1

Group Theory in Infrared Spectroscopy

This chapter reviews the use of group theory methods for the study of a molecule using infrared (IR) spectroscopy. The application of group theory involves the use of character tables in the theory of representation of a point symmetry group associated with a molecule. The focus is on the elements of the theory of representation, which are used in the following chapters for the study of ammonia (NH_3) molecules (an example of a symmetric top), and methane (CH_4) (an example of a spherical top), and their isotopologues. Elements of the tensor operator algebra are also reviewed for the study of CH_4 within the framework of tensor formalism. The permutation-inversion group CNPI is also presented with reference to NH_3, in order to distinguish between the symmetry group based on the geometry of the molecule, i.e. on its symmetry elements, and the permutation group of the identical nuclei.

1.1. Introduction

The point symmetry group of a molecule reflects the geometric form of the molecule. It is well adapted to the Hamiltonian of Schrödinger's equation, the energy operator which is the sum of the kinetic energy operator and the potential energy operator of the molecule, since it is built on space variables of the position of the electrons and nuclei. When the transformations involving identical nuclei exchanges are taken into account, the point symmetry group is not adapted to the study of the symmetries of the wave function which includes quantum variables related to the spins of identical nuclei when describing a vibration–rotation state for a given electronic state. The identical particle permutation group, which is the symmetric group S_n (not to be confused with the point group S_{2n}) of permutations of n identical particles of order $n!$, is more appropriate.

Molecules characterized by a potential energy function with several minima are not rigid molecules. To take into account the inversion in the case of semi-rigid molecules such as NH_3 and its isotopic varieties, a group of higher order that has the irreducible representations needed to list the irreducible representations used for the classification of the molecule wave functions depending on the Hamiltonian symmetry properties has been used. This group is built from the permutation-inversion group that takes into account situations in which inversion can be observed through identical nuclei exchange in the molecule [BUN 98, HOU 62, HOU 63, HOU 65, LON 63].

1.2. The point-symmetry group of a molecule

The point-group theory applies to rigid molecules, in the sense that the motions of nuclei during a vibration are described by low-amplitude motions and the rotation of the molecule as a whole is described within the framework of rigid rotators (see section 2.2). The construction of the point group relies on the geometric form of the molecule. The operators associated with the elements of a point symmetry group l of a molecule generally commute with one part of the exact or full Hamiltonian (energy operator of an effective Hamiltonian) of the molecule (at the zeroth-order approximation). The focus is on the space position variables of the electrons and nuclei and on the Schrödinger equation for vibration–rotation for a given electronic state.

In this case, the complete nuclear permutation-inversion (CNPI) group [BUN 98, HOU 62, HOU 63, HOU 65, LON 63] is built from a permutation-inversion group (see section 1.6). The elements of this group are the permutations of identical nuclei of a molecule (group of permutation S_n) and the group built on the operator whose effect is the inversion of all the coordinates of nuclei and electrons. This group operates on the exchange of nuclei independently of the observable geometric form. There is a direct link between the symmetry properties of the Hamiltonian and the operators of this group, while the link with the operators of the point symmetry group is indirect. It is worth noting that in some textbooks dedicated to group theory applications, the construction of double symmetry groups is explicitly presented [BUN 98, HAM 62, LAN 75, WIL 55] by building a higher-order group by tensor product of the point symmetry group with a second-order group built on the space coordinate inversion operator. This approach was initially proposed by H. Bethe [BET 29], who used group theory to interpret the degeneracy lifting of atomic orbitals of atoms inserted in crystallographic sites. His work was based on the effect on spin variable symmetry linked to the irreducible representation of a double group. For the structures that were not addressed by Bethe's and Opechowski's approach

[OPE 40], which showed that the classes of a double group G^* built with G, a subgroup of the three-dimensional rotation group SO(3), could be less than twice the number of G classes.

1.2.1. *Symmetry operations and symmetry elements of a molecule*

A symmetry or isometric operation that leaves distances and angles unchanged is an operation that brings a physical object from a given orientation to a new orientation that is equivalent to the former one. In the case of a molecule, the equilibrium configuration of the molecule is invariant under the symmetry operations associated with the symmetry elements of the molecule and therefore the molecule is brought to coincide with itself. There are two types of transformations: rotations of the three-dimensional space corresponding to the transformations of Euler r angles in the rotational space (direct operations) and other transformations such as inversion, reflections with respect to a plane, rotations followed by an inversion, rotations–reflections that reverse the direction of the mobile 3D reference frame (inverse operations).

The possible symmetry elements of a molecule that contribute to building a point group are rotation axes (operations termed as "direct"), inverse rotation axes, planes of reflection symmetry and an inversion center. There are five possible types of symmetry operations for a molecule (see Figure 1.1 and Table 1.1):

– identity operation E, equivalent to a rotation by 2π about C_n, ($C_z(\varphi = 2\pi)$) with $n = 1$ or an absence of operation ($C_z(\varphi = 0)$). The molecules remain unchanged under the action of E; E belongs to all the symmetry groups;

– a rotation by $2\pi/n$ about C_n, the rotation axis of order n; for a linear molecule, there are infinite possible rotations by angle φ about the internuclear axis z, the axis $C_z(\varphi)$ including the identity operation E; for $n = 2$ the molecule is an asymmetric top (H_2O); for $n = 3$, the molecule is a symmetric top (NH_3) if there is only one axis of symmetry of order 3; for $n = 4$ and because of the existence of four axes of symmetry of order 3, the CH_4 molecule is a spherical top. It is worth noting that it is a classification based on rigid rotators (see section 2.4) and on the symmetry about an axis. In general, if n is not a prime number, there is an integer k ($n = kp$), such that the p axes C_n^k are confounded with axis C_n. If there is an axis C_n with n even and a symmetry plane σ perpendicular to C_n, there is also a symmetry operation of inversion i;

– a rotation by $2\pi/n$ about the improper axis S_n, followed by the reflection operation in a plane perpendicular to the (rotation–reflection) axis; for a linear molecule, there is an infinity of improper rotations $S_z(\varphi)$ (rotation by an angle φ

about axis z followed by a reflection operation in a plane perpendicular to the axis at the center of the bond), including the reflection operation with respect to the plane *xy* (rotation by an angle 0 about the axis *z* and inversion S_2 with respect to the center of the bond); for a symmetric linear molecule, there is an infinity of rotations $C_t(\pi)$ by an angle π about axes *t* perpendicular to *z* and passing through the origin. If *n* is even, the axes C_{2n} are merged with axes S_n, ($S_n = C_{2n}$). If *n* is odd, the axes C_n are merged with axis S_n and there is a symmetry plane σ that is perpendicular to the axis S_n, ($S_n = C_n \otimes \sigma$). There is also the operation of inversion symmetry *i*. Generally, if *n* is odd and the axis is of type S_{2n}, then *i* exists;

– the symmetry planes σ_v, *v* stand for vertical (containing the highest-order rotation axis), σ_h, *h* stands for horizontal (perpendicular to the highest-order rotation axis) or σ_d, *d* stands for diagonal. For a linear symmetric molecule, there is an infinity of reflections $\sigma_{zt}(\sigma_v)$ with respect to *zt* planes containing the axis *z* and making an arbitrary angle with the *zx* plane; a molecule is invariant after the reversal of coordinates with respect to the symmetry plane σ;

– inversion *i* with respect to a center of symmetry of the molecule; for a linear symmetric molecule, S_2 corresponds to the inversion with respect to the center of the bond. Molecules that are invariant to this symmetry operation have an inversion center.

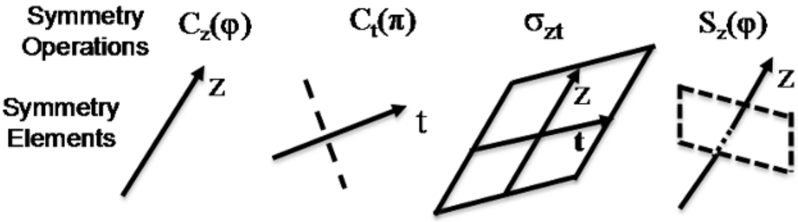

Figure 1.1. *Symmetry operations and symmetry elements of a molecule*

As an illustration, the symmetry elements of the NH$_3$ molecule are a third-order rotation axis (ternary axis: 2 rotation operations $C_z(2\pi/3)$ and $C_z(4\pi/3)$, denoted by C_3^1, and C_3^2 (see Figures 1.2(a) and 1.3), about the *Oz* axis passing through the nitrogen atom and three reflection symmetry planes $\sigma(0)$, $\sigma(2\pi/3)$ and $\sigma(4\pi/3)$, denoted by σ_v, σ_v' and σ_v'' (see Figures 1.2(b) and 1.3). If the identity operation *E* ($C_z(0)$) is added to these operations, the overlapping group of NH$_3$ and ND$_3$ molecules, denoted by C_{3v}, can be built (see Table 1.2). Generally, the *Oz* axis is placed along the highest-order rotational axis.

Symmetry operation	Herman–Mauguin	Schoenflies
Identity	1	C_1 or E
Rotation (2π/n)	n	C_n
Mirror	m	σ, C_s, S_1
Inversion	$\bar{1}$	i, C_i, S_2
Rotation-reflection	-	S_{2n}
Rotation-inversion	$\bar{n}$	-

Table 1.1. *Schoenflies and Hermann–Mauguin notations*

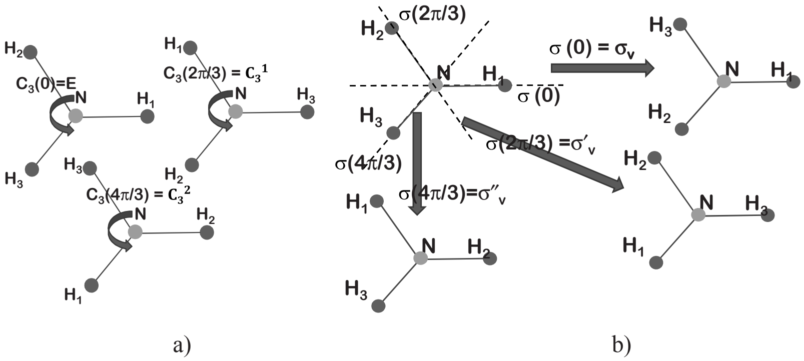

Figure 1.2. *Equivalent symmetry operations of plane rotation and reflection overlapping the equilibrium configurations of the NH_3 molecule. For a color version of this figure, see www.iste.co.uk/dahoo/infrared.zip*

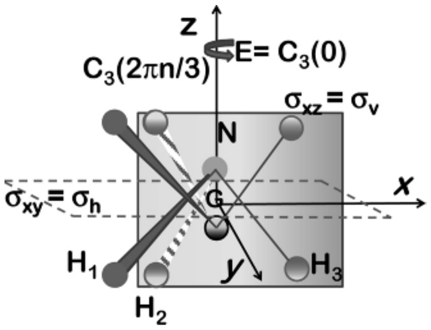

Figure 1.3. *Symmetry elements of the NH_3 molecule and its reversed equilibrium configuration. For a color version of this figure, see www.iste.co.uk/dahoo/infrared.zip*

$\mathbf{C_{3v}}$	**E**	$\mathbf{C_3^1}$	$\mathbf{C_3^2}$	$\boldsymbol{\sigma_v}$	$\boldsymbol{\sigma_v'}$	$\boldsymbol{\sigma_v''}$
E	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
$\mathbf{C_3^1}$	C_3^1	C_3^2	E	σ_v''	σ_v	σ_v'
$\mathbf{C_3^2}$	C_3^2	E	C_3^1	σ_v'	σ_v''	σ_v
$\boldsymbol{\sigma_v}$	σ_v	σ_v'	σ_v''	E	C_3^1	C_3^2
$\boldsymbol{\sigma_v'}$	σ_v'	σ_v''	σ_v	C_3^2	E	C_3^1
$\boldsymbol{\sigma_v''}$	σ_v''	σ_v	σ_v'	C_3^1	C_3^2	E

Table 1.2. *(Cayley) group C_{3v} multiplication table*

1.2.2. *Point symmetry group and laws of composition*

The set of symmetry operations of a molecule forms a point group (that leaves a point, invariant) in the mathematical sense [AMA 80a, BAR 88, BRA 72, BUN 98, CAM 88, COT 63, CRO 63, DEC 77, HAM 62, HER 45, LAN 75, MAR 83, MIX 72, TIN 03, WIG 59, WIL 55, WIL 80], and the symmetry elements can be regrouped into classes (symmetry operations that are equivalent: for NH_3, the two rotation operations $C_z(2\pi/3)$ and $C_z(4\pi/3)$, denoted by C_3^1 and C_3^2 (Figures 1.2(a) and 1.3), about the Oz axis passing through the nitrogen atom form a class, and the three planes of reflection symmetry $\sigma(0)$, $\sigma(2\pi/3)$ and $\sigma(4\pi/3)$ (Figures 1.2(b) and 1.3) form a second class.

