COMPUTER PROGRAM FOR DETERMINING ROTATIONAL LINE INTENSITY FACTORS FOR DIATOMIC MOLECULES

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SUMMARY

A Fortran IV computer program, that provides a new research tool for determining reliable rotational line intensity factors (also known as Hönl-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 Hönl-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. Hönl 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.

\[ \Delta \Sigma = 0, \Delta \Lambda = 0, \pm 1, \text{ and } \Sigma^+ \leftrightarrow \Sigma^- \text{. For spin-allowed transitions } \Delta \Omega = 0, \pm 1 \text{ and at least one of the spin-allowed conditions is violated.} \]
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.

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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 $\Lambda$-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 Λ-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

\[
E_{J', J''} = N_{J'} h \nu_{J', J''} A_{J', J''}
\]

where

- \(E_{J', J''}\) the emitted power/unit volume, W m\(^{-3}\)
- \(N_{J'}\) the population density of the \(J'\) rotational level, m\(^{-3}\)
- \(h \nu_{J', J''}\) 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, $\vec{P}$; that is,

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

(2)

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

(3)

where

$\psi_{UM'}$ the wave function of the upper Zeeman state $M'$

$\psi_{LM''}$ the wave function of the lower Zeeman state $M''$

$\vec{P}$ 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

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

(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

$$\langle S_{J',J''} \rangle = q_{J',J''} \langle \psi_{U} | R \alpha | \psi_{L} \rangle^2$$

(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 $J''$

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

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 $\vec{P}$ 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 $<R_e \alpha>$ 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 $<R_e \alpha>$ matrix is expressed in terms of the basis functions; and finally the $<R_e \alpha>$ basis matrix is transformed to the wave functions.

The transformation from the $<R_e \alpha>$ basis matrix to the $<\phi \alpha>$ 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,

$$<\psi_U | R_e \alpha | \psi_L> = T_{U}^{-1} <\phi_U | R_e \alpha | \phi_L> T_{L}$$

(6)

where

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

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 $\langle R_e \alpha \rangle$ basis matrix for a spin-forbidden $^2\Pi \leftrightarrow ^4\Sigma^+$ 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:

$$\Sigma^+ \leftrightarrow \Sigma^+$$ transitions with $\Delta S = 0, 2, \text{etc.}$

$$\Sigma^+ \leftrightarrow \Sigma^+$$ transitions with $\Delta S = 1, 3, \text{etc.}$

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

\[
\langle S_{J', J''} \rangle = q_{V' V''} R_e^2 |T^{-1}_U \langle \phi_U | \alpha | \phi_L \rangle T_L|^2
\]

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

\[
\langle J' J'' \rangle = |T^{-1}_U \langle \phi_U | \alpha | \phi_L \rangle T_L|^2
\]

\[
= | \langle \psi_U | \alpha | \psi_L \rangle |^2
\]

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

\[
\langle \psi_U | R_e \alpha | \psi_L \rangle = \langle R_e | \bar{\alpha}_1 + R_e | \bar{\alpha}_2 + \cdots \rangle
\]

where \( \bar{\alpha}_i \) is the transformed rotational matrix element associated with \( R_e | \).

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 \( R_e | \)) 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,

\[
\langle S_{J', J''} \rangle = q_{V' V''} R_e^2 | \langle \rho \bar{\alpha}_i + \sigma \bar{\alpha}_j + \tau \bar{\alpha}_k + \cdots \rangle |^2
\]
where
\[ \rho = \frac{R_{e_i}}{R_{e_j}}, \quad \sigma = \frac{R_{e_j}}{R_{e_k}}, \quad \tau = \frac{R_{e_k}}{R_{e_l}}, \quad \text{etc.} \]

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
\[ \left< \mathbf{J}, J'' \right> = \left| \sum \rho \alpha_i + \sigma \alpha_j + \tau \alpha_k + \cdots \right|^2 \tag{13} \]

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,
\[ \left< S_{J', J''} \right> = q_{v', v''} R_{e_i}^2 \left< \mathbf{J}, J'' \right> \tag{14} \]

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

1. Spin-allowed transition
\[ \Sigma \left< \mathbf{J}, J'' \right>(J) = (2 - \delta_{0, (A' + A'')})(2S + 1)(2J + 1) \tag{15} \]

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

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

where \( C = 1 \) if the transition moment occurs only once in the \( \left< R_{e\alpha} \right> \) basis matrix and \( C = 2 \) if the transition moment occurs twice in the \( \left< R_{e\alpha} \right> \) basis matrix. The only transition moments that occur only once in any \( \left< R_{e\alpha} \right> \) 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:

$$
|+\Lambda S +S \rangle |+\Lambda S +S-1 \rangle |+\Lambda S-1 J \rangle, \ldots, |+\Lambda S -S \rangle |\Lambda -S J \rangle,$$

$$|\Lambda -S +S \rangle |\Lambda +S J \rangle, |\Lambda -S +S-1 \rangle |\Lambda +S-1 J \rangle, \ldots, |\Lambda -S -S \rangle |\Lambda -S J \rangle$$

### 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 $(2 - \delta_{\Lambda,0})(2S + 1)$ 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 5. 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, $\Lambda \Sigma$, 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 $\Lambda$ (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 $\hbar^2$.

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

$$H(K,K) = -\Omega^2 - \Sigma^2 + \Lambda \Sigma$$

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

$$H(K+1,K) = H(K,K+1)$$

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2. Sigma states

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

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

where \( \eta = A/B \), 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 \( T_{\text{diag}} \) 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:

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

or

\[
\begin{align*}
N &\Rightarrow J - S \\
N &\Rightarrow J - S + 1 \\
&\vdots \\
N &\Rightarrow J + S
\end{align*}
\]

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 \( \tilde{\Omega} \), where \( \Omega = \Lambda + \Sigma \), to the \( F_\ell \) levels depends on whether the electronic state is regular or inverted. In regular states the smallest value of \( \tilde{\Omega} \) 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 $F$ 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 $F$ 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, $F_1$, 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 $N$, $F$ substate, 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 $F_L$ 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 $F'_L = F''_L$, only one subscript number is included (i.e., $R_{22} = R_2$ 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 $R_{32}$ 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 $^4\Pi \leftrightarrow ^4\Sigma$ transition and in figure 9 for a spin-forbidden $^2\Pi \leftrightarrow ^4\Pi$ transition. The rows of the matrices are labeled by the $F_L$ assignments for a given value of $J'$ and similarly the columns by $F'_L$ 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 $F_L$ 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 $<R_\alpha\sigma>$ 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 A-doublet in X↔Y transitions (X and Y represent any nonsigma electronic states), and if we combine the two submatrices in Σ↔X 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 +Λ submatrix and by neglecting the symmetrizing transformation. Thus, for spin-allowed transitions, all the required matrix elements occur in the upper left submatrix. For Σ↔Π transitions, however, Λ-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 \(3Σ \rightarrow 3Λ\) transitions are illustrated in figure 10. The \(X\) 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 \(3X \rightarrow 3Σ\) transitions is similar except that left and right submatrices replace upper and lower submatrices. The generalization to any multiplicity is straightforward.

For \(3Σ \leftrightarrow 3Y\) transitions (neither electronic state is a sigma state), the transformed rotational matrices are illustrated in figure 11. The two matrix elements for each \(Λ\)-doublet occur in symmetrical locations with respect to the center of the matrix. As we print only one component of a \(Λ\)-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 \(\bar{a}_i\) 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 $J = 1$ ($E_3$, $E_2$, and $E_1$) naturally occur in the upper leftmost portion of the matrix, which corresponds to the $F_7$, $F_6$, 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 $F_4$, $F_3$, and $F_2$, and in an inverted electronic state, they should be designated $F_6$, $F_5$, 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 \( <R_{e}\alpha> \) basis matrix for the \( Q \)-branches of a \( ^{2}\Pi \leftrightarrow ^{4}\Pi \) 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 \( <R_{e}\alpha> \) matrix in the basis functions and, hence, the transition moments \( R_{e} \) 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., \( R_{e}(\text{upper, lower}) \)).

In terms of upper and lower electronic substates, the columns of the \( <R_{e}\alpha> \) 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 \( <R_{e}\alpha> \) matrix in table 6. Similarly, the rows of the \( <R_{e}\alpha> \) 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 \( <R_{e}\alpha> \) matrix element between basis functions with opposite signs on \( \Lambda' \) and \( \Lambda'' \) (i.e., \( \langle \pm \Lambda' | R_{e} \alpha | \mp \Lambda'' \rangle \)) and at least one matrix element with the same signs on \( \Lambda' \) and \( \Lambda'' \). The \( \langle \pm \Lambda' | R_{e} \alpha | \mp \Lambda'' \rangle \) 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: \( R_{e}(-1,2), R_{e}(-1,1), \) and \( R_{e}(-2,1) \).

