MICROWAVE SPECTROSCOPY

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WITH A PLATE & 11 DIAGRAMS

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PREFACE

MICROWAVE spectroscopy began vigorous life in the post-1945 years, as a result of war-time technical advances. It rapidly proved to be a powerful instrument for both physical and chemical research. Experimental advances have caused the portion of the electro-magnetic spectrum embraced by the term microwave now to be generally considered that radiation having a wavelength from a few millimetres to a few tens of centimetres. The relevant detailed theory necessary to discuss microwave absorption phenomena had been established previous to the development of the experimental apparatus. Further necessary advances in the form of detailed application of quantum theory have been made, e.g., in the field of nuclear quadrupole effects and the Zeeman effect, so that microwave spectroscopy to-day is firmly established in both experimental and theoretical techniques.

The following discussion was undertaken by the author to make conveniently available the relevant information used to obtain and interpret microwave spectroscopic data. The emphasis has been on presenting a compact, unified treatment of the field. The treatment presupposes some familiarity with modern quantum mechanics and matrix methods. This background is readily accessible in the texts discussed in the bibliography.

The process of becoming acquainted with the material in this book may be considered several ways. It will put within the grasp of someone interested in working in the field the necessary fundamental tools. These tools are then conveniently extended either through investigation of specialized original sources or through a course of supplementary lectures. Alternatively, the material may be considered a second course in quantum theory whose framework consists of the many problems which may be precisely illustrated experimentally by microwave spectroscopic methods.

The text begins with a calculation of the quantum energy levels of a rotating molecule, and considers the various perturbations which may or must be recognized to interpret precise experimental data. The final sections deal with the instrumentation necessary to measure the frequencies in the microwave region which are characteristic of differences between these energy levels. With the resolution that microwave spectroscopy affords these frequencies are unique with each molecule. Furthermore by inverting the process, the molecular parameters which are used in the theory may be derived from a sufficient number of energy level differences or absorption frequencies. The study of these rotational levels and their measurement includes the bulk of the microwave spectroscopic material and hence they are treated to the exclusion of the also interesting electronic hyperfine structure which may come within the scope of microwave experimentation. Although microwave studies of paramagnetic materials are also justifiably termed microwave spectroscopy, they too have been omitted.

In short the material presented here, which should cover the bulk of present-day interest in microwave spectroscopy, should be qualified by the phrase "of rotating molecules." The whole field of microwave physics should be treated elsewhere in a text which even as of now would be several times the size of the present one.

CONTENTS

CHAPTER I

BACKGROUND MATERIAL

A. The General Hamiltonian

THE basic problem of determining quantum mechanically the characteristic energies of a rotating molecule is one of expressing the Hamiltonian in terms of relevant co-ordinates and their conjugate momenta. The classical Hamiltonian for a general polyatomic molecule may be written formally as a sum of terms:

$$H = H_n + H_e + H_v + H_i + H_r + H_t + H_{re} + H_{rn}$$
$$+ H_{rv} + H_{ri} + H_{rt} + H' + H_{stark} + H_{mag} \quad (I.1)$$

Such a description of the Hamiltonian in terms of separate nuclear, electronic, vibrational, inversion, rotational, and translational energy and their mutual interaction contributions may seem inappropriate at first sight. However, the description, based on the Born-Oppenheimer approximation, is adequate when the symbols are properly interpreted. We consider the construction of a molecule. The act of assembling individual nucleons into a nucleus has associated with it an energy H_n. The addition of electrons to create a molecule adds a term H_e. The nuclei may vibrate in this molecule giving rise to a term H_v; the inversion energy, if such a possibility exists, is described by H_i. The molecule, as a whole, is allowed to rotate, and the pure rotational Hamiltonian H_r is added. Finally, the existence of translational energy is accounted for by H_t. New correction terms must be added to account for the difference between the nuclear, electronic, vibrational, and inversion energies as described by H_n, H_e, H_v, H_i, and H_t and the actual energy in the presence of rotation. Terms expressing the modification of H_n due to H_e and so forth, which will not

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concern us since they are constant and small perturbations, we lump in H′. Finally, the possible presence of electric and magnetic fields, applied at will in the laboratory, is accounted for by H_{stark} and H_{mag} which describe the interaction energy of such fields with the molecular charges and currents.

The main objective of this monograph is to study concisely the allowed quantum mechanical states, or energies, that arise from the rotational term H_r. Successively, the modifications necessary to accommodate the interaction terms will be considered. The specific forms of these terms will be considered when they are studied later in detail. We consider that the ground states of the terms H_n, H_e, H_v, and H_i have been successively determined and proceed to the free rotation problem.

