.04	21 550.06	21 428.29	21 428.27
$2_{11} - 3_{12}$				
7/2 - 9/2	22 388.13	22 388.09	22 258.07	22 257.91
5/2 - 7/2	22 415.50	22 415.50	22 280.80	22 280.70
3/2 - 5/2	22 409.10	22 408.07	22 275.75	22 275.71
1/2 - 3/2	22 386.74	22 386.66	22 256.63	22 256.53
$5_{05} - 5_{14}$				
13/2 - 13/2	28 473.63	28 473.62	28 460.03	28 460.11
11/2 - 11/2	28 445.75	28 445.83	28 436.96	28 436.99
9/2 - 9/2	28 453.58	28 453.48	28 443.22	28 443.38
7/2 - 7/2	28 480.95	28 480.95	28 466.19	28 466.27
$7_{07} - 7_{16}$				
17/2 - 17/2	30 455.39	30 455.43	30 418.10	30 418.03
15/2 - 15/2	30 431.79	30 431.76	30 398.44	30 398.36
13/2 - 13/2	30 436.59	30 436.61	30 402.48	30 402.39
11/2 - 11/2	30 460.07	30 460.07	30 422.02	30 421.91

[a]As reported by Pierce and Flanagan, reference (21).

Table IIIb. Observed and calculated frequencies (Mc) of ethyl bromide.

Transition	$CH_3CH_2{}^{79}Br$		$CH_3CH_2{}^{81}Br$	
	Observed[a]	Calculated	Observed[a]	Calculated
$2_{02} - 3_{03}$				
7/2 - 9/2	19 110.67	19 110.69	18 994.08	18 994.13
5/2 - 7/2	19 109.86	19 109.99	18 993.67	18 993.72
3/2 - 5/2	19 135.33	19 135.30	19 014.75	19 014.80
1/2 - 3/2	19 133.69	19 133.67	19 013.66	19 013.69
$2_{12} - 3_{13}$				
7/2 - 9/2	18 777.32	18 777.29	18 665.63	18 665.66
5/2 - 7/2	18 801.98	18 801.93	18 686.28	18 686.34
3/2 - 5/2	18 807.27	18 807.24	18 690.79	18 690.74
1/2 - 3/2	18 782.26	18 782.19	18 669.75	18 669.77
$2_{11} - 3_{13}$				
7/2 - 9/2	19 441. 68	19 441.71	19 322.63	19 322.55
5/2 - 7/2	19 467.83	19 467.79	19 344.35	19 344.23
3/2 - 5/2	19 460.56	19 460.52	19 338.73	19 338.69
1/2 - 3/2	19 439.72	19 439.76	19 320.66	19 320.66
$6_{06} - 6_{15}$				
15/2 - 15/2	23 909.10	23 909.14	23 890.79	23 890.81
13/2 - 13/2	23 881.79	23 881.77	23 868.13	23 868.12
11/2 - 11/2	23 888.35	23 888.31	23 873.61	23 873.54
9/2 - 9/2	23 915.29	23 915.38	23 896.07	23 896.02
$7_{07} - 7_{16}$				
17/2 - 17/2	24 757.70	24 757.66	23 728.53	24 728.26
15/2 - 15/2	24 731.52	24 731.56	24 706.90	24 706.65
13/2 - 13/2	24 736.91	24 736.93	24 711.31	24 711.09
11/2 - 11/2	24 762.80	24 762.71	24 731.62	24 732.48

[a]As reported by Pierce and Flanagan, reference (21).

Table IIIc. Observed and calculated frequencies (Mc) of ethyl bromide.

Transition	$CH_3{}^{13}CH_2{}^{79}Br$		$CH_3{}^{13}CH_2{}^{81}Br$	
	Observed[a]	Calculated	Observed[a]	Calculated
$2_{02} - 3_{03}$				
7/2 - 9/2	21 718.20	21 718.04	21 590.10	21 590.15
5/2 - 7/2		21 717.79		21 590.02
3/2 - 5/2	21 744.70	21 744.22	21 612.01	21 611.96
1/2 - 3/2		21 743.35		21 611.35
$2_{12} - 3_{13}$				
7/2 - 9/2	21 289.31	21 289.21	21 166.97	21 167.04
5/2 - 7/2	21 315.48	21 315.35	21 188.89	21 188.83
3/2 - 5/2	21 320.07	21 320.03	21 192.78	21 192.68
1/2 - 3/2	21 293.52	21 293.48	21 170.52	21 170.60
$2_{11} - 3_{12}$				
7/2 - 9/2	22 149.41	22 148.94	22 017.62	22 017.58
5/2 - 7/2	22 176.84	22 176.34	22 040.21	22 040.28
3/2 - 5/2	22 170.88	22 170.44	22 035.68	22 035.73
1/2 - 3/2	22 147.69	22 147.27	22 016.12	22 016.05

Table IIId. Observed and calculated frequencies (Mc) of ethyl bromide.

Transition	$^{13}CH_3CH_2{}^{79}Br$		$^{13}CH_3CH_2{}^{81}Br$	
	Observed[a]	Calculated	Observed[a]	Calculated
$2_{02} - 3_{03}$				
7/2 - 9/2	21 208.90	21 208.64	21 083.35	21 083.56
5/2 - 7/2		21 208.49		21 083.47
3/2 - 5/2	21 233.95	21 234.32	21 104.47	21 105.12
1/2 - 3/2		21 233.57		21 104.53
$2_{12} - 3_{13}$				
7/2 - 9/2	20 809.94	20 809.94	20 689.88	20 689.90
5/2 - 7/2	20 835.57	20 835.48	20 711.40	20 711.36
3/2 - 5/2	20 840.44	20 840.41	20 715.41	20 715.35
1/2 - 3/2	20 814.35	20 814.47	20 693.57	20 693.63
$2_{11} - 3_{12}$				
7/2 - 9/2	21 606.77	21 605.91	21 477.98	21 477.90
5/2 - 7/2	21 634.34	21 633.61	21 501.20	21 501.19
3/2 - 5/2	21 626.46	21 625.82	21 494.67	21 494.76
1/2 - 3/2	21 605.90	21 605.13		21 477.44

[a]As reported by Pierce and Flanagan, Reference (21).

Table IIIe. Observed and calculated frequencies (Mc) of ethyl bromide.

Transition	$CH_3CD_2{}^{79}Br$		$CH_3CD_2{}^{81}Br$	
	Observed[a]	Calculated[b]	Observed[a]	Calculated[b]
$2_{02} - 3_{03}$				
7/2 - 9/2	21 128.81	21 128.61	21 002.59	21 002.55
5/2 - 7/2	21 132.01	21 131.94	21 005.19	21 005.19
3/2 - 5/2	21 157.81	21 157.74	21 026.68	21 026.77
1/2 - 3/2	21 162.20	21 161.48	21 030.18	21 029.71
$2_{12} - 3_{13}$				
7/2 - 9/2	20 680.26	20 680.11	20 560.17	20 560.07
5/2 - 7/2	20 707.16	20 707.21	20 582.64	20 582.75
3/2 - 5/2	20 711.43	20 711.44	20 586.21	20 586.30
1/2 - 3/2	20 684.07	20 683.89	20 563.36	20 563.31
$2_{11} - 3_{12}$[c]				
7/2 - 9/2	21 590.35	21 590.14	21 459.19	21 459.18
5/2 - 7/2	21 616.46	21 616.27	21 481.07	21 481.06
3/2 - 5/2	21 617.29	21 616.56	21 481.74	21 481.23
1/2 - 3/2	21 584.83	21 584.67	21 454.68	21 454.70
$5_{05} - 5_{14}$				
13/2 - 13/2	22 061.39	22 061.40	22 046.34	22 046.56
11/2 - 11/2	22 035.23	22 035.24	22 024.46	22 024.62
9/2 - 9/2	22 042.53	22 042.61	22 030.70	22 030.81
7/2 - 7/2	22 068.60	22 068.57	22 052.26	22 052.61
$6_{06} - 6_{15}$				
15/2 - 15/2	23 060.18	23 059.79	23 032.66	23 032.72
13/2 - 13/2	23 036.91	23 036.37	23 012.88	23 013.00
11/2 - 11/2	23 041.97	23 041.95	23 017.24	23 017.67
9/2 - 9/2	23 065.47	23 065.20	23 036.91	23 037.21
$7_{07} - 7_{16}$				
17/2 - 17/2	24 263.26	24 263.13	24 220.70	24 220.65
15/2 - 15/2	24 240.94	24 240.86	24 201.97	24 202.02
13/2 - 13/2	24 245.82	24 245.57	24 205.84	24 205.92
11/2 - 11/2	24 267.19	24 267.15	24 224.11	24 224.11

[a] As reported by Pierce and Flanagan, Reference (21).

[b] All transitions calcualted only to second-order. The 2_{02}-3_{03} and 2_{11}-3_{12} transitions are calculated to third-order in Table IIIf.

[c] The reported values of the 5/2-7/2 and 3/2-5/2 components of both species have been interchanged.

Table IIIf. Third-order corrections to the calculated spectra (Mc) of $CH_3CD_2{}^{79}Br$ and $CH_3CD_2{}^{81}Br$.

Transition	(0+1+2) ν_{calc}	(3) ν_{calc}	(0+1+2+3) ν_{calc}	ν_{obs} [a]	$\nu_{obs} - \nu_{calc}$
			$CH_3CD_2{}^{79}Br$		
$2_{02} - 3_{03}$					
7/2 - 9/2	21 128.61	--	21 128.61	21 128.81	+ 0.20
5/2 - 9/2	21 131.94	- 0.23	21 131.71	21 132.01	+ 0.30
3/2 - 5/2	21 157.74	+ 0.01	21 157.75	21 157.81	+ 0.06
1/2 - 3/2	21 161.48	+ 0.44	21 161.92	21 162.20	+ 0.28
$2_{11} - 3_{12}$ [b]					
7/2 - 9/2	21 590.14	- 0.23	21 589.91	21 590.35	+ 0.44
5/2 - 7/2	21 616.27	+ 0.01	21 616.28	21 616.46	+ 0.18
3/2 - 5/2	21 616.56	+ 0.44	21 617.00	21 617.29	+ 0.29
1/2 - 3/2	21 584.67	--	21 584.67	21 584.83	+ 0.16
			$CH_3CD_2{}^{81}Br$		
$2_{02} - 3_{03}$					
7/2 - 9/2	21 002.55	--	21 002.55	21 002.59	+ 0.04
5/2 - 7/2	21 005.19	- 0.18	21 005.01	21 005.19	+ 0.18
3/2 - 5/2	21 026.77	+ 0.01	21 026.78	21 026.68	- 0.10
1/2 - 3/2	21 029.71	+ 0.34	21 030.05	21 030.18	+ 0.13
$2_{11} - 3_{12}$ [b]					
7/2 - 9/2	21 459.18	- 0.18	21 459.00	21 459.19	+ 0.19
5/2 - 7/2	21 481.06	+ 0.01	21 481.07	21 481.07	0.00
3/2 - 5/2	21 481.23	+ 0.34	21 481.57	21 481.74	+ 0.17
1/2 - 3/2	21 454.70	--	21 454.70	21 454.68	- 0.02

[a] As reported by Pierce and Flanagan, Reference (21).