The \( P \)-branch matrix of a \( ^{4}\Pi \leftrightarrow ^{4}\Pi \) transition, shown in table 7, has five independent transition moments.

SAVE, ITRANI, ITRANS, 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 \(E_{e^a}\) 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 (\(E\)) 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_3 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

\[ \text{SUM} = R1 + QR12 + PR13 + Q1 + PQ12 + OQ13 + P1 + OP12 + NP13 \]

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, \( \bar{\alpha}_j \). The intensity factors are formed from these numbers as shown in equation (13), which is repeated here for convenience:

\[ \langle \alpha_j^{J',J''} \rangle = | \langle \rho \bar{\alpha}_j + \sigma \bar{\alpha}_j + \tau \bar{\alpha}_j + \ldots \rangle |^2 \]

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 \( \bar{\alpha}_j \) 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 Λ-doublets are not equal in all branches because three of the transition moments occur between basis functions with opposite signs on Λ' and Λ" (see page 16). These transition moments are designated by $R_e(-2,1)$, $R_e(-1,1)$, and $R_e(-1,2)$ in table 11. The intensity factor for the Λ-component not shown in the computer printout is obtained by changing the sign of these $\alpha_i^2$ terms in equation (13).

In general, when Λ-doubling occurs in spin-forbidden transitions, the intensity factor for the Λ-component not shown is obtained by changing the sign of all $\alpha_i^2$ 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 $L$ from the internuclear axis so that the intensity factors for the $p$-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 $\pm\leftrightarrow\pm$, whereas for electric dipole radiation it is $\pm\leftrightarrow\mp$, magnetic dipole transitions must be specified as $\Sigma\leftrightarrow\Sigma$, $\Sigma\leftrightarrow\Sigma^\mp$ magnetic dipole transitions must be specified as $\Sigma\leftrightarrow\Sigma^\pm$ 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 (HON-LONDON FACTORS), AND THE SQUARE ROOT
C OF THE ROTATIONAL INTENSITY FACTORS FOR FORBIDDEN TRANSITIONS.
C
C MAIN PROGRAM
C
C DIMENSION TITLE1(14),TITLE2(12),TITLE3(6),TITLE4(43),TITLE5(6),
1 TITLE6(44), HEADD(7,7,3),
2 HEAD1(119), ALPH(19,2)
C
COMMON /CSOLVE/JF,JMIN,JMAX,SI, SF, LAM1, LAMF,
1 SIGNI, ALLOW, EMISON, SIGSIG, IJ, IMAX, IMAXF,
2 NTRANR(200), NTRANQ(200), NTRANP(200),
3 ITRANI(30,200), ITRANF(30,200),
4 SAVE(9,150,200), YI(3), YF(3)
C
DOUBLE PRECISION SI, SF, LAMI, LAMF, YI, YF, JI, JF, JMIN, JMAX, SIGNI, SUM
C
LOGICAL ALLOW, SIGSIG, HALF, EMISON
C
REAL J
C
DATA ABSORB/1HA/
C
DATA TITLE1/4HSING,4HLET,4HDOUB,4HLET,4HTRIA,4HL0TET,4HL0TET/
1 4HQUAT,4HL0TET,4HL0TET,4HL0TET,4HL0TET/
C
DATA TITLE2/4HSI,4HGMA,4N PI,4H ,4HDE,4HLTA,1
1 4HGA,4HMGA,4HOT,4HHER/
C
DATA TITLE3/4HEMIS,4HSION,4N,4HABSO,4HRPTI,4HON/
C
DATA TITLE4/4MINIT,4HIAL,4FINA,4HL/
C
DATA TITLE5/4HEGUI,4HLAR,4HINVE,4HRD,4H/
C
DATA TITLE6/4HPER,4HLE,4L,4HPOWER/
C
DATA HEAD2
1 /2H1,2H12,2H13,2H14,2H15,2H16,2H17,
2 2H21,2H22,2H23,2H24,2H25,2H26,2H27,
3 2H31,2H32,2H33,2H34,2H35,2H36,2H37,
4 2H41,2H42,2H43,2H44,2H45,2H46,2H47,
5 2H51,2H52,2H53,2H54,2H55,2H56,2H57,
6 2H61,2H62,2H63,2H64,2H65,2H66,2H67,
7 2H71,2H72,2H73,2H74,2H75,2H76,2H77,
8 2H81,2H82,2H83,2H84,2H85,2H86,2H87,
9 2H91,2H92,2H93,2H94,2H95,2H96,2H97,
10 2H101,2H102,2H103,2H104,2H105,2H106,2H107,
11 2H111,2H112,2H113,2H114,2H115,2H116,2H117,
12 2H121,2H122,2H123,2H124,2H125,2H126,2H127,
13 2H131,2H132,2H133,2H134,2H135,2H136,2H137,
14 2H141,2H142,2H143,2H144,2H145,2H146,2H147,
15 2H151,2H152,2H153,2H154,2H155,2H156,2H157,
16 2H161,2H162,2H163,2H164,2H165,2H166,2H167,
17 2H171,2H172,2H173,2H174,2H175,2H176,2H177,
C
DATA ALPHA/1HZ,1HY,1HI,1HX,1HM,1HH,1TV,1HT,1HS,1HR,1HQ,1
1 1HM,1HI,1HN,1HM,1HH,1TV,1HT,1HS,1HR,1HQ,1
2 1HZ,1HY,1HI,1HX,1HM,1HH,1TV,1HT,1HS,1HR,1HQ,1
3 1HZ,1HY,1HI,1HX,1HM,1HH,1TV,1HT,1HS,1HR,1HQ,1
C
DATA BLANK/1H, R/1HR/, 0/1HQ/, P/1HP/
C
READ IN NEW CASE.
C
READS(S,501) SI, LAMI, SIGNI, YI(3), Y(3), YF(3)
READS(S,501) SF, LAMF, SIGNF, YF(3), YF(3)
READS(S,501) JMIN, JMAX
READS(S,503) TYPE
C
INITIALIZE LARGE SAVE ARRAY.
DO IS 1=1,200
DO IS 1=1,150
DO IS 1=1,1
SAVE(L,11)=0.0
C
C
INITIALIZE TRANSITION MOMENT ARRAYS.
DO IS 17=1,200
NTRANR(1,1)=0
NTRANQ(1,1)=0
NTRANP(1,1)=0
ITRANI(1,1)=0
ITRANF(1,1)=0
C
IS THIS AN EMISSION CALCULATION?
C
EMISON=.TRUE.
C
IF (TYPE.EQ. 'ABSORB') EMISON=.FALSE.
C
IF JMAX IS NOT INPUT SET JMAX TO JMIN+100.
C
IF JMAX-JMIN IS GREATER THAN 199 SET JMAX TO JMIN+199.
C
IF (JMAX.EQ.0.00) JMAX=JMIN+100.00
DEL=JMAX-JMIN
IF (DEL.LT.199.00) JMAX=JMIN+199.000
C IS THIS A SIGMA TO SIGMA TRANSITION?
C SIGSIG=.TRUE.
C IF(LAM1.GT.1.0 OR LAMF.GT.1.1 SIGSIG=.FALSE.
C
C IS THIS AN ALLOWED TRANSITION?
C IF(ISI-SF).NE.0.0 OR .OR .OR .ABS(LAM1-LAMF).GT.1.100) GO TO 20
C IF(SIGSIG.AND..SIGNF.SIGNG) GO TO 20
C THIS IS AN ALLOWED TRANSITION.
C ALLOW=.TRUE.
C IMAX1=2.*SI+1.1
C IMAXF=2.*SF+1.1
C
SET SIGN OF SYMMETRIC MATRIX ELEMENTS IN THE O BRANCH MATRIX.
C
SIGN1=1.000
C IF(SF.NE.SIGSIG) GO TO 30
C I1=1
C IF(SIGNF.NE.SIGNG) I=0
C SIGN1=(-1)**(1001+1
C
C IS SPIN HALF INTEGER OR WHOLE INTEGER?
C
IS-SH=1.000
C IF(OABS(SI-SF).LT.1.00) HALF=.FALSE.
C
JMIN AND JMAX MUST BE HALF INTEGER OR WHOLE INTEGER IN
C ACCORD WITH THE SPIN.
C
JTEST=JMIN+.100
J=JTEST
C IF(HALF) GO TO 35
C IF(.ABS(SI-.J1-.LT.1) JMIN=JMIN+.500
C GO TO 37
C IF(.ABS(SI-.J1-.LT.1) JMIN=JMIN+.500
C GO TO 40
C IF(.ABS(SI-.J1-.LT.1) JMAX=JMAX+.500
C GO TO 40
C
C FIND MINIMUM VALUES FOR J1 AND JF AND
C ADJUST JMIN IF NECESSARY.
C
J1=LAM1-SI
C IF(J1.GE.0.000) GO TO 45
J1=0.000
C IF(HALF) J1=0.500
C IF(.ABS(J1-.JMIN+.LT.1) JMIN=J1
C
JF=LAMF-SF
C IF(JF.GE.0.000) GO TO 50
JF=0.000
C IF(HALF) JF=0.500
C
C IF(JMIN-.JF).LT.5.500
C IF(.ABS(J1-.JF-.LT.1) JMIN=JF-.1000
C GO TO 65
C
CALL SOLVE
C
PRINT HEADING
C
WRITE(*,600)
C IF(ALLOW) GO TO 70
WRITE(*,601)
GO TO 75
WRITE(*,602)
70 ILAMI=LAM1+1
IF(ILAMI.LT.5) ILAMI=5
ILAMF=LAMF+1
IF(ILAMF.LT.5) ILAMF=5
INDEX=4
IF(EHISON) INDEX=1
INDEX2=INDEX
INDEX2=INDEX2+5
IF(ILAMI.LT.100.AND.SI.LT.600) GO TO 77
125 IF(HEAD(III).EQ.R) HEAD(II)=BLANK
126 CONTINUE
127 WRITE(6,604) (HEAD(I),R,HEAD2(I,I),I=1,IMAX)
128 DO 140 I=1,R
129 DELJ=I-1
130 J=JMIN+DELJ
131 WRITE(6,607)
132 KO=(K-1)*7
133 K1=KO+1
134 K2=KO+MAXF
135 K3=NTRAN(I)
136 DO 130 NTRAN=1,K3
137 SUM=0.000
138 DO 128 KK=K1,K2
139 SUM=SUM+SAVE(NTRAN,KK,II)**2
140 WRITE(6,608) J,SUM,NTRANFINTRAN,II,ITRAN(II),
141 (SAVE(NTRAN,KK,II),KK=K1,K2)
142 CONTINUE
143 PRINT Q BRANCHES.
144 DO 160 K=1,IMAX
145 DO 150 I=1,IMAXF
146 NI=I+DELJ-K+1
147 HEAD(I)=ALPHA(NI,II)
148 IF(HEAD(I).EQ.Q) HEAD(I)=BLANK
149 CONTINUE
150 WRITE(6,609) (HEAD(I),Q,HEAD2(I,K,II),I=1,IMAX)
151 DO 160 I=1,R
152 DELJ=I-1
153 J=JMIN+DELJ
154 WRITE(6,607)
155 KO=100*(K-1)*7
156 K1=KO+1
157 K2=KO+MAXF
158 K3=NTRAN(I)
159 DO 150 NTRAN=1,K3
160 SUM=0.000
161 DO 148 KK=K1,K2
162 SUM=SUM+SAVE(NTRAN,KK,II)**2
163 WRITE(6,608) J,SUM,INTRANFINTRAN,II,ITRAN(II),
164 (SAVE(NTRAN,KK,II),KK=K1,K2)
165 CONTINUE
166 PRINT P BRANCHES.
167 DO 180 K=1,IMAX
168 DO 170 I=1,IMAXF
169 NI=I+DELJ-K+1
170 HEAD(I)=ALPHA(NI,II)
171 IF(HEAD(I).EQ.P) HEAD(I)=BLANK
172 CONTINUE
173 WRITE(6,609) (HEAD(I),P,HEAD2(I,K,II),I=1,IMAX)
174 DO 180 I=1,R
175 DELJ=I-1
176 J=JMIN+DELJ
177 WRITE(6,607)
178 KO=100*(K-1)*7
179 K1=KO+1
180 K2=KO+MAXF
181 K3=NTRAN(I)
182 DO 170 NTRAN=1,K3
183 SUM=0.000
184 DO 168 KK=K1,K2
185 SUM=SUM+SAVE(NTRAN,KK,II)**2
186 WRITE(6,608) J,SUM,NTRANFINTRAN,II,ITRAN(II),
187 (SAVE(NTRAN,KK,II),KK=K1,K2)
188 CONTINUE
189 END OF CASE; READ IN NEXT CASE.
190 GO TO 10
191 THIS IS AN ALLOWED TRANSITION.
192 PRINT R BRANCHES.
193 DO 210 K=1,IMAX
194 DO 200 I=1,IMAXF
195 NI=I+DELJ-K+1
196 HEAD(I)=ALPHA(NI,II)
197 IF(HEAD(I).EQ.R) HEAD(I)=BLANK
198 CONTINUE
199 WRITE(6,609) (HEAD(I),R,HEAD2(I,K,II),I=1,IMAX)
200 DO 210 I=1,R
201 DELJ=I-1
202
J=M+DELJ
SUM=0.000

