3. Compact Course: Groups Theory

Remark: This is only a brief summary of most important results of groups theory with respect to the applications discussed in the following chapters. For a more detailed description see references.

3.1 Definition of a group

We assume a set of elements $\mathbf{G} = \{A, B, C, ...\}$. Furthermore, we assume that there is a definition of a combination of two elements AB, which we denote as the product of two elements.

$\mathbf{G}$ is a group if the following conditions are satisfied:

1. Closure: $AB \in \mathbf{G}$

   The product of two elements of the group is also an element of the group.

2. Identity element: The is an element $E \in \mathbf{G}$, such that $AE = EA = A$ for all $A \in \mathbf{G}$.

   A 'neutral' element exists, which has no 'effect' on the other elements if the group.

3. Associative law: $A(BC) = (AB)C$ for all $A, B, C \in \mathbf{G}$.

4. Inverse element: The is an element $A^{-1} \in \mathbf{G}$, such that $A^{-1}A = E$ for all $A \in \mathbf{G}$.

   In inverse element exists for all elements of the group, which inverts the 'action' of a given element.

- For some, but not for all groups, the commutative law holds (commutative law: $AB = BA$ for all $A \in \mathbf{G}$). These groups are called Abelian groups.
- Without proof (see e.g. F. A. Cotton): $(ABC)^{-1} = A^{-1}B^{-1}C^{-1}$.

(3.1: Example for a group)

3.2 Order of a group

The number of elements of a group is called the order of the group.

3.3. Multiplication table

For any group, we can set up a multiplication table, which tabulates the results of the products of two elements.

Without proof: Every line and column contains every group element exactly once. No line or column is identical to another one.

(3.2: How many types of groups are there with three elements? Derive the multiplication tables.)

3.4 Cyclic groups

In a cyclic group all n elements are generated by powers of the first element $\mathbf{G} = \{E(=A^n), A^1, A^2, \ldots A^{n-1}\}$.

(3.3: Example of a cyclic group)

An important property of cyclic groups is that they are Abelian (as $A^n A^m = A^{n+m} = A^m A^n$).

3.5 Subgroups

A subset of the elements of the group $\mathbf{G}$ can itself form a group $\mathbf{U}$. We call $\mathbf{U}$ a subgroup of $\mathbf{G}$.

(3.4: Example of a subgroup)

3.6 Symmetry groups

The complete set of symmetry elements of a molecule, surface or crystal has the mathematic structure of a group. The set is called the symmetry group.

(3.5: Example of a symmetry group. H_2O molecule: show that the symmetry elements behave like a group).

3.7 Classes

We define a similarity transformation

$$B = X^{-1}AX$$

which transform some element A by means of another element X into some other element B. If A and X are elements of the group $\mathbf{G}$, the elements are called conjugated elements. A complete set of elements, which is conjugated to one another is called a class of elements of the group.

The classes have a figurative meaning: Those symmetry operations belong to the same class, which can be reached by a transformation of the coordinate system, which is part of the symmetry group.

(3.6: Example: Divide the elements of the symmetry group C_{4v} into classes).

(The definition of classes will greatly simplify the work with symmetry groups).

3.8 Representation of symmetry operations by matrices

We can represent all symmetry operations discussed so far in the form of a matrix $\mathbf{R}$.

In the simplest case, these matrices act on points $\vec{X}$ in three-dimensional space and assign a new position $\vec{X}' = \mathbf{R}\vec{X}$ (Note: if instead we consider a basis transformation defining the new basis $\vec{B}'$ in terms of the old one as $\vec{B}' = \mathbf{A}\vec{B}$, the coordinates of the point in the new coordinated $\vec{X}'$ are $\vec{X}' = \mathbf{A}^{-1}\vec{X}$):

(3.7: Examples for matrix representations of symmetry operations).

3.9 Representations of a group

A set of matrices which upon multiplication behaves analogous to the elements of a group is called a representation of the group.

Example:

We consider the transformation of a point $\vec{X}$ in three dimensional space according to the symmetry operations of group C_{2V}.

$$E=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix};\ C_2=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix};\ \sigma_v=\begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix};\ \sigma_v{}'=\begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}$$

With respect to matrix multiplication, these matrices follow the multiplication table of group C_{2V}.

3.10 Reducible and irreducible representations

As specific case of matrices are so called block-diagonal matrices. Block-diagonal matrices are multiplied according to the scheme, i.e. the multiplication can be reduced to the multiplications of the sub-matrices of lower dimension:

$$\begin{pmatrix}\begin{pmatrix}a&\cdots\\\vdots&\ddots\end{pmatrix}&0\\0&\begin{pmatrix}b&\cdots\\\vdots&\ddots\end{pmatrix}\end{pmatrix}\cdot\begin{pmatrix}\begin{pmatrix}x&\cdots\\\vdots&\ddots\end{pmatrix}&0\\0&\begin{pmatrix}y&\cdots\\\vdots&\ddots\end{pmatrix}\end{pmatrix}=\begin{pmatrix}\begin{pmatrix}a&\cdots\\\vdots&\ddots\end{pmatrix}\begin{pmatrix}x&\cdots\\\vdots&\ddots\end{pmatrix}&0\\0&\begin{pmatrix}b&\cdots\\\vdots&\ddots\end{pmatrix}\begin{pmatrix}y&\cdots\\\vdots&\ddots\end{pmatrix}\end{pmatrix}$$

