Introduction to Group Theory with Applications in Molecular and Solid State Physics

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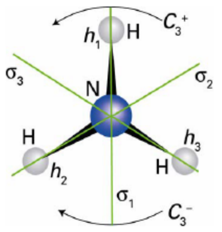
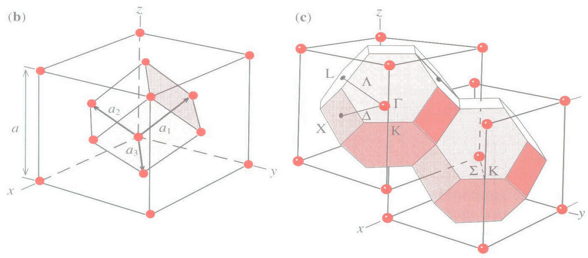


Symmetry - old concept, already known to Greek natural philosophy

Group theory: mathematical theory, developed in 19th century

Application to physics in the 1920's : Bethe 1929, Wigner 1931, Kohlrausch 1935

Why apply group theory in physics?



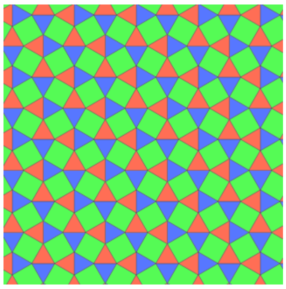
"It is often hard or even impossible to obtain a solution to the Schrödinger equation - however, a large part of qualitative results can be obtained by group theory. <u>Almost all the rules of spectroscopy follow from the symmetry of a problem</u>" E.Wigner, 1931

Outline

If you come up with a symmetry-related problem from your own work, bring it in and we can discuss it (time permitting)

At the end of this week, having followed the course, you should be able to

- determine the point group of a solid object such as a molecule or a crystalline unit cell or the space group of a translational periodic pattern
- determine the symmetry properties (in terms of irreducible representations) of
  - ⋆ tensorial properties of solids and derive those tensor elements which are "zero by symmetry"
  - ⋆ atomic wave functions in a crystal field
  - ⋆ molecular orbital wave functions
  - ⋆ molecular vibrational wave functions
  - ⋆ Bloch waves in a periodic solid
- derive symmetry selection rules for vibrational (infrared, Raman) and electronic (Vis-UV, photoemission) transition matrix elements
- identify molecular orbital and electronic band degeneracies and apply the "no-crossing-rule"
- and much more...



example of a wallpaper group; applies to surface problems

What we do **not** cover here is the Complete Nuclear Permutation Inversion Group - see book by P. R. Bunker and Per Jensen: Fundamentals of Molecular Symmetry,IOP Publishing, Bristol, 2004 (ISBN 0-7503-0941-5). However, given the successful mastering of the material discussed in this block course you should be able to extend your knowledge to this topic

Material about symmetry on the Internet

Character tables: http://symmetry.jacobs-university.de/

The platonic solids: http://www.csd.uwo.ca/~morey/archimedean.html

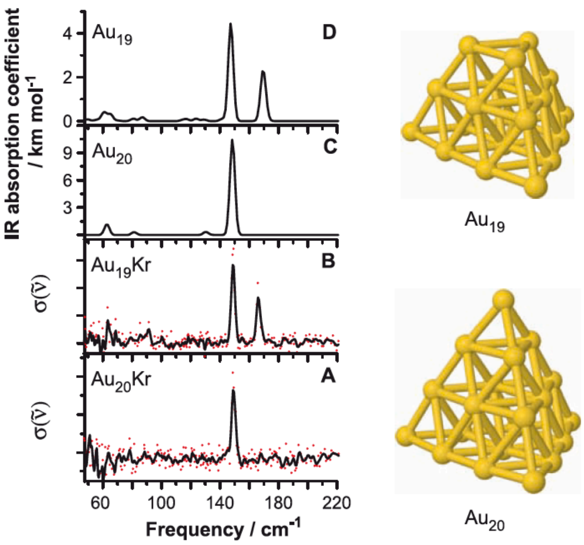
Wallpaper groups: http://www.clarku.edu/~djoyce/wallpaper/seventeen.html

Point group symmetries: http://www.staff.ncl.ac.uk/j.p.goss/symmetry/index.html

Students Online Resources of the book by Atkins & de Paula: "Physical Chemistry", 8e at http://www.oup.com/uk/orc/bin/9780198700722/01student/tables/tables_for_group_theory.pdf

Other symmetry-related links: http://www.staff.ncl.ac.uk/j.p.goss/symmetry/links.html

application: vibrational transitions in metal clusters



Photoelectron spectroscopy and quantum mechanical calculations have shown that anionic Au_{20}^- is a pyramid and has T_d symmetry. This structure has also been suggested to be the global minimum for neutral Au_{20} (14). The FIR-MPD spectrum we measured of the $Au_{20}Kr$ complex (Fig. 2A) was very simple, with a dominant absorption at 148 cm^{-1}, which already pointed to a highly symmetric structure. The calculated spectrum of tetrahedral Au_{20} was in agreement with the experiment (Fig. 2C)... The strong absorption at 148 cm^{-1} corresponds to a triply degenerate vibration (t_2) in bare Au_{20} with T_d symmetry. Theory predicts a truncated trigonal pyramid to be the minimum energy structure for neutral Au_{19} (27), **for which the removal of a corner atom of the Au20 tetrahedron reduces the symmetry from T_d to C_{3v}. As a direct consequence, the degeneracy of the t_2 vibration of Au_{20} is lifted, and this mode splits into a doubly degenerate vibration (e) and a nondegenerate vibration (a_1) inAu_{19}.** This splitting was observed in the vibrational spectrum of neutral Au_{19} (Fig. 2)… The truncated pyramidal structure of Au_{19} can thus be inferred directly from the IR spectrum.

Structures of Neutral Au_7, Au_{19}, and Au_{20} Clusters in the Gas Phase
Ph. Gruene, D. M. Rayner, B. Redlich,3 A. F. G. van der Meer, J. T. Lyon, G. Meijer, A. Fielicke, Science **329**, 5889 (2008)

application: band structure in solids, including spin-orbit coupling

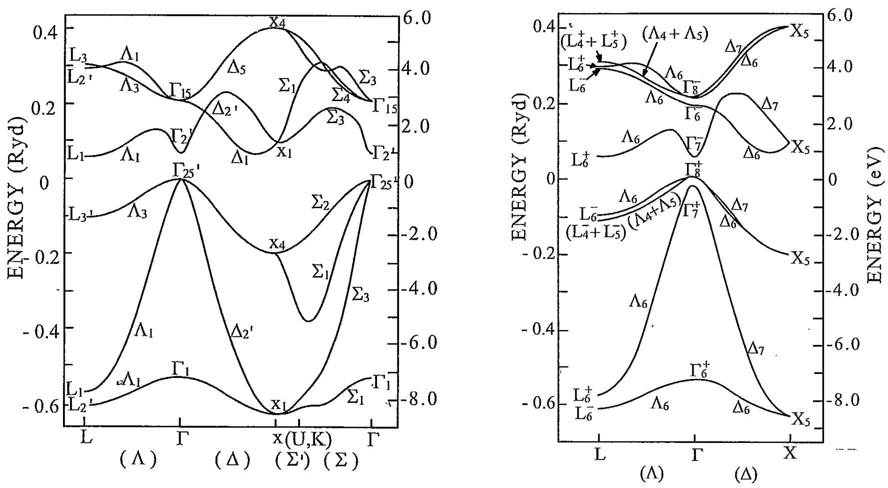


Fig. 14.1. Energy versus dimensionless wave vector for a few high-symmetry directions in germanium using standard notation. (**a**) The spin–orbit interaction has been neglected. (**b**) The spin–orbit interaction has been included and the bands are labeled by the double group representations

from: Dresselhaus, Dresselhaus and Jorio, Group Theory - Application to the Physics of Condensed Matter Springer 2008 (figure given without references)