K=K+1
K2=K+1
DO 200 KK=K1,K2
K3=KK+50
K4=KK+100

200 SUM=SUM+SAVEI1,KK,II,1)+SAVEI1,K3,II)+SAVEI1,K4,II)
WRITE(4,610) J,SUM,(SAVEI1,KK,II,1),I)
IF((SUM<1.0E-01) WRITE(4,607)

C 210 CONTINUE
C PRINT Q BRANCHES.
C DO 230 K=K1,KMAXI
DO 215 I=I1,IMAXI
N1=10-(K-1I)+1
HEADI(I)=ALPHA(N1,III)
IF(HEADI(I).EQ.0) HEADI(I)=BLANK

215 CONTINUE
WRITE(4,609) (HEADI(I)),Q,HEAD2(I,K,III,I1,IMAXI)

C 220 CONTINUE
DELJ=I-1
J=M+DELJ
SUM=0.000

K=50+K-1
K2=K+1
K3=KK=100
K4=KK+100

220 SUM=SUM+SAVEI1,KK,II,1)+SAVEI1,K3,II)+SAVEI1,K4,II)
WRITE(4,610) J,SUM,(SAVEI1,KK,II,1),I)
IF((SUM<1.0E-01) WRITE(4,607)

C 230 CONTINUE
C PRINT P BRANCHES.
C DO 250 K=K1,KMAXI
DO 235 I=I1,IMAXI
N1=10-(K-1I)+2*(I-1I)-1
HEADI(I)=ALPHA(N1,III)
IF(HEADI(I).EQ.0) HEADI(I)=BLANK

235 CONTINUE
WRITE(4,609) (HEADI(I)),P,HEAD2(I,K,III,I1,IMAXI)

C 250 CONTINUE
C END OF CASE, READ IN NEXT CASE.
C GO TO 10
C READ FORMAT STATEMENTS.
C 501 FORMAT(F3.1,2X,F2.0,2X,A1,3E10.0)
502 FORMAT(F5.1)
503 FORMAT(A1)
C WRITE FORMAT STATEMENTS.
C 600 FORMATH1,52X,2INTENSITY FACTOR PROGRAMME,
1 0.58,41NASA-AMES/CRESEE E WHITING AUGUST 1972,///)
601 FORMAT(1H3X,43OH brigade KIOF ROTATIONAL INTENSITY FACTORS,
1 1 BM FOR THE FORBIDDEN///)
602 FORMAT(12X,4HX SQUARE RIOF ROTATIONAL INTENSITY FACTORS,
1 0.58,41NASA-AMES/CRESEE E WHITING AUGUST 1972,///)
603 FORMAT(24X,3X,4H STATE SPIN-ORBIT COUPLING CONSTANT = A/B/48.3)
604 FORMAT(24X,3X,4H STATE ENERGY SEPARATION • DELTA E(l)/58.3)}
613 FORMAT(27X,5BHIN SIGMA STATES WHEN JCS, THE F DESIGNATION FOR THE LEVELS,
       /27X,5BHWITH THE SAME VALUE OF J ARE ASSIGNED AS 2S+1 FOR THE,
       /27X,5BHIHIGHEST ENERGY LEVEL, 2S FOR THE NEXT HIGHEST, ETC.)

614 FORMAT(27X,59HLAMBDA DOUBLING OCCURS IN THE SPECTRUM, BUT THE SQUARE ROOT,
       1 17H OF THE INTENSITY/27X,*OHFACTORS FOR ONLY ONE LINE OF EACH LAMBDA,
       2 4OH DOUBLET IS PRINTED. THE VALUES FOR THE/27X,12HOTHER LAMBDA,
       3 5OH COMPONENTS ARE FOUND BY CHANGING THE SIGN OF THE NUMBERS,
       4 11HPRINTED, IF/27X,42HTHE TRANSITION MOMENT DESIGNATION CONTAINS,
       5 14H A MINUS SIGN.)

615 FORMAT(27X,59HLAMBDA DOUBLING OCCURS IN THE SPECTRUM, BUT THE NON-LONDON,
       1 21H FACTORS FOR ONLY ONE/27X,59HLINE OF EACH LAMBDA DOUBLET IS PRINTED.
       2 3IH THE NON-LONDON FACTORS FOR THE OTHER/27X,17HLAMBDAS ARE THE SAME.)
END
SUBROUTINE SOLVE
C
C THIS PROGRAM:
1-DEVELOPS THE ROTATIONAL HAMILTONIAN.
2-CALLS EIGEN TO GET THE EIGEN VECTORS OF THE HAMILTONIAN.
3-DEVELOPS THE ROTATIONAL MATRIX.
4-TRANSFORMS THE ROTATIONAL MATRIX.
5-STORES, IN THE LARGE SAVE ARRAY, HORN-LONDON FACTORS
FOR ALLOWED TRANSITIONS AND THE SQUARE ROOT OF ROTATIONAL INTENSITY FACTORS FOR FORBIDDEN TRANSITIONS.

