

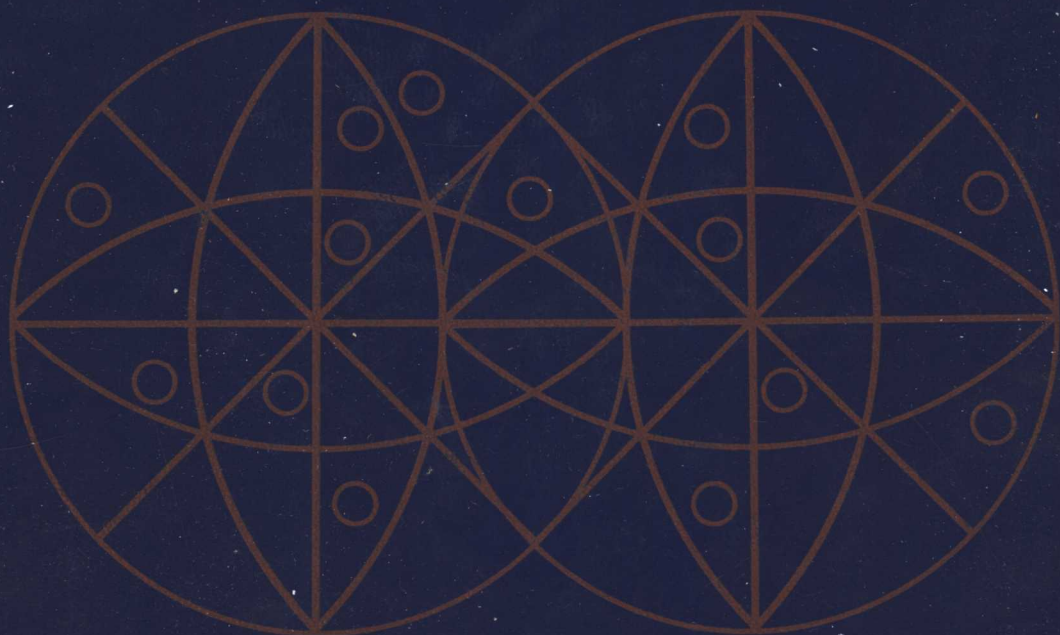
# The Theory of Molecular Spectroscopy

Volume 1:

The Quantum Mechanics and Group Theory  
of Vibrating and Rotating Molecules

C.J.H. Schutte

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# The Theory of Molecular Spectroscopy

VOLUME I

THE QUANTUM MECHANICS AND GROUP THEORY  
OF VIBRATING AND ROTATING MOLECULES

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## PREFACE

This book describes the mathematical theory of the spectroscopy of molecules and ions in the electronic ground state in a way which is as self-contained as possible. Volume I deals with the quantum-mechanical background of the vibrations and rotations of molecules, while Volume II deals with the spectroscopy of the various rotators, the vibrations of polyatomic molecules (with special emphasis upon the use of the algebraic eigenvector-eigenvalue problem). The theory is presented in such a way that the book should appeal to the post-graduate student, as well as to the research worker in the fields of infra-red and Raman spectroscopy.

In Chapter 1 of Vol. I a short survey is given of most of the mathematics which will be needed in the later chapters on group theory, with special emphasis upon the theory of linear operators, their eigenvalue equations, as well as their matrix representations. The mathematical theory of groups is described in detail in Chapter 2, emphasising the groups of operators which generate the molecular point groups that leave a point invariant. This chapter also includes complete discussions on the character tables, the correlation between a group and its sub- and super-groups, the point groups of non-rigid molecules, crystal groups, and the direct product groups. There are three appendices of group-theoretical tables which form a unit with this chapter; these tables were recalculated from first principles, and it is hoped that all the mistakes of existing tables are eliminated. Appendix I lists the complete character tables of fifty-one molecular point groups which could be of importance in molecular and crystal structure. Appendix II deals with the sub- and super-groups of these molecular point groups and the correlations between them. Appendix III contains the complete reduction of the direct products of all representations of each of the molecular point groups, the general rules of which were derived in Chapter 2. Both the *Schoenflies* and the *International System* of nomenclature (which is used by X-ray

crystallographers) are used side by side in the book; all the tables are generated through the International System, although the Schoenflies symbols are always displayed. There are tables on p. 79 and p. 393 which effectively translate the one notation into the other for each of the fifty-one molecular point groups encountered in this book. A special section on the group theory of non-rigid molecules is also included.

