COMPUTER PROGRAM FOR DETERMINING
ROTATIONAL LINE INTENSITY FACTORS
FOR DIATOMIC MOLECULES

by Ellis E. Whiting

Ames Research Center
Moffett Field, Calif. 94035

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1973
A Fortran IV computer program, that provides a new research tool for determining reliable rotational line intensity factors (also known as H"unl-London factors), for most electric and magnetic dipole allowed diatomic transitions, is described in detail. This "users' manual" includes instructions for preparing the input data, a program listing, detailed flow charts, and three sample cases. The program is applicable to spin-allowed dipole transitions with either or both states intermediate between Hund's case (a) and Hund's case (b) coupling and to spin-forbidden dipole transitions with either or both states intermediate between Hund's case (c) and Hund's case (b) coupling. It is not applicable to quadrupole transitions or to transitions involving an electronic state approximated by Hund's case (d) coupling.
COMPUTER PROGRAM FOR DETERMINING ROTATIONAL LINE INTENSITY FACTORS FOR DIATOMIC MOLECULES

Ellis E. Whiting
Ames Research Center

SUMMARY

A Fortran IV computer program, that provides a new research tool for determining reliable rotational line intensity factors (also known as Honl-London factors), for most electric and magnetic dipole allowed diatomic transitions, is described in detail. This "users' manual" includes instructions for preparing the input data, a program listing, detailed flow charts, and three sample cases. The program is applicable to spin-allowed dipole transitions with either or both states intermediate between Hund's case (a) and Hund's case (b) coupling and to spin-forbidden dipole transitions with either or both states intermediate between Hund's case (c) and Hund's case (b) coupling. It is not applicable to quadrupole transitions or to transitions involving an electronic state approximated by Hund's case (d) coupling.

INTRODUCTION

This paper describes a comprehensive computer program for the determination of rotational line intensity factors (also known as Honl-London factors) of diatomic molecules. The program is based on the theory of the intensity of rotational lines in diatomic molecular spectra presented in references 1 and 2.

The first analytic formulas for the rotational line intensity factors of diatomic molecules were derived by H. Honl and F. London (ref. 3) in 1925 for the simple singlet-singlet electronic transitions. Since that time satisfactory general formulas for the intensity factors of singlet, doublet, and triplet transitions have been developed. (See ref. 1 for a brief history of the development of analytic intensity factors.)

The availability of realistic intensity factors for all spin-allowed or spin-forbidden transitions is highly desirable. However, the algebraic difficulties associated with deriving general formulas for intensity factors, when the multiplicity is four or greater, make it unlikely that tractable formulas will be derived for them in the foreseeable future. Therefore, the provision of numerically determined intensity factors appears to be the only practical and acceptable alternative.

---

\(^1\)For spin-allowed transitions \(\Delta S = 0, \Delta \Lambda = 0, \pm 1, \) and \(\Sigma^+ \leftrightarrow \Sigma^\mp.\) For spin-forbidden transitions \(\Delta \Omega = 0, \pm 1\) and at least one of the spin-allowed conditions is violated.
The computer program described is a new research tool for determining reliable intensity factors for most electric and magnetic dipole-allowed diatomic transitions by numerical methods. It is applicable to spin-allowed dipole transitions with either or both states intermediate between Hund's case (a) and Hund's case (b) coupling and to spin-forbidden dipole transitions with either or both states intermediate between Hund's case (c) and Hund's case (b) coupling. The program is not applicable to quadrupole transitions or to transitions involving an electronic state approximated by Hund's case (d).

This paper is intended to provide an adequate users' manual for the computer program. Therefore, it includes a brief summary of the theory, a discussion of several important program operations, three sample cases, detailed flow charts, and a complete program listing liberally annotated.

The author would like to acknowledge the invaluable discussions with Dr. J. T. Hougen during the course of this work and the cheerful assistance of Cheryl Whiting in proofreading the detailed flow charts.

THEORY

The theory of rotational line intensity factors is derived from first principles, and in great detail, in reference 1. That derivation will not be duplicated here. However, in order to understand many of the definitions and operations used in the computer program, the user must be familiar with certain key concepts in the derivation. Therefore, the following abbreviated discussion of the theory is included to provide the minimal information needed to use the program with some degree of confidence.

Many of the terms used in the theory are defined in figure 1, a typical energy level diagram of an electronic transition from a $^3\Pi$ to a $^3\Sigma$ electronic state. The electronic spin-splitting and A-doubling, shown in the central portion of the figure, are greatly exaggerated. The figure illustrates the well-known fact that there are $(2S + 1)$ electronic substates for sigma electronic states and $2(2S + 1)$ electronic substates for nonsigma electronic states. The number of substates for both cases can be written in a unified fashion as $(2 - \delta_{0,\Lambda})(2S + 1)$, using the Kronecker delta symbol.

The structure of each electronic substate is composed of a series of vibrational levels each containing many rotational $J$-levels. Further, each rotational $J$-level can be split by a magnetic field into $(2J + 1)$ Zeeman states.

The basic spectral elements are Zeeman components produced by transitions between Zeeman states. The sum of all Zeeman components between two $J$-levels is a rotational line. This definition of a rotational line is identical to that of an atomic line (ref. 4, p. 237) and provides a natural bridge between atomic and molecular theory. It is also essential for the description of the theory in terms of basis functions discussed later. According to this definition of a rotational line, a $\Lambda$-doublet is composed of two rotational lines.
However, in the literature a rotational line is frequently defined to include both components of a $A$-doublet (ref. 5 and 6 for example). This difference provides one of the important sources of confusion in the theory of diatomic spectra.

A vibrational band is the composite of all rotational lines occurring between vibrational levels $v'$ and $v''$ in all electronic substates. Figure 1 shows only that part of a vibrational band formed between two substates. A band system is the composite of all rotational lines between two electronic states. Thus, a band system in molecular spectra is equivalent to a very extensive atomic multiplet in atomic spectra.

The effect of nuclear spin is not explicitly included in the analysis. However, in nearly all cases, the nuclear spin and the resultant angular momentum without nuclear spin commute. Thus, the nuclear hyperfine line components can be obtained from the rotational line intensities by the methods of angular momentum theory summarized in reference 4.

The theory of rotational line intensities is closely dependent on the various angular momentum operators and the way they couple to form their resultant. The vector model coupling diagrams for Hund's cases (a), (b), and (c) coupling and their appropriate selection rules are shown in figure 2. In this discussion, Hund's case (a) basis functions are used for spin-allowed transitions and Hund's case (c) basis functions are used for spin-forbidden transitions.

The starting point for all discussions of spectral intensities is Einstein's phenomenological equation for spontaneous emission in either an atomic line or a molecular rotational line (ref. 7); that is

$$E_{J',J''} = N_{J'} \hbar \nu_{J',J''} A_{J',J''}$$

where

$E_{J',J''}$ the emitted power/unit volume, $W \, m^{-3}$

$N_{J'}$ the population density of the $J'$ rotational level, $m^{-3}$

$\hbar \nu_{J',J''}$ the energy of each photon emitted, $W \, s$

$A_{J',J''}$ the spontaneous emission transition rate per particle, also called the Einstein $A$ coefficient, $s^{-1}$

In reference 8 Dirac derived the Einstein $A$ coefficient in terms of an expansion in the electric and magnetic moments within an atom or a molecule. The strongest term in the expansion, if it is nonzero, is that due to the
electric dipole moment, $\hat{P}$; that is,

$$A_{J',J''} = \frac{16\pi^3 v_{J',J''}^3}{3h\varepsilon_0 c^3} \sum_{M'} \sum_{M''} \frac{\langle \psi_{UM'} | \hat{P} | \psi_{LM''} \rangle^2}{(2J'' + 1)}$$

$$= \frac{16\pi^3 v_{J',J''}^3}{3h\varepsilon_0 c^3} \frac{S_{J',J''}}{(2J'' + 1)}$$

(2)  

(3)

where

- $\psi_{UM'}$ the wave function of the upper Zeeman state $M'$
- $\psi_{LM''}$ the wave function of the lower Zeeman state $M''$
- $\hat{P}$ the electric dipole moment operator in the laboratory coordinate system, C m
- $\varepsilon_0$ the permittivity of a vacuum, $8.854 \times 10^{-12} \text{C}^2\text{J}^{-1}\text{m}^{-1}$
- $S_{J',J''}$ the line strength, defined in reference 4

With equation (3), equation (1), for the power emitted in a line by spontaneous emission, can be written

$$E_{J',J''} = \frac{16\pi^3 v_{J',J''}^4}{3\varepsilon_0 c^3} \frac{S_{J',J''}}{(2J'' + 1)}$$

(4)

The advantage of using equation (4) instead of equation (1) is that the line strength $S_{J',J''}$ is symmetrical in the upper and lower states. Thus, the line strength is the same in emission and absorption (see ref. 4, p. 98).

In order to make further analytic progress in the theory of diatomic molecules, the Born-Oppenheimer approximation is introduced (see ref. 9). This approximation assumes that the total wave function can be written as a product of an electronic wave function and a vibrational-rotational wave function. Further, Pauling and Wilson (ref. 10) have shown that the vibrational-rotational wave function can also be approximated by a product of vibrational and rotational wave functions. On the basis of these approximations, it is shown in reference 1 that the line strength for isotropic radiation can be written

$$\langle S_{J',J''} \rangle = q_{v',v''} \langle \psi_U | R_\alpha | \psi_L \rangle^2$$

(5)

The derivation given herein and the computer program are based on the electric dipole moment. However, the results can also be applied to magnetic dipole transitions (see p. 19).
where

$q_{v',v''}$ the vibrational Franck-Condon factor, dimensionless

$R_e$ the electronic transition moment, C m

$\alpha$ the rotational matrix element including the summation over $M'$ and $M''$, dimensionless

$\psi_{U'}, \psi_L$ the electronic-rotational wave functions for the rotational levels $J'$ and $J''$

$$R_e = \frac{1}{\sqrt{2}} (p_x \pm ip_y)$$

for perpendicular transitions, that is, those for which $\Delta \Omega = \pm 1$.

$$R_e = p_z$$

for parallel transitions, that is, those for which $\Delta \Omega = 0$, where $p_x$, $p_y$, and $p_z$ are the components of $\hat{P}$ in the molecular coordinate system.

The matrix brackets applied to $S_{J',J''}$ in equation (5) indicate that in diatomic spectra there may be several rotational lines in the same vibrational band with the same values of $J'$ and $J''$ (see fig. 1). Further, the symbolism correctly implies that the strength of the lines can be found by regular matrix operations.

In general, it is not possible to write simple expressions for the matrix elements of $\langle R_e \alpha \rangle$ between the wave functions $\psi_U$ and $\psi_L$. Therefore, the solution proceeds in three major steps. First the wave functions are expanded in terms of a complete set of simplified basis functions $\phi$ (see ref. 2); next the $\langle R_e \alpha \rangle$ matrix is expressed in terms of the basis functions; and finally the $\langle R_e \alpha \rangle$ basis matrix is transformed to the wave functions.

The transformation from the $\langle R_e \alpha \rangle$ basis matrix to the $\langle \phi \rangle$ matrix between wave functions is given by the unitary transformations that symmetrize the basis functions $T_{sym}$ and that diagonalize the Hamiltonian matrix between symmetrized basis functions $T_{diag}$. Thus,

$$\langle \psi_U | R_e \alpha | \psi_L \rangle = T^{-1}_{U} \langle \phi_U | R_e \alpha | \phi_L \rangle T_{L}$$

where

$$\phi = | \Lambda \Sigma \rangle | \Omega J \rangle$$

is the product of an electronic and a rotational basis function with $\Omega = \Lambda + \Sigma$ and $T = T_{sym} T_{diag}$.
The electronic transition moments \( R_e \) are usually determined by comparison of theory with experimental data; they are, therefore, carried in the present analysis as unknown parameters. To calculate realistic line intensities the user must know these parameters.

The rotational matrix elements, \( \alpha \), are related to the direction cosine transformation, which expresses the components of the dipole moment operator in the laboratory coordinate system in terms of its components in the molecular coordinate system. The matrix elements of the direction cosines are expressed in terms of the rotational quantum numbers in reference 11, and these are used in reference 1 to give the expressions for \( \alpha \) (valid for isotropic radiation) listed in table 1.

The general selection rules \( \Delta J = 0, \pm 1 \) and \( \Delta \Omega = 0, \pm 1 \) are explicitly indicated in table 1. Separate matrices for the \( P \)-, \( Q \)-, and \( R \)-branches are formed, depending on the value of \( \Delta J \). The specific matrix elements for each case are given by the expressions in the appropriate column of table 1.

An example \(<R_e \alpha>\) basis matrix for a spin-forbidden \( ^2\Pi \leftarrow ^4\Sigma^+ \) transition is shown in table 2. The rows of the matrix are designated by the final state basis functions and the columns by the initial state basis functions. The number of independent matrix elements can be reduced because symmetric matrix elements are related. Symmetric matrix elements are those that interchange when the signs of both \( \Lambda \) and \( \Sigma \) are changed in both the upper and lower electronic states (\( R_{e1} \alpha_1 \) and \( R_{e10} \alpha_{10} \) in table 2, for example).

The relationship between the symmetric matrix elements is determined by the phase factors that occur naturally in the quantum mechanical description of the problem. For phase conventions consistent with those chosen by Condon and Shortley in reference 4 and by Hougen in reference 2 (eq. 2-31), the following "symmetry rules" are derived in reference 1:

1. All the transition moments are real or all are pure imaginary and, for all practical purposes, they can always be chosen to be real.

2. All of the symmetric matrix elements in any given matrix are either equal to or the negatives of each other.

3. The symmetry in the \( P \)- and \( R \)-branch matrices is always opposite to the symmetry in the \( Q \)-branch matrix.

4. The symmetric matrix elements in the \( Q \)-branch matrix can always be chosen to be equal, except for the following two cases when they must be chosen to be negatives:

\[
\Sigma^\pm \leftrightarrow \Sigma^\pm \text{ transitions with } \Delta \Sigma = 0, 2, \text{ etc.}
\]

\[
\Sigma^\pm \leftrightarrow \Sigma^\mp \text{ transitions with } \Delta \Sigma = 1, 3, \text{ etc.}
\]

As an illustration of these rules, table 2 is recast in table 3, as it would appear for a \( P \)-branch matrix.
In the case of spin-allowed transitions, the additional selection rule \( \Delta \Sigma = 0 \) applies to \( R_e \) between electronic basis functions. This additional restriction reduces the number of nonzero matrix elements in the \(< R_e \alpha >\) basis matrix for spin-allowed transitions to those along the diagonal, where \( \Delta \Omega = \Delta \Lambda, \) as \( \Omega = \Lambda + \Sigma. \)

Furthermore, for spin-allowed transitions it can be shown (see ref. 2) that the absolute values of all of the nonzero electronic transition moments \( R_e \) are equal. Thus, for spin-allowed transitions, \( R_e \) can always be factored out of the \(< R_e \alpha >\) basis matrix, and the line strength (eq. (5)) can be written as

\[
\langle S_{j',j''} \rangle = q_{V'V''} R_e^2 |T_{UL}^{-1} |^2 \langle \phi_{U|\alpha|\phi_L} > T_L |^2 \\
= q_{V'V''} R_e^2 \langle \psi_{j',j''} >
\]

(7)

(8)

and the matrix elements of \( \langle \psi_{j',j''} >\), which are the rotational line intensity factors or Hönl-London factors, only involve the transformed rotational matrix elements \( \alpha; \) that is,

\[
\langle \psi_{j',j''} > = |T_{UL}^{-1} |^2 \langle \phi_{U|\alpha|\phi_L} > T_L |^2 \\
= | \langle \psi_{U|\alpha|\psi_L} > |^2
\]

(9)

(10)

For spin-forbidden transitions it is not possible, in general, to separate the electronic and rotational parts of the problem. For these cases reference 1 shows that the transformed \( < R_e \alpha > \) matrix elements can be written

\[
\langle \psi_{U|\alpha|\psi_L} > = < R_{e_1 \alpha_1} + R_{e_2 \alpha_2} + \cdots >
\]

(11)

where \( \alpha_i \) is the transformed rotational matrix element associated with \( R_{e_i}. \)

Equation (11) illustrates the property that for spin-forbidden transitions the matrix elements of \( < R_e \alpha > \) cannot, in general, be separated into rotational and nonrotational factors. However, if one of the transition moments (denoted by \( R_{e_l} \)) is factored out of the \( < R_e \alpha > \) matrix, the expression for the rotational line strength is similar to that for spin-allowed transitions; that is,

\[
\langle S_{j',j''} \rangle = q_{V'V''} R_e^2 |\rho a_i + \sigma a_j + \tau a_k + \cdots |^2
\]

(12)
where
\[ \rho = \frac{R_{e_i}}{R_{e_L}}, \quad \sigma = \frac{R_{e_j}}{R_{e_L}}, \quad \tau = \frac{R_{e_k}}{R_{e_L}}, \quad \text{etc.} \]

The factors \( \sigma, \tau, \text{ etc.} \), are called intensity parameters. The squares of the
matrix elements in equation (12) are called the rotational line intensity factors and are defined as
\[ \langle a_{J', J''} \rangle = \left| \langle \rho \overline{\alpha}_L + \sigma \overline{\alpha}_j + \tau \overline{\alpha}_k + \cdots \rangle \right|^2 \tag{13} \]

If equations (12) and (13) are combined, the rotational line strength for
spin-forbidden transitions can be written in the same form as spin-allowed
transitions (eq. (8)); that is,
\[ \langle S_{J', J''} \rangle = q_{V', V''} R_{e_L}^2 \langle a_{J', J''} \rangle \tag{14} \]

The sum of the intensity factors for a given value of \( J' \) or \( J'' \) is:

1. Spin-allowed transition
\[ \Sigma a_{J', J''}(J) = (2 - \delta_{0,(J'+J'')}})(2S + 1)(2J + 1) \tag{15} \]

where \( \delta_{a,b} = 1 \) if \( a = b \) and \( = 0 \) if \( a \neq b \).