[b] The reported values of the 5/2 - 7/2 and 3/2 - 5/2 components have been inverted.

Table IV. Experimental and calculated hypothetical unsplit frequencies of the ethyl bromide species.

Transition	Species Observed[a]	Species Calculated	Species Observed[a]	Species Calculated
	$CH_3CH_2{}^{79}Br$		$CH_3CH_2{}^{81}Br$	
$2_{02} - 3_{03}$	21 971.45	21 971.51	21 844.01	21 843.92
$2_{12} - 3_{13}$	21 557.54	21 557.54	21 434.57	21 434.50
$2_{11} - 3_{12}$	22 400.73	22 400.69	22 268.30	22 268.20
$5_{05} - 5_{14}$	28 463.20	28 463.19	28 451.31	28 451.40
$7_{07} - 7_{16}$	30 445.81	30 445.82	30 410.11	30 410.02
	$CD_3CH_2{}^{79}Br$		$CD_3CH_2{}^{81}Br$	
$2_{02} - 3_{03}$	19 115.43	19 115.45	18 998.08	18 998.13
$2_{12} - 3_{13}$	18 788.74	18 788.69	18 675.21	18 675.22
$2_{11} - 3_{12}$	19 453.80	19 453.80	19 332.40	19 332.34
$6_{05} - 6_{15}$	23 898.36	23 898.38	23 881.89	23 881.87
$7_{07} - 7_{16}$	24 747.09	24 747.08	24 719.44	24 719.47
	$CH_3{}^{13}CH_2{}^{79}Br$		$CH_3{}^{13}CH_2{}^{81}Br$	
$2_{02} - 3_{03}$	21 723.04	21 723.08	21 594.36	21 594.36
$2_{12} - 3_{13}$	21 301.21	21 301.13	21 176.97	21 176.97
$2_{11} - 3_{12}$	22 161.80	22 161.34	22 027.69	22 027.69
	$^{13}CH_3CH_2{}^{79}Br$		$^{13}CH_3CH_2{}^{81}Br$	
$2_{02} - 3_{03}$	21 213.51	21 213.57	21 087.27	21 087.10
$2_{12} - 3_{13}$	20 821.65	20 821.65	20 699.69	20 699.72
$2_{11} - 3_{12}$	20 618.92	20 619.17	21 489.08	21 489.08

[a]As reported by Pierce and Flanagan, Reference (21).

Table V. Transformation angles derived from quadrupole theory and experimentation.

Species	I[a]	II[b]	III[c]
$CH_3CH_2{}^{79}Br$	22° 15'	23° 28'	23° 26'
$CH_3CH_2{}^{81}Br$	22° 13'	23° 16'	23° 23'
$CH_3{}^{13}CH_2{}^{79}Br$	21° 51'	22° 47'	23° 10'
$CH_3{}^{13}CH_2{}^{81}Br$	21° 49'	22° 43'	23° 2'
$^{13}CH_3CH_2{}^{79}Br$	22° 41'	23° 41'	24° 1'
$^{13}CH_3CH_2{}^{81}Br$	22° 39'	24° 9'	23° 42'
$CD_3CH_2{}^{79}Br$	24° 4'	25° 2'	25° 17'
$CD_3CH_2{}^{81}Br$	24° 2'	24° 55'	25° 8'
$CH_3CD_2{}^{79}Br$	20° 40'	21° 8'	21° 39'
$CH_3CD_2{}^{81}Br$	20° 38'	21° 3'	21° 44'

[a]The angle between the "a" inertial angle and the C-Br bond.

[b]The angle calculated from the experimental quadrupole coupling constants, $\tan 2\theta = 2\chi_{ab}/(\chi_{aa} - \chi_{bb})$, and is the angle needed to diagonalize the experimental tensor.

[c]The angle calculated assuming a cylindrical charge distribution about the C-Br bond. It is evaluated by using experimental quadrupole coupling constants by using the cylindrical restrictions:

$$\frac{\chi_{aa}}{\chi_{zz}} = \frac{\chi_{aa}}{2\chi_{cc}} = \left(\frac{3\cos^2\theta - 1}{2}\right).$$

REFERENCES

1. Schuler, H. and T. Schmidt, Z. Physik 94, 234 (1935); 98, 430 (1935).

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

3. Good, W. E., Phys. Rev. 70, 213 (1946).

4. Dailey, B. P., R. L. Kyhl, M. W. P. Strandberg, J. H. VanVieck, and E. B. Wilson, Jr., Phys. Rev. 70, 984 (1946).

5a. Casimir, H. B. G., On the Interaction Between Atomic Nuclei and Electrons, Teyler's Tweede Genootschap, E. F. Bohn, Haarlem, (1936).

5b. Reprinted by W. H. Freeman and Company, San Francisco, (1963).

6. Nordsieck, A., Phys. Rev. 58, 310 (1940).

7. Feld, B. T. and W. E. Lamb, Phys. Rev. 67, 15 (1945).

8. Coles, D. K. and W. E. Good, Phys. Rev. 70, 979 (1946).

9. VanVleck, J. H., Phys. Rev. 71, 468 (1947).

10. Bragg, J. K., Phys. Rev. 74, 533 (1948).

11. Knight, G. and B. T. Feld, Phys. Rev. 74, 354 (1948).

12. Margenau, H., G. M. Murphy, The Mathematics of Physics and Chemistry, D. VanNostrand Company, Inc., New York, (1956).

13. Ramsey, N. F., Nuclear Moments, John Wiley and Sons, Inc., New York, (1953).

14. Bragg, J. K., and S. Golden, Phys. Rev. 75, 735 (1949).

15. Wang, S. C., Phys. Rev. 34, 243 (1929).

16. Strandberg, M. W. P., Microwave Spectroscopy, Methuen and Company, Ltd., London, (1954).

17. Schwendeman, R. H., J. Mol. Spect. 7, 280 (1961).

18. Schwendeman, R. H., Technical Note: Matrix Elements of Some Products of Direction Cosines and Second-Order Quadrupole Coupling Calculations, (1964).

19. Townes, C. H. and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill, New York, (1955).

20. Wagner, R. S., B. P. Dailey and N. Solimene, J. Chem. Phys. 26, 1593 (1957).

21 Flanagan, C. and L. Pierce, J. Chem. Phys. 38, 2963 (1963).

APPENDIX

The representation used in the evaluation of the matrix elements in the Appendix assumes a prolate rotor representation I^r (i.e. a<->z, b<->x, c<->y. The procedure to convert to the oblate rotor III^r representation, (a<->x, b<->y, c<->z) and the III^1 representation (a<->y, b<->x, c<->z) is given below.

For representation III^r, the required changes are;

1. In the column labeled "g" in Table I, change a ⟶ c, b ⟶ a; c ⟶ b.
2. In the columns labeled "d" and "d'" in Table I of Reference 18, change 0 ⟶ 1 and 1 ⟶ 0 for all 0^+ and 0^- matrices.
3. Label the matrices according to Figure 7 of Reference 18.
4. Interchange K_{-1} and K_{+1} in each label.

For representations III^1, all that is required is to form and label the matrices as for I^r, then interchange "a" and "c", and K_{-1} and K_{+1}.

J				J+1				J+2			
E^+	0^+	0^-	E^-	E^+	0^+	0^-	E^-	E^+	0^+	0^-	E^-
aa 1 bb 13 cc 25	ab 37	ac 47	bc 57	bc 59	ac 49	ab 39	aa 5 bb 17 cc 29	aa 9 bb 21 cc 33	ab 43	ac 53	bc 63
	aa 2 bb 14 cc 26	bc 58	ac 48	ac 50	bc 60	aa 6 bb 18 cc 30	ab 40	ab 44	aa 10 bb 22 cc 34	bc 64	ac 54
		aa 3 bb 15 cc 27	ab 38	ab 41	aa 7 bb 19 cc 31	bc 61	ac 51	ac 55	bc 65	aa 11 bb 23 cc 35	ab 45
			aa 4 bb 16 cc 28	aa 8 bb 20 cc 32	ab 42	ac 52	bc 62	bc 66	ac 56	ab 46	aa 12 bb 24 cc 36

Figure 1. A portion of the matrices $\Phi_{Zg}\Phi_{Zg'}$, superimposed showing the separation into blocks. The letters are gg'; the numbers are the identification numbers in the first column of Table I.

Table I. **Characteristics of the blocks of the matrices of the products of direction cosines**

No.[a]	gg'	Matrix Block J	σ	J'	σ'	Pre-Matrix[b]	Post-Matrix[b]	Mult[c]	G[d]
1-1	aa	J	E^+	J	E^+	7	7^+	1	2
1-2	aa	J	E^+	J	E^+	1	1^+	1	1
2-1	aa	J	0^+	J	0^+	8	8^+	1	2
2-2	aa	J	0^+	J	0^+	2	2^+	1	1
3-1	aa	J	0^-	J	0^-	9	9^+	1	2
3-2	aa	J	0^-	J	0^-	2^+	2	1	1
4-1	aa	J	E^-	J	E^-	10	10^+	1	2
4-2	aa	J	E^-	J	E^-	1^+	1	1	1
5-1	aa	J	E^+	J+1	E^-	1	10	1	3
5-2	aa	J	E^+	J+1	E^-	7	1	1	4
6-1	aa	J	0^+	J+1	0^-	2	9	1	3
6-2	aa	J	0^+	J+1	0^-	8	2	1	4
7-1	aa	J	0^-	J+1	0^+	2^+	8	1	3
7-2	aa	J	0^-	J+1	0^+	9	2^+	1	4
8-1	aa	J	E^-	J+1	E^+	1^+	7	1	3
8-2	aa	J	E^-	J+1	E^+	10	1^+	1	4
9-1	aa	J	E^+	J+2	E^+	7	7	1	5
10-1	aa	J	0^+	J+2	0^+	8	8	1	5
11-1	aa	J	0^-	J+2	0^-	9	9	1	5
12-1	aa	J	E^-	J+2	E^-	10	10	1	5
13-1	bb	J	E^+	J	E^+	11	11^+	1	2
13-2	bb	J	E^+	J	E^+	3	3^+	1	1
14-1	bb	J	0^+	J	0^+	13	13^+	1	2
14-2	bb	J	0^+	J	0^+	4	4^+	1	1
15-1	bb	J	0^-	J	0^-	14	14^+	1	2
15-2	bb	J	0^-	J	0^-	3^+	3	1	1
16-1	bb	J	E^-	J	E^-	12	12^+	1	2
16-2	bb	J	E^-	J	E^-	4^+	4	1	1
17-1	bb	J	E^+	J+1	E^-	3	14	1	3
17-2	bb	J	E^+	J+1	E^-	11	4	-1	4
18-1	bb	J	0^+	J+1	0^-	4	12	-1	3
18-2	bb	J	0^+	J+1	0^-	13	3	1	4
19-1	bb	J	0^-	J+1	0^+	3^+	11	-1	3
19-2	bb	J	0^-	J+1	0^+	14	4^+	1	4

