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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.[1] 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.

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

The computer program described is a new research tool for determining reliable intensity factors for most electric and magnetic dipole-allowed diatomic transitions by numerical methods. It is applicable to spin-allowed dipole transitions with either or both states intermediate between Hund's case (a) and Hund's case (b) coupling and to spin-forbidden dipole transitions with either or both states intermediate between Hund's case (c) and Hund's case (b) coupling. The program is not applicable to quadrupole transitions or to transitions involving an electronic state approximated by Hund's case (d).

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

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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 Λ-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 Λ-doublet is composed of two rotational lines.

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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[2] dipole moment, $\vec{P}$; that is,

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

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

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

ε_o the permittivity of a vacuum, $8.854 \times 10^{-12} C^2 J^{-1} m^{-1}$

$S_{J'J''}$ the line strength, defined in reference 4

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

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

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

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

$$\langle S_{J'J''} \rangle = q_{v'v''} |\langle \psi_U | R_e^\alpha | \psi_L \rangle|^2 \tag{5}$$

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[2]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).

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where

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

R_e the electronic transition moment, C m

α the rotational matrix element including the summation over M' and M'', dimensionless

ψ_U, ψ_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 $\langle R_e\alpha\rangle$ between the wave functions ψ_U and ψ_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 Φ (see ref. 2); next the $\langle R_e\alpha\rangle$ matrix is expressed in terms of the basis functions; and finally the $\langle R_e\alpha\rangle$ basis matrix is transformed to the wave functions.

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

$$\left\langle \psi_U | R_e\alpha | \psi_L \right\rangle = T_U^{-1} \left\langle \Phi_U | R_e\alpha | \Phi_L \right\rangle T_L \tag{6}$$

where

$$\Phi = |\Lambda S\Sigma\rangle |\Omega J\rangle$$

is the product of an electronic and a rotational basis function with $\Omega = \Lambda + \Sigma$ and $T = T_{sym} T_{diag}$.

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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, α, 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 α (valid for isotropic radiation) listed in table 1.

The general selection rules $\Delta J = 0, \pm1$ and $\Delta\Omega = 0, \pm1$ are explicitly indicated in table 1. Separate matrices for the P-, Q-, and R-branches are formed, depending on the value of ΔJ. 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 $^2\Pi \leftarrow {}^4\Sigma^+$ transition is shown in table 2. The rows of the matrix are designated by the final state basis functions and the columns by the initial state basis functions. The number of independent matrix elements can be reduced because symmetric matrix elements are related. Symmetric matrix elements are those that interchange when the signs of both Λ and Σ are changed in both the upper and lower electronic states ($R_{e_1}\alpha_1$ and $R_{e_{10}}\alpha_{10}$ in table 2, for example).

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

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

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

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

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

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

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

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 $\langle R_e\alpha\rangle$ 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 $\langle R_e\alpha\rangle$ basis matrix, and the line strength (eq. (5)) can be written as

$$\langle S_{J'J''}\rangle = q_{v'v''}R_e^2|T_U^{-1}\langle \Phi_U|\alpha|\Phi_L\rangle T_L|^2 \tag{7}$$

$$= q_{v'v''}R_e^2\langle \mathscr{S}_{J'J''}\rangle \tag{8}$$

and the matrix elements of $\langle \mathscr{S}_{J'J''}\rangle$, which are the rotational line intensity factors or Hönl-London factors, only involve the transformed rotational matrix elements α; that is,

$$\langle \mathscr{S}_{J'J''}\rangle = |T_U^{-1}\langle \Phi_U|\alpha|\Phi_L\rangle T_L|^2 \tag{9}$$

$$= |\langle \psi_U|\alpha|\psi_L\rangle|^2 \tag{10}$$

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

$$\langle \psi_U|R_e\alpha|\psi_L\rangle = \langle R_{e_1}\bar{\alpha}_1 + R_{e_2}\bar{\alpha}_2 + \cdots\rangle \tag{11}$$

where $\bar{\alpha}_i$ is the transformed rotational matrix element associated with R_{e_i}.

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

$$\langle S_{J'J''}\rangle = q_{v'v''}R_{e_l}^2|\langle \rho\bar{\alpha}_i + \sigma\bar{\alpha}_j + \tau\bar{\alpha}_k + \cdots\rangle|^2 \tag{12}$$

where

$$\rho = \frac{R_{e_i}}{R_{e_l}} \, , \qquad \sigma = \frac{R_{e_j}}{R_{e_l}} \, , \qquad \tau = \frac{R_{e_k}}{R_{e_l}} \, , \qquad \text{etc.}$$

The factors σ, τ, etc., are called intensity parameters. The squares of the matrix elements in equation (12) are called the rotational line intensity factors and are defined as

$$\langle \mathscr{S}_{J'J''} \rangle = |\langle \rho\overline{\alpha}_i + \sigma\overline{\alpha}_j + \tau\overline{\alpha}_k + \cdots \rangle|^2 \tag{13}$$

If equations (12) and (13) are combined, the rotational line strength for spin-forbidden transitions can be written in the same form as spin-allowed transitions (eq. (8)); that is,

$$\langle S_{J'J''} \rangle = q_{v'v''} R_{e_l}^2 \langle \mathscr{S}_{J'J''} \rangle \tag{14}$$

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

1. Spin-allowed transition

$$\Sigma \mathscr{S}_{J'J''}(J) = (2 - \delta_{0,(\Lambda'+\Lambda'')})(2S + 1)(2J + 1) \tag{15}$$

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

2. For each transition moment in spin-forbidden transitions

$$\Sigma \mathscr{S}_{J'J''}(J) = C(2J + 1) \tag{16}$$

where $C = 1$ if the transition moment occurs only once in the $\langle R_e\alpha \rangle$ basis matrix and $C = 2$ if the transition moment occurs twice in the $\langle R_e\alpha \rangle$ basis matrix. The only transition moments that occur only once in any $\langle R_e\alpha \rangle$ basis matrix are those for the $\Omega' = 0$ to $\Omega'' = 0$ transition of $\Sigma \leftrightarrow \Sigma$ transitions of odd multiplicity. This transition moment is nonzero for $\Sigma^{\pm} \leftrightarrow \Sigma^{\pm}$ transitions with $\Delta S = 0$, 2, etc. and for $\Sigma^{\pm} \leftrightarrow \Sigma^{\mp}$ transitions with $\Delta S = 1$, 3, 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 $|\Lambda S \Sigma \rangle |\Omega J \rangle$ as follows:

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

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

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 $(2 - \delta_{0,\Lambda})(2S + 1)$ rows and columns. However, if $\Lambda \neq 0$ the two submatrices for $+\Lambda$ and $-\Lambda$ are mirror images. An example case is shown in table 5 for a $^2\Pi$ electronic state. As there are no off diagonal terms between $+\Lambda$ and $-\Lambda$, these two submatrices do not interact. It is therefore only necessary to operate on one of these submatrices, and, when needed, the full operator matrix can easily be constructed.

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

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

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

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

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

1. Nonsigma states

$$H(K,K) = -\Omega^2 - \Sigma^2 + Y\Lambda\Sigma \tag{17}$$

$$H(K,K+1) = -[(J - \Omega)(J + \Omega + 1)(S - \Sigma)(S + \Sigma + 1)]^{1/2} \tag{18}$$

$$H(K+1,K) = H(K,K+1) \tag{19}$$

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2. Sigma states

$$H(K,K) = -\Omega^2 - \Sigma^2 + \Delta E/B \tag{20}$$

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

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

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

Designation of Rotational Levels

In the standard notational scheme, the rotational levels of diatomic molecules are designated by two parameters in addition to J: (a) the rotational quantum number N, exclusive of spin and (b) the spin substate F_1, F_2, . . . , 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_i for the spin substates, when $J \geq \Lambda + S$, are related as follows:

$$\left. \begin{array}{lll} F_1 & \Rightarrow J = N + S & \text{or} \quad N = J - S \\[4pt] F_2 & \Rightarrow J = N + S - 1 & \text{or} \quad N = J - S + 1 \\ \quad \cdot & \quad \cdot & \qquad \cdot \\ \quad \cdot & \quad \cdot & \qquad \cdot \\ \quad \cdot & \quad \cdot & \qquad \cdot \\ F_{2S+1} & \Rightarrow J = N - S & \text{or} \quad N = J + S \end{array} \right\} \tag{21}$$

From these equations it is clear that for the group of F_i 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 $\vec{N} = \vec{\Lambda} + \vec{R}$, the difference between these N values is due to the difference in rotational energey, $\vec{R}$. Thus, for the group of F_i 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 Ω, where $\Omega = \Lambda + \Sigma$, to the F_i levels depends on whether the electronic state is regular or inverted. In regular states the smallest value of Ω 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_i, 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 Ω is assigned to each F_i substate based on whether the electronic state is regular or inverted.

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

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

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

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

Much of the discussion above for nonsigma states also holds for sigma states ($\Lambda = 0$), but the designation of the rotational levels with N, F_i, and J is the same in both regular and inverted states. The assignment for a $^3\Sigma$ electronic state is illustrated in figure 5. The concept of Ω 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_i assignment of the upper and lower substates. The assignment of letters to indicate the values of ΔJ and ΔN is summarized in figure 6. The selection rules for dipole radiation limits ΔJ to 0 or ± 1. The branch designation scheme is illustrated in figure 7. If $\Delta N = \Delta J$, the upper letter is not included and if $F_i' = F_i''$, only one subscript number is included (i.e., $^R R_{22} = R_2$ in fig. 7).

The energy change during a transition is usually more closely associated with ΔN than with ΔJ. Therefore, the form of the branch is also primarily controlled by ΔN. Hence, the $^R Q_{32}$ 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 ΔJ. 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_i' assignments for a given value of J' and similarly the columns by F_i'' 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_i 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 $\langle R_e \alpha \rangle$ 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 $\Lambda > 0$.

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 Λ-doublet in $X \leftrightarrow Y$ transitions (X and Y represent any nonsigma electronic states), and if we combine the two submatrices in $\Sigma \leftrightarrow X$ 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 $<\alpha>$ basis matrix elements from the $+\Lambda$ submatrix and by neglecting the symmetrizing transformation. Thus, for spin-allowed transitions, all the required matrix elements occur in the upper left submatrix. For $\Sigma \leftrightarrow \Pi$ transitions, however, 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 $^3\Sigma \rightarrow {}^3X$ 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 $^3X \rightarrow {}^3\Sigma$ transitions is similar except that left and right submatrices replace upper and lower submatrices. The generalization to any multiplicity is straightforward.

For $^3X \leftrightarrow {}^3Y$ 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 $\overline{\alpha}_i$ values shown in equation (13) and

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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.

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Table 6 shows the $\langle R_e \alpha \rangle$ 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 $\langle R_e \alpha \rangle$ 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(upper, lower)).

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

The rotational line intensity factors of the two lines forming a Λ-doublet in spin-forbidden transitions are not equal if the line strengths contain at least one $\langle R_e \alpha \rangle$ matrix element between basis functions with opposite signs on Λ' and Λ'' (i.e., $\langle \pm \Lambda' | R_e \alpha | \mp \Lambda'' \rangle$) and at least one matrix element with the same signs on Λ' and Λ''. 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 $^4\Sigma^+ \leftrightarrow {}^4\Sigma^-$ transition, shown in table 7, has five independent transition moments.

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

The rotational line intensity factors (Hönl-London factors) for spin-allowed transitions and the transformed rotational matrix elements for spin-forbidden transitions are stored in the SAVE array until the calculation is complete. The SAVE array is three-dimensional and can be viewed conveniently, as shown in figure 13. The three dimensions correspond to (1) the number of independent transition moments in the transition (maximum of nine), (2) the number of branches in a vibrational band (maximum of 150, there are

147 branches in spin-allowed septet-septet transitions), and (3) the number of rotational lines in each branch included in the calculation (maximum of 200). In the dimension for storing branches, the R-branches are stored in the first 50 locations, the Q-branches in the second 50, and the P-branches in the last 50. Any dimensions of the SAVE array can be changed to any desired value, limited only by the size of the computer memory.

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

Input Data and Sample Cases

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

The data needed to initiate a calculation are:

1. The resultant spin S of each state.

2. The Λ value of each state.

3. The $\pm$ symmetry for Σ states.

4. The spin-orbit and/or spin-spin parameters (see appendix C).

5. The values of J_{min} and J_{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 $^3\Pi \leftarrow {}^5\Sigma^-$ transition; and that in table 11 is a spin-forbidden $^2\Pi \leftarrow {}^4\Pi$ 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 (Σ) state $\Delta E/B$ is specified as -10; therefore, it is an inverted state. The spin-orbit coupling ($Y = A/B$) of the lower (Π) 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

$$SUM = R1 + QR12 + PR13 + Q1 + PQ12 + OQ13 + P1 + OP12 + NP13$$

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 $\Sigma \leftrightarrow \Sigma$ and for nonsigma to nonsigma transitions, and $2(2J + 1)$ for $\Sigma \leftrightarrow \Pi$ or $\Pi \leftrightarrow \Sigma$ 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, $\overline{\alpha}_i$. The intensity factors are formed from these numbers as shown in equation (13), which is repeated here for convenience:

$$\left\langle \mathscr{A}_{J'J''} \right\rangle = \left| \left\langle \rho\overline{\alpha}_i + \sigma\overline{\alpha}_j + \tau\overline{\alpha}_k + \ldots \right\rangle \right|^2$$

where ρ, σ, τ, 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 $\overline{\alpha}_i$ 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.

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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 $\overline{\alpha}_i$ 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 $\overline{\alpha}_i$ values whose associated transition moment designation contains a negative number.

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

Limitations and Capabilities of the Computer Program

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

The most important real limitation of the program is the neglect of interactions that decouple the orbital angular momentum $\vec{L}$ from the internuclear axis so that the intensity factors for the 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 $\pm\leftrightarrow\mp$, $\Sigma^{\pm}\leftrightarrow\Sigma^{\mp}$ magnetic dipole transitions must be specified as $\Sigma^{\pm}\leftrightarrow\Sigma^{\pm}$ 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

