ENERGY MOMENT TREATMENT OF THE
QUANTUM MECHANICAL ASYMMETRIC ROTATOR

DISSERTATION

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This dissertation is dedicated to my parents as a small token of gratitude for their unending and unerring help, patience, and sacrifice over the years.
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CHAPTER I

INTRODUCTION

The quantum mechanical treatment of the energies of the general configuration vibrating-rotating polyatomic molecule was first described by Wilson and Howard\(^1\) and subsequently by Darling and Dennison\(^2\) in a slightly different but equivalent form. It was soon realized by Nielsen\(^3\) that except for certain anomalous cases, a quantum mechanical Hamiltonian operator can be written down and dealt with in a most general manner to arrive at relations for the vibration-rotation energies of the general polyatomic molecule. This approach has indeed been a rewarding one, and much effort has been expended on it over the years by a number of investigators, as can be seen from a recent review article on the subject by Nielsen.\(^4\)

\(^2\) B. T. Darling and D. M. Dennison, Phys. Rev. \(57\), 128 (1940).
\(^3\) H. H. Nielsen, Phys. Rev. \(60\), 794 (1941).


To the approximation, that the vibrational part of the motion
is that of an ensemble of harmonic oscillators, and the rotational part of the motion is that involving a semi-rigid microphysical entity, the vibration-rotation energies of the molecule in question may be stated simply as the sum of two terms, one arising exclusively from the vibrational part of the motion, the other associated exclusively with the rotational part of the motion. To this approximation it is thus possible to treat the rotational problem independently of the vibrational part. The problem to be investigated then becomes one of pure rotation. In this zero-order problem the interaction of the rotational with the vibrational motion is considered negligible, the molecule is considered to be in a given fixed electronic configuration, and the rotational energies can be considered to be merely added on to a given energy of vibration of the molecule in one of its normal modes of vibration. The inclusion of centrifugal stretching effects due to the rotational motion in the zero-order part of the rotational problem may or may not meet with success, depending on whether or not they are masked by vibration-rotation interaction effects of the same order of magnitude in a particular molecule.

As in classical mechanics, quantum mechanical rotators are classified as spherical, symmetric, and asymmetric tops. If the equilibrium values of all three principal moments of inertia of the top are equal it is called a spherical top; if two are equal but different from the third it is called a symmetric top; if all are different it is called an asymmetric top; the special case of a
symmetric top whose unique moment is very much smaller than its other
two moments is the case of the linear molecule.

The evaluation of the rotational energies of spherical and
symmetric tops in terms of their moments of inertia presents no
special difficulties (in the absence of such complications as non­
zero internal angular momenta, hindered rotation, etc.). The
asymmetric top is much more difficult to deal with. An extensive
discussion of the quantum mechanical rigid asymmetric top is found
in the literature.\textsuperscript{3-22} Of special note is the work of Wang\textsuperscript{8} and

\begin{enumerate}
\item O. Klein, Z. Physik \textbf{58}, 730 (1929).
\item H. A. Kramers and G. P. Ittmann, Z. Physik \textbf{53}, 553
  (1929); \textbf{58}, 217 (1929); \textbf{60}, 663 (1929).
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\item D. M. Dennison, Rev. Mod. Phys. \textbf{3}, 280 (1931).
\item B. S. Ray, Z. Physik \textbf{78}, 71 (1932).
\item R. Mecke, Z. Physik \textbf{61}, 313 (1933).
\item H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R.
\item G. W. King, R. M. Hainer, and P. C. Cross, J. Chem.
\item R. M. Hainer, P. C. Cross, and G. W. King, J. Chem.
\item C. van Winter, Physica \textbf{20}, 274 (1954).
\end{enumerate}

\textsuperscript{12} Ray who arrive at expressions for the energies suitable for numeri-
cal calculations; the work of King, Hainer, and Cross\textsuperscript{15} whose numeri-
cal tables greatly facilitate the computational work in connection with Ray's expressions; the EDVAC electronic computer eigenvalue tables compiled by Turner, Hicks, and Reitweisner at the Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland; and the sum rules of Mecke\(^{13}\) which relate the sum of the energies of a properly chosen group of energy levels to the moments of inertia of the molecule.

The present work is principally concerned with deducing certain sum rules relating energies of the asymmetric top to some of the physical constants of the molecule. Augmented by the sum rules already given by Mecke, these rules permit in many cases the computation of the effective values of the principal moments of inertia of the molecule investigated with much less effort than is usually met in either numerical approximation methods or perturbation calculations if the latter are applicable at all.

A procedure described by Brown,\(^23\) and by Brown and Parker\(^{24, 25}\) relates the energies of a stationary quantum mechanical system to physical constants appearing in the Hamiltonian describing this system. This procedure will be described in Chapter II and then used in Chapters III and V to arrive at the sum rules. Chapters IV

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and VI deal with the application of these rules to some of the infra-red data of water vapor obtained by Benedict, Claassen, and Shaw, 26


and serve mainly as illustrative examples of the theory developed. Chapters VII and VIII describe and discuss an attempt to extend the theory to include centrifugal stretching effects explicitly, although this attempt has not met with unqualified success.

In the interest of clarity and continuity of presentation much of the corollary material of this dissertation has been relegated to a number of appendixes.
The energies $E_k$ of a stationary quantum mechanical system are obtained as the eigenvalues of the Schrödinger equation,

$$H \psi_k = E_k \psi_k,$$  \hspace{1cm} (2.1)

where $H$ is the Hamiltonian operator appropriate to the system, and where the subscript $k$ denotes the different members of the complete orthonormal set of energy eigenfunctions $\psi_k$ and their corresponding eigenvalues $E_k$. In general, the energies $E_k$ may form a finite or infinite discrete set of values, a continuous set of values, or a set partially discrete and partially continuous. In what follows, we assume for simplicity of notation a discrete set, although some of the formalism can be modified to include the continuum as well.\(^{27}\)

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If one has in addition to the set $\psi_k$ another complete orthonormal set of functions $\psi_n$ defined in the same configuration space as the set $\psi_k$, then any of the $\psi_n$ can be expanded in the set $\psi_k$,

$$\psi_n = \sum_k a_{kn} \phi_k,$$ \hspace{1cm} (2.2)

and from orthonormality in the set $\psi_k$ we obtain

$$a_{kn} = \int \phi_k^* \psi_n \, dv,$$ \hspace{1cm} (2.3)
where the asterisk denotes complex conjugate and $d\tau$ is the volume element in configuration space. The matrix $A$ of which the $a_{kn}$ are the elements, is unitary, since the product of the matrix $A$ with its adjoint $\tilde{A}$ gives the unit matrix $I$,

$$A\tilde{A} = \tilde{A}A = I, \quad (2.4)$$

because

$$(A\tilde{A})_{ki} = \sum_n a_{kn}^{\ast}a_{ni} = \sum_n a_{kn}a_{ni}^{\ast} = \\
= \sum_n \int d\tau d\tau' \phi_k^{\ast} \phi_i \phi_i^{\ast} = \delta_{ki}, \quad (2.5)$$

where $\delta$ is the Kronecker delta symbol. In similar fashion it is established that

$$(\tilde{A}A)_{ki} = \delta_{ki}, \quad (2.6)$$

hence the assertion of (2.4) is true.

The set $\psi_n$ can be used to calculate the matrix elements $H_{mn}$ of the Hamiltonian operator,

$$H_{mn} = \int \psi_m^{\ast}H\psi_n d\tau. \quad (2.7)$$

Transformation of $H$ by the unitary matrix $A$ gives

$$(AH\tilde{A})_{kj} = \sum_i a_{ki}^{\ast}H_{ni}a_{ij} = E_k\delta_{kj}, \quad (2.8)$$

with the aid of (2.7), (2.3), and (2.1).

The set of linear algebraic equations obtained by writing down the elements of (2.8) for a particular row $k$ and all columns $j$ is

$$\sum_i a_{ki}(H_{ij} - E\delta_{ij}) = 0. \quad (2.9)$$

The subscript $i$ is summed from unity to the rank $N$ of the transformation matrix $A$. Thus (2.9) may be considered a set of $N$ homogeneous algebraic equations for the elements $a_{ki}$. The necessary and
sufficient condition that these equations have a solution is that the determinant of their coefficients vanish,

\[ |H_{ij} - E\delta_{ij}| = 0. \]  \hspace{1cm} (2.10)

This yields a single equation, the secular equation, which is of degree \( N \) and which has \( N \) roots, \( E_\tau \) \((\tau = 1, 2, \ldots, N)\). These roots are the eigenvalues of the originally non-diagonal matrix of the Hamiltonian operator in the set \( \psi_n \).

Now, if the system under consideration is such that it is either adequately described by a finite set of functions \( \psi_k \) or by an infinite set \( \psi_k \) in which there exist independent subsets, then the matrix \( H \) will be of finite rank in the former case or can be brought into step form in the latter case by proper arrangement of rows and columns. In one case then, the secular equation will be a polynomial equation in \( E \) of degree \( N \); in the other case, each step will form a submatrix of \( H \) and will yield a polynomial equation in \( E \) of degree equal to the rank of the submatrix.

An example of a physical system adequately described by a finite size matrix \( H \) is the nuclear magnetic dipole and electric quadrupole moment configuration interacting with surrounding static electric and magnetic fields, \( ^{23,24} \) while an example of a system described by an infinite matrix \( H \) in step form is the rigid asymmetrical rotator to be described below.

If one attaches no particular interest to a knowledge of the detailed form of the transformation matrix but rather is interested in the allowed energies of the system, the secular equation incorpo-
rates all the information desired, although, of course, if equa-
tions of degree higher than the second are encountered, solutions 
can usually not be set down in closed form, but must be approxi-
mated or found numerically for special cases.

The problem of solving the Schrödinger equation is thus 
equivalent to diagonalizing the Hamiltonian matrix $H$ (or its sub-
matrices) when it is expressed in some arbitrary representation $\psi_n$. 
A convenient representation is obtained if one chooses for $\psi_n$ a set 
of functions which are eigenfunctions of the square of the angular 
momentum operator and of its space- or body-fixed component along 
a particular direction. This representation is of particular per-
tinence if the square of the angular momentum $P^2$ or its space- or 
body-fixed component along a particular direction $P_z$ commutes with 
the Hamiltonian, for then a set of eigenfunctions exists in which 
both the Hamiltonian and the commuting operator are diagonal. Also, 
in many cases, the matrix elements of the Hamiltonian in this 
representation can be set down with little difficulty.

It is convenient for our purposes to deal with the energy in 
units of wave numbers, and we therefore define

$$W = \frac{H}{\hbar c} \quad \text{and} \quad F = \frac{E}{\hbar c}, \quad \text{(2.11)}$$

so that the secular equation (2.10) takes the form

$$|W_{ij} - F_{ij}| = 0. \quad \text{(2.12)}$$

The way we propose to deal with (2.12) has been described by 
Brown,\textsuperscript{23} and by Brown and Parker,\textsuperscript{24,25} and will now be presented.

As was observed above, the usual procedure in this problem is
to seek by one means or another the roots $F$ of (2.12) formed from a
matrix or submatrix of finite rank, say of rank $n$. In all but very
simple systems the attempt to find general closed expressions for the
physical parameters of the system (which appear in the $W_{ij}$'s) meets
with failure. However, the inverse problem, that of finding closed
expressions for the physical parameters in terms of functions of the
energy eigenvalues, is one of much greater feasibility. Since one of
the aspects of spectral analysis is the determination of the physi­
cal parameters, and since the energy eigenvalues may be considered
to be experimentally determined quantities, the relevancy of our
viewpoint is easily recognized.

If (2.12) (or one of its finite submatrices) is expanded
into a polynomial equation of degree $n$, of the form

$$F^n + c_1 F^{n-1} + c_2 F^{n-2} + \ldots + c_n = 0,$$

(2.13)
it is known from the theory of equations\textsuperscript{28} that not only do the
$n$ roots $F$ form a complete set of invariants of the matrix (or sub-

\textsuperscript{28} L. E. Dickson, First Course in the Theory of Equations
(John Wiley and Sons, New York, 1931).

matrix) independent of representation, but so also do the $n$ coeffi­
cients $c_i$ form a complete set of invariants of the matrix (or sub-

matrix).

Now, the $c_i$'s can be expressed in two ways:

(a) In terms of the experimentally determined energy levels
by use of the well-known symmetric functions of the roots of a polynomial equation;

(b) Directly in terms of the matrix elements of \( W \) which contain the physical parameters.

Equating the expressions so obtained for corresponding \( c_i \)'s leads to \( n \) equations relating the physical parameters of the system to experimental quantities. If these \( n \) equations were all independent nothing would be gained. However, since the number of physical parameters is quite frequently less than the number of equations that can be written down, solutions can be obtained by utilizing less than the full number of coefficients \( c_i \). In the present work the calculations are limited to expressions involving \( c_1 \), \( c_2 \), and \( c_3 \). Although the treatment of the remaining coefficients follows the same pattern, the first three coefficients are the ones whose treatment is practical because of the relative simplicity of the calculations involved.

In terms of the experimentally determined energies (Part (a) above), theory of equations\(^{28}\) yields for the \( c_i \)'s:

\[
\begin{align*}
c_1 &= -\Sigma_i F_i, \\
c_2 &= \Sigma_i \Sigma_j F_i F_j, \quad i < j, \\
c_3 &= -\Sigma_i \Sigma_j \Sigma_k F_i F_j F_k, \quad i < j < k, \\
\ldots & \ldots \ldots \ldots \ldots \\
c_n &= \pi_i F_i, \\
\end{align*}
\]

(2.14)

with all summation indices ranging from unity to \( n \), except for the restrictions noted to avoid duplications in the sums. Equations (2.14)
are proved by induction (they are trivially true for \( n=1 \), reduce to a well-known theorem for \( n=2 \)).

Rather than dealing with the restricted sums occurring in (2.14), it is more convenient to rewrite the first three coefficients in terms of three summations defined as follows:

\[
S_1 = \sum_i (F_i), \\
S_2 = \sum_i (F_i)^2, \\
S_3 = \sum_i (F_i)^3; \\
\]

(2.15)

these sums may be considered as the first, second, and third "moments" of the energy levels under consideration about the zero of energy, and it is from this viewpoint that the procedure we are describing here is hereafter referred to as the "method of moments."

It is readily verified\(^{28}\) that in terms of the moments (2.15), the first three coefficients can be expressed as follows:

\[
c_1 = -S_1, \\
C_2 = \frac{1}{2}S_2 + \frac{1}{3}S_1^2, \\
c_3 = \frac{1}{3}S_3 + \frac{1}{2}S_1(S_2 - \frac{3}{4}S_1^2). \\
\]

(2.16)

As for the task outlined in (b), it is well known from the theory of equations that if the secular equation is in the form (2.13), then

\[
c_1 = -\sum_i M_i, \\
\]

(2.17)

where \( M_i \) is a 1 x 1 principal minor determinant of \( W \) and the summation index ranges over all principal minor determinants. Thus (2.17) simply states that the coefficient \( c_1 \) of the next to the
highest power of $F$ is equal to the negative of the sum of the diagonal elements of $W$, this sum being called the trace $T$ of $W$.

Each contribution to the term $c_2 F^{n-2}$ of the secular polynomial is of one of the two forms $W_{ii}W_{jj} F^{n-2}$ or $-W_{ij}W_{ji} F^{n-2}$, with $i 
eq j$. The proof of this statement is sketched in Appendix A. The two expressions $W_{ii}W_{jj} F^{n-2}$ and $-W_{ij}W_{ji} F^{n-2}$ can be combined by writing $M_{ij} F^{n-2}$, where $M_{ij}$ is the $2 \times 2$ minor determinant formed from rows $i$ and $j$; and from columns $i$ and $j$. The total contribution to $c_2$ can then be written as

$$c_2 = \sum_{i<j} M_{ij}, \quad i < j.$$ (2.18)

The restriction $i < j$ is simply to avoid repetitions in the sum.

By a similar argument one can show that the coefficient of $F^{n-3}$ is

$$c_3 = \sum_{i<j<k} M_{ijk}, \quad i < j < k,$$ (2.19)

where $M_{ijk}$ is the $3 \times 3$ minor determinant formed from rows $i$, $j$, and $k$; and from columns $i$, $j$, and $k$.

It is apparent that (2.16) would be simplified if $S_1$ were equal to zero. It also happens that manipulation of (2.18) and (2.19) is considerably facilitated if this condition is satisfied.