Table I. (Continued)

No.[a]	gg'	Matrix Block J	σ	J'	σ'	Pre-Matrix[b]	Post-Matrix[b]	Mult[c]	G[d]
20-1	bb	J	E^-	J+1	E^+	4^+	13	1	3
20-2	bb	J	E^-	J+1	E^+	12	$\underline{3^+}$	-1	4
21-1	bb	J	E^+	J+2	E^+	11	$\underline{13}$	-1	5
22-1	bb	J	0^+	J+2	0^+	13	$\underline{11}$	-1	5
23-1	bb	J	0^-	J+2	0^-	14	$\underline{12}$	-1	5
24-1	bb	J	E^-	J+2	E^-	12	$\underline{14}$	-1	5
25-1	cc	J	E^+	J	E^+	15	15^+	1	2
25-2	cc	J	E^+	J	E^+	5	5^+	1	1
26-1	cc	J	0^+	J	0^+	17	17^+	1	2
26-2	cc	J	0^+	J	0^+	5^+	5	1	1
27-1	cc	J	0^-	J	0^-	18	18^+	1	2
27-2	cc	J	0^-	J	0^-	6	6^+	1	1
28-1	cc	J	E^-	J	E^-	16	16^+	1	2
28-2	cc	J	E^-	J	E^-	6^+	6	1	1
29-1	cc	J	E^+	J+1	E^-	5	17	1	3
29-2	cc	J	E^+	J+1	E^-	15	$\underline{6}$	1	4
30-1	cc	J	0^+	J+1	0^-	5^+	15	1	3
30-2	cc	J	0^+	J+1	0^-	17	$\underline{6^+}$	1	4
31-1	cc	J	0^-	J+1	0^+	6	16	1	3
31-2	cc	J	0^-	J+1	0^+	18	$\underline{5}$	1	4
32-1	cc	J	E^-	J+1	E^+	6^+	18	1	3
32-2	cc	J	E^-	J+1	E^+	16	$\underline{5^+}$	1	4
33-1	cc	J	E^+	J+2	E^+	15	$\underline{18}$	1	5
34-1	cc	J	0^+	J+2	0^+	17	$\underline{16}$	1	5
35-1	cc	J	0^-	J+2	0^-	18	$\underline{15}$	1	5
36-1	cc	J	E^-	J+2	E^-	16	$\underline{17}$	1	5
37-1	ab	J	E^+	J	0^+	7	13^+	i	2
37-2	ab	J	E^+	J	0^+	1	4^+	i	1
38-1	ab	J	0^-	J	E^-	9	12^+	i	2
38-2	ab	J	0^-	J	E^-	2^+	4	-i	1
39-1	ab	J	E^+	J+1	0^-	1	12	-i	3
39-2	ab	J	E^+	J+1	0^-	7	$\underline{3}$	i	4

Table I. (Continued)

No.[a]	gg'	Matrix Block J	σ	J'	σ'	Pre-Matrix[b]	Post-Matrix[b]	Mult[c]	G[d]
40-1	ab	J	0^+	J+1	E^-	2	14	-i	3
40-2	ab	J	0^+	J+1	E^-	8	$\underline{4}$	-i	4
41-1	ab	J	0^-	J+1	E^+	2^+	13	-i	3
41-2	ab	J	0^-	J+1	E^+	9	$\underline{3^+}$	-i	4
42-1	ab	J	E^-	J+1	0^+	1^+	11	-i	3
42-2	ab	J	E^-	J+1	0^+	10	$\underline{4^+}$	i	4
43-1	ab	J	E^+	J+2	0^+	7	$\underline{11}$	-i	5
44-1	ab	J	0^+	J+2	E^+	8	$\underline{13}$	-i	5
45-1	ab	J	0^-	J+2	E^-	9	$\underline{14}$	-i	5
46-1	ab	J	E^-	J+2	0^-	10	$\underline{12}$	-i	5
47-1	ac	J	E^+	J	0^-	7	18^+	1	2
47-2	ac	J	E^+	J	0^-	1	6^+	1	1
48-1	ac	J	0^+	J	E^-	8	16^+	1	2
48-2	ac	J	0^+	J	E^-	2	6	1	1
49-1	ac	J	E^+	J+1	0^+	1	16	1	3
49-2	ac	J	E^+	J+1	0^+	7	$\underline{5}$	1	4
50-1	ac	J	0^+	J+1	E^+	2	18	1	3
50-2	ac	J	0^+	J+1	E^+	8	$\underline{5^+}$	1	4
51-1	ac	J	0^-	J+1	E^-	2^+	17	1	3
51-2	ac	J	0^-	J+1	E^-	9	$\underline{6}$	1	4
52-1	ac	J	E^-	J+1	0^-	1^+	15	1	3
52-2	ac	J	E^-	J+1	0^-	10	$\underline{6^+}$	1	4
53-1	ac	J	E^+	J+2	0^-	7	$\underline{15}$	1	5
54-1	ac	J	0^+	J+2	E^-	8	$\underline{17}$	1	5
55-1	ac	J	0^-	J+2	E^+	9	$\underline{18}$	1	5
56-1	ac	J	E^-	J+2	0^+	10	$\underline{16}$	1	5
57-1	bc	J	E^+	J	E^-	11	16^+	-i	2
57-2	bc	J	E^+	J	E^-	3	6	i	1
58-1	bc	J	0^+	J	0^-	13	18^+	-i	2
58-2	bc	J	0^+	J	0^-	4	6^+	-i	1
59-1	bc	J	E^+	J+1	E^+	3	18	i	3
59-2	bc	J	E^+	J+1	E^+	11	$\underline{5^+}$	-i	4

Table I. (Continued)

No.[a]	gg'	Matrix Block J	σ	J'	σ'	Pre-Matrix[b]	Post-Matrix[b]	Mult[c]	G[d]
60-1	bc	J	0^+	J+1	0^+	4	16	-i	3
60-2	bc	J	0^+	J+1	0^+	13	$\underline{5}$	-i	4
61-1	bc	J	0^-	J+1	0^-	3^+	15	-i	3
61-2	bc	J	0^-	J+1	0^-	14	$\underline{6}^+$	-i	4
62-1	bc	J	E^-	J+1	E^-	4^+	17	i	3
62-2	bc	J	E^-	J+1	E^-	12	$\underline{6}$	-i	4
63-1	bc	J	E^+	J+1	E^-	11	$\underline{17}$	-i	5
64-1	bc	J	0^+	J+1	0^-	13	$\underline{15}$	-i	5
65-1	bc	J	0^-	J+1	0^+	14	$\underline{16}$	-i	5
66-1	bc	J	E^-	J+1	E^+	12	$\underline{18}$	-i	5

[a] Number assigned for identification.

[b] Numbers of prematrix and postmatrix refer to Table I, Ref. 1. n^+ is conjugate transpose of n. $\underline{n}$ is matrix n for J = J+1.

[c] Product of mult factors from Table I, Ref. 1. Change of sign for conjugate transpose of imaginary matrix is included.

[d] Number of G factor is number assigned in Appendix A.

APPENDIX A

Table of G factors and products of G factors

The G factors in the following table are defined as:

$$G(J,J) = \frac{1}{2(J+1)}$$

$$G(J,J+1) = \frac{1}{2(J+1)(2J+3)^{1/2}}$$

$$G(J+1,J+1) = \frac{J}{2(J+1)(J+2)}$$

$$G(J+1,J+2) = \frac{(J+1)^{1/2}}{(J+2)(2J+3)^{1/2}(2J+5)^{1/2}}$$

J	G(J,J)	G(J,J+1)	G(J+1,J+1)	G(J+1,J+2)
0	0.50000000	0.28867513	0	0.12909944
1	0.25000000	0.11180340	0.08333333	0.07968191
2	0.16666667	0.06299408	0.08333333	0.05455447
3	0.12500000	0.04166667	0.07500000	0.04020151
4	0.10000000	0.03015113	0.06666667	0.03116490
5	0.08333333	0.02311251	0.05952381	0.02505880
6	0.07142857	0.01844278	0.05357143	0.02071042

	G(1)	G(2)	G(3)	G(4)	G(5)
J	$G(J,J)^2$	$G(J,J+1)^2$	G(J,J)G(J,J+1)	G(J,J+1)G(J+1,J+1)	G(J,J+1)G(J+1,J+2)
0	0.25000000	0.08333333	0.14433757	0	0.03726780
1	0.06250000	0.01250000	0.02795085	0.00931695	0.00890871
2	0.02777778	0.00396825	0.01049901	0.00524951	0.00343661
3	0.01562500	0.00173611	0.00520833	0.00312500	0.00167506
4	0.01000000	0.00090909	0.00301511	0.00201008	0.00093966
5	0.00694444	0.00053419	0.00192604	0.00137574	0.00057917
6	0.00510204	0.00034014	0.00131734	0.00098801	0.00038196

Appendix B

Numericel Values of $C(I,J,J',F)$ for $I = 3/2$ end $I = 5/2$ for $J \leq 6$.

