

# Symmetry and Order

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## Outline

1. Abstract group theory
2. Group representations
3. Application I: Character tables
4. Application II: Butadiene ( $C_4H_6$ )
5. Application III: Crystal field theory

## Literature

1. M. S. Dresselhaus, G. Dresselhaus, and A. Jorio, *Group Theory: Applications to the Physics of Condensed Matter*, Springer (2008)
2. M. Tinkham, *Group Theory and Quantum Mechanics*, Dover (2003)
3. F. A. Cotton, *Chemical Applications of Group Theory*, John Wiley (1990)
4. B. N. Figgis, and M. A. Hitchman, *Ligand Field Theory and its Applications*, Wiley-VCH (1999)

# 1 Abstract group theory (definitions/examples)

## 1.1 Definition

A set of elements  $\{E, A, B, C, \dots\}$  form a group  $G$  when the following conditions are fulfilled:

1. There exists a *multiplication* operation  $(*)$  such that the product of any two elements of  $G$  is in the set.
2. The *associative* law holds, i.e.,  $(A * B) * C = A * (B * C)$  for all  $A, B, C$  in the set.
3. There exists a *unit element*  $E$  (identity element) such that  $E * A = A * E = A$ , i.e., the product of  $E$  with any group element leaves that element unchanged.
4. For every element  $A$  there exists an *inverse element*  $A^{-1}$  such that  $A^{-1} * A = A * A^{-1} = E$ .

**Note 1.** In general, the multiplication operation is not necessarily *commutative*, i.e.,  $A * B \neq B * A$ . However, if the multiplication operation is commutative, so that  $A * B = B * A$ , the group is said to be Abelian. Usually one drops the explicit multiplication symbol  $*$  and just writes products like  $A * B = AB$ . *Multiplication* then means multiplication within the group structure, not necessarily numerical multiplication.

**Note 2.** In finite groups  $G$  considered here the number  $h$  of group elements is known as *order* of the group.

## 1.2 Some familiar examples

- The real numbers  $R$  under multiplication do *not* form a group, since the element 0 does not have an inverse  $0^{-1}$ . But the set  $R - \{0\}$  does form an Abelian group under multiplication. The identity element is unity,  $E = 1$ , because  $1A = A1 = A$ .
- The real numbers also form a group under addition, where now zero is the identity element,  $E = 0$ , and the inverse of  $A$  is  $-A$ ,  $A + (-A) = E = 0$ .
- Group of order 1. 'Trivial group' containing only one element,  $\{E\}$ , with the multiplication rule  $EE = E$ . Clearly,  $E^{-1} = E$ , and  $E(EE) = (EE)E$  and so it obeys all the axioms of group theory.

- Group of order 2. It is an Abelian group with elements  $A, A^2 = E$ . In physical applications  $A$  might represent reflection, inversion, or an interchange of two identical particles.
- Group of order 3. Group elements could be  $A, A^2 = B \neq E, A^3 = E$  (example for cyclic group to be discussed later).
- The rotations of the  $(x, y)$  around a fixed axis  $z$ , form a group. In the case where  $\theta = 2\pi/n$  the rotation element is referred to in crystallography as a  $n$ -fold axis,  $C_n$ , and the group of these rotations is obviously identical (isomorphic) to  $Z_n$ . In crystals axes can be 2, 3, 4, or 6 fold. Interestingly, 5 fold, 7 fold or other rotations are forbidden in crystals, which made the discovery of 'Penrose tiles' and 'quasicrystals' an exciting novel problem in the 1980s.
- Permutation group. One group of order  $n!$  can always be set up based on all the permutations of  $n$  distinguishable elements, where the element  $i$  shifts to the position indicated in the lower row:

$$\begin{pmatrix} 1 & 2 & \cdots & i & \cdots & n \\ \alpha_1 & \alpha_2 & \cdots & \alpha_i & \cdots & \alpha_n \end{pmatrix}$$

$$\begin{matrix} E = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix} & A = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} & B = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \\ C = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} & D = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} & F = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \end{matrix}$$

Successive permutations then form the group multiplication summarised in the group multiplication table:

	$E$	$A$	$B$	$C$	$D$	$F$
$E$	$E$	$A$	$B$	$C$	$D$	$F$
$A$	$A$	$E$	$D$	$F$	$B$	$C$
$B$	$B$	$F$	$E$	$D$	$C$	$A$
$C$	$C$	$D$	$F$	$E$	$A$	$B$
$D$	$D$	$C$	$A$	$B$	$F$	$E$
$F$	$F$	$B$	$C$	$A$	$E$	$D$

- The following six square matrices, together with ordinary matrix multiplication form a group:

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

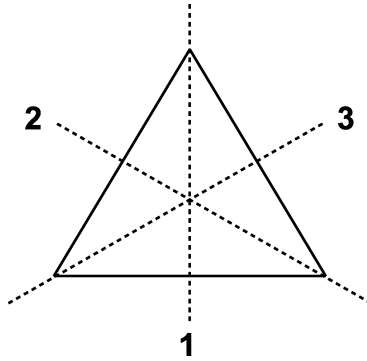


Figure 1: Symmetry operations of an equilateral triangle.

- The symmetry operations of an equilateral triangle (figure 1) form a group.  $A$ ,  $B$ , and  $C$  are rotations by  $\pi$  about the axes shown. In addition, there is a clockwise (counterclockwise) rotation by  $2\pi/3$  denoted as  $D$  ( $F$ ), and the identity operation  $E$ .
- The set of Lorentz transformations form a group. The multiplication law of the group elements leads to the rule for addition of velocities in relativity.

**Note.** The three groups (permutation group  $n = 3$ , matrix group  $3 \times 3$ , and the symmetry operations of an equilateral triangle) obey the *same* group multiplication table; they are said to be *isomorphic*. This is an example of a *one-to-one* correspondence. In case of a *many-to-one* correspondence the groups are said to be *homomorphic*.

### 1.3 Rearrangement theorem

**Theorem.** If  $E, A_2, A_3, \dots, A_h$  are the elements of a group  $G$ , then the assembly (sequence) of elements  $EA_k, A_2A_k, \dots, A_hA_k$  contains each group element  $A_i$  once and only once (in the form  $A_rA_k$ ).

**Proof.** For any  $A_i$  and  $A_k$  there exists an element  $A_r = A_iA_k^{-1}$  in the group, since the group contains inverse elements and is closed.

For this particular  $A_r$  holds  $A_rA_k = A_i$ . Therefore,  $A_i$  has to appear at least once. But there are  $h$  elements in the group and  $h$  terms in the assembly of elements. Hence, there is no opportunity for any element to make more than a single appearance.

### 1.4 Cyclic groups

For any group element  $X$  one can form the sequence  $X, X^2, X^3, \dots, X^{n-1}, X^n = E$  called the *period* of  $X$ .  $n$  is called the order of the group.