DIMENSION T(14,14),TI(14,14),TF1(14,14),TF2(14,14),AI(14,14),
C(14),SY(14),SY(17)
C
COMMON /CSOLVE/JF,JMIN,JMAX,EJ,EJ,LMJ,LMF,
1 SIGN,ALLOW,ESSION,SIGSIG,FINAL,LAM,LAMF,
2 NTRAN(200),NTRAN2(200),NTRAN3(200),
3 ITRAN(200),ITRAN2(200),ITRAN3(200),
4 SAVE(4,150,200),Y(13),YF(13)
C
COMMON /CEIGEN/H12(28),T14(491,N
C

DATA R/1HR/, 0/1HO/, P/1HP/, FINAL/1IMF/, INITAL/1HI/
C
INTEGER SAVE1,SAVE2,SAVE3,SAVE4,SAVE5,SAVE6
C
C INITIALIZE MATRICES.
C AND SET FLAG FOR FIRST COMPUTATION.
00 10 1=1,14
00 10 K-1,14
TIK,K=0.000
TF1IK,11=0.000
TF2IK,11=0.000
C(K,II=0.000
10 A{K,I>=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-LOWER FOR ABSORPTION AND IN TERMS OF
C J-UPPER FOR EMISSION.
C
DO 10 U = JMIN, JMAX
DELJ=U-UJ
JI=JMIN-DELJ
C
C SET VALUES FOR INITIAL LEVEL CALCULATION.
C
DO 15 I=1,3
Y(I)=YU(I)
GO TO 30
C
C SET VALUES FOR FINAL LEVEL CALCULATION.
C
DO 25 I=1,3
Y(I)=YFU(I)
C
C INITIALIZE HAMILTONIAN AND TRANSFORMATION MATRICES.
C
DO 30 I=1,1
DO 35 K=1,4
H(K,I)=0.000
DO 35 K=5,14
H(K,I)=0.000
30 X=1,3
DO 40 I=1,7
DO 45 K=1,4
H(K,I)=0.000
DO 45 K=5,14
H(K,I)=0.000
40 X=1,12
DO 50 I=1,7
DO 55 K=1,12
H(K,I)=0.000
DO 55 K=13,27
H(K,I)=0.000
50 X=1,12
DO 60 I=1,7
DO 65 K=1,12
TF(I,K)=0.000
DO 65 K=13,27
TF(I,K)=0.000
60 X=1,12
DO 70 I=1,7
DO 75 K=1,12
TF(I,K)=0.000
DO 75 K=13,14
TF(I,K)=0.000
70 X=1,12
DO 80 I=1,7
DO 85 K=1,12
TF(I,K)=0.000
DO 85 K=13,14
TF(I,K)=0.000
80 X=1,12
THE HAMILTONIAN MATRIX IS REDUCED AT LOW J VALUES.
C SET INDICES DEFINING WHICH ROWS AND COLUMNS HAVE NON-ZERO ELEMENT
C OMEGA=LAM
IF(IJ=11,JF,OMEGA) GO TO 50

27
C HAMILTONIAN IS FULLY DEVELOPED.
C
1=1
2=1!IMAX
GO TO 110
C HAMILTONIAN IS REDUCED.
C 50 TEST=OMEGA
DO 60 I=1,1!MAX
I=I+1
TEST=TEST-1.0
IF(1.0.EQ.1.0, GO TO 70
CONTINUE
60 CONTINUE
I=1!MAX
GO TO 80
C THERE IS ONLY ONE ELEMENT IN THE HAMILTONIAN.
C SET TRANSFORMATION MATRIX.
C
60 TEST=TEST-1.0
IF(I.EQ.1.0) GO TO 70
C THERE MAY BE MORE THAN ONE ELEMENT IN THE
C HAMILTONIAN MATRIX.
C 100 I2=I2+1
I2=I2+2
IF(I2.GT.1!MAX) I2=1!MAX
C IS THERE MORE THAN ONE ELEMENT IN THE
C HAMILTONIAN MATRIX?
C 110 IF(I2.EQ.1) GO TO 90
C THERE IS MORE THAN ONE ELEMENT IN THE
C HAMILTONIAN MATRIX. SET SIZE OF MATRIX.
C 110 IMAX=I2-I1+1
C DEVELOP UPPER HALF OF SYMMETRICAL HAMILTONIAN MATRIX.
C J(J*4) AND S(S*4) TERMS IN THE DIAGONAL ELEMENTS ARE NOT INCLUDED.
c
K=0
130 I=I+2
DO 120 K=I1,13
120 H(K,K)=OMEGA*1.000*(S-EI*1.000)**2
C IS THIS A SIGMA STATE?
C K=0
IF(LAM.LT.100) GO TO 140
C THIS IS NOT A SIGMA STATE.
C INCLUDE SPIN-ORBIT INTERACTION (Y-A/B).
C DO 130 K=I1,12
130 H(K,K)=Y*(S-EI*1.000)
GO TO 152
C THIS IS A SIGMA STATE.
C INCLUDE SPIN-ORBIT + SPIN-SPIN ENERGY SEPARATIONS (DELTA E/B).
C GO TO 152
140 DO 150 K=I1,12
150 H(K,K)=OMEGA*1.000*(S-EI*1.000)**2
GO TO 152
C IF(I.EQ.1.0) GO TO 150
134 GO TO 146
C IF(I.EQ.2.0) GO TO 150
134 GO TO 146
C IF(I.EQ.3.0) GO TO 150
134 GO TO 146
C IF(I.EQ.4.0) GO TO 150
134 GO TO 146
144 IF(I.EQ.3.OR.I.EQ.4) GO TO 150
145 IF(I.EQ.2.OR.I.EQ.5) GO TO 146
146 H(K,K)+H(K,K*Y(I)) CONTINUE
150 CONTINUE
152 IF(ALLOW.OR.LAM.GT.1.0R.S.LT.1.0) GO TO 225
155 IF(I.EQ.3.0R.I.EQ.5) I=1
156 DO 170 I=1,N
157 SYM(K,K)=0.000
159 CONTINUE
160 K=1
161 DO 170 K=N
162 SYM(K,K)=0.000
163 CONTINUE
165 NSAVE=N
167 DO 180 I=1,N
168 DO 180 K=1,N
169 SYM(K,I)=H(K,I)*C(K,I)
170 CONTINUE
171 DO 180 K=1,N
172 SYM(K,I)=H(K,I)*C(K,I)
173 CONTINUE
175 CALL F.IGEN
176 CALL SUBROUTINE TO FIND THE EIGENFUNCTIONS OF
177 THE HAMILTONIAN MATRIX BY JACOBI-VON NEUMAN METHOD.
178 EIGENFUNCTIONS ARE ORDERED IN A ONE-DIMENSIONAL ARRAY, TT WITH
179 THE LARGEST EIGENVALUE FIRST, ETC.
180 CALL EIGEN
182 DO 235 I=1,N
183 DO 235 K=1,N
184 K=K+1
186 CONTINUE
187 DO 235 I=1,N
188 DO 235 K=1,N
189 K=K+1
190 CONTINUE
192 IF(I.EQ.3.OR.I.EQ.4) GO TO 150
194 CONTINUE
196 DO 225 I=1,N
197 DO 225 K=1,N
198 K=K+1
199 CONTINUE
200 I=I+1
201 CONTINUE
202 I=I+1
203 CONTINUE
205 I=I+1
206 CONTINUE
208 I=I+1
209 CONTINUE
210 H(K,K)=SYM(K,K)*C(K,K)
211 CONTINUE
213 CALL SUBROUTINE TO EXPAND THE ONE-DIMENSIONAL ARRAY, TT INTO THE TWO-DIMENSIONAL
214 TRANSFORMATION MATRIX,TT THAT DIAGONALIZES THE HAMILTONIAN.
215 ENSURE CONSISTANT PHASE OF THE EIGENFUNCTIONS BY MAKING
216 THE FIRST ELEMENT IN EACH COLUMN NEGATIVE.
217 CALL EIGEN
219 DO 235 I=1,N
220 DO 235 K=1,N
221 K=K+1
223 CONTINUE
224 DO 235 I=1,N
225 DO 235 K=1,N
226 K=K+1
227 CONTINUE
229 I=I+1
230 CONTINUE
232 I=I+1
233 CONTINUE
235 I=I+1
236 CONTINUE
238 I=I+1
239 CONTINUE
240 M=M+1
242 CONTINUE
243 M=M+1
246 CONTINUE
249 M=M+1
250 CONTINUE
253 M=M+1
256 CONTINUE
259 M=M+1
262 CONTINUE
265 M=M+1
268 CONTINUE
271 M=M+1
274 CONTINUE
277 M=M+1
280 CONTINUE
283 M=M+1
286 CONTINUE
289 M=M+1
292 CONTINUE
295 M=M+1
DO 250 I=1,N
DO 250 K=1,N
K3=I+1