From (2.16) and (2.17) it is seen that the condition $S_1 = 0$ will be satisfied in systems which are described by traceless representations. (The zero trace property is an invariant property of the Hamiltonian describing the system, independent of the particular representation in which $H$ is expressed.) Indeed, in such
systems the condition $S_1 = 0$ can be utilized to fix the reference level from which the energies are measured in the analysis of spectroscopic data. In other systems, such as the asymmetric rotator system to be discussed, the trace does not vanish. In that event, the first moment $S_1$ is calculated using (2.17); the higher moments are then calculated about the mean of the set of energy levels under consideration; thus, the zero reference level used to compute $S_2$ and $S_3$ is different from that used to compute $S_1$ and is determined simply by requiring that $S_1 = 0$ when calculating the higher moments. The shift in reference level is introduced into the formalism in the following manner: After $S_1$ is computed, (2.12) is modified to read

$$|W_{ij} - (T/n)\delta_{ij} + (T/n)\delta_{ij} - F\delta_{ij}| = 0,$$

or

$$|W_{ij}^\circ - F^\circ\delta_{ij}| = 0,$$

where evidently

$$W_{ij}^\circ = W_{ij}, \quad i \neq j,$$

$$W_{ii}^\circ = W_{ii} - (T/n),$$

and

$$F^\circ = F - (T/n).$$

Thus in the process of modifying (2.12), the off-diagonal matrix elements of $W$ are unchanged, the diagonal matrix elements are all changed by the amount $(T/n)$, and the energies are all changed by the same amount. The result of the modifying process is to shift the zero reference of energy equally for all levels under con-
sideration, such that the representation is made traceless, but to leave all the physical aspects of the problem completely unchanged.

Combining (2.16) through (2.24) we obtain finally that

\[ S_x = 2\Sigma_i M_i, \]  
\[ S_x = -2\Sigma_i \Sigma_j M_{ij}, \quad i < j, \]  
\[ S_x = 3\Sigma_i \Sigma_j \Sigma_k M_{ijk}, \quad i < j < k. \]

For purposes of actual computation it is necessary to have (2.26) and (2.27) in more explicit form. Equation (2.25) evidently can be written as

\[ S_1 = \sum_{i=1}^{n} W_{ii}. \]  

As shown in Appendix B, one may write in a Hermitian representation,

\[ S_2 = \sum_{i=1}^{n} (W_{ii}^0)^2 + 2\sum_{i=1}^{n-1} |W_{i,i+1}|^2 + \]  
\[ + 2\sum_{i=1}^{n-2} |W_{i,i+2}|^2 + \ldots + 2|W_{i,n}|^2, \]  

and

\[ S_3 = \sum_{i=1}^{n} (W_{ii}^0)^3 + \]  
\[ + 3\sum_{i=1}^{n-1} |W_{i,i+1}|^2 \left(W_{ii}^0 + W_{i+1,i+1}^0 \right) + \]  
\[ + 3\sum_{i=1}^{n-2} |W_{i,i+2}|^2 \left(W_{ii}^0 + W_{i+2,i+2}^0 \right) + \]  
\[ + \ldots + 3|W_{in}|^2 \left(W_{in}^0 + W_{nn}^0 \right) + \]  
\[ + 3\sum_{i,j,k} \epsilon_{ijk} (W_{ij}W_{jk}W_{ki}^0 + W_{ik}W_{jk}W_{kj}^0), \quad i < j < k. \]

A more elegant (but perhaps less readily visualized) formulation of the moment equations can be given in the following manner.

In the matrix formulation of quantum mechanics the wave functions take the form of column vectors which are solutions of the
Schrödinger equation in matrix form. The Schrödinger equation (2.1) becomes

\[ \hat{H}\phi = E_k \phi, \quad (2.31) \]

and with the aid of (2.11),

\[ W\phi = F_k I\phi, \quad (2.32) \]

with \( \phi \) being one of the eigenvectors of the Hamiltonian. Taking the trace on both sides of (2.32), one finds that

\[ \text{Trace}(W) = S_1, \quad (2.33) \]

and because of the trace invariance under unitary transformations, (2.33) holds in any arbitrary representation. Furthermore, by operating on (2.32) from the left with \( W \), one finds that

\[ W^2 \phi = F_k^2 I(W\phi) = F_k^2 I\phi, \quad (2.34) \]

and therefore

\[ \text{Trace}(W^2) = S_2, \quad (2.35) \]

again, in any arbitrary representation. Operating with \( W \) on (2.34), one establishes similarly that

\[ \text{Trace}(W^3) = S_3, \quad (2.36) \]

and obviously,

\[ \text{Trace}(W^q) = S_q, \quad (2.37) \]

for any integer \( q \geq 1 \). Closer examination of (2.33), (2.35), and (2.36) shows that they are equivalent to (2.25), (2.26), and (2.27), and lead, in fact, directly to (2.28), (2.29), and (2.30).

In the computation of (2.29) and (2.30) in the present work, one needs expressions for the sum of integral powers of the first \( J \)
integers. These expressions are most conveniently established by the method of finite differences,\(^{29}\) and are compiled below.

\[ \sum K^0 = \frac{1}{2}(2J+1), \quad (2.38.0) \]

\[ \sum K^2 = \frac{1}{6}(2J+1)f, \quad (2.38.2) \]

\[ \sum K^4 = \frac{1}{30}(2J+1)f(3f-1), \quad (2.38.4) \]

\[ \sum K^6 = \frac{1}{12}(2J+1)f(3f^2-3f+1), \quad (2.38.6) \]

\[ \sum K^8 = \frac{1}{90}(2J+1)f(5f^3-10f^2+9f-3), \quad (2.38.8) \]

\[ \sum K^1 = \frac{1}{2}f, \quad (2.38.1) \]

\[ \sum K^3 = \frac{1}{12}f^2, \quad (2.38.3) \]

\[ \sum K^5 = \frac{1}{12}f^2(2f-1); \quad (2.38.5) \]

with \( f = J(J+1), \) and with \( K \) in all sums ranging from one (or zero) to \( J. \) If the summation extends from \(-J\) to \(+J,\) then evidently the sums of the odd powers of \( K \) are zero, while the sums of the even powers of \( K \) are double their values given above in \((2.38).\)
CHAPTER III
THE RIGID ROTATOR SUM RULES

The Hamiltonian for the rigid asymmetric rotator in the principal axis system of the inertia tensor is

\[ W = \frac{\hbar}{\hbar c} = A P_x^2 + B P_y^2 + C P_z^2 \]  

where \( P_x, P_y, \) and \( P_z \) are the components (in units of \( \hbar \)) of the angular momentum in the body-fixed coordinate system defined by the principal axes of the inertia tensor; and where

\[ A = \frac{\hbar}{8m^2 I_x}, \quad B = \frac{\hbar}{8m^2 I_y}, \quad C = \frac{\hbar}{8m^2 I_z}, \]  

are the rotational constants. These, apart from universal constants, are reciprocals of the effective moments of inertia of the rotator, \( I_x, I_y, \) and \( I_z. \)

In a representation such that

\[ P_x^2 \psi = J(J+1) \psi, \]  
\[ P_z \psi = K \psi, \]  

where \( J(J+1) \) is the magnitude (in units of \( \hbar^2 \)) of the square of the angular momentum; where \( J \) may be any non-negative integer; and where \( K = J, J-1, ..., -J; \) the non-zero matrix elements of \( P_x^2, P_y^2, \) and \( P_z^2 \) are

\[ (P_x^2)_{K,K} = \frac{3}{2} [ J(J+1) - K^2 ], \]  
\[ (P_x^2)_{K,K+2} = (P_x^2)_{K+2,K} = \frac{1}{14} [(J-K-1)(J-K)(J+K+2) \frac{1}{2} ], \]  

18
Consequently, the non-zero matrix elements of $W$ in this representation follow readily as

$$W_{K,K} = k^2. \tag{3.9}$$

The $W$ matrix in this representation can be arranged into step form, each step being a submatrix of size $(2J+1) \times (2J+1)$, and going with a particular value of $J$, as shown in Fig. 1. Fig. 2 shows the $J$-th submatrix in more detail.

The method of moments can now be applied to the $J$-th submatrix. There are $(2J+1)$ energies $F_\tau$ associated with this matrix. The index $\tau$ takes $(2J+1)$ values, $\tau = J$, $J-1$, ..., $-J$, with $\tau = J$ going with the largest energy, $\tau = J-1$ with the next largest energy, and so on.

The first moment $S_1$ of the $(2J+1)$ levels $F_\tau$ corresponding to a fixed value of $J$ follows readily from (2.28) and (3.10) as the trace of the $J$-th submatrix of $W$. With the aid of (2.38.0) and (2.38.2) we find

$$S_1 = (1/3)(A+B+C)J(J+1)(2J+1), \tag{3.12}$$

which is recognized as one of the Mecke sum rules. If the mean of
FIGURE 1
The matrix W arranged in step form. All elements falling into the shaded area outside the steps are zero.
FIGURE 2

The form of the J-th submatrix of W.
the energies \( F \) is defined as \( F_j \) (for given \( J \)), (3.12) takes the form

\[
F_j = \frac{1}{3}(A+B+C)J(J+1).
\]  

(3.13)

This corresponds to the energy of a spherical rotator with the single effective rotator constant \( \frac{1}{3}(A+B+C) \).

Before determining the higher moments \( S_2 \) and \( S_3 \), the \( W \) matrix is modified to make it traceless, as discussed in Chapter II. By subtracting (3.13) from the diagonal term (3.10) of \( W \), we obtain the modified form of the diagonal elements of \( W \) as

\[
W_{K,K}^0 = \begin{bmatrix} K^2 - J(J+1)/3 \end{bmatrix} \begin{bmatrix} 0 - \frac{1}{3}(A+B) \end{bmatrix}.
\]  

(3.14)

By introducing the quantities

\[
\alpha = (A+B+C),
\]

(3.15)

\[
\beta = 3(A-B)/(2C-A-B),
\]

(3.16)

\[
\gamma = (2C-A-B),
\]

(3.17)

the non-zero matrix elements of \( W^0 \) can be expressed as

\[
W_{K,K}^0 = \frac{1}{2} \gamma \begin{bmatrix} K^2 - J(J+1)/3 \end{bmatrix},
\]

(3.18)

\[
W_{K,K+2} = W_{K+2,K} = \frac{1}{12} \beta \gamma \left[ (J-K-1)(J-K) \right. \left. \times \right.
\]

\[
\left. (J+K+1)(J+K+2) \right]^{1/2}.
\]

(3.19)

The details of calculating \( S_2 \) and \( S_3 \) from (2.29) and (2.30) are given in Appendix C. One finds for the first three moments:

\[
S_1 = p_1 \alpha,
\]

(3.20)

\[
S_2 = p_2 \gamma^2 (1+\beta^2/3),
\]

(3.21)

\[
S_3 = p_3 \gamma^3 (1-\beta^2).
\]

(3.22)

The quantities \( p_1, p_2, \) and \( p_3 \) are polynomials in \( J \) as follows:

\[
p_1 = 2J(J+1)(2J+1)/3!,
\]

(3.23)
\[ p_2 = \frac{2J(J+1)(2J-1)(2J+1)(2J+3)}{3(5J)}, \quad (3.24) \]
\[ p_3 = \frac{2J(J+1)(2J-3)(2J-1)(2J+1)(2J+3)(2J+5)}{3(7I)}. \quad (3.25) \]

The quantity \( \alpha \) follows immediately from (3.20). It can be viewed as a measure of the magnitude of the rotator constants in terms of an equivalent sphere. Its range is unrestricted.

The quantities \( \beta \) and \( \gamma \) can be calculated by solving (3.21) and (3.22) simultaneously as follows:

\[ (1-\beta^2)^2/(1+\beta^2/3)^3 = p_2^3S_3^2/p_3^2S_2^3 = 1-\delta, \quad (3.26) \]

the quantity \( \delta \) being determined from the experimental moments and then used to determine \( \beta \) from a tabulation of \( \beta \) in terms of \( \delta \). This one tabulation of \( \beta=\beta(\delta) \) for \( 0 \leq \delta \leq 1, \quad -1 \leq \beta < 0 \), suffices for all values of \( J \). The curve of \( \beta \) vs. \( \delta \) is shown in Fig. 3. After \( \beta \) has been found, the magnitude of \( \gamma \) follows from either (3.21) or (3.22), and its sign follows from (3.22).

The quantity \( \gamma \) measures the deviation of the rotator from spherical symmetry, and as shown in Appendix D, has a range from a minimum of \( -(2/5)\alpha \) (oblate symmetric rotator limit), through zero (spherical rotator), to a maximum of \( 2\alpha \) (prolate symmetric rotator limit).

The deviation from a symmetric top is measured by \( \beta \), which has the range \( -1 \leq \beta < 0 \). This range of \( \beta \) follows from choosing \( B \) as the intermediate rotational constant, and \( C \) as the constant farthest removed from the mean \( (A+B+C)/3 \), i.e.,

\[ |B - \alpha/3| < |A - \alpha/3| < |C - \alpha/3|, \quad (3.27) \]

as discussed in Appendix D.
FIGURE 3

The curve (3.26) of $\delta$ vs. $\delta = 1 - (1-\beta^2)^2/(1+\beta^2/3)^3$. 
With $\alpha$, $\beta$, and $\gamma$ determined, the rotational constants are then, from (3.15), (3.16), and (3.17),

\[ A = \frac{1}{3}(\alpha - \frac{1}{2}\gamma(1-\beta)), \quad (3.28) \]
\[ B = \frac{1}{3}(\alpha - \frac{1}{2}\gamma(1+\beta)), \quad (3.29) \]
\[ C = \frac{1}{3}(\alpha + \gamma). \quad (3.30) \]

In this manner each value of $J$ for which a complete energy level scheme is available from experiment yields a set of effective rotational constants. A study of the variation of these constants with $J$ can then be performed in order to examine centrifugal stretching effects.

Values of the polynomials $p_1$, $p_2$, and $p_3$ for values of $J$ up to twelve are given in Table I.
TABLE I

VALUES OF THE POLYNOMIALS $p_1$, $p_2$, AND $p_3$

FOR $J=0$ TO $J=12$.

<table>
<thead>
<tr>
<th>$J$</th>
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<td>0</td>
<td>0</td>
</tr>
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</tr>
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</tr>
<tr>
<td>4</td>
<td>60</td>
<td>77</td>
<td>715/6</td>
</tr>
<tr>
<td>5</td>
<td>110</td>
<td>429/2</td>
<td>2145/4</td>
</tr>
<tr>
<td>6</td>
<td>182</td>
<td>1001/2</td>
<td>7293/4</td>
</tr>
<tr>
<td>7</td>
<td>280</td>
<td>3094/3</td>
<td>46189/9</td>
</tr>
<tr>
<td>8</td>
<td>408</td>
<td>1938</td>
<td>12597</td>
</tr>
<tr>
<td>9</td>
<td>570</td>
<td>6783/2</td>
<td>111435/4</td>
</tr>
<tr>
<td>10</td>
<td>770</td>
<td>33649/6</td>
<td>2042975/36</td>
</tr>
<tr>
<td>11</td>
<td>1012</td>
<td>8855</td>
<td>216315/2</td>
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<tr>
<td>12</td>
<td>1300</td>
<td>13455</td>
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CHAPTER IV
APPLICATION OF SUM RULES TO THE WATER MOLECULE

Early investigators of the absorption spectrum of water vapor in the infra-red include Paschen\textsuperscript{30} and Coblentz\textsuperscript{31} As early as 1918 Sleator\textsuperscript{32} succeeded in resolving eighty-seven lines in the

\begin{center}
\begin{tabular}{l}
\end{tabular}
\end{center}

2.7 micron region and forty-six lines in the 6.3 micron region. With the advent of the newer quantum theory the machinery became available for a better theoretical understanding of the absorption spectrum. In 1933 Mecke\textsuperscript{33} made a rotational analysis of all the water bands then known. Two important papers, one by Shaffer and Nielsen,\textsuperscript{33} and a subsequent one by Darling and Dennison,\textsuperscript{34} treat the water molecule

\begin{center}
\begin{tabular}{l}
\end{tabular}
\end{center}

theoretically in detail to the second order of perturbation, and
form an adequate basis for understanding almost all the observed experimental effects known at the present time.

More recent experimental investigators of the water vapor spectrum in the infra-red include Nielsen, Benedict and Plyler, Dalby and Nielsen, and Benedict, Claassen, and Shaw.

The data of Benedict, Claassen, and Shaw were obtained at The Ohio State University in 1951, and our calculations are based on these data.

The water molecule has three unequal moments of inertia, and is thus an asymmetric top. It has the form of an isosceles triangle, and three degrees of vibrational freedom. The three normal modes associated with the vibrational degrees of freedom are shown schematically in Fig. 4.

FIGURE 4 - The normal modes of the water molecule.
Table II shows the results of the analysis of the rotational energy level scheme associated with the vibrational ground state. This analysis has been carried out using the theory developed in Chapter III. A sample calculation is given in Appendix E.

The values found for the rotational constants and moments of inertia are, of course, only effective values of these constants. Not only do the constants differ slightly for different values of J, which is apparent from Table II, but also one must expect, especially for the higher J values, that the constants differ from level to level for a given J. Thus, since here all 2J+1 levels going with a particular value of J are used in the calculation of the constants, only effective values of the constants for a given J are obtained in this manner. This situation is, of course, ultimately due to the fact that the rigid rotator Hamiltonian is a zero-order Hamiltonian, and inadequate to describe the system under study to the accuracy implied by the experimental measurements.

The quantity $\Delta$ appearing in the table is the inertial defect described by Darling and Dennison, and is defined as

$$\Delta = I_x - I_y - I_z.$$  \hspace{1cm} (4.1)

For a planar configuration, using average or equilibrium values of the moments of inertia, the inertial defect should be zero. But since we deal here with effective rather than average values, a non-zero inertial defect arises. As might be expected, the defect is more pronounced for the higher J values.