The values tabulated here are:

$$C(I,J,J,F) = \frac{[3C(C+1) - 4\ I(I+1)J(J+1)]^2}{[8\ I(2\ I-1)J(2\ J-1)]^2}$$

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

$$C(I,J,J+1,F) = [F(F+1) - I(I+1) - J(J+2)]^2(I+J+F+2)(I-J+F)$$

$$\times \frac{(J-I+F+1)(J+I-F+1)}{[8I(2I-1)J]^2(2J+1)}$$

$$C(I,J,J+2,F) = (I+J+F+2)(I+J+F+3)(I-J+F+1)(I-J+F)$$

$$\times \frac{(J-I+F+1)(J-I+F+2)(I+J-F+1)(I+J-F+2)}{[16\ I(2\ I-1)]^2(2\ J+1)(J+1)}$$

I = 3/2

J	F	J,J	J,J+1	J,J+2
0	3/2	0.000000	0.000000	0.312500
1	5/2	0.062500	0.145833	0.583333
	3/2	1.000000	0.250000	0.218750
	1/2	1.562500	0.312500	
2	7/2	0.062500	0.187500	0.937500
	5/2	0.390625	0.100000	0.500000
	3/2	0.000000	0.350000	
	1/2	0.765625		
3	9/2	0.062500	0.229167	1.375000
	7/2	0.250000	0.059524	0.859375
	5/2	0.022500	0.372024	
	3/2	0.360000		
4	11/2	0.062500	0.270833	1.895833
	9/2	0.191406	0.041667	1.300000
	7/2	0.038584	0.401042	
	5/2	0.241151		
5	13/2	0.062500	0.312500	2.500000
	11/2	0.160000	0.031818	1.822917
	9/2	0.046944	0.434318	
	7/2	0.187778		
6	15/2	0.062500	0.354167	3.187500
	13/2	0.140625	0.025641	2.428571
	11/2	0.051653	0.470085	
	9/2	0.158187		

I = 5/2

J	F	J,J	J,J+1	J,J+2
0	5/2	0	0	0.175000
1	7/2	0.062500	0.112500	0.281250
	5/2	0.640000	0.060000	0.202500
	3/2	0.490000	0.210000	0.052500
2	9/2	0.062500	0.137500	0.412500
	7/2	0.180625	0.002500	0.412500
	5/2	0.062500	0.121500	0.202500
	3/2	0.062500	0.169000	0.045000
	1/2	0.490000	0.070000	
3	11/2	0.062500	0.162500	0.568750
	9/2	0.090000	0.001429	0.658125
	7/2	0.090000	0.078571	0.397768
	5/2	0.000400	0.178571	0.122768
	3/2	0.108900	0.133929	
	1/2	0.360000		
4	13/2	0.062500	0.187500	0.750000
	11/2	0.056406	0.008750	0.945000
	9/2	0.087870	0.056875	0.637000
	7/2	0.010727	0.180625	0.227500
	5/2	0.038584	0.171875	
	3/2	0.241151		
5	15/2	0.062500	0.212500	0.956250
	13/2	0.040000	0.018182	1.275000
	11/2	0.082178	0.044182	0.920455
	9/2	0.019600	0.183782	0.357955
	7/2	0.016900	0.202682	
	5/2	0.187778		
6	17/2	0.062500	0.237500	1.187500
	15/2	0.030625	0.028269	1.648929
	13/2	0.076880	0.035962	1.248379
	11/2	0.025310	0.188462	0.513736
	9/2	0.008264	0.230769	
	7/2	0.158187		

APPENDIX C

Table of a(J,q), b(J,q), g(J,q), and h(J,q)

The elements in the following table are defined as:

$$a(J,q) = \sqrt{[(J+1) + q][(J+1) + (q+1)]}$$

$$b(J,q) = \sqrt{[(J+1) - q][(J+1) - (q+1)]}$$

$$g(J,q) = \sqrt{J(J+1) - q(q+1)}$$

$$h(J,q) = 2\sqrt{(J+1)^2 - q^2}$$

J	q	a(J,q)	b(J,q)	g(J,q)	h(J,q)
1	0	2.449490	1.414214	1.414214	4.000000
	1	3.464102	0	0	3.464102
2	0	3.464102	2.449490	2.449490	6.000000
	1	4.472136	1.414214	2.000000	5.656854
	2	5.477226	0	0	4.472136
3	0	4.472136	3.464102	3.464102	8.000000
	1	5.477226	2.449490	3.162278	7.745966
	2	6.480741	1.414214	2.449490	6.928203
	3	7.483315	0	0	5.291502
4	0	5.477226	4.472136	4.472136	10.000000
	1	6.480741	3.464102	4.242641	9.797959
	2	7.483315	2.449490	3.741657	9.165151
	3	8.485281	1.414214	2.828427	8.000000
	4	9.486833	0	0	6.000000
5	0	6.480741	5.477226	5.477226	12.000000
	1	7.483315	4.472136	5.291503	11.832159
	2	8.485281	3.464102	4.898979	11.313709
	3	9.486833	2.449490	4.242641	10.392304
	4	10.488088	1.414214	3.162278	8.944272
	5	11.489125	0	0	0
6	0	7.483315	6.480741	6.480741	14.000000
	1	8.485281	5.477226	6.324555	13.856406
	2	9.486833	4.472136	6.000000	13.416407
	3	10.488088	3.464102	5.477226	12.649110
	4	11.489125	2.449490	4.690416	11.489125
	5	12.489996	1.414214	3.464102	9.797959
	6	13.490737	0	0	7.211102

APPENDIX D

aa-type

1-1, $G(J,J+1)G(J,J+1)$

$$\begin{bmatrix} h(J,0)^2 & 0 & 0 \\ 0 & h(J,2)^2 & 0 \\ 0 & 0 & h(J,4)^2 \end{bmatrix}$$

$J,E^+ - J,E^+$

$J+2/2 \times J+2/2$

$(7a,7a^+)$

1-2, $G(J,J)G(J,J)$

$$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 4^2 & 0 & 0 \\ 0 & 0 & 8^2 & 0 \\ 0 & 0 & 0 & 12^2 \end{bmatrix}$$

$J,E^+ - J,E^+$

$J+2/2 \times J+2/2$

$(1a,1a^+)$

2-1, $G(J,J+1)G(J,J+1)$

$$\begin{bmatrix} h(J,1)^2 & 0 & 0 \\ 0 & h(J,3)^2 & 0 \\ 0 & 0 & h(J,5)^2 \end{bmatrix}$$

$J,0^+ - J,0^+$

$J+1/2 \times J+1/2$

$(8a,8a^+)$

2-2, $G(J,J)G(J,J)$

$$\begin{bmatrix} 2^2 & 0 & 0 \\ 0 & 6^2 & 0 \\ 0 & 0 & 10^2 \end{bmatrix}$$

$J,0^+ - J,0^+$

$J+1/2 \times J+1/2$

$(2a,2a^+)$

3-1, $G(J,J+1)G(J,J+1)$

Same as M_n = 2-1

$J,0^- - J,0^-$

$J+1/2 \times J+1/2$

$(9a,9a^+)$

3-2, G(J,J)G(J,J)

Same as M_n = 2-2

$J,0^- - J,0^-$

J+1/2 x J+1/2

$(2a^+, 2a)$

4-1, G(J,J+1)G(J,J+1)

$$\begin{bmatrix} h(J,2)^2 & 0 & 0 \\ 0 & h(J,4)^2 & 0 \\ 0 & 0 & h(J,6)^2 \end{bmatrix}$$

$J,E^- - J,E^-$

J/2 x J/2

$(10a, 10a^+)$

4-2, G(J,J)G(J,J)

$$\begin{bmatrix} 4^2 & 0 & 0 \\ 0 & 8^2 & 0 \\ 0 & 0 & 12^2 \end{bmatrix}$$

$J,E^- - J,E^-$

J/2 x J/2

$(1a^+, 1a)$

5-1, G(J,J)G(J,J+1)

$$\begin{bmatrix} 0 & 0 & 0 \\ 4h(J,2) & 0 & 0 \\ 0 & 8h(J,4) & 0 \end{bmatrix}$$

$J,E^+ - J+1,E^-$

J+2/2 x J+1/2

(1a,10a)

5-2, G(J,J+1)G(J+1,J+1)

Same as M_n = 5-1

$J,E^+ - J+1,E^-$

J+2/2 x J+1/2

(7a,1a)

6-1, G(J,J)G(J,J+1)

$$\begin{bmatrix} 2h(J,1) & 0 & 0 \\ 0 & 6h(J,3) & 0 \\ 0 & 0 & 10h(J,5) \end{bmatrix}$$

$J,0^+ - J+1,0^-$

J+1/2 x J+2/2

(2a,9a)

6-2, $G(J,J+1)G(J+1,J+1)$ $J,0^+ - J+1,0^-$

Same as M_n = 6-1 $J+1/2 \times J+2/2$

$(8a,\underline{2a})$

7-1, $G(J,J)G(J,J+1)$ $J,0^- - J+1,0^+$

Same as M_n = 6-1 $J+1/2 \times J+2/2$

$(2a^+,8a)$

7-2, $G(J,J+1)G(J+1,J+1)$ $J,0^- - J+1,0^+$

Same as M_n = 6-1 $J+1/2 \times J+2/2$

$(9a,\underline{2a}^+)$

8-1, $G(J,J)G(J,J+1)$

$$\begin{bmatrix} 0 & 4h(J,2) & 0 \\ 0 & 0 & 8h(J,4) \\ 0 & 0 & 0 \end{bmatrix}$$

$J,E^- - J+1,E^+$

$J/2 \times J+3/2$

$(1a^+,7a)$

8-2, $G(J,J+1)G(J+1,J+1)$ $J,E^- - J+1,E^+$

Same as M_n = 8-1 $J/2 \times J+3/2$

$(10a,\underline{1a}^+)$

9-1, $G(J,J+1)G(J+1,J+2)$

$$\begin{bmatrix} h(J,0)h(J+1,0) & 0 & 0 \\ 0 & h(J,2)h(J+1,2) & 0 \\ 0 & 0 & h(J,4)h(J+1,4) \end{bmatrix}$$

$J,E^+ - J+2,E^+$

$J+2/2 \times J+4/2$

$(7a,\underline{7a})$

10-1, $G(J,J+1)G(J+1,J+2)$

$$\begin{bmatrix} h(J,1)h(J+1,1) & 0 & 0 \\ 0 & h(J,3)h(J+1,3) & 0 \\ 0 & 0 & h(J,5)h(J+1,5) \end{bmatrix}$$

$J,0^+ - J+2,0^+$

$J+1/2 \times J+3/2$

$(8a,\underline{8a})$

11-1, $G(J,J+1)G(J+1,J+2)$ $J,0^- - J+2,0^-$

Same as M_n = 10-1 $J+1/2 \times J+3/2$

(9a,9a)

12-1, $G(J,J+1)G(J+1,J+2)$

$$\begin{bmatrix} h(J,2)h(J,2) & 0 & 0 \\ 0 & h(J,4)h(J,4) & 0 \\ 0 & 0 & h(J,6)h(J,6) \end{bmatrix}$$

$J,E^- - J+2,E^-$

$J/2 \times J+2/2$

(10a,10a)

bb-type

13-1, $G(J,J+1)G(J,J+1)$

$$\begin{bmatrix} 2a(J,0)^2 & \sqrt{2}a(J,0)b(J,1) & 0 \\ \sqrt{2}a(J,0)b(J,1) & b(J,1)^2+a(J,2)^2 & a(J,2)b(J,3) \\ 0 & a(J,2)b(J,3) & b(J,3)^2+a(J,4)^2 \end{bmatrix}$$

$J,E^+ - J,E^+$

$J+2/2 \times J+2/2$

(11b,11b$^+$)

13-2, $G(J,J)G(J,J)$

$$\begin{bmatrix} 2g(J,0)^2 & -\sqrt{2}g(J,0)g(J,1) & 0 \\ -\sqrt{2}g(J,0)g(J,1) & g(J,1)^2+g(J,2)^2 & -g(J,2)g(J,3) \\ 0 & -g(J,2)g(J,3) & g(J,3)^2+g(J,4)^2 \end{bmatrix}$$

