TED STATES
RTMENT OF
MMERCE
LICATION

NBS MONOGRAPH 115

The Calculation of Rotational Energy Levels and Rotational Line Intensities in Diatomic Molecules

U.S.
RTMENT
OF
MMERCE
National
Bureau

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards [1] was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in four broad program areas. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Center for Radiation Research, the Center for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Measurement Services and the following technical divisions:

> Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic and Molecular Physics—Radio Physics [2]—Radio Engineering [2]—Time and Frequency [2]—Astrophysics [2]—Cryogenics.[2]

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; develops, produces, and distributes standard reference materials; relates the physical and chemical properties of materials to their behavior and their interaction with their environments; and provides advisory and research services to other Government agencies. The Institute consists of an Office of Standard Reference Materials and the following divisions:

> Analytical Chemistry—Polymers—Metallurgy—Inorganic Materials—Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations in the development of technological standards, and test methodologies; and provides advisory and research services for Federal, state, and local government agencies. The Institute consists of the following technical divisions and offices:

> Engineering Standards—Weights and Measures — Invention and Innovation — Vehicle Systems Research—Product Evaluation—Building Research—Instrument Shops—Measurement Engineering—Electronic Technology—Technical Analysis.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center consists of the following divisions:

> Reactor Radiation—Linac Radiation—Nuclear Radiation—Applied Radiation.

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in the selection, acquisition, and effective use of automatic data processing equipment; and serves as the principal focus for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

> Information Processing Standards—Computer Information — Computer Services — Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System, and provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

> Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information [3]—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

[2] Located at Boulder, Colorado 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

UNITED STATES DEPARTMENT OF COMMERCE
Maurice H. Stans, *Secretary*
NATIONAL BUREAU OF STANDARDS • Lewis M. Branscomb, *Director*

The Calculation of Rotational Energy Levels and Rotational Line Intensities in Diatomic Molecules

Jon T. Hougen

Institute for Basic Standards
National Bureau of Standards
Washington, D.C. 20234

t,
U.S. **National Bureau of Standards Monograph 115**

Nat. Bur. Stand. (U.S.), Monogr. 115, 52 pages (June 1970)
CODEN: NBSMA

Issued June 1970

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 (Order by SD Catalog No. C13.44:115), Price 55 cents

Preface

This monograph describes procedures for making quantum mechanical calculations of rotational energy levels and rotational line intensities in diatomic molecules. The procedures are illustrated by sample calculations. A familiarity with the material of this monograph should enable a practicing electronic spectroscopist to carry out, though in a rather mechanical way, his own theoretical calculations for molecules under experimental investigation.

A true understanding of the procedures described below can only be acquired by studying the theoretical reference material cited. These references are not exhaustive; they represent sources which the author finds convenient and instructive. Unfortunately, the material in the references is sometimes presented in a notation different from that used here. In addition, it is sometimes slightly too general or slightly too specific to apply directly to diatomic molecules.

The material of this monograph is aimed at electronic spectroscopists who have had the equivalent of one semester of graduate-level quantum mechanics.

Finally, I should like to point out, that the procedures described here for carrying out calculations are not new. Neither do they represent all possible correct procedures. They do represent, however, a unified approach to the problem, which, in the opinion of the author, is easier to understand than the original literature cited, and less likely to lead to error than some of the alternative calculation procedures.

Note added in proof: The reader is referred to the book *Rotational Structure in the Spectra of Diatomic Molecules* [28] by I. Kovács, which just appeared and which represents another author's discussion of much of the material in this monograph.

Library of Congress Catalog Card No. 76-604235

Contents

The Calculation of Rotational Energy Levels and Rotational Line Intensities in Diatomic Molecules

Jon T. Hougen

Procedures are described, in this pedagogical monograph, for making quantum mechanical calculations of rotational energy levels and rotational line intensities in diatomic molecules. The procedures are illustrated by sample calculations. A familiarity with the material of this report should enable a practicing electronic spectroscropist to carry out, though in a rather mechanical way, his own theoretical calculations for molecules under experimental investigation. The material of this report is aimed at electronic spectroscopists who have had the equivalent of one semester of graduate-level quantum mechanics.

Key words: Diatomic molecules; Hund's coupling cases; rotational levels; rotational line intensities; theoretical calculations.

1. Calculation of Rotational Energy Levels

1.1. Hund's Coupling Cases (a), (b), (c), and (d)

In chapter 1 we seek to calculate rotational energy level expressions for certain limiting situations known as Hund's coupling cases [1] [1] (pp. 218–237), [2] (pp. 275–302), and also for situations intermediate between the limiting coupling cases. Because any discussion of Hund's coupling cases involves a consideration of various angular momenta, it is convenient at this point to summarize the types of angular momenta considered and the notation to be used. This summary is presented in table 1. The first column of this table specifies the type of angular momentum. We consider here electronic orbital angular momentum, electronic spin angular momentum, and the angular momentum associated with the rotation of the nuclei of the diatomic molecule about the center of mass. We do not consider the nuclear spin angular momentum. Each angular momentum has associated with it a quantum number specifying its magnitude and a quantum number specifying its projection along the internuclear axis. For the purposes of this paper, the projection quantum numbers will be considered to be signed quantities.

TABLE 1. *The angular momenta involved in Hund's coupling cases*

Type of angular momentum	Operator	Quantum numbers	
		Total	Projection
Electronic orbital	$\mathbf{L}$	L	Λ
Electronic spin	$\mathbf{S}$	S	Σ
Rotational	$\mathbf{R}$	R	. . .
Total	$\mathbf{J}=\mathbf{R}+\mathbf{L}+\mathbf{S}$	J	$\Omega=\Lambda+\Sigma$
Total−Spin	$\mathbf{N}=\mathbf{R}+\mathbf{L}$	N	Λ

It can be shown that the projection of the rotational angular momentum along the internuclear axis is necessarily zero. Hence, we do not introduce a quantum number for this projection. As a further consequence of this fact, the projection of the angular momentum **N** along the internuclear axis is equal to the projection of **L** along the axis, and the projection of **J** is equal to the projection of **L**+**S**, as indicated in the table.

---

[1] Figures in brackets indicate the literature references on p. 49.

In this monograph we shall define the various Hund's coupling cases in terms of two concepts: (i) the quantum number occurring in the expression for the rotational energy levels, and (ii) the good quantum numbers in the nonrotating-molecule problem. Table 2 describes Hund's coupling cases (a), (b), (c), and (d) in these terms.

TABLE 2. *Brief description of four Hund's coupling cases*

Coupling case	Rotational energy level expression	Good quantum numbers in the nonrotating molecule (see text)	Degeneracy in the nonrotating molecule
(a)...........................	$BJ(J+1)$	$\Lambda, S, \Sigma, (\Omega=\Lambda+\Sigma)$	2 or 1
(b)...........................	$BN(N+1)$	$\Lambda, S, \Sigma, (\Omega=\Lambda+\Sigma)$	$2(2S+1)$ or $(2S+1)$
(c)...........................	$BJ(J+1)$	Ω	2 or 1
(d)...........................	$BR(R+1)$	$L, \Lambda, S, \Sigma, (\Omega=\Lambda+\Sigma)$	$(2L+1)(2S+1)$

The second column of table 2 contains a rotational energy expression of the form $BX(X+1)$, where X is one of the quantum numbers from table 1. Rotational energies are given by these simple expressions only for pure Hund's coupling cases. Rotational energies for coupling cases intermediate between these pure coupling cases are given by much more complicated expressions.

The third column of table 2 indicates which quantum numbers are good ones in the nonrotating molecule for the various Hund's coupling cases. The nonrotating-molecule quantum numbers shown in table 2 for Hund's cases (a), (b), and (d) indicate those which *must* be good; other nonrotating-molecule quantum numbers may, in fact, also be good ones. The nonrotating-molecule quantum number shown in table 2 for Hund's case (c) indicates the *only permissible* good quantum number.

The fourth column in table 2 indicates the degeneracy of the energy levels in the nonrotating molecule. (This degeneracy need not be exact, but the nearly degenerate states must be separated by energies small compared to BJ.) In Hund's cases (a) and (c) the only degeneracy in the nonrotating molecule is that associated with the two values of Ω, i.e., $\pm|\Omega|$. (States characterized by $\Omega=0^+$ or $\Omega=0^-$ are, of course, nondegenerate.) In Hund's case (b) the $2S+1$ values of Σ associated with a given value of S, and the two values of Λ, i.e., $\pm|\Lambda|$, must give rise to a set of states, all of which are degenerate in the nonrotating molecule. In Hund's case (d) the $2L+1$ values of Λ associated with a given value of L, and the $2S+1$ values of Σ associated with a given value of S must give rise to a set of states degenerate in the nonrotating molecule.

1.2. General Approach to the Calculations

The basic approach to calculations taken in this monograph derives from the fact that the Hamiltonian for a diatomic molecule [3] (pp. 3–34) can be written in the form

$$H=H_{ev}+H_r, \tag{1–1}$$

where H_{ev} is the vibrational-electronic part of the Hamiltonian, which does *not* involve the rotational variables or the total angular momentum of the molecule, and where H_r is the rotational part of the Hamiltonian, which does involve the rotational variables and the total angular momentum, and which also involves many of the coordinates and momenta occurring in H_{ev}. Since H_{ev} does not involve the rotational variables or the total angular momentum of the molecule, it is convenient to call H_{ev} the Hamiltonian for the nonrotating molecule. $H_{ev}+H_r$ is then called the Hamiltonian for the rotating molecule.

As a consequence of eq (1–1), the discussion to follow will be divided into two parts, one dealing with the *nonrotational* part of the problem, the other dealing with the *rotational* part. In both parts we consider the concepts of approximate Hamiltonian, limited set of basis functions, and matrix elements of the Hamiltonian in the basis set. (As most spectroscopists know, energy levels are commonly obtained either by evaluating perturbation-theory expressions involving matrix elements of the Hamiltonian [4] (pp. 151–179), or by solving the secular equation obtained from a truncated Hamiltonian matrix [4] (pp. 191–198).)

Actually, there is some flexibility in the exact form of the Hamiltonian (1–1), depending on whether it is written in terms of laboratory-fixed or molecule-fixed spin functions. In this monograph we shall always use molecule-fixed spin functions [3] (pp. 12–14). Loosely speaking, this choice corresponds to using Hund's case (a) or case (c) basis set functions rather than Hund's case (b) or case (d) basis set functions.

The question of which basis set functions to use is of some importance, since the same calculation in two different basis sets can appear quite different. Some authors, for example, find it desirable to use Hund's case (b) basis set functions when the rotational energy levels of the molecule under study are very close to those of pure Hund's case (b). In my opinion, however, there is less chance of confusion and error for the novice, if *all* calculations are divided into a nonrotating part and a rotating part, so that these parts can be dealt with separately. Such a division forces one to use a basis set in which the quantum numbers of the nonrotating molecule are good, and thus precludes the use of case (b) and case (d) basis sets.

In any case, the basis set functions $|ev;\,r\rangle$ used in this report can be written as simple products of the form

$$|ev;\,r\rangle = |ev\rangle|r\rangle, \tag{1–2}$$

where the functions $|ev\rangle$ are eigenfunctions of H_{ev}, i.e., wave functions for the nonrotating molecule problem, and where the functions $|r\rangle$ are appropriate rotational wave functions for diatomic molecules [2] (pp. 279–281).[2]

Units can be somewhat confusing in spectroscopic calculations. The Hamiltonian operator represents the energy of the molecule, and as such has dimensions ML^2T^{-2} in terms of the fundamental quantities Mass, Length, and Time. Diatomic spectroscopists do not normally use energy units, however. Instead, they represent energy differences by their corresponding wave numbers, which have the dimension L^{-1}, and, in particular, cm^{-1}. Conversion from energy units to cm^{-1} is carried out by dividing energies by hc, where h is Planck's constant (having dimensions ML^2T^{-1}) and c is the velocity of light (having dimensions LT^{-1}). Confusion arises because the same symbol is normally used for the "same" quantity, regardless of the units in which it is expressed. For example, the symbol E may represent $E[ML^2T^{-2}]$ or $E[\mathrm{cm}^{-1}]$, the numerical values of the two E's being related by $E[\mathrm{cm}^{-1}]=E[ML^2T^{-2}]/hc$. A second source of confusion in units arises in discussing angular momentum couplings of the form $A\mathbf{L}\cdot\mathbf{S}$ or $B\mathbf{J}^2$. These two quantities occur in the Hamiltonian operator in such a way that they have the dimensions of energy, i.e., ML^2T^{-2}. Since the matrix elements of angular momentum components are multiples of $\hbar$, this requires that A and B have dimensions $M^{-1}L^{-2}$. In formulas used by diatomic spectroscopists, however, matrix elements of $A\mathbf{L}\cdot\mathbf{S}$ and $B\mathbf{J}^2$ are normally represented by something like $A\Lambda\Sigma$ or $BJ(J+1)$, where A and B have the dimension cm^{-1}, and where Λ, Σ, and J are dimensionless. The numerical values of the two A's (or two B's) are related by $A[\mathrm{cm}^{-1}]=A[M^{-1}L^{-2}]\hbar^2/hc$. In this monograph we shall follow common practice and represent the energy of the state, the spin-orbit coupling constant, the rotational constant, etc., by a single letter each, regardless of the units being used. As a general rule, terms of the Hamiltonian *operator* may be assumed to be in energy units, whereas *matrix elements* of the terms in this operator may be assumed to be in cm^{-1}.

1.3. Nonrotating-Molecule Hamiltonian

The electronic and vibrational Hamiltonian associated with the nonrotating molecule, as well as its energy levels and wave functions, will not be considered in detail in this monograph.

Electronic energies and wave functions for the nonrotating molecule can be determined from ab initio or semi-empirical treatments of the many electron problem. The former calculations require

---

[2] The material cited here deals with a rotating diatomic molecule in which electron spin is ignored. It can be seen from the discussion in [3] that a closely analogous treatment can be carried out in which spin is included.

extremely sophisticated computer programs and many hours of computer time; the latter calculations are not always quantitatively reliable. It will be seen below that matrix elements and energy levels associated with the electronic part of the nonrotating-molecule problem can usually be represented by a small number of parameters in the calculation of the rotational energy levels.

Vibrational energies and wave functions for the nonrotating molecule can be determined more easily than electronic energies and wave functions. Thus, vibrational effects can be taken into account explicitly in many cases. We shall consider only one vibrational effect in this monograph (see section 4.7).

Because the nonrotating-molecule Hamiltonian is not considered in detail in calculations of rotational energy levels, it is often represented simply by the symbol H_{ev}. Sometimes it is of interest to consider spin-orbit interaction explicitly; then the nonrotating-molecule Hamiltonian is represented by $H^0_{ev}+A\mathbf{L}\cdot\mathbf{S}$ or by $H^0_{ev}+\Sigma_i\xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i$, where **L** and **S** are operators representing the total electronic orbital and total electronic spin angular momenta respectively, and where $\mathbf{l}_i$ and $\mathbf{s}_i$ are operators representing the same two momenta for the individual electrons. The spin-orbit interaction operator $A\mathbf{L}\cdot\mathbf{S}$ is used to compute spin splittings *within a given spin multiplet.* If interactions between states belonging to different S or L values must be taken into account, then the operator $\Sigma_i\xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i$ must be used.

1.4. Nonrotating-Molecule Basis Set

Like the Hamiltonian H_{ev}, the basis set functions $|ev\rangle$ for the nonrotating molecule are not considered in detail in calculations of rotational energy levels. Consequently, these basis set functions are often represented only formally, by symbols containing the quantum numbers used to describe the basis set, e.g., $|\Omega\rangle$, $|\Lambda S\Sigma\rangle$, or $|L\Lambda S\Sigma\rangle$ (see table 2).

At this point it is perhaps worthwhile to digress and consider the notion of good and bad quantum numbers. A basis set is said to be characterized by a good quantum number, if each function of the basis set is an eigenfunction of some particular operator, belonging to an eigenvalue which is some simple function of the good quantum number. For example, the quantum number Ω is said to be a good quantum number, if each function of the basis set satisfies an equation of the form

$$(L_z+S_z)|\Omega\rangle=\Omega\hbar|\Omega\rangle. \tag{1–3}$$

In this example, (L_z+S_z) is the operator, $|\Omega\rangle$ is the basis set function, $\Omega\hbar$ is the eigenvalue, and Ω is the quantum number. A quantum number is not good (i.e., is bad) if equations of the form (1–3) are not satisfied by the functions of the basis set. For example, if

$$L_z|\Omega\rangle\neq(\text{constant})\cdot|\Omega\rangle, \tag{1–4}$$

then the quantum number associated with L_z, namely Λ, is not a good quantum number for the basis set.

We now consider the three types of nonrotating-molecule basis set functions suggested by column 3 of table 2 in more detail [1] (pp. 212–217). It turns out that the operator L_z+S_z commutes with H_{ev}. Consequently, wave functions for the nonrotating molecule are *always* characterized by the good quantum number Ω, representing the projection of the sum of the electronic orbital angular momentum and the electronic spin angular momentum along the internuclear axis.

When spin-orbit interaction is very large, i.e., when the energy levels of the nonrotating molecule do not fall into recognizable multiplet groups, then the wave functions for the nonrotating molecule are characterized only by the good quantum number Ω. Under these circumstances it is convenient to use basis set functions which are also characterized by this single good quantum number. In eq (1–3), $|\Omega\rangle$ represents such a basis set function for the nonrotating molecule. The quantum number Ω can take on only integral values for molecules with an even number of electrons, and only half-integral values for molecules with an odd number of electrons. Both types of wave functions for the nonrotating molecule occur in degenerate pairs when $\Omega\neq0$, the members of the pair being characterized by equal and opposite values of Ω. When $\Omega=0$, the nonrotating-molecule state is nondegenerate. Nonrotating-molecule basis set functions characterized only by Ω give rise to Hund's case (c) states in the rotating molecule.

When spin orbit interaction is not large, i.e., when the energy levels of the nonrotating molecule do fall into recognizable multiplet groups, then the wave functions for the nonrotating molecule are normally characterized by three *almost* good quantum numbers, namely: the value Λ of the projection of the total electronic orbital angular momentum along the internuclear axis (corresponding to the operator L_z), the value Σ of the projection of the total electronic spin angular momentum along the internuclear axis (corresponding to the operator S_z), and the value S of the total electronic spin angular momentum (corresponding to the operator S^2). Under these circumstances it is convenient to use basis set functions $|\Lambda S\Sigma\rangle$ characterized by the three good quantum numbers Λ, S, and Σ. Since these basis set functions are eigenfunctions of L_z and S_z, belonging to the eigenvalues $\Lambda\hbar$ and $\Sigma\hbar$ respectively, they are also eigenfunctions of the operator (L_z+S_z), belonging to the eigenvalue $\Omega\hbar$, where

$$\Omega=\Lambda+\Sigma. \tag{1–5}$$

Because Ω is so simply related to Λ and Σ, it is often not explicitly indicated in the symbol for the basis set functions. (Note also, that in the true wave functions for the nonrotating molecule, the quantum number Ω is good, while Λ and Σ are only approximately good.) The recognizable multiplet groups of energy levels mentioned above consist of the $2(2S+1)$ functions characterized by $\Lambda=\pm|\Lambda|$, $S=$ fixed value, and $\Sigma=S, S-1, S-2, \ldots, -S$ (or consist of the $(2S+1)$ such functions when $\Lambda=0$). As we shall see by example in section 1.9, nonrotating-molecule wave functions characterized by Λ, S, and Σ give rise to Hund's case (a) rotational levels when the energy separations among the multiplet components of the nonrotating molecule are all large compared to BJ, and give rise to Hund's case (b) rotational levels when these energy separations are all small compared to BJ.

When spin-orbit interaction is not large, and when electrostatic interactions between the electrons and the axial field of the diatomic molecule [1] (pp. 323–330) are not large, e.g., when electrons are in Rydberg orbitals, then the wave functions of the nonrotating molecule are normally characterized by four almost good quantum numbers, namely: Λ, S, and Σ as above, and the value L of the total electronic orbital angular momentum (corresponding to the operator L^2). In addition, nearly degenerate sets of such wave functions occur, consisting of the $(2L+1)(2S+1)$ functions characterized by $L=$ fixed value, $S=$ fixed value, $\Lambda=L, L-1, \ldots, -L$, and $\Sigma=S, S-1, \ldots, -S$. Under these circumstances it is convenient to use basis set functions $|L\Lambda S\Sigma\rangle$ characterized by the four good quantum numbers L, Λ, S, and Σ. Nonrotating-molecule wave functions characterized by L, Λ, S, and Σ give rise to Hund's case (a) rotational levels when the energy separations in the nonrotating molecule among the various components of the ${}^{2S+1}L$ complex are all large compared to BJ. They give rise to Hund's case (b) rotational levels when the separations between nonrotating-molecule states of different $|\Lambda|$ are all large compared to BJ, while separations among the multiplet components within a given ${}^{2S+1}\Lambda$ state are all small compared to BJ. They give rise to Hund's case (d) rotational levels when the separations among the various components of the ${}^{2S+1}L$ complex are all small compared to BJ.

For any particular problem, it is necessary to choose which of the three basis sets for the nonrotating molecule will be used. From a calculational point of view, it is desirable to use the basis set with the most quantum numbers, since more quantum numbers mean that more matrix elements can be evaluated explicitly. However, if certain quantum numbers of the basis set are not good quantum numbers at all for the actual wave functions of the nonrotating molecule, then the advantage gained by being able to evaluate explicitly certain matrix elements involving these quantum numbers is offset by the fact that the values calculated for the matrix elements are incorrect. If the good quantum numbers of the basis set are *almost* good for the actual wave functions, then it is often convenient to allow for the slight errors made in the calculation of matrix elements by the introduction of a few small adjustable parameters. (See, for example, sect. 1.10, where B is replaced by $B - ½\gamma$.) In the final analysis, basis set functions for the calculation of rotational energy levels are chosen by trial and error, to maximize agreement between the final calculations and the experimental observations.

1.5. Nonrotating-Molecule Matrix Elements

Matrix elements [5] (pp. 90–102, 176–188) of the nonrotating-molecule Hamiltonian operator in the basis set $|\Omega\rangle$ have the following form

$$\begin{aligned} &\langle\Omega|H_{ev}|\Omega'\rangle = 0, \text{ if } |\Omega\rangle \text{ and } |\Omega'\rangle \text{ are different functions,} \\ &\langle\Omega|H_{ev}|\Omega\rangle \ = \text{the energy of the nonrotating-molecule state } |\Omega\rangle. \end{aligned} \tag{1–6}$$

Since Ω is always a good quantum number in the nonrotating molecule, the exact eigenfunctions of the operator H_{ev} can be characterized by a value of Ω. It is convenient to choose the set of exact eigenfunctions of the nonrotating-molecule Hamiltonian to be the nonrotating-molecule basis set. Such exact eigenfunctions obey the relations given in (1–6). For the purposes of calculating rotational energy levels and rotational line intensities, the energy of each state $|\Omega\rangle$ is represented by an appropriate parameter, to be fit by comparison with experimental data.

Matrix elements of the nonrotating-molecule Hamiltonian operator in the basis set $|\Lambda S\Sigma\rangle$ can be taken to have the following form

$$\begin{aligned} &\langle\Lambda S\Sigma|H^0_{ev}+A\mathbf{L}\cdot\mathbf{S}|\Lambda'S'\Sigma'\rangle = 0, \text{ if } |\Lambda S\Sigma\rangle \text{ and } |\Lambda'S'\Sigma'\rangle \text{ are different functions} \\ &\langle\Lambda S\Sigma|H^0_{ev}+A\mathbf{L}\cdot\mathbf{S}|\Lambda S\Sigma\rangle = \text{the energy of the nonrotating-molecule state } |\Lambda S\Sigma\rangle \\ &\cong \text{constant} + A\Lambda\Sigma. \end{aligned} \tag{1–7}$$

The two exact equalities in (1–7) are satisfied only if the functions involved in the matrix elements are exact eigenfunctions of H_{ev}. However, the basis set functions $|\Lambda S\Sigma\rangle$ defined above are *not* exact eigenfunctions of the nonrotating-molecule Hamiltonian, because spin-orbit coupling destroys the goodness of the three quantum numbers Λ, S, and Σ. In other words, because the spin-orbit interaction operator $\Sigma_i\xi(r_i)\mathbf{l}_i \cdot \mathbf{s}_i$ does not commute with L_z, S^2, or S_z, this part of the Hamiltonian will mix together *basis set functions* characterized by different values of Λ, S, and Σ to form final nonrotating-molecule *wave functions.*

Nevertheless, when spin-orbit splittings between the various components of a given multiplet e.g., $^2\Pi_{1/2}$, $^2\Pi_{3/2}$) are small compared to separations between different multiplet groups (e.g., $^2\Sigma$, $^4\Sigma$, $^2\Pi$, $^4\Pi$, $^2\Delta$, etc.), then the basis set functions $|\Lambda S\Sigma\rangle$ are very good approximations to the exact eigenfunctions of the nonrotating-molecule Hamiltonian. Under these circumstances *it is convenient to shift our point of view a bit,* and to consider the functions $|\Lambda S\Sigma\rangle$ to be these exact eigenfunctions. It is then necessary, however, to remember that the quantum numbers Λ, S, Σ are no longer perfectly good, i.e., the appropriate eigenvalue equations are only approximately satisfied. For example,

$$\begin{aligned} L_z|\Lambda S\Sigma\rangle &= \Lambda\hbar|\Lambda S\Sigma\rangle + |\delta_1\rangle \\ S_z|\Lambda S\Sigma\rangle &= \Sigma\hbar|\Lambda S\Sigma\rangle + |\delta_2\rangle, \end{aligned} \tag{1–8}$$

where $|\delta_1\rangle$ and $|\delta_2\rangle$ are small functions which vanish when the quantum numbers Λ and Σ are perfectly good. Because of the presence of small "left-over" functions like these $|\delta_i\rangle$, the diagonal matrix elements of the spin-orbit operator $A\mathbf{L}\cdot\mathbf{S}$ are only approximately equal to $A\Lambda\Sigma$. Thus, precise energies of the multiplet components represented by the wave functions $|\Lambda S\Sigma\rangle$ deviate somewhat from the expression: constant $+A\Lambda\Sigma$. However, the exact energies of the nonrotating-molecule problem can always be represented by a set of adjustable parameters in the rotational calculations.