LISTING OF COMPUTER PROGRAM

```
C     THIS PROGRAM COMPUTES INTENSITY FACTORS FOR ALLOWED
C     TRANSITIONS (HONL-LONDON FACTORS), AND THE SQUARE ROOT
C     OF THE ROTATIONAL INTENSITY FACTORS FOR FORBIDDEN TRANSITIONS.
C
C     MAIN PROGRAM
C
      DIMENSION TITLE1(14),TITLE2(12),TITLE3(6),TITLE4(4),TITLE5(6),
     1      TITLE6(4),HEAD2(7,7,2),
     2      HEAD1(7),ALPHA(19,2)
C
      COMMON /CSOLVE/JF,JMIN,JMAX,SI,SF,LAMI,LAMF,
     1              SIGN1,ALLOW,EMISON,SIGSIG,IJ,IMAXI,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,SIGN1,SUM
C
      LOGICAL ALLOW,SIGSIG,HALF,EMISON
C
      REAL J
C
      DATA ABSORB/1HA/
C
      DATA TITLE1/4HSING,4HLET ,4HDOUB,4HLET ,4HTRIP,4HLET ,4HQUAR,
     1           .4HTET ,4HQUIN,4HTET ,4HSEXT,4HET ,4HSEPT,4HET  /
C
      DATA TITLE2/4H  SI,4HGMA ,4H  PI,4H     ,4H  DE,4HLTA ,
     1           4H  PH,4HI   ,4H  GA,4HMMA ,4H  OT,4HHER /
C
      DATA TITLE3/4HEMIS,4HSION,4H     ,4HABSO,4HRPTI,4HON  /
C
      DATA TITLE4/4HINIT,4HIAL ,4HFINA,4HL   /
C
      DATA TITLE5/4HREGU,4HLAR ,4HINVE,4HRTED,4H    ,4H     /
C
      DATA TITLE6/4HE. U,4HPPER,4HE. L,4HOWER/
C
      DATA HEAD2
     1  /2H1 ,2H12,2H13,2H14,2H15,2H16,2H17,
     2    2H21,2H2 ,2H23,2H24,2H25,2H26,2H27,
     3    2H31,2H32,2H3 ,2H34,2H35,2H36,2H37,
     4    2H41,2H42,2H43,2H4 ,2H45,2H46,2H47,
     5    2H51,2H52,2H53,2H54,2H5 ,2H56,2H57,
     6    2H61,2H62,2H63,2H64,2H65,2H6 ,2H67,
     7    2H71,2H72,2H73,2H74,2H75,2H76,2H7 ,
     8    2H1 ,2H21,2H31,2H41,2H51,2H61,2H71,
     9    2H12,2H2 ,2H32,2H42,2H52,2H62,2H72,
     1    2H13,2H23,2H3 ,2H43,2H53,2H63,2H73,
     2    2H14,2H24,2H34,2H4 ,2H54,2H64,2H74,
     3    2H15,2H25,2H35,2H45,2H5 ,2H65,2H75,
     4    2H16,2H26,2H36,2H46,2H56,2H6 ,2H76,
     5    2H17,2H27,2H37,2H47,2H57,2H67,2H7 /
C
      DATA ALPHA/1HZ,1HY,1HX,1HW,1HV,1HU,1HT,1HS,1HR,1HQ,
     1          1HP,1HO,1HN,1HM,1HL,1HK,1HJ,1HI,1HM,1HM,
     2          1HI,1HJ,1HK,1HL,1HM,1HN,1HO,1HP,1HQ,1HR,
     3          1HS,1HT,1HU,1HV,1HW,1HX,1HY,1HZ/
C
      DATA BLANK/1H /, R/1HR/, Q/1HQ/, P/1HP/
C
C     READ IN NEW CASE.
C
10    READ(5,501)  SI,LAMI,SIGNI, YI(1),YI(2),YI(3)
      READ(5,501)  SF,LAMF,SIGNF, YF(1),YF(2),YF(3)
      READ(5,502)  JMIN,JMAX
      READ(5,503)  TYPE
C
C     INITIALIZE LARGE SAVE ARRAY.
C
      DO 15 I=1,200
      DO 15 L=1,150
      DO 15 K=1,9
15    SAVE(K,L,I)=0.0
C
C     INITIALIZE TRANSITION MOMENT ARRAYS.
C
      DO 17 I=1,200
      NTRANR(I)=0
      NTRANQ(I)=0
      NTRANP(I)=0
      DO 17 L=1,30
      ITRANI(L,I)=0
17    ITRANF(L,I)=0
C
C     IS THIS AN EMISSION CALCULATION?
C
      EMISON=.TRUE.
      IF(TYPE.EQ.ABSORB) EMISON=.FALSE.
C
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.0.0D0) JMAX=JMIN+100.D0
      DELJ=JMAX-JMIN
      IF(DELJ.GT.199.1) JMAX=JMIN+199.0D0
C
```

```
C      IS THIS A SIGMA TO SIGMA TRANSITION?
C
       SIGSIG=.TRUE.
       IF(LAMI.GT..1.OR.LAMF.GT..1) SIGSIG=.FALSE.
C
C      IS THIS AN ALLOWED TRANSITION?
C
       IF((SI-SF).NE..0D0.OR.DABS(LAMI-LAMF).GT.1.1D0) GO TO 20
C
       IF(SIGSIG.AND.SIGNI.NE.SIGNF) GO TO 20
C
C      THIS IS AN ALLOWED TRANSITION.
C
       ALLOW=.TRUE.
       IMAXI=2.*SI+1.1
       IMAXF=IMAXI
       GO TO 30
C
C      THIS IS A FORBIDDEN TRANSITION.
C
20     ALLOW=.FALSE.
       IMAXI=2.*SI+1.1
       IMAXF=2.*SF+1.1
C
C      SET SIGN OF SYMMERTRIC MATRIX ELEMENTS IN THE Q BRANCH MATRIX.
C
       SIGN1=+1.0D0
       IF(.NOT.SIGSIG) GO TO 30
       IDELS=DABS(SF-SI)+.1
       I=1
       IF(SIGNI.NE.SIGNF) I=0
       SIGN1=(-1)**(IDELS+I)
C
C      IS SPIN HALF INTEGER OR WHOLE INTEGER?
C
30     IS=SI+.1
       SI=IS
       HALF=.TRUE.
       IF(DABS(SI-SI).LT..1D0) HALF=.FALSE.
C
C      JMIN AND JMAX MUST BE HALF INTEGER OR WHOLE INTEGER IN
C      ACCORD WITH THE SPIN.
C
       JTEST=JMIN+.1D0
       J=JTEST
       IF(HALF) GO TO 35
       IF(DABS(JMIN-J).GT..1) JMIN=JMIN+0.5D0
       GO TO 37
35     IF(DABS(JMIN-J).LT..1) JMIN=JMIN+0.5D0
37     JTEST=JMAX+.1D0
       J=JTEST
       IF(HALF) GO TO 39
       IF(DABS(JMAX-J).GT..1) JMAX=JMAX+0.5D0
       GO TO 40
39     IF(DABS(JMAX-J).LT..1) JMAX=JMAX+0.5D0
C
C      FIND MINIMUM VALUES FOR JI AND JF AND
C      ADJUST JMIN IF NECESSARY.
C
40     JI=LAMI-SI
       IF(JI.GE.0.0D0) GO TO 45
       JI=0.0D0
       IF(HALF) JI=0.5D0
45     IF((JI-JMIN).GT..1) JMIN=JI
C
       JF=LAMF-SF
       IF(JF.GE.0.0D0) GO TO 50
       JF=0.0D0
       IF(HALF) JF=0.5D0
C
50     IF(JMIN-JF) 55,65,60
C
55     IF((JMIN-JF).LT.-1.1D0) JMIN=JF-1.0D0
       GO TO 65
C
60     IF((JMIN-JF).GT. 1.1D0) JF=JMIN-1.0D0
C
65     CALL SOLVE
C
C      PRINT HEADING
C
       WRITE(6,600)
C
       IF(ALLOW) GO TO 70
       WRITE(6,601)
       GO TO 75
70     WRITE(6,602)
75     ILAMI=LAMI+.1
       IF(ILAMI.GT.5) ILAMI=5
       ILAMF=LAMF+.1
       IF(ILAMF.GT.5) ILAMF=5
       INDEX=4
       IF(EMISON)    INDEX=1
       I2=INDEX+2
C
       INDEX2=5
       IF(LAMI.LT..1D0.AND.SI.LT..6D0) GO TO 77
```

```
        IF(SI.LT..1D0) GO TO 77
        INDEX2=1
        IF(YI(1).LT.0.0D0) INDEX2=3
77      INDEX3=5
        IF(LAMF.LT..1D0.AND.SF.LT..6D0) GO TO 80
        IF(SF.LT..1D0) GO TO 80
        INDEX3=1
        IF(YF(1).LT.0.0D0) INDEX3=3
C
80      WRITE(6,603) TITLE5(INDEX2),TITLE5(INDEX2+1),TITLE1(2*IMAXI-1),
     1    TITLE1(2*IMAXI),TITLE2(2*ILAMI+1),TITLE2(2*ILAMI+2),SIGNI,
     2    TITLE5(INDEX3),TITLE5(INDEX3+1),TITLE1(2*IMAXF-1),
     3    TITLE1(2*IMAXF),TITLE2(2*ILAMF+1),TITLE2(2*ILAMF+2),SIGNF,
     4    (TITLE3(I),I=INDEX,I2)
C
        IF(IMAXI.EQ.1) GO TO 85
        IF(ILAMI.EQ.0) GO TO 82
        WRITE(6,604) TITLE4(1),TITLE4(2),YI(1)
        GO TO 85
C
82      IF(SI.LT..9D0) GO TO 85
        IS=SI
        I1=1
        IF(HALF) I1=2
        WRITE(6,611) TITLE4(1),TITLE4(2),YI(1)
C
        IF(SI.LT.1.9D0) GO TO 85
        I2=1
        IF(SI.GT.2.6D0) I2=2
C
        DO 84 I=1,I2
        I3=I+1
84      WRITE(6,612) I3,YI(I+1)
C
85      IF(IMAXF.EQ.1) GO TO 90
        IF(ILAMF.EQ.0) GO TO 87
        WRITE(6,604) TITLE4(3),TITLE4(4),YF(1)
        GO TO 90
C
87      IF(SF.LT..9D0) GO TO 90
        IS=SF
        I1=1
        IF(HALF) I1=2
        WRITE(6,611) TITLE4(3),TITLE4(4),YF(1)
C
        IF(SF.LT.1.9D0) GO TO 90
        I2=1
        IF:SF.GT.2.6D0) I2=2
C
        DO 89 I=1,I2
        I3=I+1
89      WRITE(6,612) I3,YF(I+1)
C
90      IF(LAMI.LT..1D0.AND.SI.GT..6D0) GO TO 95
        IF(LAMF.GT..1D0.OR.SF.LT..6D0) GO TO 100
95      WRITE(6,613)
C
100     IF(LAMI.LT..1D0.OR.LAMF.LT..1D0) GO TO 120
        IF(ALLOW) GO TO 110
C
        WRITE(6,614)
        GO TO 120
C
110     WRITE(6,615)
C
120     INDEX=3
        IF(EMISON)    INDEX=1
        WRITE(6,605) TITLE6(INDEX),TITLE6(INDEX+1)
C
C       PRINT DATA
C
        II=2
        IF(EMISON) II=1
C
C       IS THIS AN ALLOWED TRANSITION?
C
        IF(ALLOW) GO TO 190
C
C       THIS IS A FORBIDDEN TRANSITION.
C
        IDELS=0
        DELS=SI-SF
        IF(ABS(DELS).LT..1) GO TO 124
        IF(DELS.GT.0.) GO TO 122
        IDELS=-1
        IF(DELS.LT.-1.1) IDELS=-2
        GO TO 124
122     IDELS=1
        IF(DELS.GT.1.1) IDELS=2
C
C       PRINT R BRANCHES.
C
124     DO 140 K=1,IMAXI
        DO 125 I=1,IMAXF
        N1=9+IDELS-(K-1)+(I-1)+2*(II-1)
        HEAD1(I)=ALPHA(N1,II)
```

```
       IF(HEAD1(I).EQ.R) HEAD1(I)=BLANK
125    CONTINUE
       WRITE(6,606) (HEAD1(I),R,HEAD2(I,K,II),I=1,IMAXF)
C
       DO 140 I=1,IJ
       DELJ=I-1
       J=JMIN+DELJ
       WRITE(6,607)
C
       KO=(K-1)*7
       K1=KO+1
       K2=KO+IMAXF
       K3=NTRANR(I)
       DO 130 NTRAN=1,K3
       SUM=0.ODO
       DO 128 KK=K1,K2
128    SUM=SUM+SAVE(NTRAN,KK,I)**2
130    WRITE(6,608) J,SUM,ITRANF(NTRAN,I), ITRANI(NTRAN,I),
      1               (SAVE(NTRAN,KK,I),KK=K1,K2)
C
140    CONTINUE
C
C      PRINT Q BRANCHES.
C
       DO 160 K=1,IMAXI
       DO 145 I=1,IMAXF
       N1=10+IDELS-(K-1)+(I-1)
       HEAD1(I)=ALPHA(N1,II)
       IF(HEAD1(I).EQ.Q) HEAD1(I)=BLANK
145    CONTINUE
       WRITE(6,606) (HEAD1(I),Q,HEAD2(I,K,II),I=1,IMAXF)
C
       DO 160 I=1,IJ
       DELJ=I-1
       J=JMIN+DELJ
       WRITE(6,607)
C
       KO=50+(K-1)*7
       K1=KO+1
       K2=KO+IMAXF
       K3=NTRANQ(I)
       DO 150 NTRAN=1,K3
       SUM=0.ODO
       DO 148 KK=K1,K2
148    SUM=SUM+SAVE(NTRAN,KK,I)**2
150    WRITE(6,608) J,SUM,ITRANF(NTRAN+10,I),ITRANI(NTRAN+10,I),
      1               (SAVE(NTRAN,KK,I),KK=K1,K2)
C
160       CONTINUE
C
C      PRINT P BRANCHES.
C
       DO 180 K=1,IMAXI
       DO 165 I=1,IMAXF
       N1=11+IDELS-(K-1)+(I-1)-2*(II-1)
       HEAD1(I)=ALPHA(N1,II)
       IF(HEAD1(I).EQ.P) HEAD1(I)=BLANK
165    CONTINUE
       WRITE(6,606) (HEAD1(I),P,HEAD2(I,K,II),I=1,IMAXF)
C
       DO 180 I=1,IJ
       DELJ=I-1
       J=JMIN+DELJ
       WRITE(6,607)
C
       KO=100+(K-1)*7
       K1=KO+1
       K2=KO+IMAXF
       K3=NTRANP(I)
       DO 170 NTRAN=1,K3
       SUM=0.ODO
       DO 168 KK=K1,K2
168    SUM=SUM+SAVE(NTRAN,KK,I)**2
170    WRITE(6,608) J,SUM,ITRANF(NTRAN+20,I),ITRANI(NTRAN+20,I),
      1               (SAVE(NTRAN,KK,I),KK=K1,K2)
C
180    CONTINUE
C
C      END OF CASE, READ IN NEXT CASE.
C
       GO TO 10
C
C      THIS IS AN ALLOWED TRANSITION.
C
C      PRINT R BRANCHES.
C
190    DO 210 K=1,IMAXI
       DO 195 I=1,IMAXF
       N1=9-(K-1)+(I-1)+2*(II-1)
       HEAD1(I)=ALPHA(N1,II)
       IF(HEAD1(I).EQ.R) HEAD1(I)=BLANK
195    CONTINUE
       WRITE(6,609) (HEAD1(I),R,HEAD2(I,K,II),I=1,IMAXF)
C
       DO 210 I=1,IJ
       DELJ=I-1
```

```
        J=JMIN+DELJ
        SUM=0.0D0
C
        KO=(K-1)*7
        K1=KO+1
        K2=KO+IMAXI
        DO 200 KK=K1,K2
        K3=KK+50
        K4=KK+100
200     SUM=SUM+SAVE(1,KK,I)+SAVE(1,K3,I)+SAVE(1,K4,I)
        WRITE(6,610) J,SUM,(SAVE(1,KK,I),KK=K1,K2)
        IF(((I/5)*5-I).EQ.0) WRITE(6,607)
C
210     CONTINUE
C
C       PRINT Q BRANCHES.
C
        DO 230 K=1,IMAXI
        DO 215 I=1,IMAXF
        N1=10-(K-1)+(I-1)
        HEAD1(I)=ALPHA(N1,II)
        IF(HEAD1(I).EQ.Q) HEAD1(I)=BLANK
215     CONTINUE
        WRITE(6,609) (HEAD1(I),Q,HEAD2(I,K,II),I=1,IMAXF)
C
        DO 230 I=1,IJ
        DELJ=I-1
        J=JMIN+DELJ
        SUM=0.0D0
C
        KO=50+(K-1)*7
        K1=KO+1
        K2=KO+IMAXI
        DO 220 KK=K1,K2
        K3=KK-50
        K4=KK+50
220     SUM=SUM+SAVE(1,KK,I)+SAVE(1,K3,I)+SAVE(1,K4,I)
        WRITE(6,610) J,SUM,(SAVE(1,KK,I),KK=K1,K2)
        IF(((I/5)*5-I).EQ.0) WRITE(6,607)
C
230     CONTINUE
C
C       PRINT P BRANCHES
C
        DO 250 K=1,IMAXI
        DO 235 I=1,IMAXF
        N1=11-(K-1)+(I-1)-2*(II-1)
        HEAD1(I)=ALPHA(N1,II)
        IF(HEAD1(I).EQ.P) HEAD1(I)=BLANK
235     CONTINUE
        WRITE(6,609) (HEAD1(I),P,HEAD2(I,K,II),I=1,IMAXF)
C
        DO 250 I=1,IJ
        DELJ=I-1
        J=JMIN+DELJ
        SUM=0.0D0
C
        KO=100+(K-1)*7
        K1=KO+1
        K2=KO+IMAXI
        DO 240 KK=K1,K2
        K3=KK-100
        K4=KK-50
240     SUM=SUM+SAVE(1,KK,I)+SAVE(1,K3,I)+SAVE(1,K4,I)
        WRITE(6,610) J,SUM,(SAVE(1,KK,I),KK=K1,K2)
        IF(((I/5)*5-I).EQ.0) WRITE(6,607)
C
250     CONTINUE
C
C       END OF CASE, READ IN NEXT CASE.
C
        GO TO 10
C
C       READ FORMAT STATEMENTS.
C
501     FORMAT(F3.1,2X,F2.0,2X,A1,3E10.0)
502     FORMAT(2F5.1)
503     FORMAT(A1)
C
C       WRITE FORMAT STATEMENTS.
C
600     FORMAT(1H1,52X,26HINTENSITY FACTOR PROGRAMME,/          -
       1        45X,41HNASA-AMES/CRESS/E E WHITING   AUGUST 1972,///)
601     FORMAT(32X,43HSQUARE ROOT OF ROTATIONAL INTENSITY FACTORS,  -
       1        18H FOR THE FORBIDDEN,//)
602     FORMAT(48X,35HHONL-LONDON FACTORS FOR THE ALLOWED,/)
603     FORMAT(27X,2A4,1X,4A4,A1,4H TO ,2A4,1X,4A4,A1,15H TRANSITION IN ,3A4//)
604     FORMAT(35X,2A4,47HSTATE SPIN-ORBIT COUPLING CONSTANT = A/B = Y = ,F8.3)
605     FORMAT(//,43X,29HJ VALUE IS FOR THE INITIAL (I,2A4,8H) STATE.)
606     FORMAT(//,16X,7HPARTIAL,3X,10HTRANSITION,/10X,1HJ,7X,3HSUM,6X,6HMOMENT,7(7X,A1,A1,A2,4X))
607     FORMAT(10X)
608     FORMAT(7X,0PF5.1,F11.6,5X,I2,1H,,I1,1X,7(3X,1PE12.5))
609     FORMAT(//10X,1HJ,7X,3HSUM,2X,7(7X,A1,A1,A2,4X)//)
610     FORMAT(7X,0PF5.1,F11.6,7(3X,1PE12.5))
611     FORMAT(35X,2A4,47HSTATE ENERGY SEPARATION =        DELTA E(1)/B = ,F8.3)
612     FORMAT(75X,8HDELTA E(,I1,6H)/B = ,F8.3)
```

```
613   FORMAT(//27X,58HIN SIGMA STATES WHEN J<S, THE F DESIGNATION FOR THE LEVELS,
      1            /27X,53HWITH THE SAME VALUE OF J ARE ASSIGNED AS 2S+1 FOR THE,
      2            /27X,51HHIGHEST ENERGY LEVEL, 2S FOR THE NEXT HIGHEST, ETC.)
C
614   FORMAT(//27X,59HLAMBDA DOUBLING OCCURS IN THE SPECTRUM, BUT THE SQUARE ROOT,
      1            17H OF THE INTENSITY/27X,40HFACTORS FOR ONLY ONE LINE OF EACH LAMBDA,
      2            40H DOUBLET IS PRINTED.  THE VALUES FOR THE/27X,12HOTHER LAMBDA,
      3            58H 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 HONL-LONDON,
      1            21H FACTORS FOR ONLY ONE/27X,39HLINE OF EACH LAMBDA DOUBLET IS PRINTED.
      2            39H  THE HONL-LONDON FACTORS FOR THE OTHER/27X,17HLAMBDA COMPONENTS,
      3            14H ARE THE SAME.)