Literature

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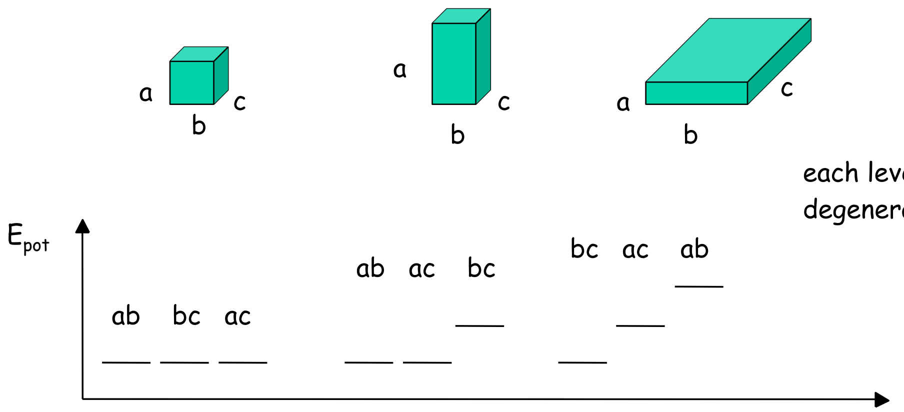
Atkins, P., Friedmann,R. “Molecular Quantum Mechanics” Oxford University Press, 2005: Chapter 5: Group Theory,

Symmetry and degeneracy

In general, the symmetry we aim to exploit is the symmetry of the Hamilton operator.

Simple example: a solid in a gravitational field. Potential energy depends on the face on which the body rests: the higher the center of mass, the higher E_{pot}



each level 2-fold degenerate (ab = ba)

As the symmetry “increases” (what does that mean?), the number of degenerate energy levels increases

Why should we care about symmetry properties in physics and chemistry ?

- Think of an surface system, e.g. a nickel atom in a (111) surface. How should we classify the d orbitals of that atom ?
  d_z^2 etc.?
- How should we classify molecular vibrations? In terms of their geometrical distortions?
- How can we classify electronic states in a molecular orbital?

1. Symmetry elements and point groups

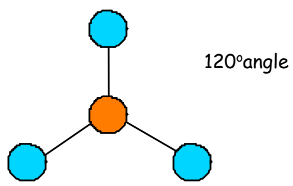
1.1 Symmmetry elements and operations

Operator gives instructions what to do: e.g. $\frac{\partial}{\partial x}$
differentiate with respect to x

Here: operator instructs to "rotate a body by $2\pi/3$ around a particular axis"

Definition: A symmetry operation is an operation which brings an object into a new orientation which is equivalent to the old one.

Example: molecule BF_3(planar)
Rotations by 120 degrees, 180 degrees, reflections.



How many different symmetry operations can one apply to this molecule ?

What kinds of symmetry operations are there? - Many! Permutation, rotation, inversion, charge, parity, time (CPT) reversal, ...

Here: **five spatial symmetry operations** which leave **one point in space fixed** (-> point group symmetry)

1. Identity: Symbol E

Transformation matrix: $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$

2. Reflection: Symbol σ

nomenclature: σ', σ'' etc, or σ_{xy} for reflection in the xy plane; also σ_v for vertical, σ_h for horizontal, σ_d for dihedral

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

3. Rotation around an axis: Symbol C_n

(here around z axis)

Nomenclature: C_n^m : apply a C_n rotation m times

$\begin{pmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$

4. Improper rotation: Symbol S_n

(Reflection in mirror plane followed by rotation normal to mirror plane, (here around z axis))

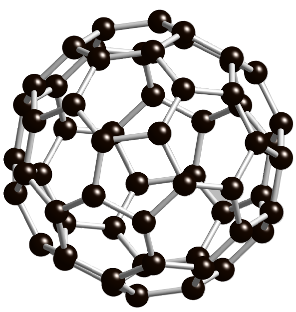
Nomenclature: S_n^m : apply a S_n rotation m times

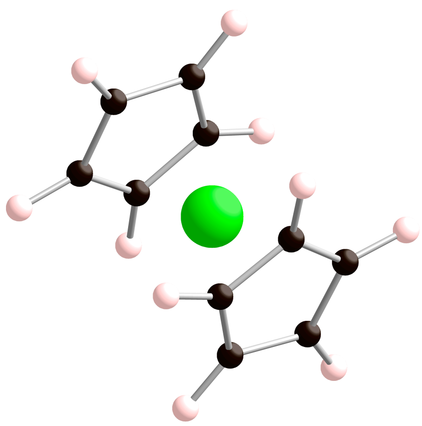
$\begin{pmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$

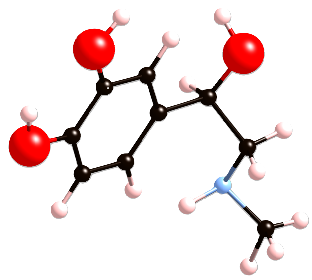
5. Inversion: Symbol i

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

Examples of objects with such symmetry elements

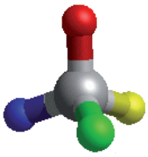


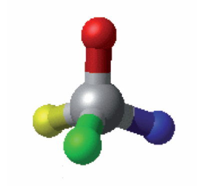




What does one need an improper axis of rotation for ?

consider a chiral object - the human hand



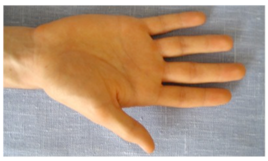
➪ an object is chiral if it cannot be superimposed on its mirror image

➪ <u>an object is chiral if it has no improper rotation axis</u>

need improper rotation also to fulfil group requirements: closure - see next section

Chirality Induction:

Adaption of a flexible, achiral object to the handedness of a chiral object – the achiral object assumes a chiral conformation


chiral object + (≠mirror image)

+


achiral object

interact ⇨

1.2 Group concepts

A group in the mathematical sense is a set of elements {a,b,c} for which an operation $\odot$ is defined such that a third element is associated with any ordered pair ("multiplication"). This operation must satisfy four requirements (group axioms).

1.2.1 Group axioms

1. Closure: the product of two elements is again an element of the group
2. One of the elements of the group is the unit element, such that
   $E \odot A = A \odot E = A$
3. To each element A there is an inverse element A^{-1} such that
   $A \odot A^{-1} = A^{-1} \odot A = E$
4. The associativity law holds: $A \odot (B \odot C) = (A \odot B) \odot C$

Notice: If the group members commute, i.e. $A \odot B = B \odot A$ for all group members, then the group is said to be Abelian.

Number of elements in the group is called "order of the group" h .

1.2.2. Examples of groups

a.) The set of all integers with addition as operation
(an infinite group). $E = 0$ $A^{-1} = -A$

b.) The set of all n x n matrices with nonvanishing determinants

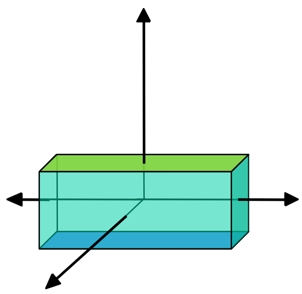
Operation is matrix multiplication, unit element is the unit matrix. Inverse of a matrix **A** is $\mathbf{A}^{-1}$

c.) The set of symmetry operations E, C_2, σ_{xz}, σ_{yz}

1).The group is closed. This applies to any symmetry group, but it must be demonstrated by means of a multiplication table

	E	C_2	σ_{xz}	σ_{yz}
E	E	C_2	σ_{xz}	σ_{yz}
C_2	C_2	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2
σ_{yz}	σ_{yz}	σ_{xz}	C_2	E

multiplication table



This object transforms into an equivalent spatial arrangement when E, C_2, σ_{xz}, and σ_{yz} are applied

But one can also say that the closure axiom is fulfilled since any of the products of symmetry operations transforms the object into an equivalent conformation

2. There is a unit element E, the identity

3. There is an inverse to each element (see multiplication table)

4. Associativity holds

In the first part of the lecture course: operations that leave a point in space fixed -> "point groups"

When including translations, glide planes and screw axes -> "space groups"

1.2.3 Multiplication tables

As seen above, group axioms can be tested by means of a multiplication table:

Consider this set of matrices

$$\underset{E}{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}} \quad \underset{A}{\frac{1}{2}\begin{pmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}} \quad \underset{B}{\frac{1}{2}\begin{pmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix}} \quad \underset{C}{\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}} \quad \underset{D}{\frac{1}{2}\begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}} \quad \underset{F}{\frac{1}{2}\begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix}}$$

From Burns p. 23

The multiplication table is then:
(try it out if you don't believe it)

	E	**A**	**B**	**C**	**D**	**F**
E	E	A	B	C	D	F
A	A	B	E	F	C	D
B	B	E	A	D	F	C
C	C	D	F	E	A	B
D	D	F	C	B	E	A
F	F	C	D	A	B	E

Theorem: Every element of the group occurs only once in each row or column of the multiplication table.