**Note 1.** The period forms a group in itself, a cyclic group (subgroup) of order  $n$ .

**Note 2.** All cyclic groups must be Abelian.

**Example.** Think of the group of symmetry operations of an equilateral triangle mentioned above. With the group multiplication table one finds  $D^1 = D$ ,  $D^2 = F$ , and  $D^3 = DF = E$ , so  $D$ ,  $E$ , and  $F$  form a cyclic subgroup of order 3 of the entire group of order 6. Similarly one finds  $A$  and  $E$ ,  $B$  and  $E$ , and  $C$  and  $E$  to be cyclic subgroups of order 2.

**Theorem.** The order  $g$  of a subgroup must be an integral divisor of the order  $h$  of the entire group. That is,  $h/g = l$ , where integer  $l$  is called the index of the subgroup in  $G$ .

## 1.5 Conjugate elements and classes

A group element  $B$  is said to be conjugate to  $A$  if  $B = XAX^{-1}$  (or  $A = X^{-1}BX$ ), where  $X$  is some element of the group  $G$ . Further, if  $B$  and  $C$  are both conjugate to  $A$ , they are conjugate to each other.

To find conjugate elements one has to form all products of the form  $EA_iE^{-1} = A_i$ ,  $A_2A_iA_2^{-1}$ ,  $\dots$ ,  $A_hA_iA_h^{-1}$ . All mutually conjugate elements of  $A_i$  form a class of elements (including  $A_i$ ).

**Example.** Consider again the symmetry operations of an equilateral triangle mentioned above. Clearly, the identity  $E$  is in a class by itself. In addition, the two rotations by  $2\pi/3$  (elements  $D$  and  $F$ ) and the three rotations by  $\pi$  (elements  $A$ ,  $B$ , and  $C$ ) form a class. Hence, for the symmetry operations of an equilateral triangle there are three classes.

## 2 Group representations (orthogonality theorem, character)

### 2.1 Definition

A representation of an abstract group is in general any group composed of concrete mathematical entities which is homomorphic to the original group. Here, we restrict our attention to representations by square matrices, with matrix multiplication as the group multiplication operation.

**Note 1.** Associate a matrix  $\Gamma(A)$  with each group element  $A$  such that  $\Gamma(A)\Gamma(B) = \Gamma(AB)$ .

**Note 2.** These matrices then satisfy the group multiplication table and therefore in every way “represent” the abstract group element.

**Note 3.** Of course, the identity element is represented by the unit matrix:  $\Gamma(E) = I$ .

**Note 4.** The number of columns and rows (dimensionality of the matrix) in the matrix is called dimensionality of the representation (similar to the order of the group).

### 2.2 Some notes about matrices

A special matrix multiplication occurs for matrices having all nonzero elements in square blocks along the diagonal, e.g.

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 3 & 2 \\ 0 & 0 & 0 & 1 & 2 & 2 \\ 0 & 0 & 0 & 4 & 0 & 1 \end{bmatrix} \begin{bmatrix} 4 & 1 & 0 & 0 & 0 & 0 \\ 2 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 2 \\ 0 & 0 & 0 & 3 & 0 & 2 \\ 0 & 0 & 0 & 2 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 4 & 1 & 0 & 0 & 0 & 0 \\ 8 & 7 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 13 & 3 & 10 \\ 0 & 0 & 0 & 10 & 3 & 8 \\ 0 & 0 & 0 & 2 & 5 & 9 \end{bmatrix}$$

The product is blocked out in exactly the same way as are its factors, i.e., the blocked out parts can be considered independently, e.g.

$$\begin{bmatrix} 1 & 0 \\ 1 & 2 \end{bmatrix} \begin{bmatrix} 4 & 1 \\ 2 & 3 \end{bmatrix} = \begin{bmatrix} 4 & 1 \\ 8 & 7 \end{bmatrix}$$

$$[3][1] = [3]$$

**Definition.** The character  $\chi$  of a square matrix  $A$  is defined as the sum of its diagonal elements:

$$\chi(A) = \sum_j a_{jj}$$

There are two important theorems concerning characters.

**Theorem 1.** If  $C = AB$  and  $D = BA$ , then the characters of  $C$  and  $D$  are equal.

**Proof.**

$$\begin{aligned}\chi(C) &= \sum_j c_{jj} = \sum_j \sum_k a_{jk} b_{kj} \\ \chi(D) &= \sum_k d_{kk} = \sum_k \sum_j b_{kj} a_{jk} \\ &= \sum_j \sum_k b_{kj} a_{jk} = \sum_j \sum_k a_{jk} b_{kj} = \chi(C)\end{aligned}$$

**Theorem 2.** Conjugate matrices have identical character.

**Proof.** Conjugate matrices are related by a similarity transformation in the same way as are conjugate elements of a group. Thus, if matrices  $A$  and  $B$  are conjugate, there is some matrix  $D$  such that  $B = D^{-1}AD$ .

$$\begin{aligned}\chi(B) &= \chi(D^{-1}AD) = \chi((D^{-1}A)D) \\ &= \chi(D(D^{-1}A)) = \chi((D^{-1}D)A) \\ &= \chi(A)\end{aligned}$$

## 2.3 Matrix notation for geometric transformations

One important application of matrix algebra lies in expressing the transformation of a point in space.

**Identity.** The identity operation  $E$  leaves the coordinates  $x$ ,  $y$ , and  $z$  of an arbitrary point unchanged and can be described by a unit matrix

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

**Inversion.** The inversion operation simply changes sign of all coordinates without permuting any. It can be understood as a negative identity matrix.

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

**Reflections.** If a plane of reflection coincides with a principal Cartesian plane ( $xy$ ,  $xz$ ,  $yz$ ), then the reflection of a general point with coordinates  $x$ ,  $y$ , and  $z$  has the effect of changing the sign of the coordinates measured perpendicular to the plane while leaving unchanged the two coordinates whose axes define the plane.

$$\sigma_{xy} : \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ \bar{z} \end{bmatrix}$$

$$\sigma_{xz} : \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ \bar{y} \\ z \end{bmatrix}$$

$$\sigma_{yz} : \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \bar{x} \\ y \\ z \end{bmatrix}$$

**Proper rotation.** Define the  $z$  axis as rotation axis. Then, the  $z$  coordinate will be unchanged by any rotation about the  $z$  axis.

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

[?] can be solved as two-dimensional problem in  $xy$  plane.