A shift in point of view similar to that above is also desirable for the basis set functions $|L\Lambda S\Sigma\rangle$. If the functions $|L\Lambda S\Sigma\rangle$ are taken to be the exact eigenfunctions of the nonrotating-molecule Hamiltonian, then we can write

$$\begin{aligned}&\langle L\Lambda S\Sigma|H_{ev}|L'\Lambda'S'\Sigma'\rangle=0, \text{ if } |L\Lambda S\Sigma\rangle \text{ and } |L'\Lambda'S'\Sigma'\rangle \text{ are two different functions}\\ &\langle L\Lambda S\Sigma|H_{ev}|L\Lambda S\Sigma\rangle=\text{the energy of the nonrotating-molecule state } |L\Lambda S\Sigma\rangle,\end{aligned} \tag{1-9}$$

where the quantum numbers L, Λ, S, Σ in these exact eigenfunctions of the nonrotating-molecule Hamiltonian are all slightly bad. The energies of these exact eigenfunctions can again be represented by appropriate adjustable parameters in the rotational calculations.

1.6. Rotating-Molecule Hamiltonian

The Hamiltonian operator corresponding to the rotational part of the problem in diatomic molecules [3] (pp. 6–16) must now be examined in some detail. H_r for any molecule can be written as a sum of three products, each product consisting of a rotational constant for the molecule and the square of one of the three components of the rotational angular momentum of the molecule [6] (pp. 273–284). Since there can be no rotational angular momentum of a diatomic molecule about its internuclear axis (the z axis), the third component of the rotational angular momentum is zero, and hence absent from H_r. H_r for diatomic molecules is thus written as

$$\begin{aligned}H_r&=B[R_x^2+R_y^2]\\ &=B[(J_x-L_x-S_x)^2+(J_y-L_y-S_y)^2],\end{aligned} \tag{1-10}$$

where the *rotational* angular momentum is expressed in the second line of (1–10) as the *total* angular momentum (**J**) *minus* the electronic *orbital* and *spin* angular momenta (**L** and **S**). For the purposes of calculation, H_r is often written in the form

$$\begin{aligned}H_r=&B(J^2-J_z^2)+B(L^2-L_z^2)+B(S^2-S_z^2)\\ &+B(L_+S_-+L_-S_+)-B(J_+L_-+J_-L_+)-B(J_+S_-+J_-S_+),\end{aligned} \tag{1-11}$$

where $J_\pm=J_x\pm iJ_y$, $L_\pm=L_x\pm iL_y$, and $S_\pm=S_x\pm iS_y$.

The extremely thorough student will find that the total angular momentum operator **J** for linear molecules is somewhat peculiar, since its molecule-fixed components do not obey angular-momentum-type commutation relations. Furthermore, the operator H_r for linear molecules does not have precisely the simple form indicated in (1–10). Nevertheless, it can be shown that correct results are obtained by ignoring the peculiarities associated with **J** in linear molecules and by treating **J** like the angular momentum operator defined for nonlinear molecules in [6].

The complete Hamiltonian H describing the nonrotational and rotational parts of the problem is of course given by (1–1). It is the matrix of the Hamiltonian (1–1) which will ultimately be diagonalized to obtain molecular energy levels and molecular wave functions.

Loosely speaking, one can see in eq (1–10) the origin of the various entries in column 2 of table 2. Forgetting for a moment the absence of R_z in (1–10), and remembering that the eigenvalue associated with the sum of the squares of the components of an angular momentum operator has the form $\hbar^2X(X+1)$, we note that: if the operators **L** and **S** in the rotational Hamiltonian (1–10) can both be ignored, then one might expect rotational energies to be given by $BJ(J+1)$, since J is the quantum number associated with $\mathbf{J}^2$; if the operator **L** in (1–10) can be ignored, but the operator **S** cannot be, then one might expect rotational energies to be given by $BN(N+1)$, since N is the quantum number associated with $(\mathbf{J}-\mathbf{S})^2$; if neither **L** nor **S** in (1–10) can be ignored, then one might expect rotational energies to be given by $BR(R+1)$, since R is the quantum number associated with $(\mathbf{J}-\mathbf{L}-\mathbf{S})^2$.

Since the operators **L** and **S** in (1–10) affect the course of the rotational energy levels only through the four cross terms J_xL_x, J_yL_y, J_xS_x, J_yS_y, and since the selection rules for nonvanishing matrix elements of L_x, L_y and S_x, S_y are $\Delta\Lambda$ and $\Delta\Sigma=\pm 1$, respectively, we see that the effects of **L** and/or **S** in (1–10) can be ignored when the separation between states of the nonrotating molecule satisfying the selection rules $\Delta\Lambda$ and/or $\Delta\Sigma=\pm 1$ is large compared to BJ.

1.7. Rotating-Molecule Basis Set

It can be shown [3] (pp. 6–16), [2] (pp. 279–281) that the wave functions $|\Omega JM\rangle$ associated with the rotational part of the problem can be characterized by one parameter and two good quantum numbers: Ω, J, M. The quantum number J specifies the *total* (not the rotational) angular momentum in the molecule. The quantum number M specifies the projection of the total angular momentum along some laboratory fixed Z axis, and takes on the values $J, J-1, \ldots, -J$. The parameter Ω, which helps to characterize the rotational wave functions of a diatomic molecule, is somewhat peculiar. It is convenient to consider the parameter Ω in the rotational wave functions to be the quantum number associated with the projection of the total angular momentum **J** along the internuclear axis. Table 1 indicates that the projection of **J** along the axis is actually equal to the projection of **L**+**S**, i.e., to the quantity represented in the nonrotating molecule by the symbol Ω. (Hence the rule $J\geqslant|\Omega|$.) Actually, however, Ω is not a *quantum number* for the rotational wave functions, since it does not correspond to an eigenvalue of some operator acting on the rotational wave functions. It arises in the rotational problem because the expression for the differential operator (1–10) [3] (p. 13) contains the operator L_z+S_z, and this latter operator, when acting on a nonrotating molecule basis set function, can be replaced by Ω.

Basis set functions for the complete problem consist of products of the basis set functions for the nonrotational problem and basis set functions for the rotational problem. Such functions are represented by one of the symbols:

$$\begin{aligned}|\Omega;\ \Omega JM\rangle &= |\Omega\rangle|\Omega JM\rangle\\ |\Lambda S\Sigma;\ \Omega JM\rangle &= |\Lambda S\Sigma\rangle|\Omega JM\rangle \qquad (1\text{–}12)\\ |L\Lambda S\Sigma;\ \Omega JM\rangle &= |L\Lambda S\Sigma\rangle|\Omega JM\rangle.\end{aligned}$$

The quantities Ω, J, M must be integers for molecules with an even number of electrons and half-integers for molecules with an odd number of electrons.

1.8. Rotating-Molecule Matrix Elements

Most of the matrix elements of the rotational Hamiltonian (1–10) can be obtained from general considerations of the matrix elements of an angular momentum operator in a basis set characterized by a quantum number specifying the total magnitude of the angular momentum and a quantum number specifying the projection along the z axis [5] (pp. 103–109), [7] (pp. 45–78). For example, the only nonvanishing matrix elements of the components of the spin angular momentum operator **S** in such a basis set are the following

$$\begin{aligned}\langle S\,\Sigma|S^2|S\,\Sigma\rangle &= \hbar^2 S(S+1)\\ \langle S\,\Sigma|S_z|S\,\Sigma\rangle &= \hbar\,\Sigma \qquad (1\text{–}13)\\ \langle S\ \Sigma\pm 1|S_\pm|S\,\Sigma\rangle &= \hbar\ [(S\mp\Sigma)(S\pm\Sigma+1)]^{1/2}.\end{aligned}$$

The nonvanishing matrix elements of the components of the orbital angular momentum **L** can be obtained from (1–13) by replacing S by L, and Σ by Λ everywhere. The nonvanishing matrix elements of the total angular momentum **J** can be obtained from (1–13) by replacing S by J, and Σ by Ω everywhere, except that $S_\pm$ must be replaced by $J_\mp$ in the third equation:

$$\langle J\ \Omega \pm 1 | J_\mp | J\ \Omega \rangle = \hbar [(J \mp \Omega)(J \pm \Omega + 1)]^{1/2}. \tag{1–14}$$

This somewhat surprising difference in behavior of **J** from **L** and **S** is discussed by Van Vleck [8].[3]

In actual calculations, two principal kinds of complications arise. First, it is possible, as discussed in section 1.5, that the angular momentum quantum numbers characterizing the basis set are not perfectly good. (Note, however, that J and Ω are always good quantum numbers in the basis sets defined above.) In that case, it is common to introduce an additional parameter in matrix elements like (1–13) to allow for the fact that eqs (1–13) are not exact. For example, part of the third equation of (1–13) might be written

$$\langle S\ \Sigma + 1 | S_+ | S\, \Sigma \rangle = (1-\gamma)\hbar [(S-\Sigma)(S+\Sigma+1)]^{1/2}, \tag{1–15}$$

where γ is a small dimensionless parameter much less than unity. This parameter can in principle be determined from accurate electronic wave functions. In practice it is usually determined by fitting the final calculated energy expressions to observed levels.

The second complication arises because sometimes a projection quantum number is used to characterize the basis set while the total-magnitude quantum number is not, e.g., the quantum number L is missing in the basis set $|\Lambda S \Sigma;\ \Omega J M\rangle$. Under these circumstances, the first and third equations of (1–13) cannot be used to obtain the matrix elements of the angular momentum concerned. Nevertheless, and this will be important below, as long as the projection quantum number is good, the selection rules on it implied by (1–13) for the components of an angular momentum operator are still valid [7] (pp. 45–78). Matrix elements which cannot be obtained from (1–13) are usually represented by a parameter, which either drops out of the calculation, or is determined from a fit to experimental data. Symmetry arguments (see chapter 2) are helpful in such cases to determine exactly how many different parameters can (or must) be used.

To illustrate the procedures described above we now consider two examples.

1.9. Example: The Hill and Van Vleck Expression for $^2\Pi$ States

The first example involves obtaining rotational energy expressions for a $^2\Pi$ state of a diatomic molecule [10], which is well separated from other electronic states, and in which the spin-orbit splitting is small compared to such electronic separations. The rotational energy levels of such an electronic state correspond to Hund's case (a), Hund's case (b), or some intermediate case between these two.

The wave functions of the nonrotating molecule are represented by $|\Lambda S \Sigma\rangle$, where the quantum numbers Λ, S, Σ are all slightly bad. The quantum number $\Omega = \Lambda + \Sigma$, however, is still good. The basis set functions for the complete (nonrotating plus rotating) problem are represented by $|\Lambda S \Sigma;\ \Omega J M\rangle$. Since we are dealing with a $^2\Pi$ state, $\Lambda = \pm 1$ and $S = 1/2$. Since $S = 1/2$, Σ takes on the values $\pm 1/2$. The quantum number M does not enter into the calculation of rotational energy levels for molecules unperturbed by the presence of external electric or magnetic fields. Hence, it will be ignored (even though the quantum number M will be carried along in the notation). The quantum number J will *not* be assigned a numerical value, since we are interested in the energy levels as a function of J. Basis set functions of interest for this problem thus have one of the following four forms: $|1\ 1/2\ 1/2;\ 3/2\ J M\rangle$, $|1\ 1/2\ -1/2;\ 1/2\ J M\rangle$, $|-1\ 1/2\ -1/2;\ -3/2\ J M\rangle$, or $|-1\ 1/2\ 1/2;\ -1/2\ J M\rangle$.

---

[3] Note that Van Vleck's paper deals with nonlinear molecules. Because of the absence of the third Eulerian angle in linear molecules, his arguments must be altered somewhat for diatomic molecules. No elegant discussion of this problem exists [9]. Note also, that we have ignored in eq (1–14) the quantum number M occurring in the wave functions $|\Omega J M\rangle$, since the operators J_+, J_-, and J_z are all diagonal in M and independent of M.

We must now set up the matrix of the Hamiltonian in the basis set given above. Let us represent a typical matrix element by the expression

$$\langle \Lambda'S'\Sigma';\ \Omega'J'M'|H|\Lambda S\Sigma;\ \Omega JM\rangle$$
$$=\langle \Lambda'S'\Sigma';\ \Omega'J'M'|H_{ev}|\Lambda S\Sigma;\ \Omega JM\rangle+\langle \Lambda'S'\Sigma';\ \Omega'J'M'|H_r|\Lambda S\Sigma;\ \Omega JM\rangle. \qquad (1\text{–}16)$$

The complete Hamiltonian for a molecule in the absence of external fields is always diagonal in the quantum numbers J and M. Thus, for the problem under consideration, the matrix element given on the left of (1–16) vanishes unless $J'=J$ and $M'=M$.

It can easily be seen, that if we restrict ourselves to matrix elements diagonal in J and M, and to the limited basis set appropriate for the rotational energy levels of a $^2\Pi$ electronic state ($\Lambda=\pm1$, $S=1/2$, $\Sigma=\pm1/2$), then the secular equation which must be solved to determine rotational energy levels is obtained from a Hamiltonian matrix having four rows and four columns. These rows and columns are labeled by the four basis set functions given just before eq (1–16). The elements of this 4× 4 matrix are calculated as follows.

Consider first the matrix elements of H_{ev}. The quantum numbers of the basis set have been divided by a semicolon into two groups, reflecting the factorization of (1–12). Because of this factorization, matrix elements of H_{ev} must be diagonal in the three rotational quantum numbers ΩJM. Values for matrix elements of H_{ev} diagonal in these three quantum numbers can be obtained from eqs (1–7) above. If we label rows and columns of a 4×4 matrix by the four functions given just before eq (1–16), then we find that the matrix of H_{ev} has the form

$$\begin{bmatrix} E+1/2A & 0 & 0 & 0 \\ 0 & E-1/2A & 0 & 0 \\ 0 & 0 & E+1/2A & 0 \\ 0 & 0 & 0 & E-1/2A \end{bmatrix}. \qquad (1\text{–}17)$$

The parameter E represents the constant given in the third line of (1–7), and $\pm 1/2A$ represents the spin splitting. We observe that only two distinct values for the energy occur, namely $E+1/2A$ and $E-1/2A$. This is consistent with the general phenomenon that energy levels in the nonrotating molecule characterized by $\Omega\neq0$ are doubly degenerate, the two degenerate functions having equal and opposite values of Ω (in this case $\Omega=\pm3/2$ and $\Omega=\pm1/2$). To be perfectly general we should allow the energy pattern to vary somewhat from that determined on the basis of simple spin-orbit interaction. However, in this case there is really only one relevant energy parameter in the nonrotating molecule, namely the distance between the $\Omega=\pm3/2$ and the $\Omega=\pm1/2$ states. This one energy separation can be described completely by the single parameter A.

Matrix elements of the rotational Hamiltonian (1–11) in a basis set consisting of the four functions labeling the matrix (1–17) can be obtained as follows. The operators $B(J^2-J_z^2)$, $B(S^2-S_z^2)$ and $-B(J_+S_-+J_-S_+)$ involve components of angular momenta for which the total magnitude quantum number and the z-axis projection quantum number characterize the basis set. Consequently, their matrix elements can be obtained immediately from (1–13).[4] Each of the operators $+B(L_+S_-+L_-S_+)$ and $-B(J_+L_-+J_-L_+)$ contains as a factor one of the quantities $L_\pm$. The operators $L_\pm$ have nonvanishing matrix elements only if the selection rule $\Delta\Lambda=\pm1$ is satisfied. (This selection rule applies to $L_\pm$ whenever Λ is a good quantum number, whether or not L is a good quantum number.) Since the limited basis set appropriate for the rotational energy levels of a $^2\Pi$ state only contains functions characterized by $\Lambda=\pm1$, it is not possible to construct matrix elements satisfying the selection rules $\Delta\Lambda=\pm1$ within this basis set. Thus, all matrix elements of $L_\pm$, and

---

[4] Actually, both S and Σ are slightly bad quantum numbers, but the results originally given by Hill and Van Vleck did not allow for this. The fact that S and Σ are not perfectly good quantum numbers can be taken into account by the introduction of small parameters γ analogous to the γ in eq (1–15).

hence of the two operators $+B(L_+S_- + L_-S_+)$ and $-B(J_+L_- + J_-L_+)$, vanish within this basis set. The remaining operator in (1–11), i.e., $B(L^2 - L_z^2)$, is more difficult to deal with. From the statements in section 1.8, this operator has only diagonal matrix elements in the limited basis set under consideration. It can be shown (see chapter 2) that these four diagonal matrix elements are all equal. They are often represented by the symbol $B\langle L_\perp^2\rangle$.

We now write down the matric of H_r analogous to the matrix of H_{er} given in (1–17). When $J \geqslant {}^3/_2$ it has the form

$$\begin{bmatrix} B[J(J+1) - {}^7/_4 + \langle L_\perp^2\rangle], & -B[(J-{}^1/_2)(J+{}^3/_2)]^{1/2}, & 0 & 0 \\ -B[(J-{}^1/_2)(J+{}^3/_2)]^{1/2}, & B[J(J+1) + {}^1/_4 + \langle L_\perp^2\rangle], & 0 & 0 \\ 0 & 0 & B[J(J+1) - {}^7/_4 + \langle L_\perp^2\rangle], & -B[(J-{}^1/_2)(J+{}^3/_2)]^{1/2} \\ 0 & 0 & -B[(J-{}^1/_2)(J+{}^3/_2)]^{1/2}, & B[J(J+1) + {}^1/_4 + \langle L_\perp^2\rangle]. \end{bmatrix} \tag{1–18}$$

The desired rotational energy levels are found by solving the secular equation obtained from the sum of the matrices for H_{ev} and H_r. It can be seen that the sum of (1–17) and (1–18), i.e., $H_{ev} + H_r$, contains two identical diagonal blocks. Individual diagonal blocks in a Hamiltonian matrix can always be diagonalized separately. Thus, we need only solve two secular equations of order two, rather than one secular equation of order four. Furthermore, these two secular equations are identical, so that the resultant energy levels occur in doubly degenerate pairs. The rotational energies obtained (twice each) from the secular equations are

$$\begin{aligned} &E + B\langle L_\perp^2\rangle + B[(J+{}^1/_2)^2 - 1] + {}^1/_2[A(A-4B) + 4B^2(J+{}^1/_2)^2]^{1/2} \\ &E + B\langle L_\perp^2\rangle + B[(J+{}^1/_2)^2 - 1] - {}^1/_2[A(A-4B) + 4B^2(J+{}^1/_2)^2]^{1/2}. \end{aligned} \tag{1–19}$$

(The algebraic operations necessary in obtaining (1–19) are simplified if one-half the trace is subtracted from each 2×2 matrix before diagonalizing it. This same quantity must then, of course, be added to the roots obtained from the secular equation.) Since the four basis set functions which label the rows and columns of (1–17) and (1–18) represent *all* the basis set functions for a given value of J, the two (doubly degenerate) energy levels given in (1–19) represent all the energy levels belonging to that value of J. The first two (J-independent) terms in (1–19) are often ignored in discussions of ${}^2\Pi$ rotational energy levels.

When $J = {}^1/_2$ the basis set functions labeling the first and third rows and columns of (1–17) and (1–18) do not exist. For this J value the Hamiltonian matrix factors into two identical 1×1 matrices, giving rise to a doubly degenerate energy level at $E - {}^1/_2A + B\langle L_\perp^2\rangle + B[J(J+1) + {}^1/_4]$.

Limiting Hund's case (a) and case (b) behavior can be obtained by expanding the square roots in (1–19) as power series. Consider first case (a) behavior, which occurs, from a mathematical point of view, when $|A| \gg BJ$. If $|A| \gg BJ$, it is convenient to approximate the radical in (1–19) as follows.

$$\begin{aligned} &[A(A-4B) + 4B^2(J+{}^1/_2)^2]^{1/2} = \{A^2[1 - 4B/A + (4B^2/A^2)(J+{}^1/_2)^2]\}^{1/2} \\ &= |A|\{1 + {}^1/_2(-4B/A) + {}^1/_2(4B^2/A^2)(J+{}^1/_2)^2 - {}^1/_8(-4B/A)^2 + O(B/A)^3\} \\ &\cong |A|\{1 - 2B/A + {}^1/_2(4B^2/A^2)[(J+{}^1/_2)^2 - 1]\}. \end{aligned} \tag{1–20}$$

The approximation (1–20) to the radical must now be substituted into (1–19). Since we must both add and subtract (1–20), it is convenient at this time to replace $|A|$ by A. The same two energy levels will be obtained by adding and subtracting $|A|$ as by adding and subtracting A (though not necessarily in the same order). Keeping only terms through order B/A, and dropping the first two terms in (1–19), we obtain the two energy levels

$$+{}^1\!/_2A+B[J(J+1)-{}^7\!/_4] \qquad (1\text{–}21\text{a})$$

$$-{}^1\!/_2A+B[J(J+1)+{}^1\!/_4], \qquad (1\text{–}21\text{b})$$

which, apart from an extra $+{}^1\!/_2B$ arising from $B\langle S_\perp^2\rangle$, agree with the familiar [1] (p. 220) Hund's case (a) energy level expression $B[J(J+1)-\Omega^2]$.[5] If we retain also the terms of order B^2/A^2 in (1–20), we see that the coefficient of $J(J+1)$ in eqs (1–21a) and (1–21b), i.e., the effective B value, must be replaced by $B(1+B/A)$ and $B(1-B/A)$ respectively. This is also a well-known Hund's case (a) result [1] (p. 233).

Hund's case (b) occurs, from a mathematical point of view, when $BJ\gg|A|$. Pure Hund's case (b) occurs when $A=0$. If $A=0$, the last two terms of eqs (1–19) can be written

$$B[(J+{}^1\!/_2)(J+{}^3\!/_2)-1] \qquad (1\text{–}22\text{a})$$

$$B[(J-{}^1\!/_2)(J+{}^1\!/_2)-1]. \qquad (1\text{–}22\text{b})$$

Both of these equations are of the form $B[N(N+1)-1]$. It is thus convenient to introduce an integer N, which is equal to $J+{}^1\!/_2$ for the higher energy level of given J, and equal to $J-{}^1\!/_2$ for the lower energy level. Equations (1–22) then have the form of the familiar [1] (pp. 221–224) Hund's case (b) expression $B[N(N+1)-\Lambda^2]$.

The significance of the quantum number N, which has arisen here in a somewhat formal way, can best be understood by examining the eigenfunctions of the matrix sum (1–17) + (1–18) when $A=0$, i.e., the case (b) eigenfunctions. The two eigenfunctions obtained by diagonalizing the 2×2 submatrix in the upper lefthand corner of (1–17) + (1–18) when $A=0$ are given on the righthand side of (1–23) as linear combinations of the basis set functions $|\Lambda S\Sigma;\,\Omega JM\rangle$ used to label the rows and columns of (1–17) and (1–18).

$$\begin{aligned}
|+1\ \ {}^1\!/_2\ \ N=J+{}^1\!/_2\ \ JM\rangle &= +[(J-{}^1\!/_2)/(2J+1)]^{1/2}|+1\ \ {}^1\!/_2\ \ +{}^1\!/_2;+{}^3\!/_2\,JM\rangle\\
&\quad -[(J+{}^3\!/_2)/(2J+1)]^{1/2}|+1\ \ {}^1\!/_2\ \ -{}^1\!/_2;+{}^1\!/_2\,JM\rangle\\
|+1\ \ {}^1\!/_2\ \ N=J-{}^1\!/_2\ \ JM\rangle &= +[(J+{}^3\!/_2)/(2J+1)]^{1/2}|+1\ \ {}^1\!/_2\ \ +{}^1\!/_2;+{}^3\!/_2\,JM\rangle\\
&\quad +[(J-{}^1\!/_2)/(2J+1)]^{1/2}|+1\ \ {}^1\!/_2\ \ -{}^1\!/_2;+{}^1\!/_2\,JM\rangle
\end{aligned} \qquad (1\text{–}23)$$

It can be seen that the two basis set functions in a given linear combination are characterized by the same values of Λ, S, J, and M, but by different values of Σ and Ω. For this reason we say that Λ, S, J, and M are good quantum numbers in Hund's case (b), but that Σ and Ω are not.

Although the linear combinations of functions given on the righthand side of (1–23) are not eigenfunctions of S_z and J_z, they do happen to be eigenfunctions of the operator $(\mathbf{J}-\mathbf{S})^2$, belonging to an eigenvalue $\hbar^2N(N+1)$. This can be demonstrated relatively easily. Since the functions $|\Lambda S\Sigma;\,\Omega JM\rangle$ are eigenfunctions of J^2, J_z, S^2, S_z, the expressions (1–13) and (1–14) can be used to determine the effect of $(\mathbf{J}-\mathbf{S})^2$ on these basis set functions and hence on any linear combination

---

[5] Hund's case (a) energy levels are obtained if all terms other than the first in (1–11) are ignored. Since we are interested here in studying a transition between Hund's case (a) and Hund's case (b), only the fourth and fifth terms in (1–11) were ignored in deriving (1–19). It is the third term in (1–11), i.e., $B(S^2-S_z^2)$, which contributes the $+{}^1\!/_2B$ present in (1–21) but normally absent in Hund's case (a) energy level expressions.

of them. Because the case (b) wave functions (1–23) belong to the eigenvalue $\hbar^2 N(N+1)$ of the operator $(\mathbf{J}-\mathbf{S})^2$, we say that N is a good quantum number in case (b).

It is sometimes convenient to label the eigenfunctions represented by the linear combinations on the righthand side of (1–23) by a single label of the form $|\Lambda SNJM\rangle$. These labels are found on the lefthand side of (1–23). The absence of a semicolon indicates that the functions $|\Lambda SNJM\rangle$ cannot be factored into a nonrotating-molecule part and a rotating-molecule part.

Some authors also find it convenient to use functions of the form $|\Lambda SNJM\rangle$ as basis set functions for diatomic molecule calculations. In this monograph we have chosen always to consider the nonrotating-molecule part of the problem separately from the rotating-molecule part. This decision requires us to use a basis set in which Ω and Σ, or perhaps just Ω, are defined, and in which N is not defined. Wave functions in which N is defined will therefore appear to arise here somewhat arbitrarily as linear combinations of the basis set functions, the linear combinations being obtained by diagonalizing appropriate Hamiltonian matrices.

