Symmetry in Condensed Matter Physics

Paolo G. Radaelli, Michaelmas Term 2013

Part 1: Group and representation theory
Lectures 1-6

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1 Lecture 1 — Introduction to group theory

1.1 Introduction: why symmetry, why CMP

- Considerations based on symmetry are important in many branches of physics, and usually lead to a simplification of the mathematical description of the problem, often requiring a suitable coordinate system.

- Staring from the 18^{th} century, mathematicians such as Leonard Euler, Évariste Gaulois and Felix Klein developed powerul mathematical theories to describe and analyse symmetries, introducing the mathematical structure of the **group**.

- Group theory and the derived theory of irreducible representations are particularly powerful tools to solve **eigenvalue problems**, both classical and quantum-mechanical. The symmetry of the problem imposes a **structure** on the space of possible solutions of eigenvalue problems, which is completely independent on the exact form of the Hamiltonian. In favourable cases, one can find the entire **multiplet structure** and at least part of the mathematical form of the solutions **entirely by symmetry**. For example, exclusively from the spherical symmetry of the hydrogen atom, one can find that the solutions will be radial functions multiplied by Légendre polynomial, organised in s, p d, $\cdots$ multiplets. One does not require the exact form of the potential to deduce this.

- Naturally, this creates a bridge between very different physical problems sharing the same symmetry, and between classical and quantum physics.

- Symmetry is also extremely useful in an important class of **non-linear** classical problems: those related to **phase transitions**, described by the famous Landau phenomenological theory. Since these problems are non-linear, the sum of two solutions is generally not a solution (minimum or maximum) of the Landau free energy. However, due to the polynomial expression of the Landau free energy, one can analyse the symmetry of the solutions for all the terms in the expansion and construct a **generalised phase diagram** (including the *order* of the phase transitions) entirely based on symmetry.

- Finally, symmetry is extremely powerful in analysing **tensors** describing the physical properties of a molecule or a crystal. One can find out entirely by symmetry whether that property is allowed at all in a certain symmetry and, if it is, how many degrees of freedom are required to

describe it. One can also find the **explicit form of the tensors** in any given coordinate system.

- In this first part of the course we will concentrate on the mathematical foundations of group and representation theory. This done very efficiently by considering **discrete** (as opposed to *continuous*) symmetry groups; in fact most of our examples are from simple *finite* symmetry groups. Discrete symmetries are particularly important in condensed matter physics: spectral properties of molecules or of ions that can be considered in isolation but still embedded in the electric field of the crystal are described by finite **point groups**. Discrete infinite *space groups* describe the symmetry of crystals as a whole, and their representations are required, for example, to study phonons, spin waves and magnetic ordering processes.

- Many of the techniques you will learn here are also applicable to *continuous* groups. These will be introduced in the next part of the course, where you will also study the applications of group and representation theory to a variety or realistic physical problems.

1.2 Transformations of patterns and symmetry

- In describing the symmetry of isolated objects or periodic systems, one defines operations (or *operators*) that describe transformations of a "pattern". With the word *pattern* here we may mean:

  - A set of *point-like objects* — for example, atoms in a molecule or in a crystal.
  - A set of *vectors* associated with discrete objects— for example, the displacement pattern of a vibrating molecule as a snapshot of its motion is taken.
  - A *continuous, real function* — for example the electron density of a molecule or a crystal.
  - A *continuous, complex function*, such as the wave function of a particular orbital.

- In this course, we will adopt the so-called *active description of transformations*, where the identity of the points in space is not changed by the transformation. Likewise, the coordinates of each points are unchanged. Rather, the transformation creates a point-by-point bijective (one-to-one in both directions) correspondence between the space and

itself, known as an *automorphism*. In the alternative *passive* description, symmetry transformations are equated to coordinate transformations.

- We create the new pattern from the old pattern by associating a point $p2$ to each point $p1$ and transferring the "attributes" of $p1$ to $p2$. We are generally interested in transformations that preserve distances and angles—in essence a combination of translations, reflections and rotations. If the transformation is a *symmetry operator*, the old and new patterns are indistinguishable.

- If one employs Cartesian coordinates, a generic transformation $T[p]$ of this kind produces the relation $\mathbf{x}(2) = \mathbf{t} + R\mathbf{x}(1)$ where $\mathbf{x}(1)$ and $\mathbf{x}(2)$ are the coordinates of $p1$ and $p2$ (written as column arrays), $\mathbf{t}$ is the translational part of the transformation and R is an orthogonal matrix. $\det R = \pm 1$, where the $+/-$ sign is for *proper*/improper rotations, respectively.

- In crystallography, one does not employ Cartesian coordinates, but the relation one obtains is very similar: $\mathbf{x}(2) = \mathbf{t} + D\mathbf{x}(1)$, where D is related to an orthogonal matrix by the transformation $U^{-1}DU$, U being the transformation matrix from crystallographic to Cartesian coordinates. $\det D = \pm 1$, as before, but U is not unitary.

1.2.1 Transformations of functions

- Scalar functions (complex- or real-valued) can be considered as patterns on the space they are defined over. Since functions (especially wavefunctions) are important for many problems involving a symmetry analysis, it is necessary to be able to transform them confidently.

- The expression for the transformation of a *function* $f(p)$ is particularly simple:

$$T[f(p)] = f(T^{-1}[p]) \tag{1}$$

  which , expressed in Cartesian or crystallographic coordinates, gives:

$$T[f(\mathbf{x})] = f(R^{-1}\mathbf{x} - R^{-1}\mathbf{t}) \tag{2}$$

- Here is the recipe to transform a function:

◇ We want to transform a function $f(x, y, z)$ with a given operator, which is expressed as $\mathbf{x}(2) = \mathbf{t} + D\mathbf{x}(1)$ in the crystallographic or Cartesian coordinate system in which the function f is defined. We will call the transformed function $f'(x, y, z)$, defined over the same space and using the same coordinates. We write:

$$f'(x, y, z) = f(X(x, y, z), Y(x, y, z), Z(x, y, z)) \tag{3}$$

◇ In other words, we have replaced the arguments of f with formal arguments X, Y and Z, which are themselves functions of the variables x, y, x.

◇ The functions X, Y and Z are defined by *back-transforming* x,y,z as follows:

$$\begin{bmatrix} X(x, y, z) \\ Y(x, y, z) \\ Z(x, y, z) \end{bmatrix} = D^{-1} \begin{bmatrix} x - t_x \\ y - t_y \\ z - t_z \end{bmatrix} \tag{4}$$

- **Example of operation on a function**: let us consider the following function, which is a representation of the so-called $3d_{x^2-y^2}$ orbital:

$$\begin{aligned} f(x, y, z) &= R(x, y, z)Y(x, y, z) \\ R &= \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \\ Y &= \frac{1}{r^2}\left(x^2 - y^2\right) = \sin^2\theta \cos 2\phi \end{aligned} \tag{5}$$

we want to apply to this function an *operator* that rotates it $20°$ counterclockwise around the z axis. The procedure is to re-write f as a function of new formal arguments $X(x, y, z)$, $Y(x, y, z)$ and $Z(x, y, z)$, and relate X, Y, Z to x, y, z through the inverse operator, i.e., a rotation by $20°$ clockwise:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \cos\phi_0 & -\sin\phi_0 & 0 \\ \sin\phi_0 & \cos\phi_0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \tag{6}$$

where $\phi_0 = -20°$. This yields:

$$
\begin{aligned}
T\left[f(x,y,z)\right] &= f(X,Y,Z) = R'(x,y,z)Y'(x,y,z) \\
R' &= R = \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \\
Y' &= \frac{1}{r^2}\left(X^2 - Y^2\right) = \sin^2\theta\cos 2(\phi - \phi_0) \qquad (7)
\end{aligned}
$$

Fig. 1 shows the original function and the function rotated with this procedure.

