Symmetry and Spectroscopy

The process of spectroscopic investigation using the interaction of matter with the electromagnetic wave can be described in terms of time dependent perturbation theory:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t) \qquad (1)$$

$\mathcal{H}_0$: characterizes the process to be investigated in matter: in the simplest case describable by solutions to the Schrödinger equation in terms of eigenfunctions and eigenstates; in the more general case approximated by a wavefunction $|\Psi(t)>$ described as a superpositions of eigenstates $|n>$

$$|\Psi(t)> = \sum_n a_n(t)|n(t)> \qquad (2)$$

$\mathcal{H}_1(t)$: interaction of the electromagnetic wave with the relevant probe in the material
NMR, EPR: oscillating magnetic field component B(t) interacting with the nuclear magnetic dipole moment
Other spectroscopies: oscillating electric field component E(t) interacting with the (permanent or induced) electric dipole moment.

$$\mathcal{H}_1(t) = -\mu E(t) = -qr\, E_o \exp(i\omega t - kr) \qquad (3)$$

The time-dependent Schrödinger equation then states

$$\mathcal{H}|\Psi(t)> = i\hbar \frac{d}{dt} |\Psi(t)> \qquad (4)$$

Applying this expression to (1) we get

$$\frac{d}{dt}|\Psi(t)> = \sum_n \frac{d}{dt}a_n(t)\,(|n(t)>) + \sum_n an(t)\,\frac{d}{dt}(|n(t)>) \quad (5)$$

change in mixing coefficients — oscillation of eigenstates

Insertion of (1), (2), and (5) into (4) results in

$$\mathcal{H}_0\sum_n a_n(t)|n(t)> + \mathcal{H}_1\sum_n a_n(t)|n(t)> = i\hbar\sum_n \frac{d}{dt}a_n(t)\,(|n(t)>) + i\hbar\sum_n an(t)\,\frac{d}{dt}(|n(t)>) \quad (6)$$

If the perturbation is absent, ($\mathcal{H}_1 = 0$) we have

$$\mathcal{H}_0\sum_n a_n(t)|n(t)> = i\hbar\sum_n an(t)\,\frac{d}{dt}(|n(t)>) \quad (7)$$

which is the Schrödinger equation itself for the unperturbed system

Subtracting (7) from (6) we get:

$\mathcal{H}_1\sum_n a_n(t)|n(t)> = i\hbar\sum_n \frac{d}{dt}a_n(t)\,(|n(t)>)$ (8). Multiplying with <m|, an eigenbra of $\mathcal{H}_0$, we see that

$\sum_n a_n(t)<m|\mathcal{H}_1|n> = i\hbar\sum_n \frac{d}{dt}a_n(t)\,(<m|n>)$ (9) . Respecting orthogonality we find

$$\frac{d}{dt}a_m(t) = -\frac{i}{\hbar}\sum_n a_n(t)<m|\mathcal{H}_1|n> \quad (10)$$

The summation term in expression (10) implies that to assess the change of the weighting factor with which state |m> contributes to the wave function we need to consider all possible transitions from |m> to the other eigenstates |n>, |o>, |p> etc. Focusing on one particular transition |m> -> |n> only, the transition probability W_{mn} can be identified with the squared rate of change of the mixing coefficients:

$W_{mn} = |\frac{d}{dt}a_m(t)|^2 = |<m|\mathcal{H}_1|n>|^2$ (11)

where the symbol $|\ldots|^2$ denotes that the complex square must be formed as $<m|\mathcal{H}_1|n>$ is typically a complex number.

Expression (11) states that the Hamiltonian H_1 connects the states |m> and |n> causing a spectroscopic transition between both states. $<m|\mathcal{H}_1|n>|$ is an expectation value describing the efficiency of this process (transition probability)

For most spectroscopies we can further simplify $\mathcal{H}_1(t) = -\mu E(t) = -qr\,E_o\exp(i\omega t - kr) \approx -qr\,E_o\exp(i\omega t)$ as the wavelength λ is usually much larger than the atomic dimension of dipole moment so that its oscillatory character in space can be neglected

With this, we arrive at an expression for the transition moment integral

$|<m|\mathcal{H}_1|n>|^2 = |\int_{-\infty}^{\infty} \Psi^*_m\, q\, r\, E_o\exp(i\omega t)\, \Psi_n dV|^2$ (12)

Expression (12) contains the scalar product of two vectors, r and E, which can be written in terms of the Cartesian components

$r \cdot E = xEx + yEy + zEz.$

Thus we can write

$W_{mn} \sim |<m|H_1|n>|^2 \sim \sim |<m|x|n>|^2$,
$|<m|y|n>|^2$, and
$|<m|z|n>|^2$

The integrand is typically a superposition of a function that is symmetric (f(x) = f(-x)) and one that is antisymmetric (f(x) = -f(-x) with regard to coordinate inversion.
As the transition moment integrals extend from -∞ to + ∞ they can only be different from zero if they contain a part that is totally symmetric.