The set of symmetry operations O_j constitutes a group if the following conditions are met:

– the product $O_k = O_iO_j$ of two operations of the set belongs to the set;

– the product is associative $O_i(O_jO_k) = (O_iO_j)O_k$;

– there is an operation E referred to as an identity such that $EO_i = O_iE = O_i$ (neutral element);

– each operation O_i can be put into correspondence with an operation O_i^{-1} known as the inverse of O_i, such that $O_iO_i^{-1} = O_i^{-1}O_i = E$.

If additionally $O_iO_j = O_jO_i$ (commutativity property), the group is referred to as “abelian”.

The number of elements of a finite group is known as the “order of the group”.

If two elements O and O' of a group G of order n are such that $O' = O_iOO_i^{-1}$ for any $O_i \in G$, the elements O and O' are conjugate. If O_i scans throughout group G, *n* elements O' are obtained. The set of distinct elements O' constitutes a class of conjugate elements (or equivalent class). The number *h* of elements is known as the order of the class. Any finite group can be decomposed into a certain number of classes of conjugate elements. For example, the group C_{3v} (Table 1.2) can be decomposed into three classes, the identity *E*, the two rotations $C_3(2\pi/3)$ or C_3^1 and $C_3(4\pi/3) = C_3(-2\pi/3)$ or $C_3^2 = C_3^{-1}$, and the three reflection operations σ_v, σ_v' and σ_v''. The order of this group is $n = 6$.

According to the Schoenflies notation (see Tables 1.1 and 1.3; Figure 1.4) used in molecular physics and in spectroscopy, the point groups are systematically denoted by C_n, S_{2n} or D_n (C for cyclic group, S for *spiegel*, which is the German word for mirror, D for dihedron) in relation, respectively, to the main symmetry axis of order *n* (a single one) that corresponds to the highest rotation order, the presence of a symmetry plane perpendicular to the main axis or of *n* axes of order 2 perpendicular to the main axis. For intermediate angles, the rotation axis $C_n(2p\pi/n)$ is denoted by C_n^p.

The indices *v*, *h* and *d* are added after the letter n in the presence of symmetry planes, *v* stands for vertical when the plane (σ_v) contains the main axis, *h* stands for horizontal when the plane (σ_h) is perpendicular to the main rotational axis, and *d* for the vertical planes containing the main bisector axis (σ_d) of axes of order 2 (C_{nv}, C_{nh}, D_{nh}, D_{nd}).

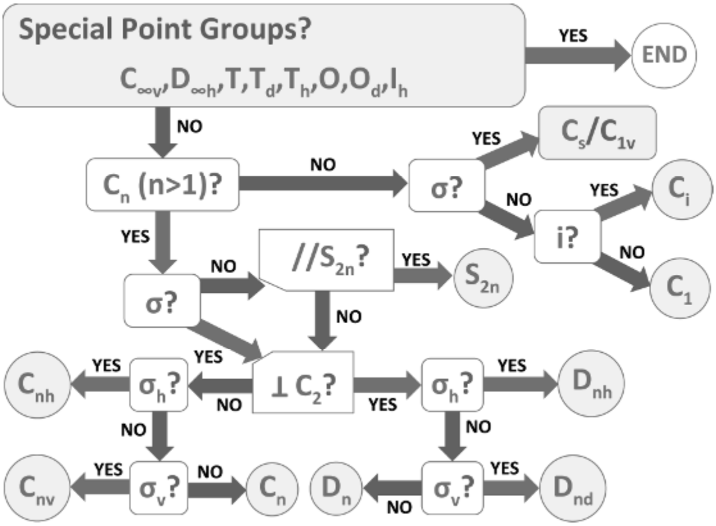

Figure 1.4. *Symmetry operations and flow diagram of point groups according to the Schoenflies notation. For a color version of this figure, see www.iste.co.uk/dahoo/infrared.zip*

A second convention, referred to as Hermann–Mauguin (see Tables 1.1 and 1.2), is preferred in crystallography: the cyclic groups are denoted by their order *n* (rotational symmetry axis of order *n*), a symmetry plane is denoted by *m* and the group is denoted by *n/m* ($C_{2v} \equiv 2m$); if the plane is perpendicular to the symmetry axis, then *n/m* ($C_{2h} \equiv 2/m$) is used; the presence of a symmetry center is indicated by a bar above the order of the group ($C_i = S_2 \equiv \bar{1}$, $S_4 \equiv \bar{4}$, $S_6 = C_i \otimes C_3 \equiv \bar{3}$). For example, $O_h \equiv m3m$, $D_{3h} \equiv \bar{3}m2$, etc. (see Tables 1.1 and 1.3).

Crystal system	Number of point groups	Herman–Mauguin	Schoenflies
Triclinic	2	$1, \bar{1}$	C_1, C_i
Monoclinic	3	2, m, 2/m	C_2, C_s, C_{2h}
Orthorhombic	3	222, 2mm, mmm	D_2, C_{2v}, D_{2h},
Rhombohedral	5	3, 32, 3m $\bar{3}$, $\bar{3}$m	C_3, D_3, C_{3v} S_6, D_{3d}
Hexagonal	7	6, 622, 6mm, 6/m, $\bar{6}$, $\bar{6}$2m, 6/mmm	C_6, D_6, C_{6v}, C_{6h} C_{3h}, D_{3h}, D_{6h}
Tetragonal	7	4, $\bar{4}$, 422, 4mm, $\bar{4}$2m, 4/m, 4/mmm	C_4, S_4, D_4, C_{4v}, D_{2d}, C_{4h}, D_{4h}
Cubic	5	23, m3, 432, $\bar{4}$3m, m3m	T, T_h, O T_d, O_h

Table 1.3. *The point groups of 32 classes of symmetry and the equivalence between Schoenflies and Hermann–Mauguin symbols*

In the condensed phase, only the rotation axes of orders 1, 2, 3, 4 and 6 can be used for a periodic paving of the space compatible with crystal lattices. Crystallography counts 32 symmetry groups (see Table 1.3) based on symmetry operations. The various symmetry elements are distributed into seven crystal systems: triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal and cubic.

In addition to these groups, there are special point groups. The continuous point groups have an infinite number of symmetry elements, the axial and spherical symmetry groups that are used to list the groups characterized by the presence of several axes of rotational symmetry of high order *n*. These axes are associated with regular polyhedrons, Plato solids, namely the tetrahedron with four triangular faces, the cube with six square faces, the octahedron with eight triangular faces, the dodecahedron with 12 regular pentagonal faces with three pentagonal faces joining in one point and the icosahedron with 20 equilateral triangular faces with five triangular faces joining in one point.

Chapter 1 of Volume 2 [DAH 19] dealt with the case of N_2O and CO_2, linear molecules characterized by the presence of a rotation axis of infinite order and planes containing the rotation axis in infinite number (group $C_{\infty v}$ for N_2O) possibly with a symmetry plane perpendicular to the rotation axis, as for CO_2, the system being symmetric with respect to its center ($D_{\infty h} = C_{\infty v} \otimes C_i$ for CO_2). Any rotation by a given angle φ about the C_∞ axis (or D_∞) constitutes a rotational group in two dimensions ($C_\infty(\varphi)$ and $C_\infty(-\varphi)$; degeneracy of modes ν_2).

The complete spherical symmetric group comprises rotations by an arbitrary angle about an axis passing through the center of the molecular system and symmetry planes passing also through the center. This group is denoted by K_h for an atom, for example. It contains the subgroup K (spatial) of spatial rotations (the three-dimensional rotation group or the symmetry group SO(3)) that serves to treat the rotational invariance of the Hamiltonian resulting from the space isotropy for a free molecule in the gas phase. Moreover, the existence of a symmetry center requires the use of $K_h = K \otimes C_i$ or symmetry group O(3). It is worth recalling that the irreducible representations of group SO(3) are described by Wigner D-matrices, which are matrix representations in the spherical harmonics basis $Y^J_m(\theta,\varphi)$.

A Plato solid is characterized by the presence of several rotation symmetry axes of high n-th order that belong to groups $T(T_d)$, $O(O_h)$ and $I(I_h)$ such as:

– The group of tetrahedron T (group of rotations that leave the tetrahedron invariant, $h = 12$, symmetry elements: $E, 4C_3, 3C_2$, and symmetry operations: $E, 4C_3, 4(C_3)^2, 3C_2$) and $T_d = T \otimes i$ (e.g. CCl_4, group of symmetry transformations of the tetrahedron, $h = 24$, symmetry elements: $E, 4C_3, 3C_2, i, 4S_6, 3\sigma_h$ and symmetry operations: $E, 4C_3, 4(C_3)^2, 3C_2, i, 4S_6, 4(S_6)^5, 3\sigma_h$).

– The group of the octahedron O (group of rotations that leave the cube invariant, $h = 24$, symmetry elements: $E, 3C_4, 4C_3, 6C_2$, and symmetry operations: $E, 6C_4, 8C_3, 3C_2, 6C'_2$), $O_h = O \otimes i$ (e.g. SF_6, group of symmetry transformations of the cube, $h = 48$, symmetry elements: $E, 3C_4, 4C_3, 6C_2, i, 3S_4, 4S_6, 3\sigma_h, 6\sigma_d$ and symmetry operations: $E, 8C_3, 6C_4, 3C_2, 6C'_2, i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d$).

– The group of the icosahedron I (group of rotations leaving the icosahedron invariant, Plato solid with 20 triangular faces or the dodecahedron with 12 pentagonal faces with rotation axes of order 5, $h = 60$, symmetry elements: $E, 6C_5, 10C_3, 15C_2$ and symmetry operations: $E, 12C_5, 12(C_5)^2, 20C_3, 15C_2$), I_h (e.g. C_{60}, group of transformations in the presence of symmetry planes that are parallel to the axes of order 5, $h = 120$, symmetry elements: E, $6C_5$, $10C_3$, $15C_2$, i, 15σ, $6S_{10}$, $10S_6$ and symmetry operations: E, $12C_5$, $12(C_5)^2$, $20C_3$, $15C_2$, i, 15σ, $12S_{10}$, $12(S_{10})^3$, $20S_6$).

1.3. Representations by square matrices (general linear group of order *n* on *R* or *C*: GLn(R) or GLn(C))

Symmetry operations can be represented by unitary square matrices in a basis built on the equilibrium configuration of the molecule. The set of matrices associated with each symmetry operation constitutes a group representation. The matrices have the same multiplication table as the group. In mathematical terms, there is an isomorphism between the overlapping group of the molecule (point symmetry group) and the matrix group, a set of invertible matrices that forms a group under matrix multiplication. The law of composition of operations is associated with the law of multiplication of matrices. It is easier to study the effects of symmetry operations on the properties of a molecule based on the set of matrices that represent these operations. The matrix representation makes it possible to replace the symmetry operations by the algebra of matrices.

1.3.1. *Irreducible representations*

A matrix can be associated with each element of group G. Given $\Gamma_{ij}(O_k)$ the matrix associated with the action of operator $\Gamma(O_k)$ identified in the representation Γ, O_k, an element of group G, then $\Gamma(O_k O_l) = \Gamma(O_k)\Gamma(O_l)$, which is written as $\Gamma_{\alpha\beta}(O_k O_l) = \sum_\gamma \Gamma_{\alpha\gamma}(O_k)\Gamma_{\gamma\beta}(O_l)$. The set of matrices $\Gamma_{ij}(O_k)$ forms an n-th order representation of the group G. The dimension of the representation is given by the dimension of matrices $\Gamma_{ij}(O_k)$. The linear space $L_n(R)$ (R for real) or $L_n(C)$ (C for complex) in which the matrices are defined is known as the space of representations, and a basis in this space is a basis of the representation. Among all the representations of a group, there is one trivial representation associated with a neutral element corresponding to the identity, and the dimension of this representation is equal to 1.

Given a representation of dimension n built on the basis $\{\Psi_1, \Psi_2, \Psi_3, ..., \Psi_n\}$, composed of the set of n x n square matrices associated each with an operation of the group, the three cases can be presented in the form of matrices:

– if all the matrices of the representation involve two blocks, with, respectively, p and n-p lines and columns aligned on the main diagonal such that

$$\begin{pmatrix} \overbrace{\begin{pmatrix} * & * \\ * & * \end{pmatrix}}^{p} & \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \\ \begin{vmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{vmatrix} & \underbrace{\begin{pmatrix} \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet \end{pmatrix}}_{n-p} \end{pmatrix} \qquad [1.1]$$

then the representation appears in reduced form. The first *p* components of the basis are transformed into themselves and constitute the basis of a representation of dimension *p*; the other *n-p* components of the basis are also transformed into themselves and constitute the basis of a representation with dimension *n-p*;

– a representation that does not appear in a reduced form is known as "reducible" if it is possible to find a new basis whose components are *n* linearly independent combinations of $\{\Psi_1, \Psi_2, \Psi_3, ..., \Psi_n\}$ by a similarity operation and such that the representation built on the new basis $\{\Psi'_1, \Psi'_2, \Psi'_3, ..., \Psi'_n\}$ appears in a reduced form. The two new representations with dimensions *p* and *n-p* may be themselves reducible;

– if through a similarity operation, the order of the set of matrices can be reduced, the representation is known as irreducible.