1.10. Example: The Schlapp Expression for $^3\Sigma$ States

The calculation of rotational energy levels for a $^3\Sigma$ state [11] proceeds in much the same fashion as for $^2\Pi$ states. The basis set functions for the complete problem are represented by $|\Lambda S\Sigma;\Omega JM\rangle$. Since we are dealing with a $^3\Sigma$ state, $\Lambda=0$ and $S=1$. Since $S=1$, Σ takes on the values $+1$, 0, -1.[6] Note that, even though the spin projection quantum number Σ will not be a good quantum number in the final $^3\Sigma$ wave functions, it is perfectly acceptable, and indeed, from the point of view of the author, desirable, to use a basis set in which Σ is a good quantum number. Basis set functions for the problem thus have one of the following forms: $|0\ 1\ 1;\ 1\ J\ M\rangle$, $|0\ 1\ 0;\ 0\ J\ M\rangle$, or $|0\ 1\ {-1};\ {-1}\ J\ M\rangle$. For $J=0$ only the second function exists, of course.

The matrix elements of the Hamiltonian in this basis set can again be represented by (1–16). Since nonvanishing matrix elements of H are again diagonal in J and M, the matrix used to determine rotational energy levels for a $^3\Sigma$ electronic state ($\Lambda=0$, $S=1$, $\Sigma=\pm1, 0$) has three rows and columns, labeled by the basis set functions given at the end of the preceeding paragraph.

Consider now the matrix elements of H_{ev}. If we employ the same reasoning used in obtaining the energies given in (1–17), we find that all three components of the nonrotating-molecule $^3\Sigma$ state lie at the same energy. (There is no first order spin-orbit interaction $A\Lambda\Sigma$ in Σ electronic states because $\Lambda=0$.) Nevertheless, states with different values of Ω do have different energies [12], except that pairs of states related to each other by a change in sign of both Λ and Σ are degenerate. From these considerations, we find that the matrix of H_{ev} is given by

$$\begin{bmatrix} E & 0 & 0 \\ 0 & E-2\lambda & 0 \\ 0 & 0 & E \end{bmatrix} \qquad (1\text{–}24)$$

The two states with $\Omega=\pm1$ have been given the energy E and the state with $\Omega=0$ has been given the energy $E-2\lambda$. Actually, in this problem, as in the $^2\Pi$ problem, there is only one relevant energy separation. That separation is represented here by the quantity 2λ. (Experimental values for λ in the $^3\Sigma$ ground state of several molecules are given in table VI of [12]).

Matrix elements of the rotational Hamiltonian (1–11) can be obtained from considerations identical to those for a $^2\Pi$ state. The matrix of H_r for $J \geqslant 1$ is thus

$$\begin{bmatrix} BJ(J+1)+B\langle L_\perp^2\rangle & -B[2J(J+1)]^{1/2} & 0 \\ -B[2J(J+1)]^{1/2} & BJ(J+1)+2B+B\langle L_\perp^2\rangle & -B[2J(J+1)]^{1/2} \\ 0 & -B[2J(J+1)]^{1/2} & BJ(J+1)+B\langle L_\perp^2\rangle \end{bmatrix}, \qquad (1\text{–}25)$$

---

[6] Standard spectroscopic notation leads to a little confusion here, since the symbol Σ represents *both* an electronic state characterized by $\Lambda=0$, e.g., a $^3\Sigma$ state, *and also* the projection of S along the internuclear axis, e.g., $\Sigma=\pm1, 0$.

where we have again used arguments (see ch. 2) to conclude that the matrix elements of $B(L^2-L_z^2)$ in the basis set under consideration are all equal.

Unfortunately the sum of (1–24) and (1–25) does not immediately factor into any smaller diagonal blocks, so we must apparently find the roots of a cubic secular equation. However, there is one simplifying procedure which has not yet been employed. For reasons of symmetry, the size of the secular determinant for rotational energy levels can often be halved by working with the basis set functions $2^{-1/2}[|\Lambda S \Sigma;\ \Omega J M\rangle \pm |-\Lambda\ S\ -\Sigma;\ -\Omega J M\rangle]$ rather than with the individual functions $|\Lambda S\Sigma;\Omega JM\rangle$ themselves. In this connection we note that

$$\langle 2^{-1/2}(a+b)|H|2^{-1/2}(c+d)\rangle = {}^1\!/_2[\langle a|H|c\rangle + \langle a|H|d\rangle + \langle b|H|c\rangle + \langle b|H|d\rangle]. \qquad (1\text{–}26)$$

Let us consider the matrices of H_{ev} and H_r in a new basis set consisting of $2^{-1/2}[|0\,1\,1;1\,J\,M\rangle + |0\,1\,-1;-1\,J\,M\rangle]$, $|0\,1\,0;0\,J\,M\rangle$, and $2^{-1/2}[|0\,1\,1;1\,J\,M\rangle - |0\,1\,-1;-1\,J\,M\rangle]$. If the three rows and columns of the Hamiltonian matrix are labeled by these functions, we find that the matrix of H_{ev} is identical to that given in (1–24), but that the matrix of H_r has the form

$$\begin{bmatrix} BJ(J+1)+B\langle L_\perp^2\rangle & -2B[J(J+1)]^{1/2} & 0 \\ -2B[J(J+1)]^{1/2} & BJ(J+1)+2B+B\langle L_\perp^2\rangle & 0 \\ 0 & 0 & BJ(J+1)+B\langle L_\perp^2\rangle \end{bmatrix} \qquad (1\text{–}27)$$

The sum of the matrices (1–24) and (1–27), i.e., $H_{ev}+H_r$, now factors into a 2×2 diagonal block and a 1×1 diagonal block.

Before actually determining the rotational energy levels, we consider one further change in the Hamiltonian matrix. As mentioned above, the matrix of H_{ev} contains a single important adjustable parameter, corresponding to the single energy difference present in the nonrotating-molecule problem. On the other hand, the matrix elements of H_r should contain more adjustable parameters than the one, i.e., B, which actually occurs in (1–25). Strictly speaking, for example, there should be three different values for B in (1–25). Because the internuclear distance will be slightly different for the states with $\Omega=\pm 1$ than it is for the state with $\Omega=0$, one value for B occurs in the matrix positions (1, 1) and (3, 3), one in the position (2, 2), and one in the off-diagonal positions (1, 2), (2, 1), (2, 3), and (3, 2). (The fact that differences in internuclear distance lead to three and only three values for B in (1–25) can be shown from symmetry considerations, as indicated in chapter 2.) In addition to the internuclear distance effect, all matrix elements of operators involving S, which were evaluated numerically from (1–13) using $S=1$ and $\Sigma=+1, -1$, or 0, are slightly wrong, since S and Σ are not quite good quantum numbers. Since these matrix elements were evaluated numerically, they are somewhat difficult to find in (1–25), but the $2^{1/2}$ occuring in the off-diagonal matrix elements, for example, is not *exactly* $2^{1/2}$, because S and Σ are not exactly good quantum numbers. Finally, $\langle L_\perp^2\rangle$ has one value for the state with $\Omega=0$, and a slightly different value for the states with $\Omega=\pm 1$. Unfortunately, the extent of the various deviations mentioned above can only be quantitatively determined at the present time from experiment. For this reason it is common to introduce, in some way, additional parameters in (1–25), which are to be determined by fitting the experimental data. Since B is the only parameter occurring in (1–25), and since each matrix element contains B, it is possible to allow for all of the above-mentioned problems in a purely formal way by replacing the single parameter B by a set of B_{eff}'s. It can be shown by symmetry arguments (see chap. 2) that a maximum of seven B_{eff}'s could be used: three of which would occur in the positions (1, 1) and (3, 3); three of which would occur in the position (2, 2); and one of which would occur in the off-diagonal positions. (A single B_{eff} in the off-diagonal positions of (1–25) corresponds to a single B_{eff} in the off-diagonal positions of (1–27).)

We shall use in our calculations one value for B on the diagonal in (1–25) or (1–27), and one value for B, written as $B-{}^1\!/\!_2\gamma$, off the diagonal. Such a decision leads ultimately to Schlapp's expression [11], and can be justified as follows. When 2λ in (1–24) is very small compared to electronic energies (less than 30 cm^{-1}, say), then the difference in equilibrium internuclear distance for the two multiplet components of a $^3\Sigma$ state is expected to be very small, and only one coefficient for $J(J+1)$ is needed on the diagonal of (1–25). On the other hand, contamination of the $^3\Sigma$ state by other electronic states through spin-orbit interaction will cause the matrix elements of the components of **S** to deviate perceptibly from those given in (1–13). On the diagonal, such deviations, as well as the differences in $B\langle L_\perp^2\rangle$, can be allowed for by adjusting the parameter λ. Off the diagonal, such deviations can be allowed for by adjusting the parameter B.

In any case, the secular equation obtained from the sum of (1–24) and (1–27) modified as described above leads to the following energies for the three states of given $J\geqslant 1$:

$$\begin{aligned}&E+B\langle L_\perp^2\rangle+BJ(J+1)\\&E+B\langle L_\perp^2\rangle+BJ(J+1)+(B-\lambda)\pm[(B-\lambda)^2+(B-{}^1\!/\!_2\gamma)^2 4J(J+1)]^{1/2}.\end{aligned}\tag{1–28}$$

For $J=0$ the energy is $E-2\lambda+BJ(J+1)+2B+B\langle L_\perp^2\rangle$. The last line of (1–28) can be rearranged to give Schlapp's expressions by expanding the square root as follows.

$$\begin{aligned}&[(B-\lambda)^2+(B-{}^1\!/\!_2\gamma)^2 4J(J+1)]^{1/2}\cong[\lambda^2-2B\lambda+B^2(2J+1)^2-4\gamma BJ(J+1)]^{1/2}\\&\cong[\lambda^2-2B\lambda+B^2(2J+1)^2]^{1/2}\{1-2\gamma BJ(J+1)/[\lambda^2-2B\lambda+B^2(2J+1)^2]\}\\&\cong[\lambda^2-2B\lambda+B^2(2J+1)^2]^{1/2}-\gamma(J+{}^1\!/\!_2).\end{aligned}\tag{1–29}$$

(The first approximate equality in (1–29) indicates the loss of terms in γ^2. The second approximate equality indicates a power series expansion of the radical. The third approximate equality represents the case (b) approximation $BJ\gg|\lambda|$ for the small γ-dependent term.) Dropping the first two (J-independent) terms in (1–28) and making the substitutions $J=N$, $J=N-1$, and $J=N+1$ in the three energy expressions given in (1–28) and in (1–29), we obtain Schlapp's expressions

$$\begin{aligned}&BN(N+1)\\&BN(N+1)-(2N-1)B-\lambda+[\lambda^2-2B\lambda+B^2(2N-1)^2]^{1/2}-\gamma N+{}^1\!/\!_2\gamma\\&BN(N+1)+(2N+3)B-\lambda-[\lambda^2-2B\lambda+B^2(2N+3)^2]^{1/2}+\gamma(N+1)+{}^1\!/\!_2\gamma,\end{aligned}\tag{1–30}$$

apart from the small J-independent term $+{}^1\!/\!_2\gamma$. (N is assigned to the three levels of given J such that the level with $N=J+1$ has the highest energy and the level with $N=J-1$ has the lowest.

It is interesting to note that the parameter γ, which was introduced here to allow for some slight discrepancies in matrix elements of the spin operators, is generally introduced as a coupling parameter between the vectors $\boldsymbol{N}$ and $\boldsymbol{S}$ [11]. For $^2\Sigma$ and $^3\Sigma$ states, there is only one such parameter γ, and the two view points lead to identical results. For $^4\Sigma$ states, however, the present approach leads in a natural way to the introduction of two parameters γ [13], whereas the vector coupling approach appears incorrectly still to require only one.

2. Symmetry Properties of the Rotational Energy Levels

In chapter 2 we discuss the symmetry properties of the rotational energy levels of diatomic molecules [1] (pp. 237–240). The rotational levels of all diatomic molecules can be classified as + or − according to their parity, i.e., according to the behavior of the complete molecular wave function (apart from translation) when the laboratory-fixed Cartesian coordinates of all particles are replaced by their negatives. The rotational energy levels of homonuclear diatomic molecules can be classified in addition as *s* (symmetric) or *a* (antisymmetric) with respect to permutation of identical nuclei. The symmetry designations +, −, *s*, *a* are very important, since perturbations and optical transitions between two rotational levels are limited by selection rules on these quantities.

It turns out that the two *permutation-inversion* symmetry operations mentioned in the preceding paragraph, i.e., the laboratory-fixed inversion operation I, and the permutation P of identical nuclei in a homonuclear diatomic molecule, are related [14–16] to the *geometric* symmetry operations found in the usual group theory tables [6] (pp. 312–340), i.e., rotation, reflection, inversion, and rotation-reflection operations. It is convenient at this time to consider these two kinds of symmetry operations in more detail.

2.1. Geometric Symmetry Operations

Heteronuclear diatomic molecules belong to the point group $C_{\infty v}$. This point group [6] (p. 330) contains as symmetry elements the identity (E), one infinite-fold rotation axis (C_∞), and an infinite number of reflection planes (σ_v) containing the rotation axis. Homonuclear diatomic molecules belong to the point group $D_{\infty h}$. This point group [6] (p. 330) contains, in addition to the symmetry elements found in $C_{\infty v}$, an inversion center (i), one infinite-fold rotation-reflection axis (S_∞), and an infinite number of twofold rotation axes (C_2) perpendicular to the C_∞ axis.

It is relatively easy to visualize the effect of these geometric symmetry operations on an electron belonging to the diatomic molecule, and to determine in this way the precise effect of these geometric symmetry operations on the coordinates of the electron. Let

$$\begin{aligned} x_e &= \rho_e \sin\theta_e \cos\varphi_e \\ y_e &= \rho_e \sin\theta_e \sin\varphi_e \\ z_e &= \rho_e \cos\theta_e \end{aligned} \tag{2–1}$$

be the Cartesian coordinates and spherical polar coordinates of an electron in an axis system fixed in the diatomic molecule such that the internuclear axis is the z axis. Table 3 indicates the new coordinates of this electron, after it has been subjected to representative symmetry operations of the point groups $C_{\infty v}$ and $D_{\infty h}$. When one of these symmetry operations acts on a function containing the electron coordinates, its effect is to replace, everywhere in the function, each coordinate by the quantity found in table 3 at the intersection of the appropriate row and column. For example,

$$\begin{aligned} C_\infty^\epsilon(z)\cdot i\cdot C_2(y)\cdot f(\,.\;.\;.\;,\varphi_e,\;.\;.\;.\,) &= C_\infty^\epsilon(z)\cdot i\cdot f(\,.\;.\;.,\pi-\varphi_e,\;.\;.\;.\,) \\ &= C_\infty^\epsilon(z)\cdot f(\,.\;.\;.,\pi-(\pi+\varphi_e),\;.\;.\;.\,) = f(\,.\;.\;.,-\varphi_e-\epsilon,\;.\;.\;.\,). \end{aligned} \tag{2–2}$$

TABLE 3. *The effect of various symmetry operations on electron coordinates*

Symmetry operation	Coordinates acted upon					
	x_e	y_e	z_e	ρ_e	θ_e	φ_e
E	x_e	y_e	z_e	ρ_e	θ_e	φ_e
$C_\infty^\epsilon(z)$	$x_e \cos\epsilon - y_e \sin\epsilon$	$y_e \cos\epsilon + x_e \sin\epsilon$	$+z_e$	ρ_e	$+\theta_e$	$\varphi_e+\epsilon$
$\sigma_v(xz)$	$+x_e$	$-y_e$	$+z_e$	ρ_e	$+\theta_e$	$-\varphi_e$
i	$-x_e$	$-y_e$	$-z_e$	ρ_e	$\pi-\theta_e$	$\pi+\varphi_e$
$S_\infty^\epsilon(z)$	$x_e \cos\epsilon - y_e \sin\epsilon$	$y_e \cos\epsilon + x_e \sin\epsilon$	$-z_e$	ρ_e	$\pi-\theta_e$	$\varphi_e+\epsilon$
$C_2(y)$	$-x_e$	$+y_e$	$-z_e$	ρ_e	$\pi-\theta_e$	$\pi-\varphi_e$

These geometric symmetry operations also act on the vibrational and rotational variables of a diatomic molecule. The transformations of the vibrational variable can be obtained by considering the effect of the various symmetry operations on the vibrational displacement vectors. Pictorially speaking, these displacement vectors are subjected to the various symmetry operations while the molecular framework, i.e., the equilibrium position of each atom in the molecule, is left unchanged [6] (pp. 77–101). Table 4 indicates quantitatively the effect of representative symmetry operations of $C_{\infty v}$ and $D_{\infty h}$ on arbitrary displacement vectors $(\mathbf{d}_1, \mathbf{d}_2)$ for the two nuclei of a diatomic molecule. The vibrational variable for diatomic molecules is usually taken to be the internuclear distance r, given by $|(\mathbf{a}_1+\mathbf{d}_1)-(\mathbf{a}_2+\mathbf{d}_2)|$, where $\mathbf{a}_1$ and $\mathbf{a}_2$ represent equilibrium positions for the two atoms. Since the equilibrium positions $\mathbf{a}_i$ lie on the z axis, and since they are not changed in value by any of the symmetry operations, it is easy to show that the transformations of table 4 leave the vibrational variable r unaltered.

TABLE 4. *The effect of various symmetry operations on nuclear displacement vectors*

Symmetry operation	Displacement vector component acted upon					
	d_{1x}	d_{1y}	d_{1z}	d_{2x}	d_{2y}	d_{2z}
E	d_{1x}	d_{1y}	d_{1z}	d_{2x}	d_{2y}	d_{2z}
$C_\infty^\epsilon(z)$	$d_{1x}\cos\epsilon-d_{1y}\sin\epsilon$	$d_{1y}\cos\epsilon+d_{1x}\sin\epsilon$	$+d_{1z}$	$d_{2x}\cos\epsilon-d_{2y}\sin\epsilon$	$d_{2y}\cos\epsilon+d_{2x}\sin\epsilon$	$+d_{2z}$
$\sigma_v(xz)$	$+d_{1x}$	$-d_{1y}$	$+d_{1z}$	$+d_{2x}$	$-d_{2y}$	$+d_{2z}$
i	$-d_{2x}$	$-d_{2y}$	$-d_{2z}$	$-d_{1x}$	$-d_{1y}$	$-d_{1z}$
$S_\infty^\epsilon(z)$	$d_{2x}\cos\epsilon-d_{2y}\sin\epsilon$	$d_{2y}\cos\epsilon+d_{2x}\sin\epsilon$	$-d_{2z}$	$d_{1x}\cos\epsilon-d_{1y}\sin\epsilon$	$d_{1y}\cos\epsilon+d_{1x}\sin\epsilon$	$-d_{1z}$
$C_2(y)$	$-d_{2x}$	$+d_{2y}$	$-d_{2z}$	$-d_{1x}$	$+d_{1y}$	$-d_{1z}$

The effect of geometric symmetry operations on rotational variables is not as obvious as the effect on electronic and vibrational variables. The rotational variables of a molecule actually represent Eulerian angles, indicating how the (right-handed) molecule-fixed axis system is rotated with respect to some (right-handed) laboratory-fixed axis system [6] (pp. 285–286). For every orientation of the molecule-fixed axis system there is a set of corresponding Eulerian angles. For every set of Eulerian angles there is a corresponding orientation of the molecule-fixed axis system. It thus seems intuitively obvious that a geometric symmetry operation corresponding to a pure rotation should effect a change in the Eulerian angles corresponding to that pure rotation. It is not possible, however, to represent the change from a right-handed to a left-handed axis system by a set of Eulerian angles. Consequently, it is not intuitively obvious how sense-reversing symmetry operations (reflections, inversion, rotation-reflections) should affect the Eulerian angles. It turns out that a consistent and useful scheme of geometric symmetry operations can be obtained if a sense-reversing operation is defined to have the same effect on the Eulerian angles as does the pure rotation obtained from the sense-reversing operation by multiplication by the inversion [15, 16]. According to this prescription, i and E have the same effect on the rotational variables; $\sigma_v(xz)$ and $C_2(y)$ have the same effect; and $S_\infty^\epsilon(z)$ and $C_\infty^{\pi+\epsilon}(z)$ have the same effect.

The rotational variables of linear molecules present an additional complication [16], since they consist of two Eulerian angles rather than three [3] (pp. 6–16). Because the third Eulerian angle is missing, it is not possible to carry out the operation $C_\infty^\epsilon(z)$ on the rotational variables. Thus, this operation and $S_\infty^\epsilon(z)$, both of which were used in classifying electronic and vibrational levels, cannot be used in classifying rotational energy levels. The remaining symmetry operations are E, σ_v, i, and C_2. Of these, we need only investigate the effect of C_2 on the rotational variables. *Note added in proof:* A recently published article by Bunker and Papoušek [27] presents a more sophisticated discussion of the complications associated with symmetry operations for linear molecules than does reference [16].

The rotational variables θ and φ represent for a diatomic molecule the polar and azimuthal angles of the internuclear axis in the laboratory-fixed axis system. Since $C_2(y)$ corresponds to a twofold rotation about an axis perpendicular to the internuclear axis, this symmetry operation reverses the direction of the internuclear axis. Thus, $C_2(y)$ acting on a function of the rotational variables replaces θ by $\pi-\theta$ and φ by $\pi+\varphi$ everywhere in the function. The functions of the rotational variables most often considered, of course, are the rotational basis set functions $|\Omega JM\rangle$ themselves. Explicit expressions for these functions, corresponding precisely to the phase conventions used in this monograph, can be obtained by setting $\alpha=\pi/2$, $\beta=\theta$, $\gamma=\varphi$, $j=J$, $\mu'=\Omega$ and $\mu=M$ in the quantity $[(2j+1)/4\pi]^{1/2}\cdot\mathcal{D}^{(j)}(\{\alpha\beta\gamma\})_{\mu'\mu}$, where $\mathcal{D}^{(j)}(\{\alpha\beta\gamma\})_{\mu'\mu}$ is given in eq (15.27) of Wigner's book on group theory [17]. In this same connection, the 3×3 rotation matrices used in eqs (2–3) below can be obtained by setting $\chi=\pi/2$, $\theta=\theta$, and $\varphi=\varphi$ in Appendix I of [6].

The effect of $C_2(y)$ on the polar and azimuthal angles of the internuclear axis, as defined above, is different from the effect of $C_2(y)$ on the polar and azimuthal angles of an electron, as given in table 3. This difference arises because $C_2(y)$ represents a rotation about an axis which is always perpendicular to the internuclear axis, but which is not in general perpendicular to the position vector from the origin to a given electron.

2.2. Permutation-Inversion Symmetry Operations

The relation between the geometric symmetry operations of section 2.1 and the permutation-inversion symmetry operations can be demonstrated most easily by considering an equation relating the laboratory-fixed Cartesian coordinates $(X_iY_iZ_i)$ of the electrons and nuclei in a diatomic molecule to the molecule-fixed electronic coordinates (xyz), the equilibrium positions of the nuclei, the displacement vectors $\mathbf{d}_i$ of the nuclei, and the two rotational angles θ, φ [15, 16].

$$\begin{bmatrix} X_e \\ Y_e \\ Z_e \end{bmatrix} = \begin{bmatrix} -\sin\varphi & -\cos\theta\cos\varphi & \sin\theta\cos\varphi \\ \cos\varphi & -\cos\theta\sin\varphi & \sin\theta\sin\varphi \\ 0 & \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} x_e \\ y_e \\ z_e \end{bmatrix}$$

$$\begin{bmatrix} X_1 \\ Y_1 \\ Z_1 \end{bmatrix} = \begin{bmatrix} -\sin\varphi & -\cos\theta\cos\varphi & \sin\theta\cos\varphi \\ \cos\varphi & -\cos\theta\sin\varphi & \sin\theta\sin\varphi \\ 0 & \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} d_{1x} \\ d_{1y} \\ -(\mu/m_1)r_e+d_{1z} \end{bmatrix} \qquad (2\text{–}3)$$

$$\begin{bmatrix} X_2 \\ Y_2 \\ Z_2 \end{bmatrix} = \begin{bmatrix} -\sin\varphi & -\cos\theta\cos\varphi & \sin\theta\cos\varphi \\ \cos\varphi & -\cos\theta\sin\varphi & \sin\theta\sin\varphi \\ 0 & \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} d_{2x} \\ d_{2y} \\ +(\mu/m_2)r_e+d_{2z} \end{bmatrix}.$$

The left-hand sides of eqs (2–3) contain the Cartesian coordinates of an electon and the two nuclei in an axis system parallel to that fixed in the laboratory, but located at the center of mass of the equilibrium configuration of the nuclei. The righthand sides of eqs (2–3) all contain a 3×3 rotation matrix, the direction cosine matrix, which transforms vector components from a molecule-fixed axis system to a laboratory-fixed axis system. This matrix is a function of the rotational variables θ and φ, specifying the direction of the internuclear axis of the diatomic molecule in the laboratory-fixed axis system. The column vector on the far right in the first of eqs (2–3) contains the molecule-fixed coordinates of an electron. The second and third column vectors on the far right contain the positions of the two nuclei in the molecule-fixed axis system. At equilibrium $(\mathbf{d}_1=\mathbf{d}_2=0)$ both nuclei lie on the z axis, with the center of mass at the origin, and with internuclear distance r_e; $\mu=m_1m_2/(m_1+m_2)$ is the reduced mass of the molecule.

Consider now the effect of the four symmetry operations E, $\sigma_v(xz)$, i, and $C_2(y)$ on the coordinates in eqs (2–3). The transformations of the coordinates on the right side of (2–3) can be obtained from tables 3 and 4 and from the text of section 2.1. It is fairly easy to show from (2–3) that these operations give rise to the transformations of laboratory-fixed coordinates shown in table 5. From table 5 we see that the geometric symmetry operation $\sigma_v(xz)$, when it is applied to the electronic, vibrational, and rotational (i.e., to all) variables, is equivalent to the laboratory-fixed inversion operation I; and that the geometric symmetry operation $C_2(y)$, when it is applied to the electronic, vibrational, and rotational variables, is equivalent to the permutation P of the two (identical) nuclei in the molecule. From table 5 we also see that the geometric symmetry operation i is equivalent to the product $P \cdot I$, i.e., to the combined permutation and laboratory-fixed inversion operation.