To make this judgement we need to apply concepts of group theory. Specifically we need to find out if there is a part of the transition moment integral that remains unchanged for all of the symmetry operations that transform the molecule into itself.

Thus, we need to develop concepts on how to characterize symmetry and how to use symmetry arguments in a quantitative way to make the above assessment.
Group theory provides us with the mathematical tools to do just that.

To develop these ideas, we first need to take a closer look at the concept of **symmetry**

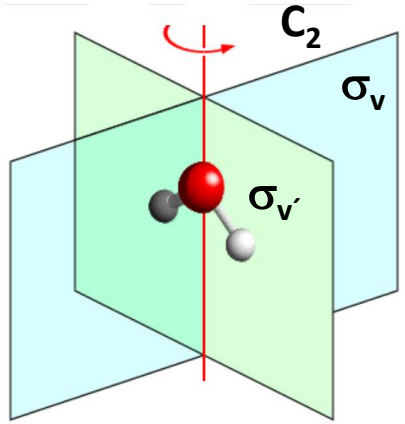
Description of molecular symmetry

Defined in terms of **symmetry operations**

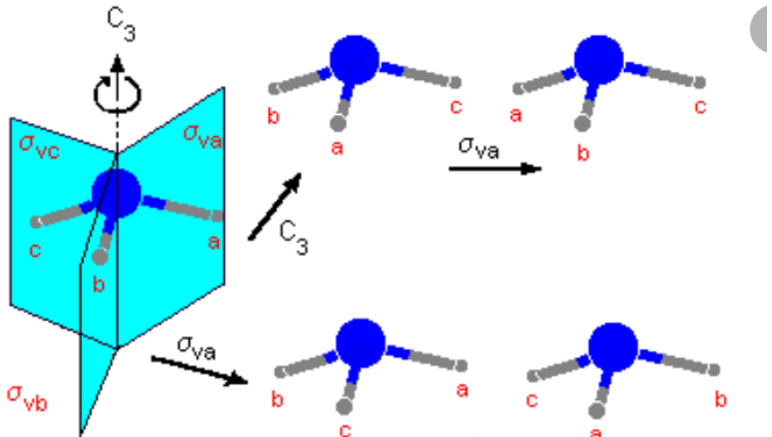
A symmetry operation is a process in which an object (such as a molecule) is moved in such a way that an identical picture of the object results. There are five principal types

Identity E	do nothing or a 360° rotation
Rotation C_n	about an axis by angle ϕ, where n = 360°/ ϕ
Reflection σ	by a plane
Inversion i	by a point.
Improper rotation S_n	rotation followed by reflection about a plane orthogonal to the rotation axis

For any molecule we can identify the set of symmetry operations it has, for example,



H_2O: C_{2v}
Set of symmetry operations:
E, C_2, σ_v, σ'_v



NH_3: C_{3v}
Set of symmetry operations:
E, C_3, C_3^2 , σ_v, σ'_v, σ''_v

The set of symmetry operations characterizing a molecule fulfills all the mathematical criteria of a group

Groups

Definition

A group $\langle G, \otimes \rangle$ is a set G, closed under a binary operation $\otimes$, such that the following axioms are satisfied:

1) Associativity of $\otimes$:

   For all a, b, c $\in$ G, we have $(a \otimes b) \otimes c = a \otimes (b \otimes c)$.

2) Identity element e for $\otimes$:

   There is an element e in G such that for all x $\in$ G, $e \otimes x = x \otimes e = x$

3) Inverse a' of a:

   For each a $\in$ G, there is an element a' in G such that

   $a \otimes a' = a' \otimes a = e$.

Any combination of two symmetry operations produces another symmetry operation belonging to the same set.
For example in the case of H_2O: $C_2 \otimes C_2 = E$, $C_2 \otimes \sigma_v = \sigma'_v$.
These relationships are summarized in the multiplication tables. The number of elements in the group is called the order of a group, h. A group may or may not contain sub-groups which by themselves satisfy the criteria of a group