$J,E^+ - J,E^+$

$J+2/2 \times J+2/2$

(3b,3b$^+$)

14-1, $G(J,J+1)G(J,J+1)$

$$\begin{bmatrix} 2b(J,0)^2+a(J,1)^2 & a(J,1)b(J,2) & 0 \\ a(J,1)b(J,2) & b(J,2)^2+a(J,3)^2 & a(J,3)b(J,4) \\ 0 & a(J,3)b(J,4) & b(J,4)^2+a(J,5)^2 \end{bmatrix}$$

14-1 (Continued)

$J,0^+ - J,0^+$

$J+1/2 \times J+1/2$

$(13b,13b^+)$

14-2, $G(J,J)G(J,J)$

$$\begin{bmatrix} g(J,1)^2 & -g(J,1)g(J,2) & 0 \\ -g(J,1)g(J,2) & g(J,2)^2+g(J,3)^2 & -g(J,3)g(J,4) \\ 0 & -g(J,3)g(J,4)^2 & g(J,4)^2g(J,5)^2 \end{bmatrix}$$

$J,0^+ - J,0^+$

$J+1/2 \times J+1/2$

$(4b,4b^+)$

15-1, $G(J,J+1)G(J,J+1)$

$$\begin{bmatrix} a(J,1)^2 & a(J,1)b(J,2) & 0 \\ a(J,1)b(J,2) & b(J,2)^2+a(J,3)^2 & a(J,3)b(J,4) \\ 0 & a(J,3)b(J,4) & b(J,4)^2+a(J,5)^2 \end{bmatrix}$$

$J,0^- - J,0^-$

$J+1/2 \times J+1/2$

$(14b,14b^+)$

15-2, $G(J,J)G(J,J)$

$$\begin{bmatrix} 2g(J,0)^2+g(J,1)^2 & -g(J,1)g(J,2) & 0 \\ -g(J,1)g(J,2) & g(J,2)^2+g(J,3)^2 & -g(J,3)g(J,4) \\ 0 & -g(J,5)g(J,4) & g(J,4)^2+g(J,5)^2 \end{bmatrix}$$

15-2 (Continued) $J,0^- - J,0^-$

$J+1/2 \times J+1/2$

$(3b^+,3b)$

16-1, $G(J,J+1)G(J,J+1)$

$$\begin{bmatrix} b(J,1)^2+a(J,2)^2 & a(J,2)b(J,3) & 0 \\ a(J,2)b(J,3) & b(J,3)^2+a(J,4)^2 & a(J,4)b(J,5) \\ 0 & a(J,4)b(J,5) & b(J,5)^2+a(J,6)^2 \end{bmatrix}$$

$J,E^- - J,E^-$

$J/2 \times J/2$

$(12b,12b^+)$

16-2, $G(J,J)G(J,J)$

$$\begin{bmatrix} g(J,1)^2+g(J,2)^2 & -g(J,4)g(J,5) & 0 \\ -g(J,2)g(J,3) & g(J,3)^2+g(J,4)^2 & -g(J,4)g(J,5) \\ 0 & -g(J,4)g(J,5) & g(J,5)^2g(J,6)^2 \end{bmatrix}$$

$J,E^- - J,E^-$

$J/2 \times J/2$

$(4b^+,4b)$

17-1, $G(J,J)G(J,J+1)$; $J,E^+ - J+1,E^-$ $J+2/2 \times J+1/2$ $(3b,14b)$

$$\begin{bmatrix} \sqrt{2}g(J,0)a(J,1) & 0 \\ -g(J,1)a(J,1)+g(J,2)b(J,2) & g(J,2)a(J,3) \\ -g(J,3)b(J,2) & -g(J,3)a(J,3)+g(J,4)b(J,4) \\ 0 & -g(J,5)b(J,4) \end{bmatrix}$$

17-2, $-G(J,J+1)G(J+1,J+1)$; $J,E^+ - J+1,E^-$ $J+2/2 \times J+1/2$ (11b,4b)

$$\begin{bmatrix} -\sqrt{2}a(J,0)g(J',1) & 0 \\ -b(J,1)g(J',1)+a(J,2)g(J',2) & -a(J,2)g(J',3) \\ b(J,3)g(J',2) & -b(J,3)g(J',3)+a(J,4)g(J',4) \\ 0 & b(J,5)g(J',4) \end{bmatrix}$$

18-1, $G(J,5)G(J,J+1) \times (-1)$; $J,0^+ - J+1,0^-$ $J+1/2 \times J+2/2$ (4b,12b)

$$\begin{bmatrix} -b(J,1)g(J,1) & -g(J,1)a(J,2) & 0 \\ b(J,1)g(J,2) & a(J,2)g(J,2)-b(J,3)g(J,3) & -g(J,3)a(J,4) \\ 0 & -b(J,3)g(J,4) & a(J,4)g(J,4)-b(J,5)g(J,5) \end{bmatrix}$$

18-2, $G(J,J+1)G(J+1,J+1) \times (+1)$; $J,0^+ - J+1,0^-$ $J+1/2 \times J+2/2$ (13b,3b)

$$\begin{bmatrix} 2b(J,0)g(J',0)-a(J,1)g(J',1) & a(J,1)g(J',2) & 0 \\ -b(J,2)g(J',1) & b(J,2)g(J',2)-a(J,3)g(J',3) & a(J,3)g(J',4) \\ 0 & -b(J,4)g(J',3) & b(J,4)g(J',4)-a(J,5)g(J',5) \end{bmatrix}$$

19-1, $G(J,J)G(J,J+1) \times (-1)$; $J,0^- - J+1,0^+$ $J+1/2 \times J+2/2$ ($3b^+$,11b)

$$\begin{bmatrix} 2a(J,0)g(J,0)-b(J,1)g(J,1) & -a(J,2)g(J,1) & 0 \\ b(J,1)g(J,2) & a(J,2)g(J,2)-b(J,3)g(J,3) & -a(J,4)g(J,3) \\ 0 & b(J,3)g(J,4) & a(J,4)g(J,4)-b(J,5)g(J,5) \end{bmatrix}$$

19-2, $G(J,J+1)G(J+1,J+1) \times (+1)$; $J,0^- - J+1,0^+$ $J+1/2 \times J+2/2$ (14b,$4b^+$)

$$\begin{bmatrix} -a(J,1)g(J',1) & a(J,1)g(J',2) & 0 \\ -b(J,2)g(J',1) & b(J,2)g(J',2)-a(J,3)g(J',3) & a(J,3)g(J',4) \\ 0 & -b(J,4)g(J',3) & b(J,4)g(J',4)-a(J,5)g(J',5) \end{bmatrix}$$

20-1, $G(J,J)G(J,J+1)$ x $(+1)$; $J,E^- - J+1,E^+$ $J/2$ x $J+3/2$ $(4b^+,13b)$

$$\begin{bmatrix} -\sqrt{2}b(J,0)g(J,1) & -a(J,1)g(J,1)+b(J,2)g(J,2) & a(J,3)g(J,2) & 0 \\ 0 & -b(J,2)g(J,3) & -a(J,3)g(J,3)+b(J,4)g(J,4) & a(J,5)g(J,4) \end{bmatrix}$$

20-2, $G(J,J+1)G(J+1,J+1)$ x (-1); $J,E^- - J+1,E^+$ $J/2$ x $J+3/2$ $(12b,\underline{3b}^+)$

$$\begin{bmatrix} \sqrt{2}b(J,1)g(J',0) & -b(J,1)g(J',1)+a(J,2)g(J',2) & -a(J,2)g(J',3) & 0 \\ 0 & b(J,3)g(J',2) & -b(J,3)g(J',3)+a(J,4)g(J',4) & -a(J,4)g(J',5) \end{bmatrix}$$

21-1, $G(J,J+1)G(J+1,J+2)$ x (-1); $J,E^+ - J+2,E^+$ $J+2/2$ x $J+4/2$ $(11b,\underline{13b})$

$$\begin{bmatrix} 2a(J,0)b(J',0) & \sqrt{2}a(J,0)a(J',1) & 0 \\ \sqrt{2}b(J,0)b(J',1) & a(J',1)b(J,1)+a(J,2)b(J',2) & a(J,2)a(J',3) \\ 0 & b(J',2)b(J,3) & a(J',3)b(J,3)+a(J,4)b(J',4) \end{bmatrix}$$

22-1, $G(J,J+1)G(J+1,J+2)$ x (-1); $J,0^+ - J+2,0^+$ $J+1/2$ x $J+3/2$ $(13b,\underline{11b})$

$$\begin{bmatrix} 2a(J',0)b(J,0)+a(J,1)b(J',1) & a(J,1)a(J',2) & 0 \\ b(J',1)b(J,2) & a(J',2)b(J,2)+a(J,3)b(J',3) & a(J,3)a(J',4) \\ 0 & b(J',3)b(J,4) & a(J',4)b(J,4)+a(J,5)b(J',5) \end{bmatrix}$$

23-1, $G(J,J+1)G(J+1,J+2)$ x (-1); $J,0^- - J+2,0^-$ $J+1/2$ x $J+3/2$ $(14b,\underline{12b})$

$$\begin{bmatrix} a(J,1)b(J',1) & a(J,1)a(J',2) & 0 \\ b(J',1)b(J,2) & a(J',2)b(J,2)+a(J,3)b(J',3) & a(J,3)a(J',4) \\ 0 & b(J',3)b(J,4) & a(J',4)b(J,4)+a(J,5)b(J',5) \end{bmatrix}$$

24-1, $G(J,J+1)G(J+1,J+2)$ x (-1); $J,E^- - J+2,E^-$ $J/2$ x $J+2/2$ $(12b,\underline{14b})$

$$\begin{bmatrix} a(J',1)b(J,1)+a(J,2)b(J',2) & a(J,2)a(J',3) & 0 \\ b(J',2)b(J,3) & a(J',3)b(J,3)+a(J,4)b(J',4) & a(J,4)a(J',5) \\ 0 & b(J',4)b(J,5) & a(J',5)b(J,5)+a(J,6)b(J',6) \end{bmatrix}$$

cc-type

25-1, $G(J,J+1)G(J,J+1)$; $J,E^+ - J,E^+$ $J+2/2 \times J+2/2$ $(15c,15c^+)$

$$\begin{bmatrix} 2a(J,0)^2 & -\sqrt{2}a(J,0)b(J,1) & 0 \\ -\sqrt{2}a(J,0)b(J,1) & b(J,1)^2+a(J,2)^2 & -a(J,2)b(J,3) \\ 0 & -a(J,2)b(J,3) & b(J,3)^2+a(J,4)^2 \end{bmatrix}$$