Table 5. *The effect of various symmetry operations on laboratory-fixed Cartesian coordinates of the electrons and of the two nuclei*

Symmetry operation	Coordinates acted upon								
	X_e	Y_e	Z_e	X_1	Y_1	Z_1	X_2	Y_2	Z_2
E	X_e	Y_e	Z_e	X_1	Y_1	Z_1	X_2	Y_2	Z_2
$\sigma_v(xz)$	$-X_e$	$-Y_e$	$-Z_e$	$-X_1$	$-Y_1$	$-Z_1$	$-X_2$	$-Y_2$	$-Z_2$
i	$-X_e$	$-Y_e$	$-Z_e$	$-X_2$	$-Y_2$	$-Z_2$	$-X_1$	$-Y_1$	$-Z_1$
$C_2(y)$	$+X_e$	$+Y_e$	$+Z_e$	$+X_2$	$+Y_2$	$+Z_2$	$+X_1$	$+Y_1$	$+Z_1$

It is evidently necessary to distinguish clearly between the "molecule-fixed" inversion operation i, and the "laboratory-fixed" inversion operation I, since these two operations are not equivalent. In particular, i exists only if the diatomic molecule is homonuclear, whereas I exists for all diatomic molecules. The precise difference between these two inversion operations can only be understood after some study [14, 15, 16].

Rotational energy levels are said to be of even (+) parity if the corresponding complete molecular wave functions are invariant to the laboratory-fixed inversion operation I; they are of odd (−) parity if the wave functions transform into their negatives. Rotational energy levels of homonuclear diatomic molecules are said to be symmetric (s) if the corresponding complete molecular wave functions are invariant to the exchange of identical nuclei P; they are antisymmetric (a) if the wave functions transform into their negatives.

2.3. The Symmetry Operation σ_v

As a further aid in understanding the geometric symmetry operation σ_v, let us consider its effect on several electronic wave functions. In particular, let us consider diatomic-molecule wave functions derived from atomic wave functions. The one-electron atomic configuration np gives rise to an orbital P state ($L=1$), which in turn gives rise to diatomic-molecule orbital $\Sigma(\Lambda=0)$ and $\Pi(\Lambda=\pm1)$ states. The wave functions for these diatomic-molecule states are

$$\begin{aligned} |p\,\Sigma\rangle &= +f(\rho_e)\cos\theta_e \\ |p\,\Pi_\pm\rangle &= \mp f(\rho_e)\,2^{-1/2}\sin\theta_e\,e^{\pm i\varphi_e}, \end{aligned} \tag{2–4}$$

if we use the phase conventions of Condon and Shortley [7] (p. 52). These functions transform as follows under the operation $\sigma_v(xz)$ (see table 3)

$$\begin{aligned} \sigma_v|p\,\Sigma\rangle &= +|p\,\Sigma\rangle \\ \sigma_v|p\,\Pi_\pm\rangle &= -\,|p\,\Pi_\mp\rangle, \end{aligned} \tag{2–5}$$

which can be written as

$$\sigma_v|L\ \Lambda\rangle = -(-1)^{L-\Lambda}|L\ -\Lambda\rangle . \tag{2–6}$$

Equations (2–4) and (2–5) can be used to illustrate a fundamental point concerning the relationship between the choice of phase factors for a set of wave functions and their transformation properties under symmetry operations. It can be seen that the first of the transformation equations (2–5) is unaltered if $|p\ \Sigma\rangle$ in (2–4) is defined to be $-f(\rho_e)\cos\theta_e$ rather than $+f(\rho_e)\cos\theta_e$. Thus the transformation property represented by this first equation is independent of the choice of phases, and is an intrinsic property of the Σ state under consideration. On the other hand, the $-$ sign on the righthand side of the second of the transformation equations (2–5) can be changed to a $+$ sign, simply by defining the functions $|p\ \Pi_\pm\rangle$ in (2–4) to be $+f(\rho_e)\,2^{-1/2}\sin\theta_e\, e^{\pm i\varphi_e}$. The transformation property represented by this second equation is thus not an intrinsic property of the Π state, but depends on the choice of phases.

It turns out that all Σ electronic wave functions are characterized by an intrinsic transformation property under the operation σ_v. Furthermore, this transformation property is customarily indicated by a superscript attached to the Σ label; i.e., we define Σ^+ and Σ^- states, such that

$$\sigma_v|\Sigma^\pm\rangle = \pm|\Sigma^\pm\rangle . \tag{2–7}$$

It further turns out that all doubly-degenerate orbital electronic states, i.e., those with $|\Lambda| > 0$, are *not* characterized by an intrinsic transformation property under the operation σ_v. Nevertheless, explicit transformation equations for such functions can be written down once a set of phases for the wave functions has been chosen. To obtain correct answers in any calculation, of course, it is necessary that the phase choice implicit in one's transformation equations be consistent with the phase choice implicit in one's expressions for the various matrix elements.

Consider now the two-election atomic configuration $np\ n'p$. This configuration also gives rise to an orbital P state, which in turn gives rise to diatomic-molecule orbital Σ and Π states. The wave functions for these diatomic-molecule states are

$$\begin{aligned}
|np\ n'p\ P\ \Sigma\rangle &= +2^{-3/2} f_1(\rho_{e1})\sin\theta_{e1}\ e^{-i\varphi_{e1}} f_2(\rho_{e2})\sin\theta_{e2}\ e^{+i\varphi_{e2}} \\
&\quad -2^{-3/2} f_1(\rho_{e1})\sin\theta_{e1}\ e^{+i\varphi_{e1}} f_2(\rho_{e2})\sin\theta_{e2}\ e^{-i\varphi_{e2}} \\
|np\ n'p\ P\ \Pi_+\rangle &= +\tfrac{1}{2} f_1(\rho_{e1})\cos\theta_{e1} f_2(\rho_{e2})\sin\theta_{e2}\ e^{+i\varphi_{e2}} \\
&\quad -\tfrac{1}{2} f_1(\rho_{e1})\sin\theta_{e1}\ e^{+i\varphi_{e1}} f_2(\rho_{e2})\cos\theta_{e2} \\
|np\ n'p\ P\ \Pi_-\rangle &= -\tfrac{1}{2} f_1(\rho_{e1})\sin\theta_{e1}\ e^{-i\varphi_{e1}} f_2(\rho_{e2})\cos\theta_{e2} \\
&\quad +\tfrac{1}{2} f_1(\rho_{e1})\cos\theta_{e1} f_2(\rho_{e2})\sin\theta_{e2}\ e^{-i\varphi_{e2}},
\end{aligned} \tag{2–8}$$

if we use the phase conventions of Condon and Shortley [7] (p. 76). These wave functions transform as follows under the symmetry operation $\sigma_v(xz)$ (see table 3)

$$\begin{aligned}
\sigma_v|np\ n'p\ P\ \Sigma\rangle &= -|np\ n'p\ P\ \Sigma\rangle \\
\sigma_v|np\ n'p\ P\ \Pi_\pm\rangle &= +|np\ n'\ p\ P\ \Pi_\mp\rangle ,
\end{aligned} \tag{2–9}$$

which can be written as

$$\sigma_v|L\ \Lambda\rangle = +(-1)^{L-\Lambda}|L\ -\Lambda\rangle . \tag{2–10}$$

We note in passing that the Σ state of (2–4) is a Σ^+ state, while that of (2–8) is a Σ^- state.

It turns out that electronic orbital wave functions $|L\Lambda\rangle$ having phase factors consistent with those of Condon and Shortley [7], and arising from atomic states of even parity, all transform according to (2–10), while wave functions having such phase factors, and arising from atomic states of odd parity, all transform according to (2–6). (The parity of an atomic state is determined by its behavior under the inversion operation i in table 3.)

There are several complications which arise in deciding whether to use (2–6) or (2–10). First, wave functions of the type $|L\Lambda\rangle$ are most often used in discussing Rydberg states. Under these circumstances, many of the electrons in the molecule are assigned to the "core" and are not considered explicitly. Since the core plays the role of the atomic nucleus, one must consider the parity of the atomic state which corresponds to the diatomic-molecule electronic wave function involving only electrons outside the core. Second, L is often not a good quantum number, so that no particular value of L suggests itself for use in (2–6) or (2–10). Under these circumstances one can often obtain consistent and correct results for states with $|\Lambda| > 0$ by arbitrarily giving L some value and arbitrarily choosing one of the two relations (2–6) or (2–10) to represent the transformation properties. This apparently casual choice of signs actually causes no difficulty. Of course, it does require a particular phase choice for the wave functions, which must be consistent with the phase choice implicit in any matrix element expressions used. However, when L is not a good quantum number, matrix elements involving the electronic orbital part of the wave function are not evaluated explicitly (they are left as adjustable parameters). Hence, contradictions between matrix elements and transformation properties are not introduced (see sect. 2.8). Finally, the transformation properties of $\Sigma^{\pm}$ states are determined by eq (2–7). Sometimes, however, it is convenient to incorporate a Σ state into a transformation scheme utilizing eq (2–6) or (2–10). It is then necessary to correlate the choice of sign and the choice of L to obtain the proper Σ state transformation properties.

Since the transformation properties of the electronic spin basis set functions $|S\Sigma\rangle$ and of the rotational basis set functions $|J\Omega\rangle$ are more difficult to illustrate with simple examples than are the transformation properties of the electronic basis set functions $|L\Lambda\rangle$, we shall merely state the final results here: The functions $|S\Sigma\rangle$ and $|J\Omega\rangle$, when chosen to have phase factors consistent with those of Condon and Shortley [7], transform like functions $|L\Lambda\rangle$ of even parity [15, 16]. We can thus summarize the effect of the operation σ_v on the various basis set functions described in chapter 1 by the following equations:

$$\sigma_v|L\,\Lambda\rangle = \pm(-1)^{L-\Lambda}\ |L\ -\Lambda\rangle \tag{2–11a}$$

$$\sigma_v|S\,\Sigma\rangle = \ (-1)^{S-\Sigma}\ |S\ -\Sigma\rangle \tag{2–11b}$$

$$\sigma_v|J\,\Omega\rangle = \ (-1)^{J-\Omega}\ |J\ -\Omega\rangle, \tag{2–11c}$$

where (2–11c) could be written more precisely as $\sigma_v|\Omega JM\rangle = (-1)^{J-\Omega}|-\Omega JM\rangle$, and where the + or − sign must be used in (2–11a) if the electronic state of the molecule correlates with a united atom state of even or odd parity, respectively. (In homonuclear diatomic molecules, this correlation is straightforward: g and u diatomic-molecule electronic states correlate with united atom states of even and odd parity, respectively.) The transformation properties given in (2–11) are, of course, consistent with the matrix elements given in (1–13) and (1–14). The transformation properties of the complete basis set functions are seen from eqs (2–11) to be

$$\sigma_v|L\ \Lambda\ S\ \Sigma;\ \Omega\ J\ M\rangle = \pm(-1)^{L-\Lambda+S-\Sigma+J-\Omega}\ |L\ -\Lambda\ S\ -\Sigma;\ -\Omega\ J\ M\rangle. \tag{2–12}$$

It was pointed out in section 2.2 that when the symmetry operation $\sigma_v(xz)$ acts on a complete basis set function (corresponding to both the nonrotational and the rotational part of the problem), then its net effect is equivalent to that obtained when the laboratory-fixed coordinates of all the particles in the molecule are replaced by their negatives. States of definite parity transform into themselves or into their negatives under this operation. It can easily be seen by application of (2–12) that functions of the form $|L\,\Lambda\,S\,\Sigma;\,\Omega\,J\,M\rangle \pm |L\ -\Lambda\ S\ -\Sigma;\ -\Omega\ J\ M\rangle$ have a definite parity. We next consider two examples of the determination of the parity of rotational energy levels.

2.4. Example: Parities of the Rotational Levels in a $^1\Sigma^-$ State

The complete basis set functions $|\,\Lambda\,S\,\Sigma;\Omega\,J\,M\rangle$ for a $^1\Sigma^-$ state can be written as $|0^-\ 0\ 0;\ 0\ J\ M\rangle$. They transform as follows under $\sigma_v(xz)$:

$$\sigma_v|0^-\ 0\ 0;\ 0\ J\ M\rangle = -(-1)^J\ |0^-\ 0\ 0;\ 0\ J\ M\rangle. \tag{2–13}$$

Thus, the rotational levels of even J are of odd parity (−), while those of odd J are of even parity (+).

2.5. Example: Parities of the Rotational Levels of a ${}^3\Sigma^+$ State

The rotational energy levels of a ${}^3\Sigma$ state were calculated in section 1.10. The three basis set functions used to label the matrix (1–27) transform as follows when the ${}^3\Sigma$ state is a ${}^3\Sigma^+$ state.

$$\begin{aligned}
\sigma_v\{2^{-1/2}[|0^+\ 1\ 1;\ 1\ J\ M\rangle+|0^+\ 1\ -1;\ -1\ J\ M\rangle]\}&\\
&=(-1)^{J-1}\{2^{-1/2}[|0^+\ 1\ -1;\ -1\ J\ M\rangle+|0^+\ 1\ 1;\ 1\ J\ M\rangle]\}\\
&=(-1)^{J-1}\{2^{-1/2}[|0^+\ 1\ 1;\ 1\ J\ M\rangle+|0^+\ 1\ -1;\ -1\ J\ M\rangle]\}\\
\sigma_v|0^+\ 1\ 0;\ 0\ J\ M\rangle=(-1)^{J+1}|0^+\ 1\ 0;\ 0\ J\ M\rangle& \qquad (2\text{–}14)\\
\sigma_v\{2^{-1/2}[|0^+\ 1\ 1;\ 1\ J\ M\rangle-|0^+\ 1\ -1;\ -1\ J\ M\rangle]\}&\\
&=(-1)^{J-1}\{2^{-1/2}[|0^+\ 1\ -1;\ -1\ J\ M\rangle-|0^+\ 1\ 1;\ 1\ J\ M\rangle]\}\\
&=(-1)^{J}\{2^{-1/2}[|0^+\ 1\ 1;\ 1\ J\ M\rangle-|0^+\ 1\ -1;\ -1\ J\ M\rangle]\}.
\end{aligned}$$

Consequently the energy levels obtained from the upper 2×2 block of (1–27) are of odd parity when J is even and of even parity when J is odd. The energy levels obtained from the lower right-hand corner of (1–27) are of even parity when J is even and of odd parity when J is odd. Since $J=N\pm 1$ for the former wave functions and $J=N$ for the latter, rotational levels of a ${}^3\Sigma^+$ state of even N are of even parity; those of odd N are of odd parity.

The wave functions in (2–14) all transform into themselves or into their negatives under the operation σ_v. This is not true in general of the functions $|\Lambda S\Sigma;\ \Omega JM\rangle$ of the original basis set. For this reason, the ${}^2\Pi$ wave functions used to label the matrix (1–18) cannot be assigned a parity, although appropriate sums and differences of such wave functions could be.

2.6. The Symmetry Operation *i*

The geometric symmetry operation i exists only if the diatomic molecule is homonuclear. Its effect on the various basis set wave functions of chapter 1 is quite simple [15, 16]. The operation i leaves the electronic spin functions $|S\Sigma\rangle$ and the rotational wave functions $|J\Omega\rangle$ invariant. The behavior of the electronic orbital wave functions under i is indicated by the subscripts g and u. For example,

$$\begin{aligned}
i[|\Sigma_g\rangle,\ |\Pi_g\rangle,\ |\Delta_g\rangle,\ \ldots]&=+[|\Sigma_g\rangle,\ |\Pi_g\rangle,\ |\Delta_g\rangle,\ \ldots]\\
i[|\Sigma_u\rangle,\ |\Pi_u\rangle,\ |\Delta_u\rangle,\ \ldots]&=-[|\Sigma_u\rangle,\ |\Pi_u\rangle,\ |\Delta_u\rangle,\ \ldots].
\end{aligned} \qquad (2\text{–}15)$$

It is important to recall that the molecule-fixed inversion operation i is not equivalent to the laboratory-fixed inversion operation I (see sect. 2.2).

2.7. The Symmetry Operation C_2

The symmetry operation C_2 also exists only if the diatomic molecule is homonuclear. Its effect on the basis set functions of chapter 1 can be determined most easily by noting that $C_2(y)\equiv\sigma_v(xz)\cdot i$. The effects of $\sigma_v(xz)$ are given in eqs (2–11). The effects of i are given in section 2.6. We thus conclude that the effect of $C_2(y)$ on the various basis set functions is given by the following equations:

$$C_2|L\ \Lambda\rangle=(-1)^{L-\Lambda}|L\ -\Lambda\rangle \qquad (2\text{–}16\text{a})$$

$$C_2|S\ \Sigma\rangle=(-1)^{S-\Sigma}|S\ -\Sigma\rangle \qquad (2\text{–}16\text{b})$$

$$C_2|J\ \Omega\rangle=(-1)^{J-\Omega}|J\ -\Omega\rangle. \qquad (2\text{–}16\text{c})$$

where (2–16c) could be written more precisely as $C_2|\Omega JM\rangle = (-1)^{J-\Omega}|-\Omega JM\rangle$. If L is not a good quantum number, it is again often possible to obtain consistent answers for the symmetry properties by arbitrarily assigning L some value. (The same value of L must be used in (2–16) as in (2–11), of course.) When $\Lambda=0$, the transformation properties of the orbital part of the electronic wave function are completely determined by the state symbol:

$$\begin{aligned} C_2|\Sigma_g^+\rangle &= +|\Sigma_g^+\rangle \qquad & C_2|\Sigma_g^-\rangle &= -|\Sigma_g^-\rangle \\ C_2|\Sigma_u^-\rangle &= +|\Sigma_u^-\rangle \qquad & C_2|\Sigma_u^+\rangle &= -|\Sigma_u^+\rangle. \end{aligned} \tag{2–17}$$

The transformation properties of the complete wave functions can be determined from the transformation properties of the individual parts as in eq (2–12) above.

It was pointed out in section 2.2 that when the symmetry operation $C_2(y)$ acts on a complete basis set function (corresponding to both the nonrotational and the rotational part of the problem), then its net effect is equivalent to that obtained when the laboratory-fixed coordinates of the two identical nuclei are permuted. Rotational states characterized as s transform into themselves under this operation; states characterized as a transform into their negatives. We next consider an example of the determination of the parity and of the s, a character of rotational energy levels.

2.8. Example: Symmetry Properties of the Rotational Levels in a $^1\Pi_u$ State

The complete basis set functions for a $^1\Pi_u$ state can be written as sums and differences of functions of the type $|\Lambda S\Sigma;\,\Omega JM\rangle$:

$$2^{-1/2}[|1_u\,0\,0;\,1\,J\,M\rangle \pm |-1_u\,0\,0;-1\,J\,M\rangle]. \tag{2–18}$$

Making use of (2–11) with an arbitrarily chosen value of $L=2$, we find

$$\sigma_v\{2^{-1/2}[|1_u\,0\,0;\,1\,J\,M\rangle \pm |-1_u\,0\,0;-1\,J\,M\rangle]\}$$

$$= \mp(-1)^J\{2^{-1/2}[|1_u\,0\,0;\,1\,J\,M\rangle \pm |-1_u\,0\,0;-1\,J\,M\rangle]\}. \tag{2–19}$$

Making use of (2–16) with the same arbitrarily chosen value of $L=2$, we find

$$C_2\{2^{-1/2}[|1_u\,0\,0;\,1\,J\,M\rangle \pm |-1_u\,0\,0;-1\,J\,M\rangle]\}$$

$$= \pm(-1)^J\{2^{-1/2}[|1_u\,0\,0;\,1\,J\,M\rangle \pm |-1_u\,0\,0;-1\,J\,M\rangle]\}. \tag{2–20}$$

We therefore conclude that the sum function in (2–18) is $-s$ for even J and $+a$ for odd J, and that the difference function is $+a$ for even J and $-s$ for odd J.

Had we arbitrarily chosen a value of $L=1$ in making use of (2–11) and (2–16), we would have concluded that the sum function was $+a$ for even J and $-s$ for odd J, and that the difference function was $-s$ for even J and $+a$ for odd J. For both values of L, we thus conclude that the rotational levels occur in pairs for given J, one member of the pair being $+a$, the other being $-s$. Whether the sum or difference function in (2–18) is $+a$ for given J actually depends on our choice of phases for the two functions $|\pm 1_u\,0\,0;\pm 1\,J\,M\rangle$. In the absence of further computations with these wave functions, neither phase choice introduces contradictions, and no further thought on the matter is necessary.

2.9. Relations Between Matrix Elements

Thus far in chapter 2, we have concerned ourselves with a determination of the symmetry properties of molecular wave functions. Symmetry operations can serve another purpose, however.

They can be used to obtain a relation between values of two different matrix elements. Their usefulness here arises from the fact that the value of any matrix element is unchanged if the two wave functions and the operator involved in the integral are subjected to a symmetry operation, since such an operation corresponds to a change in variables everywhere in the integral. Sometimes the relation obtained is equivalent to a selection rule. Suppose we have two wave functions Ψ_1, Ψ_2 and an operator L. Suppose further that these quantities obey the following transformation equations under some symmetry operation σ

$$\begin{aligned} \sigma\Psi_1 &= (-1)^{n1}\Psi_1 \\ \sigma\Psi_2 &= (-1)^{n2}\Psi_2 \\ \sigma L &= (-1)^{n3}L. \end{aligned} \tag{2-21}$$

By applying the symmetry operation σ to the integrand below, we obtain

$$\int \Psi_1^* L\Psi_2 d\tau = \int [\sigma(\Psi_1^* L\Psi_2)]d\tau = (-1)^{n_1+n_2+n_3}\int \Psi_1^* L\Psi_2 d\tau. \tag{2-22}$$

The integral given in (2–22) is therefore nonvanishing only if $n_1+n_2+n_3$ is an even integer. We have thus obtained a selection rule.

Equations (2–21) lead to a selection rule because Ψ_1, Ψ_2, and L all transform into some constant times themselves. The quantities Ψ_1, Ψ_2, and L might transform into some constant times Ψ_3, Ψ_4, and L', say. When this occurs, we do not obtain a selection rule, but obtain rather a relation between two different matrix elements. For example, H, H_{ev}, and H_r of eq (1–1) are all invariant under the symmetry operation σ_v. Thus, by applying σ_v to both wave functions and to H_{ev} in the matrix element $\langle L'\Lambda' S'\Sigma'|H_{ev}|L\Lambda S\Sigma\rangle$, and by using the transformation equations (2–11), we obtain the following equality

$$\begin{aligned} &\langle L'\,\Lambda'\,S'\,\Sigma'|H_{ev}|L\,\Lambda\,S\,\Sigma\rangle \\ &\quad = [\pm(-1)^{L'-\Lambda'+S'-\Sigma'}][\pm(-1)^{L-\Lambda+S-\Sigma}]\,\langle L'\ -\Lambda'\ S'\ -\Sigma'|H_{ev}|L\ -\Lambda\ S\ -\Sigma\rangle. \end{aligned} \tag{2-23}$$

where the first and second factors, respectively, come from the transformation properties of the first and second wave functions. Just as in (2–11), it is often possible to obtain consistent results, when some of the quantum numbers in (2–23) do not have definite values, by arbitrarily assigning them values. These values must be used throughout all calculations, however; i.e., the values chosen here must agree with those chosen for eqs (2–11) and (2–16).

As mentioned above, H_r is also invariant under σ_v. However, the individual operators occurring in H_r can be shown to transform as follows [15, 16]:

$$\begin{aligned} \sigma_v\, S_\pm &= -S_\mp \\ \sigma_v\, S_z &= -S_z \\ \sigma_v\, S^2 &= +S^2. \end{aligned} \tag{2-24}$$

Transformation equations for $L_\pm$, L_z, L^2 and $J_\pm$, J_z, J^2 can be obtained by making the obvious substitutions everywhere in (2–24). By combining the transformation properties (2–24) with those of the wave functions given in (2–11), various matrix elements of the Hamiltonian can be related to each other.

2.10. Example: $L_\perp^2 \equiv L^2 - L_z^2$

We now show that the matrix elements of $L_\perp^2$ in the basis set used to label (1–18) are all equal. By applying the symmetry operation σ_v to the wave functions and operators on the left side of the two equalities below, we obtain

$$\langle 1\ {}^1\!/_2\ {}^1\!/_2 :\ {}^3\!/_2\ J\ M|L^2 - L_z^2|1\ {}^1\!/_2\ {}^1\!/_2;\ {}^3\!/_2\ J\ M\rangle = +\langle -1\ {}^1\!/_2\ -{}^1\!/_2;\ -{}^3\!/_2\ J\ M|L^2 - L_z^2|-1\ {}^1\!/_2\ -{}^1\!/_2;\ -{}^3\!/_2\ J\ M\rangle$$

$$\langle 1\ {}^1\!/_2\ -{}^1\!/_2;\ {}^1\!/_2\ J\ M|L^2 - L_z^2|1\ {}^1\!/_2\ -{}^1\!/_2;\ {}^1\!/_2\ J\ M\rangle = +\langle -1\ {}^1\!/_2\ {}^1\!/_2;\ -{}^1\!/_2\ J\ M|L^2 - L_z^2|-1\ {}^1\!/_2\ {}^1\!/_2;\ -{}^1\!/_2\ J\ M\rangle.$$

(2–25)

In addition, if we assume that the matrix elements of the orbital operator $L_\perp^2$ do not depend on the spin quantum numbers, then we see that

$$\langle 1\ {}^1\!/_2\ {}^1\!/_2;\ {}^3\!/_2\ J\ M|L^2 - L_z^2|1\ {}^1\!/_2\ {}^1\!/_2;\ {}^3\!/_2\ J\ M\rangle = +\langle 1\ {}^1\!/_2\ -{}^1\!/_2;\ {}^1\!/_2\ J\ M|L^2 - L_z^2|1\ {}^1\!/_2\ -{}^1\!/_2;\ {}^1\!/_2\ J\ M\rangle. \quad (2\text{–}26)$$

Equation (2–26) rests ultimately on the assumption that the nonrotating-molecule basis set functions $|\Lambda S\Sigma\rangle$ can be written as the product $|\Lambda\rangle|S\Sigma\rangle$ of an orbital function $|\Lambda\rangle$ and a spin function $|S\Sigma\rangle$, and on the further assumption that the same orbital function is associated with all $2S+1$ spin functions corresponding to given S. These assumptions will be valid to the extent that Λ, S, and Σ are good quantum numbers. As a consequence of (2–25) and (2–26), the four matrix elements of $L_\perp^2$ in the basis set used to label the matrix (1–18) are all equal. The equalities represented by (2–25) are exact; that represented by (2–26) is only approximate.