For the specific example considered, the matrices are completely diagonal, i.e. all blocks are of dimension 1. Accordingly we can reduce the three dimensional representation given above into three one-dimensional representations, which again are representations of the symmetry group C_{2V}:

$$\begin{array}{llll}E=1 & C_2=-1 & \sigma_v=1 & \sigma_v{}'=-1\\ E=1; & C_2=-1; & \sigma_v=-1; & \sigma_v{}'=1\\ E=1 & C_2=1 & \sigma_v=1 & \sigma_v{}'=1\end{array}$$

We consider a representation of a group by a set of matrices $\mathbf{R}$ of dimension n. Additionally , we consider a basis transformation to a new coordinate system $\vec{B}'=\mathbf{A}\vec{B}$, with the coordinates of a vector in the new basis in terms of the old coordinates $\vec{X}'=\mathbf{A}^{-1}\vec{X}$. The representation of the group in the new basis is $\mathbf{A}'=\mathbf{A}^{-1}\mathbf{R}\mathbf{A}$. For any representation, we can search for the basis transformation, which yields a set of representations with lowest possible dimension. We denote a representation with the lowest possible dimension as an irreducible representation and a representation with higher than minimum dimension as a reducible representation.

The example shows that there are irreducible representations (brief: irreps) of different type, i.e. behaving differently with respect to the symmetry operations contained in the group.

3.11 Character of a matrix

We define the character χ_Γ of a matrix Γ as the sum over the diagonal elements:

$$\chi_\Gamma = \sum_i \Gamma_{ii} \ .$$

(3.8: Character of matrices).

The character of a matrix has an important property: It is invariant upon a transformation of the basis.

(3.9: Character of matrices).

This is quite handy, as in the following it allows us to work with characters instead of the full representation matrices, irrespective of a specific choice of the basis.

3.12 Properties of irreducible representations: GOT "great orthogonality theorem"

(for proof see textbooks)

$$\sum_R \Gamma_i(R)_{mn} \Gamma_j(R)_{m'n'}{}^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'}$$

with h : order of the group

R : symmetry operation of the group

$\Gamma_i(R)$: matrix representation for operation R of the irreducible representation of type i

l_i : dimension of the i-th type of irreducible representation

The vectors consisting of corresponding elements of the representation matrices are orthogonal and normalized. There are a number of simpler conclusions following from the GOT, which can be easily proven (see e.g. A. F. Cotton), e.g:

- $\sum_i l_i^2 = \sum_i \chi_i(E)^2 = h$; sum over the dimension squares of the irreps (sum over the character squares of the identity element) is equal to the order of the group.
- $\sum_R \chi_i(R)^2 = h$; sum over character sqares over all symmetry operation for a given type of representation is equal to the order of the group.
- $\sum_R \chi_i(R)\chi_j(R) = h\delta_{ij}$: Character vectors of different irreps are orthogonal.
- The characters of representation matrices for a given type of irrep for operations belonging to a common class are identical.
- The number of classes is equal to the number of irreps.

(3.10: Develop the characters and representation matrices for the symmetry group C_{2V} from the above statements).

3.13 Analysis of reducible representations

The following idea is a key point for a large number of applications in the next chapters of this course.

We assume that $\Gamma(R)$ is a reducible representation of the symmetry group G with the corresponding characters $\chi(R)$. We would like to know, how many irreducible representations of symmetry type i are contained in $\Gamma(R)$.

For this reason we assume that we have transformed $\Gamma(R)$ to its blockdiagonal form $\Gamma'(R)$. As the characters are invariant with respect to this transformation, we obtain:

$\chi(R) = \chi'(R) = \sum_j a_j \chi_j(R)$ with $\chi_j(R)$: character of j-th irrep of group

a_j: number of times that j-th irrep is contained in $\Gamma(R)$

By multiplying with $\chi(R)$ and summing over all operations of the group:

$$\sum_R \chi(R)\chi_i(R) = \sum_R \sum_j a_j \chi_j(R)\chi_i(R)$$
$$= \sum_R \sum_j a_j \chi_j(R)\chi_i(R)$$
$$= \sum_R a_j \underbrace{\sum_j \chi_j(R)\chi_i(R)}_{h\mathrm{d}_{ij}}$$
$$= ha_i$$

$$\Rightarrow \boxed{a_i = \frac{1}{h}\sum_R \chi(R)\chi_i(R)}$$

Here, all we need as an input is the characters of the irreps of the group. These are listed in the so called character tables.

3.14 Character tables

Most important information which is required to work with a given symmetry group is summarized in the co called character table.

Example: C_{4V}

group name (Schoenfliess)

symmetry operations ordered by classes

symmetry properties of some functions and their classification by irreps

C_{4V}	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	(x, y)	xy
E	2	0	-2	0	0	(R_x, R_y)	(xz, yz)

List of irreducible representations:

<u>Mulliken notation:</u>

(1) 1 dim. irreps: A, B
2 dim. irreps: E
3 dim. irreps: T
4 dim. irreps: G
5 dim. irreps: H

(2) A/B: symmetric / antisymmetric with respect to rotation by $2\pi/n$ around principle axis C_n.

(3) Index 1/2: symmetric / antisymmetric with respect to rotation by π around C_2 axis (perpendicular to C_n).

(4) ' or '': symmetric / antisymmetric with respect to σ_h.

(5) g/u: symmetric / antisymmetric with respect to i.