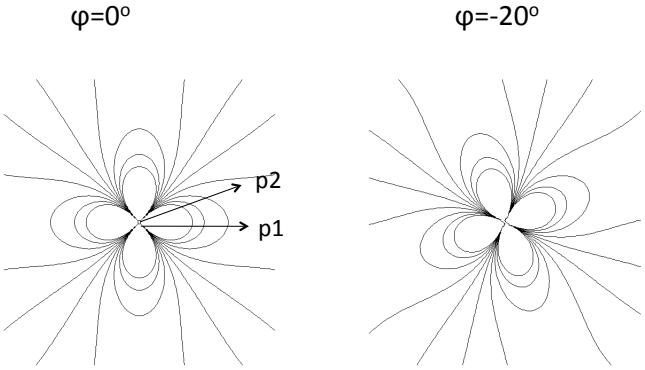


Figure 1: **Left**: the $3d_{x^2-y^2}$ orbital: function. We want to rotate it by 20° counter-clockwise around the z axis, so that the "attributes" of point $p1$ (here simply the value of the function) are transferred to point $p2$. **Right**: the rotated function, constructed using the procedure in eq. 7.

1.2.2 More on the properties of operators

- Operators can be applied one after the other, generating new operators. Taken all together they form a *finite* (for pure rotations/reflections) or *infinite* (if one includes translations) consistent set. As we shall see here below, the set of symmetry operators on a particular pattern has the mathematical structure of a *group*. In this first part of the course, we will be mainly concerned with *finite groups*, but the concepts are of much wider applicability.

- In general, operators do not commute. This is illustrated in fig. 2.

- As we see in fig. 2, some parts of the space are *left invariant* (transformed into themselves) by the application of a certain operator. For example,

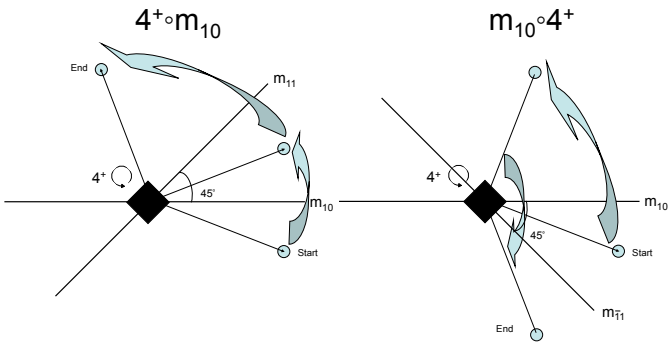


Figure 2: **Left**: A graphical illustration of the composition of the operators 4^+ and m_{10} to give $4^+ \circ m_{10} = m_{11}$. The fragment to be transformed (here a dot) is indicated with "start", and the two operators are applied in order one after the other (the rightmost first), until one reaches the "end" position. **Right**: 4^+ and m_{10} do not commute: $m_{10} \circ 4^+ = m_{\bar{1}1} \neq m_{11}$.

m_{10} leaves a horizontal plane invariant, whereas m_{11} leaves invariant a plane inclined by $45°$. Parts of the space left invariant by a certain operator are called **graphs** (more commonly known as symmetry elements) corresponding to that operator.

- **To summarise**:
  - **Operators** are maps of a space onto itself that enact transformations of a pattern defined on that space. An operator that leaves the pattern invariant is said to be a **symmetry operator**.
  - Taken together, the symmetry operators of a pattern are the **elements of a group**.
  - **Graphs** are sets of points in space that are left invariant by a certain operator.

1.3 Introduction to group theory

- The set of operators describing the symmetry of an object or pattern conforms to the mathematical structure of a **group**.
- A group is a set of elements with a defined binary operation known as composition, which obeys certain rules.

- ◇ A binary operation (usually called **composition** or **multiplication**) must be defined. We indicated this with the symbol "$\circ$". When group elements are operators, the operator to the *right* is applied *first*.
- ◇ Composition must be **associative**: for every three elements f, g and h of the set

$$f \circ (g \circ h) = (f \circ g) \circ h \tag{8}$$

- ◇ The "neutral element" (i.e., the identity, usually indicated with *E*) must exist, so that for every element g:

$$g \circ E = E \circ g = g \tag{9}$$

- ◇ Each element g has an **inverse** element g^{-1} so that

$$g \circ g^{-1} = g^{-1} \circ g = E \tag{10}$$

- ◇ A **subgroup** is a subset of a group that is also a group.
- ◇ A **set of generators** is a subset of the group (not usually a subgroup) that can generate the whole group by composition. Infinite groups (e.g., the set of all lattice translations) can have a finite set of generators (the primitive translations).
- ◇ Composition is in general not commutative: $g \circ f \neq f \circ g$
- ◇ A group for which all compositions are commutative is called an **Abelian** group.
- ◇ If the group is *finite* and has h elements, one can illustrate its action in a tabular form, by constructing a **multiplication table** (see below for an example). The table has $h \times h$ entries. By convention, the group elements running along the *top* of the table are *to the right of the composition sign*, while the elements running along the *side* of the table go to the *left* of the composition sign.

- **Composition of two symmetry operators** is the application of these one after another. We can see that the rules above hold.
- When composing symmetry operators, the notation $g \circ f$ means that f is applied *first*, followed by g.

1.4 The point group 32 (D_3): a classic example

- Fig. 3 illustrates a classic example of a crystallographic group: the point group 32 (Hermann-Mauguin notation) or D_3 (Schoenflies notation).

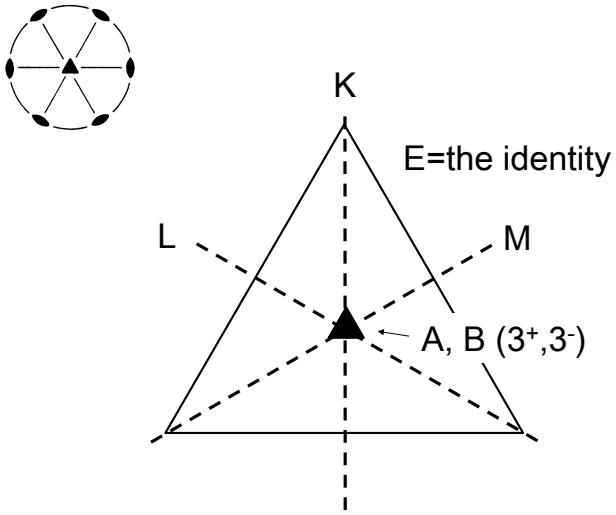


Figure 3: Schematic diagram for the the point group 32 (Hermann-Mauguin notation) or D_3 (Schoenflies notation). This group has 6 elements (symmetry operators): E (identity), A and B (rotation by $+120^\circ$ and -120°, respectively), M, K, and L (rotation by 180° around the dotted lines, as indicated). The graphical notation used in the International Tables is shown in the top left corner.

D_3 (32)

Applied first →

Applied second ↑

	E	A	B	K	L	M
E	E	A	B	K	L	M
A	A	B	E	L	M	K
B	B	E	A	M	K	L
K	K	M	L	E	B	A
L	L	K	M	A	E	B
M	M	L	K	B	A	E

Figure 4: Multiplication table for the point group 32 (D_3).

- One should take note of the following rules, since they apply generally to the composition or rotations:

◇ The composition of an axis and a 2-fold axis perpendicular to it in the order $M \circ A$ is a 2-fold axis rotated *counter-clockwise* by half the angle of rotation of A.