Tables III and IV show the results of the analysis of the
<table>
<thead>
<tr>
<th>J</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Iₓ</th>
<th>Iᵧ</th>
<th>Iₚ</th>
<th>Δ</th>
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</table>

* a, γ, A, B, C in units of cm⁻¹; β dimensionless; Iₓ, Iᵧ, Iₚ, Δ when multiplied by 10⁻⁴₀ in units of gm cm².
### TABLE III

**CALCULATED PHYSICAL PARAMETERS FOR THE WATER MOLECULE**

**FOR THE VIBRATIONAL STATE \( v_2=1, v_1=v_3=0 \)**

<table>
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<tr>
<th>( J )</th>
<th>( \alpha )</th>
<th>(-\beta)</th>
<th>( \gamma )</th>
<th>( A )</th>
<th>( B )</th>
<th>( C )</th>
<th>( I_x )</th>
<th>( I_y )</th>
<th>( I_z )</th>
<th>( \Delta )</th>
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* \( \alpha, \gamma, A, B, C \) in units of \( \text{cm}^{-1} \); \( \beta \) dimensionless; \( I_x, I_y, I_z, \Delta \) when multiplied by \( 10^{-10} \) in units of \( \text{gm cm}^2 \).
## TABLE IV

CALCULATED PHYSICAL PARAMETERS OF THE WATER MOLECULE

FOR THE VIBRATIONAL STATE $V_2=2$, $V_1=V_3=0$*

<table>
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<tr>
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<th>$-\beta$</th>
<th>$\gamma$</th>
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<th>$B$</th>
<th>$C$</th>
<th>$I_x$</th>
<th>$I_y$</th>
<th>$I_z$</th>
<th>$\Delta$</th>
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<td>15.42</td>
<td>34.15</td>
<td>3.19</td>
<td>1.81</td>
<td>0.819</td>
<td>0.56</td>
</tr>
<tr>
<td>5</td>
<td>57.91</td>
<td>0.4736</td>
<td>42.99</td>
<td>8.74</td>
<td>15.52</td>
<td>33.63</td>
<td>3.20</td>
<td>1.80</td>
<td>0.832</td>
<td>0.57</td>
</tr>
<tr>
<td>6</td>
<td>57.43</td>
<td>0.5081</td>
<td>41.61</td>
<td>8.67</td>
<td>15.73</td>
<td>33.01</td>
<td>3.23</td>
<td>1.78</td>
<td>0.848</td>
<td>0.60</td>
</tr>
</tbody>
</table>

* $\alpha$, $\gamma$, $A$, $B$, $C$ in units of cm$^{-1}$; $\beta$ dimensionless; $I_x$, $I_y$, $I_z$, $\Delta$ when multiplied by $10^{-10}$ in units of gm cm$^2$. 

---

* The table represents the calculated physical parameters of the water molecule for the vibrational state $V_2=2$, $V_1=V_3=0$. The parameters include $\alpha$, $\gamma$, $A$, $B$, and $C$, and the moments of inertia $I_x$, $I_y$, and $I_z$, along with the degree of freedom $\Delta$. All values are in units suitable for vibrational energy calculations. The parameters are given in specific units as indicated in the footnote.
rotational levels associated with the bending mode \( v_2 \), when the bending mode vibrational quantum number \( V_2 \) is equal to one and two, respectively.

One may attempt to find the effective values of the rotational constants for \( J=0 \) by fitting the calculated effective rotational constants to a curve of the form

\[
A = A_0 + A_1 J(J+1) + A_2 J^2(J+1)^2,
\]

and by using similar expressions for \( B \) and \( C \). Results of calculations of this nature must be accepted with some caution. It must be remembered that it is effective values of the constants that we are dealing with, and this makes any results obtained less meaningful, since we must not expect that an extrapolation of effective values of the constants will lead to precise values of the constants associated with the single level for which \( J=0 \). Also, it was found in the present investigation that the magnitude of the constants in \( (4.2) \) and their accuracy depend rather sensitively on how many and which values of \( J \) are used in the curve fitting, and on whether a parabolic fit or a straight line fit \( (A_2=0) \) is attempted. At least in the case of water vapor, these considerations show that not too much significance must be attached to the stretching coefficients (the coefficients of the \( J(J+1) \) terms and of the \( J^2(J+1)^2 \) terms), if they are found in this manner.

Using least square methods of curve fitting, and using all of
the rotational constants compiled in Tables II, III, and IV, one
finds (in \( \text{cm}^{-1} \)):

(a) for \( V_1=V_2=V_3=0 \),

\[
\begin{align*}
A(\pm 0.01) &= 9.27 - (0.00282)J(J+1) + (0.0000944)J^2(J+1)^2, \\
B(\pm 0.01) &= 11.51 + (0.00792)J(J+1) - (0.000236)J^2(J+1)^2, \\
C(\pm 0.01) &= 27.89 - (0.02146)J(J+1) + (0.000334)J^2(J+1)^2,
\end{align*}
\]

(b) for \( V_2=1, V_1=V_3=0 \),

\[
\begin{align*}
A(\pm 0.01) &= 9.17 - (0.00710)J(J+1) + (0.0000160)J^2(J+1)^2, \\
B(\pm 0.02) &= 11.65 + (0.0173)J(J+1) - (0.0000810)J^2(J+1)^2, \\
C(\pm 0.04) &= 31.25 - (0.03036)J(J+1) + (0.0000240)J^2(J+1)^2,
\end{align*}
\]

(c) for \( V_2=2, V_1=V_3=0 \),

\[
\begin{align*}
A(\pm 0.04) &= 9.06 - (0.0183)J(J+1) + (0.000223)J^2(J+1)^2, \\
B(\pm 0.06) &= 11.76 + (0.0401)J(J+1) - (0.000161)J^2(J+1)^2, \\
C(\pm 0.09) &= 35.73 - (0.0929)J(J+1) + (0.000688)J^2(J+1)^2.
\end{align*}
\]

In these, the probable error calculated for the \( A_0 \), \( B_0 \), and \( C_0 \) terms
is assumed to be the probable error in the \( A \), \( B \), and \( C \) terms. Because
of the smallness of the stretching coefficients this seems safe pro­
cedure. In the stretching coefficients not more than four significant
figures are retained, and only as many are retained as influence the
values of \( A \), \( B \), and \( C \) in (4.3) through (4.11) to the accuracy quoted.
Table V compares the values of the extrapolated rotational constants
found by previous investigators to those found in the present work.

The following illustrates the limited applicability of the
results obtained by curve fitting. If the term quadratic in \( J(J+1) \) is
<table>
<thead>
<tr>
<th></th>
<th>$V_2=0$</th>
<th>$V_2=1$</th>
<th>$V_2=2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>Benedict et al.</td>
<td>9.285, 14.512, 27.877</td>
<td>9.15, 14.66, 31.12</td>
<td>-</td>
</tr>
<tr>
<td>Dalby and Nielsen</td>
<td>-</td>
<td>9.15, 14.67, 31.20</td>
<td>-</td>
</tr>
<tr>
<td>Present work</td>
<td>9.27, 14.51, 27.89</td>
<td>9.17, 14.65, 31.25</td>
<td>9.06, 14.76, 35.73</td>
</tr>
</tbody>
</table>
not considered in (4.3), then a fit to the curve

\[ A = A_0 + A_1 J(J+1), \quad (4.12) \]

by least square methods of the data in Table II for \( A \) yields (in cm\(^{-1}\))

\[ A = 9.25 - (0.00112) J(J+1). \quad (4.13) \]

The stretching coefficient \( A_1 \) now differs from the one obtained in (4.3) by some 100%! And furthermore, a look at Table II shows that \( A \) now extrapolates to \( A_0 \) in an unsatisfactory manner. Even though the coefficient \( A_2 \) in (4.3) may be quite meaningless if taken by itself, its presence is necessary if \( A \) is to extrapolate to \( A_0 \) satisfactorily.

Of course, water is known to be a very "stretchy" molecule, and for other molecules the situation depicted here may be rather more reassuring.
CHAPTER V

THE RIGID ROTATOR "INCOMPLETE" SUM RULES

For the rigid rotator, the J-th submatrix of size \((2J+1) \times (2J+1)\) can be rearranged in a manner described below, such that it assumes a two-step form, one step of size \((J+1) \times (J+1)\), the other step of size \(J \times J\). The method of moments can then be applied to each of the two steps individually. The matrix can subsequently be rearranged once more. In this second rearrangement each of the steps obtained in the first rearrangement breaks up again into two steps, the "even by even" step into two steps of equal size, the "odd by odd" step into two steps, one having one more row and one more column than the other. Thus the J-th submatrix can be brought into four-step form, and the method of moments can be applied to each of the four steps individually.

While in the theory developed so far it is necessary that all \((2J+1)\) energies going with a particular value of \(J\) be known when calculating the rotational constants, it is apparent that a determination of the rotational constants can be undertaken without a knowledge of all \((2J+1)\) energies, if the sum rules applying to one of the steps of the J-th submatrix are used. In this way less complete experimental information suffices. It is in this sense that the word "incomplete" is used in the title of this chapter.
We will now describe the process of rearranging the J-th submatrix into the step form. The matrix elements of the J-th submatrix were given in (3.10) and (3.11). It is apparent from an examination of these that the J-th submatrix is diagonally symmetric about both its diagonals. Setting $W_{0,0} = A, W_{1,1} = W_{-1,-1} = B, W_{2,2} = W_{-2,-2} = C$, etc., and denoting the second off-diagonal elements by lower case letters, one may display the structure of the J-th submatrix as in Fig. 5. The $A, B,$ and $C$ introduced here should not be confused with the notation for the rotational constants. We believe the danger of confusion is rather small, and in any case we shall not use both notations concurrently. It has been pointed out by Mulliken$^{39}$ that it


is useful to introduce a representation characterized by the set of $(2J+1)$ symmetrized wavefunctions

$$(1/\sqrt{2})(\psi_K \pm \psi_{-K}); \psi_0; \ (K = 1, 2, \ldots, J), \tag{5.1}$$

instead of the set previously used here, viz., $\psi_K, K = J, J-1, \ldots, -J$. It is easily seen that if the set $\psi_K$ is orthonormal, then also the set (5.1) is orthonormal. Further examination shows that in terms of the symmetrized representation (5.1), the J-th submatrix will assume the step form shown in Fig. 6. In terms of Fig. 6, the upper left step is of size $(J+1) \times (J+1)$, and goes with the $(J+1)$ symmetrized functions $$(1/\sqrt{2})(\psi_K \pm \psi_{-K}); \psi_0.$$ The lower right step is of size $J \times J$, and goes with the $J$ antisymmetrized functions $$(1/\sqrt{2})(\psi_K - \psi_{-K}).$$
FIGURE 5

The form of the J-th submatrix of W.
FIGURE 6

The form of the J-th submatrix after the first rearrangement.
Arranging the rows and columns of the upper left step so that the elements having even values of $K$ in their subscripts stand together and the elements having odd values of $K$ in their subscripts stand together, the upper left step is further broken up into the substep $E^+$ consisting of even subscript rows and columns, and into the substep $O^+$ consisting of odd subscript rows and columns. Similarly, the lower right step is broken up into the substeps $E^-$ and $O^-$. The notation $E^+$, $E^-$, $O^+$, $O^-$ is due to King, Hainer, and Cross.\(^{15}\)

We now give the sum rules for the various steps of the $J$-th submatrix.

After the first rearrangement, the matrix is in the step form shown in Fig. 6. Since it is apparent that much of the original structure of the matrix is preserved in the symmetrizing operation described by Mulliken, it has been possible to develop the sum rules for the general case of arbitrary $J$. Details of this calculation are shown in Appendix F.

The following is found for the upper left step which is of size $(J+1) \times (J+1)$:

$$F_J = \frac{1}{3} aJ(J+1) - \frac{1}{12} J\gamma(1-\beta), \quad (5.2)$$

$$S_2 = \frac{1}{6} \gamma^2 J(J+1)(J+2)(m_o + m_1\beta + m_2\beta^2), \quad (5.3)$$

where

$$m_o = (2J+1)(8J-3), \quad (5.3.1)$$

$$m_1 = -10(2J-3), \quad (5.3.2)$$

$$m_2 = \frac{1}{3}(16J^2 + 22J - 33), \quad (5.3.3)$$
\[ S_3 = \frac{1}{6(71)}(J-1)J(J+1)(J+2)(J+3) \times \]
\[ X (n_0 + n_1 \beta + n_2 \beta^2 + n_3 \beta^3), \]
\[ (5.1) \]

where

\[ n_0 = (2J+1)(32J-15), \]
\[ (5.4.1) \]
\[ n_1 = 21(2J-15), \]
\[ (5.4.2) \]
\[ n_2 = -(64J^2 + 58J - 435), \]
\[ (5.4.3) \]
\[ n_3 = 7(2J-15). \]
\[ (5.4.4) \]

The following is found for the lower right step which is of size \( J \times J \):

\[ \overline{F}_J = (1/3)a_J(J+1) + (1/12)(J+1)\gamma(1-\beta), \]
\[ (5.5) \]
\[ S_2 = (1/61)\gamma^2(J-1)J(J+1)(m_0 + m_1 \beta + m_2 \beta^2), \]
\[ (5.6) \]

where

\[ m_0 = (2J+1)(8J+11), \]
\[ (5.6.1) \]
\[ m_1 = 10(2J+5), \]
\[ (5.6.2) \]
\[ m_2 = (1/3)(16J^2 + 10J - 39), \]
\[ (5.6.3) \]
\[ S_3 = \frac{1}{6(71)}(J-2)(J-1)J(J+1)(J+2)\gamma^3 \times \]
\[ X (n_0 + n_1 \beta + n_2 \beta^2 + n_3 \beta^3), \]
\[ (5.7) \]

where

\[ n_0 = (2J+1)(32J+17), \]
\[ (5.7.1) \]
\[ n_1 = -21(2J+17), \]
\[ (5.7.2) \]
\[ n_2 = -(64J^2 + 70J - 429), \]
\[ (5.7.3) \]
\[ n_3 = -7(2J+17). \]
\[ (5.7.4) \]

After the second rearrangement, the four steps \( E^+, E^-, 0^+, 0^- \) are obtained. So much of the original structure and symmetry of the \( J \)-th submatrix has been lost after the second rearrangement that a
calculation of the sum rules for the four steps $E^+$, $E^-$, $O^+$, $O^-$ in terms of arbitrary $J$ seems no longer practical. The method of calculation adopted here was that of calculating the sum rules for each of the four steps for all values of $J$ between zero and twelve. Subsequently the general form of the expressions was inferred from the expressions calculated for the particular $J$'s. We give here the inferred form for general $J$. We point out that, of course, rigorously, these expressions are known to hold only for $J = 0, 1, 2, \ldots, 12$. However, the consistency and relative simplicity of the general expressions obtained suggest very strongly that the expressions are indeed applicable to general $J$. The following results are secured in the manner described above:

(a) for $E^+$:

\[ F_J = \frac{1}{3}aJ(J+1), \text{ for } J \text{ even}, \quad (5.8.1) \]
\[ F_J = \frac{1}{3}aJ(J+1) - \frac{1}{3}\gamma_J, \text{ for } J \text{ odd}, \quad (5.8.2) \]
\[ S_2 = \frac{1}{3}(5!)(J+1)(J+2)(J+4)(J+5)\gamma^2 X (1+\beta^2/3), \text{ for } J \text{ even}, \quad (5.9.1) \]
\[ S_2 = \frac{1}{3}(5!)(J-1)(J+1)(J+3)\gamma^2 X \left[ (J+7) + (\beta^2/3)(J+13) \right], \text{ for } J \text{ odd}, \quad (5.9.2) \]
\[ S_3 = \frac{1}{3}(7!)(J-2)(J+1)(J+2)(J+4)(J+6)\gamma^3 X (16J-15)(1-\beta^2), \text{ for } J \text{ even}, \quad (5.10.1) \]
\[ S_3 = \frac{1}{3}(7!)(J-3)(J-1)(J+1)(J+3)(J+5)\gamma^3 X \left[ (16J-31) - \beta^2(16J+25) \right], \text{ for } J \text{ odd}; \quad (5.10.2) \]

(b) for $E^-$:

\[ F_J = \frac{1}{3}aJ(J+1) + \frac{1}{3}\gamma(J+1), \text{ for } J \text{ even}, \quad (5.11.1) \]
\( \bar{F}_j = (1/3)aJ(J+1), \) for \( J \) odd and \( \gamma \), \hfill (5.11.2)

\( S_2 = (1/3(5!))(J-2)J(J+1)(J+2)X \)
\[ X \left[ (4J+11) + (3J-3)(4J-9) \right], \text{ for } J \text{ even}, \hfill (5.12.1) \]

\( S_2 = (1/3(5!))(J-3)(J-1)J(J+1)(J+3)X \)
\[ X (1+\beta^2/3), \text{ for } J \text{ odd}, \hfill (5.12.2) \]