The total matrix for a clockwise rotation through  $\phi$  about the  $z$  axis can be written as

$$\begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

**Improper rotation.** Same as proper rotation but with additional change of sign in  $z$  coordinate (only mentioned for completeness).

$$\begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

This can be seen as a proper rotation with an additional reflection in  $xy$  plane

$$\begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & -1 \end{bmatrix}$$



Since all of these matrices represent group elements the product of any two represents a matrix of some other operation

$$\begin{matrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ \sigma_{xz} \end{matrix} \begin{matrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ \sigma_{yz} \end{matrix} = \sigma_{xz}\sigma_{yz} = \begin{matrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ C_2(z) \end{matrix}$$

## 2.4 More on representations

Representations are *not* unique.

### Examples.

1. A similarity transformation  $U^{-1}\Gamma(A)U$  generates a new set of matrices which provide an equally good representation.
2. A physical example: rotation of reference axis  $(x, y, z) \rightarrow (x', y', z')$
3. Combination of different representations

$$\begin{pmatrix} \Gamma(A) & \mathcal{O} \\ \mathcal{O} & \Gamma'(A) \end{pmatrix}$$

How many representations are there? Coming back to representations and examples of the permutation group P(3).

	$E$	$A$	$D$
$\Gamma_1$	(1)	(1)	(1)
$\Gamma_{1'}$	(1)	(-1)	(1)
$\Gamma_2$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$
$\Gamma_R$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$

Write  $\Gamma_R = \Gamma_1 + \Gamma_{1'} + \Gamma_2$  or in matrix form

$$\Gamma_R = \begin{pmatrix} \Gamma_1 & \mathcal{O} & \mathcal{O} \\ \mathcal{O} & \Gamma_{1'} & \mathcal{O} \\ \mathcal{O} & \mathcal{O} & \Gamma_2 \end{pmatrix}$$

Another example refers to the water molecule. Assign three unit vectors to each of the atoms and write down the matrices representing changes and interchanges

of these unit vectors upon applying symmetry operations. This will yield  $9 \times 9$  matrices constituting a representation of the  $\text{H}_2\text{O}$  symmetry group.

Are there special representations?

Suppose we have a set of matrices  $E, A, B, \dots$  which form a representation of a group. Now apply the *same* similarity transformation to obtain a new set of matrices, namely  $E' = S^{-1}ES, A' = S^{-1}AS, B' = S^{-1}BS, \dots$ . The new set of matrices is also a representation of the group.

**Proof.** Let  $AB = C$ . Then

$$\begin{aligned} A'B' &= (S^{-1}AS)(S^{-1}BS) \\ &= S^{-1}A(SS^{-1})BS \\ &= S^{-1}(AB)S \\ &= S^{-1}CS = C' \end{aligned}$$

Now assume  $A$  transformed to  $A'$  using  $S$  and find  $A'$  to be a block-factored matrix

$$A' = S^{-1}AS = \begin{bmatrix} A'_1 & & & & \\ & A'_2 & & & \\ & & A'_3 & & \\ & & & A'_4 & \\ & & & & A'_5 \end{bmatrix}$$

If each of the matrices  $A', B', C', \dots$  is blocked out in the same way, the corresponding blocks of each matrix can be multiplied together separately

$$\begin{aligned} A'_1B'_1 &= C'_1 \\ A'_2B'_2 &= C'_2 \\ A'_3B'_3 &= C'_3 \end{aligned}$$

Therefore,  $E'_1, A'_1, B'_1, C'_1, \dots$  are in themselves representations of the group. The set of matrices  $E, A, B, C, \dots$  is then called a *reducible* representation because it is possible, using some matrix, to transform each matrix in the set into a new one so that all of the new ones can be taken apart in the same way to give two or more representations of smaller dimension.

If it is not possible to find a similarity transformation which will reduce all of the matrices of a given representation in the above manner, the representation is said to be *irreducible*. It is the *irreducible* representations of a group that are of fundamental importance.

## 2.5 The “Great Orthogonality Theorem”

Some notations.

- The order of a group is given by  $h$ .
- The dimension of  $i$ th representation (which is the dimension of each of the matrices constituting it) will be  $l_i$ .
- Symmetry operations have the generic symbol  $R$ .
- The element in the  $m$ th row and  $n$ th column of a matrix corresponds to an operation  $R$  in the  $i$ th irreducible representation  $\Gamma_i(R)_{mn}$ .

The “Great Orthogonality Theorem”

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

Consider two irreducible representations  $\Gamma_i$  and  $\Gamma_j$ . Then, any corresponding matrix elements can be seen as vector components in a  $h$  dimensional space. Moreover, they are orthonormal (orthogonal and of unit length).

Some simpler ways to write it (under various conditions)

- vectors from different representations are orthogonal

$$\sum_R \Gamma_i(R)_{mn} \Gamma_j(R)_{mn} = 0 \text{ for } i \neq j$$

- vectors from the same representation but different sets are orthogonal

$$\sum_R \Gamma_i(R)_{mn} \Gamma_i(R)_{m'n'} = 0 \text{ } m \neq m' \text{ and/or } n \neq n'$$

- the square of length of any vector is

$$\sum_R \Gamma_i(R)_{mn} \Gamma_i(R)_{mn} = \frac{h}{l_i}$$

There are five important rules about irreducible representations and their characters which will be covered in the next lecture.

## 3 Application I: Character tables

### 3.1 Deriving character tables

In deriving character tables we basically rely on five different rules, which can all be obtained from the “Great Orthogonality Theorem”.

1. The number of irreducible representations in a character table is equal to the number of classes in the group.
2. The characters of all symmetry operations in the same class are equal in each given irreducible representation.
3. The sum of the squares of all characters in any irreducible representation is equal to the order of the group.
4. The point product of characters of any two irreducible representations is zero, e.g., irreducible representations are orthogonal.
5. The sum of squares of dimensions of the irreducible representations equals the order of the group.

**Example 1.:**  $C_{2v}$  (as for the  $\text{H}_2\text{O}$  molecule) with symmetry operations  $E$ ,  $C_2$ ,  $\sigma_v$ , and  $\sigma'_v$ . These are four classes, so according to rule 1 we have four different irreducible representations  $\Gamma_i$  with  $i = 1, \dots, 4$ . There will always be the totally symmetric representation, and according to rule 5 the characters for the identity operator  $E$  should obey  $[\Gamma_1(E)]^2 + [\Gamma_2(E)]^2 + [\Gamma_3(E)]^2 + [\Gamma_4(E)]^2 = h$  which can only be fulfilled by  $\Gamma_i(E) = 1$ . With this we arrive at the first part of our  $C_{2v}$  character table

$C_{2v}$	$E$	$C_2$	$\sigma_v$	$\sigma'_v$
$\Gamma_1$	1	1	1	1
$\Gamma_2$	1			
$\Gamma_3$	1			
$\Gamma_4$	1			

Applying now rule 3 and 4 we have to fill in permutations of two  $-1$  into the character table.