2. For each transition moment in spin-forbidden transitions
\[ \Sigma a_{J', J''}(J) = C(2J + 1) \tag{16} \]

where \( C = 1 \) if the transition moment occurs only once in the \( \langle R_{e\alpha} \rangle \) basis
matrix and \( C = 2 \) if the transition moment occurs twice in the \( \langle R_{e\alpha} \rangle \) basis
matrix. The only transition moments that occur only once in any \( \langle R_{e\alpha} \rangle \) basis
matrix are those for the \( \Omega' = 0 \) to \( \Omega'' = 0 \) transition of \( \Sigma \leftrightarrow \Sigma \) transitions
of odd multiplicity. This transition moment is nonzero for \( \Sigma \leftrightarrow \Sigma \) transitions
with \( \Delta S = 0, 2, \text{ etc.} \) and for \( \Sigma \leftrightarrow \Sigma \) transitions with \( \Delta S = 1, 3, \text{ etc.} \).

The theory is explained in more detail in references 1 and 2.

AUXILIARY PROGRAMMING CONCEPTS AND DETAILS

The major concepts involved in the program are illustrated by the conceptual
flow chart shown in table 4. In brief, the computer solution proceeds in
the following logical steps.
1. Set up the upper and lower Hamiltonian matrices for each value of $J'$ and $J''$.

2. Symmetrize and diagonalize the upper and lower state Hamiltonians.

3. Set up the relevant rotational matrix for each pair of rotational levels $J'$ and $J''$.

4. Transform the rotational matrices with the same transformations that transformed the upper and lower state Hamiltonians.

A complete listing of the computer program is given in appendix A. The listing is liberally annotated, and if it is read in conjunction with the flow charts in appendix B, it should be nearly self-explanatory. In any complicated computer program, however, there are always a few programming details for which the logic is not immediately obvious. The following topics are included to give the reader some insight into the more obscure details.

**Initial State to Final State Notation**

The computer program was organized at its inception to describe the transitions from the initial state (columns of the matrices) to the final state (rows of the matrices). Unfortunately, this choice complicates the logic necessary to print correct titles for the calculated results. However, the program works, and the substantial changes necessary to switch to the more standard notation, which describes the rows of the matrices with the upper state and the columns of the matrices with the lower state, does not seem justifiable at this time. Further, the rows and columns of all basis matrices are ordered from top to bottom and from left to right in terms of the basis functions $|\Lambda S \Sigma \Omega J \rangle$ as follows:

$$
|+\Lambda S +S \rangle |+\Lambda S +S -1 \rangle |+\Lambda S +S -2 \rangle, 
|+\Lambda S -S \rangle |+\Lambda S -S +1 \rangle |+\Lambda S -S +2 \rangle, 
|-\Lambda S +S \rangle |-\Lambda S +S -1 \rangle |-\Lambda S +S -2 \rangle, 
|-\Lambda S -S \rangle |-\Lambda S -S +1 \rangle |-\Lambda S -S +2 \rangle
$$

**Absorption and/or Emission**

The intensity factors can be calculated for either absorption (in terms of $J''$) or emission (in terms of $J'$). The accepted standard notation for rotational lines is always $J''$. However, since in quantitative calculations involving line emission it is usually more convenient to denote intensity factors by $J'$, this flexibility was provided in the program logic.

**Hamiltonian Matrix**

Hamiltonian or energy operator matrices are set up for each value of $J$ in both the initial and final electronic states. That is, the energy levels of all rotational levels with the same value of $J$, in a given vibrational level...
and electronic state, are collected into a single matrix. In general, when \( J \geq \Lambda + S \), the Hamiltonian matrix contains \( (2 - 6 \delta_0, \Lambda)(2S + 1) \) rows and columns. However, if \( \Lambda \neq 0 \) the two submatrices for \( +\Lambda \) and \( -\Lambda \) are mirror images. An example case is shown in table 5 for a \( ^2\Pi \) electronic state. As there are no off-diagonal terms between \( +\Lambda \) and \( -\Lambda \), these two submatrices do not interact. It is therefore only necessary to operate on one of these submatrices, and, when needed, the full operator matrix can easily be constructed.

The two operations performed on the Hamiltonian matrix between basis functions are those that symmetrize the basis functions and that diagonalize the Hamiltonian matrix between symmetrized basis functions. The Hamiltonian matrices between basis functions and between symmetrized basis functions are identical for nonsigma electronic states. The unitary transformations that transform the Hamiltonian matrix to symmetrized basis functions for \( ^3\Sigma \) and \( ^4\Sigma \) electronic states are shown in figure 3. The generalization to any multiplicity is straightforward.

The diagonalization of the Hamiltonian is performed by the EIGEN subroutine, which finds \( T_{\text{diag}} \) for symmetrical, real matrices. This subroutine is a slightly modified form of the EIGEN subroutine described in the IBM System 360 Scientific Subroutine Package, document H20-0205.

In this program we are concerned only with determining the rotational intensity factors and do not solve explicitly for the energies of the rotational levels. Therefore, to a very good order of approximation, it is only necessary to include in the Hamiltonian the major energy interaction terms. For nonsigma states only the first-order spin-orbit interaction term, \( A\Lambda \Sigma \), is included. For sigma states, the first-order spin-orbit interaction term is zero; therefore, both the second-order spin-orbit term and the spin-spin interaction term are included. Both terms produce a similar effect and are lumped together as \( \Delta E \), the energy separation between spin states extrapolated to \( J = 0 \) (see appendix C). If \( A \) (or \( \Delta E \)) is negative the state is an inverted state.

The unitary transformation matrix that diagonalizes the Hamiltonian is not affected by a constant value along the diagonal of the Hamiltonian matrix or by a constant times every matrix element. Therefore, as we do not need the rotational energies themselves, constant or \( J \)-dependent only terms along the diagonal are removed from the Hamiltonian and all matrix elements are divided by \( B\hbar^2 \).

General expressions for the Hamiltonian matrix elements are given in reference 2. However, on the basis of the above discussion, only the following terms are included in the computer program.

1. Nonsigma states

\[
H(K,K) = -\Omega^2 - \Sigma^2 + Y\Lambda \Sigma
\]

\[
H(K,K+1) = -[(J - \Omega)(J + \Omega + 1)(S - \Sigma)(S + \Sigma + 1)]^{1/2}
\]

\[
H(K+1,K) = H(K,K+1)
\]
2. Sigma states

\[ H(K,K) = -\Omega^2 - \Sigma^2 + \Delta E/B \]

(20)

\[ H(K,K+1) \text{ and } H(K+1,K) \text{ same as above} \]

where \( Y = A/B \), and \( K \) specifies the row and column indices with \((1,1)\) as the upper left matrix element.

After the Hamiltonian matrix is diagonalized, the largest energy level is in the upper left matrix element and the smallest is in the lower right matrix element. This organization specifies the final form of \( T_{diag} \) and, hence, determines the order in which the branch lines occur in the intensity factor matrices. In order to understand this point, it is necessary to know how the rotational levels and the branches are designated.

**Designation of Rotational Levels**

In the standard notational scheme, the rotational levels of diatomic molecules are designated by two parameters in addition to \( J \): (a) the rotational quantum number \( N \), exclusive of spin and (b) the spin substate \( F_1, F_2, \ldots, F_{2S+1} \). The designation of rotational levels by \( N \) is most appropriate for Hund's case (b) coupling, where \( N \) is a valid quantum number. However, there is a one-to-one correspondence between the rotational levels in Hund's case (b) and any other coupling case, so that a value of \( N \) can always be assigned.

The designations of \( N \) and \( F_\ell \) for the spin substates, when \( J \geq \Lambda + S \), are related as follows:

\[
\begin{align*}
F_1 & \Rightarrow J = N + S \quad \text{or} \quad N = J - S \\
F_2 & \Rightarrow J = N + S - 1 \quad \text{or} \quad N = J - S + 1 \\
\vdots & \quad \vdots \\
F_{2S} & \Rightarrow J = N - S \quad \text{or} \quad N = J + S
\end{align*}
\]

(21)

From these equations it is clear that for the group of \( F_\ell \) levels with the same value of \( J \), \( F_1 \) corresponds to the lowest value of \( N \) and \( F_{2S+1} \) corresponds to the largest value of \( N \). Because \( \tilde{N} = \tilde{\Lambda} + \tilde{R} \), the difference between these \( N \) values is due to the difference in rotational energy, \( \tilde{R} \). Thus, for the group of \( F_\ell \) levels with the same value of \( J \), the rotational energy increases from \( F_1 \), the lowest energy level, to \( F_{2S+1} \), the highest energy level.

In nonsigma electronic states (\( \Lambda \neq 0 \)), the assignment of \( \bar{\Omega} \), where \( \bar{\Omega} = \Lambda + \Sigma \), to the \( F_\ell \) levels depends on whether the electronic state is regular or inverted. In regular states the smallest value of \( \bar{\Omega} \) is associated with the lowest energy level (i.e., \( F_1 \)). In inverted states the opposite association is made. Therefore, the assignment of \( N, F_\ell, \) and \( J \) to the rotational
levels of nonsigma electronic states can be made in the following empirical fashion.

1. For \( J \geq \Lambda + S \) and for rotational levels with the same value of \( J \), \( F_1 \) is assigned to the lowest energy level, \( F_2 \) to the next higher energy level, etc.

2. The value of \( \Omega \) is assigned to each \( F_i \) substate based on whether the electronic state is regular or inverted.

3. The rotational quantum number \( J \) is assigned sequentially from the lowest rotational level in each \( F_i \) substate, where the minimum value of \( J \) is \( |\Omega| \).

4. \( N \) is assigned as specified in equations (21) with the restriction that \( N \geq \Lambda \).

The steps outlined above are applied to the rotational levels of a \( ^4\Pi \) electronic state in figure 4. The value of \( N \) is shown to the left of each row, and the value of \( J \) is shown on the line representing the rotational level. The separations of the energy levels are not drawn to any physical scale, but they do indicate that for a given value of \( J \), the energy increases with increasing \( N \).

A study of figure 4 shows that, for either regular or inverted \( ^4\Pi \) electronic states, there are only two rotational levels with \( J = 1/2 \) and only three rotational levels with \( J = 3/2 \). The full multiplicity is therefore not developed until \( J \geq \Lambda + S \). Also, note that the \( N \) designation of the lower rotational levels in regular states is not given. The empirical scheme breaks down for these levels. To find the appropriate value of \( N \), when \( J < \Lambda + S \), one must operate on the wave function with \( N^2 \). The substate designation, \( F_i \), is established for \( J \geq \Lambda + S \) and is extended to low \( J \) levels as described above.

Much of the discussion above for nonsigma states also holds for sigma states (\( \Lambda = 0 \)), but the designation of the rotational levels with \( N \), \( F_i \), and \( J \) is the same in both regular and inverted states. The assignment for a \( ^3\Sigma \) electronic state is illustrated in figure 5. The concept of \( \Omega \) used for nonsigma states is not valid for sigma states and is not shown.

A study of figure 5 shows that there is only one rotational level with \( J = 0 \) and that it fits naturally into an assignment of \( F_3 \). This assignment of \( J = 0 \) agrees with that shown by Herzberg (ref. 12, p. 223) and also is compatible with Hougen's assignment of \( F_3 \) and \( F_4 \) to the \( J = 1/2 \) levels of \( ^4\Sigma \) states (ref. 13). However, Tatum and Watson (ref. 14) chose to assign the \( J = 0 \) level of \( ^3\Sigma \) states to \( F_1 \) for regular states and to \( F_3 \) for inverted states.
Designation of Branches

The standard scheme used to designate the branches in each vibrational band, is based on using letters to indicate the changes in $J$ and $N$ occurring during the transition and on including the $F^j_\ell$ assignment of the upper and lower substates. The assignment of letters to indicate the values of $\Delta J$ and $\Delta N$ is summarized in figure 6. The selection rules for dipole radiation limits $\Delta J$ to $0$ or $\pm 1$. The branch designation scheme is illustrated in figure 7. If $\Delta N = \Delta J$, the upper letter is not included and if $F^j_\ell = F^{j'}_\ell$, only one subscript number is included (i.e., $R_{2,2} = R_2$ in fig. 7).

The energy change during a transition is usually more closely associated with $\Delta N$ than with $\Delta J$. Therefore, the form of the branch is also primarily controlled by $\Delta N$. Hence, the $R_{2,3,2}$ branch is called the $R$-form $Q$-branch; that is, even though it is a $Q$-branch ($\Delta J = 0$), it usually has the form or appearance of an $R$-branch as $\Delta N = +1$.

The proper designation of the branches can be determined by forming matrices of the branches for fixed values of $J'$, $J''$, and $\Delta J$. These matrices are illustrated in figure 8 for a spin-allowed $^4\Pi \leftrightarrow ^2\Sigma$ transition and in figure 9 for a spin-forbidden $^2\Pi \leftrightarrow ^4\Pi$ transition. The rows of the matrices are labeled by the $F^j_\ell$ assignments for a given value of $J'$ and similarly the columns by $F^{j''}_\ell$ for a given value of $J''$.

The designation scheme illustrated in figure 9, for the branches of spin-forbidden transitions, is not universally applied. For example, in reference 15 Kovács designates the $F^j_\ell$ levels in the $^2\Pi$ electronic state in $^2\Pi \leftrightarrow ^4\Pi$ transitions as $F_2$ and $F_3$ sublevels rather than $F_1$ and $F_2$, as shown in figure 9. The designations $F_1$ and $F_2$ for the $^2\Pi$ state, however, are consistent with the recommendation made by Mulliken (ref. 16), and it seems desirable to retain this designation for all types of transitions.

The physical characteristics of rotational lines, such as their wavelengths and their intensity factors, are not, of course, dependent on the notation used. Therefore, the designation of branches can be altered to suit personal preference by making appropriate substitutions in the branch symbols. This option also applies to the designation of the $J = 0$ rotational level in $^3\Sigma$ states mentioned previously. However, standard designation schemes are very desirable.

The Rotational Matrices

The rotational matrices, in terms of the basis functions, are constructed from the matrix elements given in table 1. In the case of spin-allowed transitions, the electronic transition moments are factored out of the $<R_{\alpha\alpha}>$ basis matrix (see eq. (7)), and all the matrix elements are transformed simultaneously. Further, for spin-allowed transitions the rotational matrix elements are determined individually, rather than by the symmetry rules given on page 6. Also, for spin-allowed transitions the rotational line intensity factors are unchanged when the symmetrizing transformation is neglected and when only the $+\Lambda$ submatrix is explicitly considered if $\Lambda > 0$. 

13
In the case of spin-forbidden transitions, each rotational matrix element and its symmetrical counterpart are associated with a specific independent transition moment. Thus, each pair of symmetric matrix elements must be transformed separately by both the symmetrizing and diagonalizing transformations (see eq. (6)). Because only two matrix elements are involved in each transformation, the symmetrizing transformation in the program is performed algebraically rather than by the complete unitary transformation.

Each matrix element in the transformed rotational matrices is associated with a particular branch, based only upon its location within the matrix (see figs. 8 and 9). However, for transitions involving nonsigma electronic states, two submatrices occur and the usual branch designation scheme, described previously, does not at first appear adequate. However, if we print only one line intensity factor for each \( \Lambda \)-doublet in \( \Sigma \leftrightarrow \Pi \) transitions (\( \Sigma \) and \( \Pi \) represent any nonsigma electronic states), and if we combine the two submatrices in \( \Sigma \leftrightarrow \Sigma \) transitions prior to printing the results, the designation scheme described in the previous section is adequate.

For spin-allowed transitions, the above simplification was introduced indirectly by including only the \( <a> \) basis matrix elements from the \( +\Lambda \) submatrix and by neglecting the symmetrizing transformation. Thus, for spin-allowed transitions, all the required matrix elements occur in the upper left submatrix. For \( \Sigma \leftrightarrow \Pi \) transitions, however, \( \Lambda \)-doubling does not occur and, as only one submatrix of the electronic state is included, the matrix elements must be multiplied by \( \sqrt{2} \).

