Advanced Physical Chemistry (fizkemhk17em)
Electronic Structure

Péter G. Szalay
ELTE Eötvös Loránd University
Institute of Chemsitry
szalay@chem.elte.hu

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Basic Terms of Group Theory

Basic Terms of Group Theory

A *group* ($\mathcal{G}$) is a collection of *elements* which are interrelated by an *operation*:

$$A \cdot B \quad = \quad C$$

for which the following rules must be obeyed:

- set $\mathcal{G}$ is *closed* under the operation:
  if $A, B \in \mathcal{G}$ then $C \in \mathcal{G}$
- there must be a *unit element* (E, identity) such that:
  $E \cdot A = A \cdot E = A$
- multiplication is *associative*:
  $A \cdot (B \cdot C) = (A \cdot B) \cdot C$
- all elements must have its *reciprocal* (A^{-1}) in the group:
  $A \cdot S = S \cdot A = E \qquad\qquad S \equiv A^{-1}$

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Note that the multiplication is not necessarily commutative:

$$A \cdot B \quad \neq \quad B \cdot A$$

Abelian group: the multiplication for any pair of elements *is* commutative.

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Abelian group: the multiplication for any pair of elements *is* commutative.

Dimension of the group (h):

- *finite group*: $h < \infty$
- *infinite group*: $h = \infty$

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Group multiplication table: shows the results of multiplication for any pair of group elements

	A	B	C	D
A	A	B	C	D
B	B	A	D	C
C	C	D	A	B
D	D	C	B	A

Properties:

- each element appears only once in each row and column
- multiplication is single valued

Basic Terms of Group Theory

Group multiplication table: shows the results of multiplication for any pair of group elements

	A	B	C	D
A	A	B	C	D
B	B	A	D	C
C	C	D	A	B
D	D	C	B	A

Properties:

- each element appears only once in each row and column
- multiplication is single valued

Subgroup: is a subset of elements which obey the definition of a group, i.e. multiplication does not lead out of the group.

It must always include E, and of course the invers of all elements.

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Conjugate elements: A and B are conjugate to each other, if

- $A, B, X \in \mathcal{G}$ and
- $B = X^{-1} \cdot A \cdot X$

Properties:

- If A is conjugate to B than B must be conjugate to A, i.e. the group must have an element Y such that:
  $A = Y^{-1} \cdot B \cdot Y$
- If A is conjugate to B and C then B and C are also conjugate to A.

Class: the complete set of elements which are conjugate to each other.

Basic Terms of Group Theory

Representation of a group

Remember the definitions: the group is defined by the multiplication table (relation of the elements) and not by any individual property of the elements.

The same group can also be represented for example by:

- operators (e.g. symmetry operation $\rightarrow$ symmetry groups)
- permutations (permutational groups)
- ...
- matrices (*matrix representation*)

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Assume a group with the following multiplication table:

	E	B	C	D
E	E	B	C	D
B	B	E	D	C
C	C	D	E	B
D	D	C	B	E

The following matrices obey the same multiplication table:

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{C} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{D} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Basic Terms of Group Theory

Assume a group with the following multiplication table:

C_{2v}	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

The following matrices obey the same multiplication table:

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{C}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \sigma_v' = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Basic Terms of Group Theory

Representation of a group I

How many matrix representations can a group have?

. – As many as you just generate!!!

For example, by similarity transformation we get new set of matrices which also form a representation:

$$A' = L^{-1}AL \qquad B' = L^{-1}BL$$

$$A' \cdot B' = L^{-1}AL \cdot L^{-1}BL = L^{-1}A \cdot BL = L^{-1}CL = C'$$

By similarity transformation the character of a matrix[1] does not change

$\rightarrow$ **the characters of the representing matrices will be characteristic to the representation** of the given dimensionality.

[1] Sum of the diagonal elements; also called „spur" or „trace".

Basic Terms of Group Theory

Representation of a group II

How many matrix representations can a group have?

. – As many as you just generate!!!

Also, you can create representation by forming direct sum of matices:

Basic Terms of Group Theory

Consider a group of two elements:

	A	B
A	A	B
B	B	A

Representation (1) (one dimensional):

$$\mathbf{A}^{(1)} = (1)$$

$$\mathbf{B}^{(1)} = (-1)$$

Representation (2) (two dimensional):

$$\mathbf{A}^{(2)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\mathbf{B}^{(2)} = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$$

Direct sum representation:

$$\mathbf{A} = \mathbf{A}^{(1)} \oplus \mathbf{A}^{(2)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{B} = \mathbf{B}^{(1)} \oplus \mathbf{B}^{(2)} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}$$

Basic Terms of Group Theory

Now the other way around: reducing the representation:

$$\mathbf{A} = \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right) \qquad \mathbf{B} = \left(\begin{array}{c|cc} -1 & 0 & 0 \\ \hline 0 & 0 & i \\ 0 & -i & 0 \end{array}\right)$$

In case of matrices showing block structure, the representation can be split up. Here:

$$\begin{aligned} \mathbf{A} &= \mathbf{A}^{(1)} \oplus \mathbf{A}^{(2)} \\ \mathbf{B} &= \mathbf{B}^{(1)} \oplus \mathbf{B}^{(2)} \end{aligned}$$

There are two subrepresentations in this case, matrices $\mathbf{A}^{(1)}, \mathbf{B}^{(1)}$ form representation $\Gamma^{(1)}$, and matrices $\mathbf{A}^{(2)}, \mathbf{B}^{(2)}$ form representation $\Gamma^{(2)}$.

