Chapter 4

Group theory

Group theory will be presented in this chapter as a *tool* for spectroscopy. Indeed group theory makes it possible to

- construct and classify molecular orbitals,
- classify electronic, vibrational, rotational and nuclear spin wave functions,
- predict which states are allowed,
- predict physical properties (existence of electric dipole moment, optical activity etc.),
- predict selection rules (electric dipole transitions, configuration interaction. etc.)

However, group theory does not make any *quantitative* predictions. The interest of group theory lies in *simplifying* some problems like those mentioned above that arise in molecular spectroscopy.

4.1 Symmetry operations

4.1.1 Definition of a group

A **group** G is a set of elements A, B, C, ... connected by a combination rule (written as a product, for example $A \cdot B$) which has the following properties:

1. the **closure**: for all elements A and B of the group G, $A \cdot B = C$ is also an element of the group G.

2. the **associativity**: the combination rule must be associative, *i. e.* $A \cdot (B \cdot C) = (A \cdot B) \cdot C$.

3. the **identity**: there must be an element, the identity E (also called **unit**), such that $E \cdot R = R \cdot E = R$ for all elements R of the group.

4. the **inverses**: each element R must have an inverse R^{-1} which is also a group element such that $R \cdot R^{-1} = R^{-1} \cdot R = E$.

In group theory, the elements considered are symmetry operations. For a given molecular system described by the Hamiltonian $\hat{H}$, there is a set of symmetry operations $\hat{O}_i$ which commute with $\hat{H}$:

$$\left[\hat{O}_i, \hat{H}\right] = 0. \tag{4.1}$$

$\hat{H}$ and $\hat{O}_i$ thus have a common set of eigenfunctions and the eigenvalues of $\hat{O}_i$ can be used as labels for the eigenfunctions (see Lecture Physical Chemistry III). This set of operations defines (with the multiplication operation) a symmetry group. In molecular physics and molecular spectroscopy two types of groups are particularly important, the point groups and the permutation-inversion groups.

4.1.2   Point group operations and point group symmetry

The point groups adequately describe molecules that can be considered as rigid on the timescale of the spectroscopic experiment, which means molecules that have a unique equilibrium configuration with no observable tunneling between two or more equivalent configurations.

The symmetry operations of the point groups are:

- the **identity** E which leaves all coordinates unchanged.

- the **proper rotation** C_n by an angle of $2\pi/n$ in the positive trigonometric sense (*i. e.* counter-clockwise). The symmetry axis with highest n is chosen as principal axis. If a molecule has a *unique* C_n axis with highest n, the molecule has a permanent dipole moment that lies along this axis (*e. g.* H_2O, NCl_3 in Figure 4.1). If a molecule has *several* C_n axes with highest n, the molecule has no permanent dipole moment (*e. g.* CH_4).
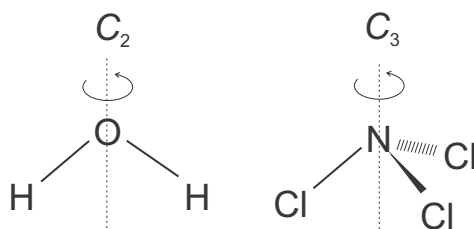

Figure 4.1: C_2 rotation of H_2O and C_3 rotation of NCl_3.

- the **reflection** through a plane σ; the reflections are classified into two categories:

- the reflections through a vertical plane, *i. e.* a plane which contains the symmetry axis z are noted σ_v,

- the reflections through an horizontal plane, *i. e.* a plane perpendicular to the symmetry axis z are noted σ_h.

- the **inversion** i of all coordinates through the inversion center.

- the **improper rotation** S_n or **rotation-reflection** which consists in a rotation by an angle of $2\pi/n$ around the z axis followed by a reflection through the plane perpendicular to the rotational axis. Figure 4.2 shows the S_4 improper rotation of allene as an example.
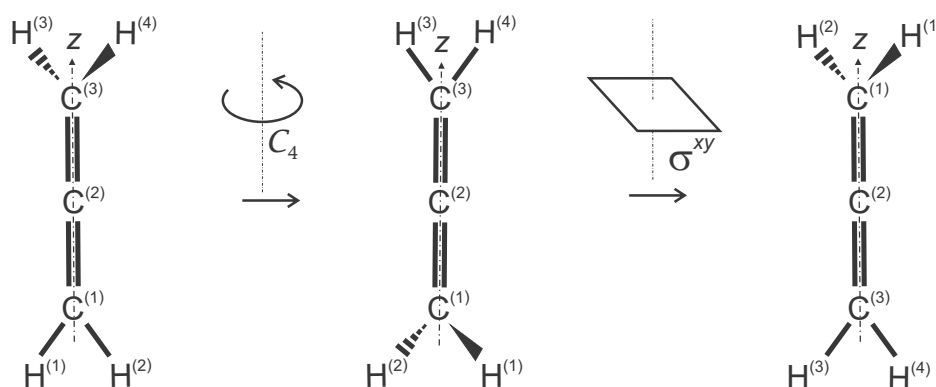

Figure 4.2: Decomposition of the improper rotation S_4 of allene.

A molecule having an improper operation as symmetry operation, *i. e.* a reflection, an improper rotation or an inversion, cannot be optically active and is therefore achiral.

4.1.3 Permutation-inversion operations and CNPI groups

As mentioned already, the point groups are well suited to describe rigid molecules. However, for floppy systems, especially clusters with tunneling splitting as shown in Figure 4.3, or when the transition between two states does not hold the same symmetry, another, more general definition is required.
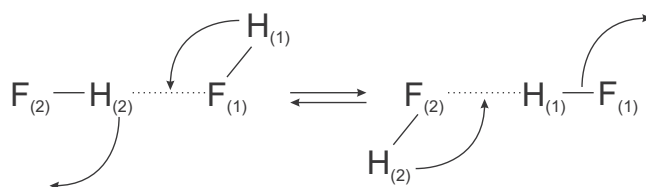

Figure 4.3: Tunneling process in $(HF)_2$.

To circumvent this problem, the complete nuclear permutation inversion (CNPI) groups have

been developed, originally by Christopher Longuet-Higgins and Jon T. Hougen (see Bunker and Jensen, *Molecular Symmetry and Spectroscopy*, 1998). Their concept relies on the fact that the symmetry operations, *i. e.* the permutation-inversion operations leave $\hat{H}$ unchanged. The symmetry operations of the CNPI groups are:

- the **permuation** (ij) of the coordinates of two identical nuclei i and j which denotes the exchange of the nucleus i with the nucleus j (see Figure 4.4 for examples),

- the **cyclic permutation** (ijk) of the coordinates of three identical nuclei i, j, and k, *i. e.* the nucleus i will be replaced by the nucleus j, j by k and k by i (see Figure 4.4 for example),
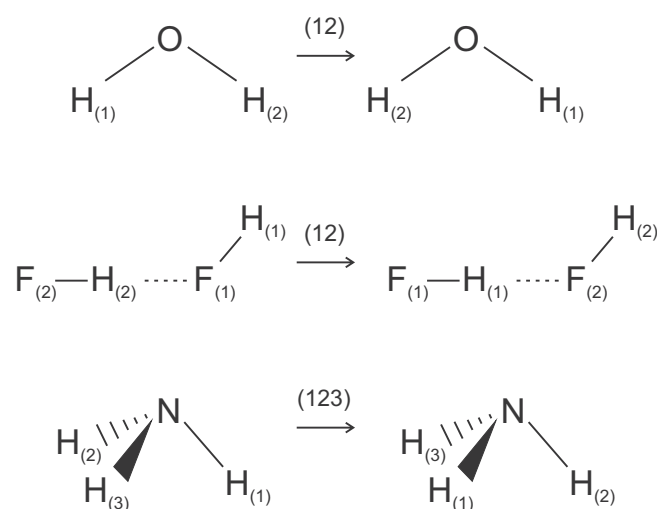

Figure 4.4: Examples of $(i\,j)$ and $(i\,j\,k)$ permutations.

- all possible circular permutations of n identical nuclei (for example, the $(1\,2\,3\,4\,5\,6)$ permutation in benzene),

- the **inversion** E^* of all coordinates of all particles through the *center of the lab-fixed frame*,

- the **permutation followed by an inversion** $(ij)^* = E^* \cdot (ij)$ of all coordinates of all particles

- the **cyclic permutation followed by an inversion** $(ijk)^*$ of all coordinates of all particles,

- all possible circular permutations followed by an inversion of all coordinates of n identical nuclei.

The permutation operations only affect *identical* nuclei, therefore the molecular Hamiltonian is left unchanged upon these operations. Moreover the molecular Hamiltonian depends on *distances* rather than positions, hence the inversion operation also leaves $\hat{H}$ unchanged.

The CNPI groups represent a more general description that can also be applied to rigid molecules. Indeed each point group is isomorphous to a CNPI group although the symmetry operations are not identical (for example, the inversion i of a point group symmetry is not the same as the inversion of a permutation inversion group E^*).

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Example: the point group C_{3v} is isomorphous to $S_3 = \{E, (1\,2\,3), (1\,3\,2), (1\,2), (1\,3), (2\,3)\}$, which means that there is a one to one correspondence between the two sets of operations.

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However, one disadvantage of the CNPI groups is their size which can become very large. For example, the CNPI for CH_4 contains 48 symmetry operations, and that of benzene 1036800! In the case of non-rigid systems, this problem is usually solved by using a subgroup, *i.e.* a subset of the group which forms a group under the same combination rule. These subgroups are called molecular symmetry (MS) groups.

In the case of rigid molecules, most of the time the point groups are used. In the following, we will consider rigid molecules only and restrict ourselves to point group symmetry, but all concepts can be extended to the CNPI and MS groups.

4.2 Important concepts in a group

4.2.1 Order, conjugated elements and classes

The **order of a group** is equal to the number of elements in the group. The **discrete** (or **finite**) groups have a finite order (for example C_{2v} is a group of fourth order), while **continuous** groups have infinite orders ($C_{\infty v}$ for example).

Let us consider two operations $\hat{O}_i$ and $\hat{O}_j$ that leave $\hat{H}$ unchanged when applied individually. Hence, they must also leave $\hat{H}$ unchanged when applied in succession. The notation $\hat{O}_i \cdot \hat{O}_j$ means that $\hat{O}_j$ acts first, and $\hat{O}_i$ second. In other words, $\hat{O}_i \cdot \hat{O}_j$ must be a symmetry operation $\hat{O}_k$ if $\hat{O}_i$ and $\hat{O}_j$ are symmetry operations, which is a corollary of the closure property of a group. Very often it is useful to build the so-called **multiplication table** which summarizes all possible $\hat{O}_i \cdot \hat{O}_j$ combinations.