For spin-forbidden transitions the situation is slightly more complicated. For example, transformed rotational matrices for \( 3\Sigma \leftrightarrow 3\Xi \) transitions are illustrated in figure 10. The \( \Sigma \) in these matrices represents the only possible nonzero matrix element and the \( F_i \) designates the rows and columns assigned as discussed on page 11. Clearly, in either of these matrices if the elements of the lower submatrix are added to the elements of the upper submatrix with the same values of \( F_i \) and \( F'_i \), we will always add a nonzero to a zero value or vice versa. Furthermore, the resultant upper submatrix will contain matrix elements for all the branches. The discussion of \( 3\Xi \leftrightarrow 3\Sigma \) transitions is similar except that left and right submatrices replace upper and lower submatrices. The generalization to any multiplicity is straightforward.

For \( 3\Sigma \leftrightarrow 3\Pi \) transitions (neither electronic state is a sigma state), the transformed rotational matrices are illustrated in figure 11. The two matrix elements for each \( \Lambda \)-doublet occur in symmetrical locations with respect to the center of the matrix. As we print only one component of a \( \Lambda \)-doublet, we can always place the required matrix elements in the upper left submatrix by adding the elements in the lower left submatrix to the elements in the upper left submatrix with the same values of \( F_i \) and \( F'_i \).

Therefore, for all cases the transformed rotational matrix elements are organized into the upper left submatrix for printing. For spin-allowed transitions these matrix elements are squared before being printed to form the rotational line intensity factors, or Hönl-London factors. For spin-forbidden transitions these matrix elements are the \( \overline{a}_i \) values shown in equation (13) and
they must be printed without being squared. Before the output is printed, however, when \( J < \Lambda + S \), the matrix elements frequently need to be shifted to ensure proper labeling.

### Shifting of Rotational Matrix Elements When \( J < \Lambda + S \)

At the conclusion of the transformation operations discussed in the previous section, the transformed rotational matrix elements are located in the upper leftmost portion of the matrix. The output section of the program prints branch headings corresponding to the location of each matrix element in the fully developed matrix. However, when \( J < \Lambda + S \), the matrix is not fully developed and the matrix elements may not be in the proper positions to correspond to the headings that are printed. In these cases the matrix elements are shifted before being stored in the SAVE array. The SAVE array is used for temporary storage, before printing, and is discussed later.

The reason for shifting the matrix elements and the logic employed for shifting is indicated in figure 12. This figure shows the \( J = 1 \) rotational levels in the \( +\Lambda \) submatrix of the Hamiltonian matrix for a \( ^7\Pi \) electronic state.

The \( F \)-level designations of the rows and columns of a fully developed \( ^7\Pi \) matrix (i.e., \( J \geq \Lambda + S = 4 \)) are shown in figure 12(a). As discussed on page 11, the highest energy level \((F_7)\) is in the upper left matrix element. The program is written so that the three energy levels for \( J = 1 \) \((E_3, E_2, \text{and } E_1)\) naturally occur in the upper leftmost portion of the matrix, which corresponds to the \( F_7, F_6, \text{and } F_5 \) levels. However, if we determine the proper designations of the \( J = 1 \) rotational levels, we see that in a regular electronic state these levels should be designated \( F_4, F_3, \text{and } F_2 \), and in an inverted electronic state, they should be designated \( F_6, F_5, \text{and } F_4 \). Thus, to correspond to the designations of the fully developed matrix, the matrix elements must be shifted three spaces for a regular electronic state and one space for an inverted electronic state. These shifts are indicated by the heavy lines in figure 12(a).

The shifting of the rotational matrix elements when \( J < \Lambda + S \) is as follows: The columns are shifted by the shift necessary in the initial state Hamiltonian matrix and the rows are shifted by the shift necessary in the final state Hamiltonian matrix. Generalization of the logic described above to other electronic states is tedious but straightforward.

#### Designation of Transition Moments in Spin-Forbidden Transitions

The discussion leading to equation (11) shows that several independent transition moments may be present in spin-forbidden transitions. Each of these transition moments is explicitly identified in the computer program, but the designation scheme, contrary to the matrix operations, must be specified in terms of upper and lower states. The designation scheme used for this purpose is illustrated in table 6.
Table 6 shows the $\langle R_\epsilon a \rangle$ basis matrix for the $Q$-branches of a $^2\Pi \rightarrow ^4\Pi$ transition. The symmetry rules given on page 6 have been used to equate the symmetrical matrix elements. As noted above, the rows of the matrix refer to the upper ($^2\Pi$) electronic state and the columns to the lower ($^4\Pi$) electronic state. The opposite choice could have been made, but the choice made corresponds to conventional matrix nomenclature. If, instead, the rows of the matrix are designated by the final electronic state and the columns by the initial electronic state, as in the program matrix operations, the same transition moment may have one designation in absorption and a different one in emission. This situation is, of course, not acceptable. Thus, the logic in the program at this point is rather complicated.

The matrix elements of the $\langle R_\epsilon a \rangle$ matrix in the basis functions and, hence, the transition moments $R_\epsilon$ are designated with two single digit numbers. The first number specifies the upper electronic substate and the second number specifies the lower electronic substate on which the transition moment operates (i.e., $R_\epsilon$ (upper, lower)).

In terms of upper and lower electronic substates, the columns of the $\langle R_\epsilon a \rangle$ matrix are numbered from 1, beginning with the rightmost column if $\Lambda'' = 0$ and with the rightmost column in the left half of the matrix if $\Lambda'' \neq 0$, as in table 6. Note the circled numbers at the top of the columns in the left half of the $\langle R_\epsilon a \rangle$ matrix in table 6. Similarly, the rows of the $\langle R_\epsilon a \rangle$ matrix are numbered from 1 upward, beginning at the bottom row if $\Lambda' = 0$. If $\Lambda' \neq 0$, the rows are numbered from 1 upward in the top half of the matrix, beginning at the dividing point, and from -1 downward in the lower half of the matrix. Note the circled numbers at the left of the rows in table 6.

The rotational line intensity factors of the two lines forming a $\Lambda$-doublet in spin-forbidden transitions are not equal if the line strengths contain at least one $\langle R_\epsilon a \rangle$ matrix element between basis functions with opposite signs on $\Lambda'$ and $\Lambda''$ (i.e., $\langle \pm \Lambda' \mid R_\epsilon a \mid \mp \Lambda'' \rangle$) and at least one matrix element with the same signs on $\Lambda'$ and $\Lambda''$. The $\langle \pm \Lambda' \mid R_\epsilon a \mid \mp \Lambda'' \rangle$ matrix elements of nonsigma to nonsigma spin-forbidden transitions are indicated in the designation scheme by a negative number in the upper (i.e., first) index location of the transition moment. There are three such matrix elements in table 6: $R_\epsilon (-1,2)$, $R_\epsilon (-1,1)$, and $R_\epsilon (-2,1)$.

The $P$-branch matrix of a $^4\Sigma^+ \rightarrow ^4\Sigma^-$ transition, shown in table 7, has five independent transition moments.

SAVE, ITRANI, ITRANSF, NTRANR, NTRANQ, and NTRANP Matrices

The rotational line intensity factors (Hönl-London factors) for spin-allowed transitions and the transformed rotational matrix elements for spin-forbidden transitions are stored in the SAVE array until the calculation is complete. The SAVE array is three-dimensional and can be viewed conveniently, as shown in figure 13. The three dimensions correspond to (1) the number of independent transition moments in the transition (maximum of nine), (2) the number of branches in a vibrational band (maximum of 150, there are
147 branches in spin-allowed septet-septet transitions), and (3) the number of rotational lines in each branch included in the calculation (maximum of 200). In the dimension for storing branches, the \( R \)-branches are stored in the first 50 locations, the \( Q \)-branches in the second 50, and the \( P \)-branches in the last 50. Any dimensions of the SAVE array can be changed to any desired value, limited only by the size of the computer memory.

In the case of spin-forbidden transitions, the designations of the independent transition moments must also be stored. These correspond to each occupied row in the short dimension of the SAVE array for each value of \( J \). The upper substate (or first) designation of the transition moments in the \( \langle R_\alpha \rangle \) basis matrix is stored in the ITRANI array and the lower substate (or second) designation is stored in the ITRANF array. The number of independent transition moments for each value of \( J \) in the \( R \)-, \( Q \)-, and \( P \)-branches is stored in the NTRANR, NTRANQ, and NTRANP arrays.

### Input Data and Sample Cases

This section is intended to give the user a general picture of the ease of operation, broad generality, and potential applications of the computer program.

The data needed to initiate a calculation are:

1. The resultant spin \( S \) of each state.
2. The \( \Lambda \) value of each state.
3. The \( \pm \) symmetry for \( \Sigma \) states.
4. The spin-orbit and/or spin-spin parameters (see appendix C).
5. The values of \( J_{\text{min}} \) and \( J_{\text{max}} \).
6. The type of calculation (i.e., emission or absorption).

The format for the data input cards is illustrated in table 8.

The computer output format is demonstrated by partial listings of the printed output for three sample cases in tables 9, 10, and 11. The sample case in table 9 is a spin-allowed \( 3\Sigma^+ \rightarrow 3\Pi \) transition; that in table 10 is a spin-forbidden \( 3\Pi \rightarrow 5\Sigma^+ \) transition; and that in table 11 is a spin-forbidden \( 2\Pi \rightarrow 4\Pi \) transition. The information in the tables is discussed below.

The heading at the top of table 9 indicates that it is an allowed \( 3\Sigma^+ \rightarrow 3\Pi \) transition. The energy separation of the upper (\( \Sigma \)) state \( \Delta E/B \) is specified as -10; therefore, it is an inverted state. The spin-orbit coupling (\( Y = A/B \)) of the lower (\( \Pi \)) state is specified as 100; therefore, it is a
regular state. The paragraph in the heading refers to the lack of a universally accepted convention for designating the low J levels of Σ states (i.e., J < 1 in this case). As noted on page 12, for this case the J = 0 rotational level in the Σ state is designated as an F_F level.

The values tabulated for each branch are the rotational line intensity factors (also called Hönl-London factors) from J_{min} = 0 to J_{max} = 4 as specified in the input data. The column titled SUM is the sum of all Hönl-London factors printed for a given value of J and for the F level designation repeated in the column headings. Therefore, SUM contains all Hönl-London factors in the R-, Q-, and P-branches from a given J level. Each value of SUM is printed three times, once in each R-, Q-, and P-subsection. In table 9, for example, the first (upper level) F designation is repeated in the column headings because it is an emission calculation. Therefore, for J = 2 and for the F_1 rotational level, SUM is given by

\[ \text{SUM} = R_1 + QR_{12} + PR_{13} + Q_1 + PQ_{12} + OQ_{13} + P_1 + OP_{12} + NP_{13} \]

This value of SUM is printed in the appropriate place in the SUM column for the R-, Q-, and P-branches. The Hönl-London factors printed are for individual rotational lines. Therefore, if Λ-doubling occurs in the spectrum, the value printed is for only one component. Thus, the value of SUM, which is only the sum of the Hönl-London factors printed, is (2J + 1) for Σ→Σ and for nonsigma to nonsigma transitions, and 2(2J + 1) for Σ→Π or Π→Σ transitions.

Two spin-forbidden sample cases are included in tables 10 and 11 to illustrate results with and without Λ-doubling in the spectrum. The information printed in the headings for these cases is similar to that described for table 9 except that table 11 also contains a comment about Λ-doubling. The primary differences from the printout for the spin-allowed cases are in the tabulations. Normally, in spin-forbidden transitions there will be more than one independent transition moment, and the transformed rotational matrix elements must be printed for each of them.

The values tabulated for each branch are the transformed rotational matrix elements, \( \alpha_j' \). The intensity factors are formed from these numbers as shown in equation (13), which is repeated here for convenience:

\[ \langle J', J'' \rangle = |\langle \rho \alpha_j + \sigma \alpha_j' + \tau \alpha_k + ... \rangle|^2 \]

where \( \rho, \sigma, \tau \), etc., are the intensity parameters defined following equation (12).

The PARTIAL SUM listed for the forbidden transitions is the sum of the squares of the \( \alpha_j' \) values printed in the row to the right of the transition moment designation. The total sum for each transition moment is found by adding the partial sums from all branches containing that transition moment.
Lambda doubling occurs in the spectrum of the sample case given in table 11. However, the strengths of the two lines composing the \( \Lambda \)-doublets are not equal in all branches because three of the transition moments occur between basis functions with opposite signs on \( \Lambda' \) and \( \Lambda'' \) (see page 16). These transition moments are designated by \( R_{\pi}(-2,1) \), \( R_{\pi}(-1,1) \), and \( R_{\pi}(-1,2) \) in table 11. The intensity factor for the \( \Lambda \)-component not shown in the computer printout is obtained by changing the sign of these \( \alpha_L \) terms in equation (13). In general, when \( \Lambda \)-doubling occurs in spin-forbidden transitions, the intensity factor for the \( \Lambda \)-component not shown is obtained by changing the sign of all \( \alpha_L \) values whose associated transition moment designation contains a negative number.

The three sample cases discussed in this section illustrate the information that is calculated by the computer and printed for both spin-allowed and spin-forbidden transitions. The following subsection discusses the range of input parameters possible and thereby indicates the comprehensive nature of the program.

**Limitations and Capabilities of the Computer Program**

Two types of limitations of the computer program need to be discussed: (a) real limitations, for which the computer program does not apply; and (b) practical limitations, such as matrix size, that can easily be altered.

The most important real limitation of the program is the neglect of interactions that decouple the orbital angular momentum \( \vec{L} \) from the internuclear axis so that the intensity factors for the \( \pi \)-complexes, applicable to Hund's case (d) coupling, cannot be determined. Another important real limit of the program is that it is only valid for diatomic molecules and for electric and magnetic dipole transitions. In fact, the computer program is written for electric dipole transitions but the results also apply to magnetic dipole transitions. However, because the parity selection rule for magnetic dipole radiation is \( \pm \to \pm \), whereas for electric dipole radiation it is \( \pm \to \mp \), \( \Sigma^+ \to \Sigma^+ \) magnetic dipole transitions must be specified as \( \Sigma^\pm \to \Sigma^\pm \) transitions and vice versa.

There are no important practical limitations to the computer program. For example, in nonsigma electronic states, only spin-orbit interactions are included in the Hamiltonian, and in sigma electronic states, only the combination of spin-spin and second-order spin-orbit interactions are included (see appendix C). However, only if precise wavelengths are desired would a more accurate Hamiltonian be necessary. The remaining practical limitations actually establish the capabilities of the program. Thus, the computer program is capable of determining intensity factors over the broad range of conditions listed below.

1. Maximum spin quantum number of three (i.e., maximum multiplicity of seven).
2. Maximum of 200 rotation levels in one computer run.
3. Spin-allowed transitions with any degree of coupling between Hund's case (a) and case (b).

4. Spin-forbidden transitions with any degree of coupling between Hund's case (c) and case (b).

5. Maximum of nine independent transition moments permitted in spin-forbidden transitions.

The maximum multiplicity, the number of rotational levels in a single computer run, and the number of independent transition moments permitted are actually only limited by the memory size of the computer. Clearly, the capabilities of the program are very extensive and permit the calculation of exact intensity factors for most of the experimentally observed diatomic transitions.