Multiplication Tables

C_{2v}

	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}_v'$	$\hat{\sigma}_v$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}_v'$	$\hat{\sigma}_v'$	$\hat{\sigma}_v$	$\hat{C}_2$	$\hat{E}$

commutative

C_{3v}

	First operation					
Second operation	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$	$\hat{\sigma}_v''$
$\hat{E}$	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$	$\hat{\sigma}_v''$
$\hat{C}_3$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{E}$	$\hat{\sigma}_v'$	$\hat{\sigma}_v''$	$\hat{\sigma}_v$
$\hat{C}_3^2$	$\hat{C}_3^2$	$\hat{E}$	$\hat{C}_3$	$\hat{\sigma}_v''$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}_v''$	$\hat{\sigma}_v'$	$\hat{E}$	$\hat{C}_3^2$	$\hat{C}_3$
$\hat{\sigma}_v'$	$\hat{\sigma}_v'$	$\hat{\sigma}_v$	$\hat{\sigma}_v''$	$\hat{C}_3$	$\hat{E}$	$\hat{C}_3^2$
$\hat{\sigma}_v''$	$\hat{\sigma}_v''$	$\hat{\sigma}_v'$	$\hat{\sigma}_v$	$\hat{C}_3^2$	$\hat{C}_3$	$\hat{E}$

non-commutative

Note that group operations are not required to be commutative.

The algorithm of combining symmetry elements is matrix multiplication.

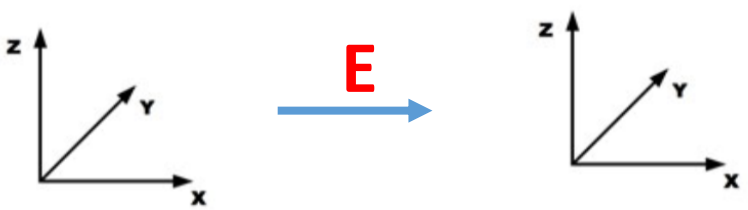
Examples:

Cartesian basis — 3×3 matrices

Molecular basis — 3N×3N matrices (N = number of atoms per molecule)

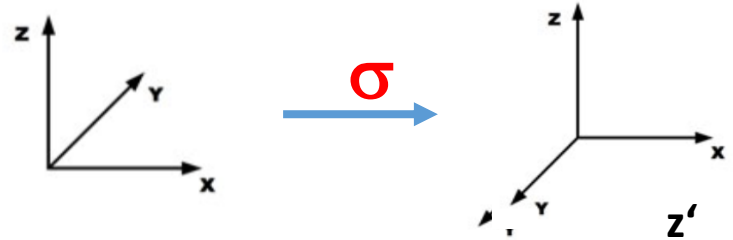
Wave vector basis — (2J+1)×(2J+1) matrices (J = angular momentum quantum number

S =1/2: 2x2 matrices: L =2 (d-orbitals): 5x5 matrices



E

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

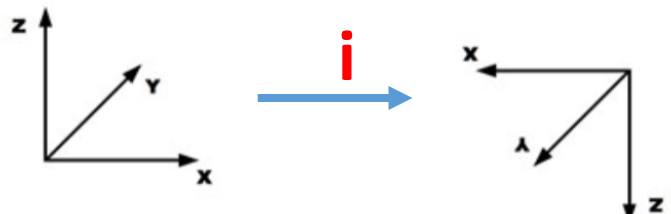


σ

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

C_2

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$



i

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}$$

General rotation matrices

Counterclockwise

$$R_x(\theta) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{bmatrix}$$

$$R_y(\theta) = \begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix}$$

$$R_z(\theta) = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

clockwise

$$R_x(\phi) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & \sin\phi \\ 0 & -\sin\phi & \cos\phi \end{pmatrix}$$

$$R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix}$$

$$R_z(\psi) = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Some common point groups

C_1: E

C_{2v}: E, C_2, σ_v, σ'_v

C_{2h}: E, C_2, σ_h, i

C_{3v}: E,C_3,C_3^2, σ_v, σ'_v σ''_v

D_{3h}: E,C_3, C_3^2, $3C_2$, σ_h

T_d: E, $4C_3$,$4C_3^2$, $3C_2$, $3S_4$,$3S_4^3$, $6\sigma_d$

O_h: E, $4C_3$,$4C_3^2$, $6C_2$, $3C_2$, $3S_4$, $3S_4^3$, $3C_2$,$3C_4$,$3C_4^3$, $4S_6$, $4S_6^5$,i,$3\sigma_h$,$6\sigma_d$