In notation:

$$\Gamma = \Gamma^{(1)} \oplus \Gamma^{(2)}$$

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Representation of a group III

Are there special ones among the representations?
. – Yes, these are the so called *irreducible representations*.

Irreducible representations: is a nonzero representation that has no proper subrepresentation.

- basic building blocks of representations
- any representation can be build up from these basic elements

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Representation of a group III

General procedure of reducing the representation:

– assume we have a group represented by matrices $\mathbf{E}, \mathbf{B}, \mathbf{C}, \mathbf{D}, ...$

– we perform the same similarity transformation on all of them:

$$\begin{aligned} \mathbf{E}' &= \mathbf{L}^{-1}\,\mathbf{E}\,\mathbf{L} \\ \mathbf{B}' &= \mathbf{L}^{-1}\,\mathbf{B}\,\mathbf{L} \\ \mathbf{C}' &= \mathbf{L}^{-1}\,\mathbf{C}\,\mathbf{L} \end{aligned}$$

– similarity transformation does not change the multiplication rules
. $\rightarrow$ transformed matrices still give a representation (same character).

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– Special transformation can lead to block diagonal matrices, e.g.:

$$\mathbf{B}' = \mathbf{L}^{-1}\mathbf{B}\mathbf{L} \quad = \quad \begin{pmatrix} \mathbf{B}'_1 & 0 & 0 & 0 & \cdots \\ 0 & \mathbf{B}'_2 & 0 & 0 & \cdots \\ 0 & 0 & \mathbf{B}'_3 & 0 & \cdots \\ 0 & 0 & 0 & \mathbf{B}'_4 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{pmatrix}$$

– Block diagonal matrices can be multiplied block-wise:

$$\begin{aligned} \mathbf{B}'_1 \cdot \mathbf{C}'_1 &= \mathbf{D}'_1 \\ \mathbf{B}'_2 \cdot \mathbf{C}'_2 &= \mathbf{D}'_2 \\ &\vdots \end{aligned}$$

obeying the same multiplication rules

$\rightarrow$ each block is a new representation.

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Therefore:

If there exists a transformation which brings all matrices of a group to the same block structure, the representation can be split into „smaller" representations $\rightarrow$ i.e. the original representation *reducible*.

Note:

- the character of the representation is changed when it is splited into smaller pieces
- the sum of the character of new representations equals the character of the original representations

Notation: $\Gamma = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \cdots$

Therefore, a representation is *Irreducible* if:

- no transformation leading simultaneously to block structure of the matrices exists

Basic Terms of Group Theory

How many *irreducible representations* of a group are there?

– One can show that the number of all irreducible representations equals to the number of the classes of the group.

Basic Terms of Group Theory

How many *irreducible representations* of a group are there?

– One can show that the number of all irreducible representations equals to the number of the classes of the group.

Character table:

Example: Character table of the C_{2v} point group

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Columns correspond to the classes (in this case elements)

Rows correspond to the irreps and show the character of the elements

Basic Terms of Group Theory

Basis of a representation

We know the relation between operators and matrices:

Consider a set of (linearly independent) functions $\{\phi_i\}$ such that the space spanned is an invariant space with respect to all operators of the group. E.g.:

$$\begin{aligned}
\hat{A}\phi_i &= \sum_j A_{ij}\phi_j \\
\hat{B}\phi_i &= \sum_j B_{ij}\phi_j \\
\hat{C}\phi_i &= \sum_j C_{ij}\phi_j \\
&\dots
\end{aligned}$$

Basic Terms of Group Theory

Basis of a representation

The matrix representation of an operator in this basis can be given as:

$$\begin{aligned} A_{ij} &= \langle \phi_i | \hat{A} | \phi_j \rangle \\ (= & \int \phi_i(x)^* \hat{A} \phi_j(x) dx \ ) \end{aligned}$$

The matrices defined this way from operators belonging to a group, form also a group with the same multiplication table:

- the matrices $\mathbf{A}, \mathbf{B}, \ldots$ are the *matrix representation of operators* $\hat{A}$, $\hat{B}$, ... on the basis $\{\phi_i\}$.

Notes:

- when transforming the matrices, in fact we transform the basis
- when finding the block diagonal form of the matrices and splitting up the representation accordingly, we divide up the space into smaller subspaces. Now the elements of subspaces will be used as basis of the representations.

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Reducing reducible representations

To split up reducible representations into irreducible ones, one can use the following formula:

$$n_i = \frac{1}{h}\sum_{k=1}^{r} N_k \, \chi^i(k) \, \chi(k)$$

with:

h: order of the group

N_k: order of the class

$\chi^i(k)$: character of kth class corresponding to irrep i

$\chi(k)$: character of kth class corresponding to the reducible representation

Basic Terms of Group Theory

To find the subspace spanning the irreducible representations, the following operator can be used, which projects into the space of the ith irrep:

$$\hat{P}_i = \sum_{\hat{R}} \chi^i(\hat{R})\, \hat{R}$$

with $\hat{R}$ being the element of the group, $\chi^i(\hat{R})$ being its character corresponding to the ith irrep.