◇ Conversely, the composition of two 2-fold axes in the order $K \circ M$ is a rotation axis of twice the angle between the two two 2-fold axes and in the direction defined by $K \times M$.

- Fig. 5 shows the multiplication table for the group of permutations of 3 objects (1,2,3). It is easy to see that the multiplication table is *identical* to that for the 32 group (with an appropriate correspondence of the elements of each group). When this happens, we say that 32 and the group of 3-element permutations are **the same abstract group**.

Permutation group

Applied first →

Applied second ↑

	123	312	231	321	132	213
123	123	312	231	321	132	213
312	312	231	123	132	213	321
231	231	123	312	213	321	132
321	321	213	132	123	231	312
132	132	321	213	312	123	231
213	213	132	321	231	312	123

Figure 5: Multiplication table for the 3-element permutation group.

1.5 Conjugation

- Two elements g and f of a group are said to be **conjugated through a third element** h if:

$$f = h^{-1} \circ g \circ h \tag{11}$$

We use the notation $g \sim f$ to indicate that g is conjugated with f.

- Conjugation has the following properties:

◇ It is **reflexive**: $g \sim g$

$$g = E^{-1} \circ g \circ E \tag{12}$$

◇ It is **symmetric**: $g \sim f \Leftrightarrow f \sim g$. In fact:

$$f = h^{-1} \circ g \circ h \Leftrightarrow h \circ f \circ h^{-1} = g \Leftrightarrow g = (h^{-1})^{-1} \circ f \circ h^{-1} \tag{13}$$

◇ It is **transitive**: $g \sim f, f \sim k \Rightarrow g \sim k$. (*proof left as an exercise*).

- A relation between elements of a set that is reflexive, symmetric and transitive is called an **equivalence relation**. An equivalence relation partitions a set into several disjoint subsets, called **equivalence classes**. All the elements in a given equivalence class are equivalent among themselves, and no element is equivalent with any element from a different class.
- Consequently, conjugation partitions a group into disjoint subsets (**usually not subgroups**), called **conjugation classes**.
- If an operator in a group commutes with all other operators, it will form a class of its own. It follows that in every group the identity is always in a class on its own.
- For Abelian groups, every elements is in a class of its own.

1.5.1 Example: the classes of the point group 422 (D_4)

- The crystallographic point group 422 and its multiplication table are illustrated in fig. 6 and fig. 7.
- One can verify from the multiplication table that 422 has the following 5 classes:
  - ◇ The identity E.
  - ◇ The two-fold rotation 2_z. This is also in a class of its own in this case, since it commutes with all other operators.
  - ◇ The two four-fold rotations 4^+ and 4^-, which are conjugated with each other through any of the in-plane 2-fold axes.
  - ◇ 2_x and 2_y, conjugated with each other through either of the 4-fold rotations.
  - ◇ 2_{xy} and $2_{x\bar{y}}$, also conjugated with each other through either of the 4-fold rotations.

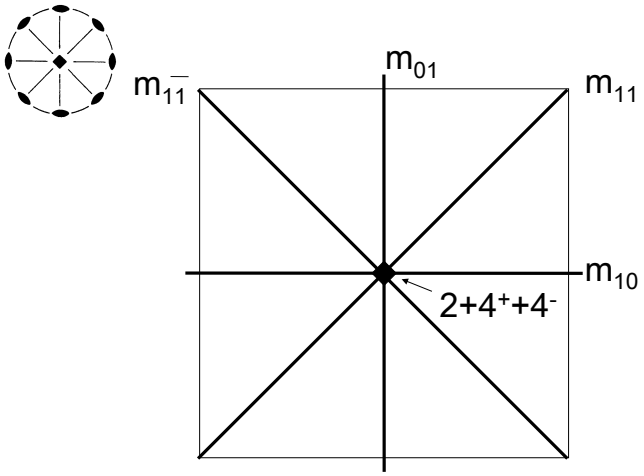


Figure 6: Schematic diagram for the the point group 422 (Hermann-Mauguin notation) or D_4 (Schoenflies notation). This group has 8 elements (symmetry operators): E (identity), 4^+ and 4^- (rotation by $+90^\circ$ and -90°, respectively), 2_z (rotation by 180° around the z axis and the four in-plane rotations 2_x, 2_y, 2_{xy}, $2_{x\bar{y}}$. The graphical notation used in the International Tables is shown in the top left corner.

Applied first →

Applied second ↑

	E	2_z	4^+	4^-	2_x	2_y	2_{xy}	2_{x-y}
E	E	2_z	4^+	4^-	2_x	2_y	2_{xy}	2_{x-y}
2_z	2_z	E	4^-	4^+	2_y	2_y	2_{x-y}	2_{xy}
4^+	4^+	4^-	2_z	E	2_{x-y}	2_{xy}	2_x	2_y
4^-	4^-	4^+	E	2_z	2_{xy}	2_{x-y}	2_y	2_x
2_x	2_x	2_y	2_{xy}	2_{x-y}	E	2_z	4^-	4^+
2_y	2_y	2_x	2_{x-y}	2_{xy}	2_z	E	4^+	4^-
2_{xy}	2_{xy}	2_{x-y}	2_y	2_x	4^+	4^-	E	2_z
2_{x-y}	2_{x-y}	2_{xy}	2_x	2_y	4^-	4^+	2_z	E

Figure 7: Multiplication table for the point group 422 (D_4).

- Once can observe the following important relation: **graphs of conjugated operators are related to each other by symmetry**.

2 Lecture 2: Introduction to the theory of representations

2.1 Formal definition of a representation

- A *representation of a group* is a **map of the group onto a set of linear operators onto a vector space**. We write:

$$g \rightarrow \hat{O}(g) \, \forall g \in G. \tag{14}$$

  The representation is said to be *faithful* if each element of the group maps onto a distinct operator.

- Physically, the **vector space** will represent the set of all possible solutions of our problem.

- More abstractly, a **vector space** is a set formed by a collection of elements called vectors, which may be added together and multiplied by numbers. To avoid confusion with ordinary vectors, we will call the elements of such a set **modes** in the remained. Some examples of vector spaces follow here below.

  - Most of the *patterns* described in Lecture 1 can be thought of as elements of a vector space. For example, the displacement patterns of atoms in a vibrating molecule can be added together and multiplied by constants, so they form a vector space.
  - The Hilbert space is a vector space (defined over the complex field), and its modes are the wavefunctions.
  - Arrays and matrices of given dimensions form vector spaces.
  - The set of magnetic configurations of a crystal are modes of a vector space.
  - Electron densities in a molecule or crystal do *not* form a vector space, since they can only be positive. However, density fluctuations away from an average density can be considered to some extent as modes of a vector space.
  - Physically, many of these modes are *real* — for example, classical magnetic moments are real (not complex) axial vectors. However, it is often advantageous to define these linear spaces over the complex field and deal with the reality of physical modes later.

- To be a representation, the map must obey the rules:

$$\begin{aligned} \hat{O}(g \circ f) &= \hat{O}(g)\hat{O}(f) \\ \hat{O}(E) &= \hat{E} \\ \hat{O}(g^{-1}) &= \hat{O}^{-1}(g) \end{aligned} \tag{15}$$

  where the operators on the right side are multiplied using the ordinary operator multiplication (which usually means applying the operators one after the other, rightmost first).

- The set of operators $\{\hat{O}(g)\}\,\forall g \in G$ is called the **image of the representation**, and is itself a group.