      END
```

```
      SUBROUTINE SOLVE
C
C     THIS PROGRAM:
C         1-DEVELOPES THE ROTATIONAL HAMILTONIAN.
C         2-CALLS EIGEN TO GET THE EIGEN VECTORS OF THE HAMILTONIAN.
C         3-DEVELOPES THE ROTATIONAL MATRIX.
C         4-TRANSFORMS THE ROTATIONAL MATRIX.
C         5-STORES, IN THE LARGE SAVE ARRAY, HONL-LONDON FACTORS
C             FOR ALLOWED TRANSITIONS AND THE SQUARE ROOT OF
C             ROTATIONAL INTENSITY FACTORS FOR FORBIDDEN TRANSITIONS.
C
      DIMENSION T(14,14),TI(14,14),TF1(14,14),TF2(14,14),A(14,14),
     1          C(14,14),H(7,7),SYM(7,7)
C
      COMMON /CSOLVE/JF,JMIN,JMAX,SI,SF,LAMI,LAMF,
     1            SIGN1,ALLOW,EMISON,SIGSIG,IJ,IMAXI,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
      COMMON/CEIGEN/HH(28),TT(49),N
C
      DOUBLE PRECISION A,DELJ,JMIN,JMAX,J,JI,JF,Y(3),YI,YF,LAM,LAMI,
     1 LAMF,S,SI,SF,H,HH,W,HOLD,TT,T,TI,TF1,TF2,OMEGA,OMEGAI,C,
     2 OMEGAF,EI,EK,SUM,FACTOR,SIGN,SIGN1,SIGN2,SIZE,SYM,
     3 C1
      LOGICAL ALLOW,EMISON,SIGSIG,FIRST
C
      REAL INITAL
C
      DATA R/1HR/, Q/1HQ/, P/1HP/, FINAL/1HF/, INITAL/1HI/
C
      INTEGER SAVE1,SAVE2,SAVE3,SAVE4,SAVE5,SAVE6
C
C     INITIALIZE MATRICES.
C     AND SET FLAG FOR FIRST COMPUTATION.
C
      DO 10  I=1,14
      DO 10  K=1,14
      TI(K,I)=0.0D0
      TF1(K,I)=0.0D0
      TF2(K,I)=0.0D0
      C(K,I)=0.0D0
10    A(K,I)=0.0D0
      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 900 IJ=1,200
      DELJ=IJ-1
      JI=JMIN+DELJ
C
C     SET VALUES FOR INITIAL LEVEL CALCULATION.
C
      J=JI
      LAM=LAMI
      S=SI
      IMAX=IMAXI
      STATE=INITAL
      DO 15 I=1,3
15    Y(I)=YI(I)
      GO TO 30
C
C     SET VALUES FOR FINAL LEVEL CALCULATION.
C
20    J=JF
      LAM=LAMF
      S=SF
      IMAX=IMAXF
      STATE=FINAL
      DO 25 I=1,3
25    Y(I)=YF(I)
C
C     INITIALIZE HAMILTONIAN AND TRANSFORMATION MATRICES.
C
30    DO 35 I=1,7
      DO 35 K=1,7
35    H(K,I)=0.0D0
      DO 40 I=1,14
      DO 40 K=1,14
40    T(K,I)=0.0D0
      DO 45 I=1,28
45    HH(I)=0.0D0
      DO 47 I=1,49
47    TT(I)=0.0D0
C
C     THE HAMILTONIAN MATRIX IS REDUCED AT LOW J VALUES.
C     SET INDECIES DEFINING WHICH ROWS AND COLUMNS HAVE NON-ZERO ELEMENT
C
      OMEGA=LAM+S
      IF((J+.1).LT.OMEGA) GO TO 50
```

```
C
C       HAMILTONIAN IS FULLY DEVELOPEC.
C
        I1=1
        I2=IMAX
        GO TO 110
C
C       HAMILTONIAN IS REDUCED.
C
50      TEST=OMEGA
        DO 60 I=1,IMAX
        I1=I+1
        TEST=TEST-1.0
        IF((J+.1).GT.TEST) GO TO 70
60      CONTINUE
        I1=IMAX
        GO TO 80
C
70      IF(J.GT..1) GO TO 100
C
C       THERE IS ONLY ONE ELEMENT IN THE HAMILTONIAN.
C       SET TRANSFORMATION MATRIX.
C
80      I2=I1
C
90      T(1,1)= (-1)**I1
        N=1
        GO TO 240
C
C       THERE MAY BE MORE THAN ONE ELEMENT IN THE
C       HAMILTONIAN MATRIX.
C
100     I2=2.*J+.1
        I2=I1+I2
        IF(I2.GT.IMAX) I2=IMAX
C
C       IS THERE MORE THAN ONE ELEMENT IN THE
C       HAMILTONIAN MATRIX?
C
110     IF(I2.EQ.I1) GO TO 90
C
C       THERE IS MORE THAN ONE ELEMENT IN THE
C       HAMILTONIAN MATRIX. SET SIZE OF MATRIX.
C
        N=I2-I1+1
C
C       DEVELOP UPPER HALF OF SYMMETRICAL HAMILTONIAN MATRIX.
C       J(J+1) AND S(S+1) TERMS IN THE DIAGONAL ELEMENTS ARE NOT INCLUDED.
C
        K=0
        I3=I2-1
        DO 120 I=I1,I3
        K=K+1
        EI=I
        H(K,K+1)=-OSQRT((J-OMEGA+EI)*(J+OMEGA-EI+1.0DO)*EI*(2.0DO*S-EI+1.0DO))
        H(K+1,K)=H(K,K+1)
120     H(K,K)=-(OMEGA-EI+1.DO)**2-(S-EI+1.DO)**2
C
        EI=I2
        K=K+1
        H(K,K)   =-(OMEGA-EI+1.DO)**2-(S-EI+1.DO)**2
C
C       IS THIS A SIGMA STATE?
C
        K=0
        IF(LAM.LT..1DO) GO TO 140
C
C       THIS IS NOT A SIGMA STATE.
C       INCLUDE SPIN-ORBIT INTERACTION (Y=A/B).
C
        DO 130 I=I1,I2
        K=K+1
        EI=I
130     H(K,K)=H(K,K)+Y(1)*LAM*(S-EI+1.DO)
        GO TO 152
C
C       THIS IS A SIGMA STATE.
C       INCLUDE SPIN-ORBIT + SPIN-SPIN ENERGY SEPERATIONS (DELTA E/B).
C
140     DO 150 I=I1,I2
        K=K+1
C
        GO TO(152,152,141,142,143,144,145), IMAX
C
141     IF(I.EQ.2) GO TO 150
        I3=1
        GO TO 146
C
142     IF(I.EQ.2.OR.I.EQ.3) GO TO 150
        I3=1
        GO TO 146
C
143     IF(I.EQ.3) GO TO 150
        I3=2
        IF(I.EQ.2.OR.I.EQ.4) I3=1
        GO TO 146
C
```

```
144   IF(I.EQ.3.OR.I.EQ.4) GO TO 150
      I3=2
      IF(I.EQ.2.OR.I.EQ.5) I3=1
      GO TO 146
145   IF(I.EQ.4) GO TO 150
      I3=3
      IF(I.NE.1.OR.I.NE.7) I3=2
      IF(I.EQ.3.OR.I.EQ.5) I3=1
C
146   H(K,K)=H(K,K)+Y(I3)
150   CONTINUE
C
C     IS SYMMETRIZING MATRIX NECESSARY?
C     NEEDED FOR NON-SINGLET SIGMA STATES IN FORBIDDEN TRANSITIONS.
C
152   IF(ALLOW.OR.LAM.GT..1.OR.S.LT..1) GO TO 225
C
C     CONSTRUCT SYMMETRIZING MATRIX.
C
      IF(N.EQ.NSAVE) GO TO 180
      NSAVE=N
      DO 155 I=1,7
      DO 155 K=1,7
155   SYM(I,K)=0.0D0
C
      C1=.707106781D0
      K=0
C
160   K=K+1
      KK=N+1-K
      IF(K.EQ.KK) GO TO 170
      SYM(K,K)=C1
      SYM(KK,K)=C1
      SYM(K,KK)=C1
      SYM(KK,KK)=-C1
C
      IF((KK-K).GT.1) GO TO 160
      GO TO 180
C
170   SYM(K,K)=1.0D0
C
C     SYMMETRIZE HAMILTONIAN MATRIX IF REQUIRED.
C
180   DO 200 I=1,N
      DO 200 K=1,N
      C(K,I)=0.0D0
      DO 190 KK=1,N
190   C(K,I)=C(K,I)+H(K,KK)*SYM(KK,I)
200   CONTINUE
C
      DO 220 I=1,N
      DO 220 K=1,N
      H(K,I)=0.0D0
      DO 210 KK=1,N
210   H(K,I)=H(K,I)+SYM(K,KK)*C(KK,I)
220   CONTINUE
C
C     TRANSFORM UPPER HALF OF SYMMETRICAL HAMILTONIAN INTO A ONE-DIMENSIONAL
C     ARRAY, HH TO BE COMPATIBLE WITH EIGENFUNCTION SUBROUTINE.
C
225   KK=0
      DO 230 I=1,N
      DO 230 K=1,I
      KK=KK+1
230   HH(KK)=H(K,I)
C
C     CALL SUBROUTINE TO FIND THE EIGENFUNCTIONS OF
C     THE HAMILTONIAN MATRIX BY JACOBI-VON NEUMAN METHOD.
C     EIGENFUNCTIONS ARE ORDERED IN A ONE-DIMENSIONAL ARRAY, TT WITH
C     THE LARGEST EIGENVALUE FIRST, ETC.
C
      CALL EIGEN
C
C     EXPAND THE ONE-DIMENSIONAL ARRAY, TT INTO THE TWO-DIMENSIONAL
C     TRANSFORMATION MATRIX,T THAT DIAGONALIZES THE HAMILTONIAN.
C     ENSURE CONSISTANT PHASE OF THE EIGENFUNCTIONS BY MAKING
C     THE FIRST ELEMENT IN EACH COLUMN NEGATIVE.
C
      KK=0
      DO 235 I=1,N
      C1=1.0D0
      IF(TT(KK+1).GT. 0.) C1=-1.0D0
      DO 235 K=1,N
      KK=KK+1
235   T(K,I)=C1*TT(KK)
C
C     IF THIS IS A FORBIDDEN TRANSITION AND IF
C     THIS STATE IS NOT A SIGMA STATE, EXPAND THE
C     TRANSFORMATION MATRIX TO ALLOW FOR LAMBDA DOUBLING.
C
240   NN=N
      IF(ALLOW.OR. LAM.LT..1) GO TO 260
C
C     EXPAND THE TRANSFORMATION MATRIX.
C
      NN=2*N
      II=NN+1
```

```
         DO 250 I=1,N
         DO 250 K=1,N
         K3=11-K
         I3=11-I
250      T(K3,I3)=T(K,I)
C
C        TRANSFER T MATRIX INTO INITIAL (TI) OR FINAL (TF)
C        MATRIX. SET FLAGS AND INDECIES FOR PROPER BRANCHES
C        PRELIMINARY TO DEVELOPING THE ROTATIONAL MATRIX.
C
C        IS THIS THE INITIAL OR THE FINAL STATE?
C
260      IF(STATE.EQ.FINAL) GO TO 280
C
C        THIS IS THE INITIAL STATE.
C        TRANSFER THE T MATRIX    INTO THE TI MATRIX.
C        SET INDECIES FOR INITIAL STATE.
C
         DO 270 I=1,NN
         DO 270 K=1,NN
270      TI(I,K)=T(I,K)
C
         II1=I1
         II2=I2
         N1=N
C
C        IF THIS IS THE FIRST TIME THRU OR IF THE Q BRANCHES
C        HAVE NOT BEEN COMPUTED, GO DIRECTLY TO THE FINAL STATE.
C
         IF(FIRST) GO TO 20
         IF(BRANCH.NE.Q) GO TO 300
C
         GO TO 330
C
C        THIS IS THE FINAL STATE.
C        ARE CONDITIONS SET FOR Q BRANCHES?
C
280      IF(DABS(JI-JF).GT..1) GO TO 310
C
C        CONDITIONS ARE SET FOR Q BRANCHES.
C        INVERT T MATRIX AND PUT INTO TF1 MATRIX.
C
         DO 290 I=1,NN
         DO 290 K=1,NN
290      TF1(I,K)=T(K,I)
C
C        SAVE INDICIES DENOTING SIZE OF HAMILTONIAN AND
C        WHICH ELEMENTS ARE FILLED.
C
         SAVE1=I1
         SAVE2=I2
         SAVE3=N
         FIRST=.FALSE.
C
C        INCREASE FINAL STATE ROTATIONAL QUANTUM NUMBER
C        BY 1 AND COMPUTE THE NEW FINAL STATE.
C
300      JF=JF+1.0D0
         GO TO 20
C
C        THIS IS EITHER A P OR AN R BRANCH.
C        NORMALLY JF WILL BE GREATER THAN JI AT THIS POINT.
C        HOWEVER, THE FIRST TIME THRU JI MAY BE GREATER.
C
310      IF(JF.GT.JI) GO TO 350
C
C        FIRST TIME THRU. INVERT T MATRIX AND PUT INTO TF1
C        MATRIX AND SET INDICIES.
C
         DO 320 I=1,NN
         DO 320 K=1,NN
320      TF1(I,K)=T(K,I)
C
         IF1=I1
         IF2=I2
         NF=N
C
C        IF THIS IS AN EMISSION CALCULATION, WE ARE READY
C        TO COMPUTE R BRANCHES. IF ABSORTION, P BRANCHES.
C
330      IF(EMISON)   GO TO 370
C
C        THIS IS A  P BRANCH CALCULATION.
C
340      BRANCH=P
C
C        SET INDEX FOR SAVING P BRANCHES IN THE LARGE SAVE ARRAY.
C
         IK=100
         SIGN2=-1.0D0
         GO TO 390
C
C        INVERT T MATRIX, PUT INTO  TF2 MATRIX AND SET INDICIES.
C
350      DO 360 I=1,NN
         DO 360 K=1,NN
360      TF2(I,K)=T(K,I)
```

```
C
      IF1=I1
      IF2=I2
      NF=N
C
C     IF THIS IS AN EMISSION CALCULATION,  WE ARE READY
C     TO COMPUTE P BRANCHES. IF ABSORPTION, R BRANCHES.
C
      IF(EMISON)   GO TO 340
C
C     THIS IS AN R BRANCH CALCULATION.
C
370   BRANCH=R
C
C     SET INDEX FOR SAVING Q BRANCHES IN THE LARGE SAVE ARRAY.
C
      IK=0
      SIGN2=-1.0D0
      GO TO 390
C
C     THIS IS A Q BRANCH CALCULATION.
C
380   BRANCH=Q
      IK=50
      SIGN2=+1.0D0
C
C     DEVELOP ROTATIONAL MATRIX.
C
C     SET INDICIES AND SIGN OF LAMBDA.
C
390   I=0
      EI=II2
      NII=NI
      NFF=NF
      NTRAN=0
      SIGN=1.0D0
C
395   IF(ALLOW.OR.LAMF.LT..1) GO TO 400
      SIGN=-1.0D0
      NFF=2*NF
C
C     SET INDICIES AND OMEGA FOR THE INITIAL STATE,
C     COLUMNS OF THE MATRIX.
C
400   I=I+1
      EI=EI-1.0D0
      OMEGAI=LAMI+SI-EI
      II=NI-I+1
C
      K=0
      EK=IF2
C
C     SET INDICIES AND OMEGA FOR THE FINAL STATE,
C     ROWS OF THE MATRIX.
C
410   K=K+1
      EK=EK-1.0D0
      KK=NFF-K+1
      IF(SIGN.LT.O.) EK=(KK-K-1)/2
      OMEGAF=SIGN*LAMF+SF-EK
C
C     FIND DELTA OMEGA AND DELTA LAMBDA.
C
      DELO=OMEGAF-OMEGAI
      DELL=LAMF-LAMI
C
C     FOR ALLOWED TRANSITIONS DELTA OMEGA MUST EQUAL DELTA LAMBDA.
C
      IF(.NOT.ALLOW) GO TO 415
      IF(ABS(DELO-DELL).GT..1) GO TO 510
C
C     WHAT TYPE OF BRANCH?
C
415   IF(BRANCH.EQ.Q) GO TO 470
      IF((JF-JI).GT. .1) GO TO 440
C
C     P BRANCH IN ABSORPTION OR
C     R BRANCH IN EMISSION.
C
      IF(JI.LT..1) GO TO 810
      IF( ABS(DELO).LT..1)GO TO 430
      IF(DELO.GT.O.) GO TO 420
      IF( DELO.LT.-1.1)GO TO 510
C
      A(KK,II)=-DSQRT((JI+OMEGAI)*(JI+OMEGAI-1.0D0)/(2.0D0*JI))
      GO TO 500
C
420   IF(DELO.GT.1.1) GO TO 520
C
      A(KK,II)=DSQRT((JI-OMEGAI)*(JI-OMEGAI-1.0D0)/(2.0D0*JI))
      GO TO 500
C
430   A(KK,II)=DSQRT((JI+OMEGAI)*(JI-OMEGAI)/JI)
      GO TO 500
C
C     R BRANCH IN ABSORPTION OR
C     P BRANCH IN EMISSION.
```

```
C
440    IF( ABS(DELO).LT..1)GO TO 460
       IF(DELO.GT.0.) GO TO 450
       IF( DELO.LT.-1.1)GO TO 510
C
       A(KK,II)=DSQRT(((JI-OMEGAI+1.0D0)*(JI-OMEGAI+2.0D0)/(2.0D0*(JI+1.0D0))))
       GO TO 500
C
450    IF( DELO.GT.1.1) GO TO 520
C
       A(KK,II)=-DSQRT(((JI+OMEGAI+1.0D0)*(JI+OMEGAI+2.0D0)/(2.0D0*(JI+1.0D0))))
       GO TO 500
C
460    A(KK,II)=DSQRT(((JI+OMEGAI+1.0D0)*(JI-OMEGAI+1.0D0)/(JI+1.0D0)))
       GO TO 500
C
C      Q BRANCH IN ABSORPTION OR EMISSION.
C
470    IF(JI.LT..1) GO TO 810
       IF( ABS(DELO).LT..1) GO TO 490
       IF(DELO.GT.0.) GO TO 480
       IF( DELO.LT.-1.1) GO TO 510
C
       A(KK,II)=DSQRT((JI+OMEGAI)*(JI-OMEGAI+1.0D0)*(2.0D0*JI+1.0D0)
      1             /(2.0D0*JI*(JI+1.0D0)))
       GO TO 500
C
480    IF( DELO.GT.1.1) GO TO 520
C
       A(KK,II)=DSQRT((JI-OMEGAI)*(JI+OMEGAI+1.0D0)*(2.0D0*JI+1.0D0)
      1             /(2.0D0*JI*(JI+1.0D0)))
       GO TO 500
C
490    A(KK,II)=OMEGAI*DSQRT((2.0D0*JI+1.0D0)/(JI*(JI+1.0D0)))
C
C      IF THIS IS AN ALLOWED TRANSITION LOOP BACK UNTIL ALL
C      ELEMENTS ARE IN THE ROTATIONAL MATRIX. IF THIS IS
C      A FORBIDDEN TRANSITION, FIND THE SYMMETRICAL ROTATIJNAL
C      MATRIX ELEMENT AND TRANSFORM THEM TOGETHER.
C
500    IF(.NOT.ALLOW) GO TO 540
C
510    IF(K.LT.NF) GO TO 410
       IF(K.GT.NF) GO TO 525
C
520    IF(SIGN..0) GO TO 530
C
C      IS FORBIDDEN BRANCH COMPLETED?
C
       IF(LAMI.GT..1.OR.(I+1).LT.II) GO TO 522
       IF(I.EQ.II) GO TO 810
C
522    SIGN=+1.0D0
       EK=IF2
       GO TO 410
C
525    IF(K.LT.NFF) GO TO 410
C
530    IF(I.EQ.NI) GO TO 535
       IF(ALLOW) GO TO 395
C
C      IS FORBIDDEN BRANCH COMPLETED?
C
       IF(LAMI.GT..1.OR.(I+1).LT.II) GO TO 395
       GO TO.810
C
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    IF(ALLOW) GO TO 580
       GO TO 810
C
C      THIS IS A FORBIDDEN TRANSITION.  FIND THE SYMETRICAL
C      ELEMENT WITH PROPER PHASE FACTORS. CHECK SIGMA TO SIGMA
C      TRANSITION FOR EXISTENCE OF TRANSITION MOMENT WHEN BOTH
C      OMEGAS EQUAL ZERO.
C
540    IF(SIGSIG) GO TO 560
C
       IF(LAMI.LT..1) GO TO 565
C
C      INITIAL STATE IS NOT A SIGMA STATE.
C
       NII=2*NI