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Reducing reducible representations

Example: Two matrices $\mathbf{A}$ and $\mathbf{B}$ considered above:

$$\mathbf{A} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}$$

Character table for this group[2]

C_s	$\hat{A}$	$\hat{B}$
A'	1	1
A''	1	-1
$\Gamma_{3\ dim}$	3	-1

The characters of the $\Gamma_{3\ dim}$ representation are given as the spur (trace) of the corresponding matrices.

[2] Note that this is the C_s point group, introduced later.

Basic Terms of Group Theory

C_s	$\hat{A}$	$\hat{B}$
A'	1	1
A"	1	-1
$\Gamma_{3\ dim}$	3	-1

$n_i = \frac{1}{h} \sum_{k=1}^{r} N_k \; \chi^i(k) \; \chi(k)$

n$_{\mathrm{A'}}$$= \frac{1}{2}(1{\cdot}1{\cdot}3+1{\cdot}1{\cdot}(-1)) = 1$

n$_{\mathrm{A''}}$$= \frac{1}{2}(1{\cdot}1{\cdot}3+1{\cdot}(-1){\cdot}(-1)) = 2$

Thus: $\Gamma_{3\ dim}$=A' $\oplus$ 2 A"

$$\mathbf{A} = \left(\begin{array}{c|c|c} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right) \qquad \mathbf{B} = \left(\begin{array}{c|c|c} 1 & 0 & 0 \\ \hline 0 & -1 & 0 \\ \hline 0 & 0 & -1 \end{array}\right)$$

Basic Terms of Group Theory

Direct product representations

Consider two representations on the two bases $\{\phi_i(x)\}$ and $\{\psi_i(y)\}$:

$$\hat{A}\phi_i(x) = \sum_j A_{ij}^{\phi}\phi_j(x) \qquad \hat{A}\psi_i(y) = \sum_j A_{ij}^{\psi}\psi_j(y)$$

Then:

$$\hat{A}\phi_i(x)\psi_j(y) \quad = \quad \sum_k \sum_l A_{ik}^{\phi} A_{jl}^{\psi} \psi_k(x)\phi_l(y)$$

i.e. the set $\{f_{ij}(x,y)\} = \{\phi_i(x) \cdot \psi_j(y)\}$ also form a basis for the representation, that of the outer product of the two matrices:

$$\mathbf{A}^{\phi\otimes\psi} \quad = \quad \mathbf{A}^{\phi} \otimes \mathbf{A}^{\psi}$$

with $\mathbf{A}^{\phi\otimes\psi}$ having a dimension as product of the dimensions of the two representations.

Basic Terms of Group Theory

Direct product representations

Outer product of two matrices:

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix}$$

$$\begin{aligned} \mathbf{A} \otimes \mathbf{B} &= \begin{pmatrix} \mathbf{A}B_{11} & \mathbf{A}B_{12} \\ \mathbf{A}B_{21} & \mathbf{A}B_{22} \end{pmatrix} \\ &= \begin{pmatrix} A_{11}B_{11} & A_{12}B_{11} & A_{11}B_{12} & A_{12}B_{12} \\ A_{21}B_{11} & A_{22}B_{11} & A_{21}B_{12} & A_{22}B_{12} \\ A_{11}B_{21} & A_{12}B_{21} & A_{11}B_{22} & A_{12}B_{22} \\ A_{21}B_{21} & A_{22}B_{21} & A_{21}B_{22} & A_{22}B_{22} \end{pmatrix} \end{aligned}$$

Character of $\mathbf{A} \otimes \mathbf{B}$?

Basic Terms of Group Theory

Direct product representations

Outer product of two matrices:

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix}$$

$$\begin{aligned} \mathbf{A} \otimes \mathbf{B} &= \begin{pmatrix} \mathbf{A}B_{11} & \mathbf{A}B_{12} \\ \mathbf{A}B_{21} & \mathbf{A}B_{22} \end{pmatrix} \\ &= \begin{pmatrix} A_{11}B_{11} & A_{12}B_{11} & A_{11}B_{12} & A_{12}B_{12} \\ A_{21}B_{11} & A_{22}B_{11} & A_{21}B_{12} & A_{22}B_{12} \\ A_{11}B_{21} & A_{12}B_{21} & A_{11}B_{22} & A_{12}B_{22} \\ A_{21}B_{21} & A_{22}B_{21} & A_{21}B_{22} & A_{22}B_{22} \end{pmatrix} \end{aligned}$$

$$\chi_{\mathbf{A}\otimes\mathbf{B}} = (A_{11} + A_{22}) \cdot (B_{11} + B_{22}) = \chi_A \cdot \chi_B$$

Basic Terms of Group Theory

Direct product representations

Notation:

$$\Gamma^{\phi\otimes\psi} \quad = \quad \Gamma^{\phi} \otimes \Gamma^{\psi}$$

Character of the direct product representation:

The characters of the direct product representation are the products of the character of the representations forming the original representations.