25-2, $G(J,J)G(J,J)$; $J,E^+ - J,E^+$ $J+2/2 \times J+2/2$ $(5c,5c^+)$

$$\begin{bmatrix} 2g(J,0)^2 & \sqrt{2}g(J,0)g(J,1) & 0 \\ \sqrt{2}g(J,0)g(J,1) & g(J,1)^2+g(J,2)^2 & g(J,2)g(J,3) \\ 0 & g(J,2)g(J,3) & g(J,3)^2+g(J,4)^2 \end{bmatrix}$$

26-1, $G(J,J+1)G(J,J+1)$; $J,0^+ - J,0^+$ $J+1/2 \times J+1/2$ $(17c,17c^+)$

$$\begin{bmatrix} a(J,1)^2 & -a(J,1)b(J,2) & 0 \\ -a(J,1)b(J,2) & b(J,2)^2+a(J,3)^2 & -a(J,3)b(J,4) \\ 0 & -a(J,3)b(J,4) & b(J,4)^2+a(J,5)^2 \end{bmatrix}$$

26-2, $G(J,J)G(J,J)$; $J,0^+ - J,0^+$ $J+1/2 \times J+1/2$ $(5c^+,5c)$

$$\begin{bmatrix} 2g(J,0)^2+g(J,1)^2 & g(J,1)g(J,2) & 0 \\ g(J,1)g(J,2) & g(J,2)^2+g(J,3)^2 & g(J,3)g(J,4) \\ 0 & g(J,3)g(J,4) & g(J,4)^2+g(J,5)^2 \end{bmatrix}$$

27-1, $G(J,J+1)G(J,J+1)$; $J,0^- - J,0^-$ $J+1/2 \times J+1/2$ $(18c,18c^+)$

$$\begin{bmatrix} 2b(J,0)^2+a(J,1)^2 & -a(J,1)b(J,2) & 0 \\ -a(J,1)b(J,2) & b(J,2)^2+a(J,3)^2 & -a(J,3)b(J,4) \\ 0 & -a(J,3)b(J,4) & b(J,4)^2+a(J,5)^2 \end{bmatrix}$$

27-2, $G(J,J)G(J,J)$; $J,0^- - J,0^-$ $J+1/2 \times J+1/2$ $(6c,6c^+)$

$$\begin{bmatrix} g(J,1)^2 & g(J,1)g(J,2) & 0 \\ g(J,1)g(J,2) & g(J,2)^2+g(J,3)^2 & g(J,3)g(J,4) \\ 0 & g(J,3)g(J,4) & g(J,4)^2+g(J,5)^2 \end{bmatrix}$$

28-1, $G(J,J+1)G(J,J+1)$; $J,E^- - J,E^-$ $J/2 \times J/2$ $(16c,16c^+)$

$$\begin{bmatrix} b(J,1)^2+a(J,2)^2 & -a(J,2)b(J,3) & 0 \\ -a(J,2)b(J,3) & b(J,3)^2+a(J,4)^2 & -a(J,4)b(J,5) \\ 0 & -a(J,4)b(J,5) & b(J,5)^2+a(J,6)^2 \end{bmatrix}$$

28-2, $G(J,J)G(J,J)$; $J,E^- - J,E^-$ $J/2 \times J/2$ $(6c^+,6c)$

$$\begin{bmatrix} g(J,1)^2+g(J,2)^2 & g(J,2)g(J,3) & 0 \\ g(J,2)g(J,3) & g(J,3)^2+g(J,4)^2 & g(J,4)g(J,5) \\ 0 & g(J,4)g(J,5) & g(J,5)^2+g(J,6)^2 \end{bmatrix}$$

29-1, $G(J,J)G(J,J+1)$; $J,E^+ - J+1,E^-$ $J+2/2 \times J+1/2$ $(5c,17c)$

$$\begin{bmatrix} -\sqrt{2}a(J,1)g(J,0) & 0 \\ -a(J,1)g(J,1)+b(J,2)g(J,2) & -a(J,3)g(J,2) \\ b(J,2)g(J,3) & -a(J,3)g(J,3)+b(J,4)g(J,4) \\ 0 & b(J,4)g(J,5) \end{bmatrix}$$

29-2, $G(J,J+1)G(J+1,J+1)$; $J,E^+ - J+1,E^-$ $J+2/2 \times J+1/2$ $(15c,\underline{6c})$

$$\begin{bmatrix} -\sqrt{2}a(J,0)g(J',1) & 0 \\ b(J,1)g(J',1)-a(J,2)g(J',2) & -a(J,2)g(J',3) \\ b(J,3)g(J',2) & b(J,3)g(J',3)-a(J,4)g(J',4) \\ 0 & b(J,5)g(J',4) \end{bmatrix}$$

30-1, $G(J,J)G(J,J+1)$; $J,0^+ - J+1,0^-$ $J+1/2 \times J+2/2$ $(5c^+,15c)$

$$\begin{bmatrix} -2a(J,0)g(J,0)+b(J,1)g(J,1) & -a(J,2)g(J,1) & 0 \\ b(J,1)g(J,2) & -a(J,2)g(J,2)+b(J,3)g(J,3) & -a(J,4)g(J,3) \\ 0 & b(J,3)g(J,4) & -a(J,4)g(J,4)+b(J,5)g(J,5) \end{bmatrix}$$

30-2, $G(J,J+1)G(J+1,J+1)$; $J,0^+ - J+1,0^-$ $J+1/2 \times J+2/2$ $(17c, \underline{6c}^+)$

$$\begin{bmatrix} -a(J,1)g(J',1) & -a(J,1)g(J',2) & 0 \\ b(J,2)g(J',1) & b(J,2)g(J',2)-a(J,3)g(J',3) & -a(J,3)g(J',4) \\ 0 & b(J,4)g(J',3) & b(J,4)g(J',4)-a(J,5)g(J',5) \end{bmatrix}$$

31-1, $G(J,J)G(J,J+1)$; $J,0^- + J+1,0^+$ $J+1/2 \times J+2/2$ $(6c,16c)$

$$\begin{bmatrix} b(J,1)g(J,1) & -a(J,2)g(J,1) & 0 \\ b(J,1)g(J,2) & -a(J,2)g(J,2)+b(J,3)g(J,3) & -a(J,4)g(J,3) \\ 0 & b(J,3)g(J,4) & -a(J,4)g(J,4)+b(J,5)g(J,5) \end{bmatrix}$$

31-2, $G(J,J+1)G(J+1,J+1)$; $J,0^- - J+1,0^+$ $J+1/2 \times J+2/2$ $(18c,\underline{5c})$

$$\begin{bmatrix} 2b(J,0)g(J',0)-a(J,1)g(J',1) & -a(J,1)g(J',2) & 0 \\ b(J,2)g(J',1) & b(J,2)g(J',2)-a(J,3)g(J',3) & -a(J,3)g(J',4) \\ 0 & b(J,4)g(J',3) & b(J,4)g(J',4)-a(J,5)g(J',5) \end{bmatrix}$$

32-1, $G(J,J)G(J,J+1)$; $J,E^- - J+1,E^+$ $J/2 \times J+3/2$ $(6c^+,18c)$

$$\begin{bmatrix} \sqrt{2}b(J,0)g(J,1) & -a(J,1)g(J,1)+b(Jc2)g(J,2) & -a(J,3)g(J,2) & 0 \\ 0 & b(J,2)g(J,3) & -a(J,3)g(J,3)+b(J,4)g(J,4) & -a(J,5)g(J,4) \end{bmatrix}$$

32-2, $G(J,J+1)G(J+1,J+1)$; $J,E^- - J+1,E^+$ $J/2$ x $J+3/2$ (16c,5c$^+$)

$$\begin{bmatrix} \sqrt{2}b(J,1)g(J',0) & b(J,1)g(J',1)-a(J,2)g(J',2) & -a(J,2)g(J',3) & 0 \\ 0 & b(J,3)g(J',2) & b(J,3)g(J',3)-a(J,4)g(J',4) & -a(J,4)g(J',5) \end{bmatrix}$$

33-1, $G(J,J+1)G(J+1,J+2)$; $J,E^+ - J+2,E^+$ $J+2/2$ x $J+4/2$ (15c,18c)

$$\begin{bmatrix} -2a(J,0)b(J',0) & 2a(J,0)a(J',1) & 0 \\ \sqrt{2}b(J',0)b(J,1) & -b(J,1)a(J',1)-a(J,2)b(J',2) & a(J,2)a(J',3) \\ 0 & b(J',2)b(J,3) & -b(J,3)a(J',3)-a(J,4)b(J',4) \end{bmatrix}$$

34-1, $G(J,J+1)G(J+1,J+2)$; $J,0^+ - J+2,0^+$ $J+1/2$ x $J+3/2$ (17c,16c)

$$\begin{bmatrix} -a(J,1)b(J',1) & a(J,1)a(J',2) & 0 \\ b(J',1)b(J,2) & -a(J',2)b(J,2)-a(J,3)b(J',3) & a(J,3)a(J',4) \\ 0 & b(J',3)b(J,4) & -a(J',4)b(J,4)-a(J,5)b(J',5) \end{bmatrix}$$

35-1, $G(J,J+1)G(J+1,J+2)$; $J,0^- - J+2,0^-$ $J+1/2$ x $J+3/2$ (18c,15c)

$$\begin{bmatrix} -2a(J',0)b(J,0)-a(J,1)b(J',1) & a(J,1)a(J',2) & 0 \\ b(J',1)b(J,2) & -a(J',2)b(J,2)-a(J,3)b(J',3) & a(J,3)a(J',4) \\ 0 & b(J',3)b(J,4) & -a(J',4)b(J,4)-a(J,5)b(J',5) \end{bmatrix}$$

36-1, $G(J,J+1)G(J+1,J+2)$; $J,E^- - J+2,E^-$ $J/2$ x $J+2/2$ (16c,17c)

$$\begin{bmatrix} -a(J',1)b(J,1)-a(J,2)b(J',2) & a(J,2)a(J',3) & 0 \\ b(J',2)b(J,3) & -a(J',3)b(J,3)-a(J,4)b(J',4) & a(J,4)a(J',5) \\ 0 & b(J',4)b(J,5) & -a(J',5)b(J,5)-a(J,6)b(J',6) \end{bmatrix}$$

ab-type

37-1, $iG(J,J+1)G(J,J+1)$; $J,E^+ - J,O^+$ $J+2/2$ **x** $J+1/2$ $(7\mathbf{a},13b^+)$

$$\begin{bmatrix} \sqrt{2}b(J,0)h(J,0) & 0 & 0 \\ \mathbf{a}(J,1)h(J,2) & b(J,2)h(J,2) & 0 \\ 0 & \mathbf{a}(J,3)h(J,4) & b(J,4)h(J,4) \end{bmatrix}$$