$C_{2v}$	$E$	$C_2$	$\sigma_v$	$\sigma'_v$
$A_1 = \Gamma_1$	1	1	1	1
$A_2 = \Gamma_2$	1	1	-1	-1
$B_1 = \Gamma_3$	1	-1	1	-1
$B_2 = \Gamma_4$	1	-1	-1	1

There is also a naming convention for the different representations in the character table of the groups.

- $A, B$  (one-dimensional representations),  $E$  (two-dimensional representations), and  $T$  (three-dimensional representations, only in cubic groups).
- If  $\chi(C_n) > 0$  ( $< 0$ ) then it is said to be symmetric (antisymmetric) with respect to the reference axis  $C_n$  and labelled with  $A$  ( $B$ ).
- Symmetric (antisymmetric) with respect to  $\sigma_h$ : ' ('').
- Symmetric (antisymmetric) with respect to inversion  $i$ :  $g$  ( $u$ ).
- Just numbering: 1, 2,  $\dots$

**Example 2.**  $C_{3v}$  (as for the  $\text{NH}_3$  molecule) with symmetry operations  $E, C_3, C_3^2, \sigma_v, \sigma'_v,$  and  $\sigma''_v$ . There are 3 classes, so according to rule 1 we have three different irreducible representations  $\Gamma_i$  with  $i = 1, \dots, 3$ . Again, there will always be the totally symmetric representation, and according to rule 5 the characters for the identity operator  $E$  should obey  $[\Gamma_1(E)]^2 + [\Gamma_2(E)]^2 + [\Gamma_3(E)]^2 = h$  which can only be fulfilled if there is one two-dimensional representation  $\Gamma_3(E) = 2$ . With this we arrive at the first part of our  $C_{3v}$  character table

$C_{3v}$	$E$	$[C_3 \ C_3^2]$	$[\sigma_v \ \sigma'_v \ \sigma''_v]$
$\Gamma_1$	1	1 1	1 1 1
$\Gamma_2$	1		
$\Gamma_3$	2		

Keeping in mind rule 2 stating that the characters of the  $C_3$  class and the  $\sigma_v$  class have to be the same, once again applying rules 3 and 4 lead to orthogonal irreducible representations.

$C_{3v}$	$E$	$[C_3 \ C_3^2]$	$[\sigma_v \ \sigma'_v \ \sigma''_v]$
$\Gamma_1$	1	1 1	1 1 1
$\Gamma_2$	1	1 1	-1 -1 -1
$\Gamma_3$	2	-1 -1	0 0 0

This can be written in a shorter form taking into account the number of elements in each class.

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$
$A_1 = \Gamma_1$	1	1	1
$A_2 = \Gamma_2$	1	1	-1
$E = \Gamma_3$	2	-1	0

**Example 3.**  $C_{4v}$  with symmetry operations  $E, C_4, C_4^2 = C_2, C_4^3, \sigma_v, \sigma'_v, \sigma_d,$  and  $\sigma'_d$ . There are now five classes, so according to rule 1 there will be five different irreducible representations  $\Gamma_i$  with  $i = 1, \dots, 5$  in the character table. Again, there will always be the totally symmetric representation, and according to rule 5 the characters for the identity operator  $E$  should obey  $[\Gamma_1(E)]^2 + [\Gamma_2(E)]^2 +$

$[\Gamma_3(E)]^2 + [\Gamma_4(E)]^2 + [\Gamma_5(E)]^2 = h$  which can only be fulfilled if there is one two-dimensional representation  $\Gamma_5(E) = 2$ . With this we arrive at the first part of our  $C_{4v}$  character table

$C_{4v}$	$E$	$[C_4 \ C_4^3]$	$[C_4^2 = C_2]$	$[\sigma_v \ \sigma'_v]$	$[\sigma_d \ \sigma'_d]$
$\Gamma_1$	1	1	1	1	1
$\Gamma_2$	1				
$\Gamma_3$	1				
$\Gamma_4$	1				
$\Gamma_5$	2				

Again, keeping in mind rule 2 stating that the characters of the  $C_4$  class, the  $\sigma_v$  class, and the  $\sigma_d$  class have to be identical, a subsequent application of rules 3 and 4 leads to the following character table

$C_{4v}$	$E$	$[C_4 \ C_4^3]$	$[C_4^2 = C_2]$	$[\sigma_v \ \sigma'_v]$	$[\sigma_d \ \sigma'_d]$
$\Gamma_1$	1	[ 1 1]	1	[ 1 1]	[ 1 1]
$\Gamma_2$	1	[ 1 1]	1	[-1 -1]	[-1 -1]
$\Gamma_3$	1	[-1 -1]	1	[-1 -1]	[ 1 1]
$\Gamma_4$	1	[-1 -1]	1	[ 1 1]	[-1 -1]
$\Gamma_5$	2	a a	b	c c	d d

The last line can only be found by explicitly writing down the pairwise orthogonality conditions among the irreducible representations (using number of symmetry elements per class times character of  $\Gamma_i$  times character of  $\Gamma_j$ )

$$\begin{aligned}
\Gamma_1\Gamma_5 &= 1 * 1 * 2 + 2 * 1 * a + 1 * 1 * b + 2 * 1 * c + 2 * 1 * d \\
&= 2 + 2a + b + 2c + 2d = 0 \\
\Gamma_2\Gamma_5 &= 2 + 2a + b - 2c - 2d = 0 \\
\Gamma_3\Gamma_5 &= 2 - 2a + b - 2c + 2d = 0 \\
\Gamma_4\Gamma_5 &= 2 - 2a + b + 2c - 2d = 0
\end{aligned}$$

This set of equations yields  $a = c = d = 0$  and  $b = -2$  and the full (simplified) character table for  $C_{4v}$

$C_{4v}$	$E$	$2C_4$	$C_2$	$2\sigma_v$	$2\sigma_d$
$A_1 = \Gamma_1$	1	1	1	1	1
$A_2 = \Gamma_2$	1	1	1	-1	-1
$B_1 = \Gamma_3$	1	-1	1	-1	1
$B_2 = \Gamma_4$	1	-1	1	1	-1
$E = \Gamma_5$	2	0	-2	0	0

### 3.2 Using character tables

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$
$A_1 = \Gamma_1$	1	1	1
$A_2 = \Gamma_2$	1	1	-1
$E = \Gamma_3$	2	-1	0

To find the representation for a direct product of representations just multiply the characters. So, for the representation of  $A_2 \times E$  one has to evaluate  $\chi(E) = 1 * 2 = 2$ ,  $\chi(C_3) = 1 * (-1) = -1$ , and  $\chi(\sigma_v) = -1 * 0 = 0$  leading to the characters of the irreducible representation  $E$ , i.e.,  $\Gamma(A_2 \times E) = E$  (the direct product of  $A_2$  and  $E$  transform like the irreducible representation of  $E$ ). This will be different for  $\Gamma(E \times E)$  where we find  $\chi(E) = 2 * 2 = 4$ ,  $\chi(C_3) = (-1) * (-1) = 1$ , and  $\chi(\sigma_v) = 0 * 0 = 0$  leading to a reducible representation of  $E \times E$  written as  $\Gamma_{red} = 4\chi(E) + \chi(C_3)$ . Based on the ‘‘Great Orthogonality Theorem’’ one can find the irreducible representations which are included in a reducible representation

$$n_i = \frac{1}{h} \sum_R l_i \chi(R) \chi_i(R)$$

with the following notation

- $n_i$  number of times the irreducible representation  $\Gamma_i$  appears in the reducible representation  $\Gamma_{red}$  under investigation.
- $h$  order of the matrix.
- $R$  symmetry operation of the group.
- $l_i$  number of symmetry elements in each class.
- $\chi(R)$  character of symmetry operation  $R$  in  $\Gamma_{red}$ .
- $\chi_i(R)$  character of symmetry operation  $R$  in  $\Gamma_i$ .