Ames Research Center
National Aeronautics and Space Administration
Moffett Field, Calif., 94035, April 26, 1973
APPENDIX A

LISTING OF COMPUTER PROGRAM

C THIS PROGRAM COMPUTES INTENSITY FACTORS FOR ALLOWED
C TRANSITIONS (GHN-, LONDON FACTORS), AND THE SQUARE ROOT
C OF THE ROTATIONAL INTENSITY FACTORS FOR FORBIDDEN TRANSITIONS.
C
C MAIN PROGRAM
C
DIMENSION TITLE1(14), TITLE2(12), TITLE3(6), TITLE6(4), HEAD1(7), ALPHA(19,2)
C
COMMON /CSOLVE/JFI(JMIN,JMAX), JF(JMIN,JMAX), TITLE1, TITLE2, TITLE3, TITLE6,HEAD1, ALPHA
C
DOUBLE PRECISION SI, SF, LAMF, YI(JMIN,JMAX)
C
READ (5,501) SI, LAMF, SIGNI, VIII(J), YI(J1, J2, J3)
READ (5,502) JMIN, JMAX
READ (5,503) TYPE
C
DO 15 1 = 1, 200
DO 15 1 = 1, 150
DO 15 1 = 1, 9
SAVE(I, J, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
DO 17 I = 1, 200
NTRANRI = 0
NTRANQI = 0
NTRANPI = 0
DO 17 J = 1, 30
ITRANRI = 0
ITRANQI = 0
ITRANPI = 0
DO 17 I = 1, 200
DO 17 J = 1, 30
DO 17 K = 1, 9
SAVE(I, J, K, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
READ(5,501) SI, LAMF, SIGNI, VIII(J), YI(J1, J2, J3)
READ(5,502) JMIN, JMAX
READ(5,503) TYPE
C
READ IN NEW CASE.
C
DO 15 1 = 1, 200
DO 15 1 = 1, 150
DO 15 1 = 1, 9
SAVE(I, J, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
DO 17 I = 1, 200
NTRANRI = 0
NTRANQI = 0
NTRANPI = 0
DO 17 J = 1, 30
ITRANRI = 0
ITRANQI = 0
ITRANPI = 0
DO 17 I = 1, 200
DO 17 J = 1, 30
DO 17 K = 1, 9
SAVE(I, J, K, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
READ IN NEW CASE.
C
DO 15 1 = 1, 200
DO 15 1 = 1, 150
DO 15 1 = 1, 9
SAVE(I, J, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
DO 17 I = 1, 200
NTRANRI = 0
NTRANQI = 0
NTRANPI = 0
DO 17 J = 1, 30
ITRANRI = 0
ITRANQI = 0
ITRANPI = 0
DO 17 I = 1, 200
DO 17 J = 1, 30
DO 17 K = 1, 9
SAVE(I, J, K, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
READ IN NEW CASE.
C
DO 15 1 = 1, 200
DO 15 1 = 1, 150
DO 15 1 = 1, 9
SAVE(I, J, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
DO 17 I = 1, 200
NTRANRI = 0
NTRANQI = 0
NTRANPI = 0
DO 17 J = 1, 30
ITRANRI = 0
ITRANQI = 0
ITRANPI = 0
DO 17 I = 1, 200
DO 17 J = 1, 30
DO 17 K = 1, 9
SAVE(I, J, K, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
READ IN NEW CASE.
C
DO 15 1 = 1, 200
DO 15 1 = 1, 150
DO 15 1 = 1, 9
SAVE(I, J, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
DO 17 I = 1, 200
NTRANRI = 0
NTRANQI = 0
NTRANPI = 0
DO 17 J = 1, 30
ITRANRI = 0
ITRANQI = 0
ITRANPI = 0
DO 17 I = 1, 200
DO 17 J = 1, 30
DO 17 K = 1, 9
SAVE(I, J, K, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
READ IN NEW CASE.
C
DO 15 1 = 1, 200
DO 15 1 = 1, 150
DO 15 1 = 1, 9
SAVE(I, J, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
DO 17 I = 1, 200
NTRANRI = 0
NTRANQI = 0
NTRANPI = 0
DO 17 J = 1, 30
ITRANRI = 0
ITRANQI = 0
ITRANPI = 0
DO 17 I = 1, 200
DO 17 J = 1, 30
DO 17 K = 1, 9
SAVE(I, J, K, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
READ IN NEW CASE.
C
DO 15 1 = 1, 200
DO 15 1 = 1, 150
DO 15 1 = 1, 9
SAVE(I, J, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
DO 17 I = 1, 200
NTRANRI = 0
NTRANQI = 0
NTRANPI = 0
DO 17 J = 1, 30
ITRANRI = 0
ITRANQI = 0
ITRANPI = 0
DO 17 I = 1, 200
DO 17 J = 1, 30
DO 17 K = 1, 9
SAVE(I, J, K, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C
READ IN NEW CASE.
C
DO 15 1 = 1, 200
DO 15 1 = 1, 150
DO 15 1 = 1, 9
SAVE(I, J, 1, 1, 1, NTRANR, NTRANQ, NTRANP, JMIN, JMAX)
C IS THIS A SIGMA TO SIGMA TRANSITION?
C SIGSIG=.TRUE.
IF(LAMI.GT..1.OR.LAMF.GT..1) SIGSIG=.FALSE.
C IS THIS AN ALLOWED TRANSITION?
IF((SI-SF).NE.0.OR.OABS(LAMI-LAMF).GT.1.100) GO TO 20
IF(SIGSIG.AND.SIGN(F).NE.SIGN(S)) GO TO 20
C THIS IS AN ALLOWED TRANSITION.
ALLOW=.TRUE.
IMAX=2.*SI+.1
IF(SIGSIG.GO TO 30
C THIS IS A FORBIDDEN TRANSITION.
ALLOW=.FALSE.
IMAX=2.*SF+.1
C SET SIGN OF SYMMETRIC MATRIX ELEMENTS IN THE 0 BRANCH MATRIX.
SIGN=1.000
IF(.NOT.SIGSIG) GO TO 30
I=1
IF(SIGSIG) I=0
SIGN=(-1)**(I+I)
C IS SPIN HALF INTEGER OR WHOLE INTEGER?
IS=SI+.1
SI=IS
HALF=.TRUE.
IF(OABS(SI-SF).LT.1.100) HALF=.FALSE.
C JMIN AND JMAX MUST BE HALF INTEGER OR WHOLE INTEGER IN
C ACCORD WITH THE SPIN.
JTEST=JMIN+.1DO
J=JTEST
IF(HALF) GO TO 35
IF(OABS(J-JI).GT.1) JMIN=JI-.5DO
GO TO 37
35 [F(OABS(J-JI).LT.1) JMIN=JI+.5DO
37 JTEST=JMAX+.1DO
J=JTEST
IF(HALF) GO TO 39
IF(OABS(J-JF).GT.1) JMAX=JF-.5DO
GO TO 40
39 [F(OABS(J-JF).LT.1) JMAX=JF+.5DO
C FIND MINIMUM VALUES FOR JI AND JF AND
C ADJUST JMIN IF NECESSARY.
40 JI=LAMI-SI
IF(JI.GE.0.000) GO TO 45
JI=0.000
IF(HALF) JI=0.500
45 JF=LAMF-SF
IF(JF.GE.0.000) GO TO 50
JF=0.000
IF(HALF) JF=0.500
C IF((JMIN-JF).LT.-1.100) JMIN=JF-.100
C IF((JMIN-JF).GT.1.100) JF=JMIN+.100
C CALL SOLVE
C PRINT HEADING
WRITE(6,600)
IF(ALLOW) GO TO 70
WRITE(6,601) GO TO 75
70 WRITE(6,602)
75 I2=INDEX+2
INDEX=INDEX2+5
IF(LAMI.LT.100.AND.SIG.LT.600) GO TO 77
IF(SI.LT.100) GO TO 77
INDEX2=1
IF(EHISON) INDEX2=3
INDEX3=5
IF(ILAMF.LT.100.AND.SF.LT.600) GO TO 80
IF(SF.LT.100) GO TO 80
INDEX3=1
IF(EHISON) INDEX3=3

80 WRITE(6,603) TITLE5(INDEX2),TITLE5(INDEX2+1),TITLE5(INDEX2+2),TITLE5(INDEX2+3),TITLE5(INDEX2+4),TITLE5(INDEX2+5),TITLE5(INDEX2+6),TITLE5(INDEX2+7)

C IF(SM.MAXX.EQ.0) GO TO 95
IF(ILAMF.EQ.0) GO TO 82
WRITE(6,604) TITLE4(INDEX2),TITLE4(INDEX2+1),TITLE4(INDEX2+2)
INDEX2=2

82 IF(SI.LT.900) GO TO 85
INDEX2=1
IF(SEMP.EQ.2) WRITE(6,605) TITLE4(INDEX2),TITLE4(INDEX2+1)

C IF(SI.LT.1.900) GO TO 85
INDEX2=1
IF(SF.GT.2.600) INDEX2=2

85 WRITE(6,606) TITLE4(INDEX2),TITLE4(INDEX2+1),TITLE4(INDEX2+2),TITLE4(INDEX2+3),TITLE4(INDEX2+4)

C IF(SI.LT.900) GO TO 85
INDEX2=1
IF(SEMP.EQ.2) WRITE(6,607) TITLE4(INDEX2),TITLE4(INDEX2+1)

INDEX2=1

89 WRITE(6,608) INDEX2,INDEX2+1

90 IF(ILAMF.LT.100.AND.S1.SF.LT.600) GO TO 95
IF(ILAMF.LT.100.AND.SF.LT.600) GO TO 100
WRITE(6,610)

95 IF(ILAMF.LT.100.AND.SF.LT.100) GO TO 120
IF(SEMP.EQ.2) GO TO 110
WRITE(6,611)

C PRINT DATA

119 INDEX=1
IF(EHISON) INDEX+1
WRITE(6,609) TITLE6(INDEX),TITLE6(INDEX+1)

C PRINT DATA

119 INDEX=1
IF(EHISON) INDEX+1

C IS THIS AN ALLOWED TRANSITION?

140 DO 140 K=1,IMAX

C THIS IS A FORBIDDEN TRANSITION.

120 IDELS=0
DO 124 IDELS=SF
DO 124 IDELS=SF
IDELS=SF
IF(IDELS<0) LAMF.LT.11 GO TO 124
IF(IDELS>0) GO TO 122
IDELS=1
IF(IDELS<1) IDELS=2
GO TO 124

122 IDELS=1
IF(IDELS<1) IDELS=2

C PRINT K BRANCHES.

124 GO TO 124
```c
125 IF (HEAD1(II).EQ.R) HEAD1(II)=BLANK

126 CONTINUE
 WRITE(6,603) (HEAD1(II),R,HEAD2(II,K,III,I-1,IMAX))

C DO 140 I=1,1,J
 DELJ=I-1
 J=JMIN+DELJ
 WRITE(6,607)

C KO=(K-1)*7
 K1=KO+1
 K2=KO+IMAX
 K3=NTRAN(II)
 DO 130 NTRAN=1,K3
 SUM=0.DO0
 DO 128 KK=K1,K2
 SUM=SUM+SAVE(NTRAN,KK,II)**2
 130 WRITE(6,608) J,SUM,NTRAN,F(NTRAN*10,1),F(NTRAN*10,2)

C 140 CONTINUE

C PRINT Q BRANCHES.
 C DO 160 K=1,MAXI
 DO 145 I=1,MAXF
 N1=I+IDELS-(K-1)*7-I+1
 HEAD1(II)=ALPHAI(11)
 IF (HEAD1(II).EQ.Q) HEAD1(II)=BLANK

149 CONTINUE
 WRITE(6,606) (HEAD1(II),Q,HEAD2(II,K,III,I-1,IMAX))

C DO 160 I=1,1,J
 DELJ=I-1
 J=JMIN+DELJ
 WRITE(6,607)

C KO=(K-1)*7
 K1=KO+1
 K2=KO+IMAX
 K3=NTRAN(II)
 DO 150 NTRAN=1,K3
 SUM=0.DO0
 DO 148 KK=K1,K2
 SUM=SUM+SAVE(NTRAN,KK,II)**2
 150 WRITE(6,608) J,SUM,NTRAN,F(NTRAN*10,1),F(NTRAN*10,2)

C END OF CASE. READ IN NEXT CASE.
 C GO TO 10

C THIS IS AN ALLOWED TRANSITION.
 C PRINT R BRANCHES.
 C DO 190 I=1,1,J
 DELJ=I-1
 WRITE(6,607)

C KO=(K-1)*7
 K1=KO+1
 K2=KO+IMAX
 K3=NTRAN(II)
 DO 170 NTRAN=1,K3
 SUM=0.DO0
 DO 168 KK=K1,K2
 SUM=SUM+SAVE(NTRAN,KK,II)**2
 170 WRITE(6,608) J,SUM,NTRAN,F(NTRAN*20,1),F(NTRAN*20,2)

C 180 CONTINUE

C END OF CASE.
 C GO TO 10

C THIS IS AN ALLOWED TRANSITION.
 C PRINT R BRANCHES.
 C DO 190 I=1,1,J
 DELJ=I-1
 WRITE(6,607)

C KO=(K-1)*7
 K1=KO+1
 K2=KO+IMAX
 K3=NTRAN(II)
 DO 170 NTRAN=1,K3
 SUM=0.DO0
 DO 168 KK=K1,K2
 SUM=SUM+SAVE(NTRAN,KK,II)**2
 170 WRITE(6,608) J,SUM,NTRAN,F(NTRAN*20,1),F(NTRAN*20,2)

C END OF CASE.
 C GO TO 10

C THIS IS AN ALLOWED TRANSITION.
 C PRINT R BRANCHES.
 C DO 190 I=1,1,J
 DELJ=I-1
 WRITE(6,607)

C KO=(K-1)*7
 K1=KO+1
 K2=KO+IMAX
 K3=NTRAN(II)
 DO 170 NTRAN=1,K3
 SUM=0.DO0
 DO 168 KK=K1,K2
 SUM=SUM+SAVE(NTRAN,KK,II)**2
 170 WRITE(6,608) J,SUM,NTRAN,F(NTRAN*20,1),F(NTRAN*20,2)
```
J=JMIN+DELJ
SUM=0.000

K0=K1+1
K1=K0+1
K2=K0+MAXI
DO 200 KK=K1,K2
K3=KK-50
K4=KK+50
200 SUM=SUM+SAVE(1,KK,I)+SAVE(1,KK+1,I)
WRITE(6,610) J,SUM,(SAVE(1,KK,I),KK=K1,K2)
IF((J+1)/5<5-1.EO.O) WRITE(6,607)

210 CONTINUE

C PRINT Q BRANCHES.
C
DO 215 K=1,MAXF
DO 210 I=1,MAXF
N1=10-(K-1)*U-1
HEAD1(I)=ALPHA(N1,I)
IF(HEAD1(I).EQ.P) HEAD1(I)="BLANK"
215 CONTINUE
WRITE(6,609) (HEAD1(I),P,HEAD2(I,K,III),I=1,MAXF)

C
DELJ=I-1
J=JMIN+DELJ
SUM=0.000

K0=50+K1+1
K1=K0+1
K2=K0+MAXF
DO 220 KK=K1,K2
K3=KK-50
K4=KK+50
220 SUM=SUM+SAVE(1,KK,I)+SAVE(1,KK+1,I)
WRITE(6,610) J,SUM,(SAVE(1,KK,I),KK=K1,K2)
IF((J+1)/5<5-1.EO.O) WRITE(6,607)

230 CONTINUE

C PRINT P BRANCHES
C
DO 235 K=1,MAXF
DO 230 I=1,MAXF
N1=11-(K-1)*U-2+(I-1)
HEAD1(I)=ALPHA(N1,I)
IF(HEAD1(I).EQ.P) HEAD1(I)="BLANK"
235 CONTINUE
WRITE(6,609) (HEAD1(I),P,HEAD2(I,K,III),I=1,MAXF)

C
DELJ=I-1
J=JMIN+DELJ
SUM=0.000

K0=100+K1+1
K1=K0+1
K2=K0+MAXF
DO 240 KK=K1,K2
K3=KK-100
K4=KK+100
240 SUM=SUM+SAVE(1,KK,I)+SAVE(1,KK+1,I)
WRITE(6,610) J,SUM,(SAVE(1,KK,I),KK=K1,K2)
IF((J+1)/5<5-1.EO.O) WRITE(6,607)

250 CONTINUE

C END OF CASE, READ IN NEXT CASE.
C
GO TO 10
C
C READ FORMAT STATEMENTS.
C
501 FORMAT(F3.1,2X,F2.0,2X,A1,3E10.0)
502 FORMAT(2F5.1)
503 FORMAT(1X)
504 FORMAT(1X)
505 FORMAT(7X,3F12.6,5X,7F8.3)
506 FORMAT(7X,2A1,15H STATE.)
507 FORMAT(3F12.6,5X,7F8.3)

C WRITE FORMAT STATEMENTS.
C
600 FORMAT(15X,2A1,6H STATE ENERGY SEPARATION = \ DELTA E(I,I/B) = \F8.3)
FORMAT //27X.5BHIN SIGMA STATES WHEN JCS, THE F DESIGNATION FOR THE LEVELS,
1 //27X.53HHITH THE SAME VALUE OF J ARE ASSIGNED AS 2S+1 FOR THE,
2 //27X.51HHIGHEST ENERGY LEVEL, 2S FOR THE NEXT HIGHEST, ETC.)

FORMAT //27X.59HLAMBDA DOUBLING OCCURS IN THE SPECTRUM, BUT THE SQUARE ROOT,
1 1TH OF THE INTENSITY/27X.40FACTORS FOR ONLY ONE LINE OF EACH LAMBDA,
2 40H DOUBLET IS PRINTED. THE VALUES FOR THE/27X.12HOTHER LAMBDA,
3 40H COMPONENTS ARE FOUND BY CHANGING THE SIGN OF THE NUMBERS ,
4 11HPRINTED, IF/27X.42HTHE TRANSITION MOMENT DESIGNATION CONTAINS,
5 14H A MINUS SIGN.)