2.11. The Time Inversion Operation θ

The time inversion operation θ [17] (pp. 325–348) is of interest here principally in connection with intensity calculations. The intensity of absorption or emission of light by diatomic molecules depends on matrix elements of the components of the dipole moment operator. These matrix elements are usually not calculated explicitly, but are rather treated as parameters, to be determined from a fit to experimental data. It sometimes happens that several such parameters occur in the intensity expressions, which then involve, for example, the squares of sums and differences of these parameters. It is clearly desirable to know which of the parameters are real and which are complex, since the arithmetic of real numbers is not identical to the arithmetic of complex numbers. Time inversion is a useful tool, since it is essentially the operation of taking complex conjugates. Indeed,

$$\theta k = k^*, \quad (2\text{–}27)$$

if k is a constant or a function of the positional coordinates of particles. However, because of the rather special nature of spin variables, time inversion, when applied to spin functions, is somewhat more complicated [17] (pp. 331–333).

Physically, time inversion would be expected to correspond to a transformation of variables in which the time t is replaced by $-t$. Thus, for example, a position coordinate x should remain invariant under time inversion, while a velocity dx/dt or a momentum $m(dx/dt)$ should transform into its negative. In quantum mechanics momenta are represented by operators of the form $-i\hbar(d/dx)$, which do not contain the time variable at all. However, in contrast to position coordinates, they do contain the pure imaginary number i. It is thus convenient in quantum mechanics to construct a formalism in which time inversion corresponds to the taking of complex conjugates rather than the replacing of t by $-t$.

Arguments such as this make the following transformation equations for angular momentum operators seem reasonable. (They are also correct [17] (pp. 329–330).)

$$\theta \mathbf{L} = -\mathbf{L}\theta$$

$$\theta \mathbf{S} = -\mathbf{S}\theta \tag{2–28}$$

$$\theta \mathbf{J} = -\mathbf{J}\theta$$

From these relations it is possible to show that when time inversion is applied to wave functions, the signs of all angular momentum projection quantum numbers are reversed. For example,

$$\theta\, L_z|L\,\Lambda\rangle = \theta\,\Lambda\hbar|L\,\Lambda\rangle = \Lambda\hbar[\theta|L\,\Lambda\rangle] = -L_z[\theta|L\,\Lambda\rangle]. \tag{2–29}$$

We thus conclude

$$\theta|L\,\Lambda\rangle \propto |L\ -\Lambda\rangle$$

$$\theta|S\,\Sigma\rangle \propto |S\ -\Sigma\rangle \tag{2–30}$$

$$\theta|\Omega\,J\,M\rangle \propto |-\Omega\ J\ -M\rangle.$$

When the system being considered contains an even number of electrons, $\theta^2 = +1$ [17] (p. 332). Under these circumstances, it happens that L, S, and J are all whole numbers, so that zero is a possible value for each of the projection quantum numbers Λ, Σ, Ω, and M. It is relatively easy to show that the phase factor of the wave function having a projection quantum number equal to zero can be chosen such that the function is unchanged when the time inversion operation is carried out. In other words, it is always possible to choose phases such that

$$\theta\,|L\,0\rangle = +|L\,0\rangle$$

$$\theta\,|S\,0\rangle = +|S\,0\rangle \tag{2–31}$$

$$\theta\,|0\,J\,0\rangle = +|0\,J\,0\rangle.$$

When the system being considered contains an odd number of electrons, $\theta^2 = -1$ [17] (p. 332). Under these circumstances, S and J are half-integers, so that a value of zero for Σ, Ω, and M is not possible. There are then no spin functions and no rotational functions which remain unchanged by the time inversion operation (see 2–30).) However, it is possible to show that one can always choose phases consistent with those of Condon and Shortley [7], such that

$$\theta\,|S\ {}^1\!/_2\rangle = +\,|S\ -{}^1\!/_2\rangle$$

$$\theta\,|{}^1\!/_2\,J\ {}^1\!/_2\rangle = +\,|-{}^1\!/_2\ J\ -{}^1\!/_2\rangle. \tag{2–32}$$

The effect of time inversion on all other functions can be obtained as follows. Our choice of phases for the ladder operators $S_\pm$ in eqs (1–13) implies that

$$|S\ {}^1\!/_2 + m\rangle = k_1(S_+)^m|S\ {}^1\!/_2\rangle$$

$$|S\ {}^1\!/_2 - n\rangle = k_2(S_-)^n|S\ {}^1\!/_2\rangle \tag{2–33}$$

where m and n are positive integers and k_1 and k_2 are positive constants. The transformation properties of components of the angular momenta given in (2–28) and eqs (2–32) and (2–33) allow us to write

$$\begin{aligned}\theta|S\ {}^1\!/_2+m\rangle &= \theta\, k_1(S_+)^m|S\ {}^1\!/_2\rangle = (-1)^m k_1(S_-)^m|S\ -{}^1\!/_2\rangle\\ &= (-1)^m|S\ -{}^1\!/_2-m\rangle\\ \theta|S\ {}^1\!/_2-n\rangle &= \theta\, k_2(S_-)^n|S\ {}^1\!/_2\rangle = (-1)^n k_2(S_+)^n|S\ -{}^1\!/_2\rangle \qquad (2\text{–}34)\\ &= (-1)^n|S\ -{}^1\!/_2+n\rangle.\end{aligned}$$

Equations (2–34) can easily be shown to be equivalent to

$$\theta|S\ \Sigma\rangle = (-1)^{\Sigma-1/2}|S\ -\Sigma\rangle \qquad (2\text{–}35)$$

for all values of Σ allowed for given half-integral S.

A set of four equations similar to (2–34) holds for the functions $|\Omega JM\rangle$ when J is half-integral, except that both laboratory-fixed $(J_X \pm iJ_Y)$ and molecule-fixed $(J_x \mp iJ_y)$ ladder operators must be used. One of these equations takes the form

$$\begin{aligned}\theta|{}^1\!/_2+m\ J\ {}^1\!/_2+n\rangle &= \theta k_3(J_x-iJ_y)^m(J_X+iJ_Y)^n|{}^1\!/_2\,J\,{}^1\!/_2\rangle\\ &= (-1)^{m+n}k_3(J_x+iJ_y)^m(J_X-iJ_Y)^n|-{}^1\!/_2\ J\ -{}^1\!/_2\rangle \qquad (2\text{–}36)\\ &= (-1)^{m+n}|-{}^1\!/_2-m\ J\ -{}^1\!/_2-n\rangle,\end{aligned}$$

where m and n are positive integers and k_3 is a positive constant. This equation and the three analogous equations obtained by using different combinations of $(J_x \mp iJ_y)^m$ and $(J_X \pm iJ_Y)^n$ can be shown to be equivalent to

$$\theta|\Omega\, J\, M\rangle = (-1)^{\Omega+M-1}|-\Omega\ J\ -M\rangle \qquad (2\text{–}37)$$

for all values of Ω and M allowed for given half-integral J.

For integral values of L, S, and J we find, by using (2–31) and equations similar to (2–34) and (2–36), that

$$\begin{aligned}\theta|L\ \Lambda\rangle &= (-1)^\Lambda|L\ -\Lambda\rangle\\ \theta|S\ \Sigma\rangle &= (-1)^\Sigma|S\ -\Sigma\rangle \qquad (2\text{–}38)\\ \theta|\Omega\, J\, M\rangle &= (-1)^{\Omega+M}|-\Omega\ J\ -M\rangle.\end{aligned}$$

Since an expression of the form $\langle a|a\rangle$ must always equal a real, positive number, we conclude that if $\theta|a\rangle = e^{i\alpha}|a'\rangle$ then $\theta\langle a| = e^{-i\alpha}\langle a'|$.

We consider an example of the use of time inversion in determining which matrix elements of the dipole moment operator are real and which are not in section 3.5.

3. Calculation of Rotational Line Intensities

In chapter 3 we discuss the determination of spectral line intensities. We shall not be concerned, however, with the total intensity of an electronic transition, nor with the vibrational distribution of intensity in a given band system. Rather, we shall consider the rotational distribution of intensity within a given band [1] (pp. 204–211).

Optical transitions in diatomic molecules are said to be electric dipole allowed, magnetic dipole allowed, or electric quadrupole allowed if the transition moment matrix element is nonvanishing when the electric dipole operator, the magnetic dipole operator, or the electric quadrupole operator, respectively, is used [7] (pp. 79–111). (These classifications are not necessarily mutually exclusive.) The vast majority of observed transitions are electric dipole allowed, and we shall consider only that case in this monograph. However, the considerations below can be applied to magnetic dipole transitions after relatively minor changes: For example, all signs on the righthand side of (3–2) must be positive, and the six signs preceding the parentheses on the righthand side of (3–4) must be changed from +, +, −, −, −, − to −, −, +, +, −, −; these sign changes lead, of course, to some changes in the selection rules. A discussion of electric quadrupole transitions is quite different from the discussion for dipole transitions, since the quadrupole operator is a tensor of the second rank, rather than a vector.

As suggested above, the intensity of most optical transitions is governed by the value of matrix elements of the electric dipole moment operator [5] (pp. 272–282). We must therefore examine this operator in some detail. Classically, the dipole moment of a system of charges e_i is a vector quantity given by an expression of the form $\Sigma_i\, e_i\, \mathbf{r}_i$, where $\mathbf{r}_i$ is a vector from the point at which the dipole moment is being defined to the charge e_i. Vector operators are sometimes a source of confusion in molecular spectroscopy, since they are often represented by their components in two different Cartesian axis systems, one fixed in the laboratory, the other fixed in the molecule. The dipole moment operator can also be resolved into components in either of these two axis systems. Matrix elements of the two sets of components have quite different interpretations.

We shall here follow the common, but not universal, practice of representing the laboratory-fixed components of the dipole moment operator by μ_X, μ_Y, μ_Z and the molecule-fixed components by μ_x, μ_y, μ_z. These two sets of components are related by an equation of the form

$$\mu_R = \Sigma_s \alpha_{Rs} \mu_s, \tag{3–1}$$

where α_{Rs}, the direction cosine matrix [3] (pp. 10–11), [6] (pp. 285–6), [8], is found on the righthand side of eqs (2–3). (Note that the direction cosine matrix for linear molecules contains only two Eulerian angles.) The subscript R in (3–1) ranges over X, Y, Z; the subscript s over x, y, z. For most of the remainder of this chapter we shall discuss the determination and interpretation of matrix elements of the quantities occurring in eq (3–1).

3.1. Laboratory-Fixed Components of the Electric Dipole Moment Operator μ

The intensity of an optical transition between two states often depends on the polarization of the light passing through the sample in an absorption experiment, or on the polarization of the light being detected in an emission experiment. This phenomenon is reflected in the theory as follows.

Theoretical calculations for experiments involving plane polarized light with the electric vector of the light in the laboratory-fixed Z direction must be performed with the laboratory-fixed Z component of the dipole moment operator [7] (pp. 90–93, 97–100), i.e., the intensity in such an experiment for a transition between an initial state i and a final state f is proportional to $|\langle f|\mu_Z|i\rangle|^2$. Clearly, by analogy, if the light is plane polarized with the electric vector in the X or Y direction, then the theoretical calculations must be performed with the laboratory-fixed X or Y component of the dipole moment operator, respectively.

Theoretical calculations for experiments involving circularly polarized light traveling in the laboratory-fixed Z direction must be performed with the combinations $\mu_X \pm i\mu_Y$ of the laboratory-fixed components of the dipole moment operator [7] (pp. 90–93, 97–100), i.e., intensities in such experiments are proportional to $|\langle f|\,\mu_X + i\mu_Y\,|\,i\rangle|^2$ or $|\langle f|\mu_X - i\mu_Y|i\rangle|^2$.

Theoretical results for experiments involving unpolarized (ordinary) light are obtained by averaging the results of calculations for plane polarized light having the electric vector in each of the three laboratory-fixed directions. If, in addition, the emitting or absorbing molecules are in an isotropic environment, then all directions are equivalent and theoretical results for experiments using unpolarized light can be obtained by considering plane polarized light with the electric vector in only one of the laboratory-fixed directions [7] (pp. 90–93, 97–100).

The laboratory-fixed components of the dipole moment operator transform as follows [15, 16] under the symmetry operations $\sigma_v(xz)$, i, and $C_2(y)$

$$\begin{aligned} \sigma_v\, \mu_R &= -\mu_R \\ i\, \mu_R &= -\mu_R \\ C_2\, \mu_R &= +\mu_R \qquad R = X, Y, Z \end{aligned} \tag{3-2}$$

These relations can be proved easily from the results given in table 5. The first of the transformation properties in (3–2) leads (see sect. 2.9) to the overall parity selection rule for electric dipole transitions $\pm \leftrightarrow \mp$. The third of the transformation properties leads to the selection rule $a \leftrightarrow a$ and $s \leftrightarrow s$. The second of the transformation properties leads to no additional selection rules, since $i \equiv \sigma_v \cdot C_2$.

3.2. Molecule-Fixed Components of $\boldsymbol{\mu}$

Molecule-fixed components of $\boldsymbol{\mu}$ come into consideration when matrix elements of the dipole moment operator are to be evaluated, because molecular wave functions are expressed in terms of molecule-fixed coordinates and not in terms of laboratory-fixed coordinates. We shall not consider in this monograph the numerical evaluation of matrix elements of the molecule-fixed components of $\boldsymbol{\mu}$, since such calculations require a knowledge of many-electron molecular wave functions. Instead, we shall treat these matrix elements as parameters, which must be determined from a fit of the calculated rotational intensity expressions to the experimental data. It is still necessary, however, to determine precisely how many such intensity parameters can occur in the rotational intensity expressions for a given electronic transition. Hence, it is necessary to investigate the circumstances under which matrix elements of the molecule-fixed components of $\boldsymbol{\mu}$ vanish.

The molecule-fixed components of $\boldsymbol{\mu}$ do not involve the rotational variables. Consequently, matrix elements of these quantities are diagonal in the rotational quantum numbers J and M, and we need only consider further matrix elements of $\boldsymbol{\mu}$ in the various nonrotating-molecule basis sets. The only nonvanishing matrix elements of the molecule-fixed components of $\boldsymbol{\mu}$ in the nonrotating-molecule basis set $|\Omega\rangle$ have the following form [7] (pp. 59–64):

$$\begin{aligned} &\langle \Omega+1 \,|\, \mu_x + i\mu_y \,|\, \Omega \rangle \\ &\langle \Omega-1 \,|\, \mu_x - i\mu_y \,|\, \Omega \rangle \\ &\langle \Omega \,|\, \mu_z \,|\, \Omega \rangle, \end{aligned} \tag{3-3}$$

with the additional restriction (see below) that μ_z has no nonvanishing matrix elements between 0^+ states and 0^- states (all diatomic molecules), and that μ_x, μ_y, μ_z have no nonvanishing matrix elements between g and g or between u and u electronic states (homonuclear diatomic molecules).

The two wave functions for the nonrotating molecule represented by $|\Omega\rangle$ in the third matrix element of (3–3) may correspond to the *same* state of the molecule or to *two different* states. If these two wave functions $|\Omega\rangle$ correspond to the same vibrational-electronic state of the molecule, then the matrix element $\langle \Omega \,|\, \mu_z \,|\, \Omega \rangle$ governs the intensity of pure rotational transitions (which are forbidden in homonuclear molecules, of course). If the two wave functions $|\Omega\rangle$ correspond to different vibrational states of the same electronic state, then the matrix element $\langle \Omega \,|\, \mu_z \,|\, \Omega \rangle$ governs the intensity of a pure vibrational transition (which is also forbidden in homonuclear molecules). If the two wave functions $|\Omega\rangle$ correspond to different electronic states of the molecule, then the matrix element $\langle \Omega | \mu_z | \Omega \rangle$ governs the intensity of an electronic transition.

Each of the matrix elements in (3–3) can be related to another matrix element by applying the symmetry operation σ_v to the two wave functions and the dipole moment operator involved in the integral. The transformation properties of the wave functions have been discussed in chapter 2. The transformation properties of the molecule-fixed components of the dipole moment operator [15, 16] can be obtained immediately from table 3:

$$\begin{aligned} \sigma_v(\mu_x \pm i\mu_y) &= +(\mu_x \mp i\mu_y) \\ \sigma_v(\mu_z) &= +(\mu_z) \\ i(\mu_x \pm i\mu_y) &= -(\mu_x \pm i\mu_y) \\ i(\mu_z) &= -(\mu_z) \\ C_2(\mu_x \pm i\mu_y) &= -(\mu_x \mp i\mu_y) \\ C_2(\mu_z) &= -(\mu_z). \end{aligned} \tag{3–4}$$

The transformation properties of μ_z under σ_v lead (see sect. 2.9) to the selection rule $0^\pm \leftrightarrow 0^\pm$ or $\Sigma^\pm \leftrightarrow \Sigma^\pm$. The transformation properties of $\boldsymbol{\mu}$ under i lead (see sect. 2.9) to the selection rule $g \leftrightarrow u$, $u \leftrightarrow g$.

Consider now the nonvanishing matrix elements of the molecule-fixed components of the dipole moment operator in the nonrotating-molecule basis set $|\Lambda S\Sigma\rangle$. These matrix elements can be classified as spin-allowed or spin-forbidden. Spin-allowed matrix elements can be obtained by considering the functions $|\Lambda S\Sigma\rangle$ to be the product of an orbital part and a spin part, i.e.,

$$|\Lambda S\Sigma\rangle = |\Lambda\rangle |S\Sigma\rangle, \tag{3–5}$$

where the quantum numbers Λ, S, and Σ are all perfectly good, and where the same orbital function $|\Lambda\rangle$ is associated with all $2S+1$ spin functions $|S\Sigma\rangle$ for given S. Since the dipole moment operator is independent of electron spin, we find

$$\langle \Lambda' S' \Sigma' | \mu_i | \Lambda S \Sigma\rangle = \langle \Lambda' | \mu_i | \Lambda\rangle \delta_{S'S} \delta_{\Sigma'\Sigma} \tag{3–6}$$

where μ_i represents μ_x, μ_y, or μ_z. The only nonvanishing spin-allowed matrix elements of the molecule-fixed components of the dipole moment operator in the nonrotating-molecule basis set $|\Lambda S\Sigma\rangle$ thus have the form [7] (pp. 59–64):

$$\begin{gathered} \langle \Lambda+1\, S\, \Sigma | \mu_x + i\mu_y | \Lambda\, S\, \Sigma\rangle \\ \langle \Lambda-1\, S\, \Sigma | \mu_x - i\mu_y | \Lambda\, S\, \Sigma\rangle \\ \langle \Lambda\, S\, \Sigma | \mu_z | \Lambda\, S\, \Sigma\rangle \end{gathered} \tag{3–7}$$

with the additional restriction that μ_z has no nonvanishing spin-allowed matrix elements between Σ^+ states and Σ^- states (all diatomic molecules), and that μ_x, μ_y, μ_z have no nonvanishing matrix elements between g and g or between u and u electronic states (homonuclear diatomic molecules). Spin-forbidden matrix elements of the dipole moment operator are those forbidden by (3–6) and (3–7), but allowed by (3–3).

The matrix elements in (3–7) can be related to other matrix elements in two ways: first, by assuming that their value is independent of the spin projection quantum number Σ (which follows from the factorization (3–5)); and second, by applying the symmetry operation σ_v to the two wave functions and the dipole moment operator involved in the integral (see sect. 2.10).

In spin-allowed transitions, the intensity of the transition comes from matrix elements involving *either* the dipole moment component μ_z *or* the components μ_x and μ_y. The former transitions are called parallel transitions because the nonvanishing matrix elements involve the component of the dipole moment parallel to the internuclear axis. The latter transitions are called perpendicular transitions because the nonvanishing matrix elements involve the components of the dipole moment perpendicular to the internuclear axis.

Allowed matrix elements of the dipole moment operator in the nonrotating molecule basis set $| L\Lambda S\Sigma \rangle$ have the form

$$\begin{gathered}\langle L' \, \Lambda+1 \, S \, \Sigma \, | \, \mu_x + i\mu_y \, | \, L \, \Lambda \, S \, \Sigma \rangle \\ \langle L' \, \Lambda-1 \, S \, \Sigma \, | \, \mu_x - i\mu_y \, | \, L \, \Lambda \, S \, \Sigma \rangle \\ \langle L' \, \Lambda \, S \, \Sigma \, | \, \mu_z \, | \, L \, \Lambda \, S \, \Sigma \rangle ,\end{gathered} \tag{3–8}$$

where the transition $L' \leftrightarrow L$ must be allowed in the united atom limit. Forbidden transitions in this basis set are those forbidden by (3–8), but allowed by (3–7) or (3–3).

3.3. The Direction Cosine Matrix α

The elements of the 3×3 direction cosine matrix α do not involve the electronic or vibrational variables of a diatomic molecule: they involve only the rotational angles (see eqs (2–3) above and [3] (pp. 10–11), [6] (pp. 285–6), [8]). Consequently, matrix elements of elements of the direction cosine matrix are diagonal in the nonrotating-molecule quantum numbers L, Λ, S, Σ. The nonvanishing matrix elements of elements of the direction cosine matrix are conveniently summarized in the form of a table [18] (p. 96).[1] This table, with some change in notation from [18], is presented here as table 6. Each matrix element of a given element of the direction cosine matrix consists of the product of three factors: one taken from the first line of table 6, one from either the second or third lines, and one from either the fourth or fifth lines; all three factors are taken from the same column of table 6. The choice of rows is determined by the particular element of the matrix α under consideration. The choice of column is determined by the value of ΔJ.

The derivation of table 6 represents a rather elaborate exercise in group theory, operator algebra, or generating functions. Furthermore, the derivation is slightly different for nonlinear molecules (three Eulerian angles) than it is for linear molecules (two Eulerian angles). We shall not consider in this monograph the derivation of table 6.

TABLE 6. *Direction cosine matrix elements* (*after* [*18*] *p. 96*).

The nonvanishing matrix elements $\langle \Omega' \, J' \, M' \, | \, \alpha_{Rs} \, | \, \Omega \, J \, M \rangle$, where $R = X$, Y, or Z and $s = x$, y, or z, are given by the product of three factors: $f(J'; J) \cdot g_s(J', \Omega'; J, \Omega) \cdot h_R(J', M'; J, M)$. The factors f, g_s, h_R 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 $J' - J$. The choice of rows depends on R and s. In all cases, the first factor f is taken from row one; the second factor g_s is chosen from rows two and three; and the third factor h_R is chosen from rows four and five.

Factor	$J' = J+1$	$J' = J$	$J' = J-1$
$f(J'; J)$	$\{4(J+1)[(2J+1)(2J+3)]^{1/2}\}^{-1}$	$[4J(J+1)]^{-1}$	$\{4J[(2J+1)(2J-1)]^{1/2}\}^{-1}$
$g_z(J', \Omega; J, \Omega)$	$2[(J+\Omega+1)(J-\Omega+1)]^{1/2}$	2Ω	$2[(J+\Omega)(J-\Omega)]^{1/2}$
$g_x(J', \Omega \pm 1; J, \Omega)$ or $\mp i g_y(J', \Omega \pm 1; J, \Omega)$	$\mp[(J \pm \Omega + 1)(J \pm \Omega + 2)]^{1/2}$	$[(J \mp \Omega)(J \pm \Omega + 1)]^{1/2}$	$\pm[(J \mp \Omega)(J \mp \Omega - 1)]^{1/2}$
$h_Z(J', M; J, M)$	$2[(J+M+1)(J-M+1)]^{1/2}$	$2M$	$2[(J+M)(J-M)]^{1/2}$
$h_X(J', M \pm 1; J, M)$ or $\pm i h_Y(J', M \pm 1; J, M)$	$\mp[(J \pm M + 1)(J \pm M + 2)]^{1/2}$	$[(J \mp M)(J \pm M + 1)]^{1/2}$	$\pm[(J \mp M)(J \mp M - 1)]^{1/2}$

The elements of the direction cosine matrix transform as follows under the symmetry operations σ_v and C_2; they are invariant under i (see eqs (2–3) and sect. 2.1).

$$\begin{gathered}(\sigma_v \text{ or } C_2)(\alpha_{Rx} \pm i\alpha_{Ry}) = -(\alpha_{Rx} \mp i\alpha_{Ry}) \\ (\sigma_v \text{ or } C_2)(\alpha_{Rz}) = -(\alpha_{Rz}).\end{gathered} \tag{3–9}$$

---

[1] Note that some early printings of [18] contain sign errors in this table. All entries in the second and fourth rows should be positive.

3.4. Example: Hönl-London Intensity Expressions for a $^1\Pi - {}^1\Sigma^+$ Transition

In order to calculate rotational line intensities, it is necessary to know the correct wave functions for both upper and lower state rotational levels. The example chosen above is relatively simple, since correct wave functions can be written very simply in terms of the basis set functions $|\Lambda S\Sigma;\Omega JM\rangle$. The wave functions for the complete problem (rotating plus nonrotating molecule) are given for the $^1\Sigma^+$ state and the $^1\Pi$ state in eqs (3–10a) and (3–10b), respectively.

$$|0^+ 0 0; 0 J M\rangle \tag{3–10a}$$

$$2^{-1/2}[|1 0 0; 1 J M\rangle \pm |-1 0 0; -1 J M\rangle] \tag{3–10b}$$

By application of the symmetry operation σ_v as described in chapter 2, we find the parities of the functions (3–10a) and (3–10b) to be

$$+(-1)^J \tag{3–11a}$$

$$\pm(-1)^J \tag{3–11b}$$

respectively, if we arbitrarily assume a value of $L=1$ for the $^1\Pi$ state, and arbitrarily assume correlation with a united atom state of odd parity (see eqs (2–11)).

Because we are interested in intensity formulas which are valid for unpolarized light and for molecules in the gas phase in the absence of external fields, all three directions in space are equivalent, and it is sufficient to calculate the matrix elements of μ_Z, the laboratory-fixed Z component of the dipole moment operator, to determine intensities. The Z component of $\boldsymbol{\mu}$, rather than the X or Y component, is chosen for intensity calculations involving unpolarized light and molecules in the absence of external fields, because nonvanishing matrix elements of the former obey the selection rule $\Delta M=0$, whereas nonvanishing matrix elements of the latter two obey the selection rule $\Delta M=\pm 1$. The selection rule $\Delta M=0$ gives rise to particularly simple summation expressions, e.g., (3–17), thus reducing the amount of algebra required to obtain the final intensity expressions, e.g., (3–20) and (3–21).