250 T(K3,IKJ)=T(KJ)
C TRANSFER T MATRIX INTO INITIAL (TI) OR FINAL (TF)
C MATRIX. SET FLAGS AND INDICES FOR PROPER BRANCHES.
C PRELIMINARY TO DEVELOPING THE ROTATIONAL MATRIX.
C IS THIS THE INITIAL OR THE FINAL STATE?
C
260 IF(State.EQ.FINAL) GO TO 280
C THIS IS THE INITIAL STATE.
C TRANSFER THE T MATRIX INTO THE TI MATRIX.
C SET INDICES FOR INITIAL STATE.
C
DO 270 I=1,N
DO 270 K=1,N

270 T(I,K)=T(I,KJ)
I1=I1
I2=I2
N1=N
C IF THIS IS THE FIRST TIME THRU OR IF THE O BRANCHES
C HAVE NOT BEEN COMPUTED, GO DIRECTLY TO THE FINAL STATE.
C IF(FIRST) GO TO 20
IF(BRANCH.NE.0) GO TO 300
C GO TO 330
C THIS IS THE FINAL STATE.
C ARE CONDITIONS SET FOR O BRANCHES?
C
280 IF(ABS(I-IJ.FT.13) GO TO 330
C CONDITIONS ARE SET FOR O BRANCHES.
C INVERT T MATRIX AND PUT INTO TF1 MATRIX.
C
DO 290 I=1,N
DO 290 K=1,N

290 T(KI,KJ)=T(IKJ)
C SAVE INDICES DENOTING SIZE OF HAMILTONIAN AND
C WHICH ELEMENTS ARE FILLED.
C SAVE1=I1
SAVE=12
SAVE3=N
FIRST=.FALSE.
C INCREASE FINAL STATE ROTATIONAL QUANTUM NUMBER
C BY 1 AND COMPUTE THE NEW FINAL STATE.
C
300 JF=JF+1.0
GO TO 20
C THIS IS EITHER A P OR AN R BRANCH.
C NORMALLY JF WILL BE GREATER THAN J1 AT THIS POINT.
C HOWEVER, THE FIRST TIME THRU J1 MAY BE GREATER.
C
310 IF(JF.NT.J1) GO TO 350
C FIRST TIME THRU. INVERT T MATRIX AND PUT INTO TF1
C MATRIX AND SET INDICES.
C
DO 320 I=1,N
DO 320 K=1,N

320 TF(I,K)=T(KJ)
I1=I1
I2=I2
N1=N
C IF THIS IS AN EMISSION CALCULATION, WE ARE READY
C TO COMPUTE R BRANCHES. IF ABSORPTION, P BRANCHES.
C
330 IF(EMISSION) GO TO 370
C THIS IS A P BRANCH CALCULATION.
C
340 BRANCH=P
C SET INDEX FOR SAVING P BRANCHES IN THE LARGE SAVE ARRAY.
C IK=100
SIGN2=-1.0
GO TO 390
C
C INVERT T MATRIX, PUT INTO TF2 MATRIX AND SET INDICES.
C
DO 360 I=1,N
DO 360 K=1,N

360 TF2(I,K)=T(KJ)
IF I = 11
IF I = 12
NF = N
C
IF THIS IS AN EMISSION CALCULATION, WE ARE READY
TO COMPUTE P BRANCHES. IF ABSORPTION, R BRANCHES.
IF (EMISSION) GO TO 340
C
THIS IS AN R BRANCH CALCULATION.
370 BRANCH = R
C
SET INDEX FOR SAVING Q BRANCHES IN THE LARGE SAVE ARRAY.
IK = 0
SIGN = -1.000
GO TO 390
C
THIS IS A Q BRANCH CALCULATION.
380 BRANCH = Q
IK = 50
SIGN = 1.000
C
DEVELOP ROTATIONAL MATRIX.
C
SET INDICES AND SIGN OF LAMBDA.
390 I = 0
E1 = E1 + 1.000
N1 = N1 + 1
NF = NF + 1
SIGMA = 1.000
SIGN = 1.000
C
IF (ALLOW OR LAMF.LT.1) GO TO 450
SIGN = -1.000
NF = 2*NF
C
SET INDICES AND OMEGA FOR THE INITIAL STATE,
COLUMNS OF THE MATRIX.
400 I = I + 1
E1 = E1 - 1.000
OMEGA1 = LAM1 + 51 - E1
I1 = N1 - I1 - 1
C
K = 0
E2 = E2 + 2
C
SET INDICES AND OMEGA FOR THE FINAL STATE,
ROWS OF THE MATRIX.
410 K = K + 1
E3 = E3 + 1.000
KK = KK - 1.000
F2 = F2 + 1.000
IF (SIGN .LT. 0.0) EK = EK + 1.000
OMEGA2 = LAM2 + 52 - EK
C
FIND DELTA OMEGA AND DELTA LAMBDA.
DEL = OMEGA2 - OMEGA1
DEL1 = LAMF - LAM1
C
FOR ALLOWED TRANSITIONS DELTA OMEGA MUST EQUAL DELTA LAMBDA.
IF (.NOT. ALLOW) GO TO 415
IF (ABS (DEL - DEL1).LT.1) GO TO 510
C
WHAT TYPE OF BRANCH?
415 IF (BRANCH.EQ.0) GO TO 470
IF (JF - J1).GT.11 GO TO 440
C
P BRANCH IN ABSORPTION OR
R BRANCH IN EMISSION.
IF (J1.LT.11) GO TO 910
IF (ABS (DEL1).LT.1100 TO 430
IF (DEL1.DT.1100 TO 910
A(KK,II) = SIGMA1(J1 + OMEGA1) * (J1 + OMEGA1 - 1.000) * (1.000 * J1)
GO TO 500
C
420 IF (DEL1.GT.11) GO TO 520
A(KK,II) = SIGMA1(J1 + OMEGA1) * (J1 + OMEGA1 - 1.000) / (1.000 * J1)
GO TO 500
C
430 A(KK,II) = SIGMA1(J1 + OMEGA1) * (J1 + OMEGA1 - 1.000) / (1.000 * J1)
GO TO 500
C
R BRANCH IN ABSORPTION OR
P BRANCH IN EMISSION.
C 440 IFI ABSDEL1.LT.1) GO TO 440
IFI DEL1.GT.1) GO TO 450
IFI DEL1.EQ.1) GO TO 510
C AIXK,11=DSQRT(IJI+OMEGA1+1.000*(IJ]+OMEGA1.*12.000*(IJ]+1.000))
GO TO 500
C 450 IFI DEL1.EQ.1) GO TO 520
C AIXK,11=DSQRT(IJI+OMEGA1+1.000*(IJ]+OMEGA1.*12.000*(IJ]+1.000))
GO TO 500
C 460 AIXK,11=DSQRT(IJI+OMEGA1+1.000*(IJ]+OMEGA1.*12.000*(IJ]+1.000))
GO TO 500
C 500 IF NOT ALLOW) GO TO 540
C 510 IF(K.LT.NF) GO TO 410
IFI (K.GT.NF) GO TO 525
C 520 IF(SIGN.GT.0) GO TO 530
C IS FORBIDDEN BRANCH COMPLETED?
C IFLAMI.GT.1.OR.IIL.LT.1) GO TO 522
IFIL.EQ.1) GO TO 810
C 522 SIGN.LT.1.000
E=IF2
GO TO 410
C 525 IF(K.LT.NF) GO TO 410
C 530 IF(I.EQ.MI) GO TO 595
IFIALLOWI) GO TO 395
C IS FORBIDDEN BRANCH COMPLETED?
C IFLAMI.GT.1.OR.IIL.LT.1) GO TO 395
GO TO 810
C IF THIS IS AN ALLOWED TRANSITION, MUST NOW TRANSFORM
C THE ROTATIONAL MATRIX, IF THIS IS A FORBIDDEN
C TRANSITION, THIS BRANCH IS COMPLETE.
C 535 IFALLOWI GO TO 580
GO TO 810
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 IFSIGSIG) GO TO 560
C 560 IF(LAMI.LT..1) GO TO 565
C INITIAL STATE IS NOT A SIGMA STATE.
C 565 I3=1
567 AIXK.13+SIGN1*SIGN2)*AIXK,11)
GO TO 571
C BOTH OMEGAS ARE ZERO.
C THERE IS NO SYMMETRICAL ELEMENT.
C FOR THE TRANSITION MOMENT TO EXIST SIGN1 MUST BE NEGATIVE.
C
IF(ISIGN1.LT.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
IF(K.EQ.KK) GO TO 576
IF(I.EQ.II) GO TO 575
IF(K.EQ.II) GO TO 573