FORMAT //27X.59HLAMBDA DOUBLING OCCURS IN THE SPECTRUM, BUT THE NON-LONDON,
1 21H FACTORS FOR ONLY ONE/27X.59LINE OF EACH LAMBDA DOUBLET IS PRINTED,
2 39H THE NON-LONDON FACTORS FOR THE OTHER/27X.17HLAMBDA COMPONENTS,
3 14H ARE THE SAME.)
END
SUBROUTINE SOLVE
C
C THIS PROGRAM:
C 1- DEVELDPES THE ROTATIONAL HAMILTONIAN.
C 2- CALLS EIGEN TO GET THE EIGEN VECTORS OF THE HAMILTONIAN.
C 3-OEVELOPES THE ROTATIONAL MATRIX.
C 4- TRANSFCRMS THE ROTATIONAL MATRIX.
C 5- STORES, IN THE LARGE SAVE ARRAY, HQL-LONOON FACTORS
C FOR ALLOWED TRANSITIONS AND THE SQUARE ROOT OF
C ROTATIONAL INTENSITY FACTORS FOR FORBIDDEN TRANSITIONS.
C
DIMENSION T(14,14),TI<14,14>,TF1I14,14>,TF2<14,14),AI14,14),
C(14)x{14},H(7x7),SY[H7]
C
COMMON /CSOLVE/JF,JMIN,JMAX,JF,J,JI,JF,Y(3),Y,LI,LAM,LAMF,
1 SIGN1,ALLOW,EMISON,SIGSIG,IJ, I MAX 1,1HAXF,
2 NTRANR(200),NTRANO(200),NTRANP(200),
3 ITRANI(30,200),ITRANF(30,200),
4 SAVE(9,150,200),YI(3),YF(3)
C
COMMON/CEIGEN/HH28),TTC49I,N
C
DOUBLE PRECISION A,OELJ,JMIN,JMAX,J,JI,JF,Y(3),YI,YF,LAM,LAMF,
1 LAMF,E1,EK, STATE-INITAL
C(15)x{15}
15 Y(I°YI(I>
GO TO 30
C
INTEGER SAVE1,SAVE2,SAVE3,SAVE4,SAVES,SAVE6
C
C INITIALIZE MATRICES.
C AND SET FLAG FOR FIRST COMPUTATION.
C
DO 10 I=1,14
DO 10 K=1,14
T(I,K)=0.000
TF1(I,K)=0.000
TF2(I,K)=0.000
10 A(I,K)=0.000
FIRST=TRUE.
SAVE3=0
NSAVE=0
C
C START PRIMARY CALCULATION AT THIS POINT.
C THE INTENSITY FACTORS ARE CALCULATED IN
C TERMS OF THE INITIAL VALUE OF J, IE. IN TERMS OF
C J-LOHER FOR ABSORPTION AND IN TERMS OF
C J-UPPER FOR EMISSION.
C
DO 90 1=1,200
DELJ=1
JI=JMIN+DELJ
C
SET VALUES FOR INITIAL LEVEL CALCULATION.
C
J=JI
LAM=LAMF
S=SI
15 STATE=INITAL
G0 15 I=1,14
Y(I)=YI(I)
GO TO 30
C
SET VALUES FOR FINAL LEVEL CALCULATION.
C
J=JF
LAM=LAMF
S=SF
15 STATE=FINAL
G0 25 I=1,14
Y(I)=YF(I)
C
SET VALUES FOR INITIAL LEVEL Calculation.
C
C(15)x{15}
15 Y(I°YI(I>
GO TO 30
C
C INITIALIZE HAMILTONIAN AND TRANSFORMATION MATRICES.
C
C(15)x{15}
15 Y(I°YI(I>
GO TO 50
C
C THE HAMILTONIAN MATRIX IS REDUCED AT LOW J VALUES.
C SET INDICES DEFINING WHICH ROWS AND COLUMNS HAVE NON-ZERO ELEMENT
C
OMEGA=LAM+F
IF(OMEGA>1.0) GO TO 50
HAMiltonian IS Fully Developed.

I1=1
I2=IMAX
GO TO 110

HAMiltonian IS Reduced.

50 TEST=OMEGA
GO TO 1*1, IMAX
TEST=TEST+1.0
IF(J,J.33,GT,TEST) GO TO 70
CONTINUE
I1=IMAX
GO TO 80
70 IF(I,J.EQ.11) GO TO 100

There IS Only One Element In The Hamiltonian.
SET TRANSFORMATION MATRIX.

80 I2=I1
90 T(J,J)=T(I,J)*I1
GO TO 240

There MMay Be More Than One Element In The Hamiltonian Matrix.

100 I2=I,J+2
I2=I2+I2
IF(I,J.GT,IMAX) I2=IMAX

There IS More Than One Element In The Hamiltonian Matrix?

110 IF(I,J.EQ.11) GO TO 90

There Is MorE Than One Element In The Hamiltonian Matrix. Set Size Of Matrix.

N=I2-I1+1

Develop upper Half of Symmetrical Hamiltonian Matrix.
J(J*1) and S(S*1) terms in the Diagonal Elements are not included.

120 H(J,J)=H(J,J)*S(I)*S(I)
GO TO 152

If this Is a Sigma State?

130 IF(I,J.GT.IA) GO TO 140

This Is Not a Sigma State. INCLUDE Spin-Orbit Interaction (Y=A/B).

140 DO 150 I1=1,I2
150 E(I1)=H(I1,11)+Y(I1)*LAMBDA*(S-I1,100)
GO TO 152

This Is a Sigma State. INCLUDE Spin-Orbit + Spin-Spin Energy Separations (DELTA E/B).

160 DO 150 I1=1,I2
150 E(I1)=H(I1,11)+Y(I1)*LAMBDA*(S-I1,100)+DELTA E/B
GO TO 152

161 IF(I,J.GT.1) GO TO 150
170 E(I1)=H(I1,11)+Y(I1)*LAMBDA*(S-I1,100)+DELTA E/B
GO TO 152

171 IF(I,J.GT.1) GO TO 150
180 E(I1)=H(I1,11)+Y(I1)*LAMBDA*(S-I1,100)+DELTA E/B
GO TO 152

28
IF I .GT. 3.OR. I .EQ. 4 GO TO 150
I = 2
IF I .EQ. 2.OR. I .EQ. 51 I = 1
GO TO 146
IF I .EQ. 4 GO TO 150
I = 3
IF I .NE. 1.OR. I .NE. 7 I = 2
IF I .EQ. 3.OR. I .EQ. 51 I = 1
GO TO 146
IF I .EQ. K OR. K .EQ. 13 GO TO 146
GO TO 145
IF I .NE. 1.OR. I .NE. 7 I = 2
IF I .EQ. 3.OR. I .EQ. 51 I = 1
H(K,K) = H(K,K) * Y(I)
CONTINUE
C IS SYMMETRIZING MATRIX NECESSARY?
C NEEDED FOR NON-SINGLET SIGMA STATES IN FORBIDDEN TRANSITIONS.
C
IF ALLOW .OR. LAM .LT. 1 GO TO 225
C CONSTRUCT SYMMETRIZING MATRIX.
C IF H(K,K) .NE. H(K,K) GO TO 180
NSAVE = M
GO TO 155
NSAVE = 0
C
K = 0
DO 170 K = 1, N
SYM(K,K) = 0.0
170 CONTINUE
C SYMMETRIZE HAMILTONIAN MATRIX IF REQUIRED.
C DO 180 I = 1, N
DO 180 K = 1, N
C(K, I) = 0.0
180 CONTINUE
C TRANSFORM UPPER HALF OF SYMMETRICAL HAMILTONIAN INTO A ONE-DIMENSIONAL
C ARRAY, HH TO BE COMPATIBLE WITH EIGENFUNCTION SUBROUTINE.
C
K = 0
DO 220 K = 1, N
H(K, I) = H(K, I) * SYM(K, K)
220 CONTINUE
C CALL SUBROUTINE TO FIND THE EIGENFUNCTIONS OF
C THE HAMILTONIAN MATRIX BY JACOBI-VON NEUMAN METHOD.
C EIGENFUNCTIONS ARE ORDERED IN A ONE-DIMENSIONAL ARRAY, TT WITH
C THE LARGEST EIGENVALUE FIRST, ETC.
C CALL EIGEN
C EXPAND THE ONE-DIMENSIONAL ARRAY, TT INTO THE TWO-DIMENSIONAL
C TRANSFORMATION MATRIX, T THAT DIAGONALIZES THE HAMILTONIAN.
C ENSURE CONSISTANT PHASE OF THE EIGENFUNCTIONS BY MAKING
C THE FIRST ELEMENT IN EACH COLUMN NEGATIVE.
C
K = 0
DO 235 I = 1, N
C(I) = 1.0
I F I ( I .GT. 0.1) C(I) = 1.0
DO 235 K = 1, N
K = K + 1
235 CONTINUE
C IF THIS IS A FORBIDDEN TRANSITION AND IF
C THIS STATE IS NOT A SIGMA STATE, EXPAND THE
C TRANSFORMATION MATRIX TO ALLOW FOR LAMBDA DOUBLING.
C
N = N
IF I .GT. 1 .OR. LAM .LT. 1.0 GO TO 260
C EXPAND THE TRANSFORMATION MATRIX.
N = 2 N
I = I + 1
DO 250 I=1,N
DO 250 K=1,N
K=1-1

270 T(K3,13)=T(K1,11)

TRANSFER T MATRIX INTO INITIAL (TI) OR FINAL (TF) MATRIX, SET FLAGS AND INDICES FOR PROPER BRANCHES
PRELIMINARY TO DEVELOPING THE ROTATIONAL MATRIX.

IS THIS THE INITIAL OR THE FINAL STATE?
260 IF (STATE.EQ.FINAL) GO TO 280

THIS IS THE INITIAL STATE.
TRANSFER THE T MATRIX INTO THE TI MATRIX.
SET INDICES FOR INITIAL STATE.
DO 270 I=1,N
DO 270 K=1,N

270 TII(IK)=TII(KI)

IF(I11=11)
I12=I2
N1=N

IF THIS IS THE FIRST TIME THRU OR IF THE Q BRANCHES
HAVE NOT BEEN COMPUTED, GO DIRECTLY TO THE FINAL STATE.
IF (FIRST) GO TO 20
IF(BRANCH.NE.0) GO TO 300

GO TO 330

THIS IS THE FINAL STATE.
ARE CONDITIONS SET FOR Q BRANCHES?
280 IF (JABS(J1-JF1.GT.0) GO TO 330

CONDITIONS ARE SET FOR Q BRANCHES.
INVERT T MATRIX AND PUT INTO TF1 MATRIX.
DO 290 I=1,N
DO 290 K=1,N

290 TF1(IK)=TI(KI)

SAVE INDICES DENOTING SIZE OF HAMILTONIAN AND
WHICH ELEMENTS ARE FILLED.
SAVEI=I1
SAVE2=I2
SAVE3=N
FIRST=.FALSE.

INCREASE FINAL STATE ROTATIONAL QUANTUM NUMBER
BY 1 AND COMPUTE THE NEW FINAL STATE.
300 JF=JF1+1
GO TO 20

THIS IS EITHER A P OR AN R BRANCH.
NORMALLY JF WILL BE GREATER THAN JI AT THIS POINT.
HOWEVER, THE FIRST TIME THRU JI MAY BE GREATER.
310 IF(JF.GT.J1) GO TO 350

FIRST TIME THRU, INVERT T MATRIX AND PUT INTO TF1
MATRIX AND SET INDICES.
DO 320 I=1,N
DO 320 K=1,N

320 TF2(IK)=TI(KI)

IF(I1=11)
I12=I2
NP=N

IF THIS IS AN EMISSION CALCULATION, WE ARE READY
TO COMPUTE R BRANCHES. IF ABSORPTION, P BRANCHES.
330 IF (EMISION) GO TO 370