The quantity μ_Z, as given in (3–1), can be rewritten in the form

$$\mu_Z = {}^1\!/\!_2(\alpha_{Zx} - i\alpha_{Zy})(\mu_x + i\mu_y) + {}^1\!/\!_2(\alpha_{Zx} + i\alpha_{Zy})(\mu_x - i\mu_y) + \alpha_{Zz}\mu_z. \tag{3–12}$$

By using the selection rule $\Delta M=0$ for elements of the direction cosine matrix of the form α_{Zs}, the selection rule $\Delta\Lambda=\pm 1$ for $\mu_x \pm i\mu_y$, and the selection rule $\Delta\Lambda=0$ for μ_z, we see that a general matrix element of μ_Z takes the form

$$\begin{aligned}\langle 2^{-1/2}[\langle 1 0 0; 1 J' M| \pm \langle -1 0 0; -1 J' M|\,] &| \mu_Z | 0^+ 0 0; 0 J M\rangle \\ = 2^{-1/2}\langle 1 0 0; 1 J' M| &{}^1\!/\!_2(\alpha_{Zx} - i\alpha_{Zy})(\mu_x + i\mu_y)\, |0^+ 0 0; 0 J M\rangle \\ \pm 2^{-1/2}\langle -1 0 0; -1 J' M| &{}^1\!/\!_2(\alpha_{Zx} + i\alpha_{Zy})(\mu_x - i\mu_y)\, |0^+ 0 0; 0 J M\rangle.\end{aligned} \tag{3–13}$$

Application of the symmetry operation σ_v (see sect. 2.9) indicates that the righthand side of (3–13) is equal to zero if the upper sign is used for $J'=J$, or if the lower sign is used for $J'=J\pm 1$. If the opposite sign choice is made in each case, the righthand side of (3–13) is equal to

$$2^{-1/2}\langle 1 0 0; 1 J' M|\,(\alpha_{Zx} - i\alpha_{Zy})(\mu_x + i\mu_y)\,|0^+ 0 0; 0 J M\rangle. \tag{3–14}$$

Note that we again assume $L=1$ for the $^1\Pi$ state, and take the lower sign choice in (2–11a), in agreement with the choice made in obtaining (3–11b). The fact that the matrix element given in (3–13) vanishes for certain sign choices and for certain ΔJ is consistent with the parities given in (3–11) and with the parity selection rule $\pm \leftrightarrow \mp$ for electric dipole transitions.

The matrix element (3–14) can be further simplified by recalling that the elements of the direction cosine matrix do not contain the variables of the nonrotating-molecule problem, whereas the molecule-fixed components of the dipole moment operator do not contain the rotational variables. Since the complete basis set functions $|\Lambda S\Sigma;\Omega JM\rangle$ are products of a function $|\Lambda S\Sigma\rangle$ containing only the variables of the nonrotating-molecule problem and a function $|\Omega JM\rangle$ containing only the rotational variables, we can write (3–14) as

$$2^{-1/2}\langle 1\,0\,0\,|\,\mu_x+i\mu_y\,|\,0^+\,0\,0\rangle\,\langle 1\,J'\,M\,|\,\alpha_{Zx}-i\alpha_{Zy}\,|\,0\,J\,M\rangle. \tag{3–15}$$

The second factor in (3–15) represents a matrix element of the type given in table 6 above. The first factor represents a matrix element which cannot be calculated from symmetry considerations alone. Hence we shall treat it as a parameter, which is to be determined by fitting the calculated intensity expressions to the experimental data. For simplicity we define a quantity $\mu_\perp$

$$\mu_\perp=2^{-1/2}\langle 1\,0\,0\,|\,\mu_x+i\mu_y\,|\,0^+\,0\,0\rangle, \tag{3–16}$$

where $\mu_\perp$ is, of course, independent of the rotational quantum numbers. In addition, we choose the phase factors for the two wave functions $|1\,0\,0\rangle$ and $|0^+\,0\,0\rangle$ such that $\mu_\perp$ is real and positive. (Such a choice is possible at this point, since we have not yet considered the phase of any matrix element connecting these two states.)

Spectral line intensities are actually proportional to the square of the dipole moment matrix elements, i.e., to the square of the quantity first given in (3–13) and later rewritten in (3–15). Furthermore, we are considering molecules in the absence of external fields, so that the $2J+1$ states having the same J but different M are all degenerate. Thus, the total intensity I is obtained by summing over all M values for the upper state and over all M values for the lower state under consideration. Since nonvanishing matrix elements of μ_Z obey the selection rule $\Delta M=0$, the sum over upper state M values, i.e., the sum over that quantum number which would be M', contributes nothing until $M'=M$. We thus write

$$I\propto\mu_\perp^2\;\Sigma_M\,|\,\langle 1\,J'\,M\,|\,\alpha_{Zx}-i\alpha_{Zy}\,|\,0\,J\,M\rangle\,|^2. \tag{3–17}$$

Consider now the intensity of an R branch ($J'=J+1$). We find from table 6 that (3–17) becomes

$$I(R\text{ branch})\propto\mu_\perp^2\Sigma_M|\,\{4(J+1)[(2J+1)(2J+3)]^{1/2}\}^{-1}$$
$$\times\{-2[(J+0+1)(J+0+2)]^{1/2}\}\,\{2[(J+M+1)(J-M+1)]^{1/2}\}\,|^2, \tag{3–18}$$

where Ω has been given its value of zero. Using the summation expressions

$$\sum_{M=-J}^{+J}1\quad=(2J+1)$$

$$\sum_{M=-J}^{J}M^2=(2J+1)J(J+1)/3 \tag{3–19}$$

we obtain

$$I(R\text{ branch})\propto 1/3\,\mu_\perp^2\,(J+2). \tag{3–20}$$

In a similar fashion we can obtain

$$I(Q\text{ branch})\propto 1/3\,\mu_\perp^2\,(2J+1)$$

$$I(P\text{ branch})\propto 1/3\,\mu_\perp^2\,(J-1). \tag{3–21}$$

The relative intensities given in (3–20) and (3–21) agree with the well-known Hönl-London expressions for a $^1\Pi-{}^1\Sigma^+$ transition in a diatomic molecule [1] (pp. 204–211).

3.5. Example: Rotational Intensity Distribution in a $^3\Sigma^- - {}^1\Sigma^+$ Transition

The wave functions and symmetry properties for the rotational levels of a $^1\Sigma^+$ state have been given in eqs (3–10a) and (3–11a) above

The rotational energy levels of a $^3\Sigma$ state have been discussed in section 1.10; the symmetry properties of the rotational levels of a $^3\Sigma^+$ state have been discussed in section 2.5. It is easy to show, by arguments analogous to those of section 2.5, that the parities of the rotational levels of a $^3\Sigma^-$ state are just the opposite of those of a $^3\Sigma^+$ state, i.e., states of even N are of odd parity and states of odd N are of even parity.

The wave functions for the rotational levels of a $^3\Sigma$ state were not determined in section 1.10. These wave functions can be determined, however, by finding the eigenvectors of the sum of the matrices given in (1–24) and (1–27) above. We consider a $^3\Sigma^-$ state which is very near case (b); for the purposes of calculating intensities, we thus set $\lambda=0$. The three normalized eigenfunctions of given J then become:

$$-[J/(2J+1)]^{1/2}2^{-1/2}[\,|0^-1\,1;1\,J\,M\rangle+|0^-1\,-1;-1\,J\,M\rangle] \\ +[(J+1)/(2J+1)]^{1/2}\,|0^-1\,0;0\,J\,M\rangle \tag{3–22a}$$

$$2^{-1/2}[\,|0^-1\,1;1\,J\,M\rangle-|0^-1\,-1;-1\,J\,M\rangle] \tag{3–22b}$$

$$[(J+1)/(2J+1)]^{1/2}2^{-1/2}[\,|0^-1\,1;1\,J\,M\rangle+|0^-1\,-1;-1\,J\,M\rangle] \\ +[J/(2J+1)]^{1/2}\,|0^-1\,0;0\,J\,M\rangle. \tag{3–22c}$$

These three functions are eigenfunctions of the matrix sum (1–24) plus (1–27) when $\lambda=0$, and belong to the eigenvalues $E+B\langle L_\perp^2\rangle+BN(N+1)$, where $N=J+1$, $N=J$, and $N=J-1$, respectively.

We must next calculate all matrix elements of μ_Z allowed by the selection rules on J and by the parity selection rule. (Alternatively, the parity selection rule can be used as a check on the calculations.) The selection rule $\Delta J=0, \pm1$, and the fact that $N=J+1$, J, or $J-1$ in the triplet state, indicates the possibility of nine rotational branches. In standard notation, i.e., $^{\Delta N}\Delta J$, these would be called ^SR, ^RR, ^QR, ^RQ, ^QQ, ^PQ, ^QP, ^PP, ^OP branches. Let us consider in detail the ^SR branch. The intensity expression for such a branch depends on a matrix element between an upper state wave function of the form (3–22a) with J replaced by $(J+1)$ everywhere ($J'=J+1$, $N'=J+2$) and a lower state wave function of the form (3–10a) with J unchanged ($J''=N''=J$). Just as in eq (3–13) above, this matrix element can be separated into parts

$$-[(J+1)/(2J+3)]^{1/2}2^{-1/2}\langle 0^-1\,1;1\;J+1\;M\,|\,\mu_Z\,|\,0^+0\,0;0\,J\,M\rangle \\ -[(J+1)/(2J+3)]^{1/2}2^{-1/2}\langle 0^-1\,-1;-1\;J+1\;M\,|\,\mu_Z\,|\,0^+0\,0;0\,J\,M\rangle \\ +[(J+2)/(2J+3)]^{1/2}\langle 0^-1\,0;0\;J+1\;M\,|\,\mu_Z\,|\,0^+0\,0;0\,J\,M\rangle. \tag{3–23}$$

Furthermore, by applying the symmetry operation σ_v (see sect. 2.9), we find that the first and second terms in (3–23) are equal.

The next step is to replace μ_Z by the righthand side of (3–12). Before doing this, however, we examine the matrix elements of the molecule-fixed components of the dipole moment operator in the nonrotating-molecule basis set under consideration. The nonrotating-molecule basis set for the $^1\Sigma^+$ state consists of one singlet function $|0^+0\,0\rangle$; that for the $^3\Sigma^-$ state consists of three triplet functions: $|0^-1\;1\rangle$, $|0^-1\;0\rangle$, and $|0^-1\;-1\rangle$. There are no spin-allowed matrix elements of the dipole moment operator between singlet functions and triplet functions, since nonvanishing dipole moment operator matrix elements obey the selection rule $\Delta S=0$ when S is a good quantum number (see eqs (3–6) and (3–7)). However, if we assume that the singlet state is slightly contaminated by triplet states, and that the triplet state is slightly contaminated by singlet states, then any matrix elements allowed by the selection rules $\Delta\Omega=0, \pm 1$ are nonvanishing (see eq (3–3)). Hence the possible nonvanishing matrix elements appear to be

$$\begin{gathered}\langle 0^- 1\, 1 |\, \mu_x + i\mu_y \,| 0^+ 0\, 0\rangle \\ \langle 0^- 1\, 0 \,|\, \mu_z \,| 0^+ 0\, 0\rangle \\ \langle 0^- 1\, -1 \,|\, \mu_x - i\mu_y \,| 0^+ 0\, 0\rangle .\end{gathered} \tag{3–24}$$

The one remaining point to check involves the matrix element between the two states having $\Omega=0$. Selection rules require that all matrix elements of μ_z vanish between 0^+ states and 0^- states. We are, of course, dealing here with a Σ^+ state and a Σ^- state, so that this electronic transition is orbitally forbidden. However, it is already known to be spin forbidden, so this orbital forbiddenness is of no great interest. What is of interest is whether or not in the strong spin-orbit coupling limit, corresponding to the nonrotating-molecule basis set $|\Omega\rangle$, the $\Delta\Omega=0$ transition is allowed or forbidden. As might be expected, it is the transformation properties of the combined spin and orbital parts of the wave function which determine whether a state having $\Omega=0$ is a 0^+ state or a 0^- state. We note that

$$\begin{gathered}\sigma_v \,| 0^+ 0\, 0\rangle = + \,| 0^+ 0\, 0\rangle \\ \sigma_v \,| 0^- 1\, 0\rangle = + \,| 0^- 1\, 0\rangle .\end{gathered} \tag{3–25}$$

Consequently, both the ${}^1\Sigma^+$ and the ${}^3\Sigma^-$ states give rise in the strong spin-orbit coupling limit to 0^+ states, and the second matrix element of (3–24) is allowed by symmetry.

Spectroscopists sometimes speak of a doubly forbidden transition. Such a label is useful, if it is employed carefully. The degree of multiple forbiddenness is best defined to be the number of first-order perturbations which must be carried out in succession before a given transition is made allowed. Thus, in the particular case of a ${}^3\Sigma^- - {}^1\Sigma^+$ transition, a single first-order spin-orbit perturbation (satisfying the selection rules $\Delta S=0, \pm 1$; $\Delta\Omega=0$) suffices to make the transition allowed (e.g., the mixing of ${}^3\Sigma^-$ and ${}^1\Pi$), so that this transition is only singly forbidden. On the other hand, a ${}^5\Sigma^- - {}^1\Sigma^+$ transition is made allowed only after two successive first-order spin-orbit perturbations, and it is therefore doubly forbidden.

Taking into account the fact that the first and second terms in (3–23) are identical, the fact that the only nonvanishing matrix elements of the molecule-fixed components of the dipole moment operator in the basis set under consideration are given in (3–24), and the fact that μ_Z can be expanded as given in (3–12), we can rewrite (3–23) in the form

$$\begin{aligned}&-[(J+1)/(2J+3)]^{1/2} 2^{-1/2} \langle 0^- 1\, 1 \,|\, \mu_x + i\mu_y \,| 0^+ 0\, 0\rangle \langle 1\, J+1\, M \,|\, \alpha_{Zx} - i\alpha_{Zy} \,| 0\, J\, M\rangle \\ &+[(J+2)/(2J+3)]^{1/2} \langle 0^- 1\, 0 \,|\, \mu_z \,| 0^+ 0\, 0\rangle \langle 0\, J+1\, M \,|\, \alpha_{Zz} \,| 0\, J\, M\rangle .\end{aligned} \tag{3–26}$$

For simplicity we define two quantities $\mu_{||}$ and $\mu_\perp$

$$\begin{gathered}\mu_{||} = \langle 0^- 1\, 0 \,|\, \mu_z \,| 0^+ 0\, 0\rangle \\ \mu_\perp = 2^{-1/2} \langle 0^- 1\, 1 \,|\, \mu_x + i\mu_y \,| 0^+ 0\, 0\rangle ,\end{gathered} \tag{3–27}$$

which can both be made real as follows. Since the two wave functions $| 0^- 1\, 0\rangle$ and $| 0^+ 0\, 0\rangle$ both have only zero values for the angular momentum projection quantum numbers, their phases can be chosen such that they transform into themselves under the time inversion operation θ (see sect. 2.11)

$$\begin{gathered}\theta \,| 0^- 1\, 0\rangle = + \,| 0^- 1\, 0\rangle \\ \theta \,| 0^+ 0\, 0\rangle = + \,| 0^+ 0\, 0\rangle .\end{gathered} \tag{3–28}$$

Applying the time inversion operation to all quantities in the first equation of (3–27) we obtain

$$\begin{aligned}\theta\mu_{\|} = \mu_{\|}^{*} &= +\langle 0^{-}\,1\,0\,|\,\mu_z^{*}\,|\,0^{+}\,0\,0\rangle \\ &= +\langle 0^{-}\,1\,0\,|\,\mu_z\,|\,0^{+}\,0\,0\rangle = +\mu_{\|}. \end{aligned} \tag{3–29}$$

Clearly, the quantity $\mu_{\|}$ is real under these conditions. Applying the time inversion operation in a similar manner to the second equation in (3–27), and using transformation properties for the wave function $|\,0^{-}\;1\;1\rangle$ obtained from eq (2–38), we find

$$\theta\mu_{\perp} = \mu_{\perp}^{*} = -2^{-1/2}\langle 0^{-}\;1\;-1\,|\,\mu_x - i\mu_y\,|\,0^{+}\;0\;0\rangle. \tag{3–30}$$

Applying the symmetry operation σ_v to the matrix element on the righthand side of (3–30) allows one to conclude that

$$\begin{aligned}&-2^{-1/2}\langle 0^{-}\,1\,-1\,|\,\mu_x - i\mu_y\,|\,0^{+}\,0\,0\rangle = \\ &+2^{-1/2}\langle 0^{-}\,1\,1\,|\,\mu_x + i\mu_y\,|\,0^{+}\,0\,0\rangle = +\mu_{\perp}. \end{aligned} \tag{3–31}$$

Thus, the quantity $\mu_{\perp}$ is also real. (Note that the time inversion operation θ was used together with the reflection operation σ_v in demonstrating that $\mu_{\perp}$ is real. The use of both θ and σ_v will generally be necessary when the matrix elements under consideration involve functions with nonzero values for angular momentum projection quantum numbers.)

If we now substitute from table 6 and eqs (3–27) in (3–26), we obtain for this matrix element of μ_Z

$$\begin{aligned}&-[(J+1)/(2J+3)]^{1/2}\mu_{\perp}\{4(J+1)[(2J+1)(2J+3)]^{1/2}\}^{-1}(-2)[(J+0+1)(J+0+2)]^{1/2} \\ &\qquad\qquad\qquad\qquad \times(2)[(J+M+1)(J-M+1)]^{1/2} \\ &+[(J+2)/(2J+3)]^{1/2}\mu_{\|}\{4(J+1)[(2J+1)(2J+3)]^{1/2}\}^{-1}(2)[(J+0+1)(J-0+1)]^{1/2} \\ &\qquad\qquad\qquad\qquad \times(2)[(J+M+1)(J-M+1)]^{1/2}, \end{aligned} \tag{3–32}$$

where Ω has been given its value of zero. The intensity is proportional to the square of this quantity summed over M. Thus,

$$I({}^{S}R\text{ branch}) \propto [+\mu_{\|}+\mu_{\perp}]^2(J+1)(J+2)/3(2J+3). \tag{3–33}$$

In a similar fashion,

$$\begin{aligned} &I({}^{Q}R\text{ branch}) \propto [+\mu_{\|}(J+1)-\mu_{\perp}(J+2)]^2/3(2J+3) \\ &I({}^{Q}Q\text{ branch}) \propto (+\mu_{\perp})^2(2J+1)/3 \\ &I({}^{Q}P\text{ branch}) \propto [+\mu_{\|}(J)-\mu_{\perp}(J-1)]^2/3(2J-1) \\ &I({}^{O}P\text{ branch}) \propto [+\mu_{\|}+\mu_{\perp}]^2J(J-1)/3(2J-1). \end{aligned} \tag{3–34}$$

These results were recently published by Watson [19], who corrected the results previously given by Schlapp [20]. An examination of Watson's eq (23) and eq (3–27) above shows that μ_0 (his notation)$=+\mu_{\|}$ (this notation), but that μ_1 (his notation)$=-\mu_{\perp}$ (this notation).

3.6. Intensity Calculations When Closed-Form Expressions Cannot Be Obtained. Example: Rotational Intensity Distribution in a $^4\Delta-{}^6\Sigma^+$ Transition

The calculation of rotational intensity distributions when some of the pertinent expressions cannot be written down in closed form can conveniently be divided into three parts: (i) determination of wave functions for rotational levels of the upper and lower electronic states of the transition, expressed in terms of basis set functions for the upper and lower states, respectively; (ii) determination of matrix elements of the dipole moment operator between functions in the upper state basis set and functions in the lower state basis set; (iii) formation of linear combinations of basis set dipole moment matrix elements to obtain dipole moment matrix elements between upper state final wave functions and lower state final wave functions. Each of these three steps must be performed numerically, presumably by a modern electronic computer. It is convenient in what follows to indicate the numerical steps in matrix notation.

Step (i). Rotational energy levels and rotational wave functions for each of the two vibrational-electronic states involved in a given optical transition can be determined as described in chapter 1. For molecules in the absence of external fields, it is thus necessary to diagonalize matrices having rows and columns labeled by a set of functions characterized by the same value of J and the same value of M (J and M are good quantum numbers in free space), but by different values of the other quantum numbers of the basis set (see sections 1.9 and 1.10). Furthermore, if numerical calculations are to be performed, it is necessary to consider a number of different matrices, corresponding to different numerical values for the quantum number J. The quantum number M need not be assigned a numerical value, since matrix elements of the Hamiltonian operator for a molecule in free space are independent of M[7] (p. 49).

For the $^4\Delta-{}^6\Sigma^+$ example considered here, we must diagonalize two sets of Hamiltonian matrices. One set is of dimension 8×8, with rows and columns labeled by functions $|\Lambda S\Sigma;\,\Omega JM\rangle$ of the $^4\Delta$ upper state, the functions being characterized by a fixed numerical value of J, a fixed algebraic value of M, and by $\Lambda=\pm 2$, $\Sigma=\pm 3/2$, $\pm 1/2$. It is convenient to represent an individual matrix from this set of 8×8 matrices by the symbol $H_u(J')$, where J' is the J-value characterizing this particular upper state Hamiltonian matrix. The other set of matrices is of dimension 6×6, with rows and columns labeled by the functions $|\Lambda S\Sigma;\,\Omega JM\rangle$ of the $^6\Sigma^+$ lower state, the functions being characterized by a fixed numerical value of J, a fixed algebraic value of M, and by $\Lambda=0$, $\Sigma=\pm 5/2, \pm 3/2, \pm 1/2$. It is convenient to represent an individual matrix from this set of 6×6 matrices by the symbol $H_l(J'')$, where J'' is the J-value characterizing this particular lower state Hamiltonian matrix.

It is often desirable to perform a factorization in intensity calculations like that used in writing (1–27) from (1–25), since this allows parity selection rules to be taken into account at once. For simplicity of presentation, such a factorization is not performed below.

The diagonalization of a given upper state Hamiltonian matrix $H_u(J')$ will be accomplished by a particular transformation matrix $U(J')$; the diagonalization of a given lower state Hamiltonian matrix $H_l(J'')$ will be accomplished by a particular transformation matrix $L(J'')$. As is well known [17] (pp. 26–28), the product matrices

$$\begin{gathered} U^{-1}(J')\,H_u(J')\,U(J') \\ L^{-1}(J'')H_l(J'')L(J'') \end{gathered} \tag{3–35}$$

are diagonal if the columns of U contain the eigenvectors of H_u and the columns of L contain the eigenvectors of H_l.

The matrices U, U^{-1}, L, and L^{-1}, obtained from step (i), will be used in step (iii).

Step (ii). The determination and systematic handling of basis set matrix elements of the dipole moment operator for a $^4\Delta-{}^6\Sigma^+$ transition can be carried out as follows. The most general matrix element of the dipole moment operator in the basis set under consideration has the form $\langle\Lambda'S'\Sigma';\,\Omega'J'M'|\mu_Z|\Lambda''S''\Sigma'';\,\Omega''J''M''\rangle$. However, nonvanishing matrix elements of μ_Z satisfy the selection rule $\Delta M = 0$; it is thus convenient to set $M' = M'' = M$ in this general matrix element. Furthermore. the Hamiltonian operator for a molecule in free space only mixes together basis set functions characterized by the same value of J and the same value of M (step (i)). Consequently, the transformation from matrix elements of the dipole moment operator between basis set functions to matrix elements of the dipole moment operator between final wave functions (step (iii)) never requires adding together basis set matrix elements characterized by different values of J', different values of J'', or different values of M. It is thus convenient to group the basis set matrix elements into submatrices $\mu_b(J', J''; M)$ characterized by fixed values of J', J'', and M. For the present example of a $^4\Delta - {}^6\Sigma^+$ transition, these submatrices are of dimension 8×6; their rows are labeled by the eight basis set functions $|\Lambda' S' \Sigma';\ \Omega' J' M\rangle$ of fixed J' and M belonging to the upper $^4\Delta$ state; their columns are labeled by the six basis set functions $|\Lambda'' S'' \Sigma'';\ \Omega'' J'' M\rangle$ of fixed J'' and M belonging to the lower $^6\Sigma^+$ state.