B. Properties of Momentum

We may express H_r in the usual way in terms of the components of the momentum on the principal inertial axes of the molecule.

$$H_r = \Sigma_g P_g{}^2/2I_g; \quad g = x, y, z \text{ (principal axes)} \quad . \quad (I.2)$$

The stationary energy states of a free molecule are thus determined by the quantum mechanical properties of the components of the angular momentum.

The algebra of non-commuting vectors is well known, so we review only briefly these properties. The commutation relations for the matrices of the components of the total angular momentum of a system resolved along molecule-fixed axes are written as:

$$P_x P_y - P_y P_x = - i\hbar P_z$$
$$P_y P_z - P_z P_y = - i\hbar P_x$$
$$P_z P_x - P_x P_z = - i\hbar P_y \quad . \quad . \quad (I.3)$$

Identical commutation relations with the sign of i changed apply for the components of the angular momentum along spaced-fixed axes (X, Y, Z = F). In a representation in which $P^2 = P_x{}^2 + P_y{}^2 + P_z{}^2 = P_X{}^2 + P_Y{}^2 + P_Z{}^2 = J(J + 1) \hbar^2$ and P_z and P_Z are simultaneously diagonal (i.e. equal to

$\hbar K$ and $\hbar M$ respectively), the solution to these matrix equations may be shown to be:

$$(J, K, M|P_y|J, K + 1, M) = -i(J, K, M|P_x|J, K + 1, M)$$

$$= \frac{\hbar}{2}[J(J + 1) - K(K + 1)]^{\frac{1}{2}}$$

$$(J, K, M|P_z|J, K, M) = \hbar K$$

$$(J, K, M|P_Y|J, K, M + 1) = i(J, K, M|P_X|J, K, M + 1)$$

$$= \frac{\hbar}{2}[J(J + 1) - M(M + 1)]^{\frac{1}{2}}$$

$$(J, K, M|P_Z|J, K, M) = \hbar M \qquad (I.4)$$

The matrices are hermitian (i.e., $(l|P_g|m) = (m|P_g|l)^*$, where the asterisk signifies complex conjugate). Hence, for example,

$$(J, K, M|P_x|J, K - 1, M) = -i\frac{\hbar}{2}[J(J + 1) - K(K - 1)]^{\frac{1}{2}}$$

Further, the space-fixed and molecule-fixed components of the angular momentum are related by a transformation matrix given by the direction cosines relating any two axes. Thus:

$$P_F = \Sigma_g \Phi_{Fg} P_g, \quad P_g = \Sigma_F \Phi_{Fg} P_F \qquad (I.5a)$$

where Φ_{Fg} is the direction cosine transformation coefficient relating the F and g axis components of a vector. The quantum mechanical matrix elements of these direction cosines may be determined by algebraically solving the set of matrix equations given by the commutation and normalization relationships:

$$\Phi_{Fg}\Phi_{F'g'} - \Phi_{F'g'}\Phi_{Fg} = 0$$

$$P_g\Phi_{Fg} - \Phi_{Fg}P_g = 0$$

$$P_F\Phi_{Fg} - \Phi_{Fg}P_F = 0$$

$$P_x\Phi_{Fy} - \Phi_{Fy}P_x = -i\hbar\Phi_{Fz}, \text{ etc.}$$

$$P_X\Phi_{Yg} - \Phi_{Yg}P_X = i\hbar\Phi_{Zg}, \text{ etc.}$$

$$\Sigma_F\Phi_{Fg}{}^2 = \Sigma_g\Phi_{Fg}{}^2 = 1 \qquad (I.5b)$$

The results may be factored into J, K, and M dependent terms in this fashion:

$$(J, K, M|\Phi_{Fg}|J', K', M')$$
$$= (J|\Phi_{Fg}|J') . (J, K|\Phi_{Fg}|J', K') . (J, M|\Phi_{Fg}|J', M') \quad (1.6)$$

Thus the direction cosine matrix elements may be displayed in the form given in Table 1.