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<u>Example</u>: the C_{2v} group of H_2O

The symmetry operations are E, C_2^z, σ^{xz} and σ^{yz}. From Figure 4.5 one can verify that the successive application of any two operations of the C_{2v} point group is equivalent to the application of a third group operation. For instance: $\sigma^{xz} \cdot \sigma^{yz} = C_2^z$, $\sigma^{xz} \cdot \sigma^{xz} = E$, $C_2^z \cdot \sigma^{xz} = \sigma^{yz}$, etc.
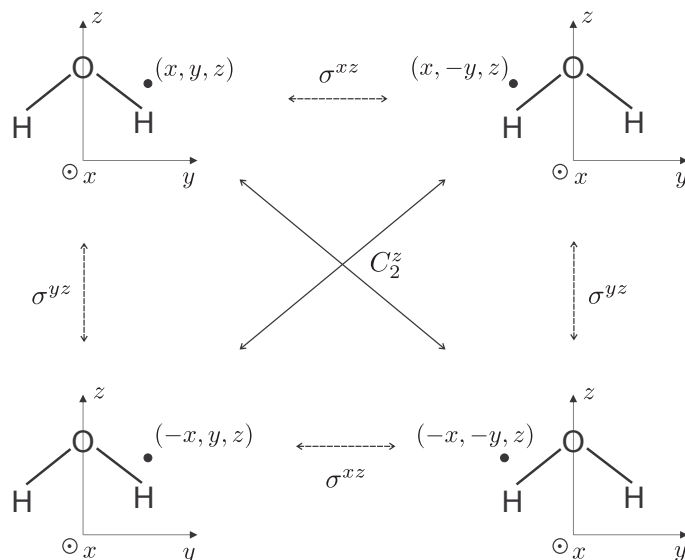

Figure 4.5: C_{2v} group operations and their effect on a water molecule. The dot indicates schematically the coordinates (x, y, z) of an electron.

The multiplication table of the C_{2v} point group with four symmetry operations (E, C_2^z, σ^{xz}, σ^{yz}) is thus a 4×4 table.

	1$^{\text{st}}$ operation (right)			
C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}
E	E	C_2^z	σ^{xz}	σ^{yz}
C_2^z	C_2^z	E	σ^{yz}	σ^{xz}
σ^{xz}	σ^{xz}	σ^{yz}	E	C_2^z
σ^{yz}	σ^{yz}	σ^{xz}	C_2^z	E

2$^{\text{nd}}$ operation (left)

Table 4.1: Multiplication table of the C_{2v} point group.

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A group G is said **abelian** or **commutative** when all operations commute:

$$\hat{O}_i \cdot \hat{O}_j = \hat{O}_j \cdot \hat{O}_i \,. \tag{4.2}$$

For example, the C_{2v} group is abelian (see Table 4.1). However, not all groups are Abelian. An example of a non-abelian group is the point group C_{3v}.

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Example: CH_3Cl in the C_{3v} group

The symmetry operations are E, C_3, C_3^2, σ^a, σ^b, σ^c, hence the group is of order 6. With the help of Figure 4.6, one can derive the multiplication table of the C_{3v} point group. One sees that the group is not Abelian because not all operations commute (e. g., $C_3 \cdot \sigma^a = \sigma^c$ and $\sigma^a \cdot C_3 = \sigma^b$). Moreover, not all operations are their own inverse (e. g., $C_3 \cdot C_3 \neq E$).
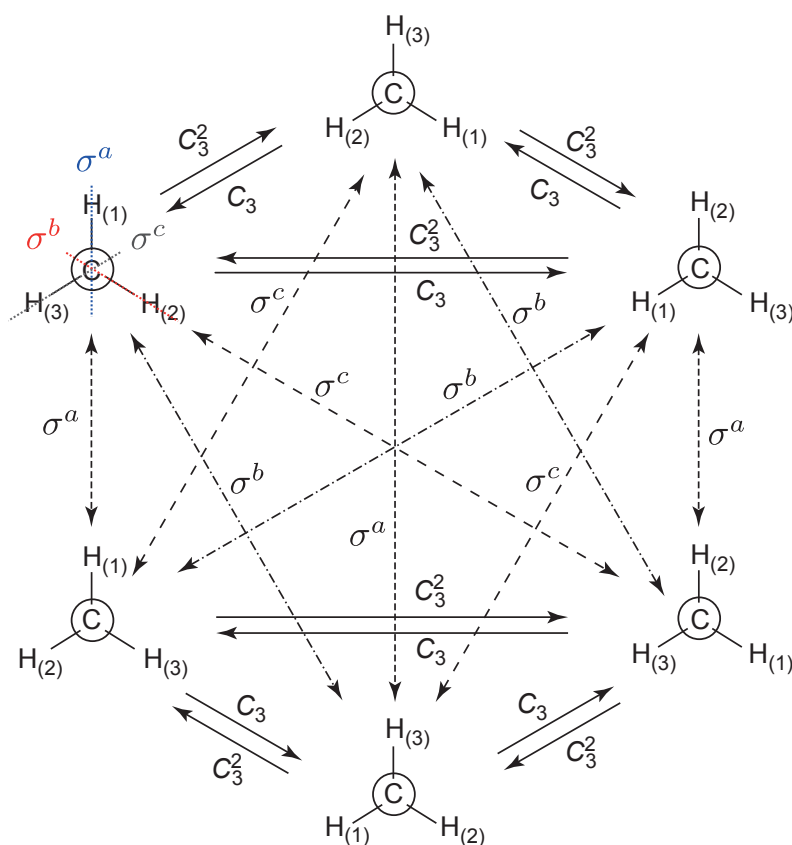

Figure 4.6: The operations of the C_{3v} point group with the example of the CH_3Cl molecule represented as a Newmann projection (adapted from F. Merkt and M. Quack in *Handbook of high-resolution spectroscopy*, 2011).

PCV - *Spectroscopy of atoms and molecules*

<div align="center">1st operation (right)</div>

C_{3v}	E	C_3	C_3^2	σ^a	σ^b	σ^c
E	E	C_3	C_3^2	σ^a	σ^b	σ^c
C_3	C_3	C_3^2	E	σ^c	σ^a	σ^b
C_3^2	C_3^2	E	C_3	σ^b	σ^c	σ^a
σ^a	σ^a	σ^b	σ^c	E	C_3	C_3^2
σ^b	σ^b	σ^c	σ^a	C_3^2	E	C_3
σ^c	σ^c	σ^a	σ^b	C_3	C_3^2	E

2nd operation (left)

Table 4.2: Multiplication table of the C_{3v} point group.

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If $\hat{O}_i$, $\hat{O}_j$, and $\hat{O}_k$ are all group elements and if they obey the relation

$$\hat{O}_k \cdot \hat{O}_i \cdot \hat{O}_k^{-1} = \hat{O}_j, \tag{4.3}$$

then $\hat{O}_i$ and $\hat{O}_j$ are called **conjugated elements**. All conjugated elements in a group form **a class**.

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Example: Elements of the point group C_{3v} that belong to the same class as C_3

We consider $C_3 = \hat{O}_i$ and apply each operation $\hat{O}_k$ of C_{3v} according to Equation (4.3) with the help of the multiplication table in order to find the conjugated elements of C_3.

$\hat{O}_i$	$\hat{O}_k$	$\hat{O}_k^{-1}$	$\hat{O}_k \cdot \hat{O}_i \cdot \hat{O}_k^{-1} = \hat{O}_j$	$\hat{O}_i$	$\hat{O}_k$	$\hat{O}_k^{-1}$	$\hat{O}_k \cdot \hat{O}_i \cdot \hat{O}_k^{-1} = \hat{O}_j$
C_3	E	E	$E \cdot C_3 \cdot E = C_3$	C_3^2	E	E	$E \cdot C_3^2 \cdot E = C_3^2$
C_3	C_3	C_3^2	$C_3 \cdot C_3 \cdot C_3^2 = C_3$	C_3^2	C_3	C_3^2	$C_3 \cdot C_3^2 \cdot C_3^2 = C_3^2$
C_3	C_3^2	C_3	$C_3^2 \cdot C_3 \cdot C_3 = C_3$	C_3^2	C_3^2	C_3	$C_3^2 \cdot C_3^2 \cdot C_3 = C_3^2$
C_3	σ^a	σ^a	$\sigma^a \cdot \underbrace{C_3 \cdot \sigma^a}_{\sigma^c} = C_3^2$	C_3^2	σ^a	σ^a	$\sigma^a \cdot \underbrace{C_3^2 \cdot \sigma^a}_{\sigma^b} = C_3$
C_3	σ^b	σ^b	$\sigma^b \cdot \underbrace{C_3 \cdot \sigma^b}_{\sigma^a} = C_3^2$	C_3^2	σ^b	σ^b	$\sigma^b \cdot \underbrace{C_3^2 \cdot \sigma^b}_{\sigma^c} = C_3^2$
C_3	σ^c	σ^c	$\sigma^c \cdot \underbrace{C_3 \cdot \sigma^c}_{\sigma^b} = C_3^2$	C_3^2	σ^c	σ^c	$\sigma^c \cdot \underbrace{C_3^2 \cdot \sigma^c}_{\sigma^a} = C_3^2$

C_3 and C_3^2 are conjugated; they are elements of the same class of order 2.

Similarly, one can show that σ^a, σ^b and σ^c form a class of order 3.

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The **order k of an element** $\hat{O}_i$ is the smallest integer $k \geq 1$ with $\hat{O}_i^k = E$. This property

exists for finite groups only.

With this definition, one can easily find that a rotation C_n is of order n and a reflection σ is of order 2. All elements of a class have the same order.

4.2.2 Representations and character table

Up to now, we have described each symmetry operation $\hat{O}$ of a group with respect to one specific molecule. Now, we would like to get a more general picture and represent each operation of the group with a $n \times n$ matrix $\boldsymbol{B}$, n being the dimensionality of the representation. This matrix represents how the vectors or functions chosen as basis set (of dimension n) transform upon the application of $\hat{O}$. Therefore, the matrix $\boldsymbol{B}$ depends on the coordinate system, *i. e.* the vectors chosen to describe the system. Given a coordinate system $\tilde{e}$, the matrix representation $\boldsymbol{B}^{(\tilde{e})}$ of the operation $\hat{O}$ fulfils

$$\vec{y} = \boldsymbol{B}^{(\tilde{e})}\vec{x}. \tag{4.4}$$

With a new coordinate system $\tilde{e}' = \boldsymbol{S}\tilde{e}$, the transformation is $\vec{y}' = \boldsymbol{S}\vec{y}$, and $\vec{x}' = \boldsymbol{S}\vec{x}$. Therefore

$$\vec{y}' = \boldsymbol{S}\vec{y} = \boldsymbol{S}\boldsymbol{B}^{(\tilde{e})}\vec{x} = \boldsymbol{S}\boldsymbol{B}^{(\tilde{e})}\boldsymbol{S}^{-1}\vec{x}' = \boldsymbol{B}^{(\tilde{e}')}\vec{x}' \tag{4.5}$$

The matrix $\boldsymbol{B}^{(\tilde{e}')} = \boldsymbol{S}\boldsymbol{B}^{(\tilde{e})}\boldsymbol{S}^{-1}$ forms a new, equivalent representation of the operation $\hat{O}$. The trace of a matrix remains unchanged upon an unitary coordinate transformation. Thus

$$\mathrm{Tr}(\boldsymbol{B}^{(\tilde{e}')}) = \mathrm{Tr}(\boldsymbol{B}^{(\tilde{e})}). \tag{4.6}$$

The trace of a matrix representing an operation is also called the **character of the operation** χ. An interesting property is that all elements of a class have the same character.