Chapter 3 describes the fundamentals of quantum mechanics; it is in effect a short reference manual on the subject, with emphasis upon the harmonic/anharmonic oscillator and the quantisation of the orbital angular momentum referred to the stationary axes; the information of this chapter will be used very much throughout the book. The complete quantum mechanical molecular Hamiltonian operator for molecules is systematically derived in Chapter 4, after the classical Hamiltonian has been fully discussed. In this chapter, the angular momentum components referred to both the stationary ( $X, Y, Z$ ) and the molecule-fixed ( $x, y, z$ ) axes, are derived after the establishing of some conventions which will be adhered to in the rest of the book, following Condon and Shortley [1963].

In Chapter 5 a description is given of those aspects of molecular quantum mechanics which are of importance for molecular spectroscopy. The Born–Oppenheimer approximation is fully described, with reference to the modern *ab-initio* computation of the vibrational rotational energy levels of  $\text{H}_2^+$  and  $\text{H}_2$ . There is also a section on the fitting of experimental data to potential energy expressions (e.g. Dunham and R.K.R.), as well as a complete description of the virial and Hellmann–Feynman theorems, and the quantum mechanical calculation of dipole moments and polarisabilities.

Chapter 6 deals with the interaction between dipole radiation and matter. The classical theory of fields is briefly reviewed, and a semi-classical derivation of the transition probabilities for the absorption/emission of dipole radiation is given, with special emphasis upon the angular momentum selection rules. The direction-cosine matrix elements for a rigid symmetrical rotator are derived, using the methods of Condon and Shortley [1963] and Shaffer and Louck [1959]; these will be required in Volume II in the section on line strengths. This chapter also describes the Raman scattering selection rules for free molecules.

The references to original papers in Vol. I are complete up to about the end of 1970, although isolated later papers are also included, especially in the sections on non-rigid molecules and the R.K.R.-method. The equations derived in many of the papers referred to, were

recalculated in order to comply with the choice of phases and other conventions (e.g. the choice of the rotations determining the Eulerian matrices) adopted in this book; this means that a systematic derivation of all the equations is given.

The semi-classical theory of radiation is used to derive the equations which describe the interaction of radiation with matter because the introduction of the fully quantised electromagnetic field would have taken up far too much space; the quantised field is briefly referred to in the section on the Raman selection rules. The coupling of two or more angular momenta is not treated in this volume, hence the Clebsch–Gordan coefficients are not fully discussed, but are briefly reviewed in Appendix V, while the Young Symbols and Tableaux are discussed in Appendix IV.

The algebraic eigenvector–eigenvalue problem is exhaustively treated in Volume II, with particular emphasis upon the theory of small vibrations and the normal modes of vibration of molecules. Although all the powerful simplifying methods of group theory are used, a chapter on direct methods of solution is included. The various potential-energy approximations are fully discussed as well as their limitations, and an introduction to anharmonic methods is given. The spectroscopy of the various vibrators is discussed in detail, as well as isotope-effects, Green's function methods, mean-square amplitudes, solid-state spectroscopy, etc. The step-by-step analysis of the normal modes and force constants of a molecule follows in an Appendix. This volume thus concentrates upon the general theoretical background of vibrational and rotational spectroscopy.