\( S_3 = (1/3(7!))(J-4)(J-2)J(J+1)(J+2)(J+4)X \)
\[ X \left[ (16J+47) - \beta^2(16J-9) \right], \text{ for } J \text{ even}, \hfill (5.13.1) \]

\( S_3 = (1/3(7!))(J-5)(J-3)(J-1)J(J+1)(J+3)X \)
\[ X (16J+31)(1-\beta^2), \text{ for } J \text{ odd}; \hfill (5.13.2) \]

\[ (c) \text{ for } 0^\pm: \]

\( \bar{F}_j = (1/3)aJ(J+1) - (1/6)(J+1)\gamma(1+\beta), \text{ for } J \text{ even}, \hfill (5.14.1) \]

\( \bar{F}_j = (1/3)aJ(J+1) + (1/6)J\gamma(1+\beta), \text{ for } J \text{ odd}, \hfill (5.14.2) \]

\( S_2 = (1/3(5!))(J-2)J(J+1)(J+2)X \)
\[ X \left[ (4J-1) + 10\beta + (3\beta^2/3)(2J+3) \right], \text{ for } J \text{ even}, \hfill (5.15.1) \]

\( S_2 = (1/3(5!))(J-1)J(J+1)(J+3)X \)
\[ X \left[ (4J-2) + 10\beta + (3\beta^2/3)(2J-1) \right], \text{ for } J \text{ odd}, \hfill (5.15.2) \]

\( S_3 = (1/3(7!))(J-4)(J-2)J(J+1)(J+2)(J+4)X \)
\[ X \left[ 16(J-1) + 2J\beta - 4\beta^2(J+3) \pm 7\beta^3 \right], \text{ for } J \text{ even}, \hfill (5.16.1) \]

\( S_3 = (1/3(7!))(J-3)(J-1)J(J+1)(J+3)(J+5)X \)
\[ X \left[ 16(J+2) + 2J\beta - 4\beta^2(J+1) \pm 7\beta^3 \right], \text{ for } J \text{ odd}. \hfill (5.16.2) \]

The expressions for \( \bar{F}_j \) have already been given by Mecke.\textsuperscript{13}

It is to be emphasized that the sums \( S_2 \) and \( S_3 \) discussed in this chapter are calculated about the mean of the energies associated with the appropriate step of the \( J \)-th submatrix rather than about the mean of the \((2J+1)\) energies going with the entire \((2J+1) \times (2J+1)\) sub-
matrix. If the latter requirement were needed, it obviously would constitute a rather serious shortcoming, since the "incomplete" sums will be most useful in those cases where all \((2J+1)\) energies are not known. In that event, of course, the mean of these \((2J+1)\) energies is also unknown.

Calculation of the rotational constants from the sum rules given in this chapter proceeds by first solving the appropriate \(S_2\) and \(S_3\) equations simultaneously for \(\beta\). With \(\beta\) known, the magnitude of \(\gamma\) follows from the \(S_2\) or \(S_3\) equation, and its sign follows from the \(S_3\) equation. Then, with \(\beta\) and \(\gamma\) determined, \(\alpha\) is found from the equation for \(F_j\), and finally the rotational constants follow from (3.28), (3.29), and (3.30).

The question that needs to be examined rather carefully now is that of "which energy levels go with which step of the \(J\)-th submatrix."

Definite answers to this question can be given from an examination of the symmetry properties of the rotational wavefunctions. Various authors have dealt with the symmetry classification of the asymmetric rotator energy levels, notably Casimir,\(^9\) Dennison,\(^10\) Ray,\(^12\) Mecke,\(^13\) Mulliken,\(^39\) and King, Hainer, and Cross.\(^15\) Various notational schemes are used, and the correlation between these schemes has been discussed by King, Hainer, and Cross,\(^15\) Herzberg,\(^40\)

van Winter,²¹ and, most recently, by Nielsen.⁴

Associated with the motion of a top, one may imagine a body-fixed ellipsoid.¹⁰ The semi-principal axes of this ellipsoid (hereafter denoted by a, b, and c) are along the coordinate axes of the principal axis system of the inertia tensor, and the lengths of the axes of the ellipsoid are chosen proportional to \(1/\sqrt{I_x}\), \(1/\sqrt{I_y}\), and \(1/\sqrt{I_z}\), respectively. It is apparent that for an asymmetric rotator the associated ellipsoid will be a general ellipsoid with its semi-principal axes all of different length. In torque- and force-free space, the motion of the rotator is such that the associated ellipsoid rolls without slipping on a space-fixed plane, the invariable plane.

The rotational wavefunctions are functions of the orientation of the body-fixed reference frame with respect to an arbitrary space-fixed reference frame. The square of the absolute magnitude of the rotational wavefunction amplitude gives, according to the postulates of quantum mechanics, the probability of finding the rotator and its associated ellipsoid in a given orientation in the space-fixed system. Because of the symmetry of the ellipsoid, an orientation that is obtained from a given one by a rotation over 180° about one of the principal axes must have the same probability as the original orientation, and therefore the rotational wavefunction must either remain unchanged or change sign under the rotation but must not undergo changes other than changes of sign under the rotation. The designation used in group theory for a
rotation by $180^\circ$ about the $i$-axis is $C_2^i$. Thus, a rotational level of an asymmetric rotator may be classified according to the behavior (+ or -) of the rotational wavefunction describing this level under the operations $C_2^a$, $C_2^b$, and $C_2^c$. Since one of the operations is equivalent to the two others carried out in succession, it is sufficient to determine the behavior with respect to two of them. Usually $C_2^c$ and $C_2^a$ are chosen. The levels may thus be classified as belonging to one of four types, briefly denoted by ++, +-, -, and --, where the first sign characterizes the behavior with respect to $C_2^c$ and the second sign characterizes the behavior with respect to $C_2^a$. The behavior with respect to $C_2^b$ is then given by the product of the two signs. This notation is the one introduced by Dennison.\(^{10}\) In the language of group theory, $C_2^a$, $C_2^b$, $C_2^c$, together with the identity operation $I$, form a four-group, the group of proper rotations of the general ellipsoid; and properties associated with the ellipsoid may be characterized as belonging to one of the four possible species defined by the four-group or to combinations of these species.

The notation introduced previously for the four steps of the rearranged $J$-th submatrix was $E^+$, $E^-$, $O^+$, and $O^-$ and the sum rules obtained for the respective steps were designated accordingly. It can be shown\(^1,15,21\) that associated with each step there are levels of one symmetry classification only. The $E,O$ notation is, of course, set up in such a manner that it classifies an energy eigenvalue relative to its origin from one of the four steps of the $J$-th submatrix. Thus, the $E,O$ notation is most convenient for designating the various sum
rules, as has been done. On the other hand, in the Dennison scheme, the emphasis is upon the symmetry operations of the associated ellipsoid and the behavior of the wavefunctions under these operations. The topic to be discussed below is best approached in terms of the Dennison scheme, and it thus becomes necessary here to relate the $E_0$ notation to the Dennison notation.

Dennison has shown that the highest level of the $(2J+1)$ levels going with a given $J$ is $+$ with respect to $C_2^c$, the two next highest are $-$, the two next highest are $+$, and so on. A similar scheme holds for $C_2^a$, but in that case the levels are labeled successively as $+- - + -$, etc., starting with the lowest level. In this way the type of each level can be deduced.

As discussed by Nielsen in the $E_0$ scheme, for $A > B > C$, and for $B$ larger than the mean $\alpha/3$ (i.e., in terms of Ray's asymmetry parameter $\mathcal{X}$, $\mathcal{X}$ is positive, $0 < \mathcal{X} < 1$; or in terms of our Fig. 8, the lower portion of the figure applies), the ordering of the $(2J+1)$ energy levels going with a given $J$ is as follows: the highest level is $E^+$, the next highest is $0^+$, the next is $0^-$, the next is $E^-$, the next is $E^+$, etc.

Thus, from the above, and under the conditions stated, the two notations are seen to be related as follows:
(a) for J even:

\[
\begin{array}{c|ccc}
\theta^c_2 & \theta^a_2 & (\theta^b_2) \\
\hline
+ & + & (+) & \sim E^+
\end{array}
\]

\[
\begin{array}{c|ccc}
\theta^c_2 & \theta^a_2 & (\theta^b_2) \\
\hline
+ & - & (-) & \sim E^-
\end{array}
\]

\[
\begin{array}{c|ccc}
\theta^c_2 & \theta^a_2 & (\theta^b_2) \\
\hline
- & + & (-) & \sim O^+
\end{array}
\]

\[
\begin{array}{c|ccc}
\theta^c_2 & \theta^a_2 & (\theta^b_2) \\
\hline
- & - & (+) & \sim O^-
\end{array}
\]

(b) for J odd:

\[
\begin{array}{c|ccc}
\theta^c_2 & \theta^a_2 & (\theta^b_2) \\
\hline
+ & - & (-) & \sim E^+
\end{array}
\]

\[
\begin{array}{c|ccc}
\theta^c_2 & \theta^a_2 & (\theta^b_2) \\
\hline
+ & + & (+) & \sim E^-
\end{array}
\]

\[
\begin{array}{c|ccc}
\theta^c_2 & \theta^a_2 & (\theta^b_2) \\
\hline
- & - & (+) & \sim O^+
\end{array}
\]

\[
\begin{array}{c|ccc}
\theta^c_2 & \theta^a_2 & (\theta^b_2) \\
\hline
- & + & (-) & \sim O^-
\end{array}
\]

Thus one may first label the levels with the Dennison notation and then use (5.17) or (5.18) to ascertain which of the levels are to be included in the calculation for a step of a given symmetry type.

We must now also examine the case in which B is smaller than the mean a/3. In this case, one may retain the ordering A>B>C, and then \( \mathcal{H} \) will change sign and lie in the range \(-1<\mathcal{H}<0\). Or, as we prefer to do here (see Appendix D), one may specify the ordering A>B>C, in which case A and C have interchanged roles, the upper part of our Fig. 8 applies, and now \( \mathcal{H} \) will retain the range \( 0<\mathcal{H}<1 \). Now, an interchange of A and C will interchange the first column of (5.17) and (5.18) with the second column of (5.17) and (5.18). This for J even will interchange the symmetry species of \( E^- \) and \( O^+ \), but will leave the species of \( E^+ \) and \( O^- \) unchanged; and for J odd, this
will interchange the symmetry species of $E^+$ and $0^-$, but will leave the species of $E^-$ and $0^+$ unchanged. Thus, in addition to (5.17) and (5.18), which apply to the case $A>B>C$, we also have the following, applying to the case $A<B<C$:

(a) for $J$ even:

$$
\begin{array}{ccc}
\mathcal{C}_2^a & \mathcal{C}_2^c & (\mathcal{C}_2^b) \\
+ & + & (+) \sim E^+ \\
+ & - & (-) \sim 0^+ \\
- & + & (-) \sim E^- \\
- & - & (+) \sim 0^- \\
\end{array}
$$

(5.19)

(b) for $J$ odd:

$$
\begin{array}{ccc}
\mathcal{C}_2^a & \mathcal{C}_2^c & (\mathcal{C}_2^b) \\
+ & - & (-) \sim 0^- \\
+ & + & (+) \sim E^- \\
- & - & (+) \sim 0^+ \\
- & + & (-) \sim E^+ \\
\end{array}
$$

(5.20)

Thus, the result of our considerations is that a calculation should start by labeling the energy levels in the manner described on page 51 with the Dennison notation. The identification between the Dennison designation of the energy levels and the sum rules designated by $E^+$, $E^-$, $0^+$, and $0^-$ is then made by using (5.17) and (5.18) if $A>B>C$; and by using (5.19) and (5.20) if $A<B<C$.

It now becomes clear why the sum rules for $E^+$ and $E^-$ contain only even powers of $\beta$ and why the sum rules for $0^-$ can be obtained from the corresponding ones for $0^+$ by changing the sign of $\beta$. Con-
Consider an interchange of A and B. This changes the sign of $\beta$, but leaves $\alpha$ and $\gamma$ unchanged. Now, reference to (5.17) through (5.20) shows that an interchange of A and B leaves the symmetry type of the E levels unchanged but interchanges the symmetry type of the $0^+$ levels with that of the $0^-$ levels. This implies that the E sum rules must contain only even powers of $\beta$ and that the $0^+$ sum rules are obtained from the $0^-$ sum rules by setting $\beta$ equal to its negative.

It is also clear that the sum rules (5.2), (5.3), and (5.4) for the $(J+1) \times (J+1)$ step go with those levels which are identified with $E^+$ and $0^+$; and that the sum rules (5.5), (5.6), and (5.7) for the $J \times J$ step go with those levels which are identified with $E^-$ and $0^-$. Finally, the sum rules for the $(J+1) \times (J+1)$ step may also be applied to the levels $E^+$ and $0^-$ if in the expressions, $\beta$ is replaced by $-\beta$; and similarly, the sum rules for the $J \times J$ step may also be applied to the levels $E^-$ and $0^+$ if in the expressions, $\beta$ is replaced by $-\beta$. 

Our purpose here in applying the "incomplete" sum rules developed in Chapter V to the water vapor data of Benedict, Claassen, and Shaw is mainly one of testing the theory developed in Chapter V. Because of this, a more complete analysis has not been carried out, but only one even value of $J$ ($J=6$) and one odd value of $J$ ($J=7$) for the case of the vibrational ground state have been considered.

As the results of Chapter IV show, the water molecule falls into the class of rotators for which the intermediate rotational constant lies below the mean $a/3$. Hence (5.19) and (5.20) apply rather than (5.17) and (5.18). The results of the calculations are summarized in Tables VI and VII, which are self-explanatory. The entries $\Delta F_j$ specify whether the mean of the levels used lies above or below the mean of all $(2J+1)$ levels going with a particular $J$.

One is hesitant to draw conclusions from an analysis as incomplete as the one presented here even though one is tempted to do so. However, if one may be allowed the luxury of theorizing, he may observe that our results show that there is very definitely an experimentally observable variation of the rotational constants within a given $J$. The variations can apparently be correlated with
### TABLE VI

CALCULATED PHYSICAL PARAMETERS OF THE WATER MOLECULE

FOR \( V_1 = V_2 = V_3 = 0, \ J = 6^* \)

<table>
<thead>
<tr>
<th>Levels: ( \tau = )</th>
<th>All</th>
<th>( E^+ )</th>
<th>( 0^+ )</th>
<th>( E^- )</th>
<th>( 0^- )</th>
<th>( E^{0+} )</th>
<th>( E^{0-} )</th>
<th>( E^{+0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 6, 2, -2, -6 )</td>
<td>11.68</td>
<td>11.71</td>
<td>11.69</td>
<td>15.18</td>
<td>14.59</td>
<td>14.78</td>
<td>15.04</td>
<td>14.73</td>
</tr>
<tr>
<td>( 3, -1, -5 )</td>
<td>27.04</td>
<td>27.01</td>
<td>27.20</td>
<td>26.96</td>
<td>27.26</td>
<td>27.04</td>
<td>26.97</td>
<td>27.06</td>
</tr>
<tr>
<td>( 5, 1, -3 )</td>
<td>51.02</td>
<td>50.93</td>
<td>51.15</td>
<td>51.11</td>
<td>51.05</td>
<td>51.03</td>
<td>50.94</td>
<td>50.95</td>
</tr>
<tr>
<td>( 4, 0, -4 )</td>
<td>0.5621</td>
<td>0.5486</td>
<td>0.5349</td>
<td>0.6269</td>
<td>0.5267</td>
<td>0.5545</td>
<td>0.6121</td>
<td>-0.5521</td>
</tr>
</tbody>
</table>

* All entries in \( \text{cm}^{-1} \) except \( \beta \) which is dimensionless.
### TABLE VII

**CALCULATED PHYSICAL PARAMETERS OF THE WATER MOLECULE**

FOR $V_1=V_2=V_3=0$, $J=7$

<table>
<thead>
<tr>
<th>Levels: $\tau =$</th>
<th>All</th>
<th>$E^+$</th>
<th>$O^+$</th>
<th>$E^-$</th>
<th>$O^-$</th>
<th>$E^+O^+$</th>
<th>$E^O^-$</th>
<th>$E^+O^-$</th>
<th>$E^O^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,1,-3,-7</td>
<td>14.88</td>
<td>14.66</td>
<td>15.03</td>
<td>14.88</td>
<td>14.98</td>
<td>14.85</td>
<td>15.13</td>
<td>14.79</td>
<td>15.02</td>
</tr>
<tr>
<td>4,0,-4</td>
<td>50.82</td>
<td>50.64</td>
<td>50.93</td>
<td>50.96</td>
<td>50.83</td>
<td>50.75</td>
<td>50.74</td>
<td>50.74</td>
<td>50.94</td>
</tr>
<tr>
<td>-$\beta$</td>
<td>0.5828</td>
<td>0.5298</td>
<td>0.6001</td>
<td>0.5768</td>
<td>0.6205</td>
<td>0.5742</td>
<td>0.6237</td>
<td>-0.5714</td>
<td>-0.5993</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>29.55</td>
<td>28.33</td>
<td>29.20</td>
<td>29.84</td>
<td>29.65</td>
<td>29.55</td>
<td>29.59</td>
<td>29.70</td>
<td>29.34</td>
</tr>
<tr>
<td>$\Delta F_j$</td>
<td>0</td>
<td>-69.51</td>
<td>+15.81</td>
<td>+2.63</td>
<td>+51.74</td>
<td>-26.85</td>
<td>+30.69</td>
<td>-8.89</td>
<td>+10.16</td>
</tr>
</tbody>
</table>

* All entries in cm$^{-1}$ except $\beta$ which is dimensionless.
\[ \Delta F_J \] as may be expected, and if so, then doubtless they may also be correlated to corresponding changes in the higher moments. Of course, this analysis still does not give rotational constants applicable to a single energy level but it represents a step in that direction. Also, it is seen that \( \alpha \) and \( \gamma \) vary but little. On the other hand, variations in \( \beta \) are appreciable. For a given relatively low \( J \) it thus seems that the character of the centrifugal distortion is such that the equivalent spherical rotator, described in terms of \( \alpha \), changes but little; such that the deviation of the spherical rotator toward the prolate symmetric top, described in terms of \( \gamma \), changes but little; however, such that the deviation from the prolate symmetric top, described in terms of the asymmetry parameter \( \beta \), shows appreciable variation from level to level.