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Example : one-dimensional representation ($n = 1$) of $C_{2\mathrm{v}}$

Case 1: one can use the functions $\Psi_1 = x$, $\Psi_2 = y$, or $\Psi_3 = z$.
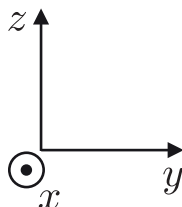
$\Psi_1 = x :$	$E\,x = x$	$\Psi_2 = y :$	$E\,y = y$	$\Psi_3 = z :$	$E\,z = z$
	$C_2^z\,x = -x$		$C_2^z\,y = -y$		$C_2^z\,z = z$
	$\sigma^{xz}\,x = x$		$\sigma^{xz}\,y = -y$		$\sigma^{xz}\,z = z$
	$\sigma^{yz}\,x = -x$		$\sigma^{yz}\,y = y$		$\sigma^{yz}\,z = z$

Therefore x, y, and z correspond to the following representations designated by Γ:

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}
$\Gamma^{(z)}$	1	1	1	1
$\Gamma^{(x)}$	1	-1	1	-1
$\Gamma^{(y)}$	1	-1	-1	1

Case 2: instead of using x, y, or z, more complicated functions can be used to generate a one-dimensional representation, such as x^2, y^2, z^2, xy, xz or yz as listed in the fourth column of the character table. For example, one takes the functions $\Psi_4 = x^2$ and $\Psi_5 = xy$:

$$\Psi_4 = x^2: \quad E\,x^2 = (E\,x)(E\,x) = x^2 \qquad\qquad \Psi_5 = xy: \quad E\,xy = (E\,x)(E\,y) = xy$$

$$C_2^z\,x^2 = (C_2^z\,x)(C_2^z\,x) = x^2 \qquad\qquad\qquad C_2^z\,xy = (C_2^z\,x)(C_2^z\,y) = xy$$

$$\sigma^{xz}\,x^2 = (\sigma^{xz}\,x)(\sigma^{xz}\,x) = x^2 \qquad\qquad\qquad \sigma^{xz}\,xy = (\sigma^{xz}\,x)(\sigma^{xz}\,y) = -xy$$

$$\sigma^{yz}\,x^2 = (\sigma^{yz}\,x)(\sigma^{yz}\,x) = x^2 \qquad\qquad\qquad \sigma^{yz}\,xy = (\sigma^{yz}\,x)(\sigma^{yz}\,y) = -xy$$

It is easy to verify that $\chi^{(xy)} = \chi^{(x)} \times \chi^{(y)}$, a result that can be written as a direct product. To evaluate a **direct product**, one multiplies the characters of each class of elements pairwise and obtains as direct product a representation of the group:

$\Gamma^{(xy)} = \Gamma^{(x)} \otimes \Gamma^{(y)} = $ (1 -1 1 -1) $\otimes$ (1 -1 -1 1) = (1 1 -1 -1).

Case 3: one can also look at the transformation properties of rotations and for example take $\Psi_6 = R_z$ as illustrated in Figure 4.7.
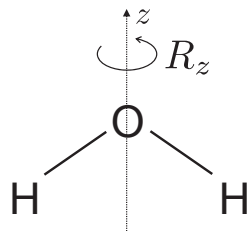

Figure 4.7: The R_z rotation of water.

$$\Psi_6 = R_z: \quad E\,R_z = R_z$$

$$C_2^z\,R_z = R_z$$

$$\sigma^{xz}\,R_z = -R_z \quad \text{Direction of rotation reversed.}$$

$$\sigma^{yz}\,R_z = -R_z \quad \text{Direction of rotation reversed.}$$

R_z transforms as follows:

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}
$\Gamma^{(R_z)}$	1	1	-1	-1

Representations of higher dimensionality can be obtained by looking at the transformation properties of two or more functions. Indeed, to construct an n-dimensional representation of a group, one takes n linear independent functions or vectors Ψ_i, $i = 1, ..., n$ spanning a given n-dimensional space. Applying the group operations on Ψ_i leads to a transformed function which is a linear combination of the original functions:

$$\hat{O}\,\Psi_i = \sum_{j=1}^{n} b_{ji}(\hat{O})\,\Psi_j. \tag{4.7}$$

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Example: two dimensional representation $\begin{pmatrix} x \\ y \end{pmatrix}$ of the $C_{2\mathrm{v}}$ group

$$E \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \qquad \text{with } \chi_E^{\binom{x}{y}} = 2$$

$$C_2^z \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -x \\ -y \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \qquad \text{with } \chi_{C_2^z}^{\binom{x}{y}} = -2$$

$$\sigma^{xz} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x \\ -y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \qquad \text{with } \chi_{\sigma^{xz}}^{\binom{x}{y}} = 0$$

$$\sigma^{yz} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -x \\ y \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \qquad \text{with } \chi_{\sigma^{yz}}^{\binom{x}{y}} = 0$$

The two-dimensional representation of $\begin{pmatrix} x \\ y \end{pmatrix}$ has thus the following characters:

$C_{2\mathrm{v}}$	E	C_2^z	σ^{xz}	σ^{yz}
2×2 Matrix	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$
$\Gamma^{\binom{x}{y}}$	2	-2	0	0

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If the matrices of all elements of a representation of a group can be simultaneously brought into block-diagonal form by a given coordinate transformation, the representation is said to be **reducible**, if not, it is **irreducible**.

The **character table** of a group lists all irreducible representations and gives for each representation the character of each class of elements.

G	$C_1 = E$	C_2	$\ldots$	C_n	T_x	T_y	T_z	R_x	R_y	R_z
$\Gamma_{\text{irr}}^{(1)}$	$\chi^{(1)}(C_1)$	$\chi^{(1)}(C_2)$	$\ldots$	$\chi^{(1)}(C_n)$						
$\Gamma_{\text{irr}}^{(2)}$	$\chi^{(2)}(C_1)$	$\chi^{(2)}(C_2)$								
$\vdots$	$\vdots$	$\vdots$								
$\Gamma_{\text{irr}}^{(n)}$	$\chi^{(n)}(C_1)$	$\chi^{(n)}(C_2)$	$\ldots$	$\chi^{(n)}(C_n)$						

In a character table, $\Gamma^{(n)}$ designates the n-th irreducible representation, C_i the i-th class of elements and $\chi^{(n)}(C_j)$ the character of the elements of class j in the n-th representation. There are as many irreducible representations as classes. Next to the characters of the elements of the different classes, the character table also gives in the last columns how the translations T_x, T_y and T_z and the rotations R_x, R_y and R_z transform.

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Example: The character table of the C_{2v} group

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z	x^2, y^2, z^2	
A_2	1	1	-1	-1		xy	R_z
B_1	1	-1	1	-1	x	xz	R_y
B_2	1	-1	-1	1	y	yz	R_x

x, y, and z correspond to the irreducible representations B_1, B_2, and A_1, respectively as indicated in the third column of the character table. R_z transforms as A_2 as indicated in the fifth column of the character table. One can verify that R_x and R_y transform as B_2 and B_1, respectively.

The $\Gamma^{\binom{x}{y}}$ representation is not an irreducible representation of C_{2v} because it is of dimension 2, and C_{2v} has one-dimensional irreducible representations only. $\Gamma^{\binom{x}{y}}$ is reducible, $i.\,e.$, it corresponds to a linear combination of irreducible representations: $\Gamma^{\binom{x}{y}} = B_1 \oplus B_2$.

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Character tables exist for all groups. Many groups have a finite number of representations, but groups with an infinite number of representations also exist such as $D_{\infty h}$ and $C_{\infty v}$.

Important remark: The character of the unity operation (E) is always equal to the dimension of the representation.

4.2.3 Reduction of reducible representations

There is a systematic mathematical procedure to perform the reduction of representations. All representations in a character table form a set of orthogonal vectors that span the complete space:

$$\sum_{\hat{O}} \chi^{(i)}(\hat{O}) \times \chi^{(j)}(\hat{O}) = h\delta_{ij}, \tag{4.8}$$

where h represents the order of the group and $\hat{O}$ runs over all the elements of the group. (Note that some classes of non-Abelian groups contain more than one element!). Any *reducible* representation can thus be expressed as a linear combination of *irreducible* representations

$$\Gamma^{\text{red}} = \sum_k c_k^{\text{red}} \Gamma^{(k)}, \tag{4.9}$$

where $\Gamma^{(k)}$ represents an irreducible representation. The expansion coefficients c_k^{red} can be determined using the **reduction formula** Equation (4.10):

$$c_k^{\text{red}} = \frac{1}{h} \sum_{\hat{O}} \chi^{\text{red}}(\hat{O}) \times \chi^k(\hat{O}) \tag{4.10}$$

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Example : two-dimensional representation spanned by 1s atomic orbitals $\begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix}$ centred on the H atoms of a water molecule H_2O in the C_{2v} group (see Figure 4.8)
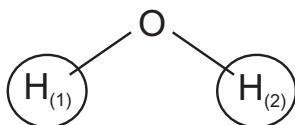

Figure 4.8: 1s atomic orbitals on the H atoms of H_2O.

$$E \begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix} = \begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix} \quad \text{thus} \quad \chi_E = 2$$

$$C_2^z \begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix} = \begin{pmatrix} 1s(2) \\ 1s(1) \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix} \quad \text{thus} \quad \chi_{C_2^z} = 0$$

$$\sigma^{xz} \begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix} = \begin{pmatrix} 1s(2) \\ 1s(1) \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix} \quad \text{thus} \quad \chi_{\sigma^{xz}} = 0$$

$$\sigma^{yz} \begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix} = \begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1s(1) \\ 1s(2) \end{pmatrix} \quad \text{thus} \quad \chi_{\sigma^{yz}} = 2$$

$C_{2\mathrm{v}}$	E	C_2^z	σ^{xz}	σ^{yz}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
2×2 Matrix	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$
$\Gamma^{(1\mathrm{s})}$	2	0	0	2

Reduction of $\Gamma^{(1\mathrm{s})} = (2\,0\,0\,2)$:

$$
\begin{aligned}
c_{\mathrm{A}_1}^{(1\mathrm{s})} &= \frac{1}{4}(2 \times 1 + 0 \times 1 + 0 \times 1 + 2 \times 1) = 1 \\
c_{\mathrm{A}_2}^{(1\mathrm{s})} &= \frac{1}{4}(2 \times 1 + 0 \times 1 + 0 \times (-1) + 2 \times (-1)) = 0 \\
c_{\mathrm{B}_1}^{(1\mathrm{s})} &= \frac{1}{4}(2 \times 1 + 0 \times (-1) + 0 \times 1 + 2 \times (-1)) = 0 \\
c_{\mathrm{B}_2}^{(1\mathrm{s})} &= \frac{1}{4}(2 \times 1 + 0 \times (-1) + 0 \times (-1) + 2 \times 1) = 1
\end{aligned}
$$

$$\Rightarrow \ \Gamma^{(1\mathrm{s})} = \mathrm{A}_1 \oplus \mathrm{B}_2.$$

This means that one can therefore construct one linear combination of the two 1s(H) orbitals of H_2O with A_1 symmetry (totally symmetric) and one with B_2 symmetry as will be shown in the following.