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## MATHEMATICAL INTRODUCTION

### §1. General

This book deals with the theory of the interaction of electromagnetic radiation with rotating and vibrating molecular and ionic species. The language which is used to describe this interaction and the energy-level sequence that the interaction reveals, is that of quantum mechanics. This means that the molecular spectroscopist must have a thorough understanding of quantum mechanics and its description of matter. Although this book is not intended to be a complete textbook on quantum mechanics and its description of molecules and ions, it is felt that it should contain a short, but self-contained introduction to the subject. This means that a chapter must be included on the relevant *mathematical* background of quantum mechanics, as well as a chapter on the mathematical theory of groups (which is of prime importance for the study of molecular spectroscopy). It is thus the aim to make the book as self-contained as possible; this, furthermore, provides the opportunity to develop a consistent nomenclature, as well as a consistent set of mathematical conventions (e.g. the conventions about the fixing of relative phases, writing of bases vectors of spaces, etc.).

The reader who wants to "delve deeper" into quantum mechanics is referred to the following textbooks by Pilar [1968], Eyring et al. [1944], Pauling and Wilson [1935], Schutte [1968], Bethe [1964], Kaempffer [1965], Kemble [1937] which cover the more elementary applications to physics and chemistry, while detailed expositions can be found in Pauli [1958], Messiah [1965, 1966], Slater [1960, 1963], Bethe and Salpeter [1957], and in Sommerfeld [1967]. The mathematical background can be found in Dennery and Krzywicki [1967], Von Neumann [1968], Jordan [1969] and Dirac [1958] while the conceptual development of quantum mechanics is described in Jammer [1966], Van der Waerden [1967] and in Ludwig [1968].

## §2. Linear vector spaces

### 2.1. Definition

Consider the set  $\{S\}$  of  $n$  objects  $| \rangle$  which are numbered in order to distinguish between them, e.g.,  $|a_1\rangle, |a_2\rangle, \dots, |a_n\rangle$ . The algebra of this set of objects is defined by the specification of the rules of manipulation or composition, just as in the case of the set of all real numbers, e.g. the well-known rules of addition and multiplication.

The  $\{S\}$  of  $n$  objects  $| \rangle$  with the following properties is called a *linear vector space*:

- (i) if  $|a_i\rangle, |a_j\rangle \in \{S\}$ , then  $|a_i\rangle + |a_j\rangle = |a_n\rangle \in \{S\}$ ;
- (ii) if  $|a_i\rangle \in \{S\}$  and  $\alpha$  is a complex number, then  $\alpha|a_i\rangle = |a_j\rangle \in \{S\}$ ;
- (iii) there exists a zero or null element  $|0\rangle \in \{S\}$  such that for any  $|a_i\rangle \in \{S\}$ ,  $|a_i\rangle + |0\rangle = |a_i\rangle$ ;
- (iv) for every  $|a_i\rangle \in \{S\}$  there exists an element  $|a_i'\rangle = |a_j\rangle \in \{S\}$  for which  $|a_i\rangle + |a_i'\rangle = |0\rangle \in \{S\}$ .

The following properties ensure that addition and multiplication are well-defined operations, with  $|a_i\rangle, |a_j\rangle \in \{S\}$ :

- (v) commutative law of addition:

$$|a_i\rangle + |a_j\rangle = |a_j\rangle + |a_i\rangle;$$

- (vi) distributive law referring to complex numbers:

$$(\alpha_i + \alpha_j)|a_i\rangle = \alpha_i|a_i\rangle + \alpha_j|a_i\rangle;$$

- (vii) distributive law referring to addition of  $| \rangle$ :

$$\alpha_i(|a_i\rangle + |a_j\rangle) = \alpha_i|a_i\rangle + \alpha_i|a_j\rangle;$$

- (viii) associative law of multiplication:

$$\alpha_i(\alpha_j|a_i\rangle) = \alpha_i\alpha_j|a_i\rangle;$$

- (ix)  $1|a_i\rangle = |a_i\rangle$ .

It is easy to see that subtraction is defined by  $|a_i\rangle - |a_j\rangle = |a_i\rangle + (-1)|a_j\rangle$ . The elements  $| \rangle$  of the linear vector space  $S$  are called *vectors*. The reader who wishes to study the properties of linear vector spaces is referred to some textbooks on the subject, like Halmos [1958], and Dean [1966], as well as to Jordan [1969] and Dennery and Krzywicki [1967, Ch. 2].