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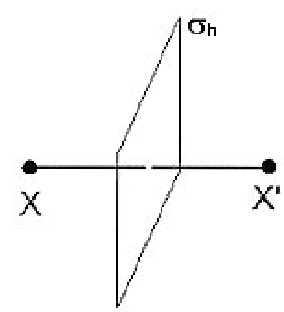
Spatial Symmetry of Molecules

Symmetry operations

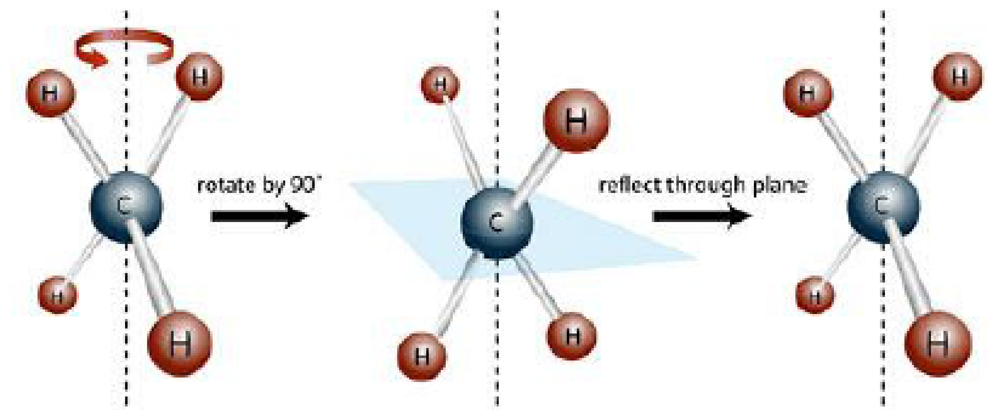
- $\hat{C}_n$ – proper rotation (around the proper axis) by $2\pi/n$

- $\hat{\sigma}$ – reflection (special cases: $\hat{\sigma}_v$, $\hat{\sigma}_h$, $\hat{\sigma}_d$)



Symmetry operations

- $\hat{S}_n$ – improper rotation: rotation ($\hat{C}_n$) followed by reflection in a plane perpendicular to the rotation axis (σ_h)



- $\hat{i}$ – inversion ($\hat{i} = \hat{S}_2$)

- $\hat{E}$ – unity: maps the object on itself (required only for mathematical purposes)

Point groups

Symmetry operations leaving an object (molecule) unchanged, form a group.

E.g. water (see next page):

Operators: $\hat{C}_2$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$

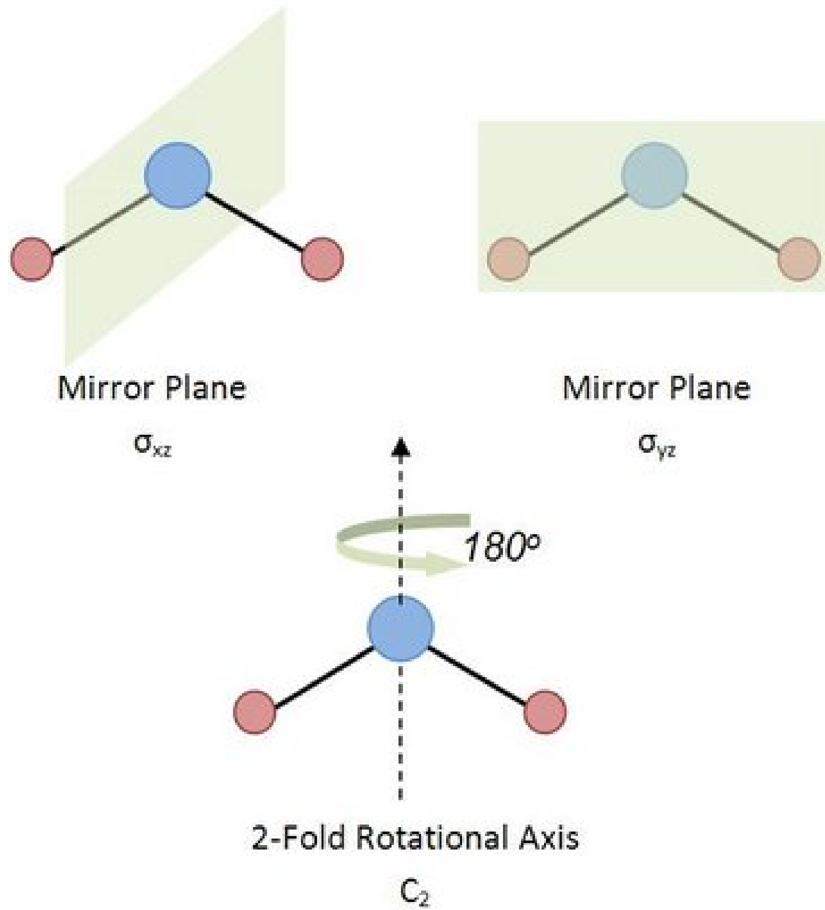
Multiplication table:

$\hat{C}_{2v}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}'_v$	σ_v
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}'_v$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$	$\hat{C}_2$	$\hat{E}$

The group formed by the symmetry operations is called the *point group*.