We see from eq (3–12) that a matrix element of μ_Z can be represented as the sum of three terms.

$$\begin{aligned}
&\langle \Lambda' S'\ \Sigma';\ \Omega' J' M | \mu_Z | \Lambda'' S''\ \Sigma'';\ \Omega'' J'' M \rangle = \\
&\qquad + {}^1\!/\!_2 \langle \Lambda' S'\ \Sigma' | \mu_x + i\mu_y | \Lambda'' S''\ \Sigma'' \rangle \langle \Omega' J' M | \alpha_{Zx} - i\alpha_{Zy} | \Omega'' J'' M \rangle \\
&\qquad + {}^1\!/\!_2 \langle \Lambda' S'\ \Sigma' | \mu_x - i\mu_y | \Lambda'' S''\ \Sigma'' \rangle \langle \Omega' J' M | \alpha_{Zx} + i\alpha_{Zy} | \Omega'' J'' M \rangle \\
&\qquad + \langle \Lambda' S'\ \Sigma' | \mu_z | \Lambda'' S''\ \Sigma'' \rangle \langle \Omega' J' M | \alpha_{Zz} | \Omega'' J'' M \rangle .
\end{aligned} \tag{3–36}$$

The first factor in each of the three terms in (3–36) represents a quantity which can only be calculated from a rather complete knowledge of the electronic wave functions. These quantities are analogous to the parameters $\mu_\parallel$ and $\mu_\perp$ introduced in sections 3.4 and 3.5. Following the selection rules of eq (3–3), and making use of various symmetry arguments (chap. 2), we find that the following independent intensity parameters μ_i must be considered for a $^4\Delta - {}^6\Sigma^+$ transition.

$$\begin{aligned}
\mu_1 &= 2^{-1/2} \langle 2\ {}^3\!/\!_2\ {}^3\!/\!_2 | \mu_x + i\mu_y | 0^+\ {}^5\!/\!_2\ {}^5\!/\!_2 \rangle = -2^{-1/2} \langle -2\ {}^3\!/\!_2\ -{}^3\!/\!_2 | \mu_x - i\mu_y | 0^+\ {}^5\!/\!_2\ -{}^5\!/\!_2 \rangle \\
\mu_2 &= 2^{-1/2} \langle 2\ {}^3\!/\!_2\ {}^1\!/\!_2 | \mu_x + i\mu_y | 0^+\ {}^5\!/\!_2\ {}^3\!/\!_2 \rangle = -2^{-1/2} \langle -2\ {}^3\!/\!_2\ -{}^1\!/\!_2 | \mu_x - i\mu_y | 0^+\ {}^5\!/\!_2\ -{}^3\!/\!_2 \rangle \\
\mu_3 &= 2^{-1/2} \langle 2\ {}^3\!/\!_2\ -{}^1\!/\!_2 | \mu_x + i\mu_y | 0^+\ {}^5\!/\!_2\ {}^1\!/\!_2 \rangle = -2^{-1/2} \langle -2\ {}^3\!/\!_2\ {}^1\!/\!_2 | \mu_x - i\mu_y | 0^+\ {}^5\!/\!_2\ -{}^1\!/\!_2 \rangle \\
\mu_4 &= 2^{-1/2} \langle 2\ {}^3\!/\!_2\ -{}^3\!/\!_2 | \mu_x + i\mu_y | 0^+\ {}^5\!/\!_2\ -{}^1\!/\!_2 \rangle = -2^{-1/2} \langle -2\ {}^3\!/\!_2\ {}^3\!/\!_2 | \mu_x - i\mu_y | 0^+\ {}^5\!/\!_2\ {}^1\!/\!_2 \rangle \\
\mu_5 &= 2^{-1/2} \langle -2\ {}^3\!/\!_2\ {}^3\!/\!_2 | \mu_x + i\mu_y | 0^+\ {}^5\!/\!_2\ -{}^3\!/\!_2 \rangle = -2^{-1/2} \langle 2\ {}^3\!/\!_2\ -{}^3\!/\!_2 | \mu_x - i\mu_y | 0^+\ {}^5\!/\!_2\ {}^3\!/\!_2 \rangle \\
\mu_6 &= 2^{-1/2} \langle -2\ {}^3\!/\!_2\ {}^1\!/\!_2 | \mu_x + i\mu_y | 0^+\ {}^5\!/\!_2\ -{}^5\!/\!_2 \rangle = -2^{-1/2} \langle 2\ {}^3\!/\!_2\ -{}^1\!/\!_2 | \mu_x - i\mu_y | 0^+\ {}^5\!/\!_2\ {}^5\!/\!_2 \rangle \\
\mu_7 &= \langle 2\ {}^3\!/\!_2\ {}^1\!/\!_2 | \mu_z | 0^+\ {}^5\!/\!_2\ {}^5\!/\!_2 \rangle = + \langle -2\ {}^3\!/\!_2\ -{}^1\!/\!_2 | \mu_z | 0^+\ {}^5\!/\!_2\ -{}^5\!/\!_2 \rangle \\
\mu_8 &= \langle 2\ {}^3\!/\!_2\ -{}^1\!/\!_2 | \mu_z | 0^+\ {}^5\!/\!_2\ {}^3\!/\!_2 \rangle = + \langle -2\ {}^3\!/\!_2\ {}^1\!/\!_2 | \mu_z | 0^+\ {}^5\!/\!_2\ -{}^3\!/\!_2 \rangle \\
\mu_9 &= \langle 2\ {}^3\!/\!_2\ -{}^3\!/\!_2 | \mu_z | 0^+\ {}^5\!/\!_2\ {}^1\!/\!_2 \rangle = + \langle -2\ {}^3\!/\!_2\ {}^3\!/\!_2 | \mu_z | 0^+\ {}^5\!/\!_2\ -{}^1\!/\!_2 \rangle .
\end{aligned} \tag{3–37}$$

The quantities μ_1 through μ_6 correspond to perpendicular transition moments; the quantities μ_7 through μ_9 correspond to parallel transition moments. The relationships between matrix elements in eqs (3–37) correspond to using $L = 2$ and the lower sign choice in eq (2–11a). It can be shown (see sections 2.11 and 3.5) that for this choice of phases, the parameters μ_1 through μ_9 are all real, though not necessarily positive. (If, for example, a value of $L = 2$ and the upper sign choice had been used in (2–11a), then the parameters μ_1 through μ_9 would all have been pure imaginary.)

The second factor in each of the three terms in (3–36) contains quantum mechanical matrix elements (in the basis set $|\Omega JM\rangle$) of elements of the direction cosine matrix. These matrix elements can be obtained from table 6.

The submatrices $\mu_b(J', J''; M)$ can thus be evaluated numerically when numerical values for J', J'', M and for the μ_i of (3–37) have been chosen.

It will become apparent in the description of step (iii) below that it is desirable to define a matrix $\mu_b(J'; J'')$, which has the same dimensions as $\mu_b(J', J''; M)$, but which is independent of the quantum number M. It can be seen from table 6 and from (3–36) that the M-dependence of each element of a given (i.e., fixed J', J'', M) matrix $\mu_b(J', J''; M)$ is the same. In fact, this M-dependence is given by the quantity $h_Z(J', M; J'', M)$ in table 6. The M-independent matrix $\mu_b(J'; J'')$ is now defined just like the M-dependent matrix $\mu_b(J', J''; M)$, except that the M-dependent quantity $h_Z(J', M; J'', M)$ given in the fourth row of table 6 is replaced by the M-independent quantity $h_Z(J'; J'')$, where

$$h_Z(J'; J'') = \left[\sum_M h_Z^2(J', M; J'', M)\right]^{1/2}. \tag{3–38}$$

It is thus possible to construct a simplified table 6, given here as table 7, to be used in calculating matrix elements of elements of the direction cosine matrix, *when these matrix elements are to be used in intensity calculations for unpolarized light and for molecules in the absence of external fields.*

TABLE 7. *A simplified table 6, for use in intensity calculations for unpolarized light and for molecules in the absence of external fields.*

Nonvanishing matrix elements $\langle\Omega' J' M|\alpha_{Zs}|\Omega JM\rangle$, where $s=x$, y, or z, can be replaced by the product of three factors: $f(J'; J)\cdot g_s(J', \Omega'; J, \Omega)\cdot h_Z(J'; J'')$. The product $f\cdot h_Z$ of the first and third factors is given in row one of this table; the second factor g_s is chosen from rows two and three.

Factor	$J'=J+1$	$J'=J$	$J'=J-1$
$f(J'; J)\cdot h_Z(J'; J)$	$[12(J+1)]^{-1/2}$	$[12J(J+1)/(2J+1)]^{-1/2}$	$[12J]^{-1/2}$
$g_z(J', \Omega; J, \Omega)$	$2[(J+\Omega+1)(J-\Omega+1)]^{1/2}$	2Ω	$2[(J+\Omega)(J-\Omega)]^{1/2}$
$g_x(J', \Omega\pm1; J, \Omega)$ or $\mp ig_y(J', \Omega\pm1; J, \Omega)$	$\mp[(J\pm\Omega+1)(J\pm\Omega+2)]^{1/2}$	$[(J\mp\Omega)(J\pm\Omega+1)]^{1/2}$	$\pm[(J\mp\Omega)(J\mp\Omega-1)]^{1/2}$

As an example of the use of table 7, we consider $\mu_b(J; J)$ for the ${}^4\Delta - {}^6\Sigma^+$ transition under discussion in this section. Making use of (3–36), (3–37), and table 7, we find that $\mu_b(J; J)$ has the form

$$\begin{bmatrix} \mu_1c_1 & 0 & 0 & 0 & 0 & 0 \\ \mu_7c_7 & \mu_2c_2 & 0 & 0 & 0 & 0 \\ -\mu_6c_6 & \mu_8c_8 & \mu_3c_3 & 0 & 0 & 0 \\ 0 & -\mu_5c_5 & \mu_9c_9 & \mu_4c_4 & 0 & 0 \\ 0 & 0 & -\mu_4c_4 & -\mu_9c_9 & \mu_5c_5 & 0 \\ 0 & 0 & 0 & -\mu_3c_3 & -\mu_8c_8 & \mu_6c_6 \\ 0 & 0 & 0 & 0 & -\mu_2c_2 & -\mu_7c_7 \\ 0 & 0 & 0 & 0 & 0 & -\mu_1c_1 \end{bmatrix}, \tag{3–39}$$

if the rows of this matrix are labeled by the ${}^4\Delta$ functions characterized by $\Lambda=+2$, $\Sigma=+3/2, +1/2, -1/2, -3/2$ and $\Lambda=-2$, $\Sigma=+3/2, +1/2, -1/2, -3/2$, respectively, and if the columns are labeled by the ${}^6\Sigma^+$ functions characterized by $\Lambda=0^+$, $\Sigma=+5/2, +3/2, +1/2, -1/2, -3/2, -5/2$, respectively.

The quantities c_i are taken from table 7 to be

$$\begin{aligned}
c_1 &= [(J+1/2)(J-5/2)(J+7/2)/3J(J+1)]^{1/2}\\
c_2 &= [(J+1/2)(J-3/2)(J+5/2)/3J(J+1)]^{1/2}\\
c_3 &= [(J+1/2)(J-1/2)(J+3/2)/3J(J+1)]^{1/2}\\
c_4 &= [(J+1/2)(J+1/2)(J+1/2)/3J(J+1)]^{1/2}\\
c_5 &= [(J+1/2)(J+3/2)(J-1/2)/3J(J+1)]^{1/2}\\
c_6 &= [(J+1/2)(J+5/2)(J-3/2)/3J(J+1)]^{1/2}\\
c_7 &= +5[(J+1/2)/6J(J+1)]^{1/2}\\
c_8 &= +3[(J+1/2)/6J(J+1)]^{1/2}\\
c_9 &= +1[(J+1/2)/6J(J+1)]^{1/2}.
\end{aligned} \tag{3–40}$$

It may occasionally be convenient to rewrite (3–39) as the sum of nine matrices, each matrix depending on only one of the intensity parameters μ_i.

Step (iii). We must now transform from matrix elements of μ_Z between *basis set functions* to matrix elements of μ_Z between *final wave functions*. This transformation can be carried out as follows [5] (pp. 208–210):

$$\mu(J', J''; M) = U^{-1}(J') \cdot \mu_b(J', J''; M) \cdot L(J''). \tag{3–41}$$

The matrix $\mu_b(J', J''; M)$ has been defined in step (ii). An element lying at the intersection of a given row and column of this matrix represents the matrix element of μ_Z between the $^4\Delta$ basis set function labeling the row and the $^6\Sigma^+$ basis set function labeling the column. The two transformation matrices $U(J)$ and $L(J)$ are defined in the text associated with (3–35). The matrix $\mu(J', J''; M)$ contains matrix elements of μ_Z between final wave functions. An element lying at the intersection of a given row and column of this matrix represents the matrix element of μ_Z between the $^4\Delta$ final wave function labeling the corresponding row of U^{-1} (the corresponding column of U) and the $^6\Sigma^+$ final wave function labeling the corresponding column of L. For bookkeeping purposes it is convenient to represent the element of $\mu(J', J''; M)$ lying at the α'th row and β'th column as $\mu(J', J''; M)_{\alpha\beta}$.

To determine the intensity $I(\alpha J', \beta J'')$ of a transition between a rotational level $\alpha J'$ of the $^4\Delta$ state and a rotational level $\beta J''$ of the $^6\Sigma^+$ state, it is necessary to square the absolute value of the matrix element of μ_Z between pairs of final wave functions $|\alpha J' M'\rangle$ and $|\beta J'' M''\rangle$, and then to sum over all M' and M''. Since nonvanishing matrix elements of μ_Z are diagonal in M, this double sum reduces immediately to a single sum. In the notation of this section we can write.

$$I(\alpha J', \beta J'') \propto \sum_M |\mu(J', J''; M)_{\alpha\beta}|^2. \tag{3–42}$$

It is at this point that the usefulness of the matrix $\mu(J'; J'')$ becomes apparent. As mentioned in the discussion of step (ii), the M dependence of all elements of a given (fixed J', J'', M) matrix $\mu_b(J', J''; M)$ is the same, and is given by the quantity $h_Z(J', M; J'', M)$ of table 6. It follows from (3–41) that the M dependence of all elements of $\mu(J', J''; M)$ is also given by $h_Z(J', M; J'', M)$. It can further be shown that the quantity $h_Z(J'; J'')$ of (3–38) and therefore the matrix $\mu(J'; J'')$ have been defined in just such a way that

$$I(\alpha J', \beta J'') \propto \sum_M |\mu(J', J''; M)_{\alpha\beta}|^2 \equiv |\mu(J'; J'')_{\alpha\beta}|^2, \tag{3–43}$$

i.e., if table 7 is used to calculate direction cosine matrix elements, then the summation over M in intensity calculations is taken care of automatically.

From the discussion of this section, it is apparent that intensity expressions obtained by squaring the appropriate element of $\mu(J'; J'')$ will in general be expressed for a $^4\Delta - {}^6\Sigma^+$ transition as functions of the nine unknown intensity parameters μ_i. The values of these parameters must be determined by fitting the calculated results to observed intensity data. For any particular transition, many of the μ_i may be negligibly small. For example, Klynning [21], who used essentially the procedure described in this section, obtained good qualitative agreement between the calculated and the observed rotational intensity distribution in a $^4\Sigma-{}^2\Pi$ transition in SnH, even though he considered as nonzero only two of the five possible intensity parameters for such a transition.

4. Perturbations

4.1. General Remarks

Perhaps the first question to consider in this chapter on perturbations in diatomic molecules [1] (pp. 280–298) is the following: What is a perturbation and what is not? From an experimental point of view, a perturbation occurs when some energy level of the molecule is found in an unexpected position, or when a transition between some pair of energy levels is observed with an unexpected intensity. From a theoretical point of view, a perturbation occurs when calculated quantities disagree with experiment because an important interaction was neglected in the calculation. Both of the preceding statements indicate that what is considered to be a perturbation and what is not depends largely on what behavior for experimentally observable quantities is initially expected, or on what interaction terms in the theoretical formalism are initially included.

For example, one sometimes speaks of the rotational levels of a $^1\Pi$ state being perturbed by the rotational levels of a nearby $^1\Sigma^+$ state. Such an interaction leads to Λ-type doubling in the Π state and to a change in the effective B value for the Σ state. Calling this interaction a perturbation implies that our experimental expectations were based on the behavior of an isolated $^1\Pi$ state and an isolated $^1\Sigma^+$ state, and that our theoretical calculations did not initially include interactions between these two states.

On the other hand, one sometimes considers the rotational levels of a $^1\Pi$ and a $^1\Sigma^+$ state simultaneously, as part of a p-complex ($L=1$; $\Lambda=0, \pm 1$). This point of view implies that our experimental expectations are not based on the behavior of an isolated $^1\Pi$ and an isolated $^1\Sigma^+$ state, and that our theoretical calculations already include interactions between the Σ state and Π state of the p-complex, including those which give rise to Λ-type doubling in the Π state and to a change in the effective B value of the Σ state. The p-complex can still be perturbed, but only by states external to itself, e.g., by a $^1\Delta$ state or by a $^3\Pi$ state.

Perturbations are sometimes a nuisance and sometimes a source of valuable information. If their origins cannot be understood, they are most often simply a nuisance. However, if a perturbation can be dealt with theoretically, it frequently yields information which cannot easily be obtained in other ways.

Many techniques have been developed for dealing theoretically with perturbation problems in molecular spectroscopy. In this chapter we do not consider all of them. Rather, we concentrate on a two-step procedure of general applicability and widespread use. The two steps consist of: (i) setting up a Hamiltonian matrix which correctly contains the effects of the perturbation(s) to be considered, and (ii) diagonalizing this matrix on a computer. It is hoped that the explanatory material and the three examples described below illustrate this procedure well enough to allow a diatomic-molecule spectroscopist to embark on his own perturbation calculations with relatively little help from a professional theoretician.

The Hamiltonian matrix for a perturbation calculation is set up by a procedure similar to that described in chapter 1, except that more electronic states must be included in the basis set. For example, if a $^3\Delta$ state were perturbed by a $^1\Pi$ state, the basis set for the perturbation calculation would contain the six wave functions of the $^3\Delta$ state *and* the two wave functions of the $^1\Pi$ state. In the absence of the perturbation, one could (and would) consider the six wave functions of the $^3\Delta$ state by themselves, and the two wave functions of the $^1\Pi$ state by themselves.

Intensity matrices for perturbed states can be set up by a procedure similar to that described in chapter 3, except that again a larger basis set must be used for the perturbed state(s).

4.2. Homogeneous and Heterogeneous Perturbations

Many perturbations in diatomic molecules can be characterized as either homogeneous or heterogeneous [1] (pp. 284–286). Homogeneous perturbations take place between electronic states satisfying the selection rule $\Delta\Lambda=0$ or $\Delta\Omega=0$. Heterogeneous perturbations take place between electronic states satisfying the selection rule $\Delta\Lambda=\pm1$ or $\Delta\Omega=\pm1$. Ambiguities can clearly arise in this classification scheme. Is, for example, the perturbation between a case (a) $^2\Pi_{1/2}$ state and a case (a) $^2\Pi_{3/2}$ state homogeneous ($\Delta\Lambda=0$) or heterogeneous ($\Delta\Omega=\pm1$)? Some measure of consistency can be achieved by requiring the nomenclature to reflect the selection rules on Ω when, as in cases (a) and (c), the rotational energy levels are given approximately by $BJ(J+1)$, and to reflect the selection rules on Λ when, as in case (b), the rotational energy levels are given approximately by $BN(N+1)$. It is interesting to note that the transition from Hund's case (a) to Hund's case (b) as J increases in a $^2\Pi$ state might thus be described as resulting from a heterogeneous perturbation of the rotational levels of the $^2\Pi_{1/2}$ state by those of the $^2\Pi_{3/2}$ state (or vice versa).

These two types of perturbations can be described in another way. Homogeneous perturbations are those which can occur in the *nonrotating* molecule, i.e., perturbations caused by H_{ev}. The rigorous selection rule is thus $\Delta\Omega=0$ for nonvanishing homogeneous-perturbation matrix elements in the basis sets used in this monograph, with the approximate selection rules $\Delta S=0$, $\Delta\Lambda=0$, $\Delta\Sigma=0$, when S, Λ, Σ are good quantum numbers in the basis set. Heterogeneous perturbations are those which can only occur in the *rotating* molecule, i.e., perturbations caused by H_r. The rigorous selection rules are thus $\Delta J=0$ and $\Delta\Omega=\pm1$ for nonvanishing heterogeneous-perturbation matrix elements in the basis sets used in this monograph, with the approximate selection rules $\Delta S=0$, and $\Delta\Lambda=\pm1$, $\Delta\Sigma=0$ or $\Delta\Sigma=\pm1$, $\Delta\Lambda=0$, when S, Λ, Σ are good quantum numbers in the basis set, as well as the approximate rule $\Delta L=0$ when L is a good quantum number in the basis set. Matrix elements for homogeneous perturbations do not involve the rotational quantum number J; matrix elements for heterogeneous perturbations do involve J. Many of the selection rules stated in this paragraph can be derived by considering the operators H_{ev} and H_r, together with appropriate angular momentum commutation relations [7] (pp. 59–64).

Homogeneous perturbations arise most frequently in practice because of spin-orbit interaction (see sect. 4.4), but they may also occur because of configuration interaction. In the latter case, the perturbations are often very large and difficult to treat accurately [22–24]. Heterogeneous perturbations occur because of uncoupling phenomena, i.e., uncoupling of the spin angular momentum (see sect. 1.9) or uncoupling of the orbital angular momentum (see sect. 4.3) from the internuclear axis because of rotation. These uncoupling phenomena can be attributed to Coriolis interactions in the rotating molecule.

4.3. Example: $^1\Pi-{}^1\Sigma^+$ Heterogeneous Perturbation

Since the two nonrotating-molecule wave functions of a $^1\Pi$ state are characterized by $\Omega=\pm1$, while the nonrotating-molecule wave function of a $^1\Sigma^+$ state is characterized by $\Omega=0^+$, there can be no interaction between these states in the nonrotating molecule. A *homogeneous* perturbation of one of these states by the other is not possible.

However, the rotating-molecule operator H_r of eq (1–10) has in general nonvanishing matrix elements between states with $\Delta\Lambda=\pm1$ and $\Delta S=0$. Consequently, a *heterogeneous* perturbation of one of these states by the other is possible. This heterogeneous perturbation can be treated theoretically as follows.

Consider a 3×3 Hamiltonian matrix with rows and columns labeled by the three interacting wave functions $|\Lambda S\Sigma;\Omega JM\rangle=|1\,0\,0;1JM\rangle$, $|-1\,0\,0;-1JM\rangle$ and $|0^+0\,0;0JM\rangle$. We find, as outlined below, that this matrix has the form

$$\begin{bmatrix} B_\Pi[J(J+1)-1]+B_\Pi\langle L_\perp^2\rangle_\Pi & 0 & -B\langle\Pi|L_+|\Sigma\rangle[J(J+1)]^{1/2} \\ 0 & B_\Pi[J(J+1)-1]+B_\Pi\langle L_\perp^2\rangle_\Pi & -B\langle\Pi|L_+|\Sigma\rangle[J(J+1)]^{1/2} \\ -B\langle\Pi|L_+|\Sigma\rangle[J(J+1)]^{1/2} & -B\langle\Pi|L_+|\Sigma\rangle[J(J+1)]^{1/2} & E_\Sigma+B_\Sigma J(J+1)+B_\Sigma\langle L_\perp^2\rangle_\Sigma \end{bmatrix} \tag{4–1}$$

where the upper lefthand 2×2 diagonal block represents the $^1\Pi$ state by itself (arbitrarily placed at the energy origin in the nonrotating molecule), where the lower righthand 1×1 diagonal block represents the $^1\Sigma^+$ state by itself (located at energy E_Σ in the nonrotating molecule), and where the off-diagonal elements represent the heterogeneous perturbation (Coriolis interaction) between the two states. Matrix elements for the 2×2 and 1×1 diagonal blocks were obtained as described in chapter 1. Off-diagonal matrix elements were obtained as follows.

The first line of terms in H_r, when H_r is written as in eq (1–11), contains operators which give rise to nonvanishing matrix elements only if $\Delta\Omega=0$. Consequently, the first line of (1–11) cannot be responsible for an interaction between the $^1\Pi$ and the $^1\Sigma^+$ states. The first and third terms of the second line of (1–11) give rise to nonvanishing matrix elements only if $\Delta\Sigma=\pm 1$. Consequently, these two terms can also not be responsible for the interaction under consideration here. The second term of the second line of (1–11) gives rise to nonvanishing matrix elements if $\Delta\Lambda=\pm 1$ and $\Delta S=\Delta\Sigma=0$. This term thus does connect the $^1\Pi$ and $^1\Sigma^+$ states under consideration.

The second term of the second line of (1–11) contains four operators: J_+, J_-, L_+, L_-. Matrix elements of J_+ and J_- can be obtained from expressions of the form (1–13) and (1–14), since both J and Ω are good quantum numbers in the basis set. Matrix elements of L_+ and L_- cannot be found from such expressions, since L is not a good quantum number. However, matrix elements of $L_\pm$ still obey the selection rule $\Delta\Lambda=\pm 1$, because Λ is a good quantum number. It can be shown by using symmetry arguments involving σ_v (see chap. 2), that

$$\langle 1\,0\,0;1\,J\,M\,|\,L_+J_-\,|\,0^+\,0\,0;0\,J\,M\rangle=\pm\langle -1\,0\,0;-1\,J\,M\,|\,L_-J_+\,|\,0^+\,0\,0;0\,J\,M\rangle, \qquad (4\text{–}2)$$

where the + or − sign on the righthand side of (4–2) allows for various possible sign choices and values of L in applying the transformation equation (2–11a) to the $^1\Pi$ state. Neither sign choice in (4–2) leads to inconsistencies elsewhere in the calculation, since no matrix elements between the two components of the $^1\Pi$ state are introduced. The relative phases of the electronic orbital wave functions $|\Lambda=+1\rangle$ and $|\Lambda=-1\rangle$ are fixed once and only once by the choice of sign in (4–2). The + sign was chosen in writing (4–1), where the quantity $B\langle\Pi\,|\,L_+\,|\,\Sigma\rangle$, given by

$$B\langle\Pi\,|\,L_+\,|\,\Sigma\rangle\equiv B\langle 1\,0\,0\,|\,L_+\,|\,0^+\,0\,0\rangle, \qquad (4\text{–}3)$$

is considered to be an unknown adjustable (real) parameter. Energy levels can be obtained by diagonalizing (4–1).

Actually, (4–1) can be factored by symmetry into a 2×2 diagonal block and a 1×1 diagonal block, by using the functions $2^{-1/2}[|+1\,0\,0;+1\,J\,M\rangle\pm|-1\,0\,0;-1\,J\,M\rangle]$ as a basis set for the $^1\Pi$ state, but this factorization will not be performed here.

Van Vleck [25] has introduced the phrase "pure precession" in connection with heterogeneous perturbations. From a quantum mechanical point of view, pure precession is said to occur whenever L is a good quantum number. If L is a good quantum number, it is possible to use (1–13) to evaluate the quantity $\langle\Pi|L_+|\Sigma\rangle$ occurring in (4–1). Since this quantity is really a matrix element of the form $\langle\Lambda=+1|L_+|\Lambda=0\rangle$ we find

$$\langle\Pi|L_+|\Sigma\rangle=\langle L,\,\Lambda=+1|L_+|L,\,\Lambda=0\rangle=\hbar[L(L+1)]^{1/2}\text{ or }0. \qquad (4\text{–}4)$$

The value $\hbar[L(L+1)]^{1/2}$ occurs when the Σ and Π states belong to the same L complex, i.e., when the Σ and Π states represent different projections of the same L along the internuclear axis. The value 0 occurs when the Σ and Π states belong to different L complexes.

It is interesting to note that the matrix (4–1) describes several apparently rather different situations. If the $^1\Sigma^+$ state and the $^1\Pi$ state are very nearly degenerate in the nonrotating molecule ($E_\Sigma\cong 0$), and if L is an approximately good quantum number equal to unity ($L=1$), then the rotational energy levels which result from diagonalizing (4–1) correspond to those of a case (d) p-complex. (Pure case (d) occurs, from a quantum mechanical point of view, when L is a perfectly good quantum number, and when all $2L+1$ states corresponding to different projections of this L along the internuclear axis are exactly degenerate in the nonrotating molecule.) If the $^1\Sigma^+$ state and the $^1\Pi$ state are separated by a distance large compared to the distance between neighboring rotational levels ($|E_\Sigma| \gg BJ$), then the rotational energy levels which result from diagonalizing (4–1) correspond to those of a normal $^1\Sigma^+$ state and those of a normal $^1\Pi$ state with some Λ-doubling. If the rotational energy levels of the $^1\Sigma^+$ state cross those of the $^1\Pi$ state for some value J_c of the rotational quantum number (i.e., if $E_\Sigma + B_\Sigma J_c(J_c+1) \cong B_\Pi J_c(J_c+1)$ for some J_c), and if the interaction between the $^1\Sigma^+$ state and the $^1\Pi$ state is very small ($|\langle\Pi|L_+|\Sigma\rangle| \ll \hbar$), then the rotational energy levels resulting from diagonalizing (4–1) will correspond to those of a normal $^1\Sigma^+$ state and those of a normal $^1\Pi$ state, except for J values in the neighborhood of J_c. The rotational levels of the $^1\Sigma^+$ state having $J \sim J_c$ and the rotational levels of one component of the $^1\Pi$ state having $J \sim J_c$ will suffer small equal and opposite displacements, corresponding to what might be called the usual heterogeneous perturbation.