Note: As the group is non-Abelian, the table does not have to be symmetric.

1.2.4 Further group concepts

a.) Subgroup

Defintion: The group S is a subgroup of the group G if all elements of S are in G, and if S satisfies the group axioms.

It can be shown that the ratio of group orders s and g, g/s is an integer.

b.) Conjugated elements

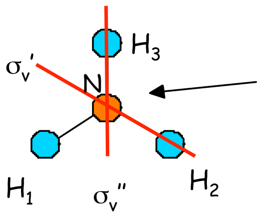
Let A, B, and C be members of a group G

Definition: A and B are conjugated, if they can be connected by a similarity transformation

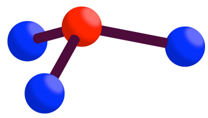
$A = X^{-1}B\,X$,   where X is also a member of the group.

- Every element is conjugated with itself.
- If A is conjugated with B, B is conjugated with A.
- If A is conjugated with B and C, then B and C are also conjugated.

Geometric illustration for a similarity



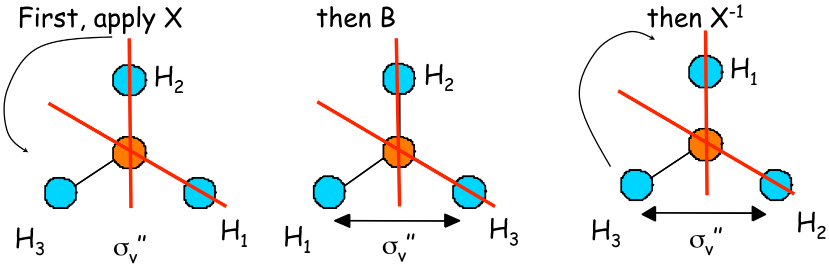
C_3 axis normal to paper plane



Ammonia NH_3
(not planar)

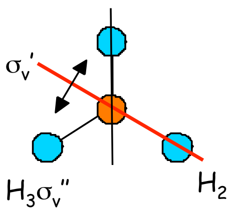
Let $X = C_3$, $A = \sigma_v'$, $B = \sigma_v''$

First, apply X   then B   then X^{-1}



This has the same effect as applying A

So indeed $A = X^{-1}\,B\;\;X$



c.) Classes of group elements

Definition: Group elements that are conjugated to one another form a **class.**

d.) Isomorphism

Definition: Two groups are isomorphic if there is a 1:1 relation between their elements. Groups are identical in the mathematical sense.

e.) Homomorphism

Definition: Two groups are homomorphic if to one element of group G_1 several elements of group G_2 are associated.

G_1 = {A_1, A_2, A_3,... }

G_2 = {B_1, B_2, B_3, B_4, B_5, B_6, B_7, B_8, B_9,... }

Homomorphism preserves products, i.e. the multiplication table !

Further reading: Serge Lang "Linear Algebra",
Paul Halmos "Finite Dimensional Vector Spaces"

Homomorphism: an example

	E	C_2	σ_v'	σ_v''
E	E	C_2	σ_v'	σ_v''
C_2	C_2	E	σ_v''	σ_v'
σ_v'	σ_v'	σ_v''	E	C_2
σ_v''	σ_v''	σ_v'	C_2	E

Example: G_1 = {+1, -1}

G_2 = {E, C_2, σ_v',σ_v'' }

	1	1	-1	-1
1	1	1	-1	-1
1	1	1	-1	-1
-1	-1	-1	1	1
-1	-1	-1	1	1

Multiplication tables give identical results for elements connected by a homomorphism.

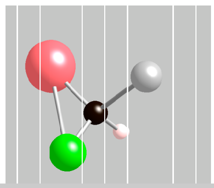
f.) Multiplication of groups

Definition: The direct product of two groups which have only E in common is the group of products of elements $A_{i.} \cdot B_{j.}$ If the two groups have orders h and g, the direct product group has h·g elements.

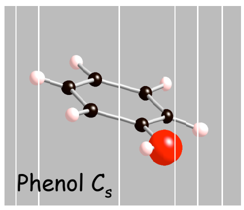
g.) Generator of a group

Definition: The generators of a group are those elements from which all elements of a group can be derived. Example: $G = \{C_6^1, C_6^2, C_6^3, C_6^4, C_6^5, C_6^6 = E\}$. All elements can be derived form successive application of C_6^1.

1.3 Classification of point groups (in Schoenflies notation)



Chloro-bromo-fluoro-methane



Phenol C_s

1.3.1 The groups C_1, C_s, C_i.

C_1 : element $E(C_1)$

C_s : E and a mirror plane

C_i : E and an inversion centre (C_i)

1.3.2 The groups C_n

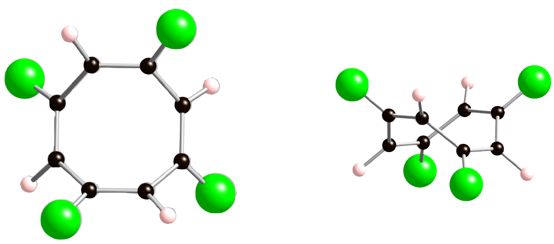
Contain E and a rotation by $2\pi/n$. C_n generates C_n^2, C_n^3, C_n^{n-1}.

Example: $C_2 = \{E, C_2\}$ H_2O_2

1.3.3 The groups S_n

Contain E and **only** an improper rotation by $2\pi/n$. If there are other symmetry elements, the object does not belong to S_n.

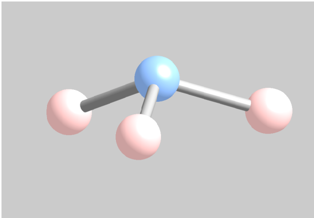
Example: 1,3,5,7 tetrafluorocyclooctatetraene S_4



1.3.4 The groups C_{nv} (frequent !)

Contain E, C_n and n mirror planes σ_v which all contain the C_n axis.

Ammonia C_{3v}

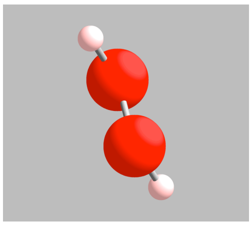


v stands for vertical. The rotation axis corresponding to C_n with the largest n is always taken as vertical:

Example: C_{2v}= {E, C_2, σ_v', σ_v''}

1.3.5 The groups C_{nh}

Contain E, $C_n$and a horizontal mirror plane. h stands for horizontal. The rotation axis corresponding to C_n with the largest n is always taken as vertical. For n even an inversion center exists.