- **Example 1 (trivial)**: mapping of the point group 32 onto a set of 2×2 matrices:

$$\begin{aligned} E &\rightarrow \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} A \rightarrow \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \\ B &\rightarrow \begin{bmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} K \rightarrow \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \\ L &\rightarrow \begin{bmatrix} +\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} M \rightarrow \begin{bmatrix} +\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \end{aligned} \tag{16}$$

  This is a simple case of **matrix representation**. Here, the matrices are linear operators onto the vector space of the 2-element column arrays.

- **Example 2 (more complex)**: mapping of the group of translations onto the Hilbert space of wavefunctions defined over a finite volume with periodic boundary conditions. Remembering that plane waves form a complete set, we can write any function $\psi(\mathbf{r})$ as:

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{17}$$

  where the summation is over $k_x = 2n_x\pi/L$ etc. Let us define a *representation* of the group of translations as $\mathbf{t} \rightarrow \hat{O}(\mathbf{t})$, so that:

$$\hat{O}(\mathbf{t}) \left[\frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \right] = e^{-i\mathbf{k}\cdot\mathbf{t}} \left[\frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \right] \tag{18}$$

and

$$\hat{O}(\mathbf{t})\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{t}} \left[\frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}\right] = \psi(\mathbf{r}-\mathbf{t}) \tag{19}$$

- In both examples given here above, the image of the group coincides with the operators as we usually define them . In particular, example of the group of translations is an illustration of the general transformation rule for functions (see Lecture 1).

- However, strictly speaking, the symmetry operators as defined in Lecture 1 are not automatically linear operators, unless the "space of patterns" has the structure of a vector space.

2.2 Basis sets for the vector space and matrix representations

- If the vector space in question has finite dimension, we can always introduce a finite **basis set** for it, which we shall call $[\mathbf{a}_\mu]$. [1] Each element $\mathbf{v}$ can be written as:

$$\begin{aligned} \mathbf{v} &= \sum_\mu v_\mu \mathbf{a}_\mu \\ \hat{O}(g)\mathbf{v} &= \sum_\mu v_\mu \hat{O}(g)\mathbf{a}_\mu \end{aligned} \tag{20}$$

Writing

$$\hat{O}(g)\mathbf{a}_\mu = \sum_\nu D_{\mu\nu}(g)\mathbf{a}_\nu \tag{21}$$

we obtain

$$\begin{aligned} \hat{O}(g)\mathbf{v} &= \sum_{\mu,\nu} D_{\mu\nu}(g) v_\mu \mathbf{a}_\nu \\ \left[\hat{O}(g)\mathbf{v}\right]_\nu &= \sum_\mu D_{\mu\nu}(g) v_\mu \end{aligned} \tag{22}$$

[1] The notation here can seem rather cumbersome, due to the proliferation of subscripts and superscripts. We will use *greek lowercase letters* such as μ and ν to indicate elements in an array. Roman subscripts will be used to label representations (see below).

- $D_{\mu\nu}(g)$ is clearly a matrix. The map $g \to D_{\mu\nu}(g)$ is called the **matrix representation** of the original representation $g \to \hat{O}(g)$ **onto the basis set** $[\mathbf{a}_\mu]$.

- For a given representation, the matrix representation will depend on the choice of the basis. If $[\mathbf{b}] = [\mathbf{a}]\, M$ then $D^b(g) = M^{-1} D^a(g) M$. Therefore **different matrix representations of the same representation are related by a similarity transformation**.

2.2.1 Abstract representations and matrix representations

- As we have just seen, all the matrix representations of the same representation onto a *given* vector space are related by a similarity transformation. Since all vector spaces with the same dimension are isomorphic, we can extend this definition to different vector spaces, and say that two representations are **the same abstract representation of a given group** if their representative matrices are related by a similarity transformation, regardless of the vector space they operate on.

Notation: we indicate such abstract representations with the greek letter Γ. Γ_1, Γ_2, etc., with be different abstract representations in a given set (typically the set of irreducible representations — see below). A particular matrix representation of an abstract representation will be denoted, for example, by $D^{\Gamma_1}_{\mu\nu}(g)$.

2.2.2 Example: Representation of the group 422 (D_4) onto the space of 3-dimensional vectors

- We have seen in Lecture 1 that 422 has 8 elements and 5 conjugation classes.

- We now consider the representation of this group on the (vector) space of 3D ordinary vectors. The representation is unique, in the sense that if we define (draw) a vector, we know precisely how it will be transformed by the action of the group operators.

- However, the *matrix* representation will depend on the choice of the basis set for the vector space. Tables 1 and 2 show the two matrix representations for Cartesian basis $[\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}]$ and $[\hat{\mathbf{i}} + \hat{\mathbf{j}}, -\hat{\mathbf{i}} + \hat{\mathbf{j}}, \hat{\mathbf{k}}]$, respectively.

- It can be shown (*left as an exercise*) that the two sets of matrices are related by a similarity transformation.

Table 1: Matrix representation of the representation of point group 422 onto the space of 3-dimensional vectors, using the usual Cartesian basis set $[\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}]$.

E	2_z	4^+	4^-
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
2_x	2_y	2_{xy}	$2_{x\bar{y}}$
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

Table 2: Matrix representation of the representation of point group 422 onto the space of 3-dimensional vectors, using the basis set $[\hat{\mathbf{i}} + \hat{\mathbf{j}}, -\hat{\mathbf{i}} + \hat{\mathbf{j}}, \hat{\mathbf{k}}]$.

E	2_z	4^+	4^-
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
2_x	2_y	2_{xy}	$2_{x\bar{y}}$
$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

- If all representative matrices of a matrix representation have non-zero determinant, it is always possible to choose the basis vector in such a way that all the representative matrices are **brought into unitary form** (i.e. , $\left[\hat{O}(g)\right]\ \left[\hat{O}(g)\right]^\dagger = 1$). The proof, which is not difficult but is rather tedious, can be found in Dresselhaus, 2.4, p19.

- Operators onto space of functions defined on a Hilbert space according to the procedure explained in section 1.2.1 are **unitary**. This is a consequence of the fact that such operator are *norm-conserving* for all elements of the Hilbert space; this is intuitive and can also be shown explicitly by writing the norm of a function f and its transform $f' = f(X, Y, Z)$, changing the integration variables to X, Y and Z and observing that symmetry operators do not change the volume element: $dxdydz = dXdYdZ$. We can therefore conclude that $\hat{O}^\dagger\hat{O}$ is the identity, so $\hat{O}$ is unitary if it is linear.

$$\forall\psi,\ \langle\psi|\hat{O}^\dagger\hat{O}|\psi\rangle = \langle\psi|\psi\rangle \Rightarrow \hat{O}^\dagger\hat{O} = \hat{E} \tag{23}$$

Note that this relation can also be satisfied by *anti-unitary, anti linear* operators, such as the time reversal operator.

2.2.3 Traces and determinants: characters of a representation

- We remind the following properties of the trace and determinant of a square matrix:
  - $\diamond$ $tr(A+B) = tr(A) + tr(B)$; $tr(cA) = c\,tr(A)$; $tr(AB) = tr(BA)$; $tr(A^T) = tr(A)$; $tr(PAP^{-1}) = tr(A)$.
  - $\diamond$ $\det(A^T) = \det(A)$; $\det(A^{-1}) = 1/\det(A)$; $det(AB) = \det(A)\det(B)$; $det(PAP^{-1}) = det(A)$.
- It follows that **the matrices of two matrix representations of the same representation have the same trace and determinant**.
- It also follows that **images of group elements in the same conjugation class have the same trace and determinant**.
- **Trace and determinant of images are properties of each conjugation class for a given representation, not of the particular matrix representation or the group element within that class**.
- Traces of representative matrices are called **characters of the representation**. Each representation is characterised by a set of characters, each associated with a conjugation class of the group.