The line of inquiry suggested in this chapter may prove a profitable one.

We point out that if an incorrect identification of the sum rules with the proper species of level was made (through ignorance of this aspect in the early stages of the investigation), absurdities in the results were encountered in all cases of incorrect identification. It was possible, in fact, to infer the schemes (5.19) and (5.20) by a process of trial and error.
CHAPTER VII

NON-RIGID ROTATOR SUM RULES

Observed rotational spectra indicate that the rotating molecular configuration is not strictly rigid. Centrifugal forces act on the nuclei, and thus the molecule is increasingly distorted in the higher rotational levels, and this leads to deviations from the energy scheme predicted by a rigid rotator Hamiltonian of the form (3.1).

The form of a more exact Hamiltonian is quite complex. Improved Hamiltonians have been discussed in detail by Wilson,\(^1\) Crawford and Cross,\(^2\) Shaffer and Nielsen,\(^3\) and by Nielsen.\(^4\) Recently Kivelson and Wilson\(^5\) have given a method of dealing with non-rigidity in asymmetric molecules. In this method, the energies are expressed as zero-order rigid top energies plus perturbation terms due to centrifugal stretching. However, fitting a spectrum (say, using the King, Hainer, and Cross tables) to a rigid top

---

Hamiltonian is already quite laborious, and consideration of the centrifugal terms substantially adds to the task.

We have already seen in Chapters IV and VI that in the case of the water molecule, centrifugal distortion effects are quite evident. In fact, in the case of water vapor the centrifugal corrections are large enough to doom to failure the technique considered in this chapter, and therefore we cannot claim unlimited applicability of the theory developed here. However, there is good reason to believe that the sum rules developed here which take centrifugal stretching effects into account explicitly will prove workable for heavier molecules (especially for relatively low values of $J$) and for molecules with less pronounced asymmetries than water. This inference is drawn from the observation that centrifugal stretching effects can be treated by approximation methods and with relative ease in symmetric tops where these effects are quite small. Also, the theory developed here should prove to be a good starting point for a more refined treatment of stretching effects.

Barring such complications as accidentally degenerate vibration frequencies, internal rotation, and certain anomalies, the work of Wilson, and Nielsen indicates that to the second order of perturbation one may set up a rotator Hamiltonian of the form

\[ W = W_0 + W_1, \]  

where $W_0$ is the Hamiltonian of an effective rigid rotator,

\[ W_0 = A \mathbf{P}_x^2 + B \mathbf{P}_y^2 + C \mathbf{P}_z^2, \]  

\[ \text{(7.1)} \]

\[ \text{(7.2)} \]
and where $W_1$ is the centrifugal distortion term and of the form

$$W_1 = \sum_{\mu} \sum_{\nu} \sum_{\gamma} \sigma_{\mu \nu \gamma} P_{\mu} P_{\nu} P_{\gamma},$$  \hspace{1cm} (7.3)$$

with the Greek letter indices ranging over the rectangular coordinates $x, y, z$ of the body-fixed coordinate system. The coefficients $\sigma$ depend on the force constants and geometrical form of the molecule and are the quantities that one would be interested to have evaluated from experimental data.

Because of the non-commutative property of the angular momentum operators $P_{\mu}$, there are, in general, eighty-one terms in the sum (7.3), and thus eighty-one coefficients $\sigma$.

The operators $P_{\mu} P_{\nu} P_{\gamma}$ may be divided into two groups: (a) the group of operators whose possibly non-zero elements (in the representation defined by (3.3) and (3.4)) are diagonal, second off-diagonal, and fourth off-diagonal elements and (b) the group of those operators whose possibly non-zero elements are first off-diagonal and third off-diagonal elements. In the representation used here, the operator $P_z$ is diagonal, and $P_x$ and $P_y$ have non-zero elements only in their first off-diagonal positions. From the definition of matrix multiplication, it follows that of the $P_{\mu}^2$ terms those that contain $P_z$ an even number of times (or not at all) will belong to Group (a) above, while those that contain $P_z$ an odd number of times will belong to Group (b). Forty-one operators are found to belong to Group (a), the remaining forty to Group (b).

We now make the assumption that terms quadratic and cubic in the coefficients $\sigma$ may be neglected compared with terms linear in $\sigma$.
It is shown in Appendix G that terms belonging to Group (b) will not contribute linearly to the moments $S_1$, $S_2$, and $S_3$. Hence, under the assumption just stated, the operators of Group (b) may be dropped. The observation that Group (b) terms are probably negligible and appear only in molecules that possess no symmetry whatsoever has already been made by Nielsen\(^3\),\(^4\) and has also been discussed by Kivelson and Wilson.\(^1\)

The work of Nielsen,\(^3\),\(^4\) Wilson,\(^1\) and Kivelson and Wilson\(^1\) indicates further that in practically all cases of interest, it is allowable to symmetrize the terms of (7.3) by taking:

\[
\sigma_{\mu \nu \mu} = \sigma_{\nu \mu \mu}, \quad (7.4)
\]

\[
\sigma_{\mu \nu \mu} = \sigma_{\mu \nu \mu} = \sigma_{\mu \mu \nu} = \sigma_{\nu \nu \mu}, \quad (7.5)
\]

\[
\sigma_{\mu \mu \nu} = \sigma_{\mu \nu \mu} = \sigma_{\nu \mu \mu}, \quad (7.6)
\]

and

\[
\sigma_{x z y} = \sigma_{y z x} = \sigma_{x z y} = \sigma_{y z x}, \quad (7.7)
\]

By using (7.4) through (7.7), we obtain now thirteen possible operator combinations in (7.3), viz.:

1. \(P_L^{1} x\)
2. \(P_L^{1} y\)
3. \(P_L^{1} z\)
4. \(P_2^{y} P_2^{x} + P_2^{z} P_2^{y}\)
5. \(P_2^{x} P_2^{y} P_2^{z}\)
6. \(P_2^{x} P_2^{y} P_2^{z}\)
7. \((P_2^{x} P_2^{y} )^2, (P_2^{y} P_2^{z} )^2, (P_2^{z} P_2^{x} )^2\)
8. \((P_2^{x} P_2^{y} )^2\)
9. \((P_2^{y} P_2^{z} )^2\)
10. \(P_2^{x} (P_2^{y} P_2^{z} ) + (P_2^{y} P_2^{z} ) P_2^{x}\)
11. \(P_2^{y} (P_2^{x} P_2^{z} ) + (P_2^{x} P_2^{z} ) P_2^{y}\)
12. \(P_2^{z} (P_2^{y} P_2^{x} ) + (P_2^{y} P_2^{x} ) P_2^{z}\)
13. \((P_2^{x} P_2^{y} ) (P_2^{y} P_2^{z} ) + (P_2^{y} P_2^{z} ) (P_2^{z} P_2^{x} ) + (P_2^{z} P_2^{x} ) (P_2^{x} P_2^{y} )\). \(7.8\)
The non-zero matrix elements of these thirteen operator combinations are compiled in Appendix H.

From Appendix H, it is seen that operators (10), (11), (12), and (13) of (7.8) have pure imaginary matrix elements and in Appendix I, it is shown that the coefficients $\sigma$ associated with these operators do not occur linearly in $S_1$, $S_2$, and $S_3$, and thus operators (10), (11), (12), and (13) can be dropped here.

Furthermore, from the angular momentum operator commutation relations, viz.:

$$ P_\mu P_\nu - P_\nu P_\mu = -i\delta_{\mu\nu}, \quad \text{(cyclic)}, \quad (7.9) $$

it is shown in Appendix J that

$$ (P_\mu P_\nu + P_\nu P_\mu)^2 = 2(P_\mu^2 P_\nu^2 + P_\nu^2 P_\mu^2) + 3P_\mu^2 - 2P_\nu^2 - 2P_\mu^2. \quad (7.10) $$

Hence operators (7), (8), and (9) can be absorbed into operators (4), (5), and (6) of (7.8), and into the zero-order Hamiltonian $W_0$, i.e., operators (7), (8), and (9) can be dropped from explicit consideration (in fact, must be dropped, otherwise linear dependence difficulties in the moment equations will occur).

After these considerations, there remains thus a Hamiltonian of the form

$$ W = W_0 + \sigma_1 P_x^1 + \sigma_2 P_y^1 + \sigma_3 P_z^1 + $$

$$ + \sigma_4 (P_x^2 P_y^2 + P_y^2 P_x^2) + \sigma_5 (P_x^2 P_z^2 + P_z^2 P_x^2) + \sigma_6 (P_y^2 P_z^2 + P_z^2 P_y^2). \quad (7.11) $$

The details of calculating the moments for this Hamiltonian are given in Appendix K. With

$$ \sigma_1 = (15/2)\gamma \lambda_i, \quad i=1,2,\ldots,6, \quad (7.12) $$

one finds for the moments of the $J$-th submatrix (with $J(J+1)=f$):
\[ F_J = (1/3)af + \]
\[ + \frac{1}{\gamma} \left[ (\lambda_1 + \lambda_2 + \lambda_3)f(3f-1) + (\lambda_4 + \lambda_5 + \lambda_6)f(2f+1) \right]; \quad (7.13) \]
\[ S_{2/P_2} = (1+\beta^2/3) - (15/7)(6f-5)[\lambda_1(1-\beta) + \lambda_2(1+\beta) - 2\lambda_3] + \]
\[ + (30/7)(f+5)[\lambda_4(1-\beta) + \lambda_5(1+\beta) - 2\lambda_6]; \quad (7.14) \]
\[ S_{3/P_3} = (1-\beta^2) - \]
\[ - (3/2)\lambda_1 \left[ 3(3f-1) + 30\beta(f-1) - \beta^2(7f-9) \right] - \]
\[ - (3/2)\lambda_2 \left[ 3(3f-1) - 30\beta(f-1) - \beta^2(7f-9) \right] + \]
\[ + 3\lambda_3 \left[ 3(6f-7) - \beta^2(4f-3) \right] - \]
\[ - 3\lambda_4 \left[ 3(f-7) - 30\beta + \beta^2(f+3) \right] - \]
\[ - 3\lambda_5 \left[ 3(f-7) + 30\beta + \beta^2(f+3) \right] - \]
\[ - 3\lambda_6 \left[ 3(f+8) + \beta^2(f-12) \right]. \quad (7.15) \]

The moment equations can be written in a more symmetric form by introducing the quantities:

\[ \alpha_1 = (\lambda_1 + \lambda_2 + \lambda_3), \quad (7.16) \]
\[ \alpha_2 = (\lambda_4 + \lambda_5 + \lambda_6), \quad (7.17) \]
\[ \beta_1 = (\lambda_1 - \lambda_2)/(2\lambda_3 - \lambda_1 - \lambda_2), \quad (7.18) \]
\[ \beta_2 = (\lambda_4 - \lambda_5)/(2\lambda_6 - \lambda_4 - \lambda_5), \quad (7.19) \]
\[ \gamma_1 = (15/11)(2\lambda_5 - \lambda_1 - \lambda_2), \quad (7.20) \]
\[ \gamma_2 = (15/11)(2\lambda_6 - \lambda_4 - \lambda_5). \quad (7.21) \]

In terms of these quantities, the moment equations are:

\[ \bar{F}_J = (1/3)af + \frac{1}{\gamma}[\alpha_1f(3f-1) + \alpha_2f(2f+1)]; \quad (7.22) \]
\[ S_{2/P_2} = (1+\beta^2/3) + 2(6f-5)\gamma_1(1+\beta_1) - \]
\[ - 4(f+5)\gamma_2(1+\beta_2); \quad (7.23) \]
\[ \frac{S_2}{\rho_3 y^3} = (1-\beta^2) + \]
\[ + 9(f-2)(1+\beta^2/3)(a_1-a_2) + \]
\[ + 2\gamma_1(f-1)[(1-\beta^2/3) - 2\beta \beta_1] - \]
\[ - 4\gamma_2 [(1-\beta^2/3) - 2\beta \beta_2] \]
\[ (7.24) \]

The moment equations contain nine physical parameters to be evaluated, viz., \( \alpha, \beta, \gamma, a_1, a_2, \beta_1, \beta_2, \gamma_1, \gamma_2 \). If the three moment equations are applied to three different values of \( J \), a set of nine equations is obtained which can be solved for the nine physical constants. However, it is simpler to find extrapolated (to \( J=0 \)) values of \( \alpha, \beta, \) and \( \gamma \) from a rigid rotator analysis of the kind illustrated in Chapters IV and VI, and then to use these values in the moment equations (7.22), (7.23), and (7.24) for the non-rigid rotator. If this procedure is followed, then the moment equations are applied to two different values of \( J \), yielding a set of six equations for the six constants associated with the stretching. This set of six equations can be solved with little difficulty. If in the calculation, a trend for the values of the constants develops, it may be necessary to readjust the assumed values of \( \alpha, \beta, \) and \( \gamma \).

After the values of the six parameters associated with the stretching are found in the manner just described, the stretching constants \( \lambda \) follow from (7.16) through (7.21) as:

\[ \lambda_1 = (1/3)[a_1 - (7/15)\gamma_1(1-3\beta_1)] \]
\[ (7.25) \]
\[ \lambda_2 = (1/3)[a_1 - (7/15)\gamma_1(1+3\beta_1)] \]
\[ (7.26) \]
\[ \lambda_3 = (1/3)[a_1 + (14/15)\gamma_1] \]
\[ (7.27) \]
\[ \lambda_4 = \frac{1}{3} \left[ a_2 - \left( \frac{7}{15} \right) \gamma_2 (1-3\beta_2) \right], \quad (7.28) \]
\[ \lambda_5 = \frac{1}{3} \left[ a_2 - \left( \frac{7}{15} \right) \gamma_2 (1+3\beta_2) \right], \quad (7.29) \]
\[ \lambda_6 = \frac{1}{3} \left[ a_2 + \left( \frac{14}{15} \right) \gamma_2 \right]. \quad (7.30) \]

From these, the constants \( \sigma \) follow from (7.12).
Centrifugal stretching effects in the water molecule are present to an extent that makes direct application of the moment equations (7.22), (7.23), and (7.24) impossible. However, in terms of the theory developed, one may discuss stretching effects in the water molecule in the following manner.

If the molecule were strictly a rigid top, then the rigid top moment equations (3.20), (3.21), and (3.22) would apply with \( a \), \( \beta \), and \( \gamma \) constants and independent of \( J \). Writing the moment equations in the form

\[
\begin{align*}
S_1/p_1 &= \alpha, \\
S_2/p_2 &= \gamma^2(1+\beta^2/3), \\
S_3/p_3 &= \gamma^3(1-\beta^2),
\end{align*}
\]

we see that if we plot \( S_i/p_i \) (\( i=1,2,3 \)) vs. \( J(J+1) \), we should obtain straight line graphs with zero slope.

From the moment equations derived from a first order stretching theory, viz., (7.22), (7.23), and (7.24), we see that a plot of \( S_1/p_1 \) vs. \( J(J+1) \) should give straight line graphs with non-zero slope.

For the vibrational ground state levels of water the quantities \( S_1/p_1 \) computed from the Benedict, Claassen, and Shaw data
are compiled in Table VIII and are plotted vs. \( J(J+1) \) in Fig. 7. It is seen that they do not give straight line graphs.

Furthermore, in order that a first order analysis meet with success, the slope of the \( S_1/p_1 \) graphs, which is a measure of the deviation from zero-order rigid top theory, must be small. As can be seen from Table VIII, while this is the case for \( S_1/p_1 \), and to a lesser extent for \( S_2/p_2 \), this is decidedly not the case for \( S_3/p_3 \).