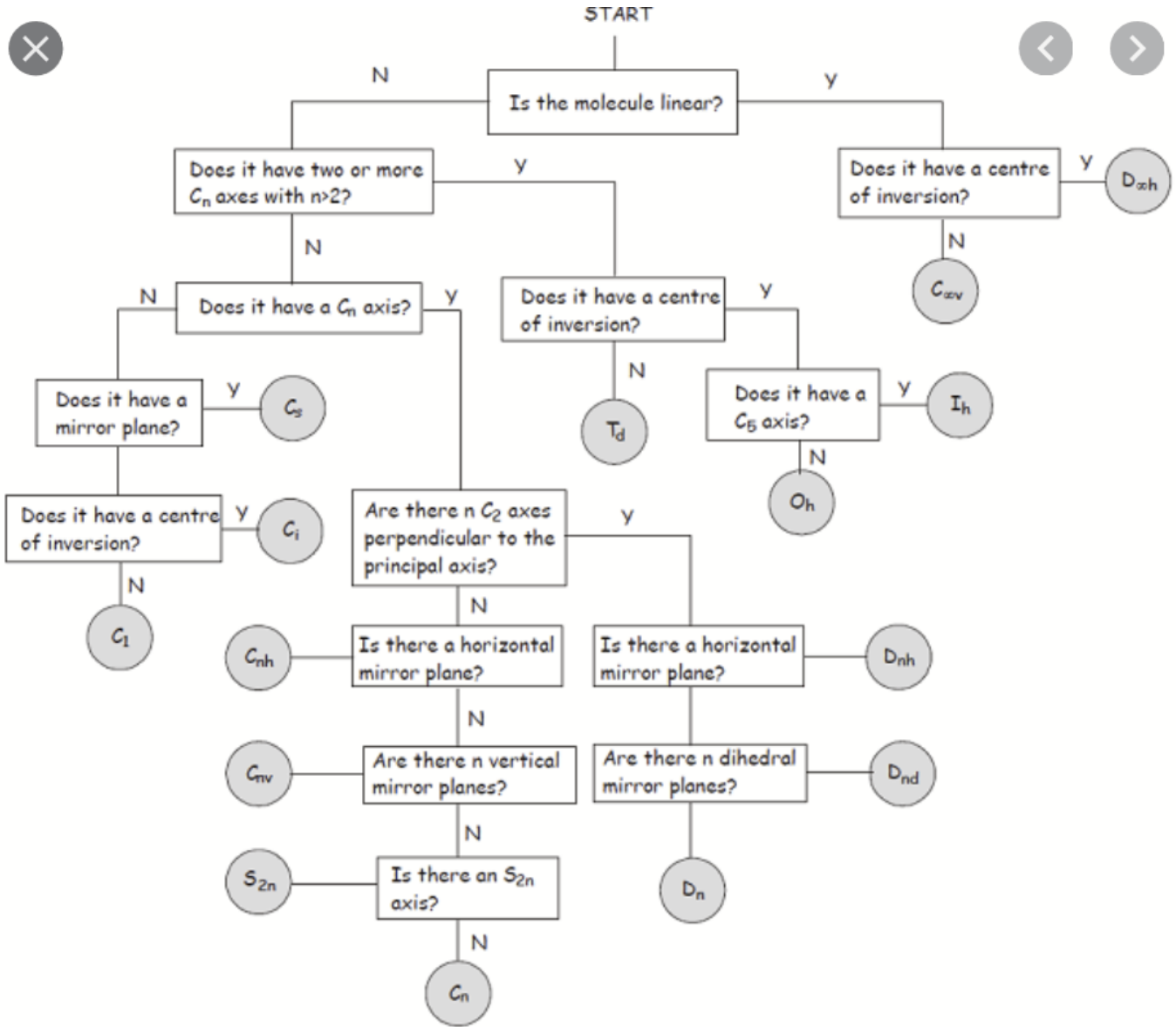
σ_v: vertical mirror plane $||C_n$

σ_h: horizontal mirror plane $\perp C_n$

σ_d: diagonal mirror plane

D_n: there are n $C_2 \perp C_n$

Flow chart for point group determination



Classes in Group theory

The elements of a group can be divided into various **classes.** The number of classes is of Interest in group theory in order to find out the number of irreducible representations (see later).

Definition: Elements that are transformed into each other by the similarity transform **$X^{-1}AX$ with X being the transformation matrix of any symmetry operation in the group and X^{-1} the inverse operation of X)** belong the same class. To find out into how many classes the elements of a group can be divided we have to do the similarity transform using all the elements of the group.

1. Example: C_{2v}, h = 4: here each element is its own inverse. Application of the similarity transform changes every element into itself. Thus each element forms its own class and there are four classes.
2. Example: C_{3v}, h = 6: Operations C_3 and C_3^2 belong to the same class. The three reflections σ_v, σ_v', and σ_v'' belong to the same class. E forms its own class. There are 3 classes.