2.3 Reducible and irreducible representations

- A representation is said to be **reducible** if there exists a choice of basis in which all matrices are simultaneously of the **same block-diagonal form**, such as, for example:

$$\left[\hat{O}(g)\right] = \begin{bmatrix} c_1 & & & & & & \\ & \begin{bmatrix} . & c_2 & . \\ c3 & . & . \\ . & . & c_4 \end{bmatrix} & & & & \\ & & & & & \\ & & & c5 & & \\ & & & & \begin{bmatrix} . & c_6 \\ c_7 & . \end{bmatrix} & \end{bmatrix} \tag{24}$$

(dots represent zeros)

- The important thing is that **the blocks must be the same shape** $\forall g \in G$.
- One can readily see that if all matrices are of this form, the vector space is subdivided into a series of subspaces, with each block defining a **representation of the original group onto the subspace**.
- A representation is said to be **fully reduced** if the blocks are as small as possible — the extreme example being that all representative matrices are diagonal.
- A representation is said to be **irreducible** if no block decomposition of this kind is possible.

2.4 Example: representation of the group 32 onto the space of distortions of a triangle

The vector space: the space of all possible configurations of polar vectors at the corners of a triangle. One such generic configuration (*mode*) is shown in fig. 8. This can represent, for example, a combination of translation, rotation and distortion of the triangle (dashed line). One can see that the set of these configurations forms a vector space, since we can add two configurations (just by summing the vectors at each vertex) and multiply them by a scalar constant. This space has 6 dimensions, and will require a 6-element basis set.

The basis set: we can start by choosing a very simple basis set, as shown in fig. 9. On this basis, modes[2] are written as column arrays — for example:

$$a\,|1\rangle + b\,|2\rangle + c\,|5\rangle = \begin{bmatrix} a \\ b \\ \cdot \\ \cdot \\ c \\ \cdot \end{bmatrix} \tag{25}$$

Representation and matrix representations: one directly constructs the representation and observes how modes are transformed into each other by the 6 operators of 32. For example, operator A transforms $|1\rangle$ into $|2\rangle$ etc. The matrix representation on this basis is (dots represent zeros):

[2] here and elsewhere we write modes as $|m\rangle$, although we stress that these particular modes are *classical*

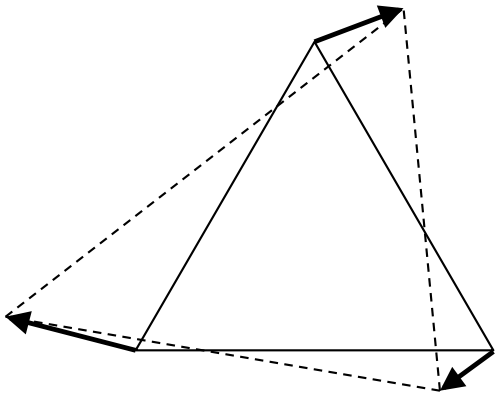


Figure 8: . A generic mode in the space of all possible configurations of polar vectors at the corners of a triangle. Modes such as this in general lose all the symmetry of the original pattern.

$$
[A] = \begin{bmatrix} . & . & 1 & . & . & . \\ 1 & . & . & . & . & . \\ . & 1 & . & . & . & . \\ . & . & . & . & . & 1 \\ . & . & . & 1 & . & . \\ . & . & . & . & 1 & . \end{bmatrix} \quad [K] = \begin{bmatrix} . & . & 1 & . & . & . \\ . & 1 & . & . & . & . \\ 1 & . & . & . & . & . \\ . & . & . & . & . & -1 \\ . & . & . & . & -1 & . \\ . & . & . & -1 & . & . \end{bmatrix}
$$

$$
[B] = \begin{bmatrix} . & 1 & . & . & . & . \\ . & . & 1 & . & . & . \\ 1 & . & . & . & . & . \\ . & . & . & . & 1 & . \\ . & . & . & . & . & 1 \\ . & . & . & 1 & . & . \end{bmatrix} \quad [L] = \begin{bmatrix} 1 & . & . & . & . & . \\ . & . & 1 & . & . & . \\ . & 1 & . & . & . & . \\ . & . & . & -1 & . & . \\ . & . & . & . & . & -1 \\ . & . & . & . & -1 & . \end{bmatrix}
$$

$$
[E] = \begin{bmatrix} 1 & . & . & . & . & . \\ . & 1 & . & . & . & . \\ . & . & 1 & . & . & . \\ . & . & . & 1 & . & . \\ . & . & . & . & 1 & . \\ . & . & . & . & . & 1 \end{bmatrix} \quad [M] = \begin{bmatrix} . & 1 & . & . & . & . \\ 1 & . & . & . & . & . \\ . & . & 1 & . & . & . \\ . & . & . & . & -1 & . \\ . & . & . & -1 & . & . \\ . & . & . & . & . & -1 \end{bmatrix}
$$

(26)

- These arrays are already in block-diagonal form (two 3×3 blocks). The representation is therefore **reducible**. This means that modes $|1\rangle$, $|2\rangle$ and $|3\rangle$ are never transformed into modes $|4\rangle$, $|5\rangle$ and $|6\rangle$ by any of the symmetry operators.

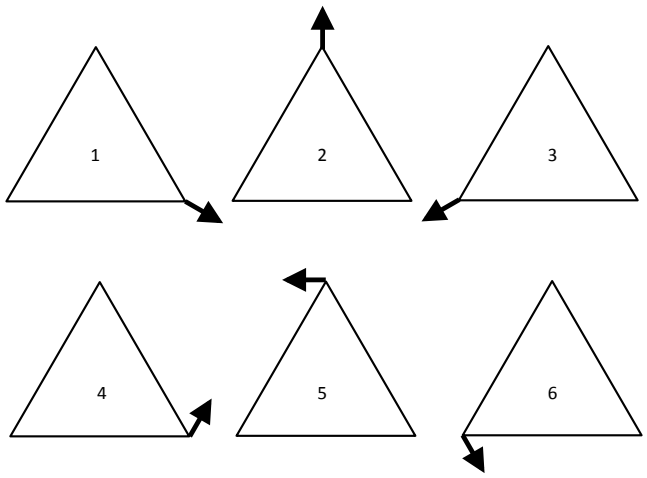


Figure 9: . A simple basis set for the space of all possible configurations of polar vectors at the corners of a triangle.

- Fig. 10 shows two modes with a higher degree of symmetry. These modes transform into either themselves or minus themselves by any of the symmetry operators. If they were chosen as basis vectors, the corresponding element of the matrix representation would lie on the diagonal and would be $+1$ or -1. This demonstrates that the representation is reducible even further by an appropriate choice of basis (see below).

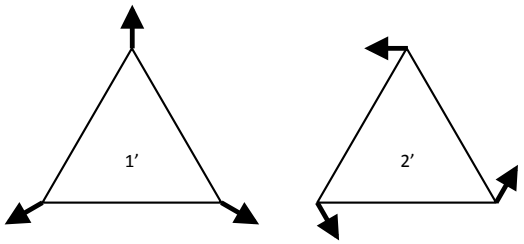


Figure 10: . Two 32 modes retaining a higher degree of symmetry. Mode m_1' is totally symmetric with respect to all symmetry operators. Mode m_2' is symmetric by the two 3-fold rotations (and the identity) and antisymmetric by the 2-fold rotations.

2.5 Example: representation of the cyclic group 3 onto the space of quadratic polynomials

The group: the cyclic group 3 is a sub-group of 32, and has only 3 elements: E, A, B. Unlike 32, 3 is an Abelian group.