MM(1)=A(KK,II)*0.500
MM(2)=0.000
MM(3)=0.000
MM(4)=A(KK,II)*0.500
GO TO 578

C
C
IF(I.EQ.KK) GO TO 574
IF(K.EQ.II) GO TO 572
IF(I.EQ.II) GO TO 570

MM(1)=A(KK,II)*0.500
MM(2)=0.000
MM(3)=0.000
MM(4)=A(KK,II)*0.500
GO TO 578

C
C
IF(K.EQ.II) GO TO 577
MM(1)=A(KK,II)*0.70710678100
MM(2)=A(KK,II)*0.70710678100
MM(3)=0.000
MM(4)=0.000
GO TO 578

C
C
IF(I.EQ.KK) GO TO 578
MM(1)=A(KK,II)*0.70710678100
MM(2)=A(KK,II)*0.70710678100
MM(3)=0.000
MM(4)=0.000

C

A(KK,II)=MM(1)*MM(2)*MM(3)*MM(4)
MM(1)=A(KK,II)*MM(2)*MM(3)*MM(4)
MM(2)=0.000
C MULTIPLY ON THE LEFT BY TF.
C
DG 600 11=-1,NNI
DG 600 K=1,NFF
C(K1,I1)=0.000
DG 590 I2=-1,NNI
C(K1,I1)=C(K1,I1)*A(K1,II)*TF(I2,I1)
GO CONTINUE
C
C
IF(BRANCH.EQ.Q.OR.(JF-JI).LT.-1) GO TO 530
C FOR P BRANCHES IN EMISSION AND R BRANCHES IN
C ABSORPTION MULTIPLY ON LEFT BY TF2.
C
DG 620 I1=-1,NNI
DG 620 K1=-1,NFF
A(K1,II)=0.000
DG 610 I2=-1,NFF
A(K1,II)=A(K1,II)*TF2(K1,I2)*C(I2,I1)
GO CONTINUE
GO TO 655
33
FOR Q BRANCHES AND FOR P BRANCHES IN ABSORPTION
AND R BRANCHES IN EMISSION MULTIPLY ON LEFT BY TF1.

DO 650 II=1,NII
DO 650 K1=1,NFF
A(K1,II)=0.0
DO 650 I2=1,NII
640 A(K1,I2)=A(K1,I2)*TF1(I1,I2)
650 CONTINUE

FOR ALLOWED TRANSITIONS LAMBDA DOUBLING WAS NOT INCLUDED. THEREFORE, THE
MATRIX ELEMENTS FOR SIGMA-PI TRANSITIONS MUST BE MULTIPLIED BY THE SQUARE
ROOT OF 2.

FOR FORBIDDEN TRANSITIONS:
IF ONLY THE INITIAL STATE IS A SIGMA STATE, THE RESULTS
IN THE UPPER AND LOWER HALVES OF THE MATRIX MUST BE COMBINED.
IF ONLY THE FINAL STATE IS A SIGMA STATE, THE RESULTS
IN THE LEFT AND RIGHT HALVES OF THE MATRIX MUST BE COMBINED.
IF NEITHER STATE IS A SIGMA STATE, THE RESULTS
ARE EITHER IN THE UPPER-LEFT AND LOWER-RIGHT QUADRANTS, OR IN
THE UPPER-RIGHT AND LOWER-LEFT QUADRANTS. THEREFORE, WE CAN ALWAYS GET
ONE LAMBDA COMPONENT BY ADDING THE MATRIX ELEMENTS IN THE UPPER-LEFT
AND LOWER-RIGHT QUADRANTS (ONE OF WHICH IS ZERO). THE OTHER LAMBDA
COMPONENT CAN BE FOUND BY SIMPLY CHANGING THE SIGN OF ALL TERMS
WHOSE TRANSITION MOMENT IS DESIGNATED WITH A MINUS SIGN IN THE
FIRST LOCATION, IE (-X,Y).

IF(SIGSIG) GO TO 666
IF(.NOT.ALLOW) GO TO 662
IF(IAMI.GT.1DO.AND.LAMF.GT.1DO) GO TO 666

Cl/l.41421356200
DO 660 K3=1,NF
DO 660 I3=1,NI
660 A(K3,I3)=C1*A(K3,I3)
GO TO 666

IF(LAMF.LT.100I) GO TO 664
DO 663 I3=1,NI
DO 663 K3=1,NF
K4=NII*1-I3
663 AIK3,I3)=AIK3,I3)*AIK4,I3)
GO TO 666

DO 665 DO 665 I3=1,NI
DO 665 K3=1,NF
665 A(K3,I3)=A(K3,14)
C

FOR STATES OTHER THAN SIGMA STATES, IF THE HAMILTONIAN
IS NOT FULLY DEVELOPED (SMALL J VALUES) THEN THE ELEMENTS
IN THE TRANSFORMED ROTATIONAL MATRIX ARE SHIFTED TO
ENABLE PROPER LABELING DURING OUTPUT.

NDELI=0
IF(LAMF.LT.10.0) GO TO 695
C
Determine column shift.
NDELI=I11=1
IF(I1I.I1.0.D0) NDELI=MAX(I11-I11-NI+1)
IF(NDELI.LE.0) GO TO 695
C
SHIFT COLUMNS
DO 670 K1=1,NF
DO 670 I3=1,NI
I2=NII-I11
I11=I2+2*NDELI
670 A(K1,I3)=A(K1,12)
C
DO 680 II=1,ND1
680 A(K1,II)=0.0
500 CONTINUE
C
NdElf=0
IF(LAMF.LT.10.0) GO TO 735
C
Determine row shift.
NdElf=I11=1
IF(I1I.I1.0.D0) NdElf=MAX(I11-NF+1)
IF(NdElf.LE.0) GO TO 735
C
SHIFT ROWS.
DO 710 K1=1,NF
DO 710 II=1,MAX1
I2=NII-NF+1
I11=I2+NdElf
710 A(K1,II)=A(I2,11)
C
DO 720 K1=1,NDELF
C
C
CONTINUE
C STORE THE TRANSFORMED ROTATIONAL MATRIX ELEMENTS
C AND INITIALIZE THE A MATRIX FOR A NEW CALCULATION.
C
K6=NOELF+NF+1
I6=NOELI+NI+1
K5=IMAXF+NOELF-NF
I5=IMAXI-NOELI-NI
C IS THIS AN ALLOWED TRANSITION?
C IF(.NOT.ALLOW) GO TO 760
C
C THIS IS AN ALLOWED TRANSITION.
C STORE THE SQUARE OF THE A MATRIX ELEMENTS.
C THESE ARE THE HOML-LONDON FACTORS FOR A SINGLE LAMBDA COMPONENT.
C
DO 755 I1=1,NI
K6=K6-1
DO 755 K1=1,NF
K7=K7+1
K6=K6-K1
SAVE(I1,K7,I1)=AIK6,163**2
755 CONTINUE
DO 757 I1=1,14
DO 757 K1=1,14
AIK1,111=0.000
757 CONTINUE
GO TO 910
C
C THIS IS A FORBIDDEN TRANSITION.
C RECORD THE NUMBER OF ELECTRONIC TRANSITION
C MOMENTS AND THEIR DESIGNATIONS.
C
NTRAN=NTRAN+1
K6=K6+1
K7=K7+1
ITRANF(K6,K7)=1MAXF-12
C IF(LAMF.LT.1I) GO TO 780
C IF(SIGN.LT.0.) GO TO 770
C ITRANF(K6,K7)=K-NF*IMAXF-IF1
C GO TO 790
C ITRANF(K6,K7)=1MAXF+IF1
C GO TO 790
C ITRANF(K6,K7)=IMAXF-KF
C
C IS THIS AN EMISSION CALCULATION?
C IF(.NOT.EMISON) GO TO 799
C
C THIS IS AN EMISSION CALCULATION. ADJUST DESIGNATION
C OF THE TRANSITION MOMENT TO CORRESPOND TO ABSORPTION.
C
K1=0
C IF(SIGN.GT.0.) GO TO 796
C I1=ITRANF(K6,K7)
C ITRANF(K6,K7)=-ITRANI(K6,II)
C ITRANI(K6,II)=IMAXF+1-I1
C GO TO 799
C
792 IF(OMEGAF.LT.-1I) GO TO 796
C I1=ITRANF(K6,K7)
C ITRANF(K6,K7)=ITRANI(K6,II)
C ITRANI(K6,II)=IMAXF+1-I1
C GO TO 799
C
794 IF(OMEGAF.GT.1I) GO TO 798
C
796 I1=ITRANF(K6,K7)
C ITRANF(K6,K7)+=K*I1
C ITRANI(K6,II)=K*I1
C GO TO 799
C
SAVE A MATRIX ELEMENTS.
C
GO 800 II+1,NI