       I3=NI+1
       GO TO 567
C
C      THIS IS A SIGMA TO SIGMA TRANSITION.
C      ARE BOTH OMEGAS EQUAL TO ZERO?
C
560    IF(DABS(OMEGAI).LT..1.AND.DABS(OMEGAF).LT..1) GO TO 570
C
C      AT LEAST ONE OMEGA IS UNEQUAL TO ZERO, SET SYMMETRICAL ELEMENT.
C
565    I3=I
567    A(K,I3)=SIGN1*SIGN2*A(KK,II)
```

```
      GO TO 571
C
C     BOTH OMEGAS ARE ZERO.
C     THERE IS NO SYMMETRICAL ELEMENT.
C     FOR THE TRANSITION MOMENT TO EXIST SIGN1 MUST BE NEGATIVE.
C
570   IF(SIGN1.LT.0.) GO TO 580
C
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)=0.0D0
      GO TO 810
C
C     TRANSFORM THE ROTATIONAL MATRIX.
C
C     SYMMETRIZE FORBIDDEN TRANSITIONS.
C
571   IF(K.EQ.KK) GO TO 576
      IF(I3.EQ.II) GO TO 575
      IF(K.GT.KK) GO TO 573
      IF(I3.GT.II) GO TO 572
C
      HH(1)=A(K,I3)*0.5D0
      HH(2)=0.0D0
      HH(3)=0.0D0
      HH(4)=A(KK,II)*0.5D0
      GO TO 578
C
572   HH(1)=0.0D0
      HH(2)=-A(K,I3)*0.5D0
      HH(3)=A(KK,II)*0.5D0
      HH(4)=0.0D0
      GO TO 578
C
573   IF(I3.GT.II) GO TO 574
      HH(1)=0.0D0
      HH(2)=A(KK,II)*0.5D0
      HH(3)=-A(K,I3)*0.5D0
      HH(4)=0.0D0
      GO TO 578
C
574   HH(1)=A(KK,II)*0.5D0
      HH(2)=0.0D0
      HH(3)=0.0D0
      HH(4)=A(K,I3)*0.5D0
      GO TO 578
C
575   HH(1)=A(K,I3)*0.70710678lD0
      HH(2)=A(KK,I3)*0.70710678lD0
      HH(3)=0.0D0
      HH(4)=0.0D0
      GO TO 578
C
576   IF(I3.GT.II) GO TO 577
      HH(1)=A(K,I3)*0.70710678lD0
      HH(2)=A(K,II)*0.70710678lD0
      HH(3)=0.0D0
      HH(4)=0.0D0
      GO TO 578
C
577   HH(1)=A(K,II)*0.70710678lD0
      HH(2)=-A(K,I3)*0.70710678lD0
      HH(3)=0.0D0
      HH(4)=0.0D0
C
578   A(K,I3)=HH(1)+HH(2)+HH(3)+HH(4)
      A(KK,II)=HH(1)-HH(2)-HH(3)+HH(4)
      IF(K.EQ.KK.OR.I3.EQ.II) GO TO 580
      A(K,II)=HH(1)-HH(2)+HH(3)-HH(4)
      A(KK,I3)=HH(1)+HH(2)-HH(3)-HH(4)
C
C     MULTIPLY ON THE RIGHT BY TI.
C
580   DO 600 I1=1,NII
      DO 600 K1=1,NFF
      C(K1,I1)=0.0D0
        DO 590 I2=1,NII
590   C(K1,I1)=C(K1,I1)+A(K1,I2)*TI(I2,I1)
600   CONTINUE
C
C     MULTIPLY ON THE LEFT BY TF
C
      IF(BRANCH.EQ.Q.OR.(JF-JI).LT..1) GO TO 630
C
C     FOR P BRANCHES IN EMISSION AND R BRANCHES IN
C     ABSORPTION MULTIPLY ON LEFT BY TF2.
C
      DO 620 I1=1,NII
      DO 620 K1=1,NFF
      A(K1,I1)=0.0D0
        DO 610 I2=1,NFF
610   A(K1,I1)=A(K1,I1)+TF2(K1,I2)*C(I2,I1)
620   CONTINUE
      GO TO 655
```

```
C
C       FOR Q BRANCHES AND FOR P BRANCHES IN ABSORPTION
C       AND R BRANCHES IN EMISSION MULTIPLY ON LEFT BY TF1.
C
630     DO 650 I1=1,NII
        DO 650 K1=1,NFF
        A(K1,I1)=0.0D0
          DO 640 I2=1,NFF
640       A(K1,I1)=A(K1,I1)+TF1(K1,I2)*C(I2,I1)
650     CONTINUE
C
C       FOR ALLOWED TRANSITIONS LAMBDA DOUBLING WAS NOT INCLUDED.  THEREFORE, THE
C       MATRIX ELEMENTS FOR SIGMA-PI TRANSITIONS MUST BE MULTIPLIED BY THE SQUARE
C       ROOT OF 2.
C
C       FOR FORBIDDEN TRANSITIONS:
C               IF ONLY THE INITIAL STATE IS A SIGMA STATE, THE  RESULTS
C               IN THE UPPER AND LOWER HALVES OF THE MATRIX MUST BE COMBINED.
C               IF ONLY THE FINAL STATE IS A SIGMA STATE, THE RESULTS IN
C               THE LEFT AND RIGHT HALVES OF THE MATRIX MUST BE COMBINED.
C
C        IF NEITHER STATE IS A SIGMA STATE, THE RESULTS
C               ARE EITHER IN THE UPPER-LEFT AND LOWER-RIGHT QUADRANTS, OR IN
C               THE UPPER-RIGHT AND LOWER-LEFT QUADRANTS.  THEREFORE, WE CAN ALWAYS GET
C               ONE LAMBDA COMPONENT BY ADDING THE MATRIX ELEMENTS IN THE UPPER-LEFT
C               AND LOWER-LEFT QUADRANTS (ONE OF WHICH IS ZERO).  THE OTHER LAMBDA
C               COMPONENT CAN BE FOUND BY SIMPLY CHANGING THE SIGN OF ALL TERMS
C               WHOSE TRANSITION MOMENT IS DESIGNATED WITH A MINUS SIGN IN THE
C               FIRST LOCATION, IE (-X,Y).
C
655     IF(SIGSIG) GO TO 666
        IF(.NOT.ALLOW) GO TO 662
        IF(LAMI.GT..1D0.AND.LAMF.GT..1D0) GO TO 666
C
        C1=1.414213562D0
        DO 660 K3=1,NF
        DO 660 I3=1,NI
660     A(K3,I3)=C1*A(K3,I3)
        GO TO 666
C
662     IF(LAMF.LT..1D0) GO TO 664
        DO 663 I3=1,NI
        DO 663 K3=1,NF
        K4=NFF+1-K3
663     A(K3,I3)=A(K3,I3)+A(K4,I3)
        GO TO 666
C
664     DO 665 I3=1,NI
        DO 665 K3=1,NF
        I4=NII+1-I3
665     A(K3,I3)=A(K3,I3)+A(K3,I4)
C
C       FOR STATES OTHER THAN SIGMA STATES, IF THE HAMILTONIAN
C       IS NOT FULLY DEVELOPED (SMALL J VALUES) THEN THE ELEMENTS
C       IN THE TRANSFORMED ROTATIONAL MATRIX ARE SHIFTED TO
C       ENABLE PROPER LABELING DURING OUTPUT.
C
666     NDELI=0
        IF(LAMI.LT..1.OR.II1.EQ.1) GO TO 695
C
C       DETERMINE COLUMN SHIFT.
C
        NDELI=II1-1
        IF(YI(1).LT.0.0D0) NDELI=IMAXI-II1-NI+1
        IF(NDELI.LE.0) GO TO 695
C
C       SHIFT COLUMNS
C
        DO 690 K1=1,NF
          DO 670 I1=1,NI
          I2=NI+1-I1
          I3=I2+NDELI
670       A(K1,I3)=A(K1,I2)
C
          DO 680 I1=1,NDELI
680       A(K1,I1)=0.0D0
C
690     CONTINUE
C
695     NDELF=0
        IF(LAMF.LT..1.OR.IF1.EQ.1) GO TO 735
C
C       DETERMINE ROW SHIFT.
C
        NDELF=IF1-1
        IF(YF(1).LT.0.0D0) NDELF=IMAXF-IF1-NF+1
        IF(NDELF.LE.0) GO TO 735
C
C       SHIFT ROWS.
C
        DO 730 I1=1,IMAXI
          DO 710 K1=1,NF
          I2=NF+1-K1
          I3=I2+NDELF
710       A(I3,I1)=A(I2,I1)
C
          DO 720 K1=1,NDELF
```

```
720      A(K1,I1)=0.0D0
C
730   CONTINUE
C
C     STORE THE TRANSFORMED ROTATIONAL MATRIX ELEMENTS
C     AND INITIALIZE THE A MATRIX FOR A NEW CALCULATION.
C
735   K4=NDELF+NF+1
      I4=NDELI+NI+1
      K5=IMAXF-NDELF-NF
      I5=IMAXI-NDELI-NI
C
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 HONL-LONDON FACTORS FOR A SINGLE LAMBDA COMPONENT.
C
      DO 755 I1=1,NI
      I6=I4-I1
      DO 750 K1=1,NF
      K7=(I5+I1-1)*7+IK+K5+K1
      K6=K4-K1
750   SAVE(1,K7,IJ)=A(K6,I6)**2
755   CONTINUE
      DO 757 I1=1,I4
      DO 757 K1=1,I4
757   A(K1,I1)=0.0D0
C
      GO TO 810
C
C     THIS IS A FORBIDDEN TRANSITION.
C     RECORD THE NUMBER OF ELECTRONIC TRANSITION
C     MOMENTS AND THEIR DESIGNATIONS.
C
760   NTRAN=NTRAN+1
      IE=EI+.1
      KE=EK+.1
      K6=NTRAN+IK/5
      ITRANI(K6,IJ)=IMAXI-IE
C
      IF(LAMF.LT..1) GO TO 780
      IF(SIGN.LT.0.) GO TO 770
C
      ITRANF(K6,IJ)=K-NF+IMAXF-IF2
      GO TO 790
C
770   ITRANF(K6,IJ)=K-IMAXF+IF1-2
      GO TO 790
C
780   ITRANF(K6,IJ)=IMAXF-KE
C
C     IS THIS AN EMISSION CALCULATION?
C
790   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=+1
      IF(SIGSIG) GO TO 794
      IF(LAMF.LT..1) GO TO 792
      IF(LAMI.LT..1) GO TO 791
C
      IF(SIGN.LT.0.) K1=-1
      GO TO 796
C
791   IF(SIGN.GT.0.) GO TO 796
C
      I1=ITRANI(K6,IJ)
      ITRANI(K6,IJ)=-ITRANF(K6,IJ)
      ITRANF(K6,IJ)=IMAXI+1-I1
      GO TO 799
C
792   IF(OMEGAF.LT.-.1) GO TO 796
C
      I1=ITRANF(K6,IJ)
      ITRANF(K6,IJ)=-ITRANI(K6,IJ)
      ITRANI(K6,IJ)=IMAXF+1-I1
      GO TO 799
C
794   IF(OMEGAF.GT..1) GO TO 798
C
796   I1=ITRANF(K6,IJ)
      ITRANF(K6,IJ)=K1*ITRANI(K6,IJ)
      ITRANI(K6,IJ)=K1*I1
      GO TO 799
C
798   I1=ITRANI(K6,IJ)
      ITRANI(K6,IJ)=IMAXF+1-ITRANF(K6,IJ)
      ITRANF(K6,IJ)=IMAXI+1-I1
C
C     SAVE A MATRIX ELEMENTS.
C
799   DO 800 I1=1,NI
```

```
          DO 800 K1=1,NF
          K7=((I5+I1-1)*7+IK+K5+K1
          K6=K4-K1
          I6=I4-I1
800       SAVE(NTRAN,K7,IJ)=A(K6,I6)
C
          DO 805 I1=1,14
          DO 805 K1=1,14
805       A(K1,I1)=0.0D0
C
          GO TO 510
C
C         A SET OF BRANCHES HAS BEEN COMPUTED.
C         STORE NUMBER OF ELECTRONIC TRANSITIONS MOMENTS
C         IN COMPUTATION JUST FINISHED AND SET FLAGS,
C         IDICIES, ETC APPROPRIATE FOR NEXT SET OF BRANCHES.
C
810       IF(BRANCH.NE.Q) GO TO 820
C
C         A SET OF Q BRANCHES HAVE BEEN COMPUTED.
C         NEXT STEP IS TO INCREASE JI AND COMPUTE A NEW INITIAL STATE.
C
          NTRANQ(IJ)=NTRAN
          GO TO 890
C
820       IF(BRANCH.EQ.P) GO TO 830
C
C         A SET OF R BRANCHES HAVE BEEN COMPUTED.
C
          NTRANR(IJ)=NTRAN
          IF(EMISON)   GO TO 840
          GO TO 860
C
C         A SET OF P BRANCHES HAVE BEEN COMPUTED.
C
830       NTRANP(IJ)=NTRAN
          IF(EMISON)   GO TO 860
C
C         REPLACE TF1 MATRIX WITH TF2 MATRIX BEFORE INCREASING JF
C         AND COMPUTING NEW FINAL STATE.
C
840       K4=SAVE3
          IF(.NOT.ALLOW.AND.LAMF.GT..1) K4=2*SAVE3
          DO 850 I1=1,K4
          DO 850 K1=1,K4
850       TF1(K1,I1)=TF2(K1,I1)
C
          JF=JF+1.0D0
          GO TO 20
C
C         IS THIS THE FIRST CALCULATION?
C
860       IF(FIRST) GO TO 870
C
C         THIS IS NOT THE FIRST CALCULATION. SAVE INDICIES
C         AND COMPUTE Q BRANCHES NEXT.
C
          SAVE4=IF1
          SAVE5=IF2
          SAVE6=NF
          IF1=SAVE1
          IF2=SAVE2
          NF=SAVE3
          SAVE1=SAVE4
          SAVE2=SAVE5
          SAVE3=SAVE6
          GO TO 380
C
C         THIS IS THE FIRST CALCULATION. SAVE INDICIES AND
C         TF2 MATRIX AND COMPUTE NEW INITIAL STATE.
C
870       FIRST=.FALSE.
          SAVE1=IF1
          SAVE2=IF2
          SAVE3=NF
C
          DO 880 I1=1,NFF
          DO 880 K1=1,NFF
880       TF1(K1,I1)=TF2(K1,I1)
C
C         WOULD NEXT VALUE OF JI BE GREATER THAN JMAX?
C
890       IF((JMAX-JI).LT..9) GO TO 910
C
C         END OF BIG DO LOOP
C
900       CONTINUE
C
          IJ=200
910       RETURN
          END
```

```
C          SUBROUTINE EIGEN
C
C          PURPOSE
C             COMPUTE EIGENVALUES AND EIGENVECTORS OF A REAL SYMMETRIC
C             MATRIX
C
C          USAGE
C
C          DESCRIPTION OF PARAMETERS
C             A - ORIGINAL MATRIX (SYMMETRIC), DESTROYED IN COMPUTATION.
C                 RESULTANT EIGENVALUES ARE DEVELOPED IN DIAGONAL OF
C                 MATRIX A IN DESCENDING ORDER.
C             R - RESULTANT MATRIX OF EIGENVECTORS (STORED COLUMNWISE,
C                 IN SAME SEQUENCE AS EIGENVALUES)
C             N - ORDER OF MATRICES A AND R
C
C          REMARKS
C             ORIGINAL MATRIX A MUST BE REAL SYMMETRIC (STORAGE MODE=1)
C             MATRIX A CANNOT BE IN THE SAME LOCATION AS MATRIX R
C
C          SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C             NONE
C
C          METHOD
C             DIAGONALIZATION METHOD ORIGINATED BY JACOBI AND ADAPTED
C             BY VON NEUMANN FOR LARGE COMPUTERS AS FOUND IN 'MATHEMATICAL
C             METHODS FOR DIGITAL COMPUTERS', EDITED BY A. RALSTON AND
C             H.S. WILF, JOHN WILEY AND SONS, NEW YORK, 1962, CHAPTER 7
C
C     .............................................................
C
       SUBROUTINE EIGEN
       COMMON/CEIGEN/A(28),R(49),N
C
       DOUBLE PRECISION A,R,ANORM,ANRMX,THR,X,Y,SINX,SINX2,COSX,
      1                 COSX2,SINCS,RANGE
C
C          GENERATE IDENTITY MATRIX
C
5      RANGE=1.0D-12
10     IQ=-N
       DO 20 J=1,N
       IQ=IQ+N
       DO 20 I=1,N
       IJ=IQ+I
       R(IJ)=0.0D0
       IF(I-J) 20,15,20
15     R(IJ)=1.0D0
20     CONTINUE
C
C          COMPUTE INITIAL AND FINAL NORMS (ANORM AND ANORMX)
C
25     ANORM=0.0D0
       DO 35 I=1,N
       DO 35 J=1,N
       IF(I-J) 30,35,30
30     IA=I+(J*J-J)/2
       ANORM=ANORM+A(IA)*A(IA)
35     CONTINUE
       IF(ANORM) 165,165,40
40     ANORM=DSQRT(2.0D0*ANORM)
       ANRMX=ANORM*RANGE/FLOAT(N)
C
C          INITIALIZE INDICATORS AND COMPUTE THRESHOLD, THR
C
       IND=0
       THR=ANORM
45     THR=THR/FLOAT(N)
50     L=1
55     M=L+1
C
C          COMPUTE SIN AND COS
C
60     MQ=(M*M-M)/2
       LQ=(L*L-L)/2
       LM=L+MQ
62     IF(DABS(A(LM))-THR) 130,65,65
65     IND=1
       LL=L+LQ
       MM=M+MQ
       X=0.5D0*(A(LL)-A(MM))
68     Y=-A(LM)/DSQRT(A(LM)*A(LM)+X*X)
       IF(X) 70,75,75
70     Y=-Y
75     SINX=Y/DSQRT(2.0D0*(1.0D0+(DSQRT(1.0D0-Y*Y))))
       SINX2=SINX*SINX
78     COSX=DSQRT(1.0D0-SINX2)
       COSX2=COSX*COSX
       SINCS =SINX*COSX
C
C          ROTATE L AND M COLUMNS
C
       ILQ=N*(L-1)
       IMQ=N*(M-1)
       DO 125 I=1,N
       IQ=(I*I-I)/2
       IF(I-L) 80,120,80
80     IF(I-M) 85,120,90
```

```
 65 IM=I+MO
    GO TO 95
 90 IM=M+IO
 95 IF(I-L) 100,105,105
100 IL=I+LO
    GO TO 110
105 IL=L+IO
110 X=A(IL)*COSX-A(IM)*SINX
    A(IM)=A(IL)*SINX+A(IM)*COSX
    A(IL)=X
120 ILR=ILQ+I
    IMR=IMQ+I
    X=R(ILR)*COSX-R(IMR)*SINX
    R(IMR)=R(ILR)*SINX+R(IMR)*COSX
    R(ILR)=X
125 CONTINUE
    X=2.0DO*A(LM)*SINCS
    Y=A(LL)*COSX2+A(MM)*SINX2-X
    X=A(LL)*SINX2+A(MM)*COSX2+X
    A(LM)=(A(LL)-A(MM))*SINCS+A(LM)*(COSX2-SINX2)
    A(LL)=Y
    A(MM)=X
C
C       TESTS FOR COMPLETION
C
C       TEST FOR M = LAST COLUMN
C
130 IF(M-N) 135,140,135
135 M=M+1
    GO TO 60
C
C       TEST FOR L = SECOND FROM LAST COLUMN
C
140 IF(L-(N-1)) 145,150,145
145 L=L+1
    GO TO 55
150 IF(IND-1) 160,155,160
155 IND=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 IQ=-N
    DO 185 I=1,N
    IQ=IQ+N
    LL=I+(I*I-I)/2
    JQ=N*(I-2)
    DO 185 J=I,N
    JQ=JQ+N
    MM=J+(J*J-J)/2
    IF(A(LL)-A(MM)) 170,185,185
170 X=A(LL)
    A(LL)=A(MM)
    A(MM)=X
175 DO 180 K=1,N
    ILR=IQ+K
    IMR=JQ+K
    X=R(ILR)
    R(ILR)=R(IMR)
180 R(IMR)=X
185 CONTINUE
    RETURN
    END
```