———————————————————————

4.3   Useful applications of group theory

4.3.1   Determination of symmetrized linear combinations of atomic orbitals

To find the symmetrized linear combination of atomic orbitals (LCAO), one uses so-called **projectors** $\hat{P}$. The projector associated with the irreducible representation Γ is defined by

$$\hat{P}^{\Gamma} = \frac{1}{h} \sum_{\hat{O}} \chi^{(\Gamma)}(\hat{O}) \times \hat{O}\,. \tag{4.11}$$

The application of $\hat{P}^{\Gamma}$ onto the atomic orbitals provides a LCAO of symmetry Γ.

_____

Example : symmetrized LCAOs of the two 1s orbitals on the H atoms of H_2O.

$$\hat{P}^{A_1} 1s(1) = \frac{1}{4}[1 \times E\,1s(1) + 1 \times C_2^z\,1s(1) + 1 \times \sigma^{xz}\,1s(1) + 1 \times \sigma^{yz}\,1s(1)]$$

$$= \frac{1}{4}[1s(1) + 1s(2) + 1s(2) + 1s(1)] = \frac{1}{2}[1s(1) + 1s(2)]$$

$$\hat{P}^{A_2} 1s(1) = \frac{1}{4}[1 \times E\,1s(1) + 1 \times C_2^z\,1s(1) - 1 \times \sigma^{xz}\,1s(1) - 1 \times \sigma^{yz}\,1s(1)]$$

$$= \frac{1}{4}[1s(1) + 1s(2) - 1s(2) - 1s(1)] = 0$$

As expected, no A_2 linear combination can be formed from the 1s(H) functions. Similarly one finds

$$\hat{P}^{B_1} 1s(1) = 0\,, \text{ and}$$

$$\hat{P}^{B_2} 1s(1) = \frac{1}{2}[1s(1) - 1s(2)]\,.$$

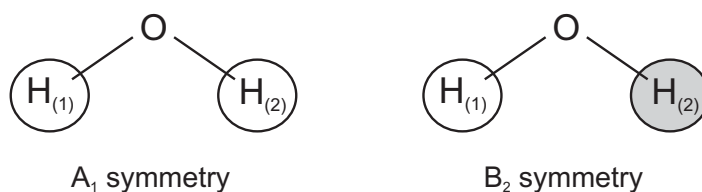The two LCAOs of symmetry A_1 and B_2 can be represented schematically in Figure 4.9.

Figure 4.9: Linear combinations of atomic orbital 1s(H) of H_2O of symmetry A_1 and B_2.

The symmetrized LCAOs can then be used to determine the chemical bonds that can be formed with the p orbitals on the O atom. First, one must determine the transformation properties of the p orbitals on the O atom depicted schematically in Figure 4.10.
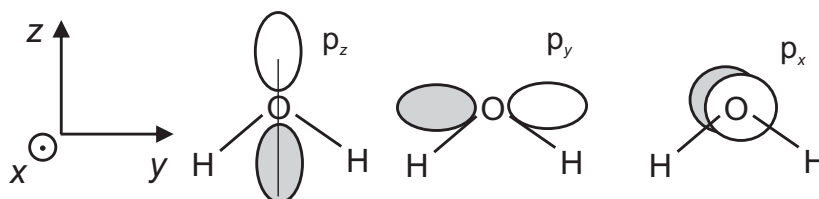

Figure 4.10: p orbitals on the O atom.

The p_x, p_y, and p_z orbitals of the O atoms transform like x, y, and z, respectively as indicated in Section 4.2.2. Hence: $\Gamma^{(p_x)} = B_1$, $\Gamma^{(p_y)} = B_2$, and $\Gamma^{(p_z)} = A_1$ as indicated in the third column of the character table.

Only orbitals of the same symmetry can be combined to form bonding or antibonding molecular

orbitals. The five symmetrized orbitals listed above can be used to form five molecular orbitals according to the following diagram (Figure 4.11) which does not take the 1s and 2s orbitals on the oxygen into account because only valence electrons are considered for the formation of chemical bonds.
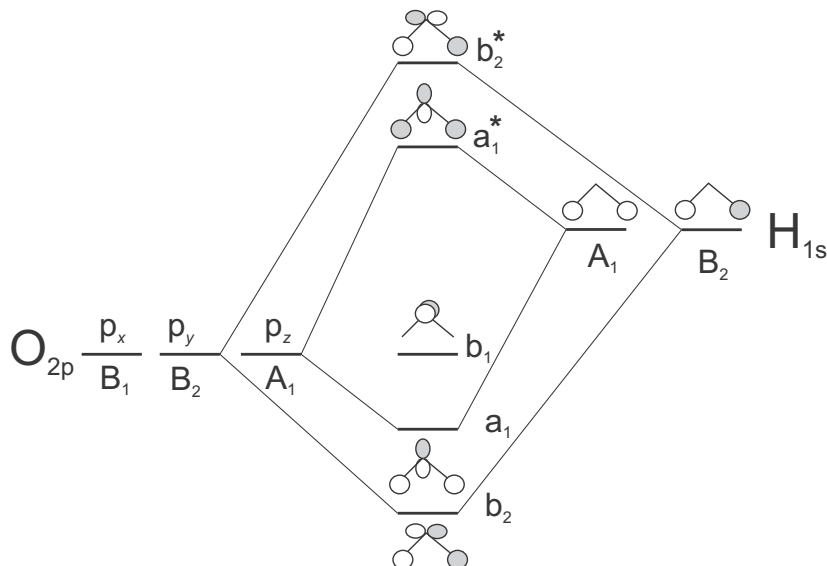

Figure 4.11: Valence molecular orbitals of H_2O built from symmetrized H(1s) "ligand" orbitals and the 2p atomic orbitals of O. The labels of the molecular orbitals refer to their symmetry in lower case letters.

From the electronic configuration of each atom, there are six valence electrons (O ... $(2p)^4$, H $(1s)^1$) to place in the Molecular Orbitals (MOs) following Pauli's Aufbau-principle gives the ground state configuration: ...$(b_2)^2(a_1)^2(b_1)^2$ with an overall symmetry A_1. Because four of the six electrons are in bonding orbitals and two in a non bonding p_x orbital, one expects two chemical bonds in H_2O. The energetical ordering of the two bonding MO of B_2 and A_1 symmetry depends on the HOH angle α defined in Figure 4.12. Whereas the a_1 orbital becomes nonbonding at $\alpha = 180°$, the b_2 orbital remains bonding at $\alpha = 180°$ but becomes antibonding at small angles.
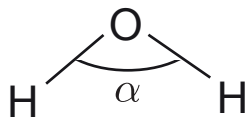

Figure 4.12: Bond angle α.

4.3.2 Symmetry of normal modes

We consider the $3N$-dimensional reducible representation Γ_{3N} spanned by the set of $3N$ Cartesian coordinates of the N atoms in a molecule and reduce it into irreducible representations of the corresponding group. The molecule can also be characterized by its $3N$ displacement coordinates *i.e.* the translations (t), rotations (r) and vibrations (v). Therefore:

$$\Gamma_{3N} = \Gamma_\text{t} \oplus \Gamma_\text{r} \oplus \Gamma_\text{v} \tag{4.12}$$

The representation of the vibrational modes Γ_v can be deduced from Γ_{3N} subtracting the representations Γ_t and Γ_r as indicated in the character table.

———————————————————————————

Example: The vibrational modes of H_2O

The total representation is $3 \times 3 = 9$-dimensional. All irreducible representations of $C_{2\text{v}}$ are one-dimensional, and only three vibrational modes ($3N$-6) exist in H_2O. The symmetry of these modes will be obtained by eliminating the six irreducible representations corresponding to the three translational and the three rotational degrees of freedom of the molecule.
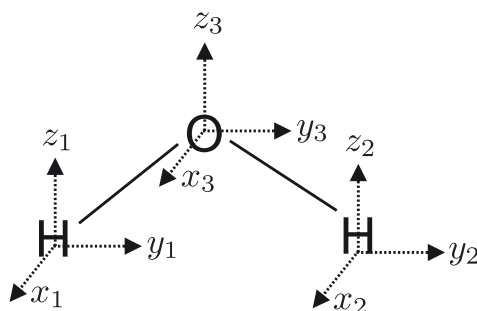

Figure 4.13: Coordinates used to derive the Γ_9 representation of H_2O in the $C_{2\text{v}}$ group.

In the basis set (or representation) $\Gamma_9 = \{x_1, y_1, ..., z_3\}$, the $C_{2\text{v}}$ symmetry operations are represented by 9×9 matrices.

The matrix representing the identity E is given by:

$$
E \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}
$$

Hence the character is $\chi^{(\Gamma_9)}(E) = 9$ (in agreement with the dimension of the representation).

The matrix representing the rotation C_2^z is given by:

$$
C_2^z \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} -x_2 \\ -y_2 \\ z_2 \\ -x_1 \\ -y_1 \\ z_1 \\ -x_3 \\ -y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}
$$

Hence the character is $\chi^{(\Gamma_9)}(C_2) = -1$.

From the construction of these two matrices we notice that only atoms that are not exchanged by the symmetry operations can contribute to the character; therefore in the following, we consider the atoms that are "invariant" by the operation $\hat{O}$ only to determine $\chi^{(\Gamma_9)}(\hat{O})$.