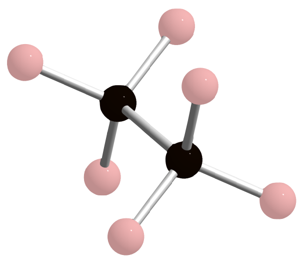
planar hydrogen peroxide C_{2h}

1.3.6The groups D_n

Groups contain E, $C_n$and n C'_2axes normal to C_n

1.3.7 The groups D_{nd}

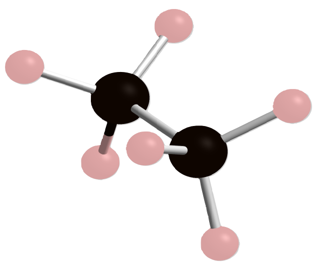
Groups contain E, C_n, n C'_2axes normal to C_n, and n mirror planes σ_d which bisect the angles between the C_2axes. If n is odd there is also an inversion center.



Staggered ethane D_{3d}

1.3.8 The groups D_{nh}

Groups contain E, C_n, n C'_2axes normal to C_n, one horizontal mirror plane. For even n there is also an inversion center, and there are n/2 mirror planes σ_d which bisect the angles between the C'_2axes, and n/2 mirror planes that contain the C_2'axes. For n odd there are n mirror planes that contain the C_2 axes.



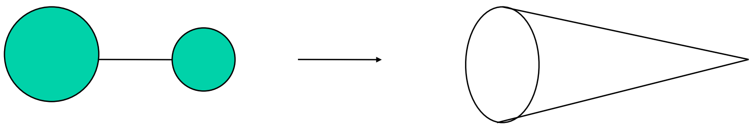
Eclipsed ethane D_{3h}

The special groups

1.3.9 The axial groups

a) $C_{\infty v}$ *one* C_∞ *axis and* ∞ σ_v *planes*

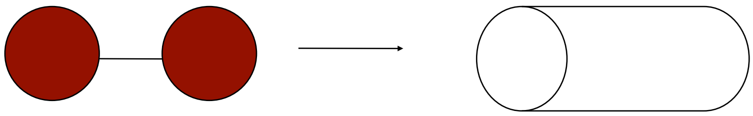
Example: carbon monoxide



heteronuclear diatomic molecule and a cone

b) $D_{\infty h}$ *one* C_∞ *axis and* ∞ σ_v *planes and* ∞ C_2 *axes*

Example: N_2, H_2

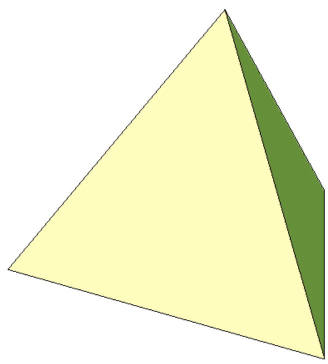


homonuclear diatomic molecule and a uniform cylinder

The special groups

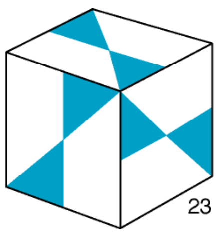
1.3.10 The platonic solids.

Plato describes them in his book "Timaios" and assigned them to his conception of the world
Made from equilateral triangles, squares, and pentaeders



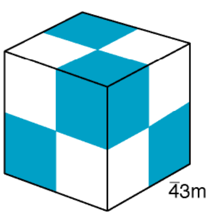
a) Tetrahedron

$$\begin{array}{l} E \\ 4 \times C_3 \\ 4 \times C_3^2 \\ 3 \times C_2 \\ \hline 12 \end{array}$$



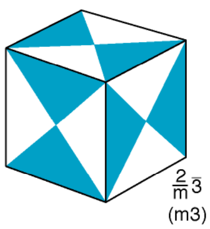
T

$$\begin{array}{ll} E & \\ 4 \times C_3 & 4 \times C_3^2 \\ 3 \times C_2 & 3 \times S_4^3 \\ 3 \times S_4 & 6 \times \sigma_d \\ \hline & 24 \end{array}$$



$\mathbf{T_d}$

$$\begin{array}{ll} E & i \\ 4 \times C_3 & 4 \times S_6 \\ 4 \times C_3^2 & 4 \times S_6^5 \\ 3 \times C_2 & 3 \times \sigma_h \\ \hline & 24 \end{array}$$

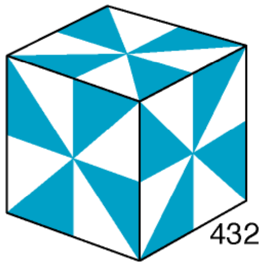


$\mathbf{T_h}$

In which molecule do you find tetrahedral bonding ?

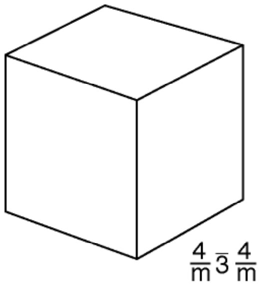
b.) The cube

E	
$3 \times C_2$	$4 \times C_3^2$
$4 \times C_3$	$3 \times C_4^3$
$6 \times C_2$	$3 \times C_4$
	24



O

E	$4 \times C_3^2$	$3 \times C_4$
$4 \times C_3$	$4 \times S_6^5$	$3 \times S_4$
$6 \times C_2$	$6 \times \sigma_d$	$3 \times \sigma_h$
$3 \times C_2 (= C_4^2)$	$4 \times S_6$	$3 \times C_4^3$
$\boxed{i}$	$3 \times S_4^3$	48

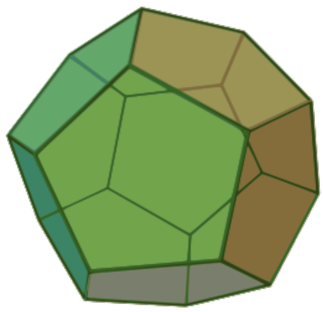


$\frac{4}{m}\bar{3}\frac{4}{m}$
(m3m)

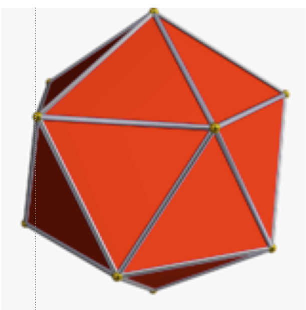
O_h

d.) Dodecahedron I_h

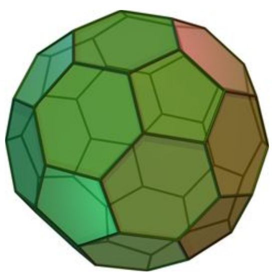
E
12 C_5 axes
20 C_3 axes
15 C_2 axes
i
12 S_{10} axes
20 S_6 axes
15 σ planes
96