1.3.1.1. *Case of the NH_3 molecule*

For the NH_3 molecule, a representation can be built by determining the matrices associated with each symmetry operation applied to the linear vector space of basis $\overrightarrow{e_1}, \overrightarrow{e_2}, \overrightarrow{e_3}$ or $\overrightarrow{e_x}, \overrightarrow{e_y}, \overrightarrow{e_z}$ (see Figure 1.5). It is worth noting that while the rotations preserve the directions of the reference frame, this is not the case for symmetries which correspond to reflection planes.

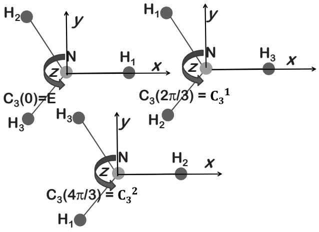

Figure 1.5. *The operations equivalent to rotational symmetry (cyclic group of order 3) overlapping the equilibrium configurations of the NH_3 molecule. For a color version of this figure, see www.iste.co.uk/dahoo/infrared.zip*

For an angle of rotation φ about the Oz axis, the rotation matrix is given by:

$$C_{\varphi}^{z} = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad [1.2]$$

The character of this matrix is $1 + 2\cos\varphi$.

These basis vectors form a certain representation Γ of the group C_{3v}. The matrices associated with each operation of the group are given by:

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},\ C_3^1 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix},\ C_3^2 = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix},\ \sigma_v' = \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix},\ \sigma_v'' = \begin{pmatrix} -'/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad [1.3]$$

All these matrices are diagonal by blocks, and can be decomposed into one 2 × 2 (two-dimensional) block and one 1 × 1 (one-dimensional) block; the spaces are disjoint so that the representation Γ has a reduced form. The disjoint spaces of basis vectors $\overrightarrow{e_1}, \overrightarrow{e_2}$ or $\overrightarrow{e_x}, \overrightarrow{e_y}$ and $\overrightarrow{e_3}$ or $\overrightarrow{e_z}$ constitute two different disjoint irreducible representations that can be denoted by Γ_1 and Γ_2, and whose matrices are, respectively, as follows:

– for the Γ_1 representation:

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},\ C_3^1 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix},\ C_3^2 = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$$

$$\sigma_v = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},\ \sigma_v' = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix},\ \sigma_v'' = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix} \qquad [1.4]$$

– for the Γ_2 representation:

$$E = 1,\ C_3^1 = 1,\ C_3^2 = 1,\ \sigma_v = 1,\ \sigma_v' = 1,\ \sigma_v'' = 1 \qquad [1.5]$$

Therefore, the Γ representation can be expressed as a direct sum of the Γ_1 and Γ_2 representations as follows:

$$\Gamma = \Gamma_1 \oplus \Gamma_2 \qquad [1.6]$$

1.3.2. *Equivalent representations*

It must first of all be noted that the elements of a matrix depend on the system of axes that is chosen. For another system of axes in the same vector space, the elements of the matrix are different and we say that another "equivalent" representation is considered. Two representations Γ' and Γ'' are equivalent if there is a non-singular (invertible, of non-zero determinant) matrix P such that:

$$\Gamma'' = P^{-1}\Gamma' P \qquad [1.7]$$

A representation is known as irreducible if it is not possible to find a matrix P that transforms all matrices $\Gamma'(O)$ or $\Gamma''(O)$ in the form of blocks or diagonal sub-matrices. A reducible representation is therefore composed of matrices that can all (for each symmetry operation) be diagonalized into blocks and expressed in the form of diagonal sub-matrices (see equation [1.1]).

The matrices of an irreducible representation depend on the chosen basis, but since the trace of matrices (sum of diagonal elements) is an invariant that does not depend on the basis, it is possible to characterize an irreducible representation by the trace, also known as the "character of the representation". It is well known that the eigenvalues of a square matrix associated with an operator O' are the same as those of the conjugate matrix of the equivalent operator $O'' = P^{-1}O'P$ and that in the basis of eigenvectors they are located on the main diagonal of the matrix. The trace being the sum of the diagonal elements, the character of a matrix associated with an operator is therefore an invariant (the same is true for the determinant which is given by the product of the eigenvalues).

An irreducible representation can therefore be represented by the character of the matrix associated with each of the symmetry operations for the considered irreducible representation. The table of characters of all the non-equivalent irreducible representations of the group can thus be built. The dimension of one representation is that of the square matrix (1, 2 (E), 3 (T or F), 4 (G), 5 (H)). The identity representation E is the one that is the easiest to find and for which all the elements of the matrix are on the main diagonal with their value equal to 1 (character = 1 if 1D), (character = 2 if 2D) or (character = 3 if 3D).

The number of irreducible representations of a group is equal to the number of classes of the group. Within the same class, the characters are identical, since the trace of a matrix is an invariant. For an abelian group, when the symmetry operations commute, each operation constitutes a class.

For the group C_{3v}, this number must be equal to 3 since there are three classes. For the above chosen representation (equation [1.6]), this means that the Γ

representation must be completed by the direct sum with another representation, so that it is written as:

$$\Gamma = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \quad [1.8]$$

$$\Gamma = A_1 \oplus A_2 \oplus E \quad [1.9]$$

where Γ_i, $i = 1, 2, 3$, are irreducible representations and are denoted by A_1, A_2 and E (Table 1.5) according to Mulliken notation, where A (symmetric with respect to axis C_n, $\chi(C_n) = 1$) or B (antisymmetric with respect to axis C_n, $\chi(C_n) = -1$) are one-dimensional representations, E is a two-dimensional representation (double degeneracy) for the molecules with rotation axes whose order is greater than 2 and T (in general in electronic spectroscopy) or F (in general in molecular spectroscopy) when there is triple degeneracy, a three-dimensional representation for molecules with more than one rotation axis of order 3. Moreover, the group C_{3v} is isomorphic to groups D_3 and S_3.

1.4. Table of characters and fundamental theorems

The theory of representations involves the substitution of the symmetry elements of a symmetry group by the square matrices representing each symmetry operation in a given basis.

These matrices can be used to build tables of characters that are the trace of the square matrices and to establish theorems that can be used for the construction of tools that facilitate the use of group theory in spectroscopy.

1.4.1. *Tables of characters, classes and irreducible representations*

The considerations developed in sections 1.3.1 and 1.3.2 on the application of the theory of representations of the point-group symmetry of a molecule can be summarized as follows:

– given $\{O_1, O_2, O_3, ..., O_p\}$, the operations associated with p symmetry elements of the group G of a molecule;

– given $\{\Psi_1, \Psi_2, \Psi_3, ..., \Psi_n\}$ (functions or states) the basis of a representation Γ that generates a vector space L;

– given $\Gamma(O_k)$ the operator associated with the operation O_k and which acts in the vector space L as a linear transformation operator;

– given $\Gamma_{ij}(O_k)$ the matrix associated with the action of operator $\Gamma(O_k)$ in the vector space L_n such that:

$$\Gamma(O_k)\Psi_j = \sum_{i=1}^{n} \Psi_i \Gamma_{ij}(O_k) \qquad [1.10]$$

The character of the representation for $\Gamma(O_k)$, the operator associated with the operation O_k, is given by the trace of matrix $\Gamma_{ij}(O_k)$ and its expression is given by:

$$\chi(O_k) = \sum_{i=1}^{n} \Gamma_{ii}(O_k) \qquad [1.11]$$

The simultaneous diagonalization of matrices $\Gamma_{ij}(O_k)$ $(k = 1,\ldots, p)$ makes it possible to split each matrix into blocks of sub-matrices and to determine the irreducible representations of the group G. The dimension of each irreducible representation is equal to the dimension (rank) of the sub-matrix.

The following relations can then be written for each O_k:

$$\Gamma(O_k) = \sum_{\mu=0}^{d} a_\mu \Gamma^\mu(O_k) \qquad [1.12]$$

$$\chi(O_k) = \sum_{\mu=0}^{d} a_\mu \chi^\mu(O_k) \qquad [1.13]$$

where $d + 1$ is the number of irreducible representations (the index 0 corresponds to a totally symmetric representation) and a_μ is the number of times the irreducible representation Γ^μ appears in the representation.

For non-abelian groups, certain operators $\Gamma(O_k)$ can be regrouped into classes, so that a group can be represented by a two-dimensional table with the classes of symmetry operations in the abscissa (for each column) and the irreducible representations in the ordinate (for each line) (see Table 1.4).

Under these conditions, there is a smaller number of symmetry operators and the p operations associated with p symmetry elements of the group G can be re-indexed depending on the number of classes equal to the number of irreducible representations, or $d + 1$, $\{E, O_1, O_2, O_3, \ldots. O_d\}$, where E is the identity operator.

Given that the number of classes and irreducible representations are identical, the table is a square one. The elements of the table are the characters of the matrices associated with symmetry operations.

$\mathbf{RI/_G}$	**E**	$\boldsymbol{h1O_1}$	$\boldsymbol{h2O_2}$	…	$\boldsymbol{hdO_d}$	**Scalar vector tensor**
$\boldsymbol{\Gamma_0}$	$\chi^{\Gamma 0}(E)$	$\chi^{\Gamma 0}(O_1)$	$\chi^{\Gamma 0}(O_2)$	…	$\chi^{\Gamma 0}(O_d)$	α
$\boldsymbol{\Gamma_1}$	$\chi^{\Gamma 1}(E)$	$\chi^{\Gamma 1}(O_1)$	$\chi^{\Gamma 1}(O_2)$	…	$\chi^{\Gamma 1}(O_d)$	β
$\boldsymbol{\Gamma_2}$	$\chi^{\Gamma 2}(E)$	$\chi^{\Gamma 2}(O_1)$	$\chi^{\Gamma 2}(O_2)$	…	$\chi^{\Gamma 2}(O_d)$	γ
…	…	…	…	…	…	…
$\boldsymbol{\Gamma_d}$	$\chi^{\Gamma d}(E)$	$\chi^{\Gamma d}(O_1)$	$\chi^{\Gamma d}(O_2)$	…	$\chi^{\Gamma d}(O_d)$	δ

Table 1.4. *Table of characters giving the classes (number of elements h_i) of the symmetry operations (O_i) and the irreducible representations (IR) of group G*

These tables constitute the table of characters associated with each type of group and to which a column is added. This column contains the coordinates *X, Y* or *Z* (components of the polar vector: T_X, T_Y or T_Z, *T* for translation) and the rotations, J_X, J_Y or J_Z (components of the axial vector: R_X, R_Y or R_Z, *R* for rotation) and the products that form a basis for the irreducible representation of the line. References [BAR 88, BRA 72, BUN 98, COT 63, CRO 63, DEC 77, HAM 62, HER 45, LAN 75, MAR 83, MIX 72, TIN 03, WIG 59, WIL 55, WIL 80] contain more detailed explanations on the application of group theory to atoms and molecules.

1.4.2. *Irreducible representation of group* C_{3v}

In the case of group C_{3v}, the table of characters is presented in Table 1.5(a) and (b); the irreducible representations are identified by Mulliken symbols (*A, E (2D)*, *T* or *F* (*3D*),…) in the first column. There are three classes comprising the one-dimensional identity operator *E*, the two-dimensional rotational operators C_3 and the three-dimensional plane symmetry operators σ_v. The order *h* of the group that corresponds to the total number of symmetry elements (operators) is equal to 6; this number is obtained by adding the dimensions of each class. Lines 1, 2 and 3 give the characters of the irreducible representations for each operator (Table 1.5(b)). The last three columns recall the symmetries in terms of irreducible representations of the operators involved in the transitions between the energy levels or those of normal coordinates.

$\mathbf{C_{3v}}$	**E**	$\mathbf{C_3^1}$	$\mathbf{C_3^2}$	$\boldsymbol{\sigma_v}$	$\boldsymbol{\sigma_v'}$	$\boldsymbol{\sigma_v''}$
$\mathbf{A_1}$	1	1	1	1	1	1
$\mathbf{A_2}$	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0

a)

C_{3v}	E	$2C_3^z$	$3\sigma_v$	Polar vector	Axial vector	Second-order tensor	Polarizability
A_1	1	1	1	z, T_Z		$x^2 + y^2$, z^2	$\alpha_{xx}+ \alpha_{yy}+ \alpha_{zz}$
A_2	1	1	-1		R_z		
E	2	-1	0	(x,y) , (T_X, T_Y)	(R_x, R_y)	$(x^2 - y^2$, xy) (xz,yz)	$(\alpha_{xx}- \alpha_{yy}, \alpha_{xy})$; $(\alpha_{yz}, \alpha_{zx})$

b)

Table 1.5. *Tables of characters of symmetry operations (O_k), classes of operations and irreducible representations (IR) of the group C_{3v}*

Similarly, the table of characters of the five types of symmetry operations for each nucleus of a molecule that is invariant under the symmetry operation can be built as given in Table 1.6.