The reflection σ^{xz} exchanges the two H atoms so that only the O atom needs to be considered:

$$
\sigma^{xz} x_3 = x_3; \quad \sigma^{xz} y_3 = -y_3; \quad \sigma^{xz} z_3 = z_3 \quad \Rightarrow \quad \chi^{(\Gamma_9)}(\sigma^{xz}) = 1.
$$

The reflection σ^{yz} does not exchange any atom. For each atom, the x coordinate is inverted and the y and z coordinates are preserved:

$$
\sigma^{xz} x_i = -x_i; \quad \sigma^{xz} y_i = y_i; \quad \sigma^{xz} z_i = z_i
$$

$$
\Rightarrow \quad \chi^{(\Gamma_9)}(\sigma^{yz}) = -1 + 1 + 1 - 1 + 1 + 1 - 1 + 1 + 1 = 3
$$

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The reducible 9-dimensional representation is therefore:

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}	
A_1	1	1	1	1	$= \Gamma^z$
A_2	1	1	-1	-1	$= \Gamma^{R_z}$
B_1	1	-1	1	-1	$= \Gamma^x = \Gamma^{R_y}$
B_2	1	-1	-1	1	$= \Gamma^y = \Gamma^{R_x}$
Γ_9	9	-1	1	3	

The Γ_9 representation can then be reduced using the reduction formula of Equation (4.10)):

$$
\begin{aligned}
c_{A_1} &= \frac{1}{4}(9 - 1 + 1 + 3) = 3 \\
c_{A_2} &= \frac{1}{4}(9 - 1 - 1 - 3) = 1 \\
c_{B_1} &= \frac{1}{4}(9 + 1 + 1 - 3) = 2 \\
c_{B_2} &= \frac{1}{4}(9 + 1 - 1 + 3) = 3
\end{aligned}
$$

$$
\Gamma_9 = 3A_1 \oplus A_2 \oplus 2B_1 \oplus 3B_2.
$$

From these nine irreducible representations, three correspond to translations ($\Gamma^x = B_1$, $\Gamma^y = B_2$, $\Gamma^z = A_1$) and three correspond to rotations ($\Gamma^{R_x} = B_2$, $\Gamma^{R_y} = B_1$, $\Gamma^{R_z} = A_2$). The remaining three, namely $2A_1 \oplus B_2$, correspond to the three vibrational modes of H_2O ($3N - 6 = 3$, because H_2O is a nonlinear molecule). To determine these modes one can use the projection formula of Equation (4.11). Let us consider the vibrational mode of symmetry B_2 as an example. In practice it is convenient to first treat the x, y and z displacements separately and then to combine the x, y, and z motions. For the x-dimension:

$$
\begin{aligned}
\hat{P}^{B_2} x_1 &= \frac{1}{4}\left(1 E x_1 - 1 C_2^z x_1 - 1 \sigma^{xz} x_1 + 1 \sigma^{yz} x_1\right) \\
&= \frac{1}{4}\left(x_1 + x_2 - x_2 - x_1\right) = 0.
\end{aligned}
$$

The B_2 mode does not involve x-coordinates.

For the y- and z-dimensions:

$$
\begin{aligned}
\hat{P}^{B_2} y_1 &= \frac{1}{4}\left(1 E y_1 - 1 C_2^z y_1 - 1 \sigma^{xz} y_1 + 1 \sigma^{yz} y_1\right) \\
&= \frac{1}{4}\left(y_1 + y_2 + y_2 + y_1\right) = \frac{1}{2}\left(y_1 + y_2\right). \\
\hat{P}^{B_2} z_1 &= \frac{1}{4}\left(1 E z_1 - 1 C_2^z z_1 - 1 \sigma^{xz} z_1 + 1 \sigma^{yz} z_1\right) \\
&= \frac{1}{4}\left(z_1 - z_2 - z_2 + z_1\right) = \frac{1}{2}\left(z_1 - z_2\right).
\end{aligned}
$$

The B_2 mode involves both y and z coordinates. Drawing the displacement vectors one obtains a vectorial representation of the motion of the H atoms in the B_2 mode. The motion of the O atom

can be estimated in a same way or reconstructed by ensuring that the center of mass of the molecule remains stationary.
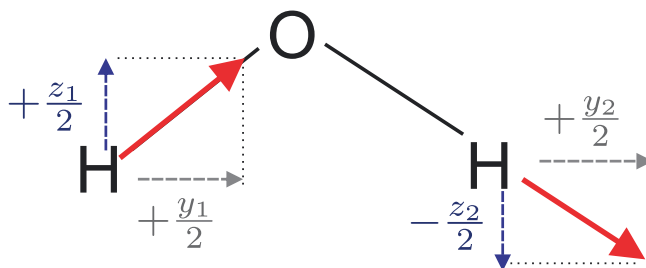

Figure 4.14: Determination of the nuclear motion of the B_2 mode of water.

The mode can be easily identified as the asymmetric stretching mode.

_____

4.3.3   Symmetry of vibrational levels

The nomenclature to label the vibrational states of a polyatomic molecule is

$$\nu_1^{v_1},\ \nu_2^{v_2}, \cdots, \nu_{3N-6}^{v_{3N-6}} \tag{4.13}$$

where ν_i designate the mode and v_i the corresponding vibrational quantum number. Usually only the modes ν_i for which $v_i \neq 0$ are indicated. The notation

$$(v_1,\ v_2, \cdots, v_{3N-6}) \tag{4.14}$$

is also often used. For the ordering of the modes, the totally symmetric modes come first in order of descending frequency, then the modes corresponding to the second irreducible representation in the character table in order of descending frequency, etc.

To find the overall symmetry of the vibrational wavefunction one must build the direct product

$$\Gamma_{\text{vib}} = (\Gamma_{\nu_1})^{v_1} \otimes (\Gamma_{\nu_2})^{v_2} \otimes \cdots \otimes (\Gamma_{\nu_{3N-6}})^{v_{3N-6}}. \tag{4.15}$$

_____

Example: The three vibrational modes of H_2O ν_1 is the O-H symmetric stretching mode ($\tilde{\nu}_1$=3585 cm^{-1}) of symmetry A_1, ν_2 is the H-O-H bending mode ($\tilde{\nu}_2$=1885 cm^{-1}) of symmetry A_1 and ν_3 is the O-H asymmetric stretching mode ($\tilde{\nu}_3$=3506 cm^{-1}).

We consider the state with $v_1 = 2$, $v_2 = 1$, $v_3 = 3$. In the first notation, this will correspond to :

$1^2\ 2^1\ 3^3$. In the second notation, it will correspond to (2 1 3). The symmetry of this vibrational state is:

$$\Gamma_{\text{vib}}(\text{H}_2\text{O},\ 1^2\ 2^1\ 3^3) = \underbrace{A_1 \otimes A_1}_{\nu_1} \otimes \underbrace{A_1}_{\nu_2} \otimes \underbrace{B_2 \otimes B_2 \otimes B_2}_{\nu_3} = B_2.$$

_____

4.3.4 Symmetry of electronic states and labels of configurations

Just as in the case of vibrational wave functions, the overall symmetry of an electronic wavefunction is obtained from the direct product

$$\Gamma_{\text{el}} = (\Gamma_1)^{n_1} \otimes (\Gamma_2)^{n_2} \otimes \cdots \otimes (\Gamma_m)^{n_m}, \tag{4.16}$$

where Γ_i is the irreducible representation of orbital i and n_i is the occupation number of orbital i in the considered configuration. As totally filled subshells are always totally symmetric they do not influence the overall symmetry and can be omitted in equation 4.16.

_____

Example: Electronic ground state configuration of H_2O and H_2O^+:

H_2O: $\underbrace{...}_{A_1}(b_2)^2(a_1)^2(b_1)^2$ (see Figure 4.11)

$$\Gamma_{\text{el}} = \underbrace{B_2 \otimes B_2}_{(b_2)^2} \otimes \underbrace{A_1 \otimes A_1}_{(a_1)^2} \otimes \underbrace{B_1 \otimes B_1}_{(b_1)^2} = A_1$$

Therefore the electronic ground state is labelled $\tilde{X}\,{}^1A_1$

H_2O^+: $\underbrace{...}_{A_1}(b_2)^2(a_1)^2(b_1)^1$

$$\Gamma_{\text{el}} = \underbrace{B_2 \otimes B_2}_{(b_2)^2} \otimes \underbrace{A_1 \otimes A_1}_{(a_1)^2} \otimes \underbrace{B_1}_{(b_1)^1} = B_1$$

Therefore the electronic ground is labelled $\tilde{X}^+\,{}^2B_1$

_____

Example: Electronic ground state configuration of the borane molecule BH_3 in the D_{3h} point group.
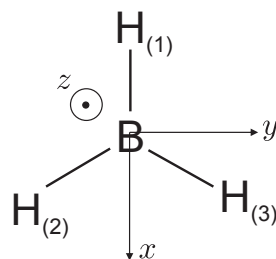

Figure 4.15: BH_3 molecule with its coordinate system.

We follow the same procedure as for H_2O in section 4.3.1, retain the 2s and 2p orbitals on the B atom and the 1s orbitals on the H atoms. First, symmetrized "ligand" orbitals are constructed from the H 1s orbitals; then these are combined with the orbitals of the B atom to form bonding and antibonding orbitals. For the ligand orbitals, a 3D-representation is spanned by the three 1s atomic orbitals on the H atom.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		
A_2'	1	1	-1	1	1	-1		R_z
E'	2	-1	0	2	-1	0	x, y	
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0		R_x, R_y
Γ^{3D}	3	0	1	3	0	1		

This representation can be reduced using the reduction formula of Equation (4.10):

$$c_{A_1'} = \frac{1}{12}[3 \times 1 \times 1 + 0 \times 2 \times 1 + 1 \times 3 \times 1 + 3 \times 1 \times 1 + 0 \times 1 \times 1 + 1 \times 3 \times 1] = 1$$

$$c_{A_2'} = \frac{1}{12}[3 \times 1 \times 1 + 0 + 1 \times 3 \times (-1) + 3 \times 1 \times 1 + 0 + 1 \times 3 \times (-1)] = 0$$

$$c_{E'} = \frac{1}{12}[3 \times 1 \times 2 + 0 + 1 \times 3 \times 0 + 3 \times 1 \times 2 + 0 + 1 \times 3 \times 0] = 1$$

$$\Gamma^{3D} = A_1' \oplus E'.$$

Figure 4.16 shows the ligand orbital of A_1' symmetry found by intuition. The ligand orbitals of E' symmetry are found by using the projection formula of Equation (4.11):

$$\hat{P}^{E'} 1s(1) = \frac{1}{12} \left[2 \times E \, 1s(1) - 1 \times C_3 \, 1s(1) - 1 \times C_3^2 \, 1s(1) + 2 \times \sigma_h \, 1s(1) - 1 \times S_3 \, 1s(1) - 1 \times S_3^2 \, 1s(1) \right]$$

$$= \frac{1}{12} \left[2 \times 1s(1) - 1s(2) - 1s(3) + 2 \times 1s(1) - 1s(2) - 1s(3) \right]$$

$$= \frac{1}{3} \left[1s(1) - \frac{1}{2} \left[1s(2) + 1s(3) \right] \right].$$

To find the second orbital of E' symmetry, we can the projector $\hat{P}^{E'}$ to the the 1s(2) and 1s(3) orbitals; we find two further molecular orbitals $\frac{1}{3}[1s(2) - \frac{1}{2}[1s(1) + 1s(3)]]$ and $\frac{1}{3}[1s(3) - \frac{1}{2}[1s(1) + 1s(2)]]$. The three orbitals are linearly dependent. One can use linear algebra to eliminate one of these three orbitals and to find an orthogonal set of two orbitals of E' symmetry (see Figure 4.16) using the Gram-Schmidt orthogonalization procedure.
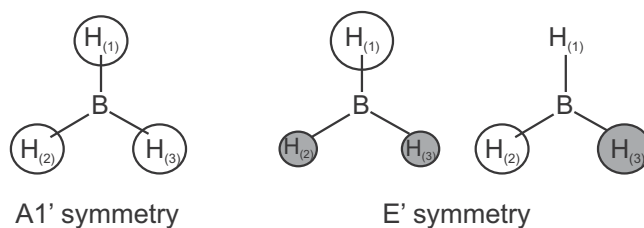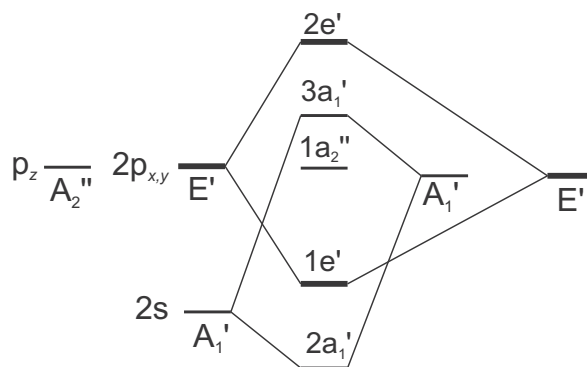
Figure 4.16: Ligand orbitals of BH_3.