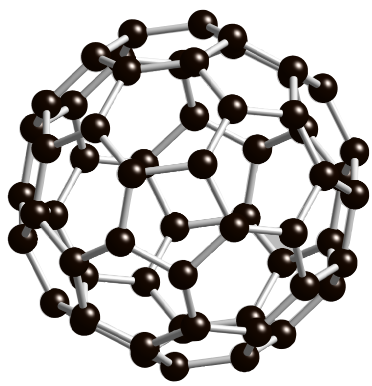


e.) Icosahedron



truncated icosahedron

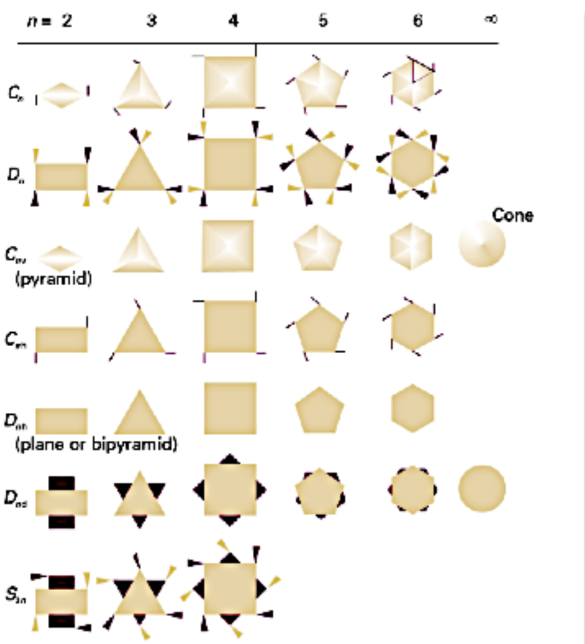




120 symmetry operations

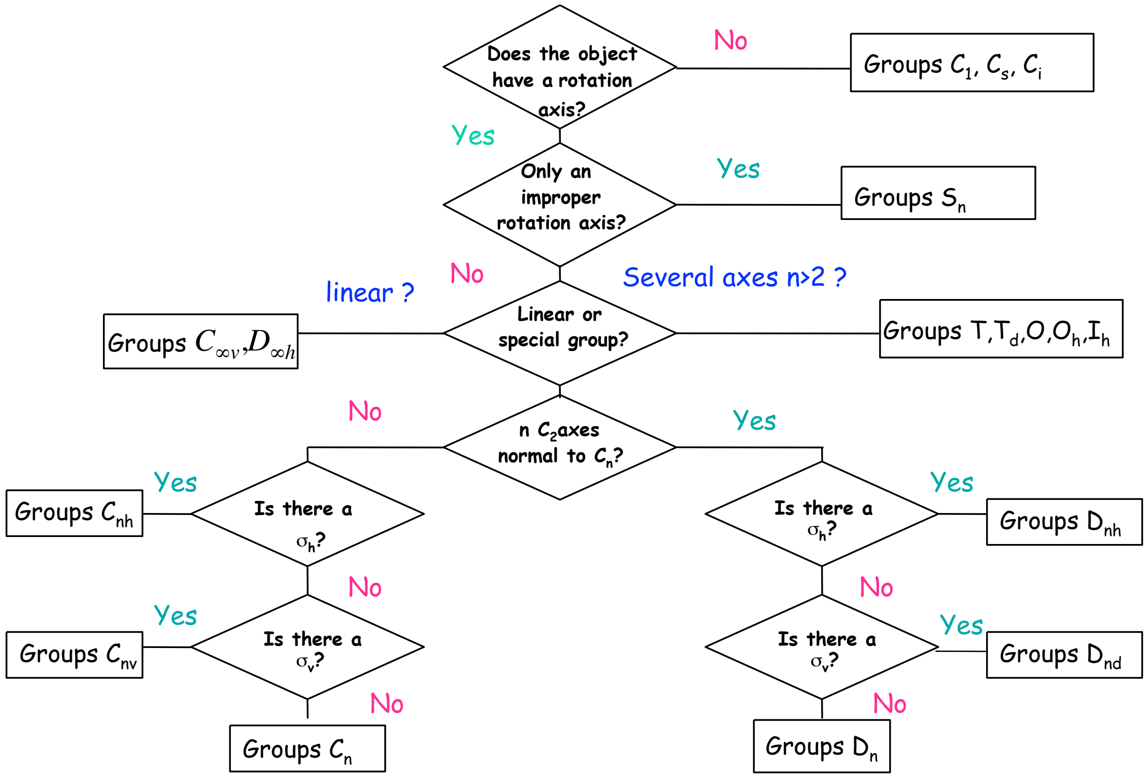
Important point groups

Nonaxial groups	C_1	C_s	C_i	-	-	-	-
C_n groups	C_2	C_3	C_4	C_5	C_6	C_7	C_8
D_n groups	D_2	D_3	D_4	D_5	D_6	D_7	D_8
C_{nv} groups	C_{2v}	C_{3v}	C_{4v}	C_{5v}	C_{6v}	C_{7v}	C_{8v}
C_{nh} groups	C_{2h}	C_{3h}	C_{4h}	C_{5h}	C_{6h}	-	-
D_{nh} groups	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}
D_{nd} groups	D_{2d}	D_{3d}	D_{4d}	D_{5d}	D_{6d}	D_{7d}	D_{8d}
S_n groups	S_2	S_4	S_6	S_8	S_{10}	S_{12}	-
Cubic groups	T	T_h	T_d	O	O_h	I	I_h
Linear groups	$C_{\infty v}$	$D_{\infty h}$	-	-	-	-	-



A useful collection of information about point groups can be found at http://symmetry.jacobs-university.de/ and in the Students Online Resources of the book by Atkins & de Paula: “Physical Chemistry”, 8e at http://www.oup.com/uk/orc

Classification of objects in terms of their point group



2. Group representations

2.1 An intuitive approach

Aim: a) Represent symmetry operations by matrices

b) Find "irreducible representations", i.e. matrices of lowest dimensions

<u>Definition</u>: A group of square matrices $\Gamma(a_i)$ is called a representation of a point group if there is an isomorphism or a homomorphism between the matrices $\Gamma(a_i)$ and the symmetry operations of the point group.

One way to obtain matrix representation: Cartesian transformation matrices - we've done this before

Transformation matrices for C_{3v}:

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

$$\sigma_v' \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \sigma_v'' \quad \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \sigma_v''' \quad \begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

matrix representations

One way to obtain matrix representation: Cartesian transformation matrices - we've done this before

Transformation matrices for C_{3v}:

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

$$\sigma_v \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \sigma_v' \quad \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \sigma_v''' \quad \begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

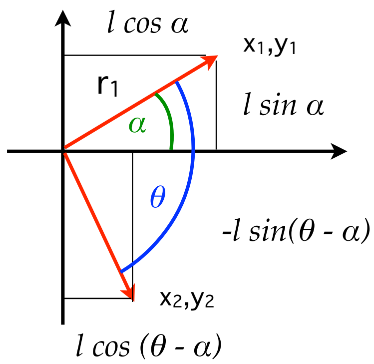
matrices to represent symmetry operations example: group C_{2h}

$$E \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} * \begin{matrix} x_1 \\ y_1 \\ z_1 \end{matrix} = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} \qquad \sigma_h \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} * \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} x_1 \\ y_1 \\ -z_1 \end{pmatrix}$$

$$i \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} -x_1 \\ -y_1 \\ -z_1 \end{pmatrix} \qquad C_2 \quad \begin{pmatrix} \cos\pi & \sin\pi & 0 \\ -\sin\pi & \cos\pi & 0 \\ 0 & 0 & 1 \end{pmatrix} * \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} -x_1 \\ -y_1 \\ z_1 \end{pmatrix}$$

$$x_2 = x_1 \cos\theta + y_1 \sin\theta$$
$$y_2 = -x_1 \sin\theta + y_1 \cos\theta$$

$$\begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} * \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} x_1' \\ y_1' \\ z_1' \end{pmatrix}$$



Transformation matrices for C_{3v}:

$$E \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \begin{pmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The matrices appear in block-diagonal form: (2 x 2) and (1 x 1) matrices, since the (x,y) and z coordinate transform into themselves always in C_{3v}.

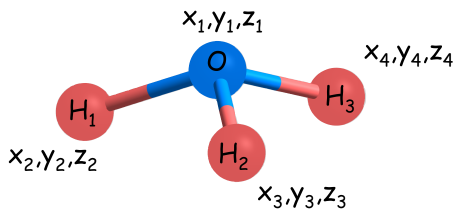
The matrices appear in block-diagonal form: (2 x 2) and (1 x 1) matrices, since the (x,y) and z coordinate transform into themselves always in C_{3v}.

Question: Are there more representations ? And more irreducible representations ?

How many in all ?

One can also take higher dimension representations: e.g. attach coordinates to each atom in a molecule:

$$\left\{ \quad 12 \times 12 \quad \right\} * \left\{ \begin{matrix} x_1 \\ y_1 \\ z_1 \\ . \\ . \\ z_4 \end{matrix} \right\} = \left\{ \begin{matrix} x_1' \\ y_1' \\ z_1' \\ . \\ . \\ z_4' \end{matrix} \right\}$$

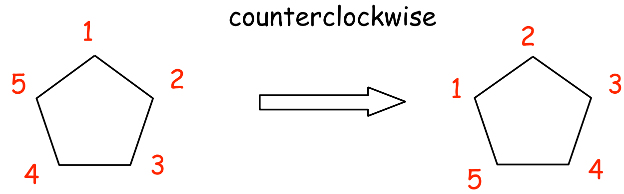


This is in fact the standard method for analysing normal mode symmetries in molecular vibrations (chapter 4).