Theory of group representations

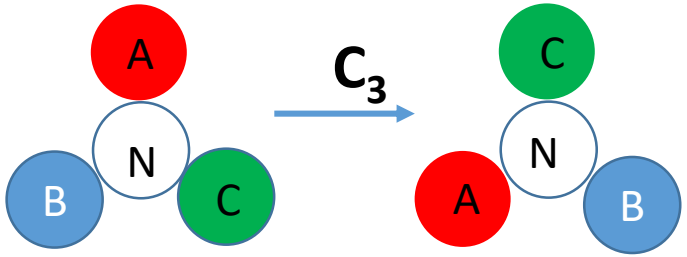
The complete set of matrices describing the symmetry operation of a particular symmetry group is called a representation of a group. The number of such representations is generally infinite, considering there are an infinite number of possible similarity transforms.

The dimensionality of the representation is defined by the basis. In the simple Cartesian basis the representation consists of a set of 3x3 matrices. We may opt for different bases, for example those that are constructed from wave functions. A simple example for the group C_{3v} (NH_3 molecule) is the set of four s-electron wavefunctions. This then leads to six 4x4 matrices. This basis may be described by the line vector

(s_N, s_A, s_B, s_C)

In this basis a symmetry operation such as C_3 is represented by a non-diagonal matrix, fulfilling the operation

$$(s_N, s_A, s_B, s_C) \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} = (s_N, s_B, s_C, s_A)$$



Change of basis:

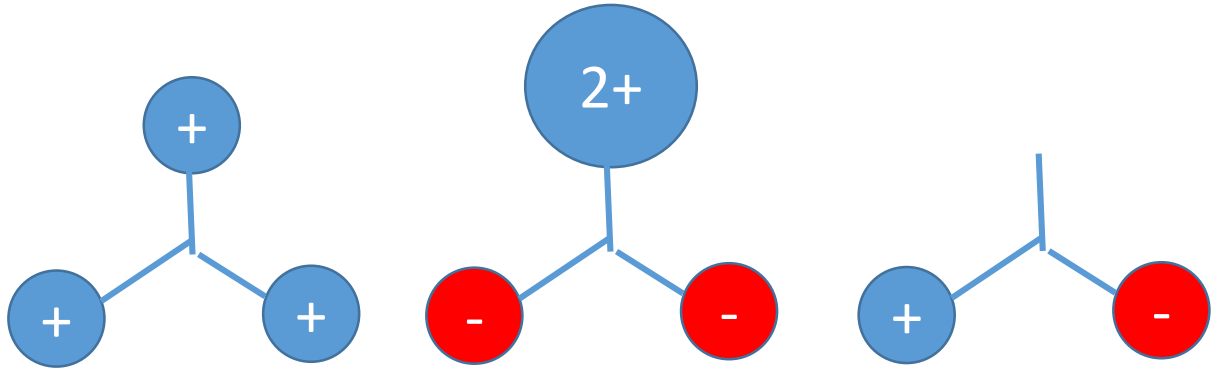
instead of the the individual s orbital we can also choose linear combinations:

(s_N, s_1, s_2, s_3) with the following properties:

$s_1 = s_A + s_B + s_C$

$s_2 = 2s_A - s_B - s_C$

$s_3 = s_B - s_C$



The transformation from the old basis to the new basis can be described by a matrix. The linear combination chosen here might seem arbitrary at first, but it will soon become evident why it is a good choice.

The matrix needed to effect this change ob basis is given by the matrix expression below:

Old vector f Matrix c new vector f'

$$(s_N, s_A, s_B, s_C) \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 2 & 0 \\ 0 & 1 & -1 & 1 \\ 0 & 1 & -1 & -1 \end{bmatrix} = (s_N, s_1, s_2, s_3)$$

$$f' = f\,c$$

$$f_i' = \sum_j f_j c_{ji}$$

Multiplication table of group C_{3v} and three reducible representations

Table 7.2 The C_{3v} group multiplication table

First	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
Second						
E	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
C_3^+	C_3^+	C_3^-	E	σ_v'	σ_v''	σ_v
C_3^-	C_3^-	E	C_3^+	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^-	C_3^+
σ_v'	σ_v'	σ_v	σ_v''	C_3^+	E	C_3^-
σ_v''	σ_v''	σ_v'	σ_v	C_3^-	C_3^+	E

Table 7.3 The matrix representation of C_{3v} in the basis (s_N, s_A, s_B, s_C)

$\mathbf{D}(E)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$\chi(E) = 4$

$\mathbf{D}(C_3^+)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$\chi(C_3^+) = 1$

$\mathbf{D}(C_3^-)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

$\chi(C_3^-) = 1$

$\mathbf{D}(\sigma_v)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$\chi(\sigma_v) = 2$

$\mathbf{D}(\sigma_v')$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$\chi(\sigma_v') = 2$