The molecular orbitals are finally found by determining the symmetry of the 2s and 2p orbitals of the central B atom and combining the orbitals of the same symmetry into bonding and antibonding orbitals (see Figure 4.17).

2s(C): $A_1' \leftrightarrow A_1'$ ligand orbital

p_x(C), p_y(C): $E' \leftrightarrow E'$ ligand orbital

$2p_z$(C): A_2''

The $2p_z$ orbital of A_2'' symmetry must remain nonbonding because there are no ligand orbitals of A_2'' symmetry.

Figure 4.17: Valence molecular orbitals of BH_3.

The electronic configuration of BH_3 (in total eight electrons) is therefore:

$$\underbrace{(1a_1')^2(2a_1')^2(1e')^4}_{A_1'}(1a_2'')^0,$$

where the $1a_1'$ orbital is the 1s orbital on the B atom. Therefore, the ground state is $\tilde{X}\,^1A_1'$.

————————————————————————————

Example: The case of a linear molecule.

As all homonuclear diatomic molecules, O_2 belongs to the point group $D_{\infty h}$. The character table and direct product tables of $D_{\infty h}$ are given in Tables 4.3 and 4.4, respectively.

$D_{\infty h}$	E	$2C_\infty^\varphi$	...	$\infty\sigma_v$	i	$2S_\infty^\varphi$	...	∞C_2		
Σ_g^+	1	1	...	1	1	1	...	1		x^2+y^2, z^2
Σ_g^-	1	1	...	-1	1	1	...	-1	R_z	
Π_g	2	$2\cos\varphi$	...	0	2	$-2\cos\varphi$	...	0	R_x, R_y	xz, yz
Δ_g	2	$2\cos 2\varphi$	...	0	2	$2\cos 2\varphi$	...	0		x^2-y^2, xy
...	...	...	...	...	...	...	...	...		
Σ_u^+	1	1	...	1	-1	-1	...	-1	z	
Σ_u^-	1	1	...	-1	-1	-1	...	1		
Π_u	2	$2\cos\varphi$	...	0	-2	$2\cos\varphi$	...	0	x, y	
Δ_u	2	$2\cos 2\varphi$	...	0	-2	$-2\cos 2\varphi$	...	0		
...	...	...	...	...	...	...	...	...		

Table 4.3: Character table of the $D_{\infty h}$ point group.

$\otimes$	Σ^+	Σ^-	Π	Δ	Φ	...
Σ^+	Σ^+	Σ^-	Π	Δ	Φ	...
Σ^-		Σ^+	Π	Δ	Φ	...
Π			$\Sigma^+ \oplus \Sigma^- \oplus \Delta$	$\Pi \oplus \Phi$	$\Delta \oplus \Gamma \oplus \ldots$	
Δ				$\Sigma^+ \oplus \Sigma^- \oplus \Gamma$	$\Pi \oplus H$	...
Φ					$\Sigma^+ \oplus \Sigma^- \oplus I$	...
...	...	...	...	...	...	...

Table 4.4: Direct product table of the point groups $C_{\infty v}$ and $D_{\infty h}$. For $D_{\infty h}$, the "gerade" (g) or "ungerade" (u) character is determined as follows: $g \otimes g = u \otimes u = g$ and $g \otimes u = u \otimes g = u$.

Referring back to Figure 3.10 we can derive the molecular orbitals of O_2 and determine the most stable electronic configuration to be

$$\underbrace{(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^2(3\sigma_u^*)^0}_{\Sigma_g^+}.$$

All fully occupied orbitals contribute the totally symmetric representation Σ_g^+ to the electronic symmetry. The irreducible representations of the electronic states resulting from the above configuration can be determined from the direct product

$$\Pi_g \otimes \Pi_g = \Sigma_g \oplus \left[\Sigma_g^-\right] \oplus \Delta_g.$$

Σ_g^- appears in square brackets because it is the *anti-symmetric* part of the direct product, whereas $\Sigma_g \oplus \Delta_g$ is the *symmetric* part. Since the total electron wave function must be antisymmetric under exchange of two electrons, the anti-symmetric spatial part combines with the symmetric spin part giving rise to the $^3\Sigma_g^-$ state, whereas the symmetric spatial part combines with the anti-symmetric spin part giving $^1\Sigma_g^+$ and $^1\Delta_g$ states.

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4.3.5 Generalized Pauli principle and allowed states

The simplistic expression of the Pauli principle states that two electrons can not occupy the same spin-orbital. In Section 2.1, we have seen that the wavefunction describing fermions (particle with half integer spin) must be antisymmetric with respect to the permutation of two particles, while the wavefunction describing bosons (particle with integer spin) must be symmetric.

The generalized form of the Pauli principle states that the total wavefunction describing a molecular system must transform under the group operations $\hat{O}_j$ as the irreducible representation whose characters $\chi^{\mathrm{irr}}(\hat{O}_j)$ are given by

$$\chi^{\mathrm{irr}}(\hat{O}_j) = \prod_i^{N_F}(-1)^{P_i(\hat{O}_j)} \tag{4.17}$$

where N_F is the number of types of identical fermions in the system. $P_i(\hat{O}_j)$ is the so-called **parity** of the permutation of the i-th kind of fermions.

If the operation $\hat{O}_j$ applies on bosons, then $\chi^{\mathrm{irr}}(\hat{O}_j) = +1$.

If the operation $\hat{O}_j$ applies on fermions, the parity is "even" (respectively "odd") if $\hat{O}_j$ can be written as an even (resp. odd) number of permutations $(n\,m)$. Therefore, $\chi^{\mathrm{irr}}(\hat{O}_j) = +1$ if the permutation of fermions has an even parity and $\chi^{\mathrm{irr}}(\hat{O}_j) = -1$ if the permutation of

fermions has an odd parity.

_____

Example: the two fermions H^+ in H_2O

The $(1\,2)$ permutation has an odd parity. Hence $\chi^{\mathrm{irr}}(1\,2) = -1$. In the $C_{2\mathrm{v}}$ group, the operation that corresponds to the permutation $(1\,2)$ is C_2^z. Two irreducible representations exhibit $\chi^{\mathrm{irr}}(C_2^z) = -1$: B_1 and B_2.

The total wavefunction of water must transform as B_1 or B_2. In the Born-Oppenheimer approximation, the total wavefunction can be written in the product form $\Psi_{\mathrm{tot}} = \Phi_{\mathrm{el}}\, \Phi_{\mathrm{vib}}\, \Phi_{\mathrm{rot}}\, \Phi_{\mathrm{ns}}\, \Phi_{\mathrm{es}}$ and its symmetry can be determined by the direct product

$$\Gamma_{\mathrm{tot}} = \Gamma_{\mathrm{el}} \otimes \Gamma_{\mathrm{vib}} \otimes \Gamma_{\mathrm{rot}} \otimes \Gamma_{\mathrm{ns}} \otimes \Gamma_{\mathrm{es}} \,.$$

Since $\Gamma_{\mathrm{el}} = A_1$ and $\Gamma_{\mathrm{vib}} = A_1$ in the vibrational and electronic ground state, it imposes $\Gamma_{\mathrm{rot}} \otimes \Gamma_{\mathrm{ns}} = B_{1/2}$. This shows that not all combinations of rotational levels and nuclear spins are allowed.

_____

Example: CO_2 in the $D_{\infty\mathrm{h}}$

In that case, all operations $\hat{O}_j$ apply on bosons only, hence $\chi^{\mathrm{irr}}(\hat{O}_j) = +1$. The total wavefunction $\Phi_{\mathrm{el}}\, \Phi_{\mathrm{vib}}\, \Phi_{\mathrm{rot}}$ should transform as Σ_{g}^+.

The vibronic (vibrational-electronic) ground state: $\Gamma_{\mathrm{el}} = \Sigma_{\mathrm{g}}^+$ and $\Gamma_{\mathrm{vib}} = \Sigma_{\mathrm{g}}^+$.

The rotational wavefunction must transform as Σ_{g}^+.

It can be shown that for the CO_2 molecule in a rigid rotor approximation, the even values of J are associated with rotational wavefunctions of Σ_{g}^+ symmetry, while the odd values of J are associated with rotational wavefunctions of Σ_{u}^+ symmetry. Therefore only half of the rotational levels, with even values of J ($J = 0, 2, 4...$) are allowed in the electronic vibrational ground state.

The antisymmetric CO stretching ν_3 vibrational state: by applying the protocol described in Section 4.3.2, one can find that $\Gamma_{\nu_3} = \Sigma_{\mathrm{u}}^+$. In that case, the rotational wavefunction must transform as Σ_{u}^+. Therefore only half of the rotational levels, with odd values of J ($J = 1, 3, 5...$) are allowed in the ν_3 vibrational state.

Rovibrational transitions $(0\,0\,1) \leftarrow (0\,0\,0)$ fulfil $\Delta J = \pm 1$, which in the spectrum gives rise to a P and an R branches. But every other line is absent compared to the spectrum of CO shown in Figure 3.11 because of the missing states.

It can be shown that for an electronic transition to an electronic state of Π symmetry, this does not hold and all J values are allowed.

_____

4.3.6 Selection rules with group theory

In the dipole approximation, the interaction between molecules and electromagnetic radiation is assumed to only come from the interaction

$$\hat{V} = -\hat{\vec{\mu}}_{\text{lab}} \cdot \vec{E}. \tag{4.18}$$

$\vec{\mu}_{\text{lab}}$ is used here to distinguish the dipole moment of the molecule in the laboratory-fixed frame from $\vec{\mu}$, which is the dipole moment in the molecule-fixed frame as illustrated in Figure 4.18 in the case of the CH_3Cl molecule.
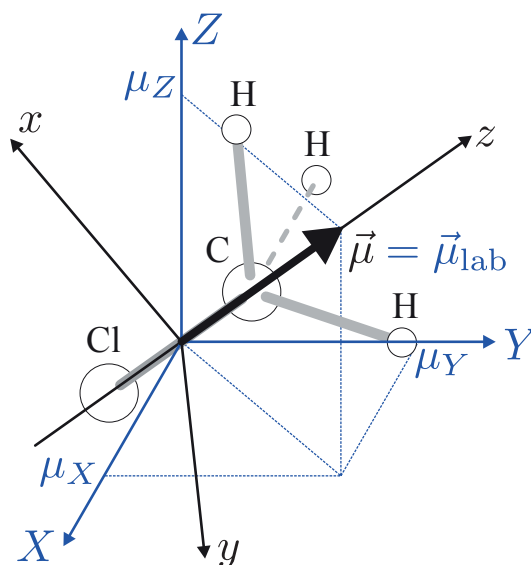

Figure 4.18: Relationship between the expression of the dipole moment $\vec{\mu} = (\mu_x, \mu_y, \mu_z)$, expressed in the molecule-fixed reference frame (x, y, z), and that $\vec{\mu}_{\text{lab}} = (\mu_X, \mu_Y, \mu_Z)$ expressed in the space-fixed (X, Y, Z) reference frame for CH_3Cl; the permanent dipole-moment vector $\vec{\mu}$ lies along the z axis of the molecule-fixed reference frame.