O_k	E	C_φ^z	σ	S_φ^z	$i=S_\pi^z$	Vector
χ_{Ok}	3	1+2cosφ	1	-1+2cosφ	-3	Polar (T)
χ_{Ok}	3	1+2cosφ	-1	1-2cosφ	3	Axial (R)

Table 1.6. *Table of characters of the symmetry operations (O_k) for each nucleus that is invariant under operation O_k*

The tables of characters given in Tables 1.5 and 1.6 can be used to determine the number of vibrations of the NH_3 molecule as well as their types of symmetry for a given system of Cartesian axes.

A fundamental theorem in group theory applications to the study of molecules is the orthogonality and normalization theorem, which refers to the orthogonality of lines and columns of a table of characters. The proof of this theorem involves Schur's lemma and its corollaries.

1.4.3. *Schur's lemma*

Given $\Gamma^\alpha(O_k)$ and $\Gamma^\beta(O_k)$, two irreducible representations of one group G, of dimensions l_α and l_β; if there is a matrix P, of dimension l_α x l_β, such that for all the O_k, the following can be written:

$$P\Gamma^\alpha(O_k) = \Gamma^\beta(O_k)P \qquad [1.14]$$

Then:

– if $l_\alpha \neq l_\beta$, P is a null matrix of dimension l_α x l_β;

– if $l_\alpha = l_\beta$, P is a square non-singular matrix (invertible, non-null determinant) and Γ^α and Γ^β are two equivalent representations.

COROLLARY 1 TO SCHUR'S LEMMA.– A matrix that commutes with each matrix of an irreducible representation of a group G, is a multiple of the identity matrix.

COROLLARY 2 TO SCHUR'S LEMMA.– An irreducible representation of an abelian group G is necessarily one-dimensional.

1.4.4. *Orthogonality and normalization theorem*

Given G a finite group of order h, Γ^α an irreducible representation of G of dimension d_α, $\Gamma^\alpha_{ij}(O_k)$ the matrix of the operator $\Gamma(O_k)$ associated with the element O_k in the representation Γ^α (considered as unitary), the following orthogonality relation is verified by the matrices, according to the orthogonality theorem:

$$\sum_{O_k \in G} \Gamma^\alpha_{ij}(O_k) \left(\Gamma^\beta_{kl}(O_k)\right)^* = \frac{h}{\sqrt{d_\alpha d_\beta}} \delta_{\alpha\beta}\delta_{jk}\delta_{il} = \frac{h}{d_\alpha}\delta_{\alpha\beta}\delta_{jk}\delta_{il} \qquad [1.15]$$

where h is the order of group G and d_α is the dimension of the Γ^α representation. It is worth noting that indices i and j take their values in the set $\{1,2,3, ..., d_\alpha\}$, and indices k and l take their values in the set $\{1,2,3, ..., d_\beta\}$, and that the dimensions of the corresponding matrices are d_α and d_β, respectively. The equivalent representations are considered as being the same representations. This theorem is not commonly used in practice because the tables of the symmetry groups are given in terms of characters. A form based on the characters is used instead (see equation [1.16]).

1.4.5. *Orthogonality of lines*

The characters of the non-equivalent unitary irreducible representations verify the orthogonality relations. The characters of the matrices verify in this case the orthogonality relation such that:

$$\sum_{O_k \in G} \chi^\alpha(O_k) \left(\chi^\beta(O_k)\right)^* = h\delta_{\alpha\beta} \qquad [1.16]$$

which corresponds to the orthogonality of lines in the table of characters. Referring to Table 1.5(a) of group C_{3v}, for example, it can be verified that for lines 1 and 2 corresponding to IR, A_1 and A_2 ($\alpha = A_1$ and $\beta = A_2$), the relation gives: $1^2 + 2 \times 1^2 + 3 \times 1 \times (-1) = 0$; similarly, for lines 1 and 3 corresponding to IR, A_1 and E ($\alpha = A_1$ and $\beta = E$), the relation gives: $1 \times 2 + 2 \times 1 \times (-1) + 3 \times 1 \times 0 = 0$; finally, for lines 2 and 3 corresponding to IR, A_2 and E ($\alpha = A_2$ and $\beta = E$), the relation gives: $1 \times 2 + 2 \times 1 \times (-1) + 3 \times (-1) \times 0 = 0$.

For the same representation, the sum of squares of characters is equal to the order of the group such that:

$$\sum_{O_k \in G} \chi^{\alpha}(O_k) \left(\chi^{\alpha}(O_k)\right)^* = h \qquad [1.17]$$

Referring to Table 1.5(a) of group C_{3v}, for example, it can be verified that for line 1 corresponding to IR, A_1, the relation gives: $1^2 + 2 \times 1^2 + 3 \times 1^2 = 6$; similarly, for line 2 corresponding to IR, A_2, the relation gives: $1^2 + 2 \times 1^2 + 3 \times 1^2 = 6$; finally, for line 3 corresponding to IR, E, the relation gives: $2^2 + 2 \times 1^2 + 3 \times 0 = 6$.

Two equivalent representations have the same system of characters. The operations O_i belonging to the same class and to the same irreducible representation have therefore the same character as a result of the equivalence of irreducible representations (similarity transformation) and the invariance of the trace of a matrix. The presentation of the table of characters of a group G can thus be simplified, grouping the symmetry operations O_i by classes i (new indices where k is replaced by i) of number of elements h_i (see Table 1.5(b)), so that equation [1.17] can be reformulated as follows:

$$\sum_{O_i \in G} h_i \chi^{\alpha}(O_i) \left(\chi^{\beta}(O_i)\right)^* = h\delta_{\alpha\beta} \qquad [1.18]$$

where h_i is the number of elements in the class to which the symmetry operation O_i belongs.

Similarly, the relation for the calculation of the order of a group on a line of the table of characters is given by:

$$\sum_{O_i \in G} h_i \chi^{\alpha}(O_i) \left(\chi^{\alpha}(O_i)\right)^* = h \qquad [1.19]$$

These relations can be readily verified with Table 1.5(b).

1.4.6. *Orthogonality of columns*

Using Schur's lemma, it is possible to prove that:

$$\Sigma_\alpha \chi^\alpha(O_i)\left(\chi^\alpha(O_j)\right)^* = \frac{h}{h_i}\delta_{ij} \qquad [1.20]$$

which corresponds to the orthogonality of columns in the table of characters.

Referring to Table 1.5(b) of group C_{3v}, for example, it can be verified that for columns 1 and 2 ($i = 1$ and $j = 2$) corresponding to identity operations E and rotations about the axis Oz, C_3^z, it can be written that: $1 \times 1 + 1 \times 1 + 2 \times (-1) = 0$; similarly, for columns 1 and 3 ($i = 1$ and $j = 3$) corresponding to identity operations E and plane symmetry σ_v, it can be written that: $1 \times 1 + 1 \times (-1) + 2 \times 0 = 0$; finally, for columns 2 and 3 ($i = 2$ and $j = 3$) corresponding to rotational operations about the axis Oz, C_3^z and plane symmetry σ_v, it can be written that: $1 \times 1 + 1 \times (-1) + (-1) \times 0 = 0$.

If O_i is assumed to be the identity operation E, then $h_i = 1$ (one class) and the sum of equation [1.20] leads to the order of group G

$$\Sigma_\alpha \chi^\alpha(E)\left(\chi^\alpha(E)\right)^* = h \qquad [1.21]$$

It can be readily verified from Table 1.5(b) of group C_{3v} for which $h = 6$, that indeed: $1 \times 1 + 1 \times 1 + 2 \times 2 = 6$.

This result can be obtained for each operation O_k of the group from equation [1.20], which leads to the calculation of the order of group G. Considering column 2 of Table 1.5(b), for rotations about the Oz axis, or the operation C_3^z it can be written that: $1^2 + 1^2 + (-1)^2 = h/2$; this leads to $h = 3 \times 2 = 6$. Similarly, for column 3, which corresponds to the plane symmetry operation σ_v, it can be written that: $1^2 + (-1)^2 + 0 = h/3$; this leads to $h = 2 \times 3 = 6$.

1.4.7. *Decomposition of a reducible representation on an irreducible basis*

Given a reducible representation Γ of a group G with h elements (order of the group) and K classes, each having a number of elements h_i. Given (l_α, l_β, …) the dimensions of its irreducible representations(Γ^α, Γ^β…).

The reducible representation Γ of group G is the direct sum of irreducible representations of the group, which is written as follows:

$$\Gamma = a_1\Gamma^1 \oplus a_2\Gamma^2 \oplus \ldots\ldots a_d\Gamma^d = \Sigma_{\oplus\alpha}\, a_\alpha\Gamma^\alpha \qquad [1.22]$$

where:

$$a_\alpha = \frac{1}{h}\Sigma_{O_i \in G}\, h_i \chi(O_i)\big(\chi^\alpha(O_i)\big)^* \qquad [1.23]$$

and

$$\chi(O_k) = \Sigma_\alpha\, a_\alpha \chi^\alpha(O_k) \qquad [1.24]$$

This relation proves to be very useful for the decomposition of a reducible representation into irreducible representations and for finding the number of vibrations belonging to a given irreducible representation from symmetries of the various types of vibrations of a molecule, stretching, bending, torsion, etc.

For the finite groups, the number of irreducible representations is equal to the number of classes of the group. The following relation (sum of squares along a column) is also verified:

$$\Sigma_\alpha\, l_\alpha^2 = h \qquad [1.25]$$

Moreover, the column of operator E (identity) makes it possible to directly determine the dimension of irreducible representations.

1.4.8. *Projection operators for irreducible representations*

Projection operators are used to build wave functions that are the bases of an irreducible representation of the symmetry group of a molecule.

Given $\left\{\Psi_i^\alpha\right\}$, the basis of an irreducible representation Γ^α of dimension l_α of the group G of order h, and given $\chi^\alpha(O_k)$ the characters of each operation O_k of the group. Applying the symmetry operation O_k to Ψ_i^α, a linear combination of $\{\Psi_i^\alpha\}$ (restriction of relation 1.10 to the irreducible representation Γ^α) is obtained for the irreducible representation $\Gamma\alpha$ of the group. This combination is transformed depending on the symmetry properties of this representation. It can be shown that these combinations can be determined by applying the projection operator given by:

$$P_{ij}^{\alpha} = \frac{l_{\alpha}}{h} \sum_{O_k \in G} \left(\Gamma_{ij}^{\alpha}(O_k) \right)^{*} O_k \qquad [1.26]$$

This method requires knowledge of matrices Γ_{ij}^{α} and the definition of the operation $O_k \Psi_i^{\alpha}$.

Since the tables of characters do not give the matrices Γ_{ij}^{α}, but only the characters of these matrices, a simplified projection operator is used, which is given depending on the characters such as:

$$P^{\alpha} = \frac{l_{\alpha}}{h} \sum_{O_k \in G} \left(\chi^{\alpha}(O_k) \right) O_k \qquad [1.27]$$

The linear combinations are not necessarily orthogonal, and this property must be built case by case.

1.4.9. *Characters of irreducible representations of the direct product of two groups*

Using this relation, it can be shown that:

– given $\{\Psi_i^{\alpha}\}$, the basis of an irreducible representation Γ_1^{α} of the group G_1 of characters $\chi_1^{\alpha}(O_k^1)$ for each operation O_k^1 of the group G_1;

– given $\{\phi_j^{\beta}\}$, the basis of an irreducible representation Γ_2^{β} of the group G_2 of characters $\chi_2^{\beta}(O_k^2)$ for each operation O_k^2 of the group G_2;

– given $\{\Psi_i^{\alpha}\phi_j^{\beta}\}$, the basis of an irreducible representation $\Gamma^{\alpha\otimes\beta}$ of the group formed by the direct product of G_1 and G_2, $G_1 \otimes G_2$, the characters of the operators that are the products of operators of G_1 by those of G_2 are given by $\{O_i^1 O_j^2\}$:

$$\chi^{\alpha\otimes\beta}\left(O_i^1 O_j^2\right) = \chi_1^{\alpha}(O_i^1)\chi_2^{\beta}(O_j^2) \qquad [1.28]$$

For example, the direct product of two representations $E \times E$ leads to the sum of three representations: $1 + A_2 + E$.

The rules and formulas given in this section can be used for building the vibration or rotation symmetry coordinates, and thus characterize each state of vibration and rotation by their type of symmetry. The tables of characters are useful for establishing the selection rules in absorption or emission spectroscopy and in Raman spectroscopy and for determining the shape of the observable spectra.