TABLE 1. Direction cosine matrix elements

Matrix Element Factor	Value of J'		
	J + 1	J	J − 1
$(J|\Phi_{Fg}|J')$	$\{4(J+1)[(2J+1)(2J+3)]^{\frac{1}{2}}\}^{-1}$	$[4J(J+1)]^{-1}$	$\{4J(4J^2-1)^{\frac{1}{2}}\}^{-1}$
$(J, K|\Phi_{Fz}|J', K)$	$2[(J+1)^2-K^2]^{\frac{1}{2}}$	$2K$	$2(J^2-K^2)^{\frac{1}{2}}$
$(J, K(\Phi_{Fy}|J', K \pm 1)$ $= \mp i(J, K|\Phi_{Fx}|J', K \pm 1)$	$\mp [(J \pm K + 1)(J \pm K + 2)]^{\frac{1}{2}}$	$[J(J+1) - K(K \pm 1)]^{\frac{1}{2}}$	$\pm [(J \mp K)(J \mp K - 1)]^{\frac{1}{2}}$
$(J, M|\Phi_{Zg}|J', M)$	$2[(J+1)^2-M^2]^{\frac{1}{2}}$	$2M$	$2(J^2-M^2)^{\frac{1}{2}}$
$(J, M|\Phi_{Yg}|J', M \pm 1)$ $= \pm i(J, M|\Phi_{Xg}|J', M \pm 1)$	$\mp [(J \pm M + 1)(J \pm M + 2)]^{\frac{1}{2}}$	$[J(J+1) - M(M \pm 1)]^{\frac{1}{2}}$	$\pm [(J \mp M)(J \mp M - 1)]^{\frac{1}{2}}$

These expressions for the components of momentum and their transformation properties form the foundation upon which the following discussions will depend. They are hastily sketched, since their application rather than their derivation is the object of this book. They should be well understood, however, so that the succeeding work will be intelligible.

CHAPTER II

CHARACTERISTIC ENERGIES OF FREE ROTATION

SINCE the free rotational energy, given in Chapter I, equation (I.2), depends only upon P_g^2, the squares of the matrices for P_x, P_y, and P_z must be formed. If n and m signify the totality of quantum or state numbers we have by matrix multiplication:

$$(n|P_g^2|m) = \Sigma_l (n|P_g|l)(l|P_g|m)$$

Since only $(J, K, M|J, K, M)$ or $(J, K, M|J, K \pm 1, M)$ elements exist for P_g then P_g^2 can have only $(J, K, M|J, K, M)$ elements (when $n = l = m$) and $(J, K, M|J, K \pm 2, M)$ elements (when $l = J, K \pm 1, M$ and $m = J, K \pm 2, M$). The non-vanishing matrix elements of P_g^2 are thus found to be:

$$(J, K, M|P_y^2|J, K \pm 2, M) = - (J, K, M|P_x^2|J, K \pm 2, M)$$

$$= \frac{\hbar^2}{4} [\{J(J + 1) - K(K \pm 1)\}$$

$$\{J(J + 1) - (K \pm 1)(K \pm 2)\}]^{\frac{1}{2}}$$

$$(J, K, M|P_y^2|J, K, M) = (J, K, M|P_x^2|J, K, M)$$

$$= \frac{\hbar^2}{2} [J(J + 1) - K^2]$$

$$(J, K, M|P_z^2|J, K, M) = \hbar^2 K^2 \qquad\qquad (II.1)$$

The characteristic energy matrix, W_r, may then be obtained by writing equation (I.2), in Chapter I, page 2, in terms of these angular momentum matrices. The energy is diagonal in J and M, so for a given value of J and M, the rotational energy matrix elements may be written:

$$(J, K|W_r|J, K) = \frac{\hbar^2}{4} \left(\frac{2}{I_z} - \frac{1}{I_y} - \frac{1}{I_x}\right) K^2 + \frac{\hbar^2}{4} \left(\frac{1}{I_y} + \frac{1}{I_x}\right) J(J + 1)$$

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$$(J, K|W_r|J, K \pm 2) = \frac{\hbar^2}{8} \{[J(J+1) - K(K \pm 1)]$$

$$[J(J+1) - (K \pm 1)(K \pm 2)]\}^{\frac{1}{2}} \left(\frac{1}{I_y} - \frac{1}{I_x}\right)$$

For reasons either immediately obvious, or soon to become apparent, it is convenient to introduce at this point a series of changes in variables. To apply the foregoing results to any particular molecule the gyrating z-axis, along which we have chosen to represent the K momentum, may be associated with any of the three principal axes of inertia of the molecule. If the principal axes are labelled a, b, and c such that $I_a \leq I_b \leq I_c$, then three right-handed associations of axes may be made: (1) with K along the axis of least inertia, so that $z \to a$, $x \to b$, $y \to c$; (2) with K along the axis of intermediate moment of inertia, so the $z \to b$, $x \to c$, $y \to a$; or (3) with K along the axis of greatest moment of inertia so that $z \to c$, $x \to a$, $y \to b$. It is evident that for the present all of these representations are equally useful, though later discussions will indicate the factors which, for reasons of simplicity, indicate the particular representation to be used in the solution of a given problem.