So for  $\Gamma_{red}(E \times E) = 4\chi(E) + \chi(C_3)$  this reads

$$\begin{aligned} n_1(A_1) &= \frac{1}{6}[1 * 4 * 1 + 2 * 1 * 1 + 3 * 1 * 0] = 1 \\ n_2(A_2) &= \frac{1}{6}[1 * 4 * 1 + 2 * 1 * 1 + 3 * (-1) * 0] = 1 \\ n_3(E) &= \frac{1}{6}[1 * 4 * 2 + 2 * 1 * (-1) + 3 * 0 * 0] = 1 \end{aligned}$$

Therefore,  $E \times E = A_1 + A_2 + E$ .

### 3.3 Vibrations of molecules

Consider again the water molecule,  $\text{H}_2\text{O}$ . In order to investigate the vibrational properties of such a molecule one has to perform the following tasks.

1. Put three orthogonal unit vectors to each of the atoms to generate the basis for a  $3N$  dimensional reducible representation  $\Gamma_{red}$  of the molecule (with  $N$  being the number of atoms).
2. In a next step the irreducible representation to this  $\Gamma_{red}$  has to be found, in addition we already know

$$\Gamma_{red} = \Gamma_{trans} + \Gamma_{rot} + \Gamma_{vib}$$

For the  $\text{H}_2\text{O}$  molecule this means  $\Gamma_{trans} = 3$  (translational degrees of freedom),  $\Gamma_{rot} = 3$  (rotational degrees of freedom), and  $\Gamma_{vib} = 3N - 6 = 3$  (vibrational degrees of freedom). From our symmetry analysis we will find a characterisation of the normal vibrations by irreducible representations of the symmetry group.

3. To evaluate above given equation we have to find the irreducible representations for  $\Gamma_{trans}$  and  $\Gamma_{rot}$ .

To find the 9-dimensional reducible representation of the water molecule just remember that we need the characters of the symmetry operations (only the traces of the matrices contribute to the characters in the group character tables). This leads to some simplified rules finding the reducible representations

1. Add “1” to the character if the basis function (in case of the water molecule the unit vectors at each atom) is unchanged by the symmetry operation.
2. Add “-1” to the character if the basis function changes sign under the symmetry operation.
3. Add “0” to the character if the basis function moves under the symmetry operation.

Remember the full character table of the point group  $C_{2v}$

$C_{2v}$			$E$	$C_2$	$\sigma_v$	$\sigma'_v$
$x^2, y^2, z^2$	$z$	$A_1$	1	1	1	1
$xy$	$R_z$	$A_2$	1	1	-1	-1
$xz$	$R_y, x$	$B_1$	1	-1	1	-1
$yz$	$R_x, y$	$B_2$	1	-1	-1	1
$\Gamma_{red}$			9	-1	3	1



The reducible representation  $\Gamma_{red}$  is shown in the last line.

To find the irreducible representations for  $\Gamma_{trans}$  and  $\Gamma_{rot}$  have a look at the *basis objects* on the left hand side of the character table and what they could be used for

- $x, y, z$ : unit vectors ( $\mathbf{e}_x, \mathbf{e}_y$ , and  $\mathbf{e}_z$ ), e.g., translations of core positions; real spherical harmonics  $S_1^m$  (atomic orbitals  $p_x, p_y$ , and  $p_z$ ); components of the dipole vector.
- Binary products of  $x, y$ , and  $z$ : real spherical harmonics  $S_2^m$  (atomic orbitals  $d_{z^2}, d_{xz}, d_{yz}, d_{x^2-y^2}$ , and  $d_{xy}$ ); polarisability.
- $R_x, R_y$ , and  $R_z$ : rotations about given axis.

Utilising the formula from above to find the irreducible parts of a given reducible representation yields

$$\begin{aligned}\Gamma_{red} &= 3a_1 + a_2 + 3b_1 + 2b_2 \\ \Gamma_{trans}(x, y, z) &= a_1 + b_1 + b_2 \\ \Gamma_{rot}(R_x, R_y, R_z) &= a_2 + b_1 + b_2\end{aligned}$$

Therefore, we find  $\Gamma_{vib} = 2a_1 + b_1$ , where the two  $a_1$  modes refer to the symmetric stretch and symmetric bend mode, and the  $b_2$  mode refers to the asymmetric stretch mode, respectively.

**Note.** It would also have been possible to use internal coordinates of the water molecule, e.g., bond lengths and bond angle. Since internal coordinates have to be linearly independent, the number of internal coordinates and the number of vibrational modes have to be identical. This approach would split the problem into bond length degrees of freedom and bond angle degrees of freedom which might allow for additional insight in structural investigations of unknown molecules.

## 4 Application II: Butadiene ( $C_4H_6$ )

### 4.1 Isomers of butadiene

Another example deals with 1,3-butadiene ( $C_4H_6$ ) which occurs in two different isomers. Having a look at the *basis objects* atomic  $p_z$  orbitals one can easily find representations for the symmetry operations of the point group  $C_{2v}$  being  $R = E, C_2, \sigma_v, \sigma'_v$  as follows

$$\Gamma(E) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \Gamma(C_2) = \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$

$$\Gamma(\sigma_v) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \Gamma(\sigma'_v) = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

with the traces given by  $\text{tr}(\Gamma(E)) = 4$ ,  $\text{tr}(\Gamma(C_2)) = 0$ ,  $\text{tr}(\Gamma(\sigma_v)) = 0$ , and  $\text{tr}(\Gamma(\sigma'_v)) = -4$ . Using the orthogonality theorem given above one can easily find an irreducible representation for this reducible one  $\Gamma_{red} = 2a_2 + 2b_1$ . Therefore, we already know that a LCAO-MO calculation will yield four molecular orbitals, two of them will transform like  $a_2$  and two like  $b_2$ . However, group theory does not give information about the energetic ordering of the molecular orbitals. For this a full calculation has to be performed.