Of all the \( F^h \) terms of the Hamiltonian (7.1) that were discarded for one reason or another in the first order theory of Chapter VII, none had diagonal matrix elements, and thus the equation for the first moment, viz., (7.22), which involves only diagonal elements is not changed by this discard. Also, obtaining this equation did not involve discarding any terms quadratic and cubic in the coefficients \( \sigma \) introduced in (7.3), because these do not occur other than linearly in (7.22). Nevertheless, \( S_1/p_1 \) does not give a straight line graph as predicted, and thus the observation of Benedict\(^{114} \) that \( F^h \) terms alone are inadequate to describe stretching effects in the water molecule is confirmed here.

If terms quadratic and cubic in \( \sigma \) are not dropped from the moment equations, these, instead of all being linear in \( f=J(J+1) \), should assume the form:

\(^{114}\) W. S. Benedict, Phys. Rev. 75, 1317A (1949).
<table>
<thead>
<tr>
<th>J</th>
<th>$S_1/P_1$</th>
<th>$S_2/P_2$</th>
<th>$S_3/P_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>51.65</td>
<td>1101</td>
<td>24640</td>
</tr>
<tr>
<td>2</td>
<td>51.58</td>
<td>1090</td>
<td>23960</td>
</tr>
<tr>
<td>3</td>
<td>51.48</td>
<td>1073</td>
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</tr>
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<td>9650</td>
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FIGURE 7
Plot of $S_1/p_1$, $S_2/p_2$, and $S_3/p_3$ vs. $J(J+1)$ for the water molecule ($V_1=V_2=V_3=0$).
with the quantities $\mu_j$ associated with the stretching. For the data of Table VIII, and with extrapolated (to $J=0$) values of $\alpha$, $\beta$, and $\gamma$, one finds by least square methods that:

$$S_1/\mu_1 = a + \mu_1 f, \quad (8.4)$$

$$S_2/\mu_2 = \gamma^2 (1+\beta^2/3) + \mu_2 f + \mu_2 f^2, \quad (8.5)$$

$$S_3/\mu_3 = \gamma^3 (1-\beta^2) + \mu_3 f + \mu_3 f^2 + \mu_3 f^3, \quad (8.6)$$

If a term in $f^2$ is added to (8.4) one finds:

$$S_1/\mu_1 = 51.67 - (0.0112)f, \quad \text{(in cm}^{-1}\text{)}, \quad (8.7)$$

$$S_2/\mu_2 = 1106 - (2.70)f + (0.0550)f^2, \quad \text{(in cm}^{-2}\text{)}, \quad (8.8)$$

$$S_3/\mu_3 = 24860 - (163)f + (1.35)f^2 - (2.85 \times 10^{-6})f^3, \quad \text{(in cm}^{-3}\text{)}. \quad (8.9)$$

Comparison of (8.7) and (8.10) shows that deviations from the straight line fit do affect $\mu_1$ appreciably. On the other hand, the smallness of the coefficient of the $f^2$ term of (8.10) indicates that the first order Hamiltonian (7.1) is pertinent even in the case of a molecule that displays considerable centrifugal distortion, such as water does.

Admittedly, there is an aura of uncertainty as to the meaning of the constants $\mu_j$, but we may claim at least as much physical meaning for these constants as one could claim for the "stretching constants" of Chapter IV.

Finally, it will be observed that even in those cases where the stretching constants are small enough to make the first order theory applicable for comparatively low values of $J$, one can always
choose a $J$ value sufficiently large to "swamp" the small stretching coefficients in the moment equations. Thus the first order theory always has its limitations no matter how small the stretching coefficients for low $J$. Another way of expressing this is to say, that, for sufficiently large values of $J$ the assumption that the displacement coordinates of the constituent nuclei of the molecule are small compared with the equilibrium values of the nuclear coordinates is no longer unassailable. For it is on the basis of this assumption, that the $P^l$ terms in the Hamiltonian (7.1) can be set down. It is unfortunate that for the water molecule this situation arises even for the very lowest values of $J$. 
CHAPTER IX

SUMMARY

A method has been presented which relates the physical parameters associated with the description of a quantum mechanical system to energy eigenvalues of the Schrödinger equation of the system in such a manner that for relatively simple systems the physical parameters can be evaluated from spectroscopic data without effecting a detailed solution for the roots of secular polynomials.

Application of the method to a system described by a rigid asymmetric rotator Hamiltonian has been carried out and has resulted in relatively simple closed expressions for effective rotational constants in terms of experimentally determined quantities.

Use of the rigid asymmetric rotator expressions obtained in this manner has been illustrated for the water molecule.

An extension of the theory to include explicitly first order stretching effects in the asymmetric top has been presented. Centrifugal stretching effects in the water molecule have been discussed in terms of this first order theory.
APPENDIX A

On page 13 it was stated that each contribution to the term $c^2F^{n-2}$ of the secular polynomial is of one of the two forms $W_{ii}W_{jj}F^{n-2}$ or $-W_{ij}W_{ji}F^{n-2}$, with $i\neq j$.

Briefly, this may be seen as follows. By definition, the value of the determinant of a square $n \times n$ array of elements $d_{pq}$ is given by

$$D = \sum d_{q_1d_2q_3 \ldots d_{n,q_n}}, \quad (A.1)$$

in which the summation extends over all $n!$ permutations $q_1, q_2, \ldots, q_n$ of the integers $1, 2, \ldots, n$, and the sign is to be taken as positive or negative according as $q_1, q_2, \ldots, q_n$ is an even or odd permutation of the integers $1, 2, \ldots, n$. Now, contributions to the term $c^2F^{n-2}$ of the secular polynomial arise from the terms of (A.1), but only if

(a) either all $n$ factors $d_{pq}$ of a typical summation term of (A.1) are the diagonal elements of (2.12), $W_{ii}$, or if

(b) $n-2$ factors $d_{pq}$ of a typical summation term of (A.1) are diagonal elements of (2.12), and then the remaining two factors are off-diagonal elements of (2.12), $W_{ij}$, $i\neq j$. (It is impossible to have $n-1$ factors $d_{pq}$ diagonal elements, because then by the definition (A.1) the remaining element must also be chosen diagonal.)

It is the type (a) term which contributes to the $W_{ii}W_{jj}F^{n-2}$ expressions, while it is the terms of type (b) which contribute to the $-W_{ij}W_{ji}F^{n-2}$ expressions. Also, the algebraic signs are consistent with the definition (A.1), since the coefficient of $F^n$ was chosen to be unity and positive.
In what follows, all summation indices range from unity to \( n \), unless restricted as noted.

Equation (2.26) states that

\[
S_2 = -2 \sum_{i<j} M_{ij}, \quad i < j; \tag{B.1}
\]

or in greater detail, that

\[
S_2 = -2 \sum_{i<j} (W_{ii} W_{jj} - W_{ij} W_{ji}), \quad i < j. \tag{B.2}
\]

Because of the modification described in (2.20) through (2.24),

\[
\sum_i W_{ii} = 0, \quad \text{whence}
\]

\[
0 = \left( \sum_i W_{ii} \right)^2 = \sum_i (W_{ii})^2 + 2 \sum_{i<j} W_{ii} W_{jj}, \quad i < j. \tag{B.3}
\]

Using (B.3) in (B.2) we find that

\[
S_2 = \sum_i (W_{ii})^2 + 2 \sum_{i<j} W_{ij} W_{ji}, \quad i < j. \tag{B.4}
\]

In a Hermitian representation

\[
W_{ij}^* = W_{ji}, \tag{B.5}
\]

hence

\[
W_{ij} W_{ji} = |W_{ij}|^2 = |W_{ji}|^2, \tag{B.6}
\]

and therefore (B.4) becomes

\[
S_2 = \sum_i (W_{ii})^2 + 2 \sum_{i<j} |W_{ij}|^2, \quad i < j, \tag{B.7}
\]

which is (2.29).

Equation (2.27) states that

\[
S_3 = 3 \sum_{i<j<k} M_{ijk}, \quad i < j < k; \tag{B.8}
\]

or in greater detail, that
because of the modification described in (2.20) through (2.24),
\[ \Sigma_i W_{ii}^o = 0, \]
whence
\[
0 = (\Sigma_i W_{ii}^o)^3 - 3 \Sigma_i (W_{ii}^o)^2 (\Sigma_j W_{jj}^o) + 6 \Sigma_i \Sigma_j \Sigma_k W_{ii}^o W_{jj}^o W_{kk}^o, \tag{B.10}
\]
which, after once more using \( \Sigma_i W_{ii}^o = 0 \), becomes
\[
0 = \Sigma_i (W_{ii}^o)^3 - 3 \Sigma_i (W_{ii}^o)^2 (\Sigma_j W_{jj}^o) + 6 \Sigma_i \Sigma_j \Sigma_k W_{ii}^o W_{jj}^o W_{kk}^o, \tag{B.11}
\]
and thus the first summation term in (B.9) may be replaced by
\[(1/3) \Sigma_i (W_{ii}^o)^3. \] This establishes (2.30.1). Term (2.30.2) follows from terms 2, 4, and 6 of (B.9) along with \( \Sigma_i W_{ii}^o = 0 \) and (B.6); and (2.30.3) is terms 3 and 5 of (B.9). This establishes (2.30) in its entirety.
Since the only non-zero matrix elements of the $W^0$ matrix are the ones given in (3.18) and (3.19), the expressions (2.29) for $S_2$ and (2.30) for $S_3$ here assume the form:

$$S_2 = \sum_{K=-J}^{J} (W_{K,K}^0)^2 + 2 \sum_{K=0}^{J-2} (W_{K,K+2}^0)^2,$$

$$S_3 = \sum_{K=-J}^{J} (W_{K,K}^0)^3 + 3 \sum_{K=0}^{J-2} (W_{K,K+2}^0)^2 (W_{K,K+2}^0 + W_{K+2,K+2}^0).$$

It will be noticed that $W_{K,K+2}^0 = 0$ for $K = J-1$ and for $K = J$. This allows extending all sums of (C.1) and (C.2) from $-J$ to $+J$. Introducing the matrix elements (3.18) and (3.19) into (C.1) there results

$$S_2 = (1/4)\gamma^2 \left\{ \sum_{K=-J}^{J} [(K^2-J(J+1)/3)^2 +$$

$$+ (1/16)\beta^2 (J-K-1)(J-K)(J+K+1)(J+K+2)] \right\}. \quad (C.3)$$

After working out the round brackets and arranging the resulting expression in powers of $K$, it is brought into the form (3.21) with the aid of the summations (2.38), and after some rearrangement.

Equation (3.22) is established in a similar manner from (C.2).
APPENDIX D

From Chapter III,
\[ a = A + B + C, \]  
\[ \beta = \frac{3(A-B)}{2C-A-B}, \]  
\[ \gamma = 2C-A-B, \]
and \( \beta \) is restricted to the range \(-1 \leq \beta \leq 0\).

For the asymmetric rotator, \( A \neq B \neq C \), and if \( B \) is chosen as the intermediate rotational constant, then either
\[ A < B < C \]
or
\[ A > B > C. \]
In the literature usually only (D.1) is admitted in the treatment of the asymmetric rotator. We prefer to admit both (D.1) and (D.5), such that (D.1) extrapolates to the prolate symmetric top (for which the unique rotational constant is larger than the remaining two) and (D.5) extrapolates to the oblate symmetric top (for which the unique rotational constant is smaller than the remaining two). Then in both limits \( A = B \neq C \). Now choosing \( C \) as the constant farthest removed from the mean \( \alpha/3 \) makes (D.1) apply when \( B \) is smaller than the mean \( \alpha/3 \), and makes (D.5) apply when \( B \) is larger than the mean \( \alpha/3 \). When \( B \) is equal to the mean, \( B = \frac{1}{2}(A+C) \), one has the case of the so-called "most asymmetric" rotator.

These observations are best visualized by referring to Fig. 8,
FIGURE 8

Variation of the rotational constants about their mean as a function of $\beta$. 
\[ \beta = 0 \text{ (prolate)} \]

\[ \frac{1}{3} \beta \gamma \]

\[ \alpha/3 \]

\[ \gamma \] positive

\[ \gamma \] negative

A, B, C

(arbitrary scale)
which shows the variation of the rotational constants about their mean in terms of $\beta$, which is zero for symmetric tops, -1 for the "most asymmetric" top, and has the range $-1 \leq \beta \leq 0$.

It is interesting to note that $\beta$ may be written as

$$\beta = \frac{(A - a/3) - (B - a/3)}{(C - a/3)}.$$  (D.6)

It describes thus in terms of the constant farthest removed from the mean, the relative separation of the remaining two constants, with all constants expressed relative to their mean. It is perhaps in the form (D.6) that $\beta$ shows most clearly its property as an asymmetry parameter.

Since $C$ is the rotational constant farthest removed from the mean, the quantity $C - a/3$ will be either the largest or the smallest of the three quantities $A - a/3$, $B - a/3$, and $C - a/3$. This means that the quantity $|C - a/3|$ will be the largest of the three quantities $|A - a/3|$, $|B - a/3|$, and $|C - a/3|$. Similarly, since $B$ is the rotational constant closest to the mean, $|B - a/3|$ will be the smallest of the three quantities $|A - a/3|$, $|B - a/3|$, and $|C - a/3|$. Thus, as asserted in (3.27),

$$|B - a/3| \leq |A - a/3| \leq |C - a/3|.$$  (D.7)

The equal sign between $|B - a/3|$ and $|A - a/3|$ is added to cover the case of the symmetric rotator, and the equal sign between $|A - a/3|$ and $|C - a/3|$ applies to the "most asymmetric" case when $A$ and $C$ are equally far removed from the mean $a/3 = B$.

Equation (D.4) applies to the asymmetric rotator extrapolating to the prolate symmetric limit and shows that $\gamma$ is positive.
in this case. Similarly, (D.5) applies to the asymmetric rotator 
extrapolating to the oblate limit and shows that $\gamma$ is negative in 
that case. For a spherical top $\gamma$ is zero. For the limiting case of 
a prolate symmetric top in the shape of a slender rod, $A = B \to 0$, 
$C \to \infty$, and $\gamma = 2a$. For the limiting case of an oblate symmetric 
top in the shape of a planar configuration, $A = B = 2C$, and $\gamma = 
-2a/5$. Hence $-2a/5 < \gamma < 2a$, with $\gamma = 0$ for a spherical top, and 
$\gamma$ may thus be viewed as a measure of the deviation of the top from 
spherical symmetry, while the quantity $\beta$ measures the deviation of 
the top from the oblate or prolate symmetric configuration.
APPENDIX E

As a sample calculation of the rotational constants, consider the case $J=7$, $V_1=V_2=V_3=0$.

The energies $F_j$ listed by Benedict, Claassen, and Shaw\textsuperscript{26} are given in the first column of Table IX. The sum of these energies $S_1$ is found to be $1h228.87$ cm\textsuperscript{-1}. From this, and using (3.13) we find $F_j = S_1/(2J+1) = 9h8.59$ cm\textsuperscript{-1}. Equation (3.20) now gives $a = 50.817$ cm\textsuperscript{-1}. Subtracting $F_j$ from each entry in the $F_j$ column of Table IX gives the modified energies $F^0_j$, as described in (2.2h). From these entries $S_2$ and $S_3$ are now computed as the sum of the squares of the modified energies and the sum of the cubes of the modified energies. We find $S_2 = 100.28 \times 10^4$ cm\textsuperscript{-2}; and $S_3 = 87.181 \times 10^6$ cm\textsuperscript{-3}. Using these values in (3.26), the quantity $\beta$ is determined from (3.26) as $\beta = 0.58278$. The quantity $\gamma$ is now found from (3.21) as $\gamma = 29.5547$ cm\textsuperscript{-1}; (3.22) shows that $\gamma > 0$, since $S_3 > 0$ and $p_3 > 0$. With $a$, $\beta$, and $\gamma$ determined, the rotational constants now follow from (3.28), (3.29), and (3.30). The effective moments of inertia then follow from (3.2).
TABLE IX

ROTATIONAL ENERGIES FOR THE CASE

\( J=7, V_1=V_2=V_3=0 \)

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<th>( F_\tau )</th>
<th>( F^{0}_\tau )</th>
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<td>cm (^{-1})</td>
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APPENDIX F

Computation of the sum rules for the steps of the J-th submatrix in the form of Fig. 6 is more involved than the computation in Appendix C of the sums for the complete J-th submatrix, principally for two reasons.

First, it is now no longer possible to extend summations of K and its powers from -J to +J as in Appendix C. This entails that of the sums (2.38) now not only those for even powers of K but also those for odd powers of K will have non-vanishing values.

Second, the diagonal matrix elements $W_{1,1}$ and $W_{-1,-1}$ in Fig. 6 are no longer equal to their corresponding values in Fig. 5 but differ by $W_{1,-1} = W_{-1,1} = a$. After modifying the step under consideration to make it traceless as described in Chapter II, the presence of the term $a$ on the diagonal will have affected every diagonal element. As will be seen, this complicates the algebra in the computation of $S_2$ and $S_3$ appreciably.

In this appendix we shall use single primes for quantities pertaining to the upper left $(J+1) \times (J+1)$ step, double primes for quantities pertaining to the lower right $J \times J$ step, and unprimed quantities when referring to the complete submatrix in the form of Fig. 5.