Another, simpler way to write down a representation matrix:

Apply C_5^1, i.e. rotation by 72° counterclockwise

example: a (planar) pentagon



etc.

This can be written as

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix} \bullet \begin{pmatrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{pmatrix} = \begin{pmatrix} 2 \\ 3 \\ 4 \\ 5 \\ 1 \end{pmatrix}$$

There is a similarity transformation with a matrix Q that can transform such matrices into block-diagonal form (no proof here!)

similarity transform ->

$$C_5' = Q^{-1} C_5 Q = \begin{pmatrix} \boxed{1} & 0 & 0 & 0 & 0 \\ 0 & \cos\frac{2\pi}{5} & \sin\frac{2\pi}{5} & 0 & 0 \\ 0 & -\sin\frac{2\pi}{5} & \cos\frac{2\pi}{5} & 0 & 0 \\ 0 & 0 & 0 & \cos\frac{4\pi}{5} & \sin\frac{4\pi}{5} \\ 0 & 0 & 0 & -\sin\frac{4\pi}{5} & \cos\frac{4\pi}{5} \end{pmatrix}$$

We then have three sets of smaller matrices that each can represent the group members, since each will fulfill the multiplication table.

representation matrices for other operations in C_5

$$C_5^1 \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix} \quad C_5^2 \begin{pmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{pmatrix} \quad C_5^3 \begin{pmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

Each of the blocks serves as a representation of the symmetry operation since it obeys the multiplication table. In fact, for the group C_5 these blocks are the irreducible representations.

Question: is there a set of matrix representations of which the dimension can be no further reduced? -> Yes!

(Important example: set of matrices consisting just of +1's).

$$\begin{pmatrix} \boxed{1} & 0 & 0 & 0 & 0 \\ 0 & \cos\frac{2\pi}{5} & \sin\frac{2\pi}{5} & 0 & 0 \\ 0 & -\sin\frac{2\pi}{5} & \cos\frac{2\pi}{5} & 0 & 0 \\ 0 & 0 & 0 & \cos\frac{4\pi}{5} & \sin\frac{4\pi}{5} \\ 0 & 0 & 0 & -\sin\frac{4\pi}{5} & \cos\frac{4\pi}{5} \end{pmatrix}$$

A quick run through matrix mathematics

Trace of a matrix: Tr $\Gamma = \sum \Gamma_{ii}$ trace, als known as "character"

Theorem: Similarity transforms leave the trace invariant

Definition: transpose matrix $\tilde{\Gamma}_{ji} = \Gamma_{ij}$

Definition: Adjunct matrix $\Gamma^{+} = \tilde{\Gamma}^{*}$

Definition: Hermitian matrix (self-adjunct): $\Gamma^{+} = \Gamma$, *i.e.* $H_{ij} = H^{*}_{ji}$

Definition: Unitary matrix $\Gamma^{+} = \Gamma^{-1}$

Note: the rows and columns of a unitary matrix form a set of n orthogonal vectors. Unitary and Hermitian matrices can always be diagonalized through a similarity transformation.

<u>Definition:</u> Let a set of matrices $\Gamma(R)$ be a representation of the symmetry operations R in the point group G . If there is a similarity transformation which converts the $\Gamma(R)$ into block-diagonal form, then the blocks Γ_1, Γ_2, ... are called irreducible representations if they cannot be further reduced.

Why are irreducible representations important? We are going to see that basis functions, e.g. electronic or vibronic wave functions, can be classified in terms of irreducible representations. This classification then decides on interactions (e.g. hybridization), term splittings, transition matrix elements etc.

in order to work on this, we need a number of central theorems ->

2.2 The Great Orthogonality Theorem

<u>Theorem (GOT)</u>: Consider all inequivalent, irreducible, unitary representations $\Gamma_i(R)$ of a group $G = \{R_1, R_2, \ldots\}$

Then

$$\sum_R \Gamma^i(R)^*_{mn} \Gamma^j(R)_{op} = \frac{h}{l_i} \delta_{ij} \delta_{mo} \delta_{np}$$

where i,j: index of element of representation matrix

mn,(op): row and column of Γ_i, (Γ_j)

h: order of the group

l_i dimension of the irreducible representation

δ Kronecker symbol

Irreducible representations for C_{3v}

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

$$\sigma_v' = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \boxed{1} \end{pmatrix} \quad \sigma''_v = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & \boxed{1} \end{pmatrix} \quad \sigma'''_v = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & \boxed{1} \end{pmatrix}$$

Blue boxes: Γ_1 Red boxes: Γ_3

We will learn in a moment that there are three irreducible representations for the group C_{3v}. The third one (Γ_2) consists of the following "matrices" (without proof)

$+1 \rightarrow E,\ C_3^{\,1},\ C_3^{\,2}$

$-1 \rightarrow \sigma_v',\ \sigma_v'',\ \sigma_v'''$

irreducible representation of C_{3v}

	E	C_3^1	C_3^2	σ_v'	σ_v''	σ_v'''
1st irr. rep	1	1	1	1	1	1
2nd irr. rep	1	1	1	-1	-1	-1
3rd irr. rep	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} -1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}$	$\frac{1}{2}\begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix}$

This table can be used to apply the GOT in detail

We write down a similar table for the traces (characters) of the representation matrices, grouped by classes of symmetry operations

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

traces or **characters**

A vector space model of the representations

In order to understand the GOT, consider the following: vectors can be formed from the irreducible representations in group element space. This space is h-dimensional (number of group elements), and its axes can be labelled by them.

Vectors are characterized by three indices:

i index of irred. rep.

m,o row of irred. rep.

n,p column of irred. rep.

Then, according to the GOT:

$$\begin{pmatrix} \Gamma^1_{m,n} \\ \Gamma^2_{m,n} \\ \cdots \\ \Gamma^n_{m,n} \end{pmatrix} \begin{pmatrix} \Gamma^1_{o,p} \\ \Gamma^2_{o,p} \\ \cdot\cdot \\ \Gamma^n_{o,p} \end{pmatrix} = 0$$

except for i=j, m=n, o=p !

In an h-dimensional space there can only be h linearly independent vectors -> upper limit to number of matrix elements that all irr. reps. together can have:

$$\Sigma l_i^2 \leq h$$

Example of C_{3v}: Correspondence between certain subspaces of the domain on which we have constructed the matrix representations (i.e. R_3), and certain irred. representations:

Transformation matrices for C_{3v}:

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

$$\sigma_v' = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma''_v = \begin{pmatrix} \tfrac{1}{2} & -\tfrac{\sqrt{3}}{2} & 0 \\ -\tfrac{\sqrt{3}}{2} & -\tfrac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma'''_v = \begin{pmatrix} \tfrac{1}{2} & \tfrac{\sqrt{3}}{2} & 0 \\ \tfrac{\sqrt{3}}{2} & -\tfrac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Blue boxes: Γ_1 Red boxes: Γ_3

The first irreducible representation only affects the z coordinate, that means any length in x and y is conserved.
The third irreducible representation only affects the x and y coordinates.
The (x,y) plane and the z coordinate are not mixed by the irr. reps.

Instead of using the irreducible representation matrices we can often just use their characters - i.e. only handle numbers not matrices. For the one-dimensional irreducible representations the character in fact is the matrix (of dimension 1).

<u>Theorem:</u> The number of irreducible representation is equal to the number of classes of group elements

<u>Theorem:</u> A necessary and sufficient condition for the equivalence of two representations is that the characters are equal.