### 4.2 LCAO-MO calculation

LCAO-MO stands for Linear Combination of Atomic Orbitals to Molecular Orbitals. Within this method (effectively a tight-binding method), each  $C$  atom contributes one  $2p_z$  orbital and one valence electron to the  $\pi$  electron system. We have four atomic orbitals  $\chi_k$  ( $k = 1 \dots 4$ ) building up four molecular orbitals  $\psi_i = \sum_{k=1}^4 c_{ik} \chi_k$ . Then we have to solve the eigenvalue problem

$$\sum_{l=1}^4 (H_{kl} - \varepsilon S_{kl}) c_l = 0$$

Thereby, the Hamilton matrix  $H_{kl} = \int \chi_k \mathcal{H} \chi_l d^3r$  and the overlap matrix  $S_{kl} = \int \chi_k \chi_l d^3r$  are approximated as  $H_{kk} = \alpha$  and  $H_{kl} = \beta$  (nearest neighbours only), and  $S_{kl} = \delta_{kl}$ , respectively. This yields

$$\begin{vmatrix} \alpha - \varepsilon & \beta & 0 & 0 \\ \beta & \alpha - \varepsilon & \beta & 0 \\ 0 & \beta & \alpha - \varepsilon & \beta \\ 0 & 0 & \beta & \alpha - \varepsilon \end{vmatrix} = 0$$

Dividing by  $\beta$  and defining  $x = (\alpha - \varepsilon)/\beta$  this yields the so-called Hückel or topological matrix

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

Solving for this equation yields the energies and associated molecular orbitals (shown in figure 2).

$$\varepsilon_4 = \alpha - 1.618\beta, \psi_4 = 0.372\chi_1 - 0.602\chi_2 + 0.602\chi_3 - 0.372\chi_4$$

$$\varepsilon_3 = \alpha - 0.618\beta, \psi_3 = 0.602\chi_1 - 0.372\chi_2 - 0.372\chi_3 + 0.602\chi_4$$

$$\varepsilon_2 = \alpha + 0.618\beta, \psi_2 = 0.602\chi_1 + 0.372\chi_2 - 0.372\chi_3 - 0.602\chi_4$$

$$\varepsilon_1 = \alpha + 1.618\beta, \psi_1 = 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4$$

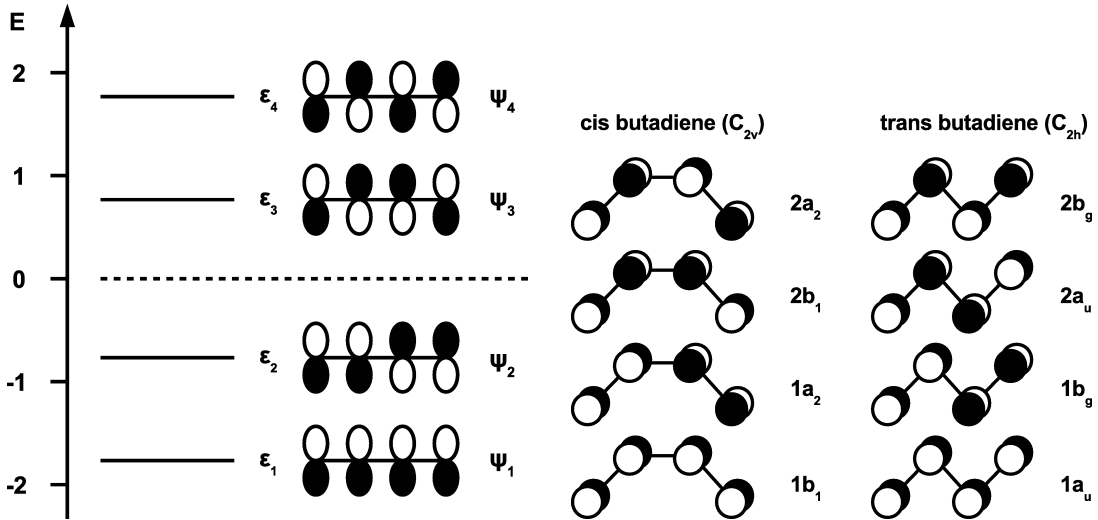


Figure 2: (Left) Eigenvalues and eigenfunctions of butadiene (shown as  $p_z$  orbitals). (Right) Molecular orbitals for cis and trans butadiene (top view) including irreducible representations of the respective symmetry group.

### 4.3 Transitions

Looking again at the energy levels of the butadiene molecule depicted in the left part of figure 2, we can now populate separate energy levels with electrons, e.g., in the molecular ground state we would have two electrons in level  $1b_1$  ( $1a_u$ ) and  $1a_2$  ( $1b_g$ ) for cis (trans) butadiene, respectively. The symmetry of the molecular ground state, denoted by  $\Psi_0$  (many-electron states are characterised by capital letters), can be derived as the direct product of the symmetry of the populated

one-electron levels. For cis (trans) butadiene this yields  $\Psi_0 = (1b_1)^2(1a_2)^2 = A_1$  ( $\Psi_0 = (1a_u)^2(1b_g)^2 = A_g$ ).

Being interested in electronic transition from the molecular ground state  $\Psi_0$  to an excited state, we want to decide whether a specific transition is allowed by symmetry or not. This can be accomplished by analysing transition matrix elements given by

$$\int \Psi_{\text{initial}} \mathbf{r} \Psi_{\text{final}}$$

with  $\Psi_{\text{initial}}$  and  $\Psi_{\text{final}}$  being the initial and final states of the transition and  $\mathbf{r}$  will carry the  $x$ ,  $y$  and  $z$  coordinate of the dipole vector  $\mu = e\mathbf{r}$ , respectively. The electronic transition under investigation is forbidden by symmetry if the integral given above vanishes. From group theory we know that this happens if the integrand does not transform as the totally symmetric representation of the respective group. Once again, taking into account only the topology of the molecules (how the atoms are connected) is not enough to judge whether electronic transitions are allowed by symmetry or not. For this we need to know information about the symmetry of initial and final states, e.g., we would expect different results for the topologically equal cis and trans butadiene. Looking at the transition of one electron from  $1a_2$  to  $2b_1$  for cis butadiene this reads for the  $x$ ,  $y$ , and  $z$  coordinate of the dipole vector

$$\begin{aligned} x : a_2 \times b_1 \times b_1 &= a_2(-) \\ y : a_2 \times b_2 \times b_1 &= a_1(+) \\ z : a_2 \times a_1 \times b_1 &= b_2(-) \end{aligned}$$

The transition is allowed only for the  $y$  component (+) and forbidden for the  $x$  and  $z$  component (-). Looking at the transition of one electron from  $1b_g$  to  $2a_u$  in trans butadiene a similar analysis yields

$$\begin{aligned} x : b_g \times b_u \times a_u &= a_g(+) \\ y : b_g \times b_u \times a_u &= a_g(+) \\ z : b_g \times a_u \times a_u &= b_g(-) \end{aligned}$$

The transition is now allowed for the  $x$  and  $y$  component (+) and forbidden only for the  $z$  component (-). This kind of symmetry analysis of allowed and forbidden electronic transitions can be used for structural investigations.