$\mathbf{D}(\sigma_v'')$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

$\chi(\sigma_v'') = 2$

Table 7.4 The matrix representation of C_{3v} in the basis (s_N, s_1, s_2, s_3)

$\mathbf{D}(E)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$\chi(E) = 4$

$\mathbf{D}(C_3^+)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & \frac{3}{2} & -\frac{1}{2} \end{bmatrix}$$

$\chi(C_3^+) = 1$

$\mathbf{D}(C_3^-)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & -\frac{3}{2} & -\frac{1}{2} \end{bmatrix}$$

$\chi(C_3^-) = 1$

$\mathbf{D}(\sigma_v)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

$\chi(\sigma_v) = 2$

$\mathbf{D}(\sigma_v')$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & \frac{3}{2} & \frac{1}{2} \end{bmatrix}$$

$\chi(\sigma_v') = 2$

$\mathbf{D}(\sigma_v'')$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & -\frac{3}{2} & \frac{1}{2} \end{bmatrix}$$

$\chi(\sigma_v'') = 2$

Table 7.6 The matrix representation of C_{3v} in the basis (x, y, z)

$\mathbf{D}(E)$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\chi(E) = 3$

$\mathbf{D}(C_3^+)$

$$\begin{bmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\chi(C_3^-) = 0$

$\mathbf{D}(C_3^-)$

$$\begin{bmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\chi(C_3^+) = 0$

$\mathbf{D}(\sigma_v)$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\chi(\sigma_v) = 1$

$\mathbf{D}(\sigma_v')$

$$\begin{bmatrix} \frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\chi(\sigma_v') = 1$

$\mathbf{D}(\sigma_v'')$

$$\begin{bmatrix} \frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\chi(\sigma_v'') = 1$

Symmetry –Operations after Basis Change:

How does the change in basis affect the matrices describing the symmetry operations ? We characterize the symmetry operation by the symbol $\mathcal{R}$ and the corresponding matrix $\mathcal{D}(\mathcal{R})$ with the elements $D_{ki}(R)$. We have:

$\mathcal{R}f_i = \sum_k f_k D_{ki}(R)$ **in the old basis**

$\mathcal{R}f'_i = \sum_k f'_k D'_{ki}(R)$ **in the new basis**

$$\mathcal{R}f = f\,\mathcal{D}(\mathcal{R})$$
$$\mathcal{R}f' = f'\mathcal{D}'(\mathcal{R})$$

$$\mathcal{R}f' = f'\mathcal{D}'(\mathcal{R}) \quad \Leftrightarrow \quad \mathcal{R}fc = fc\mathcal{D}'(\mathcal{R})$$
$$\mathcal{R}fcc^{-1} = fc\mathcal{D}'(\mathcal{R})\,c^{-1} \quad \Leftrightarrow \quad \mathcal{R}f = fc\mathcal{D}'(\mathcal{R})\,c^{-1}$$
$$f\,\mathcal{D}(\mathcal{R}) = fc\mathcal{D}'(\mathcal{R})\,c^{-1} \quad \Leftrightarrow \quad \mathcal{D}(\mathcal{R}) = c\mathcal{D}'(\mathcal{R})\,c^{-1}$$

$$\mathcal{D}'(\mathcal{R}) = c^{-1}\mathcal{D}(\mathcal{R})c$$

Thus, we need to perform a similarity transform using the matrix with which f' is generated from f

Example

$$\mathcal{D}'(C_3) = c^{-1}\mathcal{D}(C_3)c$$

$$\mathcal{D}'(C_3) = \frac{1}{6}\begin{bmatrix} 6 & 0 & 0 & 0 \\ 0 & 2 & 2 & 2 \\ 0 & 2 & -1 & -1 \\ 0 & 0 & -3 & -3 \end{bmatrix}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 2 & 0 \\ 0 & 1 & -1 & 1 \\ 0 & 1 & -1 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1/2 & -1/2 \\ 0 & 0 & 3/2 & -1/2 \end{bmatrix}$$

Block-diagonal form

Irreducible representations:

Special consequence of block-diagonality: each block by itself satisfies the group multiplication table. Instead of six 4x4 matrices we are now dealing with two times six 1x1 matrices and one time six 2x2 matrices. This process has resulted in a reduced representation. A representation with the smallest dimensionality, which cannot be reduced further, is called the **irreducible representation**. It has a particular significance in group theory. In practice we don't need to know the form of these matrices, it suffices to know their trace, also known as the **character: Value +1: the representation is symmetric with respect to the symmetry operation. Value -1: the representation is anti-symmetric with respect to the symmetry operation**

Classification and terminology of representations:

A: one-dimensional, symmetric with respect to the highest C_n
B: one-dimensional, anti-symmetric with respect to the highest C_n
E: two-dimensional
T: three-dimensional

Sub_1: symmetric with respect to the next highest C_n or σ
Sub_2: antisymmetric with with respect to the next highest C_n or σ
Super_' symmetric with respect to reflection
Super_'' antisymmetric with respect to reflection
g: symmetric with respect to inversion (*gerade*)
u: antisymmetric with respect to inversion (*ungerade*).