Now define reciprocal moments of inertia such that

$$a = \frac{h}{8\pi^2 I_a} \text{ c.p.s., etc.}$$

Further define an asymmetry factor κ such that

$$\kappa = \frac{2b - a - c}{a - c}$$

In terms of these definitions the rotational energy matrix elements for the three equivalent right-handed representations become:

$$(I) \quad (J, K|W_r|J, K) = \frac{a + c}{2} J(J+1)h$$

$$+ \frac{a - c}{2} \{\tfrac{1}{2}(\kappa - 1)[J(J+1) - K^2] + K^2\}h$$

$$(J, K|W_r|J, K \pm 2) = -\frac{a-c}{8}(\kappa+1)\{[J(J+1)$$

$$- K(K \pm 1)][J(J+1) - (K \pm 1)(K \pm 2)]\}^{\frac{1}{2}}h$$

(II) $(J, K|W_r|J, K) = \dfrac{a+c}{2}J(J+1)h + \dfrac{a-c}{2}\kappa K^2 h$

$$(J, K|W_r|J, K \pm 2) = \frac{a-c}{4}\{[J(J+1)$$

$$- K(K \pm 1)][J(J+1) - (K \pm 1)(K \pm 2)]\}^{\frac{1}{2}}h$$

(III) $(J, K|W_r|J, K) = \dfrac{a+c}{2}J(J+1)h$

$$+\frac{a-c}{2}\{\tfrac{1}{2}(\kappa+1)[J(J+1) - K^2] - K^2\}h$$

$$(J, K|W_r|J, K \pm 2) = \frac{a-c}{8}(\kappa-1)\{[J(J+1)$$

$$- K(K \pm 1)][J(J+1) - (K \pm 1)(K \pm 2)]\}^{\frac{1}{2}}h \quad \text{(II.2)}$$

These three forms of the characteristic rotational energy may be further factored to good purpose into the form:

$$W_r = \frac{a+c}{2}J(J+1)h + \frac{a-c}{2}E(\kappa)h \qquad . \quad \text{(II.3)}$$

where, in general, the matrix elements of the reduced energy, $E(\kappa)$, are given as:

$$(J, K|E(\kappa)|J, K) = F[J(J+1) - K^2] + GK^2$$

$$(J, K|E(\kappa)|J, K \pm 2) = \frac{H}{2}\{[J(J+1)$$

$$- K(K \pm 1)][J(J+1) - (K \pm 1)(K \pm 2)]\}^{\frac{1}{2}} \quad \text{(II.4)}$$

The values of the new coefficients F, G, and H are given in terms of κ and the type of axis identification by Table 2.

TABLE 2. Reduced energy factors

	I	II	III
F	$\frac{1}{2}(\kappa - 1)$	0	$\frac{1}{2}(\kappa + 1)$
G	1	κ	-1
H	$-\frac{1}{2}(\kappa + 1)$	1	$\frac{1}{2}(\kappa - 1)$

The $E(\kappa)$ matrix is infinite in extent because of the possible infinite number of values of J. However, since it is diagonal in J, it is immediately factored into separate J blocks, each of a given value of J. The general form of one such factored component would be given as:

$$E^J(\kappa) = \begin{bmatrix} E_{J,J} & 0 & E_{J,J-2} & 0 & & & & \\ 0 & E_{J-1,J-1} & 0 & E_{J-1,J-3} & & & & \\ E_{J-2,J} & 0 & E_{J-2,J-2} & 0 & & & & \\ 0 & & & & & & & 0 \\ & & & & & & & \\ & & & & E_{-J+2,-J+2} & 0 & E_{-J+2,-J} \\ & & & & 0 & E_{-J+1,-J+1} & 0 \\ & & & 0 & E_{-J,-J+2} & 0 & E_{-J,-J} \end{bmatrix}$$

(II.5)

Where $E_{K,K'} = (J, K|E(\kappa)|J, K')$.