APPENDIX B

DETAILED FLOW CHARTS OF COMPUTER PROGRAM

PERTINENT BRANCHING SYMBOLS

BRANCHING ON SAME PAGE

OR

TO PAGE

BRANCHING BETWEEN PAGES

OR

FROM PAGE

START

10

SI,AI,SIGNI,YI(1),YI(2),YI(3)
SF,AF,SIGNF,YF(1),YF(2),YF(3)
JMIN,JMAX
TYPE

DO 15 I = 1,200
DO 15 L = 1,150
DO 15 K = 1,8
15 SAVE(K,L,I) = 0.

DO 17 I = 1,200
NTRANR(I) = 0
NTRANQ(I) = 0
NTRANP(I) = 0

DO 17 L = 1,30
17 ITRANI(L,I) = 0
ITRANF(L,I) = 0

EMISON = .TRUE.

TYPE .EQ. ABSORB   T → EMISON = .FALSE.
F

JMAX .EQ. 0.0   T → JMAX = JMIN + 100.
F

DELJ = JMAX - JMIN

DELJ .GT. 199.1   F
T

JMAX = JMIN + 199.

SIGSIG = .TRUE.

SIGSIG = .FALSE. ← T   LAMI.GT. .1
F
T   LAMF.GT. .1
F

ALLOW = .FALSE.
IMAXI = 2.*SI + 1.1
IMAXF = 2.*SF + 1.1
20

SI - SF .NE. 0.   T
F

|AI - AF| .GT. 1.1   T
F

SIGNI.NE. SIGNF   T   SIGSIG
F

ALLOW = .TRUE.
IMAXI = 2.*SI + 1.1
IMAXF = IMAXI
30

SIGN1 = + 1.0

.NOT. SIGSIG   T
F

IDELS = |SF - SI|+.1
I = 1

SIGNI.NE. SIGNF   F → SIGN1 = (-1)^(IDELS + I)
T

I = 0

IS = SI+.1
SI = IS
HALF = .TRUE.

SI - SI1 .LT. .1   F
T

HALF = .FALSE.

JTEST = JMIN + .1
J = JTEST

3

3

HALF   F
T

JMIN - JI .GT. .1   T → JMIN = JMIN + .5
F
35

JMIN - JI .LT. .1   T
T

JMIN = JMIN+.5

37
JTEST = JMAX + .1
J = JTEST

HALF   F

JMAX-JI .GT. .1   F
39 T

JMAX-JI .LT. .1   F
T

JMAX = JMAX + .5   JMAX = JMAX + .5

40

JI = AI - SI

JI .GE. 0.   F → JI = 0.
T

HALF
T

45   JI = 0.5

JMIN = JI ← T   JI - JMIN .GT. .1
F

JF = AF - SF

JF .GE. 0.   F → JF = 0.
T

HALF
T

50   JF = 0.5

55   <0   JMIN - JF   >0   60

JMIN - JF .LT. - 1.1   F   = 0   JMIN - JF .GT. 1.1   F
T   T

JMIN = JF - 1.0   65   JF = JMIN - 1.0

CALL SOLVE

PRINT HEADINGS

PRINT DATA

2

2

SUBROUTINE SOLVE

START

DO 10 ▼ I = 1, 14
DO 10 ▼ K = 1,14

TI(K,I) = 0.0
TF1(K,I) = 0.0
TF2(K,I) = 0.0
C(K,I) = 0.0
A(K,I) = 0.0

10

FIRST = .TRUE.
SAVE3 = 0
NSAVE = 0

DO 900 ▼ IJ = 1,200

DELJ = IJ - 1
JI = JMIN + DELJ

J = JI
Λ = ΛI
S = SI
IMAX = IMAXI
STATE = INITAL

J = JF
Λ = ΛF
S = SF
IMAX = IMAXF
STATE = FINAL

20

FROM PAGE
43 OR 45

DO 15 ▼ I = 1,3
15 Y(I) = YI(I)

DO 25 ▼ I = 1,3
25 Y(I) = YF(I)

30

DO 35 ▼ I = 1,7
DO 35 ▼ K = 1,7
35 H(K,I) = 0.0

DO 40 ▼ I = 1,14
DO 40 ▼ K = 1,14
40 T(K,I) = 0.0

DO 45 ▼ I = 1,28
45 HH(I) = 0.0

DO 47 ▼ I = 1,49
47 TT(I) = 0.0

OMEGA = Λ + S

(J + .1) ＜
LT. OMEGA

50 TEST = OMEGA

DO 60 ▼ I = 1,IMAX
I1 = I+1
TEST = TEST -1.0

(J + .1)
GT. TEST

T

70 J .GT. .1   F

T

60 CONTINUE

F

I1 = 1
I2 = IMAX

I1 = IMAX

100 I2 = 2.*J + .1
I2 = I1 + I2

I2. GT.
IMAX

F

T

110 I2 = IMAX

80 I2 = I1

I2 .EQ. I1

T

F

N = I2-I1+1

K = 0
I3 = I2 - 1

DO 120 ▼ I = I1,I3
K = K + 1
EI = I

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

120

90 T(1,1) = (-1)^I1
N = 1

TO PAGE 42

EI = I2
K = K+1

H(K,K) = -(OMEGA-EI+1.)^2 -(S-EI+1.)^2

K = 0

DO 130 ▼ I = I1,I2
EI = I
K = K + 1

130 H(K,K) = H(K,K)+Y(I)*Λ*(S-EI+1.)

Λ .LT. .1

F

T

TO PAGE 42

TO PAGE 42

5

4

140

DO 150 I = I1,I2

K = K+1

1,2   7

IMAX

3   4   5   6

141   142   143   144   145

I.EQ.2   I.EQ.2   I.EQ.3   I.EQ.3   I.EQ.4

T   T   T   T   T

F   F   F   F

I.EQ.3   I3 = 2   I.EQ.4   I3 = 3

F   I.EQ.2   I3 = 2   I.NE.1

T   T

F   T   I.EQ.2   I.NE.7

I.EQ.4   F   F

T   I3 = 2

I.EQ.5   I.EQ.3

F

T   F   F

I.EQ.5   I.EQ.5

T   F

I3 = 1   I3 = 1   I3 = 1   I3 = 1   I3 = 1

146

H(K,K) = H(K,K) + Y(I3)

150   CONTINUE

152

KK = 0   225

T

ALLOW

F

DO 230   I = 1,N
DO 230   K = 1,I
KK = KK+1
230   HH(KK) = H(K,I)

CALL EIGEN

KK = 0

DO 235   I = 1,N
C1 = 1.0

TT(KK+1)
GT. 0.   T   C1 = -1.0

F

DO 235   K = 1,N
KK = KK+1
235   T(K,I) = C1•TT(KK)

3

FROM PAGE 41

240

NN = N

T

ALLOW

F

T

A .LT. .1

F

NN = 2•N
II = NN+1

DO 250   I = 1,N
DO 250   K = 1,N
K3 = II−K
I3 = II−I
250   T(K3,I3) = T(K,I)

6

TO PAGE 43

T

LAM
GT. .1

T

S
.LT. .1

N

N
.EQ.NSAVE   T

F

NSAVE = N

DO 155   I = 1,7
DO 155   K = 1,7
155   SYM(I,K) = 0.0

C1 = √2/2.
K = 0

160

K = K+1
KK = N+1−K

K
.EQ.KK   T

F

SYM(K,K) = C1
SYM(K,KK) = C1
SYM(KK,K) = C1
SYM(KK,KK) = −C1

T

(KK−K)
.GT. .1

F

170

SYM(K,K) = 1.0

180

DO 220   I = 1,N
DO 220   K = 1,N

H(K,I) = 0.0

DO 210   KK = 1,N
210   H(K,I) = H(K,I) + SYM(K,KK) • C(KK,I)

220   CONTINUE

DO 200   I = 1,N
DO 200   K = 1,N

C(K,I) = 0.0

DO 190   KK = 1,N
190   C(K,I) = C(K,I) + H(K,KK) • SYM(KK,I)

200   CONTINUE

260 STATE EQ. FINAL

DO 270 K=1,NN
DO 270 I=1,NN
270 TI(I,K)=T(I,K)

II1=I1
II2=I2
NII=N

280 |JI-JF| GT..1

310 JF.GT.JI

350 DO 360 I=1,NN
DO 360 K=1,NN
360 TF2(I,K)=T(K,I)

360 IF1=J1
IF2=I2
NF=N

EMISON

DO 320 I=1,NN
DO 320 K=1,NN
320 TF1(I,K)=T(K,I)

IF1=I1
IF2=I2
NF=N

330 EMISON

DO 290 I=1,NN
DO 290 K=1,NN
290 TF1(I,K)=T(K,I)

SAVE1=I1
SAVE2=I2
SAVE3=N
FIRST=.FALSE.

FIRST → TO PAGE 41 (2)

BRANCH .NE. Q → 300 JF=JF+1

370 BRANCH=R
IK=0
SIGN2=-1.0

340 BRANCH=P
IK=100
SIGN2=-1.0

380 BRANCH=Q
IK=50
SIGN2=+1.0

870 FROM PAGE 45 (7)
SAVE4=IF1
SAVE5=IF2
SAVE6=NF
IF1=SAVE1
IF2=SAVE2
NF=SAVE3
SAVE1=SAVE4
SAVE2=SAVE5
SAVE3=SAVE6

390 EI=II2
I=0
NII=NI
NFF=NF
SIGN=1.0
NTRAN=Q

395 ALLOW

ΔF .LT. .1 → SIGN=-1.0 / NFF=2*NF

400 I=I+1
EI=EI-1.0
OMEGAI=ΛI*SI-EI
II=NI-I+1
K=0
EK=IF2

410 K=K+1
EK=EK-1.0
KK=NFF-K+1

SIGN .LT. 0. → EK=(KK-K-1)/2

OMEGAF=SIGN*ΛF*SF-EK
DELO=OMEGAF-OMEGAI
DELL=ΛF-ΛI

.NOT. ALLOW

|ΔΩ-ΔΛ| GT..1

415 BRANCH EQ. Q

470 JI.LT..1

|DELO| LT..1

440 (JF-JI) GT..1

450 DELO GT.1.1
DELO GT.0.
DELO LT.-1.1

A(KK,II)=   A(KK,II)=   460 A(KK,II)=

J1.LT..1 → TO PAGE 45 (8)

|DELO| LT..1

420 DELO GT.1.1
DELO GT.0.
DELO LT.-1.1

A(KK,II)=   A(KK,II)=   430 A(KK,II)=

480 DELO GT.1.1
DELO GT.0.
DELO LT.-1.1

A(KK,II)=   A(KK,II)=   490 A(KK,II)=

9 FROM PAGE 45

500 .NOT. ALLOW

510 K.LT.NF

K.GT.NF → 525 K.LT.NFF

522 SIGN=1.0
EK=IF2

520 SIGN GT.0.

ΛI.GT..1

(I+1).LT.II

530 I.EQ.NI   ALLOW   I.EQ.II

535 ΛI.GT..1   (I+1).LT.II

ALLOW

640 SIGSIG

560 |OMEGAI| LT..1

|OMEGAF| LT..1

570 SIGN1 LT.0.

ΛI.GT..1 → NII=2*NI / I3=NI+1

565 I3=I

A(KK,II)=0.

567 A(K,I3)=SIGN1*SIGN2*A(KK,II)

10 TO PAGE 44
11 TO PAGE 44
8 TO PAGE 45

FROM PAGE 43

10

571

K .EQ. KK

576

I2 .GT. II

573

I3 .GT. II

K .GT. KK

I3 .EQ. II

I3 .GT. II

577

HH(1) = A(K,II) · √2/2
HH(2) = –A(K,I3) · √2/2
HH(3) = 0.
HH(4) = 0.

574

HH(1) = A(K,I3) · √2/2
HH(2) = A(K,II) · √2/2
HH(3) = 0.
HH(4) = 0.

HH(1) = A(KK,II) · 1/2
HH(2) = 0.
HH(3) = 0.
HH(4) = A(K,I3) · 1/2

HH(1) = 0.
HH(2) = A(KK,II) · 1/2
HH(3) = –A(K,I3) · 1/2
HH(4) = 0.

HH(1) = A(K,I3) · 1/2
HH(2) = 0.
HH(3) = 0.
HH(4) = A(KK,II) · 1/2

572

HH(1) = 0.
HH(2) = –A(K,I3) · 1/2
HH(3) = A(KK,II) · 1/2
HH(4) = 0.

575

HH(1) = A(K,I3) · √2/2
HH(2) = A(KK,I3) · √2/2
HH(3) = 0.
HH(4) = 0.