1.5. Overall rotation group symmetry of a molecule

The point-group symmetry of a molecule is defined by the geometry of the molecule and does not involve the overall rotation of this molecule. The symmetry operations of the point group do not commute with the full molecular Hamiltonian, but only with the vibration and electronic Hamiltonian. A more detailed presentation of the considerations given below can be found in the following (non-exhaustive) references, such as: [BUN 98, EDM 74, GRI 64, HER 45, LAN 75, MES 64, SAK 94, WAT 66].

The symmetry group of the Hamiltonian of the rigid rotator is the infinite group of rotations K (J integer; or SO(3)) about an axis passing through the center of mass. The group of spherical symmetry contains the rotations by an arbitrary angle about any axis passing through the center and the reflections in any plane passing through the same point. It is denoted by K_h and contains the group K (group of rotations in the three-dimensional space SO(3)) as subgroup with $K_h = K \otimes C_i$ (group O (3)). All the axes being equivalent in group K, the classes are the rotations by an angle of given absolute value about an arbitrary axis. The group K comprises an infinite number of finite rotations achieved by continuous variation of infinitesimal angles.

The natural approach for the study of overall rotations of a molecule relies on the identification of the rotation axis defined by a unit vector $\hat{n}$ and the angle of rotation ϕ. The two angles (polar angle, θ and azimuthal angle, φ), which in the system of spherical coordinates can be used to identify the unit vector and the angle of rotation, ϕ, show that three parameters are needed for the definition of a rotation in the three-dimensional space. The same rotation can also be defined by means of three Cartesian components of vector $\hat{n}\phi$. Applying this method to study the properties of rotations is not convenient because it is not possible to add vectors of type $\hat{n}\phi$ when characterizing successive rotations.

It is more convenient to use orthogonal 3 × 3 matrices that form the group SO(3) under the operation of matrix multiplication (S for special with the determinant equal to 1, O for orthogonal and 3 for dimension 3). Hence, it is customary to define the rotation of the reference system attached to the molecule in terms of three Euler angles that can be used for positioning the mobile reference frame with respect to the fixed reference frame by means of three rotations about three axes. These rotations and the axes were defined in section 2.7.3 of Volume 2 [DAH 19] as the rotation by an angle $\theta\,(0 \leq \theta \leq 2\pi)$ about the Z axis of the fixed reference frame, the rotation by an angle φ $(0 \leq \varphi \leq \pi)$ about the line of nodes (new position of the OY axis of the initial fixed reference frame after the first rotation) and the rotation by an angle $\chi\,(0 \leq \chi \leq 2\pi)$ about the axis $z = z'$ of the mobile reference frame (final position of the OZ axis of the initial fixed reference frame).

Given $R(\theta, \varphi, \chi)$ – the operator corresponding to the three rotations defined by: $R(\theta,\varphi,\chi) = exp(\frac{-i\chi}{\hbar}J_{z'})exp(\frac{-i\varphi}{\hbar}J_{y'})exp(\frac{-i\theta}{\hbar}J_Z)$, it can be proved that the rotation operation can be defined with respect to the fixed axes such that: $R(\theta,\varphi,\chi) = exp(\frac{i\chi}{\hbar}J_Z)exp(\frac{i\varphi}{\hbar}J_Y)exp(\frac{i\theta}{\hbar}J_Z)$, using the transformations: $R_{y'}(\varphi) = R_Z(\theta)\,R_Y(\varphi)\,R_Z^{-1}(\theta)$ and $R_{z'}(\chi) = R_{y'}(\varphi)\,R_Z(\chi)\,R_{y'}^{-1}(\varphi)$, where the three matrices refer to rotations about fixed axes. It is in fact appropriate to consider the rotations with respect to fixed axes rather than to mobile axes, since spin variables can be dealt with by rotation operators following the same properties and for which the notion of mobile axes is not relevant. In the space of spins, R is a 2 × 2 matrix defined in a two-dimensional space and the matrix is associated with an operator $D(R)$ acting on the spin variables $|\alpha\rangle$ and $|\beta\rangle$ or $\left| +1/2 \right\rangle$ and $|1/2\rangle$.

The angular momenta operators $\hat{\mathcal{J}}_X$, $\hat{\mathcal{J}}_Y$ and $\hat{\mathcal{J}}_Z$ of a molecule are proportional to the operators associated with rotations by an infinitesimal angle about an axis passing through a center. Consequently, the common eigenfunctions $|JM\rangle$ of the operators $\hat{\mathcal{J}}^2$ and $\hat{\mathcal{J}}_Z$ ($\left[H, \hat{\mathcal{J}}^2\right] = 0, \left[H, \hat{\mathcal{J}}_Z\right] = 0$) identified by the quantum numbers J and M constitute a basis for the irreducible representation of the rotation group. Each irreducible representation contains a continuous set of matrices, but the dimension of the representation is finite, meaning that the rank of the matrix remains finite. The number of various irreducible representations is infinite, but countable. At a fixed j, the $2j + 1$ eigenfunctions common to operators J^2 and J_Z, form the basis of the irreducible representation of angular momenta operators. Finite rotations are achieved by iteration of infinitesimal rotations $D\left(\hat{Z}, d\phi\right) = 1 - i\left(\frac{J_Z}{\hbar}\right)d\phi$ so that:

$$D_Z(\phi) = \lim_{n \to \infty}\left(1 - i\left(\frac{J_Z}{\hbar}\right)\left(\frac{\phi}{n}\right)\right)^n = exp\left(\frac{-iJ_Z\phi}{\hbar}\right)$$

For a fixed j, the $2j + 1$ eigenfunctions $|JM\rangle$ transform into themselves under the action of operator $D(\theta, \varphi, \chi)$.

Designating by $D(\theta, \varphi, \chi)$ the operator corresponding to three rotations and defined by: $D(\theta,\varphi,\chi) = exp(\frac{-i\chi}{\hbar} J_Z) exp(\frac{-i\varphi}{\hbar} J_Y) exp(\frac{-i\theta}{\hbar} J_Z)$, the following expression can be written:

$$D(\theta,\varphi,\chi)|Jm\rangle = \sum_{m'=-J}^{m'=+J} |Jm'\rangle D^J_{m'm}(\theta,\varphi,\chi) \qquad [1.29]$$

where

$$D^J_{m'm}(\theta,\varphi,\chi) = exp\left(\frac{-im'\chi}{\hbar}\right) \left\langle Jm' \right| exp\left(\frac{-i\varphi}{\hbar} J_{y'}\right) |Jm\rangle \, exp\left(\frac{-im\theta}{\hbar}\right)$$

and

$$D^J_{m'm}(0,\varphi,0) = d^J_{m'm}(\theta,\varphi,\chi) = \left\langle Jm' \right| exp\left(\frac{-i\varphi}{\hbar} J_{y'}\right) |Jm\rangle$$

The irreducible representations of group K are $D^{(0)}$ (totally symmetric representation), $D^{(1)}$, $D^{(2)}$, $...D^{(j)}$, …, where j is an integer (for rotations). The dimension of each matrix of the representation j is $(2j + 1)$. The lines and columns can be identified from the indices m' and m that take values in the set $\{-j, -j + 1, ..., j\}$. The trace of a matrix $D^J_{m'm}(\theta,\varphi,\chi)$ for j constant can be evaluated using the equivalence between the operator $R(\theta,\varphi,\chi)$, product of three rotation operators and the operator $R(\hat{n},\varphi)$ (using the fact that the characters of the irreducible elements of a class are identical) to determine the character $\chi^J(\varphi) = \frac{sin(j + 1/2)\varphi}{sin(1/2)\varphi}$. For $j = 1$, for example: $\chi^J(\varphi) = 1 + 2cos\varphi$. When j is a half-integer, the character $\chi^J(\varphi)$ can take two distinct values for φ and $\varphi + \pi$, and it can be written that: $\chi^J(\varphi + \pi) = -(\varphi)$ since $\chi^J(\varphi)$ is a periodic function in φ of period 4π, as $\chi^J(\varphi) = sinj\varphi cot\ 1/2\,\varphi + cos\varphi$. Given that the two rotations φ and $\varphi + \pi$ represent the same rotation in the three-dimensional space, there is a 2:1 correspondence between the characters or the matrices, when j is a half-integer and the rotations in the three-dimensional space. A 1:1 correspondence can be established by applying Bethe method [BET 29], which involves the introduction of a new operation Q that commutes with the rotation operators ($QR = RQ$) such that $Q^2 = E$. The new rotation group comprises twice more elements as the initial group and constitutes the double rotation group.

It is worth noting that the analytical expression of the elements of $D^J_{m'm}(\theta,\varphi,\chi)$ (see section 2.7.5, Volume 2 [DAH 19]); (θ,φ,χ) depends on how the rotations are defined. Indeed, the molecule and therefore the reference frame attached to it can be rotated: this point of view is known as "active", or the fixed axes attached to the laboratory system can be given an inverse rotation motion: this point of view is known as "passive". In both cases, the effect of rotations on the rotational Hamiltonian of the molecule is identical. In the first case, the spatial positions $\vec{R}(\vec{r})$ become $\vec{R}(\vec{r}) + \vec{A}$, and in the second case the fixed axes shift by $-\vec{A}$, which leads to the same spatial coordinates of the transformed Hamiltonian. It should be noted that in Volume 2, we use (φ, θ, χ) instead of (θ, φ, χ); it suffices to invert θ and φ to find the correct expressions of the matrices.

For irreducible representations $j = 1/2$ (spin variables) and $j = 1$, the matrix elements of $d^{(j)}_{m'm}(\theta,\varphi,\chi)$ are given by:

$\mathbf{d}^{(\frac{1}{2})}_{\mathbf{m'm}}$		
m'/m	**-1/2**	**1/2**
-1/2	cos(φ/2)	-sin(φ/2)
1/2	sin(φ/2)	cos(φ/2)

a)

$\mathbf{d}^{(1)}_{\mathbf{m'm}}$			
m'/m	**−1**	**0**	**1**
-1	(1/2)(1+ cos φ)	$-(1/\sqrt{2})$ sin φ	(1/2)(1- cos φ)
0	$(1/\sqrt{2})$ sin φ	cos φ	$-(1/\sqrt{2})$ sin φ
1	(1/2)(1- cos φ)	$(1/\sqrt{2})$ sin φ	(1/2)(1+ cos φ)

b)

Table 1.7. *Elements of the rotation matrix $d^{(j)}_{m'm}$ for irreducible representations:* (*a*) *for j = 1/2 and* (*b*) *for j = 1*

1.6. Full symmetry group of the Hamiltonian of a molecule

The theory of permutation-inversion (PI) groups is a concept that uses molecular symmetry making it possible to describe both rigid and non-rigid molecular systems. This concept differs from that of Schönflies point-group symmetry based on equilibrium configuration geometry of nucleï, which is limited to rigid species. Non-rigid systems easily modify their conformation, and therefore their symmetry properties, by high-amplitude motions [BUN 98, HOU 62, HOU 63, LON 63]. The effects of high-amplitude motions can be observed in the form of degeneracy lifting by tunneling effect in high resolution spectra. The theory of PI groups can be used to adequately describe the high-amplitude motions that modify the molecular symmetry.

1.6.1. *Permutation operations*

Given a set denoted by $\{abc \bullet\bullet\bullet yz\}$. Given the symbol $(abc \bullet\bullet\bullet yz)$ that represents a permutation such that *a* is replaced by *b*, *b* by *c*, *c* by *d*, …, *y* by *z* and *z* by *a*. For example, for the set $\{123\}$, a possible permutation is to swap 1 and 2, while 3 maintains its place. In mathematics, this operation is represented by:

$$\begin{pmatrix}123\\213\end{pmatrix} = (12)$$

where the abbreviated notation *(12)* is used for the permutation operation, which corresponds to a transposition.

A further example is the cyclic permutation of three numbers such that:

$$\begin{pmatrix}123\\231\end{pmatrix} = (231) = (123)$$

Such a permutation is known as a cycle. A group can be built from all the permutations of 3 numbers by adding the identity element E (no change).

For example, if the permutation operators *(12)* and *(123)* are applied to the ordered set *321*, the following results are obtained:

$$(12)321 = 312$$

$$(123)321 = 132$$

where in the first case, 1 is replaced by 2 and 2 by 1 and in the second case, 1 is replaced by 2, 2 is replaced by 3 and 3 is replaced by 1.

A permutation involving only two elements, for example *(12)*, is known as a transposition. Based on this definition, the following relations can be written:

$$(12) = (21),\ (23) = (32),\ (13) = (31),$$

and

$$(123) = (312) = (231),\ (132) = (321) = (213).$$

1.6.2. *Permutation group* S_n

The set of all the possible permutation operations of *n* objects meets the axioms of the group. This is known as the *n*-th degree permutation group and is denoted by S_n. There are *n!* elements in S_n. It is an *n!*-th order group. This group is composed of transpositions with two elements and cyclic subgroups. The *k*-cycles (of dimension *k*) are thus counted by searching the *k* elements that form a cycle after permutation.