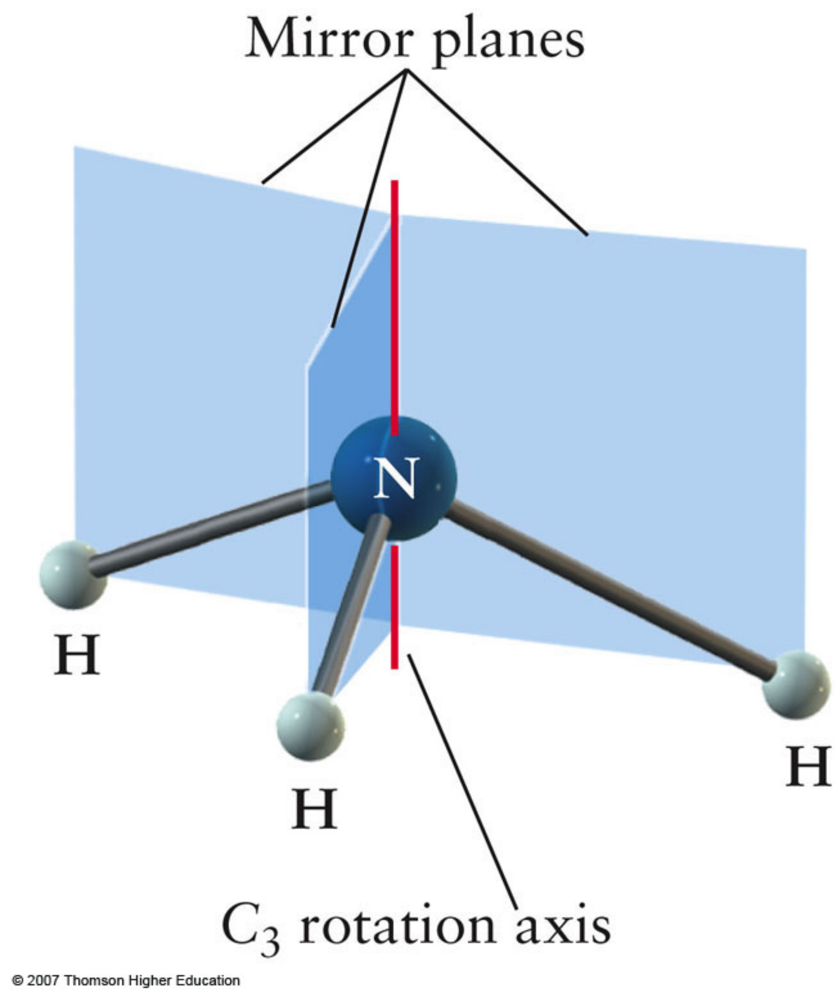
Point groups

Water: $\hat{C}_2$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$



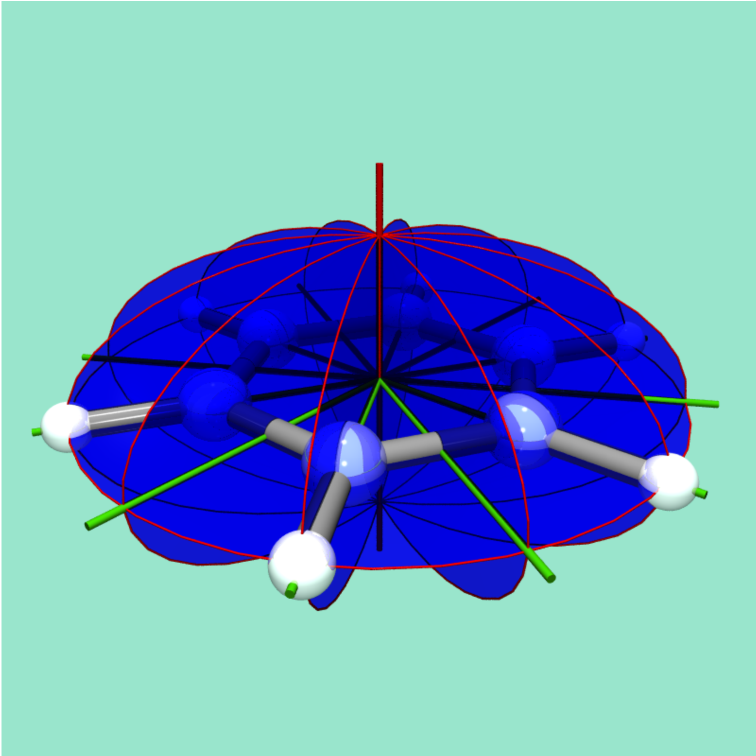
Point groups

Ammonia: $\hat{C}_3$, 3 times $\hat{\sigma}_v$, $\hat{E}$



Point groups

Benzene: $\hat{C}_6$, 6 times $\hat{C}_2$, $\hat{\sigma}_h$ (horizontal, perpendicular to the main axis), 6 times $\hat{\sigma}_v$ (including the main axis), $\hat{i}$, etc.