The vector space: the space of all quadratic polynomials in x, y and z with real (or complex) coefficients. This space has 6 dimension.

The basis set: we choose the basis set formed by the following 6 functions:

$$f_1 = x^2;\ f_2 = y^2;\ f_3 = z^2;\ f_4 = xy;\ f_5 = xz;\ f_6 = yz \tag{27}$$

The transformations: to transform the functions, we follow the recipe given in Lecture 1: we replace the arguments x, y and z of the original functions with new formal arguments $X(x,y,z)$, $Y(x,y,z)$ and $Z(x,y,z)$, which are the back-transformations of the original arguments. For example, for the 3^+ operator:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \frac{1}{2}(-x+\sqrt{3}y) \\ \frac{1}{2}(-\sqrt{3}x-y) \\ z \end{bmatrix} \tag{28}$$

this produced the following set of rotated basis functions:

$$\begin{aligned} f_1' &= \frac{1}{4}\left(x^2 + 3y^2 - 2\sqrt{3}xy\right) \\ f_2' &= \frac{1}{4}\left(3x^2 + y^2 + 2\sqrt{3}xy\right) \\ f_3' &= z^2 \\ f_4' &= \frac{1}{4}\left(\sqrt{3}x^2 - \sqrt{3}y^2 - 2xy\right) \\ f_5' &= \frac{1}{2}\left(-xz + \sqrt{3}yz\right) \\ f_6' &= \frac{1}{2}\left(-\sqrt{3}xz - yz\right) \end{aligned} \tag{29}$$

The matrix representation for the 3^+ operator can therefore be written as

$$\begin{bmatrix} \frac{1}{4} & \frac{3}{4} & 0 & \frac{\sqrt{3}}{4} & 0 & 0 \\ \frac{3}{4} & \frac{1}{4} & 0 & -\frac{\sqrt{3}}{4} & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & +\frac{\sqrt{3}}{2} & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \tag{30}$$

By exchanging columns 3 & 4 and rows 3 & 4 (which is equivalent to exchanging f_3 with f_4 and f_3' with f_4'), the matrix can be rewritten as

$$\begin{bmatrix} \frac{1}{4} & \frac{3}{4} & \frac{\sqrt{3}}{4} & 0 & 0 & 0 \\ \frac{3}{4} & \frac{1}{4} & -\frac{\sqrt{3}}{4} & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \tag{31}$$

which is in block-diagonal form. Note that on this particular basis set the matrix is *not* unitary, and $[3^-] = [3^+]^{-1} \neq [3^+]^T$, although $[3^-]$ is in the same block-diagonal form (for a basis set with unitary matrix representation, see Problem 4 of Problem Sheet 1, since C_3 is a subgroup of D_3). The latter demonstrates that the representation is **reducible**. One can prove that all representations of Abelian groups can be fully reduced to *diagonal* form.

2.6 * Example: scalar functions on a square.

The group is 422 — the group of the square in 2D, which we have already encountered. Note that this group is the *same abstract group* as the group of permutations of 4 objects (it has the same multiplication table).

The vector space: the space of all possible combinations of 4 numbers at the corners of the square. It is a 4-dimensional space.

The basis set: we employ the basis set shown in fig. 11, where $+$ and $-$ indicates $+1$ and -1.

The matrix representation on this basis set is block-diagonal. Modes $|1\rangle$ and $|2\rangle$ transform either into themselves or minus themselves by all symmetry operators, and their matrix elements lie on the diagonal of the 4×4 matrix representation. Modes $|3\rangle$ and $|4\rangle$ are transformed either into themselves or into each other. This is illustrated in tab. 3.

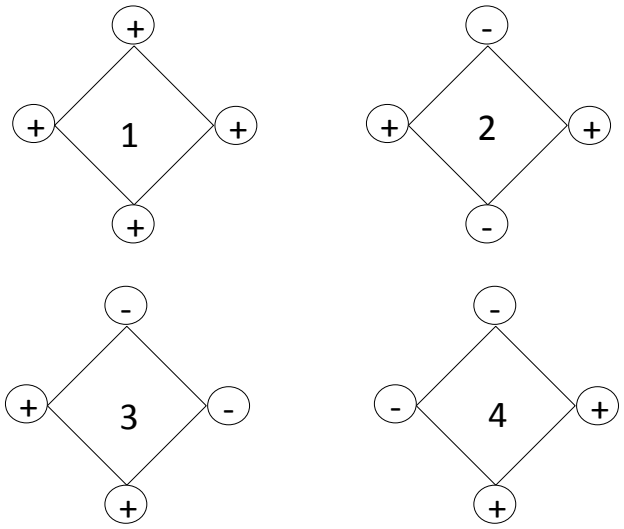


Figure 11: . A basis set for the space of scalar functions on a square.

Table 3: Matrix representation of the representation of point group 422 onto the space of the scalar functions on a square.

	E	2_z	4^+	4^-
$\|1\rangle$	1	1	1	1
$\|2\rangle$	1	1	-1	-1
$\begin{bmatrix} \|3\rangle \\ \|4\rangle \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$

	2_x	2_y	2_{xy}	$2_{x\bar{y}}$
$\|1\rangle$	1	1	1	1
$\|2\rangle$	1	1	-1	-1
$\begin{bmatrix} \|3\rangle \\ \|4\rangle \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$

- Let us now consider a closely related problem where, instead of scalar functions, we have vectors in the z direction. An appropriate basis set is shown in fig. 12. One can see that the transformations on individual vectors will be the same as for the scalars, except for the fact the in-plane 2-fold axes have an additional sign reversal. The transformation for modes $|3\rangle$ and $|4\rangle$ are the same as for the scalar case. Modes $|1\rangle$ and $|2\rangle$ transform as shown in tab. 4.

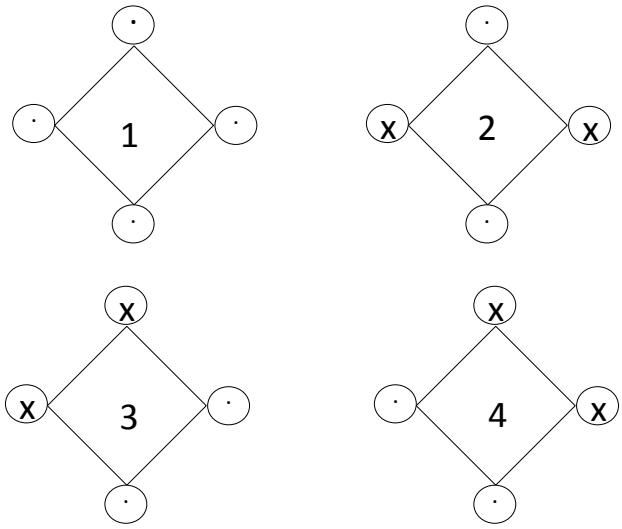


Figure 12: . A basis set for the space of z-vector functions on a square.

Table 4: Matrix representation of the representation of point group 422 onto the space of the z-vector functions on a square.

	E	2_z	4^+	4^-
$\|1\rangle$	1	1	1	1
$\|2\rangle$	1	1	-1	-1

	2_x	2_y	2_{xy}	$2_{x\bar{y}}$
$\|1\rangle$	-1	-1	-1	-1
$\|2\rangle$	-1	-1	1	1

3 Lecture 3: Key theorems about irreducible representations

- In the previous section, we have introduced the concepts of reducible and irreducible representations and seen some example of both. Abstract irreducible representations, or ***irreps*** for short, are extremely important in both group theory and its applications in physics, and are governed by a series of powerful, one would be tempted to say "magical" theorems. Before we introduce them, we will start by asking ourselves a series of questions about *irreps*:

  1. Are *irreps* a property of the group?
  2. How many are they for a given group?
  3. How can we characterise them, since for each there is clearly an

infinite number of matrix representations, all related by similarity transformations?