Classification with respect to degeneracy and symmetry properties in relation to the symmetry operations of the group

The basis that leads to the irreducible representation is called the **symmetry-adapted basis.** In the NH_3 example chosen this is **(s_N, s_1, s_2, s_3).** In this problem we found two times the representation **A_1** and one time the representation **E**:

Applications in Spectroscopy

The mathematical formalism of group theory can be used for numerous practical applications in spectroscopy. Topics that can be solved include the following:

1) Symmetry character of the 3N-6 normal vibrational modes of a molecule: **FTIR/Raman**
2) Identify and classify electronic configurations with different symmetries/energies: **UV/Vis**
3) Based on the symmetry character it is possible to decide whether a spectroscopic transition is allowed or not
   - IR absorption spectroscopy: „*the dipole moment must change during the course of the atomic movement*“
   - Raman spectroscopy: „*the molecular polarizability must change during the course of the atomic movement*“
   - Electronic spectroscopy: *change in angular momentum quantum number.* **Selection rules.**
   - Group theory helps to **understand these rules** and to develop **quantitative criteria** for their application.

Task: Based on the molecular symmetry group find and identify the irreducible representations defining the problem

1. **Which irreducible representations are possible within a given group ?**
2. **Which of those occur in the spectroscopic problem considered ?**
3. **Does the irreducible representation of** $W_{mn} \sim |\langle m|H_1|n\rangle|^2$ **contain a totally symmetric part ?**
   Type A_1, A‘, A_{1g}

1 **Answers from the Great Orthogonality Theorem (GOT) of Group Theory**

$$\sum_R \mathrm{D}_{ij}^{(l)}(R)\mathrm{D}_{i'j'}^{(l')}(R) = \frac{h}{d_l}\,\delta_{ii'}\delta_{jj'}\delta_{ll'}$$

h = order of the group

l, l‘ = different irreducible representations that occur for a given group

D_{ij}, $D_{i'j'}$: matrix elements of the transformation matrix describing the symmetry operation R

d_l = dimensionality of the representation l.

The expression states that each summation results from the scalar product of two vectors. These vectors are orthogonal, i.e. their scalar product is zero unless i = i‘, j =j‘, and l = l‘.

To work with this formula, we apply it to the characters (sum of the diagonal elements) of the two matrices. The left side turns into:

$$\sum_R \sum_i \mathbf{D}_{ii}^{(l)}(\mathbf{R}) \sum_{i'} \mathbf{D}_{i'i'}^{(l')}(\mathbf{R}) = \sum_R \chi^{(l)}(\mathbf{R})\,\chi^{(l')}(\mathbf{R})$$

The right side turns into

$$\sum_i \sum_{i'} \frac{h}{d_l}\,\delta_{ii'}\delta_{jj'}\delta_{ll'} = \frac{h}{d_l}\,\delta_{ll'}\underbrace{\sum_i \delta_{ii}}_{d_l} = h\,\delta_{ll'}$$

In this way we arrive at the orthogonality theorem of characters (little orthogonality theorem (LOT)

$$\sum_R \chi^{(l)}(R)\, \chi^{(l')}(R) = h\, \delta_{ll'}$$

The LOT allows us to provide the answers to question 1 **and to construct the character tables. They detail numbers and types of the irreducible representations occurring in a given group. These can be derived according to the following rules:**

Rule 1: The number of irreducible representations of a group equals the number of classes

Rule 2: $\sum_l d_l^2 = h$

Rule 3: $\sum_R \chi^{(l)}(R)\, \chi^{(l')}(R) = h$ for l = l‘

Rule 4: $\sum_R \chi^{(l)}(R)\, \chi^{(l')}(R) = 0$ for l ≠ l‘

Link for the Character tables: https://global.oup.com/uk/orc/chemistry/qchem2e/student/tables/

Translation and rotation operators

Classes of symmetry operations

Bilinear position operators

Irred. Repres.