Generators of a group

Set of elements ($\mathcal{S}$) of the group $\mathcal{G}$ are called *generators* if all elements of $\mathcal{G}$ can be generated by multiplication of the elements of $\mathcal{S}$.

Example: benzene

Elements of the point group $\mathrm{D_{6h}}$:

$$\hat{E},\ 2\hat{C}_6,\ 2\hat{C}_3,\ \hat{C}_2,\ 3\hat{C}_2',\ 3\hat{C}_2\text{"},\ \hat{i},\ 2\hat{S}_6,\ 2\hat{S}_3,\ \hat{\sigma}_h,\ 3\hat{\sigma}_v,\ 3\hat{\sigma}_d$$

Three generators are able to produce these elements.

Set 1: $\hat{C}_6, \hat{C}_2'$ and $\hat{i}$.

$$\hat{C}_3 = \hat{C}_6 \cdot \hat{C}_6, \quad \hat{C}_2 = \hat{C}_6 \cdot \hat{C}_6 \cdot \hat{C}_6, \quad \hat{C}_2\text{"} = \hat{C}_6 \cdot \hat{C}_2', \quad \hat{\sigma}_v = \hat{C}_2' \cdot \hat{i} \text{ etc.}$$

Set 2: $\hat{C}_6$, $\hat{\sigma}_v$, $\hat{\sigma}_v$

Set 3:..... several others

The set of the generators is not unique!

Point groups

Symmetry of molecules are represented by the collection of symmetry operations leaving it unchanged, i.e. by the *point group*.

Point groups are represented by the so called *Schoenflies-symboles*:

- C_n: groups including proper rotation $\hat{C}_n$ only
- C_{nv}: groups including proper rotation $\hat{C}_n$ and reflection to a plain including the axis $\hat{\sigma}_v$
- C_{nh}: groups including proper rotation $\hat{C}_n$ and reflection to a plain perpendicular to the axis $\hat{\sigma}_h$
- D_n: groups including proper rotation $\hat{C}_n$ and n additional proper rotation $\hat{C}_2$ perpendicular to the main axis
- D_{nh}: same as D_n with and additional reflection to a plane perpendicular to the main axis.

Point groups

- D_{nd}: same as D_n with and additional reflection to a plane including the main axis.
- S_n: includes improper rotation $\hat{S}_n$
- T_d: tetrahedral point group
- ...
- $C_{\infty v}$: proper rotation with arbitrary angle ($\hat{C}_\infty$) and reflection to a plane including this axis ($\hat{\sigma}_v$)
- $D_{\infty h}$: proper rotation with arbitrary angle ($\hat{C}_\infty$) and reflection to a plane perpendicular to this axis ($\hat{\sigma}_h$)
- O_3^+: spherical symmetry