THIS IS A P BRANCH CALCULATION.
340 BRANCH=P

SET INDEX FOR SAVING P BRANCHES IN THE LARGE SAVE ARRAY.
IK=100
SIGN2=-1
GO TO 390

INVERT T MATRIX, PUT INTO TF2 MATRIX AND SET INDICES.
DO 360 I=1,N
DO 360 K=1,N

360 TF2(IK)=TI(KI)
IF2 = I2
NF = N

C IF THIS IS AN EMISSION CALCULATION, WE ARE READY
C TO COMPUTE P BRANCHES. IF ABSORPTION, R BRANCHES.
C IF(EMISSION) GO TO 340
C
C THIS IS AN R BRANCH CALCULATION.
C
370 BRANCH = R
C
SET INDEX FOR SAVING Q BRANCHES IN THE LARGE SAVE ARRAY.
C
IK = 0
SIGN 2 = 1.000
GO TO 390
C
C THIS IS A Q BRANCH CALCULATION.
C
380 BRANCH = Q
IK = 50
SIGN 2 = 1.000
C
DEVELOP ROTATIONAL MATRIX.
C
C SET INDICES AND SIGN OF LAMBDA.
C
390 1 = 0
E1 = I2
N1 = N1
NFF = NF
NTRAN = 0
SIGN 2 = 1.000
C
IF(ALLOW OR LAMF.LT.1.1) GO TO 450
SIGN 2 = 1.000
NFF = 2*NF
C
C SET INDICES AND OMEGA FOR THE INITIAL STATE,
C COLUMNS OF THE MATRIX.
C
400 1 = 1
E1 = E1 - 1.000
OMEGA1 = LAMM + S1 - E1
II = II + 1
C
K = 0
EK = E1
C
C SET INDICES AND OMEGA FOR THE FINAL STATE,
C ROWS OF THE MATRIX.
C
410 K = K + 1
EK = EK - 1.000
KE = NFF - K1
IF(SIGNSIGNLT.1.0) EK = EK - K1/2
OMEGA2 = SIGMLAMF + 3F - EK
C
C FIND DELTA OMEGA AND DELTA LAMBDA.
C
DELO = OMEGAF - OMEGAI
DELL = LAMF - LAM1
C
C FOR ALLOWED TRANSITIONS DELTA OMEGA MUST EQUAL DELTA LAMBDA.
C
IF( .NOT. ALLOW) GO TO 415
IF(ABS(DELO - DELL).GT.1.1) GO TO 415
C
WHAT TYPE OF BRANCH?
C
415 IF(BRANCH.EQ.0) GO TO 470
IF(JF-J1).GT.1.1) GO TO 440
C
P BRANCH IN ABSORPTION OR
C R BRANCH IN EMISSION.
C
IF(J1.LT.1) GO TO 410
IFIABSDELO.LT.1.100 TO 430
IFIDELO.GT.0.0) GO TO 470
IFI DELO.LT.-1.100 TO 510
C
A(KK,II) = DSQRT((J1*OMEGAII - (J1-OMEGAI)/JII
GO TO 500
C
A(KK,II) = DSQRT((J1+OMEGAII)*(J1+OMEGAI-1.000)/(2.000*JII)
GO TO 500
C
420 IF(DELO.GT.1.1) GO TO 520
C
A(KK,II) = DSQRT((J1+OMEGAII)*(J1-OMEGAI-1.000)/(2.000*JII)
GO TO 500
C
430 IF(IN.1.0) DGRT((J1+OMEGAII)*(J1+OMEGAI)/JII
GO TO 500
C
R BRANCH IN ABSORPTION OR
P BRANCH IN EMISSION.
C
C 440 IF(ABS(DEL0.LT.1))GO TO 440
  IF(DEL0.GT.1)GO TO 450
  IF(DEL0.LT.-1)GO TO 510
  A(KK,II)=SQRT(IJ+OMEGA*1.000*IJ+OMEGA*1.000)*IJ+OMEGA*1.000
  GO TO 500
C 450 IF(DEL0.GT.1.1)GO TO 520
  A(KK,II)=OMEGA*IJ+OMEGA*1.000*IJ+OMEGA*1.000
  GO TO 500
C 460 A(KK,II)=OMEGA*IJ+OMEGA*1.000*IJ+OMEGA*1.000
  GO TO 500
C 0 BRANCH IN ABSORPTION OR EMISSION.
C 470 IF(ABS(DEL0.LT.1))GO TO 490
  IF(ABS(DEL0.LT.1))GO TO 490
  IF(DEL0.GT.1)GO TO 480
  IF(DEL0.LT.-1.1)GO TO 510
  A(KK,II)=SQRT(IJ+OMEGA*1.000*IJ+OMEGA*1.000)*IJ+OMEGA*1.000
  GO TO 500
C 480 IF(DEL0.GT.1.1)GO TO 520
  A(KK,II)=OMEGA*IJ+OMEGA*1.000*IJ+OMEGA*1.000
  GO TO 500
C 490 A(KK,II)=OMEGA*IJ+OMEGA*1.000*IJ+OMEGA*1.000
  GO TO 500
C IF THIS IS AN ALLOWED TRANSITION LOOP BACK UNTIL ALL
C ELEMENTS ARE IN THE ROTATIONAL MATRIX. IF THIS IS
C A FORBIDDEN TRANSITION, FIND THE SYMMETRICAL ROTATIONAL
C MATRIX ELEMENT AND TRANSFORM THEM TOGETHER.
C 500 IF.(NOT.ALLOW)GO TO 540
C 510 IF(K.LT.NF)GO TO 410
  IF(K.GT.NF)GO TO 525
C 520 IF(SIGN.GT.0)GO TO 530
C IS FORBIDDEN BRANCH COMPLETED?
C 530 IF(I.EQ.NI)GO TO 535
  IF(I.EQ.NI)GO TO 535
C IS FORBIDDEN BRANCH COMPLETED?
C 535 IF(ALLOW)GO TO 580
  IF(ALLOW)GO TO 580
C THIS IS A FORBIDDEN TRANSITION, FIND THE SYMMETRICAL
C ELEMENT WITH PROPER PHASE FACTORS. CHECK SIGMA TO SIGMA
C TRANSITION FOR EXISTENCE OF TRANSITION MOMENT WHEN BOTH
C OMEGAS EQUAL ZERO.
C 540 IF(SIGSIG)GO TO 560
C INITIAL STATE IS NOT A SIGMA STATE.
C 550 IF(I.EQ.NI)GO TO 535
  IF(I.EQ.NI)GO TO 535
C IS FORBIDDEN BRANCH COMPLETED?
C 535 IF(ALLOW)GO TO 580
  IF(ALLOW)GO TO 580
C THIS IS A FORBIDDEN TRANSITION, MUST NOW TRANSFORM
C THE ROTATIONAL MATRIX. IF THIS IS A FORBIDDEN
C TRANSITION, THIS BRANCH IS COMPLETE.
C 535 IF(ALLOW)GO TO 580
C THIS IS A FORBIDDEN TRANSITION, FIND THE SYMMETRICAL
C ELEMENT WITH PROPER PHASE FACTORS. CHECK SIGMA TO SIGMA
C TRANSITION FOR EXISTENCE OF TRANSITION MOMENT WHEN BOTH
C OMEGAS EQUAL ZERO.
C 540 IF(SIGSIG)GO TO 560
C INITIAL STATE IS NOT A SIGMA STATE.
C 550 IF(I.EQ.NI)GO TO 535
  IF(I.EQ.NI)GO TO 535
C IS FORBIDDEN BRANCH COMPLETED?
C 535 IF(ALLOW)GO TO 580
  IF(ALLOW)GO TO 580
C THIS IS A SIGMA TO SIGMA TRANSITION.
C ARE BOTH OMEGAS EQUAL TO ZERO?
C 550 IF(ABS(OMEGA.LT.1.1AND.DABS(OMEGA.LT.1.1))GO TO 570
C AT LEAST ONE OMEGA IS UNEQUAL TO ZERO. SET SYMMETRICAL ELEMENT.
C 560 IF(ABS(OMEGA.LT.1.1AND.DABS(OMEGA.LT.1.1))GO TO 570
C AT LEAST ONE OMEGA IS UNEQUAL TO ZERO. SET SYMMETRICAL ELEMENT.
C 565 I3+1
C 567 A(KK,II)=SIGN1*SIGN2*AIKK,II}
C BOTH OMEGAS ARE ZERO.
C THERE IS NO SYMMETRICAL ELEMENT.
C FOR THE TRANSITION MOMENT TO EXIST SIG1 MUST BE NEGATIVE.
C
570 IFSIG1.LT.0.0 GO TO 580
C THE TRANSITION MOMENT CORRESPONDING TO THIS MATRIX
C ELEMENT DOES NOT EXIST. WE CAN ALLOW FOR THIS BY
C SETTING THE MATRIX ELEMENT EQUAL TO ZERO. ALSO THIS
C BRANCH IS COMPLETE.
C
A(KK,II)=0.000
GO TO 810
C TRANSFORM THE ROTATIONAL MATRIX.
C SYMMETRIZE FORBIDDEN TRANSITIONS.
C
571 IF(K,EQ.KK) GO TO 576
IF(K1,EQ.13) GO TO 575
IF(K1,GT.III) GO TO 572
MH(1)=A(KK,13)*0.500
MH(2)=0.000
MH(3)=A(KK,II)*0.500
MH(4)=0.000
GO TO 578
C
572 MH(1)=0.000
MH(2)=A(K,13)*0.500
MH(3)=A(K,11)*0.500
MH(4)=0.000
GO TO 578
C
573 IF(II,GT.III) GO TO 574
MH(1)=-A(K,13)*0.500
MH(2)=A(K,11)*0.500
MH(3)=0.000
MH(4)=0.000
GO TO 578
C
574 MH(1)=A(K,11)*0.500
MH(2)=0.000
MH(3)=A(K,13)*0.500
MH(4)=0.000
GO TO 578
C
575 MH(1)=A(K,13)*0.70710678100
MH(2)=A(K,11)*0.70710678100
MH(3)=0.000
MH(4)=0.000
GO TO 578
C
576 IF(13,GT.III) GO TO 577
MH(1)=A(K,13)*0.70710678100
MH(2)=A(K,11)*0.70710678100
MH(3)=0.000
MH(4)=0.000
GO TO 578
C
577 MH(1)=A(K,11)*0.70710678100
MH(2)=A(K,13)*0.70710678100
MH(3)=0.000
MH(4)=0.000
C
578 A(K,K)=MH(1)+MH(3)-MH(2)-MH(4)
A(K,13)=MH(1)-MH(3)+MH(2)-MH(4)
A(K,11)=MH(1)+MH(3)-MH(2)+MH(4)
IF(K,EQ.KK.OR.III,EQ.13) GO TO 580
A(K,13)=MH(1)-MH(2)+MH(3)-MH(4)
A(K,11)=MH(1)+MH(2)-MH(3)-MH(4)
C MULTIPLY ON THE RIGHT BY T1.
C
580 DO 400 11=1,NNI
DO 400 K1=1,NPF
C(K1,1)=0.000
DO 590 J1=1,NNI
C(K1,J1)=C(K1,1)+A(K1,12)*T1(J1,12)
400 CONTINUE
C
590 CONTINUE
C MULTIPLY ON THE LEFT BY TF
C IF(BRANCH.EQ.Q.OR.JF-J1.EQ.-1) GO TO 530
C FOR R BRANCHES IN EMISSION AND P BRANCHES IN
C ABSORPTION MULTIPLY ON LEFT BY TF2.
C
580 DO 400 11=1,NNI
DO 400 K1=1,NPF
A(K1,1)=0.000
DO 610 J1=1,NPF
A(K1,J1)=A(K1,J1)*TF2(K1,12)*C(J1,12)
600 CONTINUE
GO TO 655
C FOR Q BRANCHES AND FOR P BRANCHES IN ABSORPTION
C AND R BRANCHES IN EMISSION MULTIPLY ON LEFT BY TF1.
C DO 650 II=1,NII
DO 650 K1=1,NFF
AK1,II=0.0D0
DO 640 I2=1,NFF
AK1,II=AK1,II+TF1(K1,II)*C(I2,II)
650 CONTINUE
C FOR ALLOWED TRANSITIONS LAMBDA DOUBLING WAS NOT INCLUDED. THEREFORE, THE
C MATRIX ELEMENTS FOR SIGMA-PI TRANSITIONS MUST BE MULTIPLIED BY THE SQUARE
C ROOT OF 2.
C FOR FORBIDDEN TRANSITIONS:
C IF ONLY THE INITIAL STATE IS A SIGMA STATE, THE RESULTS
C IN THE UPPER AND LOWER HALVES OF THE MATRIX MUST BE COMBINED.
C IF ONLY THE FINAL STATE IS A SIGMA STATE, THE RESULTS IN
C THE LEFT AND RIGHT HALVES OF THE MATRIX MUST BE COMBINED.
C IF NEITHER STATE IS A SIGMA STATE, THE RESULTS
C ARE EITHER IN THE UPPER-LEFT AND LOWER-RIGHT QUADRANTS, OR IN
C THE UPPER-RIGHT AND LOWER-LEFT QUADRANTS. THEREFORE, WE CAN ALWAYS GET
C ONE LAMBDA COMPONENT BY ADDING THE MATRIX ELEMENTS IN THE UPPER-LEFT
C AND LOWER-RIGHT QUADRANTS (ONE OF WHICH IS ZERO). THE OTHER LAMBDA
C COMPONENT CAN BE FOUND BY SIMPLY CHANGING THE SIGN OF ALL TERMS
C WHOSE TRANSITION MOMENT IS DESIGNATED WITH A MINUS SIGN IN THE
C FIRST LOCATION, IE (I-X,Y).
C IF(SIGSIG) GO TO 666
IF(.NOT.ALLOW) GO TO 662
IF(UAMI.GT..LDO.AND.LAMF.GT..1DO) GO TO 666
C Cl=1.41421356200
DO 660 K3=1,NF
DO 660 I3=1,NI
660 AK3,I3=Cl*AK3,I3
GO TO 666
C 662 IF(LAMF.LT..1.0D0) GO TO 666
DO 663 I3=1,NI
DO 663 K3=1,NF
K4=NII-I3-I4
663 AK3,I3=AK3,I3*AK4,I3
GO TO 666
C 664 DO 665 I3=1,NI
DO 665 K3=1,NF
K4=NII-I3-I4
665 AK3,I3=AK3,I3*AKK4,I4
C FOR STATES OTHER THAN SIGMA STATES, IF THE HAMILTONIAN
C IS NOT FULLY DEVELOPED (SMALL J VALUES) THEN THE ELEMENTS
C IN THE TRANSFORMED ROTATIONAL MATRIX ARE SHIFTED TO
C ENABLE PROPER LABELING DURING OUTPUT.
C NDELF=0
IF(LAMF.LT..1.0D0) GO TO 695
C DETERMINE COLUMN SHIFT.
C NDELF=I11-I
IF(I11.IEQ.0) GO TO 695
IF(I11.LE.0) GO TO 695
C SHIFT COLUMNS
DO 670 K1=1,NF
DO 670 I1=1,NI
I2=NII-I1-I2
670 AK1,I1=AK1,I1*AKK1,I2
C DO 680 I1=1,N1
680 CONTINUE
C CONTINUE
C NDELF=0
IF(LAMF.LT..1.0D0) GO TO 735
C DETERMINE ROW SHIFT.
C NDELF=I11-I
IF(I11.IEQ.0) GO TO 735
IF(I11.LE.0) GO TO 735
C SHIFT ROWS.
DO 710 K1=1,NF
DO 710 I1=1,NI
I2=NII-I1-I2
710 AK1,I1=AK1,I1*AKK1,I2
C DO 720 K1=1,N1
720 CONTINUE
C
CONTINUE

C STORE THE TRANSFORMED ROTATIONAL MATRIX ELEMENTS AND INITIALIZE THE A MATRIX FOR A NEW CALCULATION.

K4=NOELF*NF+1
I4=NDELI+NI*1
K5=IMAF-NDEL-NF
I5=1MAXI-NDEL-NI

C IS THIS AN ALLOWED TRANSITION?
IF (.NOT. ALLOW) GO TO 740

C THIS IS AN ALLOWED TRANSITION.
STORE THE SQUARE OF THE A MATRIX ELEMENTS.
C THESE ARE THE HONL-LONDON FACTORS FOR A SINGLE LAMBDA COMPONENT.
DO 755 1,11=1,NI
K6=I4-I1
DO 750 K1=1,NF
K7=(I5+I1-I2)*K6+K5*K1
K6=K6-K1
SAVE(I7,K7,IJ)=AI(K6,I6)*2
750 CONTINUE
DO 757 11=1,14
DO 757 Kl=1,14
757 AI(K1,111)=0.000
GO TO 810

C GO TO 810
C
C THIS IS A FORBIDDEN TRANSITION.
C RECORD THE NUMBER OF ELECTRONIC TRANSITION MOMENTS AND THEIR DESIGNATIONS.
NTRAN=NTRAN+1
IE=EI*.1
KE=EK*.1
K6=NTRAN*IK/5
ITRANI(K6,U)=IMAXI-I1
C IF(LAMF.LT..1I GO TO 780
IF(SIGN.LT.0.I GO TO 770
C ITRANF(K6,U)=IFAKF-1F2
GO TO 790
770 ITRANF(K6,U)=1-MAXF+IF1-1
GO TO 790
780 ITRANF(K6,U)=1-MAXF-KF
C
C IS THIS AN EMISSION CALCULATION?
C IF (.NOT. EMISON) GO TO 799
C
C THIS IS AN EMISSION CALCULATION. ADJUST DESIGNATION OF THE TRANSITION MOMENT TO CORRESPOND TO ABSORPTION.
K1=1
IF (.NOT. SIG) GO TO 794
IF(LAMF.LT..1I GO TO 792
IF(LAM.GT..1I GO TO 791
C IF(SIGN.LT.0.I K1=-1
GO TO 796
791 IF(SIGN.GT.0.I GO TO 796
C
C IF(SIGN.GT.0.I GO TO 796
C
C IF(SIGN.GT.0.I K1=-1
GO TO 796
791 IF(SIGN.GT.0.I GO TO 796
C
C I1=ITRANI(K6,U)
ITRANF(K6,U)=ITRANI(K6,U)
GO TO 799
C
C I1=ITRANF(K6,U)
ITRANF(K6,U)=1-MAXF+1-M11
GO TO 799
C
C IF(MEGAF.LT..1I GO TO 794
C 11=ITRANI(K6,U)
ITRANI(K6,U)=ITRANF(K6,U)
GO TO 799
C
C I1=ITRANF(K6,U)
ITRANF(K6,U)=1-MAXF+1-M11
GO TO 799
C
C IF(MEGAF.GT..1I GO TO 794
C 11=ITRANI(K6,U)
ITRANI(K6,U)=ITRANF(K6,U)
GO TO 799
C
C I1=ITRANI(K6,U)
ITRANF(K6,U)=1-MAXF+1-M11
GO TO 799
C
C IF(MEGAF.LT..1I GO TO 794
C 11=ITRANF(K6,U)
ITRANF(K6,U)=1-MAXF+1-M11
GO TO 799
C
C I1=ITRANI(K6,U)
ITRANI(K6,U)=ITRANF(K6,U)
GO TO 799
C
C I1=ITRANF(K6,U)
ITRANF(K6,U)=1-MAXF+1-M11
GO TO 799
C
C SAVE A MATRIX ELEMENTS.
C DO 800 11=1,NI
800
CO 800 K1=1,14
K7=15+11-13+16+5+1
F6=84-11
G6=16-11
SAVE(ENTRAN,K1J)+A(K6,16)
C GO 805 I1=1,14
G0 805 K1=1,14
805 A(K1J)+Q,0,0,0
C GO TO 510
C A SET OF BRANCHES HAS BEEN COMPUTED.
C STORE NUMBER OF ELECTRONIC TRANSITIONS MOMENTS
C IN COMPUTATION JUST FINISHED AND SET FLAGS.
C IN DI CIES, ETC APPROPRIATE FOR NEXT SET OF BRANCHES.
C 610 IF(BRANCH.NE.0) GO TO 820
C A SET OF 0 BRANCHES HAVE BEEN COMPUTED.
C NEXT STEP IS TO INCREASE J1 AND COMPUTE A NEW INITIAL STATE.
C NTRAN0(J1)+NTRAN
GO TO 890
C 820 IF(BRANCH.EQ.P) GO TO 830
C A SET OF P BRANCHES HAVE BEEN COMPUTED.
C IF(EMISSION) GO TO 840
840 K4=SAVE3
IF(.NOT.ALLOW.ANO.LAMF.GT.1> K4*2*SAVE3
CO 850 11=1,K4
DO 850 K1=1,K4
850 TF1(K1,I1I)+TF2(K1,I1I)
C WCULD NEXT VALUE OF J1 BE GREATER THAN JMAX?
C 890 IF(J1-JMAX-J1LT..9) GO TO 910
C END OF BIG DD LOOP
C 900 CONTINUE
C IJ+200
910 RETURN
END
SUBROUTINE EIGEN

PURPOSE
COMPUTE EIGENVALUES AND EIGENVECTORS OF A REAL SYMMETRIC MATRIX

USAGE

DESCRIPTION OF PARAMETERS
A - ORIGINAL MATRIX (SYMMETRIC), DESTROYED IN COMPUTATION.
RESULTANT EIGENVALUES ARE DEVELOPED IN DIAGONAL OF
MATRIX A IN DESCENDING ORDER.
R - RESULTANT MATRIX OF EIGENVECTORS (STORED COLUMNWISE,
IN SAME SEQUENCE AS EIGENVALUES)
N - ORDER OF MATRICES A AND R

REMARKS
ORIGINAL MATRIX A MUST BE REAL SYMMETRIC (STORAGE MODE=1)
MATRIX A CANNOT BE IN THE SAME LOCATION AS MATRIX R

SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
NONE

METHOD
DIAGONALIZATION METHOD ORIGINATED BY JACOBI AND ADAPTED
BY VON NEUMANN FOR LARGE COMPUTERS AS FOUND IN "MATHEMATICAL
METHODS FOR DIGITAL COMPUTERS", EDITED BY A. RALSTON AND
H.S. WILF, JOHN WILEY AND SONS, NEW YORK, 1962, CHAPTER 7

********************************************************************************

SUBROUTINE EIGEN
COMMON/CEIGEN/A(28),R(49),N

DOUBLE PRECISION A,R,ANORH,ANRMX,THR,X,Y,SINX,SINX2,COSX,
1 CQSX2,SINCS,RANGE

GENERATE IDENTITY MATRIX

5 RANGE=1.0D-12
10 IO=-N
GG 20 J=1,N
10 20 IO=IO+1
20 CONTINUE

COMPUTE INITIAL AND FINAL NORMS (ANORM AND ANORMX)