4. How can we construct all of them?
5. How can we decompose a reducible representation in its irreducible (block-diagonal) "components"?
6. Once we have an *irrep* and one of its matrix representations, how can we construct the corresponding basis vectors in a given space?

Point group *32* – variant 1

	E	A	B	K	L	M
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	-1	-1	-1
Γ_3	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} +\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} +\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$

Figure 13: . A matrix representation for 3 *irreps* of for the point group 32 . The modes in fig. 10 are basis vectors for Γ_1 and Γ_2. The appropriate basis vectors for Γ_3 in the space of ordinary 2D vectors are indicated.

- To start answering these questions, let us look at 3 *irreps* of the point group 32 we have already encountered (see figs 13, 14 and 15). The modes in fig. 10 are basis vectors for Γ_1 and Γ_2, which are obviously irreducible since they are 1-dimensional. Γ_3 is the "trivial" mapping onto the space of ordinary vector. We have not proven that this is an *irrep*, but let us assume it for the moment. Figs 13, 14 and 15 show 3 different matrix representations (and basis vectors) for Γ_3.
- We shall remember that 32 has 3 classes: $\{E\}$, $\{A, B\}$ and $\{K, L, M\}$.
- We can verify explicitly the properties of the trace of the representative matrices, as explained above: the trace is a characteristic of the *class*

Point group *32* – variant 2 $U = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$

UMU^{-1}

	E	A	B	K	L	M
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	-1	-1	-1
Γ_3	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} +\frac{\sqrt{3}}{2} & +\frac{1}{2} \\ +\frac{1}{2} & -\frac{\sqrt{3}}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{\sqrt{3}}{2} & +\frac{1}{2} \\ +\frac{1}{2} & +\frac{\sqrt{3}}{2} \end{pmatrix}$

Figure 14: . Same as fig. 13, but with a different set of basis vector and matrix representation for Γ_3. The transformation matrix from the basis in fig. 13 is indicated.

Point group *32* – variant 3 $U = \frac{\sqrt{2}}{3}\begin{pmatrix} \frac{\sqrt{3}}{2}\left(1-e^{-i\omega}\right) & -\frac{1}{2}\left(1+e^{-i\omega}\right)+e^{+i\omega} \\ \frac{\sqrt{3}}{2}\left(1-e^{+i\omega}\right) & -\frac{1}{2}\left(1+e^{+i\omega}\right)+e^{-i\omega} \end{pmatrix}$

UMU^{-1}

	E	A	B	K	L	M
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	-1	-1	-1
Γ_3	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2}+i\frac{\sqrt{3}}{2} & 0 \\ 0 & -\frac{1}{2}-i\frac{\sqrt{3}}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2}-i\frac{\sqrt{3}}{2} & 0 \\ 0 & -\frac{1}{2}+i\frac{\sqrt{3}}{2} \end{pmatrix}$	$\begin{pmatrix} 0 & -\frac{1}{2}-i\frac{\sqrt{3}}{2} \\ -\frac{1}{2}+i\frac{\sqrt{3}}{2} & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -\frac{1}{2}+i\frac{\sqrt{3}}{2} \\ -\frac{1}{2}-i\frac{\sqrt{3}}{2} & 0 \end{pmatrix}$

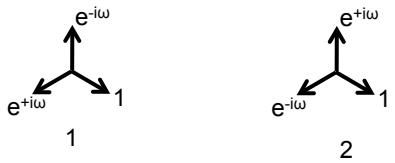


Figure 15: . Same as fig. 13 and 14 , but with a different set of (complex) basis vector and matrix representation for Γ_3. The transformation matrix from the basis in fig. 13 is indicated.

and of the *irrep*, not of the group element in the class or of the matrix representation. For example, the trace of all representative elements

for $\{K, L, M\}$ is 1 for Γ_1, -1 for Γ_2 and 0 for Γ_3. As already mentioned, we call this trace the **character** of the *irrep* for a given class[3]. The set of characters will be used to *characterise* the *irreps* — see below for theorems that put this on solid foundation.

- By examining each of the tables separately, we can determine the following:
  - ◇ Let us construct 6 arrays, of 6 elements by taking the representative number of each operator for the 1D *irreps* Γ_1 and Γ_2 and one of the 4 elements of the representative matrices for the 2D *irrep* Γ_3. For example, for the table in fig. 13 we get the following 6 arrays:

$$\begin{array}{cccccc} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 & -1 \\ 1 & -\frac{1}{2} & -\frac{1}{2} & -1 & +\frac{1}{2} & +\frac{1}{2} \\ 0 & -\frac{\sqrt{3}}{2} & +\frac{\sqrt{3}}{2} & 0 & -\frac{\sqrt{3}}{2} & +\frac{\sqrt{3}}{2} \\ 0 & +\frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 & -\frac{\sqrt{3}}{2} & +\frac{\sqrt{3}}{2} \\ 1 & -\frac{1}{2} & -\frac{1}{2} & 1 & -\frac{1}{2} & -\frac{1}{2} \end{array} \tag{32}$$

  - ◇ The 6 arrays are **orthogonal with each other** (in the ordinary sense of orthogonality of arrays).
  - ◇ The **norm** of each array is $\sqrt{6}$ for Γ_1 and Γ_2 and $\sqrt{3}$ for Γ_3, which can all be written as $\sqrt{h/l_j}$, where h is the number of elements in the group and l_j is the dimension of the *irrep*.
- We can verify that the same properties apply to the table in figs 14, although the arrays for Γ_3 are clearly different.
- We can also verify that the same properties apply to the table in fig 16, which contains 5 *irreps* of the point group 422.
- The table in figs 15, is slightly different, because the matrix elements are complex[4]. The 6 arrays are:

[3] Note that all the characters for all the *irreps* of this group and group 422 below are *real*. We can prove that if $g \sim g^{-1}$, then the character of any unitary representation of g is real. In fact, $g \sim g^{-1} \rightarrow U(g) = MU^{-1}(g)M^{-1} = MU^{\dagger}(g)M^{-1}$. Taking the trace, $tr(U(g)) = tr(U^*(g)) = tr^*(U(g))$, so the character is *real*. $g \sim g^{-1}$ for all operators in 32 and 422.

[4] Somewhat surprisingly, this is the **standard setting** for these matrices, as shown, for example, in http://www.cryst.ehu.es/rep/point.html. The reason is that the cyclic subgroup of D_3, C_3, is Abelian, and all the representations of an Abelian group can be fully reduced into 1D *irreps*, which usually have complex characters. The one shown here is the basis that fully reduces C_3. For Abelian groups, each element is in a class of its own, so it obviously cannot be $g \sim g^{-1}$ unless $g = g^{-1}$.

$$\begin{array}{cccccc} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 & -1 \\ 1 & -\frac{1}{2}+i\frac{\sqrt{3}}{2} & -\frac{1}{2}-i\frac{\sqrt{3}}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2}-i\frac{\sqrt{3}}{2} & 1 & -\frac{1}{2}+i\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & -\frac{1}{2}+i\frac{\sqrt{3}}{2} & 1 & -\frac{1}{2}-i\frac{\sqrt{3}}{2} \\ 1 & -\frac{1}{2}-i\frac{\sqrt{3}}{2} & -\frac{1}{2}+i\frac{\sqrt{3}}{2} & 0 & 0 & 0 \end{array} \tag{33}$$

- One can verify that line 3 is actually orthogonal to the *complex conjugate* of line 6 etc.