A further important aspect to be considered is that any permutation can be expressed as a product of transpositions. A given permutation is known as even or odd when it has an even or odd number of transpositions in its product of transposition. For example, *(abcdef)(gh)* = *(ab)(bc)(cd)(de)(ef)(gh)* is an even permutation. For example:

S_2 = *{E, (12)}* forms an abelian group;

S_3 = {*E*, *(12), (23), (31), (123), (132)*}.

The transpositions are *(12)*, *(23)* and *(31)*. The cycles are *(123)* and *(132)*. A cycle is built from an even number of transpositions. The set of operations *{E, (123), (132)}* forms a subgroup of S_n. For *n* > *2*, the groups S_n are not commutative.

The multiplication or Cayley table of the symmetric group S_3 is given in Table 1.8. An element of line *i* and of column *j* is the product of the operator of the first column *j* and the operator of line *i*.

S₃	**E**	**(12)**	**(23)**	**(13)**	**(123)**	**(132)**
E	E	(12)	(23)	(13)	(123)	(132)
(12)	(12)	*E*	(123)	(132)	(23)	(13)
(23)	(23)	(132)	*E*	(123)	(13)	(12)
(13)	(13)	(123)	(132)	E	(12)	(23)
(123)	(123)	(13)	(12)	(23)	(132)	*E*
(132)	(132)	(23)	(13)	(12)	*E*	(123)

Table 1.8. *Multiplication (Cayley) table of the symmetric group* S_3

Table 1.9(a) and (b) gives the table of characters of the symmetric groups S_2 and S_3 and the irreducible representations of the groups and the classes.

S_2	E	(12)
	1	1
A	1	1
B	1	1

a)

S_3	E	(12)	(123)
	1	3	2
A_1	1	1	1
A_2	1	-1	1
E	2	0	-1

b)

Table 1.9. *Table of characters of symmetric groups: a) for S_2 and b) for S_3*

Two important results are that symmetric groups are finite (of finite dimension) and that each finite group (particularly finite point group) is isomorphic to a subgroup of a given symmetric group (Cayley or Jordan theorem) [HAM 62].

The symmetry group of the Hamiltonian operator of a system of particles should not be confused with the symmetric group. The symmetry group is composed of operators that commute all with the Hamiltonian operator. The total wave function of the Hamiltonian of a molecular system must be invariant in a symmetry operation that leads to a simultaneous inversion of the coordinates of all the particles (electrons and nucleons of the nuclei) and that belongs to the symmetry group C_i isomorphic to the symmetry group S_2. The irreducible representations of group S_2 are one-dimensional and denoted by $\Gamma(2)$ and $\Gamma(1^2)$ for the symmetric and antisymmetric representations, respectively. The wave functions belong to one or the other of these representations and are designated as positive or negative states.

Generally speaking, each symmetric group S_n (of order $n!$) has two one-dimensional irreducible representations, denoted by $\Gamma(n)$ and $\Gamma(1^n)$, for the symmetric and antisymmetric representations, respectively. $\Gamma(n)$ is homomorphic to S_n for $n > 2$ and $\Gamma(1^n)$ is homomorphic to S_n for $n > 3$. The other irreducible representations have dimensions above 1 and are isomorphic to S_n. The latter are known as faithful representations.

Furthermore, given that the identical elementary particles are not discernible, this involves that the Hamiltonian of a system of n indiscernible particles (electrons and nucleons of nuclei) commutes with each operator of the symmetric group S_n so that S_n is a symmetry group of the Hamiltonian. According to Pauli's principle, electrons, nucleons and all the half spin elementary particles belong to the fully antisymmetric irreducible representation $\Gamma(1^n)$. Indeed, if the irreducible representation was fully symmetric $\Gamma(n)$, Bose–Einstein condensate could be possible, which would lead to the formation of aggregates generating a single atom structure and the absence of molecules with a structure.

It is worth noting that $\Gamma(n)$ and $\Gamma(1^n)$ are the only stable irreducible representations to which electrons or nucleons can belong.

1.6.3. *Complete nuclear permutation group (G^{CNP}) of a molecule*

The CNP group of a molecule is a group that contains all the possible permutations of identical nuclei in the molecule. If the chemical formula of the molecule is $A_tB_mC_n$ • • •, the CNP group is the direct product group, $G^{CNP} = S_t \otimes S_m \otimes S_n \otimes \ldots$, and the order of the group is *t!* x *m!* x *n!* x, etc.

A permutation operation (*123*) on the three H nuclei of the CH_3D molecule:

$$
\begin{aligned}
&(123)\,[X_1,Y_1,Z_1,X_2,Y_2,Z_2,X_3,Y_3,Z_3]\\
&= \left[\tilde{X}_1,\tilde{Y}_1,\tilde{Z}_1,\tilde{X}_2,\tilde{Y}_2,\tilde{Z}_2,\tilde{X}_3,\tilde{Y}_3,\tilde{Z}_3\right]\\
&= [X_2,Y_2,Z_2,X_3,Y_3,Z_3,X_1,Y_1,Z_1]
\end{aligned}
$$

where $(X_i,\ Y_i,\ Z_i)$ are the initial fixed coordinates of H_i nucleus in the space and $\left(\tilde{X}_i,\tilde{Y}_i,\tilde{Z}_i\right)$ are its coordinates after permutation. For example:

$G^{CNP} = S_3$ for CH_3D and $G^{CNP} = S_2 \otimes S_2$ for H_2O_2

1.6.4. *Inversion group ε and inversion operations* E* *and permutation-inversion operations* P*

The inversion operation E^* is defined as the inversion operation of the spatial coordinates of all the particles (nuclei and electrons) of a molecule through its center of mass (Figure 1.6.). Using the system of axes (X, Y, Z) fixed in space with the origin in the center of mass, the following can be written: the inversion group $\varepsilon = \{E, E^*\}$.

A permutation-inversion (PI) operation is denoted by P^*. When the inversion operation E^* commutes with an arbitrary permutation operation P, the (PI) operation can be written in the form $P^* = PE^* = E^*P$.

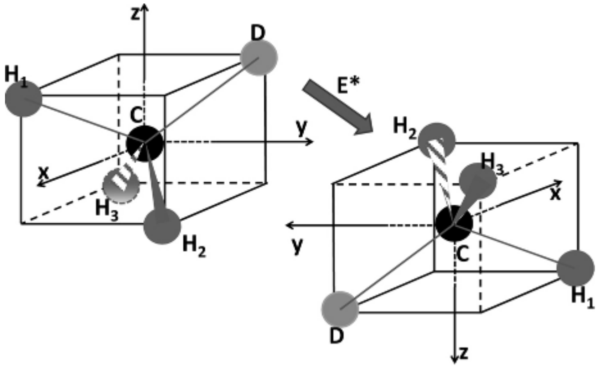

Figure 1.6. *The effect of operation E* on a CH_3D molecule. For a color version of this figure, see www.iste.co.uk/dahoo/infrared.zip*

1.6.5. *Permutation-inversion group G^{CNPI}*

The CNPI (complete nuclear permutation-inversion) group G^{CNPI} is built by the direct tensor product of the G^{CNP} group and of the inversion group ε: $G^{CNPI} = G^{CNP} \otimes \varepsilon$. The CNPI group of a molecule is a group that contains all the possible permutations of identical nuclei in the molecule with and without inversion. The order of the CNPI group is twice that of the CNP group. For example:

$$C_2H_4 \quad G^{CNPI} = G^{CNP} \otimes \varepsilon = S_2 \otimes S_4 \otimes \varepsilon$$

$$H_2O \quad G^{CNPI} = G^{CNP} \otimes \varepsilon = S_2 \otimes \varepsilon = \{E, (12), E^*, (12)^*\}$$

The theory of PI groups makes it possible to determine the spectroscopic selection rules and to calculate the statistical weights of nuclear spin as well as the number and the degeneracy lifting of sub-levels due to tunneling effect. It can therefore be used to predict and analyze the rotation spectra. The complete permutation-inversion (PI) group of a molecule comprises the identity operation *E*, all the permutations *P* of identical nuclei, the inversion *E** and the product of *E* with all the permutations *P* of identical nuclei. Nevertheless, for many molecules, it is not necessary to take all the elements into account. Limiting the group to achievable operations leads to the "molecular symmetry" (MS) group. The feasibility of an operation with respect to the tunneling effect is limited by the experimental time scale, hence by the resolution of the experiment. The MS group is therefore a subgroup of the complete (PI) group and can be adapted to the problem under study. For nonlinear rigid molecules, the group is isomorphic to the point group of the molecule. The operations of the point-group symmetry have an effect on the vibration and electronic coordinates of a molecule and are denoted by: C_n for rotation, σ for reflection, i for inversion and S_n for improper rotation. These operations are described by permutation, inversion and inversion-permutation in the theory of PI groups, which act on the rotation and spin coordinates. The group SO(3) termed as "molecular" [BUN 98] must also be considered. It contains the rotation group isomorphic to the group of molecular symmetry.

1.6.6. *Group SO(3) isomorphic to permutation-inversion group G^{CNPI}*

In the set of subgroups of SO(3), the cyclic groups as well as the dihedral groups are specific in the sense that their elements can be reduced to two representative operators, either a rotation by β about an axis z attached to the molecule in the mobile reference frame, or a rotation by π about an axis in the plane xy, which forms an angle α with the x axis. For the molecules belonging to groups of symmetry isomorphic to one cyclic group or one dihedral group, it is generally assumed that the rotation motion is approximately described by a symmetric rigid rotator. The eigenfunctions $|JKM\rangle\rangle$ of the rigid rotator can therefore be used as basis states for the solution of Schrödinger's molecular equation. The action of operators representative for the cyclic and dihedral groups is given by:

$$R_z^{\beta}|JKM\rangle = e^{iK\beta}|JKM\rangle \qquad [1.30]$$

$$R_\alpha^{\pi}|JKM\rangle = \left(-1\right)^J e^{-2iK\alpha}\left|J{-}KM\right\rangle \qquad [1.31]$$

The transformations of Euler angles by these rotations are given in Table 1.10.

R_α^π is a (direct) rotation of the reference frame attached to the molecule (mobile reference frame: *Oxyz*) by an angle π about the axis making an angle α with the *Ox* axis. R_z^β is a (direct) rotation of the reference frame attached to the molecule (mobile reference frame: *Oxyz*) by an angle β about the *Oz* axis. The effect of these rotation operators on the Euler angles can be determined by multiplying the rotation matrix corresponding to these operators by the transformation matrix depending on Euler angles (see section 2.7.2 of Chapter 2, Volume 2 [DAH 19]), allowing the switch from the fixed reference frame (OXYZ) to the mobile reference frame (*Oxyz*). Based on the matrix product, the elements are expressed as a function of new Euler angles, allowing the move from the fixed reference frame (OXYZ) to the mobile reference frame (*Oxyz*), taking into account the rotation R_α^π or R_z^β.

The rotation matrices corresponding to the two operators are given by:

$$R_z^{\beta} = \begin{pmatrix} cos\beta & sin\beta & 0 \\ -sin\beta & cos\beta & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad [1.32]$$

$$R_{\alpha}^{\pi} = \begin{pmatrix} cos2\alpha & sin2\alpha & 0 \\ sin2\alpha & -cos2\alpha & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad [1.33]$$

	$\mathbf{R}_{\alpha}^{\pi}$	$\mathbf{R}_{z}^{\beta}$
θ	$\pi-\theta$	θ
φ	$\pi+\varphi$	φ
χ	$2\pi-2\alpha-\chi$	$\chi+\beta$
J_x	$J_x\cos2\alpha+J_y\sin2\alpha$	$J_x\cos\beta+J_y\sin\beta$
J_y	$J_x\sin2\alpha-J_y\cos2\alpha$	$-J_x\sin\beta+J_y\cos\beta$
J_z	$-J_z$	J_z

Table 1.10. *Transformations of Euler angles and components of rovibronic angular momenta during rotations R_{α}^{π} and R_z^{β}*

Consequently, the representations $D^{(J)}$ such that $D^{(J_1)} \otimes D^{(J_2)} = D^{(J_1+J_2)} \oplus D^{(J_1+J_2-1)} \oplus \ldots \oplus D^{(|J_1-J_2|)}$ (vector addition) and generated by functions $|JKM\rangle$ for a fixed J and $K = -J, -J+1, \ldots, J$, can be subdivided into a one-dimensional representation for $K = 0$ (type A) and two-dimensional representation $|J-|K|M\rangle$ and $|J|K|M\rangle$ when $K \neq 0$ (type E). The characters are given by equations [1.30] and [1.31].