The characteristic values of $E^J(\kappa)$ are given as usual by the roots of the secular determinant formed from the $E^J(\kappa)$

matrix, i.e., $|E^J(\kappa) - \delta_{KK'}\lambda| = 0$, where $\delta_{KK'} = 1$ when $K = K'$ and $\delta_{KK'} = 0$ when $K \neq K'$. Since the $E^J(\kappa)$ matrix (and hence the secular determinant) is of order $2J + 1$, there will be $2J + 1$ roots or characteristic values. As a book-keeping procedure we shall label each root by a number τ such that $J \geq \tau \geq - J$ and such that the magnitude of τ decreases with decreasing characteristic value. In short any general characteristic value of the reduced energy matrix will be given as $E_\tau^J(\kappa)$. Since the only off diagonal matrix elements are off the diagonal by an even number (± 2), the $E(\kappa)$ matrix may be factored further into four submatrices by the Wang symmetrizing transformation X,

$$X = X^{-1} = \frac{1}{\sqrt{2}} \begin{bmatrix} & & & & & & \\ & & -1 & & 1 & & \\ & & -1 & 1 & & & \\ & & & \sqrt{2} & & & \\ & & 1 & 1 & & & \\ & 1 & & & 1 & & \\ & & & & & & \end{bmatrix} \quad \text{(II.6)}$$

when use is made of the relationships:

$$E_{K, K} = E_{-K, -K}$$
$$E_{K, K+2} = E_{K+2, K} = E_{-K, -K-2}$$
$$= E_{-K-2, -K}$$

The transformation $X^{-1}EX$ essentially switches from an expansion in terms of function vectors $|J, K, M)$ to an expansion in terms of vectors $|J, 0, M)$ and $2^{-\frac{1}{2}}[|J, |K|, M) \pm |J, - |K|, M)]$, thus; with evident notation, these four submatrices may be written compactly as follows.

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$$E_{E+}^{J}(\kappa) = \begin{bmatrix} E_{00} & \sqrt{2}E_{02} & 0 & \cdot & \cdot & \cdot \\ \sqrt{2}E_{02} & F_{22} & E_{24} & 0 & \cdot & \cdot \\ 0 & E_{24} & E_{44} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

$$E_{E-}^{J}(\kappa) = \begin{bmatrix} E_{22}' & E_{24} & 0 & \cdot & \cdot & \cdot \\ E_{24} & E_{44} & E_{46} & 0 & \cdot & \cdot \\ 0 & E_{46}^{*} & E_{66} & E_{68} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

$$E_{0+}^{J}(\kappa) = \begin{bmatrix} E_{11} + E_{-11} & E_{13} & 0 & \cdot & \cdot & \cdot \\ E_{13} & E_{33} & E_{35} & \cdot & \cdot & \cdot \\ 0 & E_{35} & E_{55} & E_{57} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

$$E_{0-}^{J}(\kappa) = \begin{bmatrix} E_{11} - E_{-11} & E_{13} & 0 & \cdot & \cdot & \cdot \\ E_{13} & E_{33} & E_{35} & \cdot & \cdot & \cdot \\ 0 & E_{35} & E_{55} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

$$\tag{II.7}$$

Each of these sub-matrices $E_{E+}{}^J$, $E_{E-}{}^J$, $E_{0+}{}^J$, and $E_{0-}{}^J$ is roughly the order of $J/2$, so that the solution of the secular determinant is considerably less onerous than might appear at first thought. For all the values of J less than or equal to three and for some states with J values of four or five the secular equation is quadratic, and hence the roots may be explicitly determined. For higher J values the continued fraction expansion of the roots may be fruitfully applied. Transform first to the unsymmetrical matrix

$$D = L^{-1}E^J L = L^{-1}\begin{bmatrix} k_0 & b_1^{\frac{1}{2}} & 0 & & & \\ b_1^{\frac{1}{2}} & k_1 & b_2^{\frac{1}{2}} & & & \\ 0 & b_2^{\frac{1}{2}} & k_3 & & & \\ & & & & & \\ & & & & & \\ & & & & & \end{bmatrix} L$$

$$D = \begin{bmatrix} k_0 & 1 & 0 & & & \\ b_1 & k_1 & 1 & & & \\ 0 & b_2 & k_2 & 1 & & \\ & & & & & \\ & & & & & \\ & & & & & \end{bmatrix}$$

where

$$L = \begin{bmatrix} 1 & 0 & & & \\ 0 & b_1^{-\frac{1}{2}} & 0 & & \\ & 0 & b_1^{-\frac{1}{2}}b_2^{-\frac{1}{2}} & 0 & \\ & & 0 & b_2^{-\frac{1}{2}}b_3^{-\frac{1}{2}} & \end{bmatrix} = [l_{ii}]$$

$$(II.8)$$