37-2, $iG(J,J)G(J,J)$; $J,E^+ - J,O^+$ $J+2/2$ **x** $J+1/2$ $(1\mathbf{a},4b^+)$

$$\begin{bmatrix} 0 & 0 & 0 \\ -4g(J,1) & 4g(J,2) & 0 \\ 0 & -8g(J,3) & 8g(J,4) \end{bmatrix}$$

38-1, $iG(J,J+1)G(J,J+1)$; $J,O^- - J,E^-$ $J+1/2$ **x** $J/2$ $(9\mathbf{a},12b^+)$

$$\begin{bmatrix} b(J,1)h(J,1) & 0 & 0 \\ \mathbf{a}(J,2)h(J,3) & b(J,3)h(J,3) & 0 \\ 0 & \mathbf{a}(J,4)h(J,5) & b(J,5)h(J,5) \end{bmatrix}$$

38-2, $-iG(J,J)G(J+J)$; $J,O^- - J,E^-$ $J+1/2$ **x** $J/2$ $(2\mathbf{a}^+,4b)$

$$\begin{bmatrix} -2g(J,1) & 0 & 0 \\ 6g(J,2) & -6g(J,3) & 0 \\ 0 & 10g(J,4) & -10g(J,5) \end{bmatrix}$$

39-1, $-iG(J,J)G(J,J+1)$; $J,E^+ - J+1,O^-$ $J+2/2$ **x** $J+2/2$ $(1\mathbf{a},12b)$

$$\begin{bmatrix} 0 & 0 & 0 \\ 4b(J,1) & 4\mathbf{a}(J,2) & 0 \\ 0 & 8b(J,3) & 8\mathbf{a}(J,4) \end{bmatrix}$$

39-2, $iG(J,J+1)G(J+1,J+1)$; $J,E^+ - J+1,0^-$ J+2/2 x J+2/2 (7a,3b)

$$\begin{bmatrix} \sqrt{2}h(J,0)g(J',0) & 0 & 0 \\ -h(J,2)g(J',1) & h(J,2)g(J',2) & 0 \\ 0 & -h(J,4)g(J',3) & h(J,4)g(J',4) \end{bmatrix}$$

40-1, $-iG(J,J)G(J,J+1)$; $J,0^+ - J+1,E^-$ J+1/2 x J+1/2 (2a,14b)

$$\begin{bmatrix} 2a(J,1) & 0 & 0 \\ 6b(J,2) & 6a(J,3) & 0 \\ 0 & 10b(J,4) & 10a(J,5) \end{bmatrix}$$

40-2, $-iG(J,J+1)G(J+1,J+1)$; $J,0^+ - J+1,E^-$ J+1/2 x J+1/2 (8a,4b)

$$\begin{bmatrix} -h(J,1)g(J',1) & 0 & 0 \\ h(J,3)g(J',2) & -h(J,3)g(J',3) & 0 \\ 0 & h(J,5)g(J',4) & -h(J,5)g(J',5) \end{bmatrix}$$

41-1, $-iG(J,J)G(J,J+1)$; $J,0^- - J+1,E^+$ J+1/2 x J+3/2 ($2a^+$,13b)

$$\begin{bmatrix} 2\sqrt{2}b(J,0) & 2a(J,1) & 0 \\ 0 & 6b(J,2) & 6a(J,3) \\ 0 & 0 & 10b(J,4) \end{bmatrix}$$

41-2, $-iG(J,J+1)G(J+1,J+1)$; $J,0^- - J+1,E^+$ J+1/2 x J+3/2 (9a,$3b^+$)

$$\begin{bmatrix} \sqrt{2}h(J,1)g(J',0) & -h(J,1)g(J',1) & 0 \\ 0 & h(J,3)g(J',2) & -h(J,3)g(J',3) \\ 0 & 0 & h(J,5)g(J',4) \end{bmatrix}$$

42-1, $-iG(J,J)G(J,J+1)$; $J,E^- - J+1,0^+$ J/2 x J+2/2 ($1a^+$,11b)

$$\begin{bmatrix} 4b(J,1) & 4a(J,2) & 0 \\ 0 & 8b(J,3) & 8a(J,4) \\ 0 & 0 & 12b(J,5) \end{bmatrix}$$

42-2, $iG(J,J+1)G(J+1,J+1)$; $J,E^- - J+1,0^+$ $J/2 \times J+2/2$ (10a,4b$^+$)

$$\begin{bmatrix} -h(J,2)g(J',1) & h(J,2)g(J',2) & 0 \\ 0 & -h(J,4)g(J',3) & h(J,4)g(J',4) \\ 0 & 0 & -h(J,6)g(J',5) \end{bmatrix}$$

43-1, $-iG(J,J+1)G(J+1,J+2)$; $J,E^+ - J+2,0^+$ $J+2/2 \times J+3/2$ (7a,11b)

$$\begin{bmatrix} \sqrt{2}a(J',0)h(J,0) & 0 & 0 \\ b(J',1)h(J,2) & a(J',2)h(J,2) & 0 \\ 0 & b(J',3)h(J,4) & a(J',4)h(J,4) \end{bmatrix}$$

44-1, $-iG(J,J+1)G(J+1,J+2)$; $J,0^+ - J+2,E^+$ $J+1/2 \times J+4/2$ (8a,13b)

$$\begin{bmatrix} \sqrt{2}b(J',0)h(J,1) & a(J',1)h(J,1) & 0 \\ 0 & b(J',2)h(J,3) & a(J',3)h(J,3) \\ 0 & 0 & b(J',4)h(J,5) \end{bmatrix}$$

45-1, $-iG(J,J+1)G(J+1,J+2)$; $J,0^- - J+2,E^-$ $J+1/2 \times J+2/2$ (9a,14b)

$$\begin{bmatrix} a(J',1)h(J,1) & 0 & 0 \\ b(J',2)h(J,3) & a(J',3)h(J,3) & 0 \\ 0 & b(J',4)h(J,5) & a(J',5)h(J,5) \end{bmatrix}$$

46-1, $-iG(J,J+1)G(J+1,J+2)$; $J,E^- - J+2,0^-$ $J/2 \times J+3/2$ (10a,12b)

$$\begin{bmatrix} b(J',1)h(J,2) & a(J',2)h(J,2) & 0 \\ 0 & b(J',3)h(J,4) & a(J',4)h(J,4) \\ 0 & 0 & b(J',5)h(J,6) \end{bmatrix}$$

a-type

47-1, $G(J,J+1)G(J,J+1)$; $J,E^+ - J,0^-$ $J+2/2$ x $J+1/2$ (7a,18c$^+$)

$$\begin{bmatrix} \sqrt{2}b(J,0)h(J,0) & 0 & 0 \\ -a(J,1)h(J,2) & b(J,2)h(J,2) & 0 \\ 0 & -a(J,3)h(J,4) & b(J,4)h(J,4) \end{bmatrix}$$

47-2, $G(J,J)G(J,J)$; $J,E^+ - J,0^-$ $J+2/2$ x $J+1/2$ (1a,6c$^+$)

$$\begin{bmatrix} 0 & 0 & 0 \\ 4g(J,1) & 4g(J,2) & 0 \\ 0 & 8g(J,3) & 8g(J,4) \end{bmatrix}$$

48-1, $G(J,J+1)G(J,J+1)$; $J,0^+ - J,E^-$ $J+1/2$ x $J/2$ (8a,16c$^+$)

$$\begin{bmatrix} b(J,1)h(J,1) & 0 & 0 \\ -a(J,2)h(J,3) & b(J,3)h(J,3) & 0 \\ 0 & -a(J,4)h(J,5) & b(J,5)h(J,5) \end{bmatrix}$$

48-2, $G(J,J)G(J,J)$; $J,0^+ - J,E^-$ $J+1/2$ x $J/2$ (2a,6c)

$$\begin{bmatrix} 2g(J,1) & 0 & 0 \\ 6g(J,2) & 6g(J,3) & 0 \\ 0 & 10g(J,4) & 10g(J,5) \end{bmatrix}$$

49-1, $G(J,J)G(J,J+1)$; $J,E^+ - J+1,0^+$ $J+2/2$ x $J+2/2$ (1a,16c)

$$\begin{bmatrix} 0 & 0 & 0 \\ 4b(J,1) & -4a(J,2) & 0 \\ 0 & 8b(J,3) & -8a(J,4) \end{bmatrix}$$

49-2, $G(J,J+1)G(J+1,J+1)$; $J,E^+ - J+1,0^+$ $J+2/2$ x $J+2/2$ (7a,5c)

$$\begin{bmatrix} \sqrt{2}h(J,0)g(J',0) & 0 & 0 \\ h(J,2)g(J',1) & h(J,2)g(J',2) & 0 \\ 0 & h(J,4)g(J',3) & h(J,4)g(J',4) \end{bmatrix}$$

50-1, G(J,J)G(J,J+1); $J,O^+ - J+1,E^+$ J+1/2 x J+3/2 (2a,18c)

$$\begin{bmatrix} 2\ 2b(J,0) & -2a(J,1) & 0 \\ 0 & 6b(J,2) & -6a(J,3) \\ 0 & 0 & 10b(J,4) \end{bmatrix}$$

50-2, G(J,J+1)G(J+1,J+1); $J,O^+ - J+1,E^+$ J+1/2 x J+3/2 (8a,$\underline{5c}^+$)

$$\begin{bmatrix} 2h(J,1)g(J',0) & h(J,L)g(J',1) & 0 \\ 0 & h(J,3)g(J',2) & h(J,3)g(J',3) \\ 0 & 0 & h(j,5)g(J',4) \end{bmatrix}$$

51-1, G(J,J)G(J,J+1); $J,O^- - J+1,E^-$ J+1/2 x J+1/2 ($2a^+$,17c)

$$\begin{bmatrix} -2a(J,1) & 0 & 0 \\ 6b(J,2) & -6a(J,3) & 0 \\ 0 & 10b(J,4) & -10a(J,5) \end{bmatrix}$$

51-2, G(J,J+1)G(J+1,J+1); $J,O^- - J+1,E^-$ J+1/2 x J+1/2 (9a,$\underline{6c}$)

$$\begin{bmatrix} h(J,1)g(J',1) & 0 & 0 \\ h(J,3)g(J',2) & h(J,3)g(J',3) & 0 \\ 0 & h(J,5)g(J',4) & h(J,5)g(J',5) \end{bmatrix}$$

52-1, G(J,J(G(J,J+1); $J,E^- - J+1,O^-$ J/2 x J+2/2 ($1a^+$,15c)

$$\begin{bmatrix} 4b(J,1) & -4a(J,2) & 0 \\ 0 & 8b(J,3) & -8a(J,4) \\ 0 & 0 & 12b(J,5) \end{bmatrix}$$