35
CO 300 KIM, NF
K7 = U5 \cdot I1 - I1 \cdot K5 \cdot K1
K6 = K4 - K1
I6M4 - I1
800 SAVE(NTRAN, KT, IJ) = A(K6, I6)
DO 805 I1 = 1, 14
00 805 K1 = 1, 14
805 A(K1, I1) = 0.000
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 INDICES, 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 JI AND COMPUTE A NEW INITIAL STATE.
C NTRAN(IIJ) = NTRAN
C GO TO 890
C 820 IF(BRANCH.EQ.0) GO TO 830
C A SET OF 0 BRANCHES HAVE BEEN COMPUTED.
C NEXT STEP IS TO INCREASE JI AND COMPUTE A NEW INITIAL STATE.
C NTRAN(IIJ) = NTRAN
C IF(EMISSION) GO TO 840
C IF(EMISION) GO TO 860
C A SET OF P BRANCHES HAVE BEEN COMPUTED.
C IF(EMISSION) GO TO 860
C REPLACE TF1 MATRIX WITH TF2 MATRIX BEFORE INCREASING JF
C AND COMPUTING NEW FINAL STATE.
C 840 K4 = SAVE3
K4 = K4 - 2 \cdot SAVE3
K4 = K4 - 2 \cdot SAVE3
DO 850 K1 = 1, K4
850 TF1(K1, I1) = TF2(K1, I1)
C IS THIS THE FIRST CALCULATION?
C 860 IF(FIRST) GO TO 870
C THIS IS NOT THE FIRST CALCULATION. SAVE INDICES AND
C Compute Q BRANCHES NEXT.
C SAVE1 = IF1
SAVE2 = IF2
SAVE3 = IF3
SAVE4 = E
SAVE5 = E
SAVE6 = E
SAVE7 = E
SAVE8 = E
GO TO 380
C THIS IS THE FIRST CALCULATION. SAVE INDICES AND
C TF2 MATRIX AND COMPUTE NEW INITIAL STATE.
C 870 FIRST = .FALSE.
SAVE1 = I1
SAVE2 = I1
SAVE3 = MF
DO 880 I1 = 1, NFF
880 TF(I1, I1) = TF(I1, I1)
C WOULD NEXT VALUE OF JI BE GREATER THAN JMAX?
C 890 IF(JMAX - JI - 1) .GT. 91 GO TO 910
C END OF BIG DO LOOP
C 910 RETURN
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,S1NX2,COSX,
1 CQSX2,SIHCS,RANGE

GENERATE IDENTITY MATRIX

5 RANGE=1.0D-12
10 IO=-N
20 20 IO=-N
30 R(IO)=0.0DO
40 IF(I-J) 20,15,20
15 R(IJ)=1.0DO
50 CONTINUE

COMPUTE INITIAL AND FINAL NORMS (ANORM AND ANORMX)

25 ANORM=0.0DO
30 35 DO 35 J=1,N
40 IF(I-J) 30,35,30
35 ANORM=ANORM+111A(I)»AI
40 CONTINUE

IFIANORM) 165,165,40
40 ANORMX=DSORT(2.000*ANORMX/RANGE/FLOAT(N))

INITIALIZE INDICATORS AND COMPUTE THRESHOLD, THR

50 IND=0
55 THRaANORM
60 THR=THR/FLOAT(N)
65 L=1
70 CONTINUE

COMPUTE SIN AND COS

75 SINX=Y/SQRT(1.0DO1-SINX2)
80 COSX=11112COSX/SINX
85 SIHCS=COSX*COSX
90 CQSX2=SINX*COSX

ROTATE L AND M COLUMNS

95 95 ILO=-M+1
96 IM=-L+1
97 DO 97 L=1,H
98 IF(L-M) 95,96,90
90 IF(L-M) 95,96,90
95 CONTINUE

90 CONTINUE

**********************************************************************
65 IP=1
GO TO 99
99 IP=IP+1
100 IP=1
105 IL=IL+1
GO TO 110
110 IF(IL-1) 100,105,105
103 IL=IL+1
GO TO 110
110 X=AILM+AILM*SINC
AILM=AILM*SINX-AILM*COSX
AILM=X
120 ILR=IL+1
IMR=IM+1
X=AILR*SINX-AILR*COSX
AILR=AILR*SINX-AILR*COSX
AILR=X
125 CONTINUE
X=2.000*AILM*SINC
Y=AILL*COSX2+AILL*SINC2-X
AILL=AILL-AIMM*SINC+AILM*(COSX2-SINC2)
AILL=Y
AILL=X
C
C TESTS FOR COMPLETION
C
C TEST FOR K = LAST COLUMN
C
130 IF(IN=N) 135,140,135
135 M=M+1
GO TO 60
C
C TEST FOR L = SECOND FROM LAST COLUMN
C
140 IF(LL-N-1) 145,150,145
145 L=L+1
GO TO 55
150 IF(NL=1) 160,155,160
155 A=0
GO TO 50
C
C COMPARE THRESHOLD WITH FINAL NORM
C
160 IF(THR=ANRMX) 165,165,45
C
C SORT EIGENVALUES AND EIGENVECTORS
C
165 I=1
GO TO 166
166 I=I+1
LL=I+J-11/2
JO=JN-2
GO 185, J=1,N
JO=JN
MM=J-11/2
IFAILL=A(ALL)
170 X=AILL
AILL=A(MM)
AILL=X
175 DC=180-K-1,N
ILR=IL+K
IMR=JKK
X=AILR
AILR=A(IMR)
180 RETURN
185 CONTINUE
RETURN
END
APPENDIX B

DETAILED FLOW CHARTS OF COMPUTER PROGRAM

PERTINENT BRANCHING SYMBOLS

BRANCHING ON SAME PAGE

OR

BRANCHING BETWEEN PAGES

TO PAGE

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, $H(i,i)$, of the Hamiltonian matrix in terms of the basis functions for nonsigma electronic states, are given by

$$\frac{H(i,i)}{\hbar^2} = BJ(J + 1) - Br_i^2 + BS(S + 1) - Bl_i^2 + A\lambda_i \Sigma_i$$  \hspace{1cm} (C1)

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

$$\frac{H(i,i)}{\hbar^2} = J(J + 1) + S(S + 1) - (\Lambda + \Sigma_i)^2 - \Sigma_i^2 + Y\Lambda \Sigma_i$$  \hspace{1cm} (C2)

where $Y = A/B$, or as

$$\frac{H(i,i)}{\hbar^2} = J(J + 1) + S(S + 1) - \Lambda^2 - 2\Sigma_i^2 + (Y - 2)\Lambda \Sigma_i$$  \hspace{1cm} (C3)

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

$$\frac{H(i,i)}{\hbar^2} = J(J + 1) + S(S + 1) - 2\Sigma_i^2 + \frac{\Delta \Sigma_i^2}{B}$$  \hspace{1cm} (C4)
where $\Delta E_i$ 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 $\Delta E_i$ in equation (C4) are found by extrapolating the energy separations shown in Figure 14, to $N = 0$. The reference level for $\Delta E_i$ 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 \( \langle \Omega'|J'|a|\Omega J \rangle \), where \( \langle a \rangle = f(J',J)g(J',\Omega';J,\Omega) \). 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>( 4(J+1) )^{-1/2}</td>
<td>( 4J/(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>2J \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+\Omega+1)(J+\Omega+2)]^{1/2} )</td>
<td>( \pm [2(J+\Omega)(J+\Omega-1)]^{1/2} )</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2.—\( <\xi a> \) BASIS MATRIX FOR A SPIN-FORBIDDEN \( 2\pi \leftrightarrow 4\Sigma^+ \) TRANSITION

TABLE 3.—\( <\xi a> \) 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

Store transformed rotational matrix elements and code for transition moments.

Test if all transition moments have been included.

No

Yes

\(J \neq J_{\text{max}}\)

\(J = J + 1\)

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

Square transformed rotational matrix elements to get H"onl-London factors.

Store H"onl-London factors.