*Example 1.* The set  $\{S\}$  of all vectors  $| \rangle$  in a plane around the origin  $o$  can be used to familiarise these abstract concepts. The well-known parallelogram rule of addition, where the components of vectors are added, as shown in Fig. 1.1, operates here. Multiplication of  $|a_i\rangle \in \{S\}$  by a real number  $b$  elongates the vector:  $b|a_i\rangle = b(a_{xi}, a_{yi}) = (ba_{xi}, ba_{yi}) = |a_j\rangle \in \{S\}$ , where  $a_{xi}$  and  $a_{yi}$  are the Cartesian components of  $|a_i\rangle$  along the basis vectors (i.e. the coordinates). It is easy to show, using the above definition, that  $S$  is a linear vector space, the null element being the vector  $(0, 0) = \mathbf{0}$  and  $|a_i\rangle + |a_j\rangle = (a_{xi} + a_{xj}, a_{yi} + a_{yj}) = |a_k\rangle \in \{S\}$ , as said above. This set of vectors in a plane is just a special case of the  $n$ -dimensional vector space where the vectors are written as  $n$ -tuples of numbers (i.e.  $n$  components or coordinates), e.g.  $|a_i\rangle = (a_1, a_2, \dots, a_n)$  with addition defined *component-wise*, as above. In the case with  $n = 3$  the vector space is called three-dimensional Euclidian space.

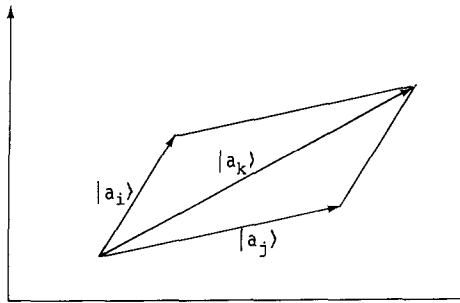


Fig. 1.1. Component-wise addition of two vectors in a plane.

*Example 2.* The set  $\{S\}$  of all continuous functions of a real variable  $x$ . The operation addition is defined *point-wise*  $|a_i\rangle_x + |a_j\rangle_x = |a_k\rangle_x \in \{S\}$ , where the subscript  $x$  indicates that the addition of the vectors  $|a_i\rangle$ ,  $|a_j\rangle \in \{S\}$  is defined point by point. A concrete example here is the set  $\{S\}$  of solutions of the harmonic oscillator differential equation which will be met very often in this book, that is, the solutions of

$$\frac{d^2\psi(t)}{dt^2} + \lambda^2\psi(t) = 0 \quad (1.1)$$

which are

$$\psi_\gamma(t) = A \sin(\lambda t + \gamma) = |a_\gamma\rangle_t \quad (1.2)$$

where  $A$  is the amplitude and  $\gamma$  the phase. If, as an example  $\gamma$  is taken as

0 and  $\pi/2$  respectively, the solutions are

$$\psi_0(t) = A \sin \lambda t = |a_0\rangle_t; \quad \psi_{90}(t) = A \cos \lambda t = |a_{90}\rangle_t,$$

yielding  $|a_0\rangle_t + |a_{90}\rangle_t = |a\rangle_t$ , which is equivalent to the statement  $\psi_0(t) + \psi_{90}(t) = A(\sin \lambda t + \cos \lambda t) = \psi_t$ , which is the general solution.

## 2.2. Linear independence of the vectors; basis of space $S$

Consider the set  $\{S\}$  of  $n$  vectors  $|a_n\rangle$  in the space  $S$ . The set  $\{S\}$  is called a *linearly independent set of vectors* if the relation

$$\sum_i^n k_i |a_i\rangle = 0 \quad (1.3)$$

can only be satisfied by the requirement that all the scalars  $k_i$  are equal to zero; if not all  $k_i = 0$  (i.e. at least two of them), then the set  $\{S\}$  is called linearly dependent. It is said that a set  $\{S\}$  of  $n$  linearly independent vectors  $|a_n\rangle$  spans the  $n$ -dimensional space  $S$  if all vectors  $|a\rangle \in \{S\}$  can be expressed as a linear combination of the set *basis vectors*