(a) Sum Rules for the Upper Left $(J+1) \times (J+1)$ Step

Referring to Figs. 5 and 6, it is seen that
\[ S_1' = T' = \frac{1}{2}(T+A) + a, \]  

is the trace of the upper left step. Using the value of \( T \) from (3.20), forming \( \bar{F}_{J}' = T'/(J+1) \), and subtracting \( \bar{F}_{J}' \) from the diagonal elements, gives the modified diagonal elements as:

\[ W_{K,K}^{o'} = \frac{3}{2}YK^2 - (1/12)\gamma J(2J+1+\beta), \quad K=0,2,3,...,J; \quad (F.2) \]

\[ W_{1,1}^{o'} = \frac{3}{2}Y - (1/12)\gamma J(2J+1-\beta J). \quad (F.3) \]

It is quickly verified that with these diagonal elements,

\[ \sum_{K=0}^{J} W_{K,K}^{o'} = 0, \quad (F.4) \]

i.e., the step is now traceless, as required for the calculation of \( S_2 \) and \( S_3 \).

The explicit form of \( \bar{F}_{J}' \) is

\[ \bar{F}_{J}' = (1/3)\alpha J(J+1) - (1/12)\gamma J(1-\beta), \quad (F.5) \]

as asserted in (5.2).

Since only diagonal elements and second off-diagonal elements of the step are non-vanishing, the expression (2.29) for \( S_2 \) here assumes the form

\[ S_{2}' = \sum_{K=0}^{J} (W_{K,K}^{o'})^2 + 2\sum_{K=0}^{J-2} (W_{K,K+2})^2; \quad (F.6) \]

denoting the first sum of (F.6) by \( \sigma_2' \), and using (F.2) and (F.3), we find:

\[ \sigma_2' = \sum_{K=0}^{J} (W_{K,K}^{o'})^2 + (W_{1,1}^{o'})^2 = \]

\[ = (1/12)\gamma^2 \left[ \sum_{K=0}^{J} [K^2 - (1/6)J(2J+1+\beta)]^2 \right] - \]

\[ = \left[ 1 - (1/6)J(2J+1+\beta) \right]^2 + \left[ 1 - (1/6)J(2J+1-\beta J) \right]^2. \quad (F.7) \]

Here, the restriction in the sum, viz., \( K \neq 1 \), has been removed, and
the terms introduced by removing the restriction have been subtracted out. The expression (F.7) can now be evaluated in the manner described in Appendix C.

Denoting the second sum of (F.6) by \( \tau_2' \), we have in terms of the notation of Fig. 6,

\[
\tau_2' = 2\sum_{K=0}^{J} (W_{K+2,K})^2 = 2(2b^2+c^2+d^2+\ldots). \quad (F.8)
\]

The sum is extended from \( K=0 \) to \( K=J \), because \( W_{K+2,K+1} = 0 \) for \( K=J-1 \) and for \( K=J \). Now the expression corresponding to \( \tau_2' \) in the entire \( J \)-th submatrix of Fig. 5 is

\[
\tau_2 = 2(a^2+2b^2+2c^2+2d^2+\ldots), \quad (F.9)
\]

and as indicated in Appendix C and (3.21), has the value

\[
\tau_2 = (1/3)p_2\gamma^2p^2. \quad (F.10)
\]

It follows that

\[
\tau_2' = \frac{1}{2}\tau_2 - a^2 + 2b^2 = \frac{1}{6}p_2\gamma^2p^2 + (1/144)\gamma^2p^2J(J+1)(J^2+J-1). \quad (F.11)
\]

From (F.7) and (F.11), and after some rearrangement of the expression, the value of \( S_2' = \sigma_2' + \tau_2' \) now follows as the one given in (5.3).

The general expression (2.30) for \( S_3 \) here assumes the form:

\[
S_3' = \sum_{K=0}^{J} (W_{K,K}^{0'})^3 + 2\sum_{K=0}^{J-2} (W_{K,K+2}')^2 \times (W_{K,K}^{0'} + W_{K+2,K+2}^{0'}). \quad (F.12)
\]

Denoting the first sum of (F.12) by \( \sigma_3' \), we have:
\[ \sigma_3' = \frac{1}{8} \gamma^3 \left[ \sum_{K=0}^{J} \left[ J^2 - \frac{1}{6} J (2J+1+\beta) \right] \right] - \left[ 1 - \frac{1}{6} J (2J+1+\beta) \right]^3 + \left[ 1 - \frac{1}{6} J (2J+1-\beta) \right]^3 \]

which can now be evaluated in the usual manner.

Denoting the second sum of (F.12) by \( \tau_3' \), we find:

\[ \tau_3' = \frac{3}{8} \gamma^3 \left[ \sum_{K=0}^{J} \left( \frac{1}{36} \beta^2 (J-\frac{1}{2} J (J+1) (J+2) \right) \left[ K^2 + (K+2)^2 - \frac{1}{3} J (2J+1+\beta) \right] \right] + \left( \frac{1}{288} \right) \beta^2 \gamma^3 \left[ \frac{1}{3} (J-1) (J+1) (J+2) \right] + \left( \frac{1}{288} \right) \beta^2 \gamma^3 \left[ \frac{1}{6} J (J+1) \right] \left[ (J-2) (J-1) (J+2) (J+3) \right] \]

where the second term compensates for the fact that the element \( W_{0,2} \) in Fig. 6 is not equal to the element \( W_{0,2} \) of Fig. 5, and where the third term compensates for the fact that the element \( W_{1,1} \) does not have the general form (F.2) but is given by (F.3). The expression (F.114) can now be evaluated in the usual manner. Finally, from (F.13) and (F.114), and after rearrangement of the expression, the value of \( S_3' = \sigma_3' + \tau_3' \) follows as the one given in (5.4). Extensive algebraic manipulation is involved in the calculation of \( S_3' \). The remarkable simplicity of the result (5.4) for \( S_3' \) is indeed very impressive after one has gone through much tedious detail.

(b) Sum Rules for the Lower Right \( J \times J \) Step

The calculation proceeds in a manner similar to the one just outlined in Part (a) above.

Reference to Figs. 5 and 6 shows that

\[ T'' = \frac{1}{2} (T-A) - a. \]
From this follows

\[ F_j'' = T''/J = (1/3)a_j(J+1) + (1/12)(J+1)\gamma (1-\beta) , \quad \text{(F.16)} \]

and the modified diagonal elements follow as

\[ W_{K,K}^{0''} = \frac{3}{2}YK^2 - (1/12)\gamma (J+1)(2J+1-\beta) , \quad K=-2,-3,\ldots,-J ; \quad \text{(F.17)} \]

\[ W_{-1,-1}^{0''} = \frac{3}{2}Y - (1/12)\gamma (J+1)[2J+\beta(J-1)] . \quad \text{(F.18)} \]

Furthermore, here we have

\[ S_2'' = \sum_{K=-J}^{K=+J} (W_{K,K}^{0''})^2 + 2\sum_{K=-J}^{K=+J} (W_{K,K+2}^{0''})^2 = \sigma_2'' + \tau_2'' , \quad \text{(F.19)} \]

and

\[ \sigma_2'' = (1/4)\gamma^2 \left[ \sum_{K=1}^{J} [K^2-(1/6)(J+1)(2J+1-\beta)]^2 \right] - \left[ 1 - (1/6)(J+1)(2J+1-\beta) \right]^2 + \left[ 1 - (1/6)(J+1)(2J+\beta(J-1)) \right]^2 . \quad \text{(F.20)} \]

The summation in (F.20) can be extended from K=+1 to K=+J, because only even powers of K occur.

In terms of \( \tau_2 \) for the entire J-th submatrix,

\[ \tau_2'' = \frac{1}{2}\tau_2 - a^2 - 2b^2 = \]

\[ = (1/6)p_2\gamma^2\beta^2 - (1/1144)\gamma^2\beta^2J(J+1)(3J^2+3J-4) . \quad \text{(F.21)} \]

\( S_2'' \) is now found by combining (F.20) and (F.21), and by putting it into the form (5.6).

Also, here

\[ S_3'' = \sum_{K=-J}^{K=+J} (W_{K,K}^{0''})^3 + 3\sum_{K=-J}^{K=+J} (W_{K,K+2}^{0''})^2 X \]

\[ X (W_{K,K}^{0''} + W_{K+2,K+2}^{0''}) = \sigma_3'' + \tau_3'' , \quad \text{(F.22)} \]

and

\[ \sigma_3'' = (1/8)\gamma^3 \left[ \sum_{K=+1}^{J} [K^2-(1/6)(J+1)(2J+1-\beta)]^3 \right] - \left[ 1 - (1/6)(J+1)(2J+1-\beta) \right]^3 + \left[ 1 - (1/6)(J+1)(2J+\beta(J-1)) \right]^3 . \quad \text{(F.23)} \]
The summation in (F.23) can be extended from \( K=+1 \) to \( K=+J \) because only even powers of \( K \) occur.

Now, the summation

\[
\tau_3'' = 32 \sum_{K=-J}^{-1} (W_{K,K+2}')^2 (W_{K,K}^{0''} + W_{K+2,K+2}^{0''})
\]

may not be extended from \( K=-J \) to \( K=-1 \) without changing its value, because \( W_{K,K+2}' \not= 0 \) for \( K=-2 \) and for \( K=-1 \). However, (F.24) can be expressed in the equivalent form

\[
\tau_3'' = 32 \sum_{K=-J}^{-1} (W_{K,K-2}')^2 (W_{K,K}^{0''} + W_{K-2,K-2}^{0''}),
\]

and now the summation may be extended from \( K=-1 \) to \( K=-J \) without changing the value of the sum. More explicitly we have:

\[
\tau_3'' = (3/8) \gamma^3 \sum_{K=-J}^{-1} (1/36) \beta^2 (J-K+1)(J-K+2)(J+K-1)(J+K) \times \\
\left[ K^2 - (K-2)^2 - (J+1)(J+1+2) \right] - \\
\left[ (1/144) \beta^2 \gamma^2 [ (1/12)(J+1)[(J-2)(J-1)(J+2)(J+3)] \right],
\]

where the last term of (F.26) compensates for the fact that the element \( W_{-1,-1}^{0''} \) does not have the general form (F.17) but is given by (F.18). For convenience, the sum in (F.26) can be extended from \( K=+1 \) to \( K=+J \) by replacing \( K \) with \( -K \) in the expressions to be summed. Then the calculation proceeds in the usual manner. The sum \( S_3'' \) is then found by combining (F.23) and (F.26), and again after straightforward but extensive manipulation can be put into the form (5.7).
It is to be shown that stretching constants $\sigma$ associated with first and third off-diagonal matrix elements do not occur linearly in $S_1$, $S_2$, and $S_3$.

For brevity, we shall call first and third off-diagonal matrix elements "odd elements" and call diagonal, second and fourth off-diagonal matrix elements "even elements."

Since no zero-order (rigid rotator) terms contribute to the odd elements, all odd elements are of the form

$$(\text{stretching constant } \sigma') \times (\text{appropriate angular momentum matrix element}),$$

or a sum of such terms.

We have $S_1 = \sum_K W_{k,k}$, hence obviously no odd elements occur in $S_1$.

Further, from (2.29) the appropriate form of $S_2$ here is

$$S_2 = \sum_K \left[ (W_{k,k})^2 + 2|W_{k,k+1}|^2 + 2|W_{k,k+2}|^2 + 2|W_{k,k+3}|^2 + 2|W_{k,k+4}|^2 \right],$$

and it is evident that $S_2$ is quadratic in the odd elements, hence quadratic in the stretching constants.

In $S_3$, from (B.9) three types of term occur:

(I) A term which is a product of diagonal elements only, of the form $W_{ii} W_{jj} W_{kk} (i < j < k)$, in which obviously no odd elements occur.

(II) Terms containing one diagonal element, which are of the
form $W_{ii} W_{jk} W_{kj}$ ($i \neq j \neq k$). Because of the Hermitian property of the representation, $W_{ii} W_{jk} W_{kj} = W_{ii} W_{jk} W_{kj}^2$. It follows that these terms contain no odd elements or that they are quadratic in the odd elements.

(III) Terms of the type $W_{ij} W_{jk} W_{ki}$ ($i < j < k$). This term has only off-diagonal elements as factors. If $W_{ki}$ is an $n$-th off-diagonal element, then

(a) if $n$ is odd, $k-i$ is an odd integer. Since we must have that

$$(j-i) + (k-j) = (k-i),$$
either $j-i$ is an odd integer or $k-j$ is an odd integer, hence either $W_{ij}$ or $W_{jk}$ is an odd element. Since we assumed $W_{ki}$ to be an odd element, the term $W_{ij} W_{jk} W_{ki}$ is quadratic in the odd elements.

(b) if $n$ is even, by similar reasoning we ascertain that in this case either both $j-i$ and $k-j$ are even integers or both are odd integers. Then the term $W_{ij} W_{jk} W_{ki}$ either does not contain odd elements or it is quadratic in the odd elements.

Similar reasoning shows that the other terms of Type III, viz., $W_{ik} W_{ji} W_{kj}$, $i < j < k$, give rise to an analogous conclusion. This completes the proof.
APPENDIX H

The non-zero matrix elements of $P_x$, $P_y$, and $P_z$, in the body-fixed reference frame are given by Klein as:

\[
(P_x)^{K,K+1}_{K+1,K} = \frac{1}{2} [(J-K)(J+K+1)]^{1/2}, \quad (H.1)
\]

\[
(P_y)^{K,K+1}_{K+1,K} = -\frac{1}{2} [(J-K)(J+K+1)]^{1/2}, \quad (H.2)
\]

\[
(P_z)^{K,K}_{K+1,K} = K. \quad (H.3)
\]

From these, the non-zero matrix elements of the operators of (7.8) are found by matrix multiplication. In this appendix we shall denote the matrix elements with row index $K$ and column index $L$ of a certain operator of (7.8) by $(K|L)$. The non-vanishing matrix elements of the various operators of (7.8) follow below.

(1) $P_x^l$:

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

\[
X (J+K+2) + (1/4)(J-K)(J+K)(J+K+1)(J+K+2), \quad (H.4)
\]

\[
(K|K+2) = (K+2|K) = \frac{1}{16} \left[ (J-K)(J+K)(J+K+1)(J+K+2) \right]^{1/2} X
\]

\[
X \left[ 2J(J+1) - (K+2)^2 \right], \quad (H.5)
\]

\[
(K|K+4) = (K+4|K) = \frac{1}{16} \left[ (J-K)(J+K)(J+K+1)(J+K+2) \right]^{1/2} X
\]

\[
\]

(2) $P_y^l$:

The diagonal and fourth off-diagonal matrix elements of this operator are equal to the corresponding ones of $(P_x^2)^2$. The second off-diagonal elements are equal to the negative of the corresponding ones of $P_x^l$.

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(3) $p_{2z}^{1/2}$:

$$(K|K) = K_{2}^{1/2}. \quad (H.7)$$

(4) $p_{y}^{2}p_{z}^{2} + p_{z}^{2}p_{y}^{2}$:

$$
(K|K) = K^{2}[J(J+1)-K^{2}], \quad (H.8)

(K|K+2) = (K+2|K) = -\frac{1}{8} [(J-K-1)(J-K)(J+K+1)(J+K+2)]^{\frac{3}{2}} 
X \ (K^{2}+2K+2). \quad (H.9)
$$

(5) $p_{x}^{2}p_{z}^{2} + p_{z}^{2}p_{x}^{2}$:

The diagonal elements are equal to those of operator (4). The second off-diagonal elements are equal to the negative of the corresponding ones of (4).

(6) $p_{x}^{2}p_{y}^{2} + p_{y}^{2}p_{x}^{2}$:

$$
(K|K) = \frac{3}{2} [J(J+1)-K^{2}]^{2} - (1/4) (J-K)(J+K+1)(J+K+2) \left( J-K-1 \right) (J-K+2) (J+K-1) (J+K) 
- (1/4) (J-K-1) (J-K) (J+K+1) (J+K+2), \quad (H.10)

(K|K+1) = (K+1|K) = -(1/8) [(J-K-1)(J-K)(J+K+1)(J+K+2)] X
$$

(7) $(p_{y}^{2}p_{z}^{2} + p_{z}^{2}p_{y}^{2})^{2}$:

$$
(K|K) = (1/4) [2K^{2}+1] (J-K)(J+K+1) + (2K^{2}+1)(J-K+1)(J+K), \quad (H.12)

(K|K+2) = (K+2|K) = -(1/4) (2K+1)(2K+3) X
X [(J-K)(J-K-1)(J+K+1)(J+K+2)]^{\frac{3}{2}}. \quad (H.13)
$$

(8) $(p_{x}^{2}p_{y}^{2} + p_{y}^{2}p_{x}^{2})^{2}$:

The diagonal elements are equal to those of operator (7). The second off-diagonal elements are equal to the negative of the corresponding ones of (7).
The second off-diagonal elements are the same as the corresponding ones of (10). The fourth off-diagonal elements are the negative of the corresponding ones of (10).
APPENDIX I

From the matrix elements compiled in Appendix H it is seen that the non-vanishing matrix elements of the non-rigid rotator Hamiltonian (7.1), when written in terms of the thirteen operators (7.8), have the general structure:

\[
\begin{align*}
W_{K,K}^0 &= A^{(0)} + \sum_{j=1}^{9} \sigma_j A_j^{(1)}, \\
W_{K,K+2} &= W_{K+2,K}^* = B^{(0)} + \sum_{j=1}^{9} \sigma_j B_j^{(1)} + i\sum_{j=10}^{13} \sigma_j B_j^{(2)}, \\
W_{K,K+4} &= W_{K+4,K}^* = \sum_{j=1}^{9} \sigma_j C_j^{(1)} + i\sum_{j=10}^{13} \sigma_j C_j^{(2)},
\end{align*}
\]

with all \( A^{(n)} \), \( B^{(n)} \), \( C^{(n)} \), functions of \( K, K, K+1, \ldots, K \); not all \( \sigma_j \) are necessarily non-zero.