C_{2v} (2mm)	E	C_2	$\sigma_v(xz)$	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

C_{3v} (3m)	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, 2xy)(xz, yz)$

C_{4v} (4mm)	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

Combined Symmetry properties via direct product

A B A⊗B

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} \otimes \begin{bmatrix} e & f \\ g & h \end{bmatrix} = \begin{bmatrix} ae & cf & be & bf \\ ag & ah & bg & bh \\ ce & cf & de & df \\ cg & ch & dg & dh \end{bmatrix}$$

Characters

$(a + d)(e + h) = ae+ah+de +dh$

$\chi_A\chi_B = \chi(A\otimes B)$

Character of direct product = Product of characters

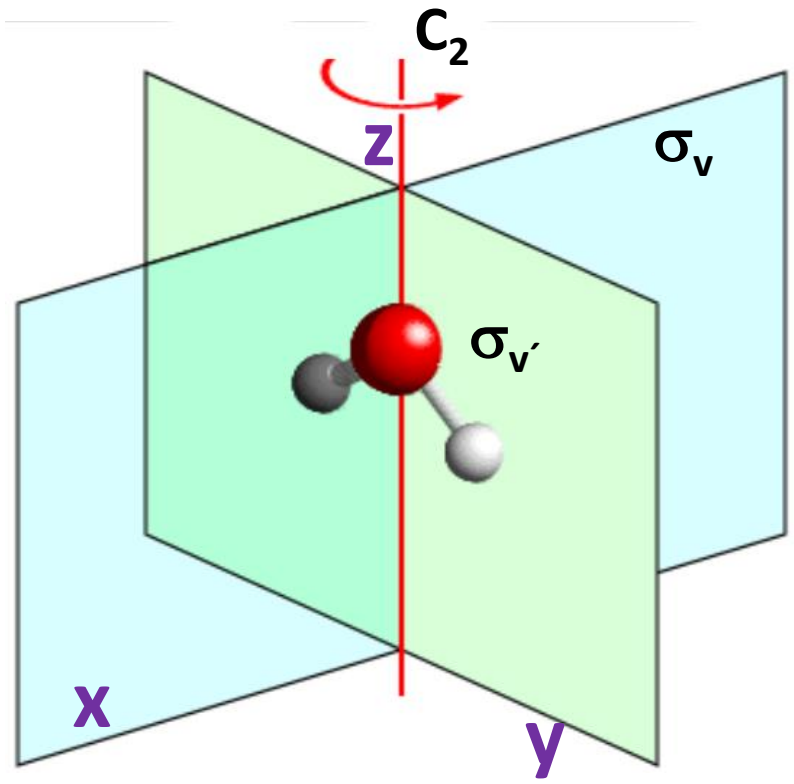
$A\otimes A = A$ $A\otimes B = B\otimes A = B$ $B\otimes B = A$

$1\otimes 1 = 1$ $1\otimes 2 = 2\otimes 1 = 2$ $2\otimes 2 = 1$

$g\otimes g = g$ $g\otimes u = u\otimes g = u$ $u\otimes u = g$

Irreducible representations of the translation and rotation operators:

C_{2v} (2mm)	E	C_2	$\sigma_v(xz)$	$\sigma'_v\ (yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz



Translation along z: conserves all symmetry elements
Translation along y: conserves σ_v‘
Translation along x: conserves σ_v
Rotation about z: conserves C_2
Rotation ablut x: conserves σ_v‘
Rotation about y: conserves σ_v

Now we are ready to address Question 2

Which irreducible representations occur in the spectroscopic problem considered ?

The problem always is approached in two steps:

1. **Develop the characters of the reducible representation $\chi_T(R)$ (problem specific)**
2. **Decompose this representation into the irreducible representations $\sum_l \Gamma_l$.**

For step 2 we can develop a simple formula, which is based on the fact that the character of a matrix is always maintained upon similarity transforms. So the trace of the transformation matrices of the reducible and the irreducible representations is conserved.

$$\chi_T(R) = \sum_l a_l \chi^{(l)} \qquad | \times \chi^{(l')}(R)$$

$$\chi_T(R)\,\chi^{(l')}(R) = \sum_l a_l \chi^{(l)}(R)\,\chi^{(l')}(R)$$

Here a_l is the number of times the irreducible representation appears after reduction

Summation over all symmetryoperations leads to $h a_l \delta_{ll'}$

$$\sum_R \chi_T(R)\,\chi^{(l')}(R) = \sum_R \sum_l a_l \chi^{(l)}(R)\,\chi^{(l')}(R) = \sum_l \sum_R a_l \chi^{(l)}(R)\,\chi^{(l')}(R)$$

This leads to the decomposition formula:

$$a_l = \frac{1}{h} \sum_R \chi_T(R)\,\chi^{(l')}(R)$$

Using this formula we determine from the χ_T how many times the various Irreducible representations of the group appear in the problem considered.