## 5 Application III: Crystal field theory

### 5.1 Central atom

Consider transition metal oxides crystallising in the perovskite structure. There, the central transition metal atom is octahedrally surrounded by oxygen atoms. Crystal field theory aims at a description of the orbital splittings of the central transition metal atom due to the electrostatic potential of assumed point charges, i.e., oxygen atoms. Thereby, the central transition metal atom is described by a hydrogen-like Schrödinger equation

$$\mathcal{H}_0\Psi = E\Psi$$

and the electrostatic potential of the point charges is treated as a perturbation

$$\mathcal{H}_1 = \sum_{i=1}^6 v_i(x, y, z)$$

The question is, what can group theory tell us about the orbital splittings? Consider for a moment a free central atom with five degenerate  $d$  orbitals. Since it shall be described by a hydrogen-like Schrödinger equation, the basis functions are chosen naturally as complex spherical harmonics  $Y_l^{m_l}(\theta, \phi)$  with  $m_l = -l, \dots, l$ . A group theoretical analysis requires to check the influence of symmetry operations on all  $(2l + 1)$  orbitals, thereby yielding a  $(2l + 1)$  dimensional reducible representation  $\Gamma_{red}$ .

Starting point of our investigation will be the full rotation group where we then reduce the symmetry to the octahedral group  $O_h$ . Within  $O_h$  we then have to find  $\Gamma_{red}$  and its irreducible representation which will provide us with information about the orbital splitting.

### 5.2 Representations

Within the full rotation group, a rotation by an angle  $\alpha$  about an arbitrary axis (chosen as  $z$  axis here) affects the complex spherical harmonics

$$Y_l^{m_l}(\theta, \phi) = N_l^{m_l} P_l(\cos \theta) e^{im_l \phi}$$

in the following way. The prefactor

$$N_l^{m_l} = \sqrt{\frac{2l + 1}{4\pi} \frac{(l - |m_l|)!}{(l + |m_l|)!}}$$

is unaffected by rotations about  $\alpha$  as are the Legendre polynomials  $P_l(\cos \theta)$ . A rotation about  $\alpha$  only changes the exponential part of the complex spherical

harmonics  $e^{im_l\phi} \rightarrow e^{im_l(\phi+\alpha)}$ . In matrix notation covering the whole  $(2l + 1)$  dimensional basis this reads

$$\begin{pmatrix} e^{il(\phi+\alpha)} \\ e^{i(l-1)(\phi+\alpha)} \\ \dots \\ e^{-il(\phi+\alpha)} \end{pmatrix} = \begin{pmatrix} e^{i\alpha} & & & \\ & e^{i(l-1)\alpha} & & \\ & & \dots & \\ & & & e^{-i\alpha} \end{pmatrix} \begin{pmatrix} e^{il\phi} \\ e^{i(l-1)\phi} \\ \dots \\ e^{-il\phi} \end{pmatrix}$$

The matrix on the right side is the representation matrix for arbitrary rotations  $C_{2\pi/\alpha}$  with respect to the utilised basis of  $(2l + 1)$  orbitals. From this representation matrix only the character is of interest, i.e., the sum of the diagonal elements. This reads

$$\begin{aligned} \chi^{(l)}(C_{2\pi/\alpha}) &= e^{i\alpha} + e^{i(l-1)\alpha} + \dots + e^{-i\alpha} \\ &= \sum_{m_l=-l}^{+l} e^{im_l\alpha} \\ &= \frac{e^{i(l+1)\alpha} - e^{-i\alpha}}{e^{i\alpha} - 1} \\ &= \frac{\sin(l + \frac{1}{2})\alpha}{\sin \frac{1}{2}\alpha} \end{aligned}$$

For the five  $d$  orbitals in an octahedral field  $l = 2$  and the character reads

$$\chi^{(d)}(C_{2\pi/\alpha}) = \frac{\sin \frac{5}{2}\alpha}{\sin \frac{1}{2}\alpha}$$

Evaluating this expression exemplary for some of the rotations present in the octahedral group  $O_h$  we find  $\chi^{(d)}(C_2) = +1$ ,  $\chi^{(d)}(C_3) = -1$ , and  $\chi^{(d)}(C_4) = -1$ . Further simplifications make use of the fact that the remaining symmetry operations can be written as products of rotations and the inversion element  $i$ , e.g.,  $\sigma_h = iC_2$  and  $S_6 = iC_3$ . With this we can find  $\Gamma_{red}^{(d)}$  now containing 48 quadratic  $5 \times 5$  matrices

$O_h$	$E$	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	$i$	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
$\Gamma_{red}^{(d)}$	5	-1	1	-1	1	5	-1	1	-1	1

Finding the irreducible representation for  $\Gamma_{red}^{(d)}$  yields  $\Gamma^{(d)} = e_g + t_{2g}$ , i.e., a two-dimensional representation  $e_g$  accounting for the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals, and a three-dimensional representation accounting for the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals, respectively. Finally, group theory tells us that the fivefold degeneracy of the  $d$  orbitals will be lifted in an octahedral crystal field resulting in a twofold degenerated level transforming like  $e_g$  and a threefold degenerated level transforming like  $t_{2g}$ . Once again, group theory does not tell us about the energetic order of the splitted levels. For this we still have to do the calculations.

### 5.3 Octahedral crystal field

Consider an ideal octahedral arrangement of point charges. In order to find at any point in space the potential that arises from the octahedron of charges the individual charge contributions have to be added together

$$V(x, y, z) = \sum_{i=1}^6 v_i(x, y, z) = \sum_{i=1}^6 \frac{ez_i}{r_{ij}}$$

where  $r_{ij}$  denotes the distance from the  $i$ th charge to the point  $(x, y, z)$ .