4.4. Example: $^3\Delta - {}^1\Pi$ Homogeneous Perturbation

A $^3\Delta$ state cannot easily interact with a $^1\Pi$ state via the operator H_r, since terms of this operator give rise to nonvanishing matrix elements only if the selection rule $\Delta S = 0$ is satisfied. To the extent that S is a good quantum number, a heterogeneous perturbation of one of these states by the other is not possible. Actually, of course, S is not a perfectly good quantum number and heterogeneous perturbations between a $^3\Delta$ state and a $^1\Pi$ state can take place.

The nonrotating-molecule $^3\Delta$ state gives rise to multiplet components characterized by $\Omega = \pm 3$, ± 2, ± 1; the nonrotating-molecule $^1\Pi$ state gives rise to "multiplet components" characterized by $\Omega = \pm 1$. Thus a homogeneous perturbation (caused by the spin-orbit interaction term in H_{ev}) is also possible between the $^3\Delta$ state and the $^1\Pi$ state, corresponding to an interaction between the two multiplet components with $\Omega = +1$ and between the two multiplet components with $\Omega = -1$. We now consider this homogeneous perturbation.

The full Hamiltonian matrix for this problem is of dimension 8×8. However, this matrix immediately factors into two identical 4×4 diagonal blocks. We consider only one of these below, with rows and columns labeled by the wave functions $|\Lambda S \Sigma;\, \Omega J M\rangle = |2\,1\,1;\,3\,J\,M\rangle$, $|2\,1\,0;\,2\,J\,M\rangle$, $|2\,1\,{-1};\,1\,J\,M\rangle$, and $|1\,0\,0;\,1\,J\,M\rangle$. This Hamiltonian matrix has the following form.

$$\begin{bmatrix} B_\Delta[J(J+1)-8] + B_\Delta\langle L_\perp^2\rangle_\Delta + 2A, & -B_\Delta[2(J-2)(J+3)]^{1/2}, & 0, & 0 \\ -B_\Delta[2(J-2)(J+3)]^{1/2}, & B_\Delta[J(J+1)-2] + B_\Delta\langle L_\perp^2\rangle_\Delta, & -B_\Delta[2(J-1)(J+2)]^{1/2}, & 0 \\ 0, & -B_\Delta[2(J-1)(J+2)]^{1/2}, & B_\Delta J(J+1) + B_\Delta\langle L_\perp^2\rangle_\Delta - 2A, & \eta \\ 0, & 0, & \eta & E_\Pi + B_\Pi[J(J+1)-1] + B_\Pi\langle L_\perp^2\rangle_\Pi \end{bmatrix} . \tag{4–5}$$

The upper left 3×3 diagonal block is just the Hamiltonian matrix for a $^3\Delta$ state, set up as described in chapter 1. (In this block we have written the spin-orbit energies as $A\Lambda\Sigma$, which results in three evenly spaced components of the $^3\Delta$ state in the nonrotating molecule.) The lower 1×1 diagonal block is the Hamiltonian matrix for a $^1\Pi$ state. The off-diagonal element η represents the spin-orbit interaction between the two states with $\Omega = +1$ and is given by (see sect. 1.3)

$$\begin{aligned}\eta &= \langle 2\,1\,-1;\,1\,J\,M|\sum_i \xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i|1\,0\,0;\,1\,J\,M\rangle \\ &= \langle 2\,1\,-1|\sum_i \xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i|1\,0\,0\rangle \qquad (4\text{–}6) \\ &= \pm\langle -2\,1\,1|\sum_i \xi(r_i)\mathbf{l}_i\cdot\mathbf{s}_i|-1\,0\,0\rangle,\end{aligned}$$

where the second line results from the fact that the spin-orbit interaction operator does not involve the rotational variables, and where the third line results from symmetry arguments (see chapt. 2). The second line of (4–6) shows that η is independent of J. The third line represents part of the algebra leading to the factorization of the original 8×8 Hamiltonian matrix into two identical 4×4 diagonal blocks. The matrix element η can only be evaluated theoretically if the electronic wave functions for the $^3\Delta$ state and for the $^1\Pi$ state are rather well known. Such information is usually not available, so that this matrix element must be treated as an unknown adjustable (real) parameter, to be determined from a fit of calculated results to experimental data. Rotational energy levels are calculated, of course, by diagonalizing (4–5).

The effect of a heterogeneous perturbation ($\Delta\Omega=\pm 1$) between the $^3\Delta$ state and the $^1\Pi$ state can be taken into account by placing the quantity $\lambda[(J-1)(J+2)]^{1/2}$ in the (2, 4) and (4, 2) positions of (4–5). This quantity consists of a J-dependent part, determined as in section 4.3 from (1–13) and (1–14), and a small J-independent adjustable (real) parameter λ, which is analogous to the parameter $B\langle\Pi|L_+|\Sigma\rangle$ in section 4.3. (The fact that η and λ can simultaneously be taken as real must, of course, be proven (see chapt. 2 and sect. 3.5)).

4.5. Van Vleck Transformations

It is sometimes desirable to take into account perturbations arising from rather distant states without actually including these states in the matrix to be diagonalized exactly. Under these circumstances, it is convenient to use a Van Vleck transformation [26] (pp. 394–396) to correct the matrix elements within the submatrix to be diagonalized for effects arising from interactions with the distant states. (A Van Vleck transformation is essentially a transformation from the original Hamiltonian to a new Hamiltonian in which first-order interactions between the states under consideration and the distant states are eliminated. For more information, the reader is referred to reference [26].) If the Hamiltonian is divided into a zeroth-order part, a first-order part, and a second-order part

$$H=H_0+H_1+H_2 \qquad (4\text{–}7)$$

where the matrix of H_0 is diagonal in the basis set under consideration, then the corrected matrix elements (to second order) within the block actually to be diagonalized are given by

$$\langle i|H_0|j\rangle+\langle i|H_1|j\rangle+\langle i|H_2|j\rangle+\sum_{k\neq i,j}\langle i|H_1|k\rangle\langle k|H_1|j\rangle[\tfrac{1}{2}(E_i^\circ+E_j^\circ)-E_k^\circ]/(E_i^\circ-E_k^\circ)(E_j^\circ-E_k^\circ). \qquad (4\text{–}8)$$

In (4–8), the indices i and j are chosen from within the block to be diagonalized; the summation index k runs over all values outside this block. The energies E_i° are those calculated for each state from H_0.

4.6. Example: Λ-type Doubling in a $^1\Pi$ State

Λ-type doubling in a $^1\Pi$ state arises from perturbations of the rotational levels of the $^1\Pi$ state by the rotational levels of a distant $^1\Sigma$ state [25]. In section 4.3, we considered a $^1\Pi-{}^1\Sigma^+$ perturbation problem in which the two electronic states were both included in the matrix to be diagonalized. In this section we consider the same problem, but take into account the effect of the $^1\Sigma$ state by a Van Vleck transformation.

We thus intend to diagonalize exactly only the upper left 2×2 diagonal block of the matrix given in (4–1). This block can be corrected, according to eq (4–8), by adding the quantity

$$-[B^2|\langle\Pi|L_+|\Sigma\rangle|^2/E_\Sigma]J(J+1) \tag{4–9}$$

to each of the four matrix elements in the block. Diagonalization of the resulting 2×2 matrix yields the desired Λ-doubled rotational energy levels.

$$\begin{aligned} E_{\text{rot}} &= B_\Pi J(J+1)-B_\Pi+B_\Pi\langle L_\perp^2\rangle_\Pi \\ E_{\text{rot}} &= [B_\Pi-2B^2|\langle\Pi|L_+|\Sigma\rangle|^2/E_\Sigma]J(J+1)-B_\Pi+B_\Pi\langle L_\perp^2\rangle_\Pi \end{aligned} \tag{4–10}$$

The Λ-doubled rotational levels of the $^1\Pi$ state are often represented as symmetrically split about some mean position. Such a representation causes no difficulty when the $^1\Pi$ and $^1\Sigma$ states are well separated. However, if the states are approaching case (d) coupling, it is essential to represent the probelm as indicated here, namely only one-half of the $^1\Pi$ rotational levels are perturbed by interaction with the $^1\Sigma^+$ state. The other half of the levels are completely unaffected.

4.7. Centrifugal Distortion Corrections to Rotational Energy Levels

Centrifugal distortion, which can be considered from one point of view as a perturbation of rigid-rotor rotational energy levels, may be treated in diatomic molecules as follows. We rewrite eq (1–10), making two changes.

$$\begin{aligned} H_r &= B(Q)\hbar^{-2}[R_x^2+R_y^2] \\ &= B(Q)\hbar^{-2}[(J_x-L_x-S_x)^2+(J_y-L_y-S_y)^2]. \end{aligned} \tag{4–11}$$

First, careful attention is paid to units, and dimensionless angular momentum operators are obtained by considering $\hbar^{-2}[R_x^2+R_y^2]$ rather than $R_x^2+R_y^2$. Second, the quantity B is no longer taken to be a constant, but is rather given its true functional form [3] (p. 13) in terms of the vibrational coordinate $Q=r-r_e$

$$\begin{aligned} B(Q) &= \hbar^2/2\mu(r_e+Q)^2=[\hbar^2/2\mu r_e^2][1+Q/r_e]^{-2} \\ &= B_e-2(B_e/r_e)Q+3(B_e/r_e^2)Q^2-\ .\ .\ .\ . \end{aligned} \tag{4–12}$$

Note that μ is the reduced mass $m_1m_2/(m_1+m_2)$ of the diatomic molecule and that $B(Q)$ has the dimensions of energy, i.e., ML^2T^{-2}.

The next step is to apply a Van Vleck transformation (see sect. 4.5) to the problem. The complete Hamiltonian $H=H_{ev}+H_r$ is considered to be divided into two parts $H=H_0+H_1$, such that $H_0=H_{ev}$ and $H_1=H_r$. Energies of the unperturbed states are thus equal to energies of the nonrotating-molecule states. Wave functions for the unperturbed states (the basis set functions) have one of the forms (see sections 1.4 and 1.7): $|\Omega;\, v;\, \Omega JM\rangle$, $|\Lambda S\Sigma;\, v;\, \Omega JM\rangle$ or $|L\Lambda S\Sigma;\, v;\, \Omega JM\rangle$. Since centrifugal distortion involves an interaction between rotation and vibration, a vibrational quantum number v is included in these basis set functions. They are still taken to be simple products, however, of the form $|\Omega\rangle|v\rangle|\Omega JM\rangle$, $|\Lambda S\Sigma\rangle|v\rangle|\Omega JM\rangle$, or $|L\Lambda S\Sigma\rangle|v\rangle|\Omega JM\rangle$, respectively. We consider, in the submatrix to be diagonalized exactly (sect. 4.5), states characterized by fixed J and M, by fixed vibrational quantum number v, and by fixed $|\Omega|$, or by fixed $|\Lambda|$ and S, with $\Sigma=S$, $S-1$, . . ., $-S$, or by fixed L and S with $\Lambda=L$, $L-1$, . . ., $-L$ and $\Sigma=S$, $S-1$, . . ., $-S$, respectively, for the three types of wave functions given above. For the purpose of calculating centrifugal distortion corrections to the rotational energy levels, the distant perturbing states (sect. 4.5) are taken to be states characterized by the same fixed value of J and M, by different values of the vibrational quantum number v, and by electronic quantum numbers from the same set Ω, $\Lambda S\Sigma$, or $L\Lambda S\Sigma$, respectively.

Consider now centrifugal distortion corrections for a situation in which the $(2L+1)(2S+1)$ states of fixed L, S, J, M, and v having wave functions of the form $|L\Lambda\Sigma;\, v;\, \Omega JM\rangle$ lie close together in energy compared to the separation between adjacent vibrational levels. Under these circumstances the fourth term of (4–8) can be written

$$\sum_{v''}\sum_{\Lambda''\Sigma''}\frac{\langle L\Lambda S\,\Sigma;\, v;\Omega\, JM|H_r|L\Lambda'' S\,\Sigma'';\, v'';\, \Omega'' JM\rangle\,\langle L\Lambda'' S\,\Sigma'';\, v'';\, \Omega'' JM|H_r|L\Lambda' S\,\Sigma' :\, v;\, \Omega'\, J\, M\rangle}{(E_v-E_{v''})}, \tag{4–13}$$

where the energy separation between two states $|L\Lambda S\Sigma;\, v;\, \Omega JM\rangle$ and $|L\Lambda'' S\Sigma'';\, v'';\, \Omega'' JM\rangle$ has been approximated by the purely vibrational energy separation $E_v - E_{v''} \equiv (v-v'')h\nu$, and where the summation indices take on the values $v'' \neq v$; $\Lambda''=L,\, L-1,\, .\, .\, .,-L$; and $\Sigma''=S,\, S-1,\, .\, .\, .,-S$.

Since the basis set functions are simple products of a vibrational part, and a rotational and electronic part, and since H_r of (4–11) is also a simple product of a vibrational part and a rotational-electronic part, (4–13) can be written as the product of a vibrational part and a rotational-electronic part. If we make a further approximation and consider only the constant and linear terms in the series expansion (4–12) for $B(Q)$, we find that (4–13) can be written as

$$\sum_{v''}\langle v|-2(B_e/r_e)Q|v''\rangle\langle v''|-2(B_e/r_e)Q|v\rangle\,(E_v-E_{v''})^{-1}\times$$

$$\sum_{\Lambda''\Sigma''}\langle L\Lambda S\,\Sigma;\, \Omega JM|\hbar^{-2}[R_x^2+R_y^2]\,|L\Lambda'' S\,\Sigma'';\, \Omega'' JM\rangle\,\langle L\Lambda'' S\,\Sigma'';\, \Omega'' JM|\hbar^{-2}[R_x^2+R_y^2]\,|L\Lambda' S\,\Sigma';\, \Omega' JM\rangle \tag{4–14}$$

The sum over v'' in (4–14), i.e., the vibrational factor in the product, can be evaluated explicitly since [4] (pp. 67–82)

$$\begin{aligned}\langle v+1|Q|v\rangle &= [(v+1)\hbar/4\pi\mu\nu]^{1/2}\\ \langle v-1|Q|v\rangle &= [v\hbar/4\pi\mu\nu]^{1/2}\end{aligned} \tag{4–15}$$

Representing the sum over v'' by the symbol $-D_e$, we find for the vibrational factor in (4–14)

$$-D_e = -4B_e^3/(h\nu)^2 \tag{4–16}$$

where D_e, B_e, and $h\nu$ are all in units of energy, i.e., ML^2T^{-2}. D_e can be expressed in its more common units of cm^{-1} by (mentally) changing the units of B_e to cm^{-1} and replacing the vibrational energy interval $h\nu$ by its equivalent in cm^{-1}. If at the same time we drop the subscript e, we find [1] (p. 103)

$$D = 4B^3/\omega^2. \tag{4–17}$$

The sum over Λ'' and Σ'' in (4–14), i.e., the rotational-electronic factor in the product, can also be evaluated explicitly. It can be shown by considering various commutation relations [7] (pp. 45–78), [8], that the operator $R_x^2+R_y^2$, when acting on a function of the form $|L\Lambda' S\Sigma';\, \Omega' JM\rangle$ transforms it into a linear combination of functions characterized by the same L, S, J, and M, but by various values of Λ', Σ', and $\Omega' \equiv \Lambda' + \Sigma'$. Consequently, the sum in (4–14) over all values of Λ'' and Σ'' permitted for the given (fixed) values of L and S can be collapsed, just as if the sum were carried out over *all possible* basis set functions, to give for the rotational-electronic factor

$$\langle L\Lambda S\,\Sigma;\, \Omega JM|\hbar^{-4}[R_x^2+R_y^2]^2|L\Lambda' S\,\Sigma';\, \Omega' JM\rangle. \tag{4–18}$$

Combining the vibrational factor (4–16) and the rotational-electronic factor (4–18), we rewrite the Van Vleck correction (4–13) as

$$\langle L\Lambda S\Sigma;v;\Omega JM|-D\hbar^{-4}[R_x^2+R_y^2]^2|L\Lambda' S\Sigma';v;\Omega' JM\rangle \tag{4–19}$$

where D is a constant. The centrifugal distortion correction to the rigid-rotor rotational energy levels for a set of states characterized by fixed L and S, and by the fact that the $(2L+1)(2S+1)$ components of differing Λ and Σ lie close together compared to the vibrational spacing, can thus be determined to a good approximation by including matrix elements of the operator

$$-D\hbar^{-4}[(J_x-L_x-S_x)^2+(J_y-L_y-S_y)^2]^2 \tag{4–20}$$

in the $(2L+1)(2S+1)\times(2L+1)(2S+1)$ Hamiltonian matrices of fixed L, S, J, M, and v to be diagonalized exactly. By analogy, higher order centrifugal distortion corrections can be obtained by including matrix elements of $H\hbar^{-6}[R_x^2+R_y^2]^3$, $K\hbar^{-8}[R_x^2+R_y^2]^4$, etc.

Consider as a second example of centrifugal distortion corrections a situation in which the $2(2S+1)$ or $(2S+1)$ states of fixed $|\Lambda|$, S, J, M, and v having wave functions of the form $|\Lambda S\Sigma;v;\Omega JM\rangle$ lie close together in energy compared to the separation between adjacent vibrational levels. Under these circumstances, the fourth term of (4–8) can be written

$$\sum_{v''}\sum_{\Lambda''\Sigma''}\frac{\langle\Lambda S\Sigma;v;\Omega JM|H_r|\Lambda'' S\Sigma'';v'';\Omega'' JM\rangle\langle\Lambda'' S\Sigma'';v'';\Omega'' JM|H_r|\Lambda' S\Sigma';v;\Omega' JM\rangle}{(E_v-E_{v''})}, \tag{4–21}$$

where we have approximated the energy separation between two states $|\Lambda S\Sigma;v;\Omega JM\rangle$ and $|\Lambda'' S\Sigma'';v'';\Omega'' JM\rangle$ by the purely vibrational energy separation, and where the summation indices take on the values $v''\neq v$; $\Lambda''=\pm|\Lambda|$; and $\Sigma''=S, S-1, \ldots, -S$.

The expression (4–21) can be written as the product of a vibrational factor and a rotational-electronic factor, just as (4–13) was, giving an expression identical to (4–14) except for the absence of the quantum number L and the new significance of the sum over Λ''.

The sum over v'' can again be evaluated explicitly, yielding for the vibrational factor the same quantity $-D_e$ given in (4–16).

The sum over Λ'' and Σ'' this time does not include all functions generated when the operator $R_x^2+R_y^2$ acts on a function of the form $|\Lambda' S\Sigma';\Omega' JM\rangle$. Consequently, the summation over Λ'' and Σ'' cannot be collapsed to give an expression like (4–18). However, the sum over Λ'' and Σ'' does include all functions produced when **J** and **S** act on a function of the form $|\Lambda' S\Sigma';\Omega' JM\rangle$. By a series of arguments it is possible to show that the centrifugal distortion correction to the rigid-rotor rotational energy levels for a set of states characterized by fixed $|\Lambda|$ and S, and by the fact that the spin-multiplet components of this state lie close together compared to the vibrational spacing, can be determined to a good approximation by including matrix elements of the operator

$$-D\hbar^{-4}[(J_x-S_x)^2+(J_y-S_y)^2+\langle L_\perp^2\rangle]^2 \tag{4–22}$$

in the $2(2S+1)\times 2(2S+1)$ or $(2S+1)\times(2S+1)$ Hamiltonian matrices of fixed $|\Lambda|$, S, J, M, and v to be diagonalized exactly. When centrifugal distortion corrections of the order of DJ^2 are negligible, (4–22) can be replaced by

$$-D\hbar^{-4}[\mathbf{J}^4-4(J_xS_x+J_yS_y)\mathbf{J}^2]. \tag{4–23}$$

There are many other situations for which centrifugal distortion corrections could be considered, e.g., the situation corresponding to basis set functions of the form $|\Omega;v;\Omega JM\rangle$, or the situation which arises when one of the multiplet splittings is approximately equal to a vibrational interval. We shall not consider these here.

The author is extremely grateful to Dr. W. J. Balfour, Dr. G. Herzberg, Dr. Ch. Jungen, Dr. I. Kopp, and Dr. C. M. Woodman for reading a draft of this monograph, and for communicating to the author their own comments as well as comments from some of their colleagues. This combined criticism was invaluable in reshaping certain sections of each chapter.

5. References

[1] Herzberg, G., Spectra of Diatomic Molecules (D. Van Nostrand Co., New York, N.Y., 1950).
[2] Landau, L. D., and Lifshitz, E. M., Quantum Mechanics, translated from the Russian by J. B. Sykes and J. S. Bell (Pergamon Press, London, England, 1958).
[3] Kronig, R. de L., Band Spectra and Molecular Structure (Cambridge Univ. Press, Cambridge, England, 1930).
[4] Pauling, L., and Wilson, E. B., Jr., Introduction to Quantum Mechanics (McGraw-Hill Book Co., New York, N.Y., 1935).
[5] Dicke, R. H., and Wittke, J. P., Introduction to Quantum Mechanics (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1960).
[6] Wilson, E. B., Jr., Decius, J. C., and Cross, P. C., Molecular Vibrations (McGraw-Hill Book Co., New York, N.Y., 1955).
[7] Condon, E. U., and Shortley, G. H., The Theory of Atomic Spectra (Cambridge Univ. Press, Cambridge, England, 1951).
[8] Van Vleck, J. H., Revs. Mod. Phys. **23**, 213 (1951).
[9] Hougen, J. T., J. Chem. Phys. **36**, 519 (1962).
[10] Hill, E., and Van Vleck, J. H., Phys. Rev. **32**, 250 (1928).
[11] Schlapp, R., Phys. Rev. **51**, 342 (1937).
[12] Kayama, K., and Baird, J. C., J. Chem. Phys. **46**, 2604 (1967).
[13] Hougen, J. T., Can. J. Phys. **40**, 598 (1962).
[14] Longuet-Higgins, H. C., Mol. Phys. **6**, 445 (1963).
[15] Hougen, J. T., J. Chem. Phys. **37**, 1433 (1962).
[16] Hougen, J. T., J. Chem. Phys. **39**, 358 (1963).
[17] Wigner, E. P., Group Theory (Academic Press, New York, N.Y., 1959).
[18] Townes, C. H., and Schawlow, A. L., Microwave Spectroscopy (McGraw-Hill Book Co., New York, N.Y., 1955).
[19] Watson, J. K. G., Can. J. Phys. **46**, 1637 (1968).
[20] Schlapp, R., Phys. Rev. **39**, 806 (1932).
[21] Klynning, L., Arkiv för Fysik **31**, 281 (1966).
[22] Lagerqvist, A., and Miescher, E., Helv. Phys. Acta **31**, 221 (1958).
[23] Felenbok, P., and Lefebvre-Brion, H., Can. J. Phys. **44**, 1677 (1966).
[24] Lewis, J. K., and Hougen, J. T., J. Chem. Phys. **48**, 5329 (1968).
[25] Van Vleck, J. H., Phys. Rev. **33**, 467 (1929).
[26] Kemble, E. C., Quantum Mechanics (Dover Publications, New York, N.Y., 1958).
[27] Bunker, P. R., and Papoušek, D., J. Mol. Spectr. **32**, 419 (1969).
[28] Kovács, I., Rotational Structure in the Spectra of Diatomic Molecules, translated from the Hungarian by L. Nemes (Adam Hilger Ltd., London, 1969).

U. S. GOVERNMENT PRINTING OFFICE : 1970 O - 371-908

NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, chemistry, and engineering. Comprehensive scientific papers give complete details of the work, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Illustrated with photographs, drawings, and charts.

Published in three sections, available separately:

• Physics and Chemistry

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, $9.50; foreign, $11.75*

• Mathematical Sciences

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, $5.00; foreign, $6.25*

• Engineering and Instrumentation

Reporting results of interest chiefly to the engineer and the applied scientist. This section includes many of the new developments in instrumentation resulting from the Bureau's work in physical measurement, data processing, and development of test methods. It will also cover some of the work in acoustics, applied mechanics, building research, and cryogenic engineering. Issued quarterly. Annual subscription: Domestic, $5.00; foreign, $6.25*.

TECHNICAL NEWS BULLETIN

The best single source of information concerning the Bureau's research, developmental, cooperative and publication activities, this monthly publication is designed for the industry-oriented individual whose daily work involves intimate contact with science and technology—*for engineers, chemists, physicists, research managers, product-development managers, and company executives.* Annual subscription: Domestic, $3.00; foreign, $4.00*.

NONPERIODICALS

Applied Mathematics Series. Mathematical tables, manuals, and studies.

Building Science Series. Research results, test methods, and performance criteria of building materials, components, systems, and structures.

Handbooks. Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications. Proceedings of NBS conferences, bibliographies, annual reports, wall charts, pamphlets, etc.

Monographs. Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

National Standard Reference Data Series. NSRDS provides quantitive data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated.

Product Standards. Provide requirements for sizes, types, quality and methods for testing various industrial products. These standards are developed cooperatively with interested Government and industry groups and provide the basis for common understanding of product characteristics for both buyers and sellers. Their use is voluntary.

Technical Notes. This series consists of communications and reports (covering both other agency and NBS-sponsored work) of limited or transitory interest.

Federal Information Processing Standards Publications. This series is the official publication within the Federal Government for information on standards adopted and promulgated under the Public Law 89–306, and Bureau of the Budget Circular A–86 entitled, Standardization of Data Elements and Codes in Data Systems.

CLEARINGHOUSE

The Clearinghouse for Federal Scientific and Technical Information, operated by NBS, supplies unclassified information related to Government-generated science and technology in defense, space, atomic energy, and other national programs. For further information on Clearinghouse services, write:

Clearinghouse
U.S. Department of Commerce
Springfield, Virginia 22151

* Difference in price is due to extra cost of foreign mailing.

Order NBS publications from:

Superintendent of Documents
Government Printing Office
Washington, D.C. 20402

U.S. DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20230

OFFICIAL BUSINESS

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF COMMERCE