578

A(K,I3) = HH(1)+HH(2)+HH(3)+HH(4)
A(KK,II) = HH(1)–HH(2)–HH(3)+HH(4)

K .EQ. KK

I3 .EQ. II

A(K,II) = HH(1)–HH(2)+HH(3)–HH(4)
A(KK,I3) = HH(1)+HH(2)–HH(3)–HH(4)

580

FROM PAGE 43

11

DO 600 I1 = 1,NII
DO 800 K1 = 1,NFF
C(K1,I1) = 0.0
DO 590 I2 = 1,NII
C(K1,I1) = C(K1,I1) + A(K1,I2) · TI(I2,I1)
600 CONTINUE

BRANCH .EQ. 0

(JF–JI) .LT. 0.1

630
DO 650 I1 = 1,NII
DO 650 K1 = 1,NFF
A(K1,I1) = 0.0
DO 640 I2 = 1,NFF
A(K1,I1) = A(K1,I1) + TF1(K1,I2) · C(I2,I1)
650 CONTINUE

DO 620 I1 = 1,NII
DO 620 K1 = 1,NFF
A(K1,I1) = 0.0
DO 610 I2 = 1,NFF
A(K1,I1) = A(K1,I1) + TF2(K1,I2) · C(I2,I1)
620 CONTINUE

655

SIGSIG

.NOT. ALLOW

LAMF .LT. .1

682

LAMI .GT. .1

LAMF .GT. .1

C1 = √2

684
DO 665 I3 = 1,NI
DO 665 K3 = 1,NF
I4 = NII+1–I3
665 A(K3,I3) = A(K3,I3)+A(K3,I4)

DO 663 I3 = 1,NI
DO 663 K3 = 1,NF
K4 = NFF+1–K3
663 A(K3,I3) = A(K3,I3)+A(K4,I3)

DO 660 K3 = 1,NF
DO 660 I3 = 1,NI
660 A(K3,I3) = C1·A(K3,I3)

12

TO PAGE 45

44
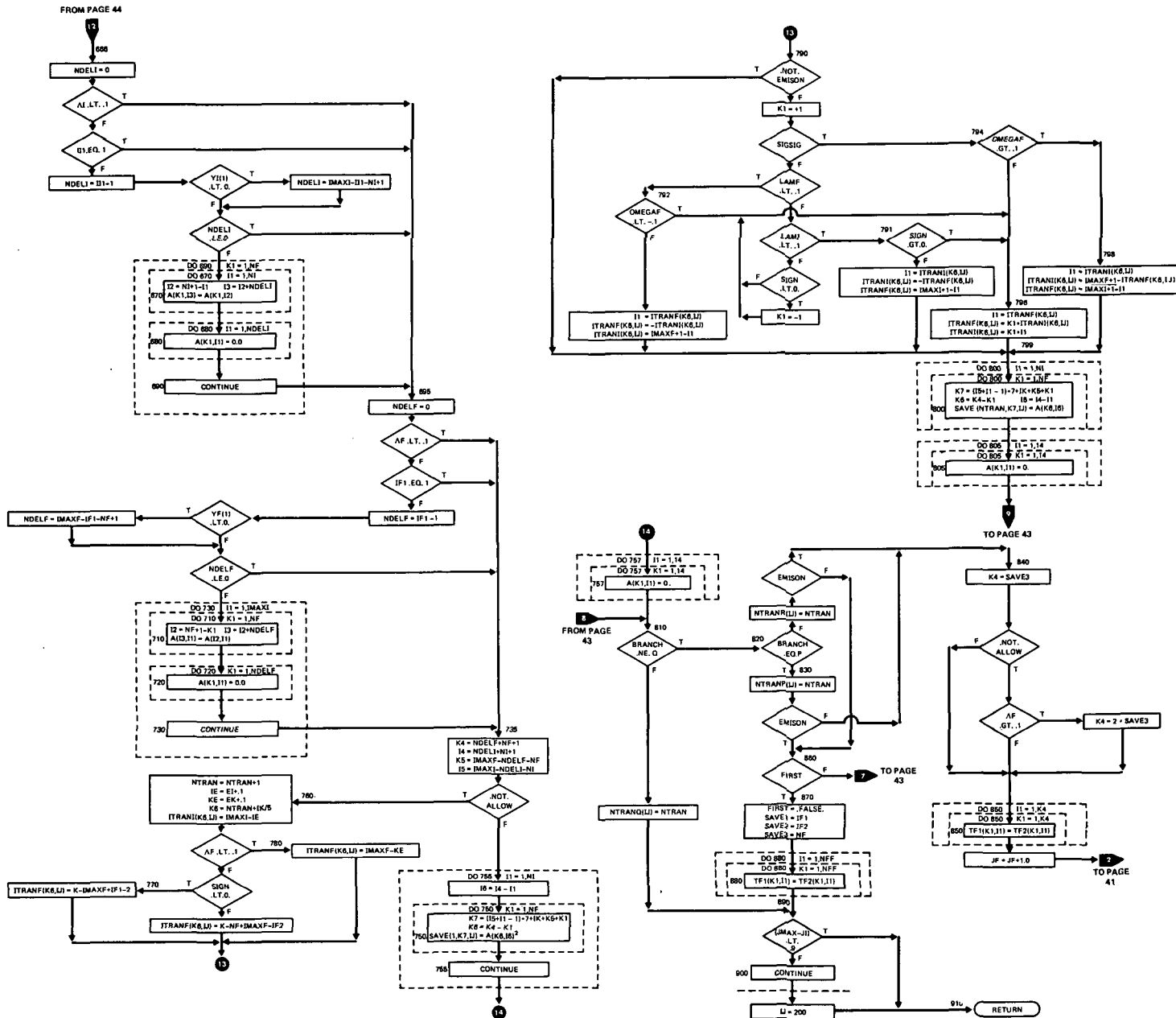
APPENDIX C

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

$$\frac{H(i,i)}{\hbar^2} = BJ(J + 1) - B\Omega_i^2 + BS(S + 1) - B\Sigma_i^2 + A\Lambda_i\Sigma_i \qquad (C1)$$

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

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

where $Y = A/B$, or as

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

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

$$\frac{H(i,i)}{B\hbar^2} = J(J + 1) + S(S + 1) - 2\Sigma_i^2 + \frac{\Delta E_i}{B} \qquad (C4)$$

where ΔE_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 ΔE_i in equation (C4) are found by extrapolating the energy separations shown in figure 14, to $N = 0$. The reference level for ΔE_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 ΔE. If $\Delta E \geq 0$, the state is regular, and if $\Delta E < 0$, the state is inverted.

REFERENCES

1. Whiting, Ellis E.: Rotational Line Intensity Factors for Dipole Transitions in Diatomic Molecules. Ph.D. Thesis, York Univ., Toronto, Canada, 1972.

2. Hougen, J. T.: The Calculation of Rotational Energy Levels and Rotational Line Intensities in Diatomic Molecules. NBS Monograph 115, 1970.

3. Hönl, H.; and London, F.: The Intensities of Band Lines. Z. Physik, vol. 33, 1925, pp. 803–809.

4. Condon, Edward U.; and Shortley, G. H.: The Theory of Atomic Spectra. Cambridge Univ. Press (London), 1935.

5. Tatum, J. B.: The Interpretation of Intensities in Diatomic Molecular Spectra. Astrophys. J. Supp., vol. 14, no. 124, Mar. 1967, pp. 21–55.

6. Schadee, Aert: On the Normalization of Hönl-London Factors. Astronomy Astrophys., vol. 14, no. 3, Oct. 1971, pp. 401–404.

7. Einstein, A.: On the Quanta Theory of Radiation. Z. Physik, no. 18, Mar. 1917, pp. 121–128.

8. Dirac, P. A. M.: The Quantum Theory of the Emission and Absorption of Radiation. Proc. Roy. Soc. (London), vol. 114, Mar. 1927, pp. 243–265.

9. Born, M.; and Oppenheimer, R.: Quantum Theory of Molecules. Ann. Physik, vol. 84, no. 4, Nov. 1927, pp. 457–484.

10. Pauling, Linus; and Wilson, E. B., Jr.: Introduction to Quantum Mechanics With Applications to Chemistry. McGraw Hill, N.Y., 1935.

11. Townes, Charles H.; and Schawlow, A. L.: Microwave Spectroscopy. McGraw Hill, N.Y., 1955.

12. Herzberg, Gerhard: Molecular Spectra and Molecular Structure. Vol. I. Spectra of Diatomic Molecules. Second ed., D. Van Nostrand, N.Y., 1950.

13. Hougen, Jon T.: The Rotational Energy Levels of Diatomic Molecules in $^4\Sigma$ Electronic States. Can. J. Phys., vol. 40, no. 5, May 1962, pp. 598–606.

14. Tatum, J. B.; and Watson, J. K. G.: Rotational Line Strengths in $^3\Sigma^\pm \leftrightarrow {}^3\Sigma^\pm$ Transitions With Intermediate Coupling. Can. J. Phys., vol. 49, no. 21, Nov. 1971, pp. 2693–2703.

48

15. Kovács, I.: Rotational Structure in the Spectra of Diatomic Molecules. Adam Hilger Ltd., London, 1969.

16. Mulliken, R. S.: Notation For Spectra of Diatomic Molecules. Phys. Rev., vol. 36, Aug. 1930, pp. 611–629.

TABLE 1.— ROTATIONAL MATRIX ELEMENTS

[The nonvanishing matrix elements $\langle \Omega'J'|\alpha|\Omega J\rangle$, where $\langle\alpha\rangle = f(J',J)g(J'\Omega';J,\Omega)$. 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.]

Factor	R Branch $J' = J+1$	Q Branch $J' = J$	P Branch $J' = J-1$
$f(J',J)$	$\left[4(J+1)\right]^{-1/2}$	$\left[4J(J+1)/(2J+1)\right]^{-1/2}$	$\left[4J\right]^{-1/2}$
$g(J',\Omega;J\Omega)$	$2\left[(J+\Omega+1)(J-\Omega+1)\right]^{1/2}$	2Ω	$2\left[(J+\Omega)(J-\Omega)\right]^{1/2}$
$g(J',\Omega\pm1;J\Omega)$	$\mp\left[2(J\pm\Omega+1)(J\pm\Omega+2)\right]^{1/2}$	$\left[2(J\mp\Omega)(J\pm\Omega+1)\right]^{1/2}$	$\pm\left[2(J\mp\Omega)(J\mp\Omega-1)\right]^{1/2}$

TABLE 2.— $\langle R_e\alpha\rangle$ BASIS MATRIX FOR A SPIN-FORBIDDEN $^2\Pi \leftarrow {}^4\Sigma^+$ TRANSITION

$^2\Pi$ $\langle\Lambda'S'\Sigma'K\Omega'J'|$ \ $^4\Sigma^+$ $|\Lambda'S''\Sigma''\Omega''J''\rangle$	$\left\|0+\frac{3}{2}\frac{3}{2}J''\right\rangle$	$\left\|0+\frac{1}{2}\frac{1}{2}J''\right\rangle$	$\left\|0+\frac{3}{2}-\frac{1}{2}J''\right\rangle$	$\left\|0+\frac{3}{2}-\frac{3}{2}J''\right\rangle$
$\left\langle1\frac{1}{2}\frac{1}{2}\right\|\left\langle\frac{3}{2}J'\right\|$	$R_{e_1}\alpha_1$	$R_{e_2}\alpha_2$		
$\left\langle1\frac{1}{2}-\frac{1}{2}\right\|\left\langle\frac{1}{2}J'\right\|$	$R_{e_3}\alpha_3$	$R_{e_4}\alpha_4$	$R_{e_5}\alpha_5$	
$\left\langle-1\frac{1}{2}\frac{1}{2}\right\|\left\langle-\frac{1}{2}J'\right\|$		$R_{e_6}\alpha_6$	$R_{e_7}\alpha_7$	$R_{e_8}\alpha_8$
$\left\langle-1\frac{1}{2}-\frac{1}{2}\right\|\left\langle-\frac{3}{2}J'\right\|$			$R_{e_9}\alpha_9$	$R_{e_{10}}\alpha_{10}$

TABLE 3.— $\langle R_e\alpha\rangle$ P-BRANCH BASIS MATRIX FOR A SPIN-FORBIDDEN $^2\Pi \leftarrow {}^4\Sigma^+$ TRANSITION

$^2\Pi$ $\langle\Lambda'S'\Sigma'K\Omega'J'|$ \ $^4\Sigma^+$ $|\Lambda'S''\Sigma''\Omega'J'\rangle$	$\left\|0+\frac{3}{2}\frac{3}{2}J''\right\rangle$	$\left\|0+\frac{1}{2}\frac{1}{2}J''\right\rangle$	$\left\|0+\frac{3}{2}-\frac{1}{2}J''\right\rangle$	$\left\|0+\frac{3}{2}-\frac{3}{2}J''\right\rangle$
$\left\langle1\frac{1}{2}\frac{1}{2}\right\|\left\langle\frac{3}{2}J'\right\|$	$R_{e_1}\alpha_1$	$R_{e_2}\alpha_2$		
$\left\langle1\frac{1}{2}-\frac{1}{2}\right\|\left\langle\frac{1}{2}J'\right\|$	$R_{e_3}\alpha_3$	$R_{e_4}\alpha_4$	$R_{e_5}\alpha_5$	
$\left\langle-1\frac{1}{2}\frac{1}{2}\right\|\left\langle-\frac{1}{2}J'\right\|$		$-R_{e_5}\alpha_5$	$-R_{e_4}\alpha_4$	$-R_{e_3}\alpha_3$
$\left\langle-1\frac{1}{2}-\frac{1}{2}\right\|\left\langle-\frac{3}{2}J'\right\|$			$-R_{e_2}\alpha_2$	$-R_{e_1}\alpha_1$

TABLE 4.— SIMPLIFIED FLOW CHART OF COMPUTER PROGRAM

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

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

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

Forbidden transitions   Allowed transitions

Store transformed rotat-
ional matrix elements and
code for transition moments.

Square transformed rotat-
ional matrix elements to get
Hönl-London factors.

No Test if all transition moments
have been included.

Store Hönl-London factors.

Yes

$J = J + 1$ $J \neq J_{max}$ Test if J is equal to J_{max}.

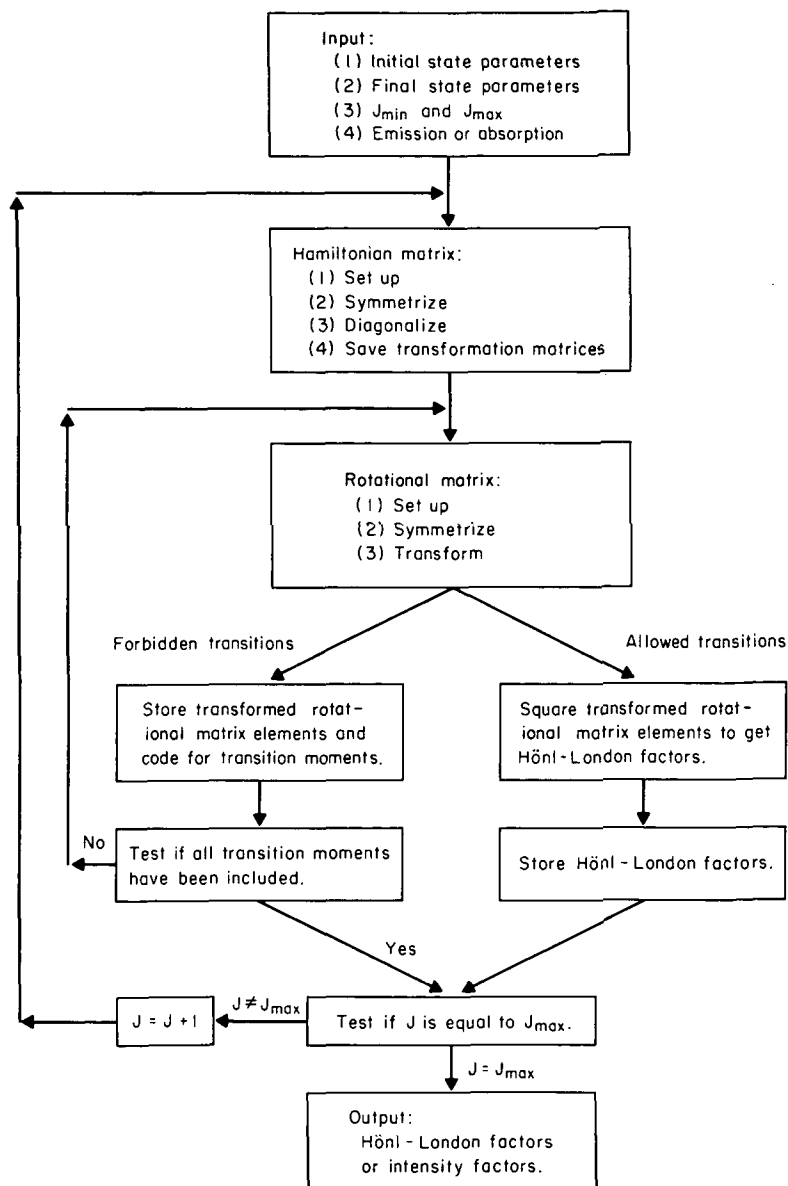$J = J_{max}$

Output:
Hönl-London factors
or intensity factors.