<u>Theorem:</u> Let l_i be the dimension of the i-th irreducible representation of a group of order h. Then

$$\sum l_i^2 = h$$

e.g. in C_{3v}: $1^2 + 1^2 + 2^2 = 6 = h(C_{3v})$. There is always a unique solution. The character of the symmetry operation E (the identity), which is the unit matrix, then gives the dimension of the irreducible representation.

nomenclature

Nomenclature:

a) Bethe: irr. reps just named $\Gamma^1, \Gamma^2, \Gamma^3 \ldots$; (used in mathematical treatments, for simplicity

b) Bouckaert, Smoluchowski, Wigner (BSW) (used in solid state physics)

$\Gamma_1, \Gamma_{15}, \Gamma_{25}, \Gamma_{25}'$ etc.

Mulliken (widely used in chemistry, spectroscopy in general)

A,B	1-dimensional irr. reps
E	2-dimensional irr. reps
T	3-dimensional irr. reps

Indices 1,2,3 no meaning

' and " symmetric or antisymmetric with respect to a horizontal mirror plane σ_h

g,u gerade/ungerade with respect to inversion

Example: irreducible representation A_{1g} in point group D_{6h}
A means 1-dimensional, index 1 has no meaning
g means functions transforming as A_{1g} are even under inversion

Example: irreducible representation T_{1u}: representation matrices are 3 dimensional, and functions transforming as T_{1u} are odd under inversion

2.3 Theorems about irreducible representations

In the following, the symbol χ means "take the trace of"

Theorem: (**Little orthogonality theorem, LOT**) When summing over all symmetry operations R of a group G, the system of **characters** of an irreducible representation is orthogonal

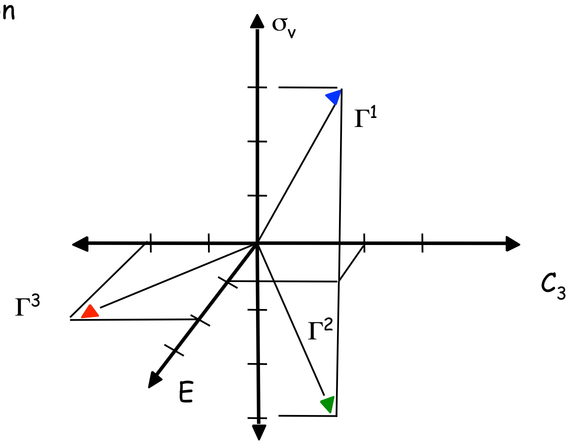
$$\sum_R \chi\left[\Gamma^i(R)\right]^* \chi\left[\Gamma^j(R)\right] = h\delta_{ij}$$

and normalized to the order h of a group:

So for a test whether a representation is irreducible one can set i=j and carry out the summation

example:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0



$$\sum_R \chi\left[\Gamma^i(R)\right]^* \chi\left[\Gamma^j(R)\right] \; = \; h\delta_{ij}$$

C_{3v}	1E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

example: Γ_1, Γ_3

$$[1 \cdot 2] \cdot 1 + [1 \cdot (-1)] \cdot 2 + [1 \cdot 0] \cdot 3 = 0$$

A typical character table

Mulliken notation for irr.reps

A,B	1-dimensional irr. reps
E	2-dimensional irr. reps
T	3-dimensional irr. reps

Indices 1,2,3 no meaning
' and " symmetric or antisymmetric with respect to a horizontal mirror plane σ_h g,u gerade/ungerade with respect to inversion

group symbol

C_{4v}	E	$2C_4$ (z)	C_2	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions	cub functi
A_1	+1	+1	+1	+1	+1	z	x^2+y^2, z^2	$z^3, z(x^2+y^2)$
A_2	+1	+1	+1	-1	-1	R_z	-	-
B_1	+1	-1	+1	+1	-1	-	x^2-y^2	$z(x^2-y^2)$
B_2	+1	-1	+1	-1	+1	-	xy	xyz
E	+2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)	(xz^2, yz^2) $(xy^2,$

irr.reps

characters

basis functions

So the point group C_{4v} has five classes of symmetry operations, hence five irreducible representations.
Four of them are one-dimensional, one is two-dimensional.

And these are their characters, i.e. the traces of the representation matrices

A useful collection of character tables can be found at http://symmetry.jacobs-university.de/

Example of nomenclature

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Chemical Physics Letters 393 (2004) 361–366

CHEMICAL PHYSICS LETTERS

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The C 1s NEXAFS spectrum of benzene below threshold: Rydberg or valence character of the unoccupied σ-type orbitals

R. Püttner [a,*], C. Kolczewski [b], M. Martins [a,1], A.S. Schlachter [c], G. Snell [c,d], M. Sant'Anna [c,2], J. Viefhaus [b], K. Hermann [b], G. Kaindl [a]

the observation that the experimental excitation energies are higher than the calculated values by ≅ 150–200 meV.

Peaks A and D have been assigned in the literature to the transitions C $1s^{-1}\pi^*\boxed{e_{2u}}$ and C $1s^{-1}\pi^*\boxed{b_{2g}}$, respectively. The assignments given in the literature for peaks B and C agree only in assigning σ-symmetry to the final-state orbitals, i.e., they exhibit no node in the molecular plane. The detailed character of these orbitals, however, has been described quite differently, as summarized in Table 1.

In the presence of a localized core hole, the symmetry of benzene is reduced from D_{6h} to C_{2v}. In this case, the degenerate orbital $\boxed{e_{2u}}$ (peak A) splits into two orbitals with b_1 and a_2 symmetry. Furthermore, an excitation from the localized core hole into the $\boxed{a_2}$ orbital is forbidden by dipole-selection rules. Thus, the main peak A at 285.1 eV can be assigned to the C $1s^{-1}\pi^*\boxed{e_{2u}(b_1)}$ transition. This transition exhibits a rich fine structure

Reduction of reducible representations

We have seen how large dimensional representations can be obtained by considering spatial coordinates of atoms etc. Obviously we would like to find out how to decompose these into the constituent irreducible representations.

<u>Theorem:</u> The character of a reducible representation is the sum of the characters of the irreducible representations that make up the reducible representation:

$$\chi\left[\Gamma^{red}(R)\right] = \sum_j a_j \chi\left[\Gamma(R)\right] \qquad (1)$$

a_j is the number of times Γ^j appears in Γ^{red}. This theorem becomes clear if we look at the block-diagonal form of a representation matrix, and remember that the character of a matrix does not change upon a similarity transformation.

Now we multiply (1) by $\sum_j \chi\left[\Gamma(R)\right]^*$:

$$\sum_R \chi\left[\Gamma^{j'}(R)\right]^* \chi\left[\Gamma^{red}(R)\right] = \sum_R \sum_j a_j \chi\left[\Gamma^{j'}(R)\right]^* \chi\left[\Gamma^{j}(R)\right]$$

apply the "Little Orthogonality Theorem"

$$\sum_R \chi\left[\Gamma^{j'}(R)\right]^* \chi\left[\Gamma^{red}(R)\right] = h\sum_j a_j \delta_{jj'} \qquad \left| j \to j' \right.$$

$$= h\sum_j a_j \delta_{jj'} = h \cdot a_j$$

Reduction of reducible representations

Thus:

$$\sum_R \chi\left[\Gamma^{j'}(R)\right]^* \chi\left[\Gamma^{red}(R)\right] = h \ a_j$$

-> find out how many times an irreducible representation is contained in a reducible representation:

<u>Theorem:</u> A unique decomposition of a reducible representation into irred. reps. can be obtained from its characters