The molecular symmetry under rotation is thus double. There is a spatial group SO(3), in which the application of an external field may remove the degeneracy in M, and there is a molecular group SO(3), which contains the rotation, a group that is isomorphic to the molecular symmetry group. In Bunker and Jensen [BUN 98], these groups are referred to as K (spatial) and K (mol), respectively. Consequently, the set of functions$(2J+1)^2$ $|JKM\rangle$, here K and M, span each over the set $\{-J, -J+1, \ldots, J\}$, cover the irreducible representations $D^{(J)}$ in spatial SO(3) and the restricted $D^{(J)}$ covers the molecular symmetry group. The isomorphisms of the molecular symmetry groups of A_4, A_5 or S_4 cannot be found by the equivalent rotation technique of Longuet-Higgins [LON 63]. It is nevertheless possible to find the respective isomorphisms with an appropriate approach [HOU 63].

1.7. Correlation between the rotation group and a point-group symmetry of a molecule

The Hamiltonian of a molecule must be invariant under a rotation operation (SO(3) group) and an inversion operation with respect to the origin (I) so that the Hamiltonian must be invariant in a rotation-inversion symmetry operation (O(3) group). Each representation of a rotation group SO(3) generates two representations of the group O(3). The representations of type $D^{(J)}$ (of dimension $2J + 1$) in SO(3) for which the character of the operation I is equal to 1, respectively – 1, lead to representations of type $D^{(J+)}$ (positive levels), respectively $D^{(J-)}$ (negative levels), in O(3). When considering the terms that should be added to the zeroth-order Hamiltonian in order to describe the full Hamiltonian of the molecule, it can be considered that these terms constitute a perturbation susceptible to removing the $2J + 1$ degeneracy of an irreducible representation of type $D^{(J+)}$.

If it is possible to determine the lower-order symmetry group to which the new Hamiltonian including the higher orders belongs, the degenerate levels will be labeled with the terms identifying the irreducible representation of the lower-order symmetry group. The decomposition of the type of irreducible representation of the higher-order group (here the one associated with the $2J + 1$-dimensional space of $D^{(J+)}$ representation) must be determined in terms of those of the lower-order group.

The same procedure is applicable to the decomposition of the type of irreducible representation of the rotation symmetry group of the representation $D^{(J+)}$ in the $2J + 1$-dimensional space, in terms of those of the point symmetry group of the molecule (C_{3v}, D_{3h}, T_d, C_{2v}) or of the symmetry group of the environment (point group of a nanocage or of a trapping surface) in which the molecule is placed. In this case the reduction formula [1.23] is used:

$$a_\alpha = \frac{1}{h}\sum_{O_i \in G} h_i \chi(O_i)\left(\chi^\alpha(O_i)\right)^* .$$

Consequently, this requires the identification of the rotational symmetry operations contained in the molecular symmetry group or that imposed by the environment that limits the degrees of freedom of the molecule.

In a three-dimensional crystal structure, the only rotation operations that allow the paving of the three-dimensional space are the rotations of type C_2, C_3, C_4 and C_6. In the case of the symmetry group C_{3v}, the symmetry axes C_3 must therefore be considered, which amounts to considering the subgroup C_3 of the group C_{3v}. Additionally, the second-order rotation symmetry axes of type C_2 perpendicular to the symmetry planes σ_v can also be considered, because a symmetry operation of type σ_v can always be written in the form of a product $i \otimes C_3$.

The characters of the rotation symmetry operations C_2, C_3, C_4 and C_6 are summarized in Table 1.11 for j varying from 0 to 5. They are calculated with the formula: $\chi^J(\varphi) = \frac{sin(j+1/2)\varphi}{sin(1/2)\varphi}$, where φ takes the values π, $2\pi/3$, $\pi/2$ and $\pi/3$ for the operations C_2, C_3, C_4 and C_6, respectively.

J =	0	1	2	3	4	5
$\chi^{j}(C_2)$	1	-1				
$\chi^{j}(C_3)$	1	0	1			
$\chi^{j}(C_4)$	1	1	-1	-1		
$\chi^{j}(C_6)$	1	2	1	-1	-2	-1

Table 1.11. *Characters of the rotation symmetry operations of type C_2, C_3, C_4 and C_6 in the irreducible representation $D^{(j)}$ of dimension 2j+1*

Considering a nanocage characterized by the symmetry group of type $O_h = I \otimes O$, for example, a substitution site of a face-centered cubic (fcc) structured noble gas matrix, the type of symmetry of the rotation levels of a molecule trapped in the site can be determined as follows. Just as for the irreducible representations of type $D^{(J+)}$ and $D^{(J-)}$ of the group K_h (O(3) group) that can be built from those of group K (SO(3) group), it is sufficient to consider group O in order to establish the symmetries of the rotation levels in the substitutional site and then add the suffix + or – to the types of symmetry when the character of the inversion operation I is equal to 1 or – 1.

Characters of operations of O in the representation $D^{(J)}$ of the rotation group K or SO(3)						Resolution of $D^{(J)}$ into irreducible representations of the group O
J	**E**	**C_2**	**C_4^2**	**C_3**	**C_4**	
0 (S)	1	1	1	1	1	A_1
1 (P)	3	-1	-1	0	1	F_1
2 (D)	5	1	1	-1	-1	$E + F_2$
3 (F)	7	-1	-1	1	-1	$A_2 + F_1 + F_2$
4 (G)	9	1	1	0	1	$A_1 + E + F_1 + F_2$
5 (H)	11	-1	-1	-1	1	$E + 2F_1 + F_2$
6 (I)	13	1	1	1	-1	$A_1 + A_2 + E + F_1 + 2F_2$
12 (O)	25	1	1	1	1	$2A_1 + A_2 + 2E + 3F_1 + 3F_2$

Table 1.12. *Table of correlation and characters of symmetry operations of group O in the irreducible representation $D^{(j)}$ of the rotation group SO(3) of dimension 2j+1*

The group O, of order 24, comprises the symmetry operations $E, C_2(6), C_3(8), C_4^2(3)$ and $C_4(6)$. In the symmetry group SO(3), the two operations C_4^2 and C_2 are equivalent. The characters summarized in Table 1.11 are used to determine those of operations of group SO(3) in the representation $D^{(J)}$. Table 1.12 gives the characters of the classes of group O in the representation $D^{(J)}$ of dimension $2J + 1$ of the rotation group as well as the correlations of irreducible representations of O in $D^{(J)}$.

Since 12 is the least common multiple of 2, 3 and 4 associated with operators C_2, C_3 and C_4, it is possible to establish the table of correlation between the group O and the group $D^{(J)}$ up to 13. When examining the decomposition of characters of classes of group O in the representation $D^{(J)}$ of dimension $2J + 1$, it can be noted that the character is given by the number 25 for the identity representation E and that it corresponds to the dimension of the representation $D^{(J)}$, for $J = 12$ since $2J + 1 = 25$. For $J = 12$, the character of each rotation is equal to 1. This for $J = 12$, the characters are the sum of two sets, that of the identity representation for which the character of each operation is 1, and the character of E in O which must be equal to 24 (order of the group), the characters of other symmetry operations being all equal to zero. For the decomposition of the representation $D^{(J)}$, for $J = 12$, $D^{(12)} = A_1 \oplus reg$ (where reg is the regular representation [HAM 62] for which each irreducible representation appears once multiplied by the dimension of the space such that $reg = A_1 \oplus A_2 \oplus 2E \oplus 3F_1 \oplus 3F_2$). Moreover, if the following relation is written as: $D^{(J)} \oplus D^{(11-J)} = reg$ then $D^{(6)} \oplus D^{(5)} = reg$. The table can thus be filled up to $J = 5$ from which the decompositions for $J = 6, 7, 8, 9, 10$ and 11 can be deduced according to the formula. For $J = 12m$, it can be written that:

$$D^{(12m+p)} = m(reg) \oplus D^{(p)} \text{ where } p < 13$$

The table of correspondence between the symmetry group T_d of the spherical top CH_4 and the representation $D^{(J)}$ can similarly be built. The symmetry operations are $E, C_3(8), S_4^2(3), \sigma_d(6)$ and $S_4(6)$ (order 24). The correspondence between the group O and the group T_d makes it possible to easily establish Table 1.13.

The table of correspondence between the symmetry group C_{3v} of the symmetric top NH_3 and the representation $D^{(J)}$ can be established by the same method. The symmetry operations are $E, C_3(2)$ and $\sigma_v(3)$. Either the subgroup C_3 of C_{3v} is used, or the rotation operations equivalent to the symmetry operations $C_3(2)$ and $\sigma_v(3)$, i.e. $R_z^{2\pi/3}$ and $R_{\pi/2}^{\pi}$, are used to build the table of correlation between the rotation group and the group C_{3v}. Using a similar approach to that for group O, Table 1.14 can be established.

Characters of operations of T_d in the representation $D^{(J)}$ of the rotation group K or SO(3)						**Resolution of $D^{(J)}$ into irreducible representations of the group *Td***
Equivalent Rotations	**E**	**C_2**	**C_4^2**	**C_3**	**C_4**	
J	**E**	**σ_d**	**S_4^2**	**C_3**	**S_4**	
0 (S)	1	1	1	1	1	A_1
1 (P)	3	-1	-1	0	1	F_1
2 (D)	5	1	1	-1	-1	$E + F_2$
3 (F)	7	-1	-1	1	-1	$A_2 + F_1 + F_2$
4 (G)	9	1	1	0	1	$A_1 + E + F_1 + F_2$
5 (H)	11	-1	-1	-1	1	$E + 2F_1 + F_2$
6 (I)	13	1	1	1	-1	$A_1 + A_2 + E + F_1 + 2F_2$
7 (J)	15	-1	-1	0	-1	$A_2 + E + 2F_1 + 2F_2$
8 (K)	17	1	1	-1	1	$A_1 + 2E + 2F_1 + 2F_2$
9 (L)	19	-1	-1	1	1	$A_1 + A_2 + E + 3F_1 + 2F_2$
10 (M)	21	1	1	0	-1	$A_1 + A_2 + 2E + 2F_1 + 3F_2$
11 (N)	23	-1	-1	-1	-1	$A_2 + 2E + 3F_1 + 3F_2$
12 (O)	**25**	**1**	**1**	**1**	**1**	$\mathbf{2A_1 + A_2 + 2E + 3F_1 + 3F_2}$

Table 1.13. *Table of correlation and characters of the symmetry operations of group T_d in the irreducible representation of $D^{(j)}$ of the rotation group SO(3) of dimension 2j+1*

Characters of operations of C_{3v} in the representation $D^{(J)}$ of the rotation group K or SO(3)				**Resolution of $D^{(J)}$ into irreducible representations of group C_{3v}**
Equivalent Rotations	**R^0**	**$R_z^{2\pi/3}$**	**$R_{\pi/2}\pi$**	
J	**E**	**$2C_3$**	**$3\sigma_v$**	
0 (S)	1	1	1	A_1
1 (P)	3	0	-1	$A_2 + E$
2 (D)	5	-1	1	$A_1 + 2E$
3 (F)	7	1	-1	$A_1 + 2A_2 + 2E$
4 (G)	9	0	1	$2A_1 + A_2 + 3E$
5 (H)	11	-1	-1	$A_1 + 2A_2 + 4E$
6 (I)	13	1	1	$3A_1 + 2A_2 + 4E$

Table 1.14. *Table of correlation and characters of symmetry operations of group C_{3v} in the irreducible representation $D^{(j)}$ of the rotation group SO(3) of dimension 2j+1*

The representations $D^{(J)}$ are generated by rotational functions of symmetric tops $|JKM\rangle$. These representations can be divided into a one-dimensional representation when $K = 0$ and a two-dimensional representation for each pair $|J,|K|,M\rangle$ and $|J,-|K|,M\rangle$. The characters of the symmetry operations of group T in this basis are summarized in Table 1.15.

T	$\chi^{\mathrm{j}}(\boldsymbol{E})$	$\chi^{\mathrm{j}}(\boldsymbol{C_2})$	$\chi^{\mathrm{j}}(\boldsymbol{C_3})$	$\chi^{\mathrm{j}}(\boldsymbol{C_3^2})$
$J = 6p + k$	12p+2k+1	$(-1)^k$	(2/√3)sin(2(1-k)/3)	(2/√3)sin(2(1-k)/3)

Table 1.15. *Table of characters of representation of group T generated by the basis /JKM〉. p,k=,1,2,3 … in the irreducible representation $D^{(j)}$ of dimension 2j+1*

When determining the statistical weight of the vibration–rotation levels for a given electronic and vibration state, tensor products of the irreducible representations of the rotation functions and spin functions must be evaluated. Tables X–12 and X–13 of reference [WIL 55] provide the rules of multiplication of direct products of irreducible representations.

By applying these rules, it is possible to build the following tables for the groups C_{3v}, D_{3h} and T_d applicable to symmetric and spherical tops.