Output:
H"onl-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 $<\Lambda \Sigma \sigma |<\Omega \Sigma |$

| $<\Lambda \Sigma \sigma |<\Omega \Sigma |$ | | | |
|---|---|---|---|
| $<\Lambda \Sigma \sigma |<\Omega \Sigma |$ | $H_{11}$ | $H_{12}$ | $H_{23}$ |
| $<\Omega \Sigma ; \sigma \Lambda$ | $H_{12}$ | $H_{22}$ | $H_{23}$ |
| $<\Omega \Sigma ; \sigma \Lambda$ | $H_{23}$ | $H_{23}$ | $H_{23}$ |
| $<\Omega \Sigma ; \sigma \Lambda$ | $H_{23}$ | $H_{23}$ | $H_{23}$ |

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

| $4\pi$ | $2\pi$ | $\alpha \beta \gamma |\alpha \beta \gamma |$ | $\alpha \beta \gamma |\alpha \beta \gamma$ | $\alpha \beta \gamma |\alpha \beta \gamma$ | $\alpha \beta \gamma |\alpha \beta \gamma$ | $\alpha \beta \gamma |\alpha \beta \gamma$ | $\alpha \beta \gamma |\alpha \beta \gamma$ |
|---|---|---|---|---|---|---|---|
| $<\Omega \Sigma ; \sigma \Lambda$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ |
| $<\Omega \Sigma ; \sigma \Lambda$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ |
| $<\Omega \Sigma ; \sigma \Lambda$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ |
| $<\Omega \Sigma ; \sigma \Lambda$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ | $R_{\pi}(2, 4)$ |
TABLE 7. – $<R \rho \alpha>$ BASIS MATRIX FOR THE P-BRANCHES OF A $^4\Sigma^+ \leftrightarrow ^4\Sigma^-$ TRANSITION

![Basis Matrix Diagram]

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>6-7</td>
<td>F2.0</td>
<td>+ or -; i.e., symbol for $\Sigma$ states</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>A</td>
<td>$\Lambda$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11-20</td>
<td>E10.0</td>
<td>Y for nonsigma states, $\Delta\epsilon(1)/\Gamma$ for $\Sigma$ states, $\Delta\epsilon(2)/\Gamma$ for $\Sigma$ states</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>21-30</td>
<td>E10.0</td>
<td>$\Delta\epsilon(2)/\Gamma$ for $\Sigma$ states</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>31-40</td>
<td>E10.0</td>
<td>$\Delta\epsilon(3)/\Gamma$ for $\Sigma$ states</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>*as needed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1-5</td>
<td>F5.1</td>
<td>$J_{\text{min}}$</td>
<td>1</td>
<td>It is recommended that ABSORPTION or EMISSION always be used.</td>
</tr>
<tr>
<td></td>
<td>6-10</td>
<td>F5.1</td>
<td>$J_{\text{max}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>A</td>
<td>$\Lambda$ for absorption. Anything for emission.</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 9.— COMPUTER PRINTOUT FOR SAMPLE CASE 1

<table>
<thead>
<tr>
<th>J</th>
<th>R1</th>
<th>QR12</th>
<th>QR13</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td>1.0</td>
<td>4.999999</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td>5.0</td>
<td>9.999999</td>
<td>1.34364E-01</td>
<td>9.70087E-02</td>
</tr>
<tr>
<td>10.0</td>
<td>17.999998</td>
<td>2.0573E-03</td>
<td>6.9933E-03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>J</th>
<th>R2</th>
<th>Q2</th>
<th>QR23</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td>1.0</td>
<td>5.999999</td>
<td>1.000000E-00</td>
<td>0.000000</td>
</tr>
<tr>
<td>2.0</td>
<td>9.999999</td>
<td>1.3384E-01</td>
<td>9.7361E-02</td>
</tr>
<tr>
<td>3.0</td>
<td>13.999999</td>
<td>2.0478E-01</td>
<td>1.0855E-01</td>
</tr>
<tr>
<td>4.0</td>
<td>17.999998</td>
<td>3.0009E-02</td>
<td>1.1911E-02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>J</th>
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### Table 10. - Partial Printout for Sample Case 2

**SQUARE ROOT OF ROTATIONAL INTENSITY FACTORS FOR THE EMB1100X**

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<th>UT1</th>
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**INITIAL STATE ENERGY SEPARATION:**
- Delta E1/L = 5.000
- Delta E1/7 = 10.000

**FINAL STATE SPIN-ORBIT COUPLING CONSTANT = 4xRA + Y = -5.000**

**IN SIGMA STATES, WHEN J, K, THE F DESIGNATION FOR THE LEVELS WITH THE SAME VALUE OF J ARE ASSIGNED AS 2J+1 FOR THE HIGHEST ENERGY LEVEL, PS FOR THE NEXT HIGHEST, ETC.**

**J VALUE IS FOR THE INITIAL (IE, LOWER) STATE.**
**TABLE 11.— PARTIAL PRINTOUT FOR SAMPLE CASE 3**

**SQUARE ROOT OF ROTATIONAL INTENSITY FACTORS FOR THF**

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<th>TO REGULAR DOUBLET PI</th>
<th>TRANSITION IN ABSORPTION</th>
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<tr>
<td>INIT. STATE SPIN-ORBIT COUPLING CONSTANT = ( A / \lambda' = 5.0 )</td>
<td>FNL. STATE SPIN-ORBIT COUPLING CONSTANT = ( A / \lambda' = 0.0 )</td>
<td>LAMBDA DOUBLING OCCURS IN THE SPECTRUM, BUT THE SQUARE ROOT OF THE INTENSITY FACTORS FOR ONLY ONE LINE OF EACH LAMBDA DOUBLET IS PRINTED. THE VALUE FOR THE OTHER LAMBDA COMPONENTS ARE FOUND BY CHANGING THE SIGN OF THE NUMBERS PRINTED, IF THE TRANSITION MOMENT DESIGNATION CONTAINS A MINUS SIGN. J VALUE IS FOR THE INITIAL (IE. LOWER) STATE.</td>
</tr>
</tbody>
</table>

<table>
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Figure 1. — Typical energy level diagram of a $^3\Pi \rightarrow ^3\Sigma$ electronic transition.

(a) Hund's case (a) coupling
\[ \Delta S = 0 \]
\[ \Delta \Sigma = 0 \]
\[ \Delta \Lambda = 0, \pm 1 \]
\[ \Delta J = 0, \pm 1 \]

(b) Hund's case (b) coupling
\[ \Delta S = 0 \]
\[ \Delta N = 0, \pm 1 \]
\[ \Delta \Lambda = 0, \pm 1 \]
\[ \Delta J = 0, \pm 1 \]

(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.

\[
\begin{array}{ccc}
1/\sqrt{2} & 0 & 1/\sqrt{2} \\
0 & 1 & 0 \\
1/\sqrt{2} & 0 & -1/\sqrt{2}
\end{array}
\]

(a) $^3\Sigma$

\[
\begin{array}{ccc}
1/\sqrt{2} & 0 & 0 & 1/\sqrt{2} \\
0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\
0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 \\
1/\sqrt{2} & 0 & 0 & -1/\sqrt{2}
\end{array}
\]

(b) $^4\Sigma$

(a) Regular electronic state

(b) Inverted electronic state

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

\[
\begin{array}{cccc}
F_i & F_1 & F_2 & F_3 \\
\Omega & -1/2 & 1/2 & 3/2 & 5/2 & 5/2 & 3/2 & 1/2 & -1/2 \\
J & 15/2 & 13/2 & 11/2 & 9/2 & 13/2 & 11/2 & 9/2 & 7/2 \\
N = 6 & 11/2 & 9/2 & 7/2 & 5/2 & 11/2 & 9/2 & 7/2 & 5/2 \\
J = 15/2 & 13/2 & 11/2 & 9/2 & 7/2 & 13/2 & 11/2 & 9/2 & 7/2 \\
J = 13/2 & 11/2 & 9/2 & 7/2 & 5/2 & 11/2 & 9/2 & 7/2 & 5/2 \\
J = 11/2 & 9/2 & 7/2 & 5/2 & 11/2 & 9/2 & 7/2 & 5/2 & 3/2 \\
J = 9/2 & 7/2 & 5/2 & 3/2 & 7/2 & 5/2 & 3/2 & 1/2 & 3/2 \\
J = 7/2 & 5/2 & 3/2 & 1/2 & 5/2 & 3/2 & 1/2 & 3/2 \\
J = 5/2 & 3/2 & 1/2 & 3/2 & 5/2 & 3/2 & 1/2 & 3/2 \\
J = 3/2 & 1/2 & 3/2 & 5/2 & 3/2 & 1/2 & 3/2 \\
J = 1/2 & 3/2 & 1/2 & 3/2 & 5/2 & 3/2 & 1/2 & 3/2 \\
J = -1/2 & 1/2 & 3/2 & 5/2 & 3/2 & 1/2 & 3/2 & 1/2 \\
J = -3/2 & 1/2 & 3/2 & 5/2 & 3/2 & 1/2 & 3/2 & 1/2 \\
J = -5/2 & 1/2 & 3/2 & 5/2 & 3/2 & 1/2 & 3/2 & 1/2 \\
J = -7/2 & 1/2 & 3/2 & 5/2 & 3/2 & 1/2 & 3/2 & 1/2
\end{array}
\]

Figure 5.— Designation of the rotational levels for a $^3\Sigma$ electronic state.
AN => N O P Q R S T

\[ \Delta N \Rightarrow \cdots -3 -2 -1 0 1 2 3 \cdots \]
\[ \Delta J \]

Figure 6. – Letter designations for changes in \( N \) and \( J \) during a transition.

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.

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 $^3X \rightarrow ^3Y$ transition; X and Y any nonsigma electronic states.

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.

Figure 14.— Illustration of spin splitting in sigma electronic states.
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