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TABLE 5.— A DIAGRAMMATIC REPRESENTATION OF THE ELECTRONIC-ROTATIONAL HAMILTONIAN FOR A $^2\Pi$ ELECTRONIC STATE IN TERMS OF BASIS FUNCTIONS $<\Lambda S\Sigma\,|<\Omega J\,|$

$<\Lambda S\Sigma\,|<\Omega J\,|$	$\lvert\tfrac{1}{2}\tfrac{1}{2}\rangle\lvert\tfrac{3}{2}J\rangle$	$\lvert\tfrac{1}{2}-\tfrac{1}{2}\rangle\lvert\tfrac{1}{2}J\rangle$	$\lvert-\tfrac{1}{2}\tfrac{1}{2}\rangle\lvert-\tfrac{1}{2}J\rangle$	$\lvert-\tfrac{1}{2}-\tfrac{1}{2}\rangle\lvert-\tfrac{3}{2}J\rangle$
$\langle\tfrac{1}{2}\tfrac{1}{2}\lvert\langle\tfrac{3}{2}J\rvert$	H_{11}	H_{12}		
$\langle\tfrac{1}{2}-\tfrac{1}{2}\lvert\langle\tfrac{1}{2}J\rvert$	H_{12}	H_{22}		
$\langle-\tfrac{1}{2}\tfrac{1}{2}\lvert\langle-\tfrac{1}{2}J\rvert$			H_{22}	H_{12}
$\langle-\tfrac{1}{2}-\tfrac{1}{2}\lvert\langle-\tfrac{3}{2}J\rvert$			H_{12}	H_{11}

TABLE 6.— $\langle R_e\alpha\rangle$ BASIS MATRIX FOR THE Q-BRANCHES OF A $^2\Pi\leftrightarrow{}^4\Pi$ TRANSITION

$^4\Pi$ / $^2\Pi$ $\langle\Lambda'S'\Sigma'\lvert\langle\Omega'J'\rvert$	④ $\lvert\tfrac{3}{2}\tfrac{5}{2}\rangle\lvert\tfrac{3}{2}J\rangle$	③ $\lvert\tfrac{3}{2}\tfrac{3}{2}\rangle\lvert\tfrac{3}{2}J\rangle$	② $\lvert\tfrac{3}{2}\tfrac{1}{2}\rangle\lvert\tfrac{1}{2}J\rangle$	① $\lvert\tfrac{3}{2}-\tfrac{1}{2}\rangle\lvert-\tfrac{1}{2}J\rangle$	$\lvert\tfrac{3}{2}-\tfrac{3}{2}\rangle\lvert-\tfrac{1}{2}J\rangle$	$\lvert\tfrac{3}{2}-\tfrac{1}{2}\rangle\lvert-\tfrac{1}{2}J\rangle$	$\lvert\tfrac{3}{2}-\tfrac{3}{2}\rangle\lvert-\tfrac{3}{2}J\rangle$	$\lvert-\tfrac{3}{2}-\tfrac{3}{2}\rangle\lvert-\tfrac{5}{2}J\rangle$
$\langle\tfrac{1}{2}\tfrac{1}{2}\lvert\langle\tfrac{3}{2}J\rvert$ ②	$R_e(2,4)\times\alpha(2,4)$	$R_e(2,3)\times\alpha(2,3)$	$R_e(2,2)\times\alpha(2,2)$		$R_e(-2,1)\times\alpha(-2,1)$			
$\langle\tfrac{1}{2}-\tfrac{1}{2}\lvert\langle\tfrac{1}{2}J\rvert$ ①		$R_e(1,3)\times\alpha(1,3)$	$R_e(1,2)\times\alpha(1,2)$	$R_e(1,1)\times\alpha(1,1)$	$R_e(-1,1)\times\alpha(-1,1)$	$R_e(-1,2)\times\alpha(-1,2)$		
$\langle-\tfrac{1}{2}\tfrac{1}{2}\lvert\langle\tfrac{1}{2}J\rvert$ ⊖①			$R_e(-1,2)\times\alpha(-1,2)$	$R_e(-1,1)\times\alpha(-1,1)$	$R_e(1,1)\times\alpha(1,1)$	$R_e(1,2)\times\alpha(1,2)$	$R_e(1,3)\times\alpha(1,3)$	
$\langle-\tfrac{1}{2}-\tfrac{1}{2}\lvert\langle\tfrac{3}{2}J\rvert$ ⊖②				$R_e(-2,1)\times\alpha(-2,1)$		$R_e(2,2)\times\alpha(2,2)$	$R_e(2,3)\times\alpha(2,3)$	$R_e(2,4)\times\alpha(2,4)$

TABLE 7.— $\langle R_e \alpha \rangle$ BASIS MATRIX FOR THE P-BRANCHES OF A $^4\Sigma^+ \leftrightarrow\ ^4\Sigma^-$ TRANSITION

$\langle \Lambda'S'\Sigma\|\Omega'J'\| \quad \backslash \quad \|\Lambda''S''\Sigma''\rangle\|\Omega''J''\rangle$	④ $\langle\frac{3}{2}\frac{3}{2}\|0\,J-1\rangle$	③ $\langle\frac{3}{2}\frac{1}{2}\|0\,J-1\rangle$	② $\langle\frac{1}{2}-\frac{1}{2}\|0\,J-1\rangle$	① $\langle\frac{3}{2}-\frac{3}{2}\|0\,J-1\rangle$
$\langle 0^+\frac{3}{2}\frac{3}{2}\|\langle\frac{3}{2}J-1\|$ ④	$-R_e(1,1)\times\alpha(1,1)$	$-R_e(1,2)\times\alpha(1,2)$		
$\langle 0^+\frac{3}{2}\frac{1}{2}\|\langle\frac{1}{2}J-1\|$ ③	$-R_e(2,1)\times\alpha(2,1)$	$-R_e(2,2)\times\alpha(2,2)$	$R_e(3,2)\times\alpha(3,2)$	
$\langle 0^+\frac{3}{2}-\frac{1}{2}\|\langle-\frac{1}{2}J-1\|$ ②		$-R_e(3,2)\times\alpha(3,2)$	$R_e(2,2)\times\alpha(2,2)$	$R_e(2,1)\times\alpha(2,1)$
$\langle 0^+\frac{3}{2}-\frac{3}{2}\|\langle-\frac{3}{2}J-1\|$ ①			$R_e(1,2)\times\alpha(1,2)$	$R_e(1,1)\times\alpha(1,1)$

TABLE 8.— DESCRIPTION OF INPUT CARDS FOR PROGRAM

Card number	Columns	Format	Content	Number of cards per case	Comments
1	1–3	F 3.1	Spin	2	The first card contains the information for the initial state and the second card contains the information for the final state.
	6–7	F2.0	Λ		
	10	A1	+ or − ; i.e. symbol for Σ states		
	11–20	E10.0	Y for nonsigma states. $\Delta E(1)/B$ for Σ states.		
	21–30	E10.0	$\Delta E(2)/B$ for Σ states.*		
	31–40	E10.0	$\Delta E(3)/B$ for Σ states.* *as needed		
2	1–5	F5.1	J_{min}	1	
	6–10	F5.1	J_{max}		
3	1	A1	A for absorption. Anything for emission.	1	It is recommended that ABSORPTION or EMISSION always be used.

TABLE 9.— COMPUTER PRINTOUT FOR SAMPLE CASE 1

HONL-LONDON FACTORS FOR THE ALLOWED

INVERTED TRIPLET   SIGMA + TO REGULAR TRIPLET   PI   TRANSITION IN EMISSION

INITIAL STATE ENERGY SEPARATION =   DELTA E(1)/B = -10.000
FINAL   STATE SPIN-ORBIT COUPLING CONSTANT = A/B = Y =   100.000

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

J VALUE IS FOR THE INITIAL (IE. UPPER) STATE.

J	SUM	R1	QR12	PR13
0.0	0.000000	0.00000	0.00000	0.00000
1.0	5.999999	9.52267E-01	0.00000	0.00000
2.0	9.999997	1.34594E 00	9.77088E-02	0.00000
3.0	13.999997	1.70604E 00	3.11386E-01	2.58351E-01
4.0	17.999998	2.05673E 00	6.09323E-01	5.28580E-01

J	SUM	SR21	R2	QP23
0.0	0.000000	0.00000	0.00000	0.00000
1.0	5.999999	1.00000E 00	0.00000	0.00000
2.0	9.999998	1.49940E 00	5.99281E-04	0.00000
3.0	13.999997	1.99679E 00	4.34552E-03	3.22196E-01
4.0	17.999998	2.49098E 00	1.38119E-02	7.45205E-01

J	SUM	TR31	SR32	P3
0.0	2.000000	0.00000	0.00000	0.00000
1.0	5.999999	4.77330E-02	0.00000	0.00000
2.0	9.999999	1.53860E-01	9.02491E-01	0.00000
3.0	13.999999	2.94775E-01	1.68551E 00	7.72769E-02
4.0	17.999998	4.47505E-01	2.37440E 00	2.29461E-01

J	SUM	Q1	PQ12	OQ13
0.0	0.000000	0.00000	0.00000	0.00000
1.0	5.999999	1.44596E 00	1.25636E-01	0.00000
2.0	9.999997	2.29541E 00	5.39022E-01	1.42615E 00
3.0	13.999997	3.08029E 00	1.17937E 00	2.25773E 00
4.0	17.999998	3.84303E 00	1.95697E 00	2.84966E 00

J	SUM	RQ21	Q2	PQ23
0.0	0.000000	0.00000	0.00000	0.00000
1.0	5.999999	1.49940E 00	5.99281E-04	0.00000
2.0	9.999998	2.49497E 00	8.59462E-03	1.66310E 00
3.0	13.999997	3.48453E 00	2.91786E-02	2.90295E 00
4.0	17.999998	4.46575E 00	6.70398E-02	4.01721E 00

J	SUM	SQ31	RQ32	Q3
0.0	2.000000	0.00000	0.00000	0.00000
1.0	5.999999	5.46360E-02	2.87376E 00	0.00000
2.0	9.999999	2.09618E-01	4.45094E 00	2.45525E-01
3.0	13.999999	4.35169E-01	5.78893E 00	6.75173E-01
4.0	17.999998	6.91215E-01	6.97250E 00	1.23663E 00

J	SUM	P1	OP12	NP13
0.0	0.000000	0.00000	0.00000	0.00000
1.0	5.999999	4.94976E-01	1.63153E-01	2.81800E 00
2.0	9.999997	9.51723E-01	4.95369E-01	2.84967E 00
3.0	13.999997	1.37756E 00	9.31311E-01	2.89796E 00
4.0	17.999998	1.79069E 00	1.41583E 00	2.94918E 00

J	SUM	QP21	P2	OP23
0.0	0.000000	0.00000	0.00000	0.00000
1.0	5.999999	4.98181E-01	5.69398E-03	2.99612E 00
2.0	9.999998	9.93554E-01	1.78887E-02	3.32189E 00
3.0	13.999997	1.48495E 00	3.90941E-02	3.72596E 00
4.0	17.999998	1.97123E 00	7.16605E-02	4.15711E 00

J	SUM	RP31	QP32	P3
0.0	2.000000	7.99041E-04	1.99920E 00	0.00000
1.0	5.999999	9.23808E-03	2.83136E 00	1.83268E-01
2.0	9.999999	5.95046E-02	3.48773E 00	4.90331E-01
3.0	13.999999	1.45440E-01	4.03135E 00	8.66373E-01
4.0	17.999998	2.49970E-01	4.51507E 00	1.27925E 00

TABLE 10.— PARTIAL PRINTOUT FOR SAMPLE CASE 2

SQUARE ROOT OF ROTATIONAL INTENSITY FACTORS FOR THE FORBIDDEN

REGULAR QUINTET SIGMA - TO INVERTED TRIPLET PI TRANSITION IN ABSORPTION

INITIAL STATE ENERGY SEPARATION =   DELTA E(1)/B =   5.000
                                       DELTA E(2)/B =   10.000
FINAL STATE SPIN-ORBIT COUPLING CONSTANT = A/B = Y = -50.000

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

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

J	PARTIAL SUM	TRANSITION MOMENT	SR1	TR21	UR31
0.0	0.000000	-2,3	0.00000	0.00000	0.00000
0.0	0.000000	-1,3	0.00000	0.00000	0.00000
1.0	0.000000	-3,2	0.00000	0.00000	0.00000
1.0	0.000000	-2,2	0.00000	0.00000	0.00000
1.0	0.000000	-1,2	0.00000	0.00000	0.00000
1.0	0.000000	1,2	0.00000	0.00000	0.00000
1.0	0.000000	-2,3	0.00000	0.00000	0.00000
1.0	0.000000	-1,3	0.00000	0.00000	0.00000
2.0	0.117959	-3,1	-3.42283E-01	-2.82693E-02	-1.42549E-03
2.0	0.023592	-2,1	1.26445E-02	-1.52349E-01	-1.48931E-02
2.0	1.423921	-3,2	-1.18922E 00	-9.92179E-02	-4.95269E-03
2.0	1.139137	-2,2	-8.78636E-02	1.05863E 00	1.03489E-01
2.0	0.427177	-1,2	2.52556E-03	-6.33814E-02	6.50502E-01
2.0	0.427177	1,2	-2.52556E-03	6.33814E-02	-6.50502E-01
2.0	2.008190	-2,3	-1.16660E-01	1.40560E 00	1.37407E-01
2.0	3.012286	-1,3	-6.70659E-03	1.68308E-01	-1.72740E 00
3.0	0.278747	-3,1	-5.24757E-01	-5.79885E-02	-3.76012E-03
3.0	0.069687	-2,1	2.90022E-02	-2.60322E-01	-3.28352E-02
3.0	1.691597	-3,2	-1.29271E 00	-1.42852E-01	-9.26287E-03
3.0	1.691598	-2,2	-1.42891E-01	1.28258E 00	1.61780E-01
3.0	0.676639	-1,2	5.46099E-03	-1.02341E-01	8.16171E-01
3.0	0.676639	1,2	-5.46099E-03	1.02341E-01	-8.16171E-01
3.0	2.279954	-2,3	-1.65890E-01	1.48901E 00	1.87819E-01
3.0	3.647928	-1,3	-1.26799E-02	2.37626E-01	-1.89507E 00
4.0	0.432154	-3,1	-6.51231E-01	-8.94542E-02	-7.06959E-03
4.0	0.123473	-2,1	4.78345E-02	-3.44040E-01	-5.31151E-02
4.0	1.944692	-3,2	-1.38147E 00	-1.89761E-01	-1.49069E-02
4.0	2.222507	-2,2	-2.02945E-01	1.45964E 00	2.25349E-01
4.0	0.926045	-1,2	9.66142E-03	-1.45509E-01	9.31199E-01
4.0	0.926045	1,2	-9.66142E-03	1.45509E-01	-9.51199E-01
4.0	2.604501	-2,3	-2.19694E-01	1.58010E 00	2.43947E-01
4.0	4.340835	-1,3	-2.09176E-02	3.15036E-01	-2.05941E 00

J	PARTIAL SUM	TRANSITION MOMENT	R12	SR2	TR32
0.0	0.000000	-2,3	0.00000	0.00000	0.00000
0.0	0.000000	-1,3	0.00000	0.00000	0.00000
1.0	0.000000	-3,2	0.00000	0.00000	0.00000
1.0	0.000000	-2,2	0.00000	0.00000	0.00000
1.0	0.000000	-1,2	0.00000	0.00000	0.00000
1.0	0.000000	1,2	0.00000	0.00000	0.00000
1.0	0.000000	-2,3	0.00000	0.00000	0.00000
1.0	0.000000	-1,3	0.00000	0.00000	0.00000
2.0	0.936696	-3,1	9.64538E-01	7.96612E-02	4.01695E-03
2.0	0.187339	-2,1	-3.56316E-02	4.29311E-01	4.19681E-02
2.0	1.459941	-3,2	1.20417E 00	9.94524E-02	5.31494E-03
2.0	1.167952	-2,2	8.89680E-02	-1.07194E 00	-1.04789E-01
2.0	0.437983	-1,2	-2.55730E-03	6.41780E-02	-6.58678E-01
2.0	0.437983	1,2	-2.55730E-03	6.41780E-02	-6.58678E-01
2.0	0.000000	-2,3	0.00000	0.00000	0.00000
2.0	0.000000	-1,3	0.00000	0.00000	0.00000
3.0	1.618215	-3,1	1.26436E 00	1.39719E-01	9.05972E-03
3.0	0.404554	-2,1	-6.93787E-02	6.27225E-01	7.91162E-02
3.0	1.727227	-3,2	1.30626E 00	1.44348E-01	9.35991E-03
3.0	1.727228	-2,2	1.44388E-01	-1.29602E 00	-1.63475E-01
3.0	0.690892	-1,2	-5.51820E-03	1.03413E-01	-8.24722E-01
3.0	0.690892	1,2	-5.51820E-03	1.03413E-01	-8.24722E-01
3.0	0.000000	-2,3	0.00000	0.00000	0.00000
3.0	0.000000	-1,3	0.00000	0.00000	0.00000
4.0	2.223528	-3,1	1.47719E 00	2.02910E-01	1.60360E-02
4.0	0.635294	-2,1	-1.08503E-01	7.80388E-01	1.20481E-01
4.0	1.976469	-3,2	1.39271E 00	1.91305E-01	1.51189E-02
4.0	2.258820	-2,2	2.04596E-01	-1.47151E 00	-2.27182E-01
4.0	0.941176	-1,2	-9.74003E-03	1.46693E-01	-9.58938E-01
4.0	0.941176	1,2	-9.74003E-03	1.46693E-01	-9.58938E-01
4.0	0.000000	-2,3	0.00000	0.00000	0.00000
4.0	0.000000	-1,3	0.00000	0.00000	0.00000

TABLE 11.— PARTIAL PRINTOUT FOR SAMPLE CASE 3

SQUARE ROOT OF ROTATIONAL INTENSITY FACTORS FOR THE FORBIDDEN

REGULAR   QUARTET   PI   TO REGULAR   DOUBLET   PI   TRANSITION IN ABSORPTION

INITIAL STATE SPIN-ORBIT COUPLING CONSTANT = A/B = Y =   50.000
FINAL   STATE SPIN-ORBIT COUPLING CONSTANT = A/B = Y =   0.000

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 VALUES 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.