25 ANORM=0.0D0
35 GD 35 I=1,N
30 IF(I-J) 30,35,30
30 IA=I-J*(J*J-JI/2
ANGRH=ANORM*A(IA)*A(IA)
35 CONTINUE
40 ANORM=DSORT(2.000*ANORMX)ANORM/RANGE/FLOAT(N)

INITIALIZE INDICATORS AND COMPUTE THRESHOLD, THR

IND=0
45 THR=ANORM
50 L=1
55 M=L+1

COMPUTE SIN AND COS

60 MQ=MM-M/2
LO=LM-L/2
LM=LM+MQ
65 PH=ABS(A(LM)-THR) 130,65,65
65 IND=2
70 LL=L+LQ
MQ=MQ
X=0.5D0*(A(LM)-AMQ)
66 Y=-ALLM/DESBAL(MQ),A(LM)+X)
75 IF(I) 70,75,75
70 Y=-Y
75 SINK=SINK*Y
78 COSK=COSK+Y
SINCS=SINCS+COSK

ROTATE L AND M COLUMNS

IL=MM-M/2
M=M+1
DO 80 I=1,M
10 IQ=I-I/2
20 IF(I) 20,80,80
80 CONTINUE

END
65 IP=1:GO
66 GO TO 95
60 IM=H:GO
70 IF(E=1) 100,105,105
103 IL=H:GO
105 GO TO 110
110 X=A(LL)*COSX-A(MM)*SINX
A(LL)=A(LL)*COSX+A(MM)*COSX
A(MM)=A(LL)*COSX+A(MM)*SINX
GO TO 110
115 CONTINUE
X=2.000*A(LL)*SINX
V=A(LL)*COSX-A(MM)*SINX-
X=A(LL)*SINX-A(MM)*COSX
A(LL)=A(LL)*SINX-A(MM)*COSX
A(MM)=A(LL)*COSX+A(MM)*SINX
A(LL)*X

C TESTS FOR COMPLETION
C TEST FOR K = LAST COLUMN
130 IF(H-N-1) 135,140,135
135 H=M+1
GO TO 60
C TEST FOR L = SECOND FROM LAST COLUMN
140 IF(H-N-1) 145,150,145
145 L=L+1
GO TO 55
150 IF(N-1) 160,155,160
155 N=0
GO TO 50
C COMPARE THRESHOLD WITH FINAL NORM
160 IF(THR-ANRMX1) 165
C SORT EIGENVALUES AND EIGENVECTORS
165 IO=N
170 DO 185 J=1,N
175 LD=1
180 A(LL)=A(MM)
A(MM)=X
185 CONTINUE
RETURN
END
APPENDIX B

DETAILED FLOW CHARTS OF COMPUTER PROGRAM

PERTINENT BRANCHING SYMBOLS

3
OR

3

BRANCHING ON SAME PAGE

4
TO PAGE

BRANCHING BETWEEN PAGES

4
FROM PAGE
APPENDIX C

INTERACTION TERMS INCLUDED IN HAMILTONIAN MATRIX

In nonsigma states the spin-orbit interaction is of first order and is usually the dominant interaction. In sigma states the spin-orbit interaction is very small and, in fact, is on the same order as the spin-spin interactions. Therefore, nonsigma and sigma electronic states are discussed separately.

NONSIGMA ELECTRONIC STATES

The diagonal elements, $\hat{H}(i,i)$, of the Hamiltonian matrix in terms of the basis functions for nonsigma electronic states, are given by

$$\frac{\hat{H}(i,i)}{\hbar^2} = BJ(J + 1) - Br_i^2 + BS(S + 1) - BL_i^2 + AL_i \Sigma_i$$

where $A$ is the spin-orbit coupling constant. The result is the same for both lambda substates; therefore, for this discussion $A_i$ can be considered positive. Equation (C1) can be written

$$\frac{\hat{H}(i,i)}{\hbar^2} = J(J + 1) + S(S + 1) - (A + \Sigma_i)^2 - \Sigma_i^2 + Y\Lambda \Sigma_i$$

where $Y = A/B$, or as

$$\frac{\hat{H}(i,i)}{\hbar^2} = J(J + 1) + S(S + 1) - A^2 - 2\Sigma_i^2 + (Y - 2)\Lambda \Sigma_i$$

The criterion for regular or inverted electronic states is specified by the sign of $A$ or $Y$; that is, if $A \geq 0$, the state is regular, and if $A < 0$, the state is inverted.

SIGMA ELECTRONIC STATES

The spin-orbit interaction of sigma electronic states is of second order and $A = 0$. Therefore, the spin-orbit and spin-spin interactions are of the same order and both should be considered. Both of these interactions depend on the $|\Sigma|$, and their combined effect is included in the following analysis.

The diagonal elements of the Hamiltonian matrix in terms of the basis functions for sigma electronic states can be written

$$\frac{\hat{H}(i,i)}{\hbar^2} = J(J + 1) + S(S + 1) - 2\Sigma_i^2 + \frac{\Delta E_i}{B}$$

(C4)
where $\Delta E_i^z$ is the separation of the spin substates for $N = 0$ caused by spin-spin and second-order spin-orbit interactions. Figure 14 illustrates this separation and indicates the degeneracy of the rotational levels with the same value of $N$ and $|\Sigma|$. The number of energy separations is obviously related to the spin multiplicity. There are, for example, zero energy separations for singlet and doublet states, one for triplet and quartet states, two for quartet and sextet states, etc.

The values of $\Delta E_i^z$ in equation (C4) are found by extrapolating the energy separations shown in Figure 14, to $N = 0$. The reference level for $\Delta E_i^z$ is usually chosen to be the matrix element(s) with the lowest value of $|\Sigma|$.

Whether a sigma electronic state is a regular or an inverted state is determined by the sign of $\Delta E$. If $\Delta E \geq 0$, the state is regular, and if $\Delta E < 0$, the state is inverted.
REFERENCES


TABLE 1.—ROTATIONAL MATRIX ELEMENTS

The nonvanishing matrix elements $<\Omega'|J'|\alpha|\Omega J>$, where $\alpha = f (J',J)g(J',\Omega';J,\Omega)$. The factors for a given matrix element are taken from different rows of the same column of this table. The choice of columns depends on the value of $J'-J$. In all cases, the first factor is taken from row one and the second factor from row two or three.

<table>
<thead>
<tr>
<th>Factor</th>
<th>R Branch $J' = J+1$</th>
<th>Q Branch $J' = J$</th>
<th>P Branch $J' = J-1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f(J', J)$</td>
<td>$[4J(J+1)]^{-1/2}$</td>
<td>$[4J(J+1)/(2J+1)]^{-1/2}$</td>
<td>$[4J]^{-1/2}$</td>
</tr>
<tr>
<td>$g(J', \Omega; J, \Omega)$</td>
<td>$2[(J+\Omega+1)(J-\Omega+1)]^{1/2}$</td>
<td>$2\Omega$</td>
<td>$2[(J+\Omega)(J-\Omega)]^{1/2}$</td>
</tr>
<tr>
<td>$g(J', \Omega \pm 1; J, \Omega)$</td>
<td>$\pm[2(J \pm \Omega+1)(J \pm \Omega+2)]^{1/2}$</td>
<td>$\pm[2(J \pm \Omega)(J \pm \Omega-1)]^{1/2}$</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2.—$<R_\alpha>$ BASIS MATRIX FOR A SPIN-FORBIDDEN $^2\Pi \leftrightarrow ^4\Sigma^+$ TRANSITION

TABLE 3.—$<R_\alpha>$ P-BRANCH BASIS MATRIX FOR A SPIN-FORBIDDEN $^2\Pi \leftrightarrow ^4\Sigma^+$ TRANSITION
TABLE 4.—SIMPLIFIED FLOW CHART OF COMPUTER PROGRAM

Input:
(1) Initial state parameters
(2) Final state parameters
(3) $J_{\text{min}}$ and $J_{\text{max}}$
(4) Emission or absorption

Hamiltonian matrix:
(1) Set up
(2) Symmetrize
(3) Diagonalize
(4) Save transformation matrices

Rotational matrix:
(1) Set up
(2) Symmetrize
(3) Transform

Forbidden transitions
Allowed transitions

Store transformed rotational matrix elements and code for transition moments.
Square transformed rotational matrix elements to get H"{o}nl-London factors.

Test if all transition moments have been included.
Store H"{o}nl-London factors.

Yes

No

$J = J + 1$
$J \neq J_{\text{max}}$

Test if $J$ is equal to $J_{\text{max}}$.

Output:
H"{o}nl-London factors or intensity factors.

Output: H"{o}nl-London factors or intensity factors.
TABLE 5.— A DIAGRAMMATIC REPRESENTATION OF THE ELECTRONIC-ROTATIONAL HAMILTONIAN FOR A $^2\Pi$ ELECTRONIC STATE IN TERMS OF BASIS FUNCTIONS $<\Lambda \Sigma \Omega |<\Omega J>$

\[
\begin{array}{c|cc}
<\Lambda \Sigma \Omega |<\Omega J> & M_{11} & M_{12} \\
\hline
<\frac{1}{2} \frac{3}{2} K = \frac{3}{2} J & M_{11} & M_{12} \\
<\frac{1}{2} \frac{3}{2} K = \frac{1}{2} J & M_{12} & M_{22} \\
<\frac{1}{2} \frac{3}{2} K = \frac{3}{2} J & M_{22} & M_{12} \\
<\frac{1}{2} \frac{1}{2} K = \frac{3}{2} J & M_{12} & M_{11} \\
\end{array}
\]

TABLE 6.— $<\xi | a> \text{ BASIS MATRIX FOR THE Q-BRANCHES OF A } ^2\Pi \leftrightarrow ^4\Pi \text{ TRANSITION}$

\[
\begin{array}{cccccccc}
& ^4\Pi & & ^2\Pi & & ^4\Pi & & ^2\Pi & \\
\hline
\langle \xi \Sigma \Omega |<\Omega J> & \langle \xi \Sigma \Omega |<\Omega J> & \langle \xi \Sigma \Omega |<\Omega J> & \langle \xi \Sigma \Omega |<\Omega J> & \langle \xi \Sigma \Omega |<\Omega J> & \langle \xi \Sigma \Omega |<\Omega J> & \langle \xi \Sigma \Omega |<\Omega J> & \langle \xi \Sigma \Omega |<\Omega J> \\
\hline
\langle \frac{1}{2} \frac{3}{2} K = \frac{3}{2} J \rangle & R_{e}(2,4) & \times & a(2,4) & R_{e}(2,3) & \times & a(2,3) & R_{e}(-2,2) & \times & a(-2,2) \\
\langle \frac{1}{2} \frac{3}{2} K = \frac{1}{2} J \rangle & R_{e}(1,2) & \times & a(1,2) & R_{e}(1,3) & \times & a(1,3) & R_{e}(-1,2) & \times & a(-1,2) \\
\langle \frac{1}{2} \frac{3}{2} K = \frac{3}{2} J \rangle & R_{e}(1,2) & \times & a(1,2) & R_{e}(1,3) & \times & a(1,3) & R_{e}(-1,2) & \times & a(-1,2) \\
\langle \frac{1}{2} \frac{1}{2} K = \frac{3}{2} J \rangle & R_{e}(2,3) & \times & a(2,3) & R_{e}(2,2) & \times & a(2,2) & R_{e}(2,3) & \times & a(2,3) \\
\langle \frac{1}{2} \frac{1}{2} K = \frac{1}{2} J \rangle & R_{e}(1,2) & \times & a(1,2) & R_{e}(1,3) & \times & a(1,3) & R_{e}(-1,2) & \times & a(-1,2) \\
\langle \frac{1}{2} \frac{1}{2} K = \frac{3}{2} J \rangle & R_{e}(2,4) & \times & a(2,4) & R_{e}(2,3) & \times & a(2,3) & R_{e}(2,2) & \times & a(2,2) \\
\end{array}
\]
TABLE 7.—<Formula> Basis Matrix for the P-Branches of a $^4\Sigma^+ \leftrightarrow ^4\Sigma^-$ Transition

<table>
<thead>
<tr>
<th>Transition</th>
<th>Matrix Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4\Sigma^+$</td>
<td>$^4\Sigma^-$</td>
</tr>
<tr>
<td>$^4\Sigma^+$</td>
<td>$^4\Sigma^-$</td>
</tr>
</tbody>
</table>

TABLE 8.— Description of Input Cards for Program

<table>
<thead>
<tr>
<th>Card number</th>
<th>Columns</th>
<th>Format</th>
<th>Content</th>
<th>Number of cards per case</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-3</td>
<td>F3.1</td>
<td>Spin</td>
<td>2</td>
<td>The first card contains the information for the initial state and the second card contains the information for the final state.</td>
</tr>
<tr>
<td></td>
<td>6-10</td>
<td>F2.0</td>
<td>+ or -</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>A</td>
<td>i.e., symbol for $\Sigma$ states</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11-20</td>
<td>E10.O</td>
<td>Y for nonsigma states, $\Delta \varepsilon (1)/B$ for $\Sigma$ states, $\Delta \varepsilon (2)/B$ for $\Sigma$ states</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>21-30</td>
<td>E10.O</td>
<td>$\Delta \varepsilon (3)/B$ for $\Sigma$ states</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>31-40</td>
<td>E10.O</td>
<td>*as needed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1-5</td>
<td>F5.1</td>
<td>$J_{min}$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6-10</td>
<td>F5.1</td>
<td>$J_{max}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>A</td>
<td>A for absorption. Anything for emission.</td>
<td>1</td>
<td>It is recommended that ABSORPTION or EMISSION always be used.</td>
</tr>
</tbody>
</table>

53
### Table 9: Computer Printout for Sample Case 1

<table>
<thead>
<tr>
<th>J</th>
<th>ΔE (0)</th>
<th>ΣR1</th>
<th>ΣQ12</th>
<th>ΣP13</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1.0</td>
<td>4.999999</td>
<td>9.3228E-01</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>5.0</td>
<td>9.8224E-01</td>
<td>9.7008E-02</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>10.0</td>
<td>13.9999E-01</td>
<td>1.7064E-02</td>
<td>3.1138E-01</td>
<td>2.6851E-01</td>
</tr>
<tr>
<td>20.0</td>
<td>17.9999E-01</td>
<td>2.0573E-02</td>
<td>6.9373E-01</td>
<td>5.2858E-01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>J</th>
<th>ΔE (1)</th>
<th>ΣR21</th>
<th>ΣR22</th>
<th>ΣP1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1.0</td>
<td>5.999999</td>
<td>4.7823E-02</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>2.0</td>
<td>9.999999</td>
<td>1.8246E-02</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>20.0</td>
<td>13.9999E-01</td>
<td>2.0475E-02</td>
<td>1.0651E+00</td>
<td>7.7976E-01</td>
</tr>
<tr>
<td>40.0</td>
<td>17.9999E-01</td>
<td>4.4705E-02</td>
<td>1.7811E+00</td>
<td>7.4205E-01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>J</th>
<th>ΔE (2)</th>
<th>ΣQ1</th>
<th>ΣQ12</th>
<th>ΣQ13</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1.0</td>
<td>5.999999</td>
<td>1.4489E+00</td>
<td>1.2163E+00</td>
<td>0.00000</td>
</tr>
<tr>
<td>2.0</td>
<td>9.999999</td>
<td>2.2163E+00</td>
<td>5.3052E+00</td>
<td>1.6227E+00</td>
</tr>
<tr>
<td>4.0</td>
<td>17.9999E-01</td>
<td>3.0829E+00</td>
<td>1.7063E+00</td>
<td>2.9777E+00</td>
</tr>
<tr>
<td>40.0</td>
<td>17.9999E-01</td>
<td>3.8423E+00</td>
<td>1.9569E+00</td>
<td>2.8466E+00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>J</th>
<th>ΔE (3)</th>
<th>ΣQ2</th>
<th>ΣQ21</th>
<th>ΣQ23</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1.0</td>
<td>5.999999</td>
<td>2.4464E+00</td>
<td>2.4464E+00</td>
<td>0.00000</td>
</tr>
<tr>
<td>2.0</td>
<td>9.999999</td>
<td>6.0636E+00</td>
<td>6.0636E+00</td>
<td>0.00000</td>
</tr>
<tr>
<td>4.0</td>
<td>17.9999E-01</td>
<td>3.0829E+00</td>
<td>1.7063E+00</td>
<td>2.9777E+00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>J</th>
<th>ΔE (4)</th>
<th>ΣP1</th>
<th>ΣP12</th>
<th>ΣP13</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1.0</td>
<td>5.999999</td>
<td>4.9430E-01</td>
<td>4.9430E-01</td>
<td>0.00000</td>
</tr>
<tr>
<td>2.0</td>
<td>9.999999</td>
<td>7.2777E-01</td>
<td>7.2777E-01</td>
<td>0.00000</td>
</tr>
<tr>
<td>4.0</td>
<td>17.9999E-01</td>
<td>1.7066E-01</td>
<td>1.7066E-01</td>
<td>0.00000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>J</th>
<th>ΔE (5)</th>
<th>ΣP2</th>
<th>ΣP21</th>
<th>ΣP23</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1.0</td>
<td>5.999999</td>
<td>6.9613E-01</td>
<td>6.9613E-01</td>
<td>0.00000</td>
</tr>
<tr>
<td>2.0</td>
<td>9.999999</td>
<td>1.2163E+00</td>
<td>1.2163E+00</td>
<td>0.00000</td>
</tr>
<tr>
<td>4.0</td>
<td>17.9999E-01</td>
<td>1.7066E-01</td>
<td>1.7066E-01</td>
<td>0.00000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>J</th>
<th>ΔE (6)</th>
<th>ΣP3</th>
<th>ΣP31</th>
<th>ΣP32</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>1.0</td>
<td>5.999999</td>
<td>9.3228E-01</td>
<td>9.3228E-01</td>
<td>0.00000</td>
</tr>
<tr>
<td>2.0</td>
<td>9.999999</td>
<td>1.7064E-02</td>
<td>1.7064E-02</td>
<td>0.00000</td>
</tr>
<tr>
<td>4.0</td>
<td>17.9999E-01</td>
<td>2.0573E-02</td>
<td>2.0573E-02</td>
<td>0.00000</td>
</tr>
</tbody>
</table>
### TABLE 10.—PARTIAL PRINTOUT FOR SAMPLE CASE 2