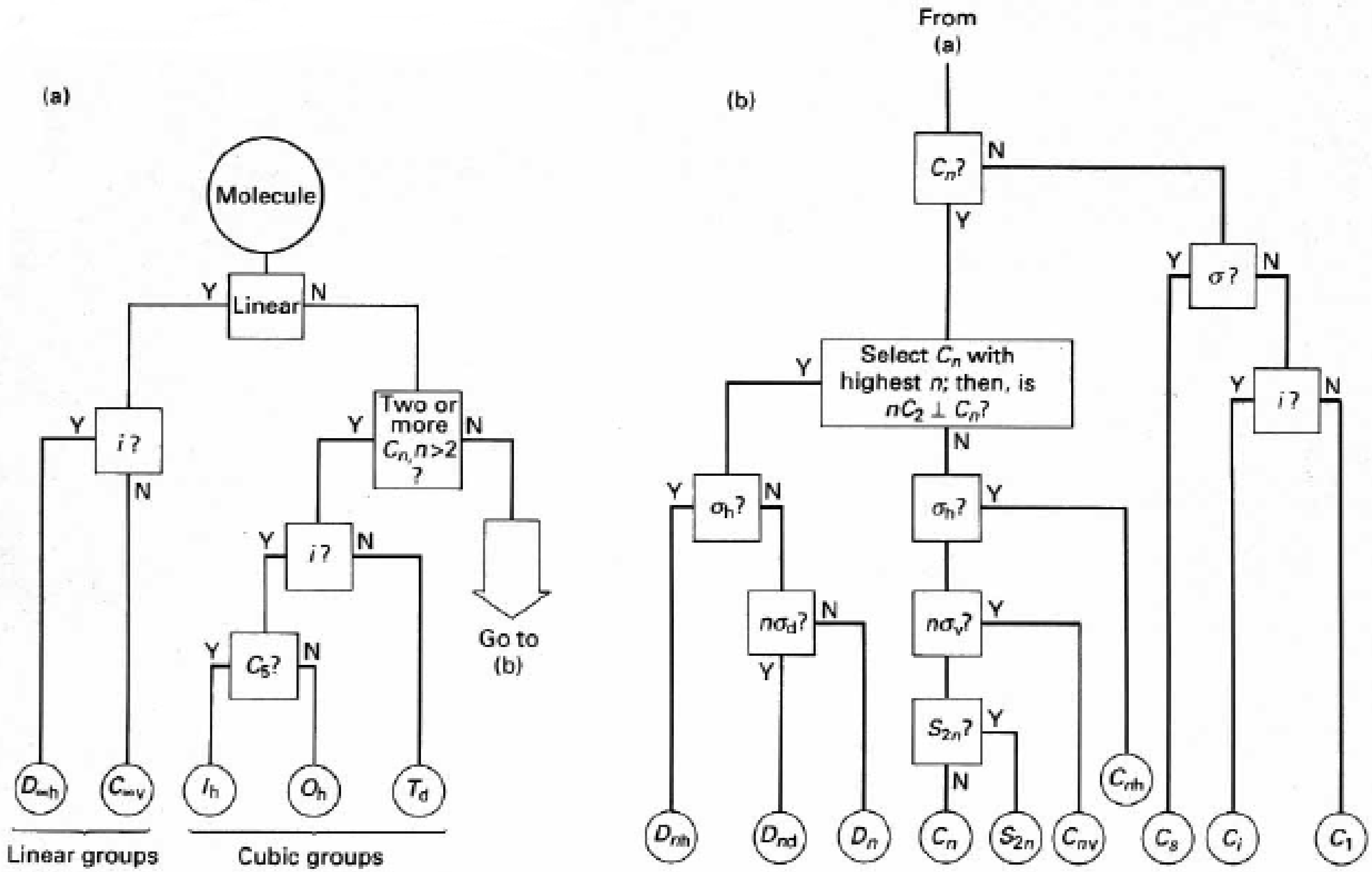
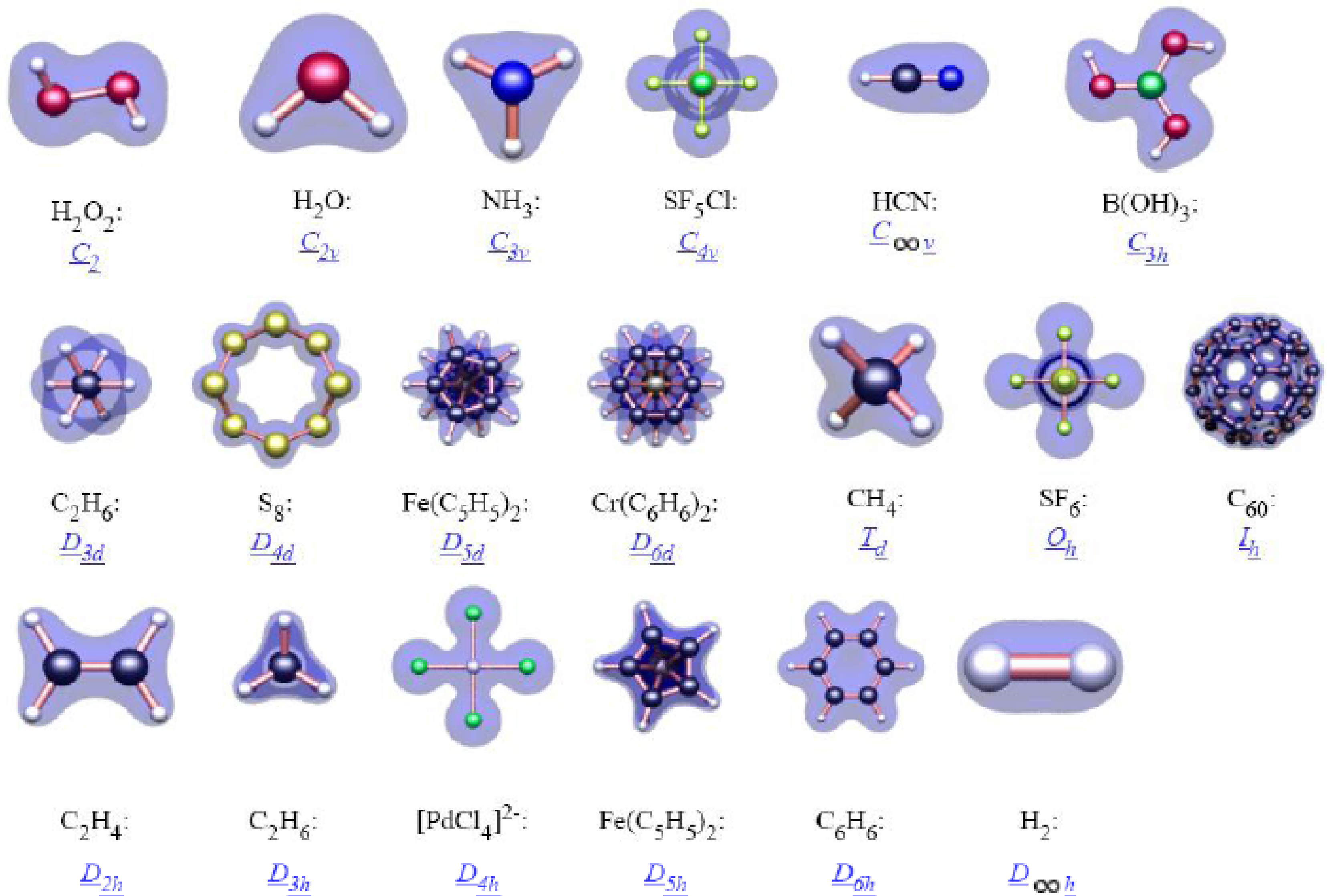