J	PARTIAL SUM	TRANSITION MOMENT	SR1	TR21
0.5	1.997786	-2.1	-1.22407E 00	-7.06716E-01
0.5	1.331859	-1.1	-5.77031E-01	9.94447E-01
0.5	0.665929	1.1	-4.08022E-01	7.06716E-01
0.5	0.000737	-1.2	-1.35756E-02	2.35137E-02
0.5	0.001474	1.2	1.91989E-02	-3.32534E-02
0.5	0.002212	2.2	-4.07269E-02	-2.35137E-02
1.5	2.389426	-2.1	-1.26212E 00	-8.92455E-01
1.5	2.389426	-1.1	-8.92455E-01	1.26212E 00
1.5	1.194714	1.1	-6.31061E-01	8.92455E-01
1.5	0.005280	-1.2	-4.19504E-02	5.93268E-02
1.5	0.010559	1.2	5.93268E-02	-8.39008E-02
1.5	0.010559	2.2	-8.39008E-02	-5.93268E-02
1.5	0.000002	1.3	8.37081E-04	-1.18381E-03
1.5	0.000008	2.3	2.36762E-03	1.67416E-03
2.5	2.829018	-2.1	-1.32971E 00	-1.02999E 00
2.5	3.394822	-1.1	-1.12830E 00	1.45663E 00
2.5	1.697411	1.1	-7.97828E-01	1.02999E 00
2.5	0.016820	-1.2	-7.94204E-02	1.02531E-01
2.5	0.033641	1.2	1.12318E-01	-1.45001E-01
2.5	0.028034	2.2	-1.32367E-01	-1.02531E-01
2.5	0.000027	1.3	3.16374E-03	-4.08437E-03
2.5	0.000089	2.3	7.45700E-03	5.77617E-03
2.5	0.000000	2.4	6.31961E-05	4.89515E-05
3.5	3.275557	-2.1	-1.40190E 00	-1.14465E 00
3.5	4.367409	-1.1	-1.32173E 00	1.51878E 00
3.5	2.183704	1.1	-9.34603E-01	1.14465E 00
3.5	0.038289	-1.2	-1.23757E-01	1.51570E-01
3.5	0.076578	1.2	1.75018E-01	-2.14353E-01
3.5	0.057434	2.2	-1.85635E-01	-1.51570E-01
3.5	0.000136	1.3	7.37605E-03	-9.03378E-03
3.5	0.000408	2.3	1.56470E-02	1.27757E-02
3.5	0.000000	2.4	2.64475E-04	2.15943E-04
4.5	3.716023	-2.1	-1.47230E 00	-1.24432E 00
4.5	5.308606	-1.1	-1.48725E 00	1.75974E 00
4.5	2.654303	1.1	-1.05165E 00	1.24432E 00
4.5	0.072285	-1.2	-1.73547E-01	2.05344E-01
4.5	0.144570	1.2	2.45433E-01	-2.90400E-01
4.5	0.101199	2.2	-2.42966E-01	-2.05344E-01
4.5	0.000454	1.3	1.37465E-02	-1.62655E-02
4.5	0.001270	2.3	2.72174E-02	2.30029E-02
4.5	0.000001	2.4	6.97642E-04	5.81164E-04
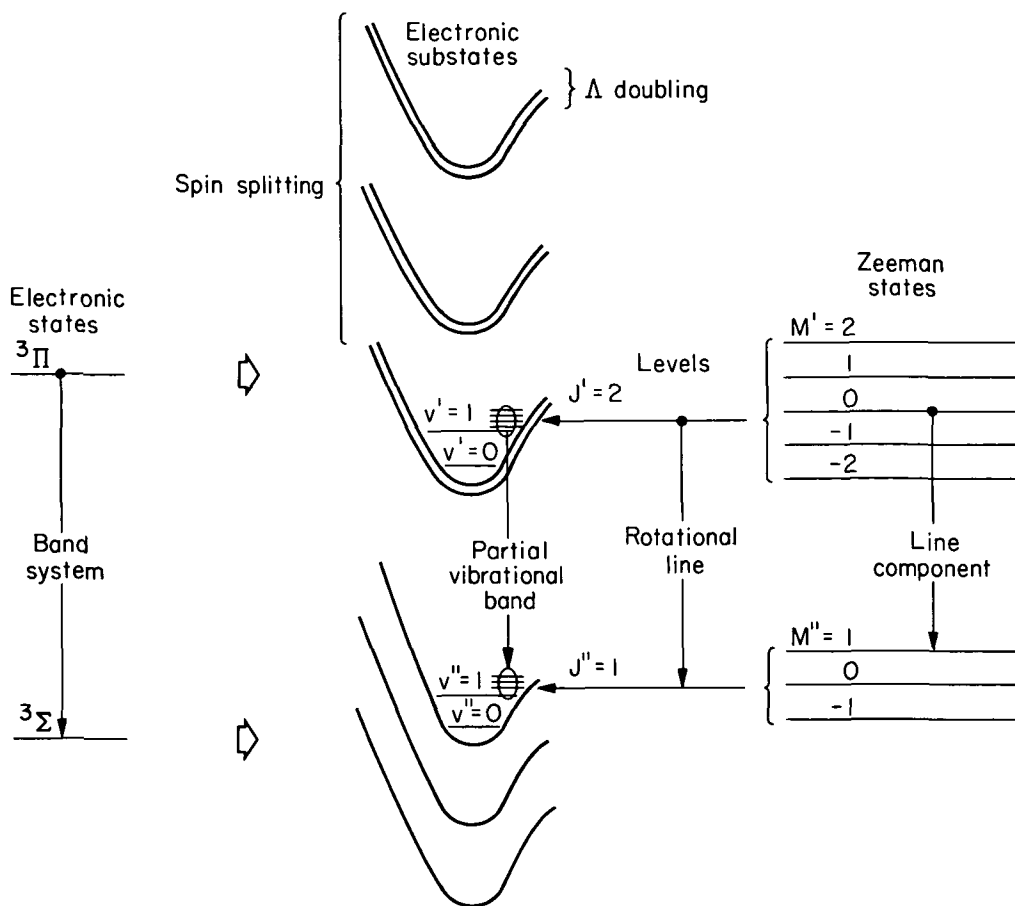
Figure 1.— Typical energy level diagram of a $^3\Pi \rightarrow {}^3\Sigma$ electronic transition.
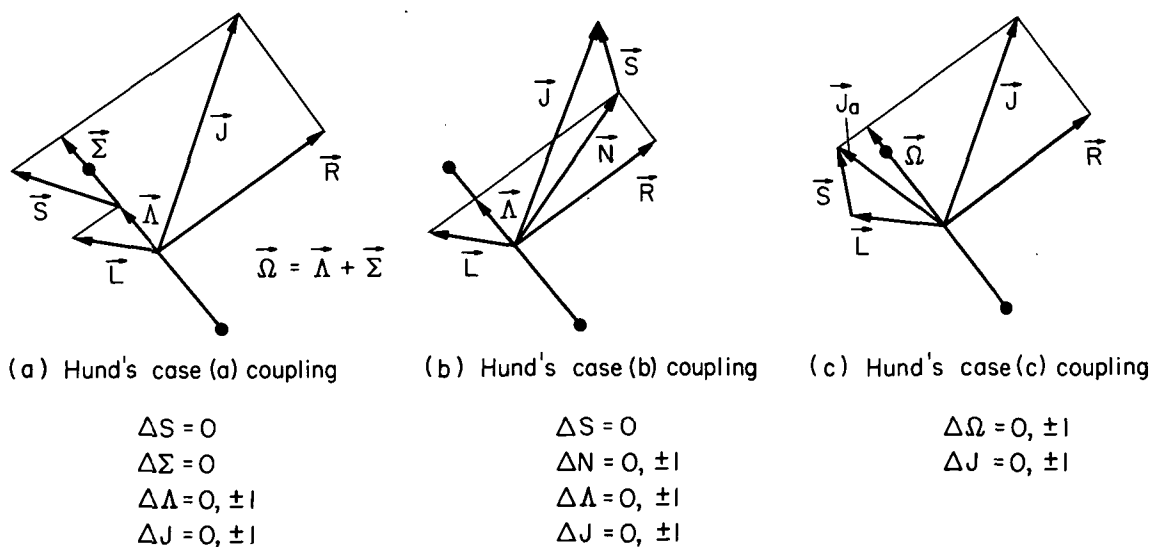

(a) Hund's case (a) coupling

$\Delta S = 0$
$\Delta \Sigma = 0$
$\Delta \Lambda = 0, \pm 1$
$\Delta J = 0, \pm 1$

(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).

$$\begin{bmatrix} 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1 & 0 \\ 1/\sqrt{2} & 0 & -1/\sqrt{2} \end{bmatrix}$$

(a) $^3\Sigma$

$$\begin{bmatrix} 1/\sqrt{2} & 0 & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 0 & -1/\sqrt{2} \end{bmatrix}$$

(b) $^4\Sigma$

Figure 3.— Unitary transformations that transform the Hamiltonian matrix from basis functions to symmetrized basis functions for $^3\Sigma$ and $^4\Sigma$ electronic states.

$F_j =$	F_1	F_2	F_3	F_4		F_1	F_2	F_3	F_4
$\Omega =$	$-1/2$	$1/2$	$3/2$	$5/2$		$5/2$	$3/2$	$1/2$	$-1/2$
$N=6$	$J=15/2$	$13/2$	$11/2$	$9/2$		$J=15/2$	$13/2$	$11/2$	$9/2$
5	$13/2$	$11/2$	$9/2$	$7/2$		$13/2$	$11/2$	$9/2$	$7/2$
4	$11/2$	$9/2$	$7/2$	$5/2$		$11/2$	$9/2$	$7/2$	$5/2$
3	$9/2$	$7/2$	$5/2$			$9/2$	$7/2$	$5/2$	$3/2$
2	$7/2$	$5/2$	$3/2$			$7/2$	$5/2$	$3/2$	$1/2$
1	$5/2$	$3/2$				$5/2$	$3/2$	$1/2$	
	$3/2$	$1/2$							
	$1/2$								

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

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

	F_1	F_2	F_3
$N=4$	$J=5$	4	3
3	4	3	2
2	3	2	1
1	2	1	0
0	1		

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

Letter	=>	. . .	N	O	P	Q	R	S	T	. . .
ΔN	=>	. . .	-3	-2	-1	0	1	2	3	. . .

$$\underbrace{\qquad\qquad\qquad}_{\Delta J}$$

Figure 6.— Letter designations for changes in N and J during a transition.

$\Delta N = N' - N'' = +1$

$\Delta J = J' - J'' = 0$

$^R Q_{32}(4)$

F_i level in upper state

F_i level in lower state
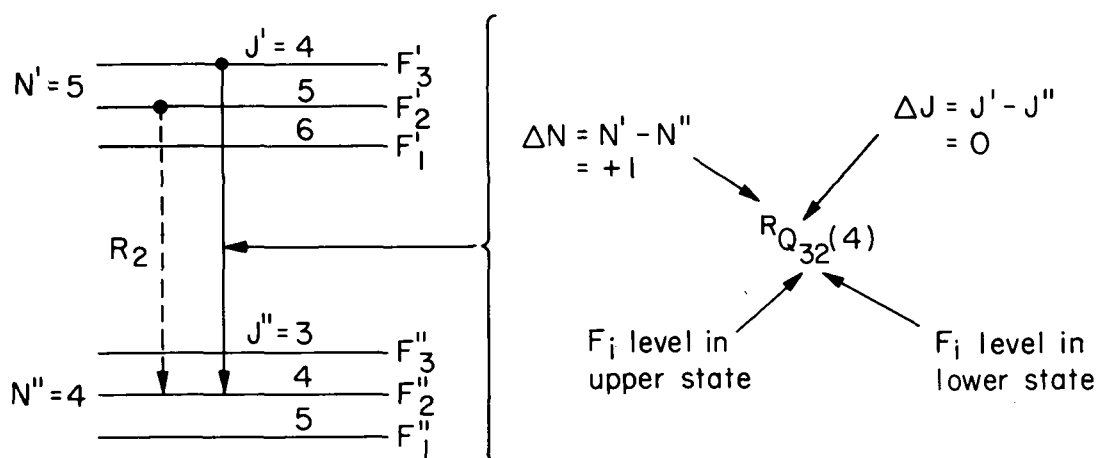
Figure 7.— Illustration of branch designation.

$^4\Sigma$

	F_4''	F_3''	F_2''	F_1''
F_4'	P_4	$^QP_{43}$	$^RP_{42}$	$^SP_{41}$
F_3'	$^OP_{34}$	P_3	$^QP_{32}$	$^RP_{31}$
F_2'	$^NP_{24}$	$^OP_{23}$	P_2	$^QP_{21}$
F_1'	$^MP_{14}$	$^NP_{13}$	$^OP_{12}$	P_1

$^4\Pi$

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

$^4\Sigma$

	F_4''	F_3''	F_2''	F_1''
	Q_4	$^RQ_{43}$	$^SQ_{42}$	$^TQ_{41}$
	$^PQ_{34}$	Q_3	$^RQ_{32}$	$^SQ_{31}$
	$^OQ_{24}$	$^PQ_{23}$	Q_2	$^RQ_{21}$
	$^NQ_{14}$	$^OQ_{13}$	$^PQ_{12}$	Q_1

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

$^4\Sigma$

	F_4''	F_3''	F_2''	F_1''
	R_4	$^SR_{43}$	$^TR_{42}$	$^UR_{41}$
	$^QR_{34}$	R_3	$^SR_{32}$	$^TR_{31}$
	$^PR_{24}$	$^QR_{23}$	R_2	$^SR_{21}$
	$^OR_{14}$	$^PR_{13}$	$^QR_{12}$	R_1

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

Figure 8.— Branch designation scheme for spin-allowed $^4\Pi \leftrightarrow {}^4\Sigma$ transitions.

$^2\Pi$	$^4\Sigma$			
	F_4''	F_3''	F_2''	F_1''
F_2'	$^OP_{24}$	P_{23}	$^QP_2$	$^RP_{21}$
F_1'	$^NP_{14}$	$^OP_{13}$	P_{12}	$^QP_1$

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

	$^4\Sigma$			
	F_4''	F_3''	F_2''	F_1''
	$^PQ_{24}$	Q_{23}	$^RQ_2$	$^SQ_{21}$
	$^OQ_{14}$	$^PQ_{13}$	Q_{12}	$^RQ_1$

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

	$^4\Sigma$			
	F_4''	F_3''	F_2''	F_1''
	$^QR_{24}$	R_{23}	$^SR_2$	$^TR_{21}$
	$^PR_{14}$	$^QR_{13}$	R_{12}	$^SR_1$

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

Figure 9.— Branch designation scheme for spin-forbidden $^2\Pi \leftrightarrow {}^4\Pi$ transitions.

^3X	$^3\Sigma$		
	F_3	F_2	F_1
F_3	X	O	X
F_2	X	O	X
F_1	X	O	X
F_1	O	X	O
F_2	O	X	O
F_3	O	X	O

(a)

^3X	$^3\Sigma$		
	F_3	F_2	F_1
F_3	O	X	O
F_2	O	X	O
F_1	O	X	O
F_1	X	O	X
F_2	X	O	X
F_3	X	O	X

(b)

Figure 10.— Possible nonzero matrix elements in the transformed rotational matrix of a $^3\Sigma \rightarrow {}^3X$ transition; X any nonsigma electronic state.

Figure 11.— Possible nonzero matrix elements in the transformed matrix of a $^3X \to {}^3Y$ transition; X and Y any nonsigma electronic states.

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

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

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

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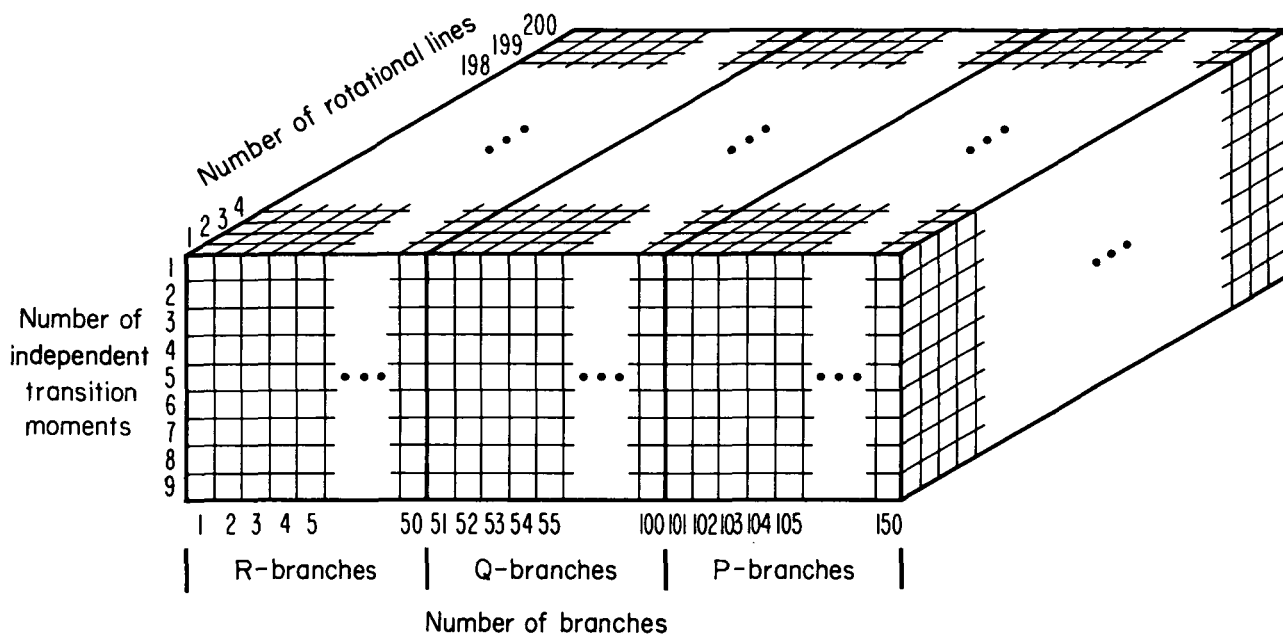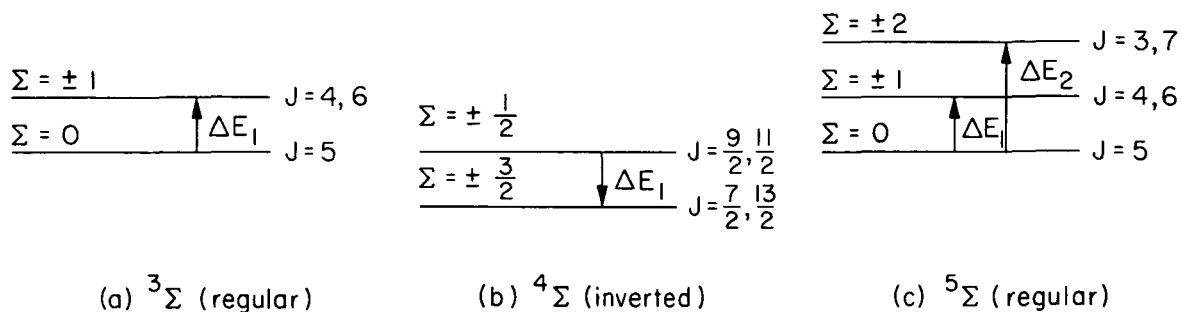
Figure 13.— Sketch of the SAVE (9, 150, 200) array.

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

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

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