The polarization vector $\vec{E}$ of the radiation is defined in the laboratory-fixed frame (X, Y, Z), whereas the components of $\vec{\mu}$ are defined in the molecule-fixed frame (x, y, z) as follows:

$$\mu_\xi = \sum_{i=1}^{N} q_i \xi_i$$

with $\xi = x, y, z$ and q_i is the charge of particle i. The space-fixed components μ_X, μ_X, and μ_Z of $\vec{\mu}_{\text{lab}}$ vary as the molecule rotates while the molecule-fixed components μ_x, μ_y, and μ_z remain the same.

For a linearly polarized light $\vec{E} = (0, 0, E)$,

$$\hat{V} = -\hat{\mu}_Z E. \tag{4.19}$$

As the intensity of an electric dipole transition between an initial state Ψ_i and a final state Ψ_f is proportional to $\langle \Psi_f | \hat{V} | \Psi_i \rangle$, the selection rule can be written as follows:

$$\langle \Psi_f | \hat{\mu}_Z | \Psi_i \rangle \neq 0. \tag{4.20}$$

The wavefunctions Ψ_i and Ψ_f are expressed in the molecule-fixed frame (x, y, z); for simplicity, the selection rules are usually expressed in terms of μ_x, μ_y, and μ_z instead of μ_X, μ_Y, and μ_Z. Therefore one needs to express μ_X, μ_Y, and μ_Z as functions of μ_x, μ_y, and μ_z $i.e.$ the transformation from the space-fixed frame to the molecule-fixed frame.

The relative orientation of the space-fixed and molecule-fixed coordinate systems is given by the three Euler angles (φ, θ, χ) defined by three successive rotations depicted in Figure 4.19:

1. the rotation around Z by φ which generates the coordinate system (x', y', z') in grey in Figure 4.19

2. the rotation around y' by θ which generates the coordinate system (x'', y'', z'') in red in Figure 4.19

3. the rotation around z'' by χ which generates the coordinate system (x, y, z) in black in Figure 4.19.

The transformation 1 can be written as follows:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \boldsymbol{R_Z}(\varphi) \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} \tag{4.21}$$

The transformation 2 can be written as follows:

$$\begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} = \boldsymbol{R_{y'}}(\theta) \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \tag{4.22}$$

The transformation 3 can be written as follows:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \boldsymbol{R_{z''}}(\chi) \begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} = \begin{pmatrix} \cos\chi & \sin\chi & 0 \\ -\sin\chi & \cos\chi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} \tag{4.23}$$
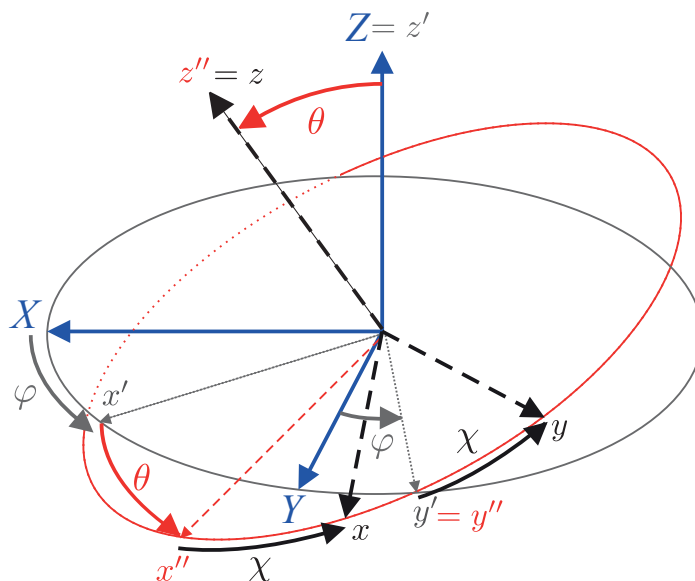
Figure 4.19: Euler angles θ, ϕ, χ defining the relative orientation of the space-fixed reference frame (X, Y, Z) in blue and the molecule-fixed reference frame (x, y, z) in black. Starting from the space-fixed reference frame, the molecule-fixed reference frame is obtained by 1) rotation by an angle φ around the Z axis, leading to the intermediate $(x', y', z'$ in grey) frame; 2) rotation by an angle θ around the y' axis, leading to the second intermediate $(x'', y'', z''$ in red) frame; and 3) rotation by an angle χ around the z'' axis.

Using these three equations, the laboratory- and molecule-fixed frames can be linked by the following transformation:

$$
\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \boldsymbol{R_{z''}}(\chi)\boldsymbol{R_{y'}}(\theta)\boldsymbol{R_Z}(\varphi) \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \tag{4.24}
$$

$$
= \begin{bmatrix} \cos\varphi\cos\theta\cos\chi - \sin\varphi\sin\chi & \sin\varphi\cos\theta\cos\chi + \cos\varphi\sin\chi & -\sin\theta\cos\chi \\ -\cos\varphi\cos\theta\sin\chi - \sin\varphi\cos\chi & -\sin\varphi\cos\theta\sin\chi + \cos\varphi\cos\chi & \sin\theta\sin\chi \\ \cos\varphi\sin\theta & \sin\varphi\sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}
$$

or its inverse

$$
\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \cos\varphi\cos\theta\cos\chi - \sin\varphi\sin\chi & -\cos\varphi\cos\theta\sin\chi - \sin\varphi\cos\chi & \cos\varphi\sin\theta \\ \sin\varphi\cos\theta\cos\chi + \cos\varphi\sin\chi & -\sin\varphi\cos\theta\sin\chi + \cos\varphi\cos\chi & \sin\varphi\sin\theta \\ -\sin\theta\cos\chi & \sin\theta\sin\chi & \cos\theta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}
$$

$$
= \boldsymbol{\lambda} \begin{bmatrix} x \\ y \\ z \end{bmatrix}, \tag{4.25}
$$

where $\boldsymbol{\lambda}$ is the direction cosine matrix. $\boldsymbol{\lambda}$ can thus be used to express the components of a vector in the laboratory-fixed frame as a function of the components of the same vector in the molecule-fixed frame, and especially μ_Z as a function of μ_x, μ_y, and μ_z:

$$
\mu_Z = \lambda_{Zx}\mu_x + \lambda_{Zy}\mu_y + \lambda_{Zz}\mu_z. \tag{4.26}
$$

In the Born-Oppenheimer approximation, the molecular wavefunctions Ψ_{f} and Ψ_{i} are expressed in the product form

$$
\Psi_{\mathrm{f}} = \phi'_{\mathrm{el}}\ \phi'_{\mathrm{vib}}\ \phi'_{\mathrm{rot}}\ \phi'_{\mathrm{nspin}}\ \phi'_{\mathrm{espin}}, \text{ and} \tag{4.27}
$$

$$
\Psi_{\mathrm{i}} = \phi''_{\mathrm{el}}\ \phi''_{\mathrm{vib}}\ \phi''_{\mathrm{rot}}\ \phi''_{\mathrm{nspin}}\ \phi''_{\mathrm{espin}}. \tag{4.28}
$$

The transition moment $\langle \Psi_{\mathrm{f}} | \hat{\mu}_Z | \Psi_{\mathrm{i}} \rangle$ can now be written as follows:

$$
\langle \phi'_{\mathrm{el}}\ \phi'_{\mathrm{vib}}\ \phi'_{\mathrm{rot}}\ \phi'_{\mathrm{nspin}}\ \phi'_{\mathrm{espin}} | \sum_{\alpha} \lambda_{Z\alpha}\ \hat{\mu}_\alpha | \phi''_{\mathrm{el}}\ \phi''_{\mathrm{vib}}\ \phi''_{\mathrm{rot}}\ \phi''_{\mathrm{nspin}}\ \phi''_{\mathrm{espin}} \rangle. \tag{4.29}
$$

Equations (4.20) and (4.29) lead to the selection rules for an electric dipole transition.

Spin conservation upon electric dipole transition

The ϕ_{nspin} functions depend on the nuclear spin variables only, and the ϕ_{espin} functions depend on the electron spin variables only. Their integration in Equation (4.29) can thus be separated:

$$
\langle \phi'_{\mathrm{espin}} | \phi''_{\mathrm{espin}} \rangle \langle \phi'_{\mathrm{nspin}} | \phi''_{\mathrm{nspin}} \rangle \langle \phi'_{\mathrm{el}}\ \phi'_{\mathrm{vib}}\ \phi'_{\mathrm{rot}} | \sum_{\alpha} \lambda_{Z\alpha}\ \hat{\mu}_\alpha | \phi''_{\mathrm{el}}\ \phi''_{\mathrm{vib}}\ \phi''_{\mathrm{rot}} \rangle. \tag{4.30}
$$

Because electron- and nuclear-spin functions are orthogonal, Equation (4.30) vanishes (transition forbidden) unless $\phi'_{\mathrm{espin}} = \phi''_{\mathrm{espin}}$ and $\phi'_{\mathrm{nspin}} = \phi''_{\mathrm{nspin}}$, which bring the selection rules:

- $\Delta S = 0$ **interdiction of intercombination**

- $\Delta I = 0$ **nuclear-spin conservation rule**

Angular momentum selection rules

The remaining rovibronic (rotational-vibrational-electronic) transition moment in Equation (4.30) $\langle \phi'_{\text{el}} \ \phi'_{\text{vib}} \ \phi'_{\text{rot}} | \sum_\alpha \lambda_{Z\alpha} \ \mu_\alpha | \phi''_{\text{el}} \ \phi''_{\text{vib}} \ \phi''_{\text{rot}} \rangle$ can be further simplified.