Figure 3.15
Shriver, Atkins, and Langford: *INORGANIC CHEMISTRY*, second edition
©1990, 1994 D. F. Shriver, P. W. Atkins, and C. H. Langford
W. H. Freeman and Company

Point groups

Molecular examples:

molecule	symmetry operations	point group
water	$\hat{C}_2$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$	C_{2v}
ammonia	$\hat{C}_3(z)$, 3 x $\hat{\sigma}_v$, $\hat{E}$	C_{3v}
benzene	$\hat{C}_6$, 6 x $\hat{C}_2$, $\hat{\sigma}_h$, 6 x $\hat{\sigma}_v$, $\hat{i}$, etc.	D_{6h}
formaldehyde	$\hat{C}_2(z)$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$	C_{2v}
ethene		D_{2h}
acetylene		$D_{\infty h}$
carbon monoxide		$C_{\infty v}$



http://newton.ex.ac.uk/research/qsystems/people/goss/symmetry/Molecules.html

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Symmetry and quantum mechanics

Symmetry and quantum mechanics

Symmetry operations are represented by operators ($\hat{R}$).

What does it mean mathematically: „The operations leave the molecule unchanged"?

It does not change the properties $\rightarrow$ The symmetry operators commute with the corresponding operators (e.g. Hamiltonian):

$$\hat{R}\hat{H} \quad = \quad \hat{H}\hat{R}$$

Symmetry and quantum mechanics

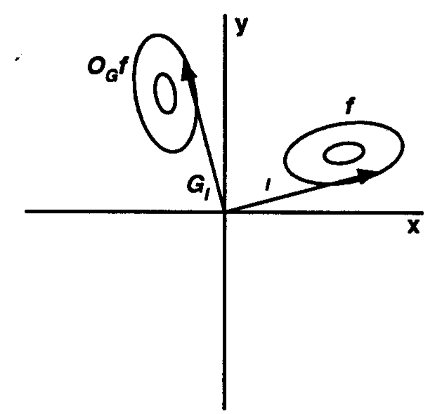
Symmetry operations are represented by operators ($\hat{R}$).

What does it mean mathematically: „The operations leave the molecule unchanged"?

It does not change the properties $\rightarrow$ The symmetry operators commute with the corresponding operators (e.g. Hamiltonian):

$$\hat{R}\hat{H} = \hat{H}\hat{R}$$

Figure 10.2: Transformation of functions



Action of a symmetry operator on a function:

$$\hat{R}f(\mathbf{x}) = f(\hat{R}^{-1}\mathbf{x})$$

Symmetry and quantum mechanics

$$\hat{R}\hat{H} = \hat{H}\hat{R}$$

Commuting operators have a common set of eigenfunctions[3]

$\Downarrow$

The eigenfunction of the Hamiltonian must also be eigenfunction of the symmetry operators.

$$\hat{R}\Psi = r\Psi$$

[3] For easier understanding we disregard degeneracy for the time being.

Symmetry and quantum mechanics

$$\hat{R}\Psi = r\Psi$$

What are the eigenvalues?

- Like the object (molecule), the wave function is unchanged under the symmetry operation: $r = 1$
- The wave function can also change sign under the symmetry operation, since in this case the density $|\Psi|^2$ is still unchanged: $r = -1$

This eigenvalue will be representative for the wave function („good quantum numbers"):

- $r = 1$: symmetric
- $r = -1$: antisymmetric

Symmetry and quantum mechanics

$$\hat{R}\Psi = r\Psi$$

What about the eigenfunctions?

- They form a basis for a representation of the symmetry operations.

Symmetry axiom: the eigenfunctions of the Hamiltonian form an *irreducible representation* of the symmetry operations.

Symmetry and quantum mechanics

We have several symmetry operations, all can have two eigenvalues.

For water, this means 2^3 possibilities ($\hat{E}$ has only one eigenvalue).

Are all of these possible?? No, only four combinations are possible:

C_{2v}	E	C_2	σ_{zx}	σ_{zy}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

The four possibilities are the *irreducible representation*.

The *character table* shows the eigenvalue of the individual operators corresponding to the irreps.

Thus, wave functions can be classified according to the rows of the character table, i.e. according to the irreps.

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The four possibilities are the *irreducible representation*.

The *character table* shows the eigenvalue of the individual operators corresponding to the irreps.

Thus, the wave function of water can be classified as A_1, A_2, B_1 or B_2.

Symmetry and quantum mechanics

Other example: ammonia

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Here there is also two-dimensional irrep. This means:

- there are two eigenfunctions of the Hamiltonian which have the same symmetry property
- any combination of these two functions still define a representation of the group (with the same character)

Symmetry and quantum mechanics

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$\Rightarrow$ it follows that these functions belong to the same eigenvalue of the Hamiltonian, i.e. *degenerate*!

Symmetry and quantum mechanics

In summary:

It is worth to use symmetry:

- to classify states
- to speed up calculations
- predict degeneracy