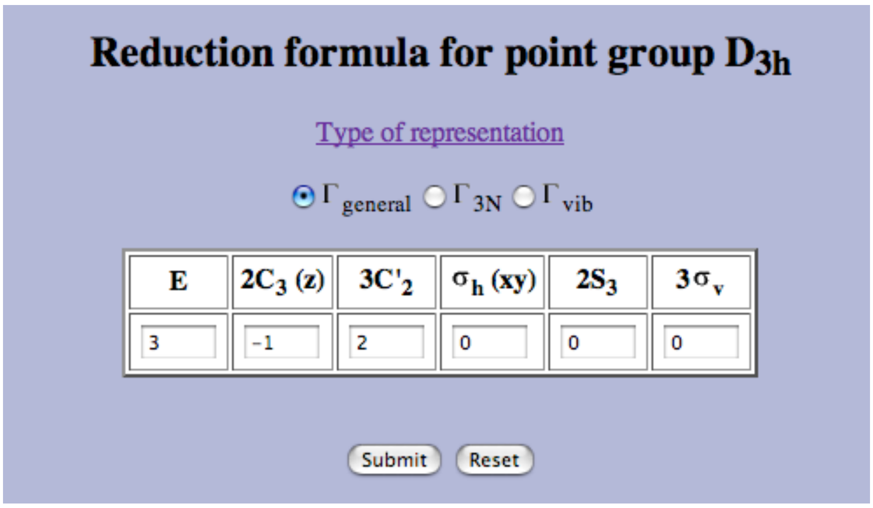
$$a_j = \frac{1}{h}\sum_R \chi\left[\Gamma^{j}(R)^*\right] \chi\left[\Gamma^{red}(R)\right]$$

In the matrix on the right hand side, Γ^1 is contained twice ($a_j(\Gamma^1) = 2$), Γ^2 is also contained twice, and Γ^3 is contained once.

$$\begin{pmatrix}
\Gamma^1_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \Gamma^1_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \Gamma^2_{11} & \Gamma^2_{12} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \Gamma^2_{21} & \Gamma^2_{22} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \Gamma^2_{11} & \Gamma^2_{12} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \Gamma^2_{21} & \Gamma^2_{22} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \Gamma^3_{11} & \Gamma^3_{12} & \Gamma^3_{13} \\
0 & 0 & 0 & 0 & 0 & 0 & \Gamma^3_{21} & \Gamma^3_{22} & \Gamma^3_{23} \\
0 & 0 & 0 & 0 & 0 & 0 & \Gamma^3_{31} & \Gamma^3_{32} & \Gamma^3_{33}
\end{pmatrix}$$

Reduction of reducible representations made easy though the internet

type in the characters of the reducible representation that you are working on, and get the resulting decomposition



http://symmetry.jacobs-university.de/cgi-bin/group.cgi?group=603&option=4

reduction of representations: a worked example

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(xz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
Γ^{red}	3	1	3	1

reduce Γ^{red} "by inspection"

$\Gamma^{red} = 2A_1 + B_1$

correctly, use formula $$a_j = \frac{1}{h}\sum_R \chi\left[\Gamma^j(R)^*\right]\,\chi\left[\Gamma^{red}(R)\right]$$

$a_{A1} = 1/4([3\cdot1\cdot1 + 1\cdot1\cdot1 + 3\cdot1\cdot1 + 1\cdot1\cdot1] = 2$

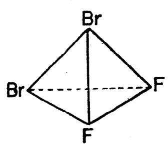
$a_{A2} = 1/4([3\cdot1\cdot1 + 1\cdot1\cdot1 + 3\cdot(-1)\cdot1 + 1\cdot(-1)\cdot1] = 0$

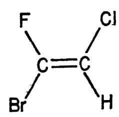
$a_{B1} = 1/4([3\cdot1\cdot1 + 1\cdot(-1)\cdot1 + 3\cdot1\cdot1 + 1\cdot(-1)\cdot1] = 1$

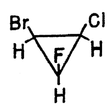
$a_{B2} = 1/4([3\cdot1\cdot1 + 1\cdot(-1)\cdot1 + 3\cdot(-1)\cdot1 + 1\cdot1\cdot1] = 0$

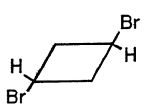
Exercises

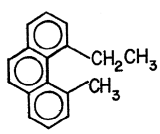
1. Molecules with a mirror plane, a center of inversion, or an improper axis of rotation cannot be optically active (i.e. exhibit circular dichroism) – those that have not may be optically active. Which of the following molecules may be optically active?


a.


b.


c.


d.

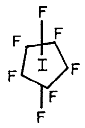

e.

2. Assign each molecule below to the proper point group

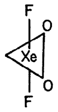
a. O=C=C=C=O (linear)

b. HF

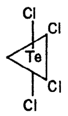
c. IF_7



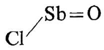
d. XeO_2F_2



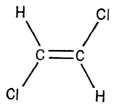
e. $TeCl_4$



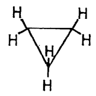
f.



g. *trans*-dichloroethylene



h. cyclopropane



3.What group is obtained by adding to or deleting from each of the following groups the indicated symmetry operation? Use the character table.

C_3 plus i	S_6 minus i	D_{3d} minus S_6
C_{3v} plus i	T_d plus i	S_4 plus i
C_{5v} plus σ_h	C_3 plus S_6	C_{3h} minus S_6^5

4. Decompose the following reducible representations of the point group D4:

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
Γ_1	3	-1	-1	1	-1
Γ_2	2	2	2	0	0
Γ_3	8	0	0	0	0
Γ_4	4	-2	0	-2	2

allene

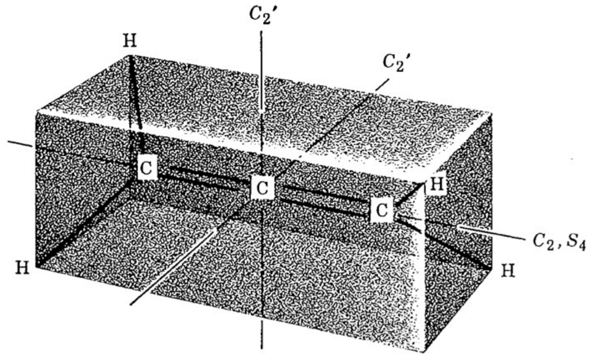
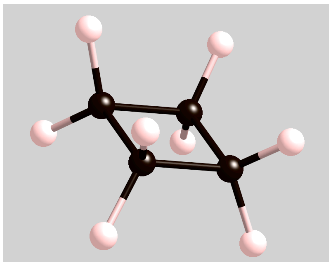
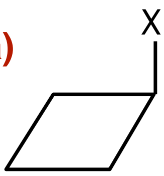


Figure 3.11 The allene molecule.

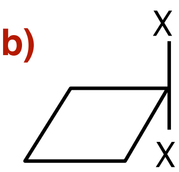
5. What is the point group for each of the following substituted cyclobutanes? Assume that (idealized) C_4H_8 itself has D_{4h} symmetry and that replacing an H by X or Y changes no other structure parameters.



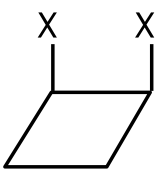
a)



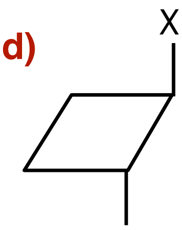
b)



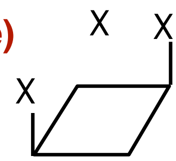
c)



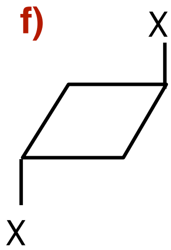
d)



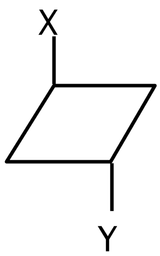
e)



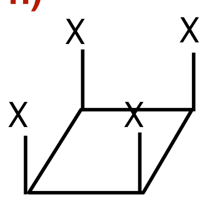
f)



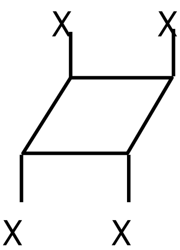
g)



h)



k)



l)