52-2, G(J,J+1)G(J+1,J+1); $J,E^- - J+1,O^-$ J/2 x J+2/2 (10a,$\underline{6c}^+$)

$$\begin{bmatrix} h(J,2)g(J',1) & h(J,2)g(J',2) & \\ 0 & h(J,4)g(J',3) & h(J,4)g(J',4) \\ 0 & 0 & h(J,6)g(J',5) \end{bmatrix}$$

53-1, $G(J,J+1)G(J+1,J+2)$; $J,E^+ - J+2,0^-$ $J+2/2 \times J+3/2$ (7a,15c)

$$\begin{bmatrix} -\sqrt{2}a(J',0)h(J,0) & 0 & 0 \\ b(J',1)h(J,2) & -a(J',2)h(J,2) & 0 \\ 0 & b(J',3)h(J,4) & -a(J',4)h(J,4) \end{bmatrix}$$

54-1, $G(J,J+1)G(J+1,J+2)$; $J,0^+ - J+2,E^-$ $J+1/2 \times J+2/2$ (8a,17c)

$$\begin{bmatrix} -a(J',1)h(J,1) & 0 & 0 \\ b(J',2)h(J,3) & -a(J',3)h(J,3) & 0 \\ 0 & b(J',4)h(J,5) & -a(J',5)h(J,5) \end{bmatrix}$$

55-1, $G(J,J+1)G(J+1,J+2)$; $J,0^- - J+2,E^+$ $J+1/2 \times J+4/2$ (9a,18c)

$$\begin{bmatrix} \sqrt{2}b(J',0)h(J,1) & -a(J',1)h(J,1) & 0 \\ 0 & b(J',2)h(J,3) & -a(J',3)h(J,3) \\ 0 & 0 & b(J',4)h(J,5) \end{bmatrix}$$

56-1, $G(J,J+1)G(J+1,J+2)$; $J,E^- - J+2,0^+$ $J/2 \times J+3/2$ (10a,16c)

$$\begin{bmatrix} b(J',1)h(J,2) & -a(J',2)h(J,2) & 0 \\ 0 & b(J',3)h(J,4) & -a(J',4)h(J,4) \\ 0 & 0 & b(J',5)h(J,6) \end{bmatrix}$$

bc-type

57-1, $-iG(J,J+1)G(J,J+1)$; $J,E^+ - J,E^-$ $J+2/2 \times J/2$ (11b,16c$^+$)

$$\begin{bmatrix} \sqrt{2}a(J,0)b(J,1) & 0 & 0 \\ b(J,1)^2-a(J,2)^2 & a(J,2)b(J,3) & 0 \\ -a(J,2)b(J,3) & b(J,3)^2-a(J,4)^2 & a(J,4)b(J,5) \end{bmatrix}$$

57-2, $iG(J,J)G(J,J)$; $J,E^+ - J,E^-$ $J+2/2 \times J/2$ (3b,6c)

$$\begin{bmatrix} \sqrt{2}g(J,0)g(J,1) & 0 & 0 \\ -g(J,1)^2+g(J,2)^2 & g(J,2)g(J,3) & 0 \\ -g(J,2)g(J,3) & -g(J,3)^2+g(J,4)^2 & g(J,4)g(J,5) \end{bmatrix}$$

58-1, $-iG(J,J+1)G(J,J+1)$; $J,0^+ - J,0^-$ $J+1/2 \times J+1/2$ ($13b,18c^+$)

$$\begin{bmatrix} 2b(J,0)^2-a(J,1)^2 & a(J,1)b(J,2) & 0 \\ -a(J,1)b(J,2) & b(J,2)^2-a(J,3)^2 & a(J,3)b(J,4) \\ 0 & -a(J,3)b(J,4) & b(J,4)^2-a(J,5)^2 \end{bmatrix}$$

58-2, $-iG(J,J)G(J,J)$; $J,0^+ - J,0^-$ $J+1/2 \times J+1/2$ ($4b,6c^+$)

$$\begin{bmatrix} -g(J,1)^2 & -g(J,1)g(J,2) & 0 \\ g(J,1)g(J,2) & g(J,2)^2-g(J,3)^2 & -g(J,3)g(J,4) \\ 0 & g(J,3)g(J,4) & g(J,4)^2-g(J,5)^2 \end{bmatrix}$$

59-1, $iG(J,J)G(J,J+1)$; $J,E^+ - J+1,E^+$ $J+2/2 \times J+3/2$ (3b,18c)

$$\begin{bmatrix} 2b(J,0)g(J,0) & \sqrt{2}a(J,0)g(J,1) & 0 \\ \sqrt{2}b(J,1)g(J,0) & a(J,1)g(J,1)+b(J,2)g(J,2) & a(J,2)g(J,3) \\ 0 & b(J,3)g(J,2) & a(J,3)g(J,3)+b(J,4)g(J,4) \end{bmatrix}$$

59-2, $-iG(J,J+1)G(J+1,J+1)$; $J,E^+ - J+1,E^+$ $J+2/2 \times J+3/2$ (11b,$\underline{5c}^+$)

$$\begin{bmatrix} 2a(J,0)g(J',0) & \sqrt{2}a(J,0)g(J',1) & 0 \\ \sqrt{2}b(J,1)g(J',0) & b(J,1)g(J',1)+a(J,2)g(J',2) & a(J,2)g(J',3) \\ 0 & b(J,3)g(J',2) & b(J,3)g(J',3)+a(J,4)g(J',4) \end{bmatrix}$$

60-1, $-iG(J,J)G(J,J+1)$; $J,0^+ - J+1,0^+$ $J+1/2 \times J+2/2$ (4b,16c)

$$\begin{bmatrix} -b(J,1)g(J,1) & a(J,2)g(J,1) & 0 \\ b(J,1)g(J,2) & -a(J,2)g(J,2)-b(J,3)g(J,3) & a(J,4)g(J,3) \\ 0 & b(J,3)g(J,4) & -a(J,4)g(J,4)-b(J,5)g(J,5) \end{bmatrix}$$

60-2, $-iG(J,J+1)G(J+1,J+1)$; $J,0^+ - J+1,0^+$ $J+1/2 \times J+2/2$ (13b,5c)

$$\begin{bmatrix} 2b(J,0)g(J',0)+a(J,1)g(J',1) & a(J,1)g(J',2) & 0 \\ b(J,2)g(J',1) & b(J,2)g(J',2)+a(J,3)g(J',3) & a(J,3)g(J',4) \\ 0 & b(J,4)g(J',3) & b(J,4)g(J',4)+a(J,5)g(J',5) \end{bmatrix}$$

61-1, $-iG(J,J)G(J,J+1)$; $J,0^- - J+1,0^-$ $J+1/2 \times J+2/2$ ($3b^+$,15c)

$$\begin{bmatrix} -2a(J,0)g(J,0)-b(J,1)g(J,1) & a(J,2)g(J,1) & 0 \\ b(J,1)g(J,2) & -a(J,2)g(J,2)-b(J,3)g(J,3) & a(J,4)g(J,3) \\ 0 & b(J,3)g(J,4) & -a(J,4)g(J,4)-b(J,5)g(J,5) \end{bmatrix}$$

61-2, $-iG(J,J+1)G(J+1,J+1)$; $J,0^- - J+1,0^-$ $J+1/2 \times J+2/2$ ($14b,6c^+$)

$$\begin{bmatrix} a(J,1)g(J',1) & a(J,1)g(J',2) & 0 \\ b(J,2)g(J',1) & b(J,2)g(J',2)+a(J,3)g(J',3) & a(J,3)g(J',4) \\ 0 & b(J,4)g(J',3) & b(J,4)g(J',4)+a(J,5)g(J',5) \end{bmatrix}$$

62-1, $iG(J,J)G(J,J+1)$; $J,E^- - J+1,E^-$ $J/2 \times J+1/2$ ($4b^+$,17c)

$$\begin{bmatrix} a(J,1)g(J,1)+b(J,2)g(J,2) & -a(J,3)g(J,2) & 0 \\ -b(J,2)g(J,3) & a(J,3)g(J,3)+b(J,4)g(J,4) & -a(J,5)g(J,4) \\ 0 & -b(J,4)g(J,5) & a(J,5)g(J,5)+b(J,6)g(J,6) \end{bmatrix}$$

62-2, $-iG(J,J+1)G(J+1,J+1)$; $J,E^- - J+1,E^-$ $J/2 \times J+2/2$ (12b,6c)

$$\begin{bmatrix} b(J,1)g(J',1)+a(J,2)g(J',2) & a(J,2)g(J,3) & 0 \\ b(J,3)g(J',2) & b(J,3)g(J',3)+a(J,4)g(J',4) & a(J,4)g(J',5) \\ 0 & b(J,5)g(J',4) & b(J,5)g(J',5)+a(J,6)g(J',6) \end{bmatrix}$$

63-1, $-iG(J,J+1)G(J+1,J+2)$; $J,E^+ - J+2,E^-$ $J+2/2 \times J+2/2$ (11b,17c)

$$\begin{bmatrix} -\sqrt{2}a(J,0)a(J',1) & 0 \\ -a(J',1)b(J,1)+a(J,2)b(J',2) & -a(J,2)a(J',3) \\ b(J',2)b(J,3) & -a(J',3)b(J,3)+a(J,4)b(J',4) \\ 0 & b(J',4)b(J,5) \end{bmatrix}$$

64-1, $-iG(J,J+1)G(J+1,J+2)$; $J,0^+ - J+2,0^-$ $J+1/2 \times J+3/2$ (13b,15c)

$$\begin{bmatrix} -2a(J',0)b(J,0)+a(J,1)b(J',1) & -a(J,1)a(J',2) & 0 \\ b(J',1)b(J,2) & -a(J',2)b(J,2)+a(J,3)b(J',3) & -a(J,3)a(J',4) \\ 0 & b(J',3)b(J,4) & -a(J',4)b(J,4)+a(J,5)b(J',5) \end{bmatrix}$$

65-1, $-iG(J,J+1)G(J+1,J+2)$; $J,0^- - J+2,0^+$ $J+1/2 \times J+3/2$ (14b,16c)

$$\begin{bmatrix} a(J,1)b(J',1) & -a(J,1)a(J',2) & 0 \\ b(J',1)b(J,2) & -a(J',2)b(J,2)+a(J,3)b(J',3) & -a(J,3)a(J',4) \\ 0 & b(J',3)b(J,4) & -a(J',4)b(J,4)+a(J,5)b(J',5) \end{bmatrix}$$

66-1, $-iG(J,J+1)G(J+1,J+2)$; $J,E^- - J+2,E^+$ $J/2 \times J+4/2$ (12b,18c)

$$\begin{bmatrix} \sqrt{2}b(J',0)b(J,1) & -a(J',1)b(J,1)+a(J,2)b(J',2) & -a(J,2)a(J',3) \\ 0 & b(J',2)b(J,3) & -a(J',3)b(J,3)+a(J,4)b(J',4) \\ 0 & 0 & b(J',4)b(J,5) \end{bmatrix}$$