$$\sum_i^n b_i |a_i\rangle = |a\rangle; \quad (1.4)$$

this relation can be written in another way by writing the  $n$ -tuple of real scalars  $b_i$  ( $i = 1, 2, \dots, n$ ) as a row vector  $\mathbf{b}$  and the basis vectors as a column vector  $\mathbf{X}$ , so that Eq. (1.4) can be written as

$$|a\rangle = \mathbf{b} \cdot \mathbf{X} = (b_1, b_2, b_3, \dots, b_n) \begin{pmatrix} |a_1\rangle \\ |a_2\rangle \\ \vdots \\ |a_n\rangle \end{pmatrix} \quad (1.5)$$

a form familiar in vector calculus. The numbers  $b_i$  are the components of  $|a\rangle$  with respect to the basis vectors  $|a_i\rangle$ ,  $i = 1, 2, \dots, n$ , respectively;  $n$  is called the *dimension* of the space  $S$ .

*Example 1.* The basis vectors in the two-dimension Euclidian space of Fig. 1.1 are  $i$  and  $j$ , or equivalently  $|a_1\rangle$  and  $|a_2\rangle$

$$\mathbf{i} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \mathbf{j} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

so that every vector can be decomposed into  $|a\rangle = k_1|a_1\rangle + k_2|a_2\rangle$ .



In this book vectors will be written as either *bold-face italics* or as brackets of the type  $| \rangle$  wherever convenient and as normal convention prescribes. It is easy to extend this to three dimensions, with basis vectors

$$|a_1\rangle = i = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}; \quad |a_2\rangle = j = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}; \quad |a_3\rangle = k = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (1.6)$$

or to  $n$ -dimensional spaces.

### 2.3. The scalar or inner product

The scalar or inner product in the space  $S$  is a complex number  $\alpha$  associated with every pair of vectors  $|a_i\rangle, |a_j\rangle \in \{S\}$  and is written as follows:

$$\langle |a_i\rangle, |a_j\rangle \rangle = \alpha. \quad (1.7)$$

The scalar product has the following defined properties, the two members of the pair  $(, )$  being known as the first factor and the second factor, respectively:

(i) distribution of the second factor:

$$\langle |a_i\rangle, |a_j\rangle + |a_k\rangle \rangle = \langle |a_i\rangle, |a_j\rangle \rangle + \langle |a_i\rangle, |a_k\rangle \rangle;$$

(ii) association of the second factor:

$$\langle |a_i\rangle, \beta |a_j\rangle \rangle = \beta \langle |a_i\rangle, |a_j\rangle \rangle.$$

(This definition can also be given to be  $\langle \beta |a_i\rangle, |a_j\rangle \rangle = \beta \langle |a_i\rangle, |a_j\rangle \rangle$ , i.e. associative for the first factor, so that  $\langle |a_i\rangle, \beta |a_j\rangle \rangle = \beta^* \langle |a_i\rangle, |a_j\rangle \rangle$ , where the asterisk indicates complex conjugation; this means that for the vectors of quantum mechanics which will be discussed below, the equivalent scalar product becomes  $\langle a_i | a_j \rangle = \int_{\Omega} \phi_i \phi_j^* d\Omega$ —this notation is followed by Von Neumann [1932], Green [1965], Bethe and Salpeter [1957] and Kato [1966], but not by the majority of the other textbooks, hence definition (ii) is adopted here.)

(iii) Hermitian symmetry:

$$\langle |a_i\rangle, |a_j\rangle \rangle = \langle |a_j\rangle, |a_i\rangle \rangle^*; \quad \text{and}$$

(iv)  $\langle |a_i\rangle, |a_j\rangle \rangle \geq 0$ , where the equality sign only appears for  $|a_i\rangle = |0\rangle$  (this derived property ensures that the scalar product of a vector with itself is a real number, because of (iii)).