Writing now the hydrogen-like Schrödinger equation with the unperturbed wave functions  $\Psi_i$  as before  $\mathcal{H}_0\Psi_i = E_0\Psi_i$  we can easily find the influence of a small perturbation  $\mathcal{H}'$  (the crystal field potential) on the wave functions from  $(\mathcal{H}_0 + \mathcal{H}')\Psi'_j = E'_j\Psi'_j$ . The new wave functions read  $\Psi'_j = \sum_{i=1}^n c_{ij}\Psi_i$  with  $\sum c_{ij}^*c_{ij} = 1$ . The secular determinant we have to solve for then reads

$$\begin{array}{cccccc} & (2) & (1) & (0) & (-1) & (-2) \\ (2) & \mathcal{H}'_{2,2} - E & \mathcal{H}'_{2,1} & \mathcal{H}'_{2,0} & \mathcal{H}'_{2,-1} & \mathcal{H}'_{2,-2} \\ (1) & \mathcal{H}'_{1,2} & \mathcal{H}'_{1,1} - E & \mathcal{H}'_{1,0} & \dots & \\ (0) & & & \dots & & \\ (-1) & & \dots & & & \\ (-2) & & & & \mathcal{H}'_{-2,-1} & \mathcal{H}'_{-2,-2} - E \end{array}$$

with

$$\mathcal{H}'_{m,m'} = e \int (m)^* V(x, y, z) (m') d\tau$$

The next step involves evaluation of

$$V(x, y, z) = \sum_{i=1}^6 v_i(x, y, z) = \sum_{i=1}^6 \frac{ez_i}{r_{ij}}$$

with an expression of  $r_{ij}^{-1}$  suitable for integration

$$\frac{1}{r_{ij}} = \sum_{n=0}^{\infty} \sum_{m=-n}^n \frac{4\pi}{2n+1} \frac{r_{<}^n}{r_{>}^{n+1}} Y_{nj}^m Y_{ni}^{m*}$$

with  $r_{<}$  and  $r_{>}$  being the lesser and larger distance of the origin to points  $i$  and  $j$ . Being interested only in the contributions within the octahedron they read  $r_{<} = r$  and  $r_{>} = a$ . As an example we evaluate the first term in the sum for  $n = 0$ . Each term contributes

$$\left( \frac{4\pi ze}{a} \right) Y_0^0 Y_0^0 = \frac{ze}{a}$$

so the whole contribution from  $n = 0$  to the potential  $V(x, y, z)$  is  $6ze/a$ . It can be shown that  $n = 2$  does not contribute to  $V(x, y, z)$ , and the next (and final) contribution to  $V(x, y, z)$  comes from  $n = 4$ . The whole potential then reads

$$V(x, y, z) = \frac{6ze}{a} + \sqrt{\frac{49}{18}} \sqrt{\frac{1}{2\pi}} \left( \frac{zer^4}{a^5} \right) \left[ Y_4^0 + \sqrt{\frac{5}{14}} (Y_4^4 + Y_4^{-4}) \right]$$

With this expression for  $V(x, y, z)$  we can now evaluate  $\mathcal{H}'_{m,m'} = e \int (m)^* V(x, y, z) (m') d\tau$ . Starting with the first constant term in  $V(x, y, z)$

$$\begin{aligned} & \int (m^*) \left( \frac{6ze}{a} \right) (m') d\tau \\ &= \frac{6ze}{a} \int (m^*) (m') d\tau \\ &= \frac{6ze}{a} \text{ if } m = m' \text{ otherwise zero} \end{aligned}$$

i.e., it affects all  $d$  orbitals and leads to an identical change in energy. It is the second term in  $V(x, y, z)$  that is responsible for the orbital splittings and hence gets renamed as  $V_{\text{oct}}$ . Evaluating now the remaining integrals as

$$\begin{aligned} \int (0)^* V_{\text{oct}}(0) d\tau &= \left( \frac{zer^4}{a^5} \right) \\ \int (\pm 1)^* V_{\text{oct}}(\pm 1) d\tau &= - \left( \frac{2}{3} \right) \left( \frac{zer^4}{a^5} \right) \\ \int (\pm 2)^* V_{\text{oct}}(\pm 2) d\tau &= \left( \frac{1}{6} \right) \left( \frac{zer^4}{a^5} \right) \\ \int (\pm 2)^* V_{\text{oct}}(\mp 2) d\tau &= \left( \frac{5}{6} \right) \left( \frac{zer^4}{a^5} \right) \end{aligned}$$

and defining  $Dq = (1/6)(zer^4/a)$  the eigenvalue problem now reads

$$\begin{vmatrix} Dq - E & & & & 5Dq \\ & -4Dq - E & & & \\ & & 6Dq - E & & \\ & & & -4Dq - E & \\ 5Dq & & & & Dq - E \end{vmatrix}$$

Solving for the eigenvalues yields  $E_1 = -4Dq$  and  $E_2 = 6Dq$  with  $\Delta_{\text{oct}} = 10Dq$  being the octahedral crystal field splitting, respectively. The energy levels are shown in figure 3.



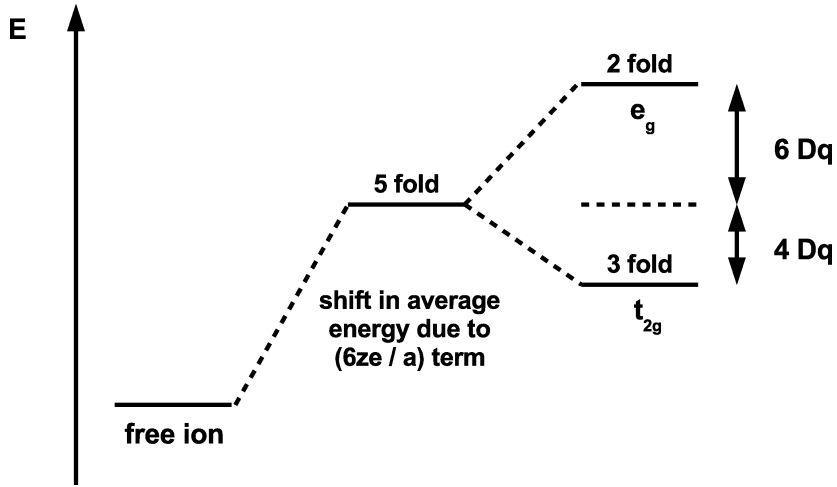


Figure 3: Energy levels of a free ion (left), constant shift in energy when brought into an octahedral environment of point charges (oxygen) due to the  $(6ze/a)$  term (middle), and splitting of orbital levels into lower  $t_{2g}$  (threefold) and upper  $e_g$  (twofold) due to the octahedral crystal field  $V_{\text{oct}}$ .

Similarly, one can derive the expression for the equally important tetrahedral crystal field by summing over four point charges only  $V_{(x,y,z)} = \sum_{i=1}^4 z_i e / r_{ij}$ . The octahedral and tetrahedral crystal field are related by  $V_{\text{tet}} = -4/9 V_{\text{oct}}$  with the respective splittings given as  $\Delta_{\text{tet}} = -4/9 \Delta_{\text{oct}}$ , respectively. The lower energy level is now twofold degenerate with an energy of  $6Dq$  and transform like  $e$  in the tetrahedral group, whereas the upper energy level is now threefold degenerate with an energy of  $4Dq$  and transforms like  $t_2$  in the tetrahedral group.