It is desired to show that the stretching constants \( \sigma_j \) associated with the imaginary part of the off-diagonal elements (hereafter in this appendix referred to as "imaginary stretching constants") do not occur linearly in the moment equations.

This conclusion follows immediately for \( S_1 \), since \( S_1 \) is formed from diagonal elements of \( W \) only.

Also, from the general form (2.29) of \( S_2 \) we have here,

\[
S_2 = \sum_K (W_{K,K}^0)^2 + 2\sum_K |W_{K,K+2}|^2 + 2\sum_K |W_{K,K+4}|^2,
\]

and it is apparent that the imaginary stretching constants do not occur in the first sum of (I.14) and will occur quadratically in the second and third sums of (I.14).
As in Appendix G we consider separately the three types of term of $S_3$:

(I) Obviously no imaginary stretching constants occur in this type, since it is made up of diagonal elements only.

(II) Since our representation is Hermitian, the terms of type (II) have the form $W_{ij}^0 |W_{jk}|^2$ as in Appendix G, and thus they are quadratic in the imaginary stretching constants.

(III) From (E.9) it is seen that the terms of type (III) occur in $S_3$ in pairs as

$$W_{ij}W_{jk}W_{ki} + W_{ik}W_{ji}W_{kj}, \quad i < j < k; \tag{I.5}$$

in our Hermitian representation (I.5) may be written as

$$W_{ij}W_{jk}W_{ki} + W_{ij}W_{jk}W_{ki}^*, \quad i \neq j \neq k. \tag{I.6}$$

Since all elements of (I.6) are off-diagonal elements and therefore from (I.2) and (I.3) they are complex, the expression (I.6) has the structure:

$$(a_1 + ib_1)(a_2 + ib_2)(a_3 + ib_3) + (a_1 - ib_1)(a_2 - ib_2)(a_3 - ib_3) = 2(a_1a_2a_3 - a_1b_2b_3 - a_2b_1b_3 - a_3b_2b_1). \tag{I.7}$$

No $a_n$ of (I.7) is associated with imaginary stretching constants.

Each $b_n$ of (I.7) has the form

$$b_n = \Sigma_j \delta_j B_j^{(2)}, \tag{I.8}$$

or has the form

$$b_n = \Sigma_j \delta_j C_j^{(2)}, \tag{I.9}$$

with the $\delta_j$'s imaginary stretching constants. It is evident from (I.7) that the imaginary stretching constants do not occur linearly in the terms of type (III).
The identities (7.10) may be established in the following manner.

From the commutation relations,

\[ P_{x y} P_{y x} = -i P_z, \quad \text{(cyclic)}, \quad (J.1) \]

we have that

\[
P_{x y} P_{y x} P_{x y} + P_{x y} P_{x y} = P_{x y} (P_{x y} + i P_z) + P_{x y} (P_{x y} - i P_z) = \]

\[
= P_{x y} P_{x y} + P_{x y} P_{x y} + i(P_{x y} - P_{x y}) P_z = \]

\[
= P_{x y} P_{x y} + P_{x y} P_{x y} + P^2_z. \quad (J.2)\]

Hence,

\[
(P_{x y} P_{x y})^2 = P_{x y} P_{x y} P_{x y} + P_{x y} P_{x y} P_{x y} + P_{x y} P_{x y} + P_{x y} P_{x y} = \]

\[
= 2(P_{x y} P_{x y} + P_{x y} P_{x y}) + P^2_z = \]

\[
= 2[P_{x y} (P_{x y} + i P_z) P_{x y} + P_{x y} (P_{x y} - i P_z) P_{x y}] + P^2_z = \]

\[
= 2P^2_{x y} + 2P^2_{x y} + 2i(P_{x y} P_{x y} - P_{x y} P_{x y}) + P^2_z. \quad (J.3)\]

But

\[
2i(P_{x y} P_{x y} - P_{x y} P_{x y}) = 2i[P_{x y} (P_{x y} + i P_z) - P_{x y} (P_{x y} - i P_z)] = \]

\[
= 2i[P_{x y} P_{x y} + i P^2_z - P_{x y} P_{x y} + i P^2_z] = \]

\[
= -2P^2_x - 2P^2_y + 2i(P_{x y} P_{x y} - P_{x y} P_{x y}) P_z = \]

\[
= -2P^2_x - 2P^2_y + 2P^2_z. \quad (J.4)\]

Using (J.4) in (J.3) gives

\[
(P_{x y} P_{x y})^2 = 2(P^2_{x y} + P^2_{x y}) + 3P^2_z - 2P^2_x - 2P^2_y, \quad (J.5)\]

and cyclic permutation of indices establishes (7.10).
APPENDIX K

From (3.10), (3.11), and Appendix H, the non-zero matrix elements of the Hamiltonian (7.11) are:

\[ W_{K,K} = \frac{3}{2} f (A+B) + \frac{3}{2} \gamma K^2 + (\lambda_1 + \lambda_2) (15/8) \gamma (f-K^2)^2 + \]
\[ + (1/14) (J-K-1)(J-K)(J+K+1)(J+K+2) + \]
\[ + (1/14) (J-K+1)(J-K+2)(J+K-1)(J+K) + \]
\[ + \lambda_3 (15/2) \gamma K^4 + (\lambda_4 + \lambda_5) (15/2) \gamma K^2 (f-K^2) + \lambda_6 (15/14) \gamma (f-K^2)^2 - \]
\[ - (1/14) (J-K-1)(J-K)(J+K+1)(J+K+2) - \]
\[ - (1/14) (J-K+1)(J-K+2)(J+K-1)(J+K) \]  

\(W_{K,K+2} = W_{K+2,K} = \frac{1}{12} \beta \gamma [(J-K-1)(J-K)(J+K+1)(J+K+2) \frac{3}{2} + \]
\[ + (15/8) \gamma (\lambda_3 - \lambda_2) [(J-K-1)(J-K)(J+K+1)(J+K+2) \frac{3}{2} (K^2+2K+f+2) + \]
\[ + (15/14) \gamma (\lambda_5 - \lambda_4) [(J-K-1)(J-K)(J+K+1)(J+K+2) \frac{3}{2} (K^2+2K+2); \]

\(W_{K,K+4} = W_{K+4,K} = (15/32) \gamma (\lambda_1 + \lambda_2 - 2\lambda_6) X \]

Arranging (K.1) in powers of K, computing \( S_1 = \sum_{K=1}^{J} W_{K,K} \) with the aid of (2.38), and forming \( \tilde{F}_j = S_j / (2J+1) \), we find (7.13), i.e.,
\[ \tilde{F}_j = (1/3) a f + \frac{3}{4} \gamma [(\lambda_1 + \lambda_2 + \lambda_3) f(3f-1) + (\lambda_4 + \lambda_5 + \lambda_6) f(2f+1)]. \]

Subtracting \( \tilde{F}_j \) from the diagonal elements \( W_{K,K} \) of (K.1) gives the modified form of the diagonal elements as
\[ W_{K,K}^o = \frac{3}{2} \gamma (K^2-3f) + (\lambda_1 + \lambda_2) (1/16) \gamma [15K^4 - 15K^2 (6f-5)+f(21f-22)] + \]
\[ + \frac{3}{2} \lambda_3 \gamma [15K^4 - f(3f-1)] + \frac{3}{2} (\lambda_4 + \lambda_5) \gamma [-15K^4 + 15K^2 f-f(2f+1)] + \]
\[ + \lambda_6 (1/8) \gamma [15K^4 - 15K^2 (2f+5)+f(7f+26)]. \]

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The general expression (2.29) for $S_2$ here specializes to

$$S_2 = \sum_{K=-J}^{J} (W_{K,K}^{0})^2 + 2\sum_{K=-J}^{J} (W_{K,K+2}^{0})^2 + 2\sum_{K=-J}^{J} (W_{K,K+4}^{0})^2.$$  \hspace{1cm} (K.6)

Introducing the matrix elements (K.2), (K.3), and (K.5) into (K.6) but dropping all terms quadratic in $\lambda$ results in:

$$S_2 = \sum_{K=-J}^{J} (1/4)\gamma^2(K^2-\frac{3}{2}f)^2 +$$

$$+ (\lambda_1+\lambda_2)(1/16)\gamma^2[45K^4-15K^2(6f-5)+f(21f-22)][K^2-\frac{3}{2}f] +$$

$$+ \lambda_3(1/2)\gamma^2[15K^4-f(3f-1)][K^2-\frac{3}{2}f] +$$

$$+ (\lambda_4+\lambda_5)(3/2)\gamma^2[-15K^4+15K^2f-f(2f+1)][K^2-\frac{3}{2}f] +$$

$$+ \lambda_6(1/8)\gamma^2[15K^4-15K^2(2f+5)+f(7f+26)][K^2-\frac{3}{2}f] +$$

$$+ (1/72)\beta^2\gamma^2(J-K-1)(J-K)(J+K+1)(J+K+2) +$$

$$+ (\lambda_1-\lambda_4)(5/4)\gamma^2(J-K-1)(J-K)(J+K+1)(J+K+2)(K^2+2K-f+2) +$$

$$+ (\lambda_2-\lambda_1)(5/4)\beta^2(J-K-1)(J-K)(J+K+1)(J+K+2)(K^2+2K+2) \hspace{1cm} (K.7)$$

Here again, as in Appendix C, all terms can be summed from $-J$ to $+J$ without changing the value of the expression. Upon summing (K.7) in the usual manner we find:

$$S_2 (p_2\gamma^2)^{-1} = 1 + (\lambda_1+\lambda_2)(-15/7)(6f-5) + \lambda_3(30/7)(6f-5) +$$

$$+ (\lambda_4+\lambda_5)(30/7)(f+5) + \lambda_6(-60/7)(f+5) + \frac{3}{2}\beta^2 +$$

$$+ (\lambda_2-\lambda_1)(-15/7)\beta(6f-5) + (\lambda_2-\lambda_1)(30/7)\beta(f+5), \hspace{1cm} (K.8)$$

with the order of the terms in (K.8) corresponding to the order of the terms in (K.7). Equation (K.8) can now be rearranged into the form (7.114).

The general expression (2.30) for $S_3$ here specializes to

$$S_3 = \sum_{K=-J}^{J} (W_{K,K}^{0})^3 + 3\sum_{K=-J}^{J} (W_{K,K+2}^{0})^2(W_{K,K}^{0}+W_{K+2,K}^{0}) +$$

$$+ 3\sum_{K=-J}^{J} (W_{K,K+4}^{0})^2(W_{K,K}^{0}+W_{K+4,K}^{0}) +$$

$$+ 6\sum_{K=-J}^{J} (W_{K,K+2}W_{K+2,K}^{0}+W_{K+4,K}^{0}) +$$

$$+ 6\sum_{K=-J}^{J} (W_{K,K+2}W_{K+2,K}^{0}+W_{K+4,K}^{0}) +$$

$$+ 6\sum_{K=-J}^{J} (W_{K,K+2}W_{K+2,K}^{0}+W_{K+4,K}^{0}). \hspace{1cm} (K.9)$$
Introducing the matrix elements (K.2), (K.3), and (K.5) into (K.9) but dropping all terms quadratic and cubic in $\lambda$ results in:

\[
S_3 = \sum_{K=J} \left\{ (1/8) \gamma^3 (K^2 - \frac{1}{3} \lambda)^3 + \right. \\
+ (\lambda_1 + \lambda_2) (3/64) \gamma^3 (K^2 - \frac{1}{3} \lambda)^2 \left[ 15 K^4 - 15 K^2 (6f - 5) + 7f (21f - 22) \right] + \\
+ \lambda_3 (3/8) \gamma^3 (K^2 - \frac{1}{3} \lambda)^2 \left[ 15 K^4 - f (3f - 1) \right] + \\
+ (\lambda_4 + \lambda_5) (3/8) \gamma^3 (K^2 - \frac{1}{3} \lambda)^2 \left[ -15 K^4 + 15 K^2 f - f (2f + 1) \right] + \\
+ \lambda_6 (3/32) \gamma^3 (K^2 - \frac{1}{3} \lambda)^2 \left[ 15 K^4 - 15 K^2 (2f + 5) + f (7f + 26) \right] + \\
+ (1/96) \beta^2 \gamma^3 (J-K-1) (J-K) (J+K+1) (J+K+2) \left[ K^2 + (K+2)^2 - \frac{3}{2} f \right] + \\
+ (\lambda_1 + \lambda_2) (1/768) \beta^2 \gamma^3 (J-K-1) (J-K) (J+K+1) (J+K+2) X \\
\left[ 45 (K^4 + (K+2)^4) - 15 (K^2 + (K+2)^2) (6f - 5) + 2f (21f - 22) \right] + \\
+ \lambda_3 (1/96) \beta^2 \gamma^3 (J-K-1) (J-K) (J+K+1) (J+K+2) X \\
\left[ 15 (K^4 + (K+2)^4) - 2f (3f - 1) \right] + \\
+ (\lambda_4 + \lambda_5) (1/96) \beta^2 \gamma^3 (J-K-1) (J-K) (J+K+1) (J+K+2) X \\
\left[ -15 (K^4 + (K+2)^4) + 15 (K^2 + (K+2)^2) f - 2f (2f + 1) \right] + \\
+ \lambda_6 (1/384) \beta^2 \gamma^3 (J-K-1) (J-K) (J+K+1) (J+K+2) X \\
\left[ 15 (K^4 + (K+2)^4) - 15 (K^2 + (K+2)^2) (2f + 5) + 2f (7f + 26) \right] + \\
+ (\lambda_2 - \lambda_3) (15/32) \beta \gamma^3 (J-K-1) (J-K) (J+K+1) (J+K+2) X \\
\left[ K^2 + 2K f + 2 \right] \left[ K^2 + (K+2)^2 - \frac{3}{2} f \right] + \\
+ (\lambda_5 - \lambda_4) (15/16) \beta \gamma^3 (J-K-1) (J-K) (J+K+1) (J+K+2) X \\
\left[ K^2 + 2K f + 2 \right] \left[ K^2 + (K+2)^2 - \frac{3}{2} f \right] + \\
+ (\lambda_1 + \lambda_2) (5/256) \beta \gamma^3 (J-K-3) (J-K-2) (J-K-1) (J-K) (J+K+1) X \\
\left[ (J+K+2) (J+K+3) (J+K+4) \right] + \\
+ \lambda_6 (-5/128) \beta \gamma^3 (J-K-3) (J-K-2) (J-K-1) (J-K) (J+K+1) X \\
\left[ (J+K+2) (J+K+3) (J+K+4) \right], \quad (K.10)\]
Once again here it is permissible to sum all terms from \(-J\) to \(+J\) without changing the value of the expression. Upon summing (K.10) in the usual manner we find:

\[ S_3(p_3 r^3)^{-1} = 1 + (\lambda_1 + \lambda_2)(-9/2)(3f-1) + \lambda_3(9)(6f-7) + \\
+ (\lambda_4 + \lambda_5)(-9)(f-7) + \lambda_6(-9)(f+8) - \beta^2 + \\
+ (\lambda_4 + \lambda_5)(3/4)(9f-8) + \lambda_3(-3)\beta^2(4f-3) + \\
+ (\lambda_4 + \lambda_5)(-3)\beta^2(f+3) + \lambda_6(3/2)\beta^2(3f+14) + \\
+ (\lambda_2 - \lambda_1)(15/4)\beta(f-1) + (\lambda_5 - \lambda_4)(-90)\beta + \\
+ (\lambda_1 + \lambda_2)(15/4)\beta^2(f-2) + \lambda_6(-15/2)\beta^2(f-2), \]  

(K.11)

with the order of the terms in (K.11) corresponding to the order of the terms in (K.10). Equation (K.11) can now be rearranged into the form (7.11). One cannot refrain from commenting once more on the surprisingly simple form of the final expression, in view of the mass of detail involved in the calculation of \(S_3\).
I, Paul Michael Parker, was born in Vienna, Austria, June 21, 1928. I received my secondary school education in the public schools of Vienna, and my undergraduate training at the City College of New York, which granted me the Bachelor of Science degree in 1953. From the Ohio State University, I received the Master of Science degree in 1955. In 1956 I was awarded a General Electric Company fellowship. While completing requirements for the Doctor of Philosophy degree I held the positions of assistant, research assistant, and instructor in the Department of Physics and Astronomy.