A rotation of the molecule in space leads to a change of the Euler angles, and the rotational wave-functions $\phi_{\text{rot}}(\varphi, \theta, \chi)$ are expressed in the space-fixed frame as a function of these angles, while the functions ϕ_{el}, ϕ_{vib} and μ_α do not depend on the Euler angles: $\phi_{\text{el}}(q_i, Q)$, $\phi_{\text{vib}}(Q)$, $\mu_\alpha(q_i, Q)$. The direction cosine elements $\lambda_{Z\alpha}$ and ϕ_{rot} only depend on φ, θ, χ and the integration can be further separated in an integral over angular variables and an integral over electronic coordinates and normal modes:

$$\sum_\alpha \langle \phi'_{\text{rot}} | \lambda_{Z\alpha} | \phi''_{\text{rot}} \rangle \langle \phi'_{\text{el}} \phi'_{\text{vib}} | \hat{\mu}_\alpha | \phi''_{\text{el}} \phi''_{\text{vib}} \rangle. \tag{4.31}$$

The integral $\langle \phi'_{\text{rot}} | \lambda_{Z\alpha} | \phi''_{\text{rot}} \rangle$ leads to angular momentum selection rules:

- $\Delta J = 0, \pm 1; \ 0 \nleftrightarrow 0$ **angular momentum conservation** (see also Chapter 2)

The projection quantum number M of J on the Z axis leads to further selection rules:

- if the polarization is along the Z axis, then $\Delta M = 0$

- if the polarization is along the X or Y axis, then $\Delta M = \pm 1$

Finally,

- if the dipole moment lies on the z axis, the transition is said **parallel** and $\Delta \Lambda = 0$ for diatomic molecules

- if the dipole moment lies on the x or y axis, the transition is said **perpendicular** and $\Delta \Lambda = \pm 1$ for diatomic molecules

Further selection rules

The integral $\langle \phi'_{\text{el}} \ \phi'_{\text{vib}} | \hat{\mu}_\alpha | \phi''_{\text{el}} \ \phi''_{\text{vib}} \rangle$ of Equation (4.31) represents a selection rule for transitions between electronic and vibrational levels. Depending of the type of transitions investigated, its evaluation can be simplified using the **vanishing integral theorem** and group theory: this theorem states that the product $\langle \Psi_2 | \hat{O} | \Psi_1 \rangle$ vanishes if the product of the symmetry representation of Ψ_2^*, $\hat{O}$ and Ψ_1 does not contain the totally symmetric irreducible representation $\Gamma_{\text{irr}}^{(\text{sym})}$ of the group, *i.e.*

$$\langle \Psi_2 | \hat{O} | \Psi_1 \rangle \neq 0 \Rightarrow \Gamma(\Psi_2^*) \otimes \Gamma(\hat{O}) \otimes \Gamma(\Psi_1) \supset \Gamma_{\text{irr}}^{(\text{sym})} \tag{4.32}$$

This theorem will be used in three cases in the following.

Rotational spectroscopy: $\phi'_{\text{el}} = \phi''_{\text{el}}$, $\phi'_{\text{vib}} = \phi''_{\text{vib}}$
The integral $\langle \phi'_{\text{el}} \ \phi'_{\text{vib}} | \hat{\mu}_\alpha | \phi''_{\text{el}} \ \phi''_{\text{vib}} \rangle$ of Equation (4.31) represents the expectation value of $\hat{\mu}_\alpha$. Transitions are only allowed for molecules with a *permanent* dipole moment. The angular momentum selection rules are as above.

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Vibrational spectroscopy: $\phi'_{\text{el}} = \phi''_{\text{el}}$, $\phi'_{\text{vib}} \neq \phi''_{\text{vib}}$

Since, in the BO approximation, only ϕ_{el} and μ_α depend on electron coordinates q_i, the integration over q_i can be done first:

$$\langle \phi'_{\text{vib}}(Q)| \underbrace{\langle \phi'_{\text{el}}(Q, q_i)|\hat{\mu}_\alpha(Q, q_i)|\phi''_{\text{el}}(Q, q_i)\rangle_{q_i}}_{\hat{\mu}_{\text{el},\alpha}(Q)} |\phi''_{\text{vib}}(Q)\rangle_Q = \langle \phi'_{\text{vib}}(Q)|\hat{\mu}_{\text{el},\alpha}(Q)|\phi''_{\text{vib}}(Q)\rangle. \qquad (4.33)$$

Whether Equation (4.33) vanishes or not, can be determined using the vanishing integral theorem. Therefore the transition is allowed if

$$\Gamma'_{\text{vib}} \otimes \Gamma_\alpha \otimes \Gamma''_{\text{vib}} \supset \Gamma^{(\text{sym})}_{\text{irr}}, \qquad (4.34)$$

where Γ_α $(\alpha = x, y, z)$ transforms as the components of a vector and thus as α.

—————————————————————————

Example: the case of H_2O

The vibrational ground state $\phi''_{\text{vib}} = (0,0,0)$ has the symmetry $\Gamma''_{\text{vib}} = A_1$

The components of the dipole moment have the symmetries $\Gamma_{\mu_x} = B_1$, $\Gamma_{\mu_y} = B_2$, and $\Gamma_{\mu_z} = A_1$.

The vibrational state $\phi'_{\text{vib}} = (1,0,0)$ has the symmetry $\Gamma'_{\text{vib}} = A_1$.

$$\Gamma'_{\text{vib}} \otimes \Gamma_\alpha \otimes \Gamma''_{\text{vib}} = A_1 \otimes \left\{ \begin{array}{c} B_1 \\ B_2 \\ A_1 \end{array} \right\} \otimes A_1 = \left\{ \begin{array}{c} B_1 \\ B_2 \\ A_1 \end{array} \right\}$$

The allowed vibrational transition originates from the z component of the transition dipole moment.

The vibrational $\phi'_{\text{vib}} = (0,0,1)$ has the symmetry $\Gamma'_{\text{vib}} = B_2$.

$$B_2 \otimes \left\{ \begin{array}{c} B_1 \\ B_2 \\ A_1 \end{array} \right\} \otimes A_1 = \left\{ \begin{array}{c} A_2 \\ A_1 \\ B_2 \end{array} \right\}$$

The allowed vibrational transition originates here from the y component of the transition dipole moment. The component of the permanent dipole moment along the y axis is zero in H_2O. Nevertheless a transition can be observed. The condition for a vibrational transition to be observable is that a *change* of the dipole moment must occur when exciting the vibration. This is obviously the case when the antisymmetric stretching mode is excited in H_2O.

One can show that transitions to all vibrational levels are allowed by symmetry in H_2O. However, overtones are weaker than fundamental excitations as discussed in the case of diatomic molecules in Section 3.5.1.

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Electronic spectroscopy: $\phi'_{el} \neq \phi''_{el}$

The left hand side of Equation (4.33) can be written as

$$\langle \phi'_{vib}(Q) | \underbrace{\langle \phi'_{el}(Q, q_i) | \hat{\mu}_\alpha(Q, q_i) | \phi''_{el}(Q, q_i) \rangle_{q_i}}_{\mu^{fi}_{el,\alpha}} | \phi''_{vib}(Q) \rangle_Q, \qquad (4.35)$$

where the inner integral represents an electronic transition moment $\mu^{fi}_{el,\alpha}$ obtained by integration over the electronic coordinates.

A transition is *electronically allowed* when $\mu^{fi}_{el,\alpha} \neq 0$, which is fulfilled if

$$\Gamma'_{el} \otimes \Gamma_\alpha \otimes \Gamma''_{el} \supset \Gamma^{(sym)}_{irr}. \qquad (4.36)$$

––

Example: the case of H_2O

The electronic ground state is $\tilde{X}\ ^1A_1$

$$\Gamma'_{el} \otimes \Gamma_\alpha \otimes \Gamma''_{el} = \left\{ \begin{array}{c} B_1 \\ B_2 \\ A_1 \end{array} \right\} \otimes \left\{ \begin{array}{c} B_1 \\ B_2 \\ A_1 \end{array} \right\} \otimes A_1 = \left\{ \begin{array}{c} A_1 \\ A_1 \\ A_1 \end{array} \right\}$$

Electric dipole transitions to electronic states of B_1, B_2 and A_1 symmetry are electronically allowed and transitions to electronic states of A_2 symmetry are electronically forbidden in H_2O.

––

If one assumes that the transition moment function $\mu^{fi}_{el,\alpha}(Q)$ varies slowly with Q, then $\mu^{fi}_{el,\alpha}(Q)$ can be described by a Taylor series and one can in good approximation neglect higher terms:

$$\mu^{fi}_{el,\alpha}(Q) = \left(\mu^{fi}_{el,\alpha} \right)_{eq} + \sum_{j}^{3N-6} \left(\frac{\partial \mu^{fi}_{el,\alpha}}{\partial Q_j} \right)_{eq} Q_j + ... \qquad (4.37)$$

In electronically allowed transitions the first term in Equation (4.37) is often the dominant one and the transition moment (Equation (4.35)) becomes:

$$\langle \phi'_{vib}(Q) | \phi''_{vib}(Q) \rangle \left(\mu^{fi}_{el,\alpha} \right)_{eq}. \qquad (4.38)$$

The intensity of a transition is proportional to the square of the transition moment and thus,

$$I \propto \left| \langle \phi'_{vib}(Q) | \phi''_{vib}(Q) \rangle \right|^2. \qquad (4.39)$$

$\left| \langle \phi'_{vib}(Q) | \phi''_{vib}(Q) \rangle \right|^2$ is called a **Franck-Condon factor** and represents the square of the overlap of the vibrational wavefunctions. Equation (4.39) implies the vibrational selection rule for electronically allowed transitions:

$$\Gamma'_{vib} \otimes \Gamma''_{vib} \supset \Gamma^{(sym)}_{irr}. \qquad (4.40)$$

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Example: H_2O $\tilde{X}\,^1A_1(0,0,0) \rightarrow H_2O$ $\tilde{C}\,^1B_1$

$\Gamma''_{\text{vib}} = A_1 \Rightarrow \Gamma'_{\text{vib}} \overset{!}{=} A_1$

Only the symmetric stretching mode ν_1 and the bending mode ν_2 can be excited. The asymmetric stretching mode ν_3 of B_2 symmetry can only be excited if v_3 is even.

———————————————————————————

Electronically forbidden transitions can become weakly allowed if the electronic and vibrational degrees of freedom cannot be separated as in Equation (4.35). The condition for them to be weakly observable is that

$$\underbrace{\Gamma'_{\text{vib}} \otimes \Gamma'_{\text{el}}}_{\Gamma'_{\text{ev}}} \otimes \Gamma_\alpha \otimes \underbrace{\Gamma''_{\text{vib}} \otimes \Gamma''_{\text{el}}}_{\Gamma''_{\text{ev}}} \supset A_1. \tag{4.41}$$

———————————————————————————

Example:

Transitions from H_2O $\tilde{X}\,^1A_1$ (0,0,0) to electronically excited states of A_2 symmetry (electronically forbidden) may become weakly allowed (vibronically allowed) if a non totally symmetric mode is excited.

$\tilde{X}\,^1A_1$ (0,0,0): $\Gamma''_{\text{el}} = A_1$, $\Gamma''_{\text{vib}} = A_1$, $\Gamma''_{\text{ev}} = A_1 \otimes A_1 = A_1$

A_2 (0,0,1): $\Gamma'_{\text{el}} = A_2$, $\Gamma'_{\text{vib}} = B_2$, $\Gamma'_{\text{ev}} = A_2 \otimes B_2 = B_1$

$$\Gamma'_{\text{ev}} \otimes \Gamma_\alpha \otimes \Gamma''_{\text{ev}} = B_1 \otimes \left\{ \begin{array}{c} B_1 \\ B_2 \\ A_1 \end{array} \right\} \otimes A_1 = \left\{ \begin{array}{c} A_1 \\ A_2 \\ B_1 \end{array} \right\}$$

The vibronically allowed transition originates from μ_x.

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