$\mathbf{C_{3v}}$	$\mathbf{A_1}$	$\mathbf{A_2}$	**E**
$\mathbf{A_1}$	A_1	A_2	E
$\mathbf{A_2}$	A_2	A_1	E
E	E	E	$A_1 \oplus A_2 \oplus E$

Table 1.16. *Direct product of irreducible representations of group C_{3v}*

$\mathbf{D_{3h}}$	$\mathbf{A'_1}$	$\mathbf{A'_2}$	**E'**	$\mathbf{A''_1}$	$\mathbf{A''_2}$	**E''**
$\mathbf{A'_1}$	A'_1	A'_2	E'	A''_1	A''_2	E''
$\mathbf{A'_2}$	A'_2	A'_1	E'	A''_2	A''_1	E''
E'	E'	E'	$A'_1 \oplus A'_2 \oplus E'$	E''	E''	$A''_1 \oplus A''_2 \oplus E''$
$\mathbf{A''_1}$	A''_1	A''_2	E''	A'_1	A'_2	E'
$\mathbf{A''_2}$	A''_2	A''_1	E''	A_2	A_1	E
E''	E''	E''	$A''_1 \oplus A''_2 \oplus E''$	E'	E'	$A'_1 \oplus A'_2 \oplus E'$

Table 1.17. *Direct product of irreducible representations of group D_{3h}*

T_d	A_1	A_2	E	T_1	T_2
A_1	A_1	A_2	E	T_1	T_2
A_2	A_2	A_1	E	T_2	T_1
E	E	E	$A_1 \oplus A_2 \oplus E$	$T_1 \oplus T_2$	$T_1 \oplus T_2$
T_1	T_1	T_2	$T_1 \oplus T_2$	$A_1 \oplus E \oplus T_1 \oplus T_2$	$A_2 \oplus E \oplus T_1 \oplus T_2$
T_2	T_2	T_1	$T_1 \oplus T_2$	$A_2 \oplus E \oplus T_1 \oplus T_2$	$A_1 \oplus E \oplus T_1 \oplus T_2$

Table 1.18. *Direct product of irreducible representations of group T_d (for group T, remove the indices 1 and 2)*

1.8. Example of group theory applications

An application of symmetry operations involves the determination of the existence of electric dipole moments in a molecule taking into account the symmetry of its structure. Given that a symmetry operation leaves a molecule in a configuration that is indiscernible from the one it had before the transformation, the direction of the dipole moment vector (polar vector) must be invariant with respect to the operation.

Consequently:

– If the molecule has an *n*-th order symmetry axis, C_n, the permanent dipole moment must be along this axis.

– If the molecule has a symmetry plane, its dipole moment must be in this plane.

– If there are several symmetry planes, the moment must be at the intersection of the planes of symmetry (in NH_3, it is along the axis C_3).

– If the molecule has two or more axes of symmetry, it has no permanent dipole moment (CH_4).

– If the molecule has a center of symmetry, it has no dipole moment, as the inversion changes the direction of a vector.

The molecules whose structures cannot be superimposed to their images in a mirror (enantiomer) can rotate the plane of polarization of light, as the two possible forms (isomer) have opposite optical properties. A molecule that has a symmetry axis S_n is optically inactive ($S_1 = i$ and $S_2 = \sigma$). In general, the absence of axis S_n involves the existence of an optical activity.

1.9. Conclusion

The groups generated by geometric transformations are not the only ones that can be applied in physics, as is revealed by the use of permutation groups that are better adapted for the study of molecules composed of identical nuclei. According to Bose and Fermi statistics, the permutations of N identical particles are associated with two different irreducible representations, but they are very easy to deal with, so the group theory is unnecessary. Point-group symmetry is adapted for dealing with electron, vibrational and rotational degrees of freedom. To deal with the exchange of identical nuclei in a molecule or tunneling effect inversion that are observable in experiments, it is more convenient to use the permutation-inversion group. The elements of the theory of group representation and the methods developed in group theory were presented for the study of molecules from their point-group symmetry. The theory of permutation-inversion groups was also introduced. These methods will be applied in Chapters 2 and 3 in order to determine the symmetries of the wave functions of vibration, rotation and spin degrees of freedom of the various types of molecules considered as well as the selection rules leading to IR spectra of these molecules.

1.10. Appendices: Groups and Lie algebra of SU(2) and SO(3)

1.10.1. *Appendix A: Groups SU(2) and SO(3)*

The study of angular momenta involves operators that can act in a quantum space (spin space with $S = 1/2$) or in a physical space (rotation space with $J = 1$). There is a correspondence between the rotation group SO(3) defined in the physical space of rotations and the group SU(2) defined in the quantum space of spins. The following elements can be found in the references [HAM 62] (see Chapter 8) or [GIL 74] (see Chapter 5) or [LIP 65] (see Chapters 1 and 2).

1.10.1.1. *The relation between the group SU(2) and the group SO(3)*

SU(2) is the set of complex 2×2 matrices, M, of determinants equal to $+1$ and which have the property that: $M^{\dagger}M = I$

$$M = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} \text{ with } |a|^2 + |b|^2 = 1 \qquad [1.34]$$

Only three independent parameters are needed to determine the elements of the matrix M of SU(2). A commonly used form is given by:

$$M = \begin{pmatrix} \cos\frac{\theta}{2} e^{\frac{i}{2}(\psi+\phi)} & \sin\frac{\theta}{2} e^{\frac{i}{2}(\psi-\phi)} \\ -\sin\frac{\theta}{2} e^{\frac{-i}{2}(\psi-\phi)} & \cos\frac{\theta}{2} e^{-\frac{i}{2}(\psi+\phi)} \end{pmatrix} \qquad [1.35]$$

with $0 \leq \theta \leq \pi$, $0 \leq \psi \leq 4\pi$ and $0 \leq \phi \leq 2\pi$.

The 2 x 2 matrix that is a representation of the rotation group O(3) is known as the irreducible representation $D_{1/2}$.

The vectors transformed in SU(2) are spinors that can form a basis for the spin operator $\widehat{S}$. The spinors are used to represent the half-spin fermions [LAN 75] used in Dirac's theory (Dirac used Pauli matrices to build 4 x 4 matrices defined from Dirac's[1] equation and referred to this four-dimensional space as the bispinor space, which comprises the particles and the anti-particles; the study is limited to the space of particles) which can be denoted as Φ_α where $\alpha = 1, 2$. An analogy can be drawn with the $3D$ vectors in the case of the rotation group SO(3). It can be written as $\Phi_\alpha^{'} = M_{\alpha\beta}\Phi_\beta$.

There is a homomorphism between group SU(2) and group SO(3) (where each element of SO(3) has two corresponding elements in SU(2)). If the image of $M \in$ SU(2) is $R(M) \in$ SO(3), then $R(M) = R(-M)$ The application of SU(2) in SO(3) can be chosen in the following form:

$$R_{ik}(M) = \frac{1}{2} Tr\left(\sigma_i M \sigma_k M^{-1}\right) \text{ with } i,k = 1,2,3 \qquad [1.36]$$

where σ_i are Pauli matrices defined by:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \text{ and } \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad [1.37]$$

Therefore, the representations of SO(3) are representations of SU(2). However, the spinor representations of SU(2) have no analogue in SO(3). The representation of SU(2) by 2 x 2 matrices corresponds to the lowest dimension of spinor representations of SU(2).

1.10.1.2. *Representations of SU(2) and SO(3)*

The representation of SU(2) is the one used in the theory of angular momenta in quantum mechanics.

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[1] Dirac used Pauli matrices to construct the defined 4 x 4 matrices of the Dirac equation, and called this four-dimensional space the bispinor space, which includes particles and antiparticles; we therefore restrict ourselves to particle space.

Indeed, kets are defined from eigenfunctions common to operators l^2 and l_z denoted by $|lm\rangle$ with $l = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$ and $m = -l, -l+1, \ldots, l-1, l$. For each l, there is a corresponding distinct irreducible representation of SU(2) and the number of possible values of m, which is $2l + 1$, gives the dimension of the representation.

The representations for which l is an integer number are equivalent to the representations of SO(3) and correspond to the representations of bosons, and those for which l is a half-integer number are equivalent to the representations of SU(2) and correspond to the representations of fermions.

1.10.2. *Appendix B: Lie algebra and SO(3)*

1.10.2.1. *Definition of an algebra*

An algebra is a vector space E over the field K with a law of composition or vector product $E \otimes E \rightarrow E : (a,b) \rightarrow ab \in E, \ (A,b \in E)$ that obeys the following distributive laws:

$$a(\lambda b + \mu c) = \lambda ab + \mu ac \text{ and } (\lambda a + \mu b)c = \lambda ac + \mu bc \qquad [1.38]$$

where $(\lambda,\mu) \in K$ and $(a,b,c) \in E$.

1.10.2.2. *Generators of elements of group SO(3)*

The following 3 x 3 matrix is the starting point:

$$J_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix} \qquad [1.39]$$

The following expansion can be written as:

$$e^{i\phi J_x} = 1 + i\phi J_x + \frac{1}{2!}(i\phi J_x)^2 + \ldots = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & \sin\phi \\ 0 & -\sin\phi & \cos\phi \end{pmatrix} \qquad [1.40]$$

which is a rotation about the Ox axis. J_x is said to be a generator of rotations about the Ox axis. The term generator takes its root from the way the operator is built. An infinitesimal rotation by an angle $\delta\phi$ about the Ox axis is proportional to ϕ and the complete rotation is realized (or generated) by composing an infinity of infinitesimal rotations such that:

$$R_x(\phi) = lim_{N\to\infty}\left(1 + i\frac{\phi}{N}J_x\right)^N \to e^{i\phi J_x} \qquad [1.41]$$

Similarly, the rotations about Oy and Oz axes are generated by:

$$J_y = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix} \text{ and } J_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad [1.42]$$

The set of three generators J_x, J_y and J_z of SO(3) forms a Lie algebra.

1.10.2.3. *Definition of a Lie algebra*

A real Lie algebra denoted by L, of dimension n ($n \geq 1$), is a real vector space with a Lie product or a commutator $[a, b]$ defined for each element a and b of L such that:

$[a,b] \in L$ for any a and $b \in L$ [1.43a]

$[\alpha a + \beta b,c] = \alpha[a,c] + \beta[b,c]$ for any a and $b \in L$ and any real α and β [1.43b]

$[a,b] = -[b,a]$ for any a and $b \in L$ [1.43c]

$\left[a,[b,c]\right] + \left[b,[c,a]\right] + \left[c,[a,b]\right] = 0$ for any a, b and $c \in L$ [1.43d]

The last property is the Jacobi identity.

1.10.2.4. *Lie algebra of SU(2) and SO(3)*

The algebra of SO(3) generator commutators verifies:

$$\left[J_x,J_y\right] = iJ_z \qquad [1.44a]$$

$$\left[J_y,J_z\right] = iJ_x \qquad [1.44b]$$

$$[J_z,J_x] = iJ_y \qquad [1.44c]$$

$$\left[J_i,J_j\right] = i\varepsilon_{ijk}J_k \qquad [1.44d]$$

where J_x, J_y and J_z constitute the basis of the vector space and ε_{ijk} is the Levi-Civita tensor, $\varepsilon_{123} = \varepsilon_{312} = \varepsilon_{213} = 1$ and $\varepsilon_{132} = \varepsilon_{321} = \varepsilon_{231} = -1$ (where $x = 1$, $y = 2$ and

$z = 3$). Each rotation operator is obtained by the integration of three independent infinitesimal rotation operators:

$$1 + i\frac{\phi}{N}J_i,\ i = x,y \text{ or } z$$

For example, the π mesons form a triplet of isotopic spin $I = 1$. The infinitesimal generators are 3 x 3 matrices represented by structure constants of the Lie algebra.

Similarly in SU(2), the following relations between Pauli matrices can be written as:

$$\left[\frac{\sigma_1}{2}, \frac{\sigma_2}{2}\right] = i\frac{\sigma_3}{2} \qquad [1.45a]$$

$$\left[\frac{\sigma_2}{2}, \frac{\sigma_3}{2}\right] = i\frac{\sigma_1}{2} \qquad [1.45b]$$

$$\left[\frac{\sigma_3}{2}, \frac{\sigma_1}{2}\right] = i\frac{\sigma_2}{2} \qquad [1.45c]$$

$$\left[\frac{\sigma_i}{2}, \frac{\sigma_j}{2}\right] = i\varepsilon_{ijk}\frac{\sigma_k}{2} \qquad [1.45d]$$

where $\frac{\sigma_1}{2}, \frac{\sigma_2}{2}$ and $\frac{\sigma_3}{2}$ constitute the basis of the vector space.

Though the groups SU(2) and SO(3) are not isomorphic, the Lie algebras of SU(2) and SO(3) are isomorphic. The nucleons form a doublet of isotopic spin $I = 1/2$. The infinitesimal generators are Pauli matrices.