**REGULAR QUINTET SIGMA TO INVERTED TRIPLET PI TRANSITION**

**INITIAL STATE ENERGY SEPARATION** = \( \Delta E(1/2) = 5.009 \)

**FINAL STATE SPIN-ORBIT COUPLING CONSTANT** = \( a = 6 \)

**J VALUE FOR THE INITIAL (IE. LOWER) STATE**

<table>
<thead>
<tr>
<th>J</th>
<th>PARTIAL SUM</th>
<th>TRANSITION MOMENT</th>
<th>SIG1</th>
<th>SIG2</th>
<th>URT1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>-2.2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>-1.3</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0</td>
<td>0.000000</td>
<td>-1.0</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0</td>
<td>0.000000</td>
<td>-1.2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0</td>
<td>0.000000</td>
<td>-1.2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0</td>
<td>0.000000</td>
<td>-1.5</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>2.0</td>
<td>0.177959</td>
<td>-3.1</td>
<td>-3.422FE-01</td>
<td>-2.8762E-01</td>
<td>-1.6754FE-01</td>
</tr>
<tr>
<td>2.0</td>
<td>0.278747</td>
<td>-3.1</td>
<td>-5.2476E-01</td>
<td>-5.7985E-01</td>
<td>-3.7102FE-01</td>
</tr>
<tr>
<td>2.0</td>
<td>0.069387</td>
<td>-2.1</td>
<td>-1.022PE-01</td>
<td>-2.6932E-01</td>
<td>-3.2835E-02</td>
</tr>
<tr>
<td>2.0</td>
<td>1.691508</td>
<td>-2.2</td>
<td>-1.2304E+00</td>
<td>-1.6398E+00</td>
<td>-1.8423E+00</td>
</tr>
<tr>
<td>3.0</td>
<td>0.000000</td>
<td>-1.0</td>
<td>-1.0332E+00</td>
<td>-1.0422E+00</td>
<td>-1.0537E+00</td>
</tr>
<tr>
<td>3.0</td>
<td>0.000000</td>
<td>-1.0</td>
<td>-1.0332E+00</td>
<td>-1.0422E+00</td>
<td>-1.0537E+00</td>
</tr>
<tr>
<td>3.0</td>
<td>0.000000</td>
<td>-1.5</td>
<td>-1.0332E+00</td>
<td>-1.0422E+00</td>
<td>-1.0537E+00</td>
</tr>
<tr>
<td>4.0</td>
<td>0.000000</td>
<td>-2.2</td>
<td>-1.2612E+00</td>
<td>-1.4394E+00</td>
<td>-1.5184E+00</td>
</tr>
<tr>
<td>4.0</td>
<td>0.000000</td>
<td>-2.2</td>
<td>-1.2612E+00</td>
<td>-1.4394E+00</td>
<td>-1.5184E+00</td>
</tr>
<tr>
<td>4.0</td>
<td>0.000000</td>
<td>-2.2</td>
<td>-1.2612E+00</td>
<td>-1.4394E+00</td>
<td>-1.5184E+00</td>
</tr>
</tbody>
</table>

**FINAL STATE SPIN-ORBIT COUPLING CONSTANT** = \( a = 6 \)

**J VALUE FOR THE INITIAL (IE. LOWER) STATE**

<table>
<thead>
<tr>
<th>J</th>
<th>PARTIAL SUM</th>
<th>TRANSITION MOMENT</th>
<th>SIG1</th>
<th>SIG2</th>
<th>URT1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>-2.3</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>-1.3</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0</td>
<td>0.000000</td>
<td>-2.7</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0</td>
<td>0.000000</td>
<td>-1.2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0</td>
<td>0.000000</td>
<td>-1.2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1.0</td>
<td>0.000000</td>
<td>-1.5</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>2.0</td>
<td>0.177959</td>
<td>-3.1</td>
<td>-1.422PF-01</td>
<td>-2.8762E-01</td>
<td>-1.6754FE-01</td>
</tr>
<tr>
<td>2.0</td>
<td>0.278747</td>
<td>-3.1</td>
<td>-5.2476E-01</td>
<td>-5.7985E-01</td>
<td>-3.7102FE-01</td>
</tr>
<tr>
<td>2.0</td>
<td>0.069387</td>
<td>-2.1</td>
<td>-1.022PE-01</td>
<td>-2.6932E-01</td>
<td>-3.2835E-02</td>
</tr>
<tr>
<td>2.0</td>
<td>1.691508</td>
<td>-2.2</td>
<td>-1.2304E+00</td>
<td>-1.6398E+00</td>
<td>-1.8423E+00</td>
</tr>
<tr>
<td>3.0</td>
<td>0.000000</td>
<td>-1.0</td>
<td>-1.0332E+00</td>
<td>-1.0422E+00</td>
<td>-1.0537E+00</td>
</tr>
<tr>
<td>3.0</td>
<td>0.000000</td>
<td>-1.0</td>
<td>-1.0332E+00</td>
<td>-1.0422E+00</td>
<td>-1.0537E+00</td>
</tr>
<tr>
<td>3.0</td>
<td>0.000000</td>
<td>-1.5</td>
<td>-1.0332E+00</td>
<td>-1.0422E+00</td>
<td>-1.0537E+00</td>
</tr>
<tr>
<td>4.0</td>
<td>0.000000</td>
<td>-2.2</td>
<td>-1.2612E+00</td>
<td>-1.4394E+00</td>
<td>-1.5184E+00</td>
</tr>
<tr>
<td>4.0</td>
<td>0.000000</td>
<td>-2.2</td>
<td>-1.2612E+00</td>
<td>-1.4394E+00</td>
<td>-1.5184E+00</td>
</tr>
<tr>
<td>4.0</td>
<td>0.000000</td>
<td>-2.2</td>
<td>-1.2612E+00</td>
<td>-1.4394E+00</td>
<td>-1.5184E+00</td>
</tr>
<tr>
<td>J</td>
<td>PARTIAL SUM</td>
<td>TRANSITION MOMENT</td>
<td>SRI</td>
<td>TR2</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------------</td>
<td>-------------------</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>-2.1</td>
<td>-1.22607E-00</td>
<td>-7.06716E-01</td>
<td>0.6947E-01</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1.231859</td>
<td>-1.1</td>
<td>-5.77031E-01</td>
<td>5.97447E-01</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.665929</td>
<td>1.1</td>
<td>-4.06027E-01</td>
<td>7.06714E-01</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.00077</td>
<td>-1.2</td>
<td>-1.35756E-02</td>
<td>2.15137E-02</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.0017</td>
<td>1.2</td>
<td>-1.35756E-02</td>
<td>2.15137E-02</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.002712</td>
<td>2.2</td>
<td>-4.07692E-02</td>
<td>-2.39137E-02</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>2.389426</td>
<td>-1.1</td>
<td>-8.29256E-00</td>
<td>1.26212E-00</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.94714</td>
<td>1.1</td>
<td>-6.31061E-01</td>
<td>8.92455E-01</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.00528</td>
<td>-1.2</td>
<td>-4.19504E-02</td>
<td>5.32686E-02</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.01059</td>
<td>1.2</td>
<td>5.32686E-02</td>
<td>-8.19027E-02</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.01059</td>
<td>2.2</td>
<td>-8.39008E-02</td>
<td>-5.53264E-02</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.0000</td>
<td>1.3</td>
<td>8.39008E-02</td>
<td>-5.53264E-02</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.00008</td>
<td>2.3</td>
<td>2.26672E-03</td>
<td>1.67616E-03</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>7.82901E-01</td>
<td>-1.1</td>
<td>-1.32971E00</td>
<td>-1.02999E00</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>3.18442</td>
<td>-1.1</td>
<td>-1.17910E00</td>
<td>1.45463E00</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>1.66741</td>
<td>1.1</td>
<td>-7.87822E-01</td>
<td>1.02999E00</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.01625</td>
<td>-1.2</td>
<td>-7.04256E-02</td>
<td>1.92931E-02</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.03364</td>
<td>1.2</td>
<td>-1.12316E01</td>
<td>-1.45001E01</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.00884</td>
<td>2.2</td>
<td>-1.13238E01</td>
<td>-1.45001E01</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.00007</td>
<td>1.3</td>
<td>3.16376E-04</td>
<td>-4.08437E-04</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.00009</td>
<td>2.7</td>
<td>7.45700E-05</td>
<td>5.77617E-05</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.00000</td>
<td>2.4</td>
<td>6.31961E-05</td>
<td>4.89515E-05</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>3.27555</td>
<td>-2.1</td>
<td>-1.40190E00</td>
<td>-1.14465E00</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>4.36760</td>
<td>-1.1</td>
<td>-1.32173E00</td>
<td>1.51878E00</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>2.18304</td>
<td>1.1</td>
<td>-8.36606E-01</td>
<td>1.14465E00</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>0.03828</td>
<td>-1.2</td>
<td>-1.23575E01</td>
<td>1.45001E01</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>0.07668</td>
<td>1.2</td>
<td>1.75108E-01</td>
<td>-7.04256E-02</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>0.05747</td>
<td>2.2</td>
<td>-1.65659E-01</td>
<td>-1.45001E01</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>0.000136</td>
<td>1.3</td>
<td>7.97605E-05</td>
<td>-4.08437E-05</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>0.00009</td>
<td>2.3</td>
<td>1.56470E-02</td>
<td>1.77977E-02</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>0.00000</td>
<td>2.4</td>
<td>6.64475E-04</td>
<td>2.15947E-04</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>3.71602</td>
<td>-2.1</td>
<td>-1.47730E00</td>
<td>-1.24432E00</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>5.38684</td>
<td>-1.1</td>
<td>-1.49725E00</td>
<td>1.75974E00</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>2.64203</td>
<td>1.1</td>
<td>-1.05135E00</td>
<td>1.74432E00</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>0.07280</td>
<td>-1.2</td>
<td>-1.73547E01</td>
<td>2.05344E01</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>0.14477</td>
<td>1.2</td>
<td>2.45437E-01</td>
<td>-2.05344E01</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>0.10199</td>
<td>2.2</td>
<td>-2.42966E-02</td>
<td>-2.05344E01</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>0.00054</td>
<td>1.3</td>
<td>1.37463E-02</td>
<td>-1.62859E-02</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>0.00170</td>
<td>2.3</td>
<td>2.70714E-02</td>
<td>2.15947E-02</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>0.00001</td>
<td>2.4</td>
<td>6.87642E-04</td>
<td>5.81164E-04</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1.— Typical energy level diagram of a $^3\Pi \rightarrow ^3\Sigma$ electronic transition.

(a) Hund’s case (a) coupling

$\Delta S = 0$

$\Delta \Sigma = 0$

$\Delta \Delta = 0, \pm 1$

$\Delta J = 0, \pm 1$

(b) Hund’s case (b) coupling

$\Delta S = 0$

$\Delta N = 0, \pm 1$

$\Delta \Delta = 0, \pm 1$

$\Delta J = 0, \pm 1$

(c) Hund’s case (c) coupling

$\Delta \Omega = 0, \pm 1$

$\Delta J = 0, \pm 1$

Figure 2.— Vector coupling diagrams and selection rules for Hund’s cases (a), (b), and (c).
Figure 3.— Unitary transformations that transform the Hamiltonian matrix from basis functions to symmetrized basis functions for $^3\Sigma$ and $^4\Sigma$ electronic states.

\[
\begin{pmatrix}
\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\
0 & 1 & 0 \\
\frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\
\end{pmatrix}
\] (a) $^3\Sigma$

\[
\begin{pmatrix}
\frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} \\
0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\
0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\
\frac{1}{\sqrt{2}} & 0 & 0 & -\frac{1}{\sqrt{2}} \\
\end{pmatrix}
\] (b) $^4\Sigma$

Figure 4.— Designation of the rotational levels for a $^4\Sigma$ electronic state.

\[
\begin{align*}
F_I &= F_1 F_2 F_3 F_4 \\
\Omega &= -\frac{1}{2} \quad \frac{1}{2} \quad \frac{3}{2} \quad \frac{5}{2} \\
N = 6 & \quad J = \frac{15}{2} \quad \frac{13}{2} \quad \frac{11}{2} \quad \frac{9}{2} \\
5 & \quad \frac{13}{2} \quad \frac{11}{2} \quad \frac{9}{2} \quad \frac{7}{2} \\
4 & \quad \frac{11}{2} \quad \frac{9}{2} \quad \frac{7}{2} \quad \frac{5}{2} \\
3 & \quad \frac{9}{2} \quad \frac{7}{2} \quad \frac{5}{2} \\
2 & \quad \frac{7}{2} \quad \frac{5}{2} \quad \frac{3}{2} \\
1 & \quad \frac{5}{2} \quad \frac{3}{2} \quad \frac{1}{2} \\
\frac{1}{2}
\end{align*}
\]

(a) Regular electronic state  (b) Inverted electronic state

Figure 5.— Designation of the rotational levels for a $^3\Sigma$ electronic state.

\[
\begin{align*}
F_1 & \quad F_2 & \quad F_3 \\
N = 4 & \quad J = \frac{5}{2} & \quad \frac{4}{2} & \quad \frac{3}{2} \\
3 & \quad \frac{4}{2} & \quad \frac{3}{2} & \quad \frac{2}{2} \\
2 & \quad \frac{3}{2} & \quad \frac{2}{2} & \quad \frac{1}{2} \\
1 & \quad \frac{2}{2} & \quad \frac{1}{2} & \quad \frac{0}{2} \\
0 & \quad \frac{1}{2} & \quad \frac{0}{2}
\end{align*}
\]
Figure 6.— Letter designations for changes in \( N \) and \( J \) during a transition.

\[
\begin{align*}
\text{Letter} \Rightarrow & \quad \ldots \quad \text{N} \quad \text{O} \quad \text{P} \quad \text{Q} \quad \text{R} \quad \text{S} \quad \text{T} \quad \ldots \\
\Delta N \Rightarrow & \quad \ldots \quad -3 \quad -2 \quad -1 \quad 0 \quad 1 \quad 2 \quad 3 \quad \ldots \\
\end{align*}
\]

\[\Delta J\]

Figure 7.— Illustration of branch designation.

Figure 8.— Branch designation scheme for spin-allowed \( ^4 \Pi \leftrightarrow ^4 \Sigma \) transitions.
Figure 9.— Branch designation scheme for spin-forbidden $^2\Pi \leftrightarrow ^4\Pi$ transitions.

(a) P-Branches
$\Delta J = -1$

(b) Q-Branches
$\Delta J = 0$

(c) R-Branches
$\Delta J = +1$

Figure 10.— Possible nonzero matrix elements in the transformed rotational matrix of a $^3\Sigma \rightarrow ^3\chi$ transition; $\chi$ any nonsigma electronic state.
Figure 11.— Possible nonzero matrix elements in the transformed matrix of a $^3X \to ^3Y$ transition; X and Y any nonsigma electronic states.

(a) + A Hamiltonian submatrix for the J=1 rotational levels of a $^7\Pi$ electronic state

(b) Designation of the rotational levels for a regular electronic state.

(c) Designation of the rotational levels for an inverted electronic state.

Figure 12.— Shifting of the J = 1 matrix elements of a $^7\Pi$ electronic state so that the position of the elements in the matrix correspond to the designations for the fully developed matrix.
Figure 13.— Sketch of the SAVE (9, 150, 200) array.

(a) $3\Sigma$ (regular)  
(b) $4\Sigma$ (inverted)  
(c) $5\Sigma$ (regular)

Figure 14.— Illustration of spin splitting in sigma electronic states.
"The aeronautical and space activities of the United States shall be conducted so as to contribute ... to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—National Aeronautics and Space Act of 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons. Also includes conference proceedings with either limited or unlimited distribution.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include final reports of major projects, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546