- Remembering that each array element is actually an element of the representative matrix of an *irrep*, we can summarise all these results as an **orthogonality relation**:

$$\sum_g D(g)^{\Gamma_i}_{\mu\nu} D^*(g)^{\Gamma_j}_{\mu'\nu'} = \frac{h}{l_i}\delta_{ij}\delta_{\mu\mu'}\delta_{\nu\nu'} \tag{34}$$

Point group *422* (one of the variants)

	E	2_z	4^+	4^-	2_x	2_y	2_{xy}	$2_{x\bar{y}}$
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	-1	-1	-1	-1
Γ_3	1	1	-1	-1	1	1	-1	-1
Γ_4	1	1	-1	-1	-1	-1	1	1
Γ_5	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$

Figure 16: . A matrix representation for 5 *irreps* of for the point group 422 .

- The *orthogonality* relation in eq. 34 can be easily converted into an *orthonormality relation* by normalising all the arrays with the coefficient $\sqrt{l_j/h}$.

3.1 The Wonderful Orthogonality Theorem and its implications

- Amazingly, eq. 34 **represents a general theorem applicable to all unitary matrix representations of all *irreps* of all finite groups**. This is the so-called *Wonderful Orthogonality Theorem* (WOT), due to physicist and Nobel prize winner John Van Vleck (this tells a story of its own about the importance of group theory in the early days of quantum theory). The theorem can be easily extended to non-unitary matrix representations (see Dresselhaus, p 25, eq. 2.52), but we will be content here with its version for unitary representations. The proof of the WOT is not conceptually difficult, but it is rather convoluted. One proves the so-called Schur's Lemma (in 2 parts) to begin with, then moves to the actual proof. This is done in detail in Dresselhaus, pp 21-27.

- It is important to stress that the WOT is only valid for **irreducible representations**. Indeed, if a representation is reducible, the matrix elements of any of its matrix representations **will not be orthogonal** to those of the *irreps* it can be decomposed into.

- The importance of the WOT cannot be overestimated, since it goes a long way to answer the questions stated at the beginning of this section.

- One can immediately see that the number of *irreps* of a given group and their dimensionality is limited by the fact that only h mutually orthogonal vectors can be constructed in the space of arrays of dimensionality h. Since the number of such arrays arising from a given *irrep* of dimension l_j is l_j^2, it must be:

$$\sum_j l_j^2 \leq h \tag{35}$$

  As we will see later it is the strict $=$ sign that holds in eq. 35.

3.2 The Wonderful Orthogonality Theorems for Characters

- We can go even further by constructing the so-called **character tables**, which can be done for the full group or for the classes (remember that group elements in the same conjugation class have the same characters, since their representative matrices are similar). For example, group 32 has the character tables shown in fig. 17.

- Turning our attention first to the full-group table, we can see that each element is simply:

Point group *32* – Character Table (full group)

	E	A	B	K	L	M
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	-1	-1	-1
Γ_3	2	-1	-1	0	0	0

Point group *32* – Character Table(classes)

	E	2A	3K
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

Figure 17: Character tables for the point group 32 . In the class table, the number preceding the *representative element* (e.g., 2A, 3K), indicates the number of elements in the class.

$$tr(D(g)^{\Gamma_i}) = \sum_{\mu} D(g)^{\Gamma_i}_{\mu\mu} \tag{36}$$

- The three arrays in the table must remain orthogonal to each other because of the way they are constructed. For example, the array corresponding to Γ_3 is:

$$\begin{aligned} \left[\begin{array}{cccccc} 2 & -1 & -1 & 0 & 0 & 0 \end{array}\right] &= \left[\begin{array}{cccccc} 1 & -\frac{1}{2} & -\frac{1}{2} & -1 & +\frac{1}{2} & +\frac{1}{2} \end{array}\right] \\ &+ \left[\begin{array}{cccccc} 1 & -\frac{1}{2} & -\frac{1}{2} & +1 & -\frac{1}{2} & -\frac{1}{2} \end{array}\right] \end{aligned} \tag{37}$$

the arrays to the right of the $=$ sign being arrays 3 and 6 in eq. 32. Since these are orthogonal to all the other arrays in eq. 32, their sum must also be orthogonal. However, the normalisation has now changed, since the squared norm of these arrays will be multiplied by l_j. If we indicate with $\chi(g)^{\Gamma_i}$ the character of group element g in *irrep* Γ_i, we obtain the following **WOT for characters - full group version**.

$$\sum_g \chi(g)^{\Gamma_i}\chi^*(g)^{\Gamma_j} = h\delta_{ij} \tag{38}$$

- This can be easily modified for application to the class version of the character table, e.g., fig. 17 (bottom panel). All the element in each class have the same character, so if we call N_k the number of group elements in class C_k (for clarity, this is usually indicated in class character tables such as fig. 17 — bottom panel), eq. 38 becomes the **WOT for characters - classes version**:

$$\sum_k N_k\chi(C_k)^{\Gamma_i}\chi^*(C_k)^{\Gamma_j} = h\delta_{ij} \tag{39}$$

- Once again, one can easily construct orthonormal arrays of dimensionality equal to the number of *classes* by normalising each array. The arrays

$$\left[\sqrt{\frac{N_1}{h}}\chi(C_1)^{\Gamma_i}, \sqrt{\frac{N_2}{h}}\chi(C_2)^{\Gamma_i}, \cdots \sqrt{\frac{N_n}{h}}\chi(C_n)^{\Gamma_i}\right] \tag{40}$$

  are orthonormal for different i's.

- Eq. 39 further restricts the number of *irreps* for a group. If the number of classes is n, the number of independent mutually orthogonal vectors of dimension n is at most n, so it must be

$$N_{\textit{irreps}} \leq N_{classes} \tag{41}$$

  where, once again, the strictly $=$ sign holds (see below).

3.3 Reducible representations and their decomposition

- **The trace of a block-diagonal matrix is the sum of the traces of its diagonal blocks**. This is quite obvious from the definition of the trace. If a representation is *reducible*, the representative matrices of all the group elements can be written in the same identical diagonal form. It follows that **the array of characters of a *reducible* representation is a linear combination of the character arrays of the *irreps* of the group**. Calling the *reducible* representation Γ_{red}:

$$\left[\chi(g_1)^{\Gamma_{red}}, \chi(g_2)^{\Gamma_{red}}, \cdots \chi(g_h)^{\Gamma_{red}}\right] = \sum_i a_i \left[\chi(g_1)^{\Gamma_i}, \chi(g_2)^{\Gamma_i}, \cdots \chi(g_h)^{\Gamma_i}\right] \tag{42}$$

or

$$\left[\chi(C_1)^{\Gamma_{red}}, \chi(C_2)^{\Gamma_{red}}, \cdots \chi(C_n)^{\Gamma_{red}}\right] = \sum_i a_i \left[\chi(C_1)^{\Gamma_i}, \chi(C_2)^{\Gamma_i}, \cdots \chi(C_n)^{\Gamma_i}\right] \tag{43}$$

- The coefficients a_i are integers indicating the **number of *times irrep*** Γ_i **appears in the decomposition of reducible representation** Γ — in other words, the number of identical (or better similar) diagonal blocks corresponding to *irrep* Γ_i along the diagonal, once Γ is fully decomposed.

- Eq. 42 can be inverted exploiting the orthonormality relation, to find the coefficients:

$$a_j = \frac{1}{h} \sum_g \left[\chi(g)^{\Gamma_j}\right]^* \chi(g)^{\Gamma_{red}} \tag{44}$$

or, for classes

$$a_j = \sum_k \frac{N_k}{h} \left[\chi(C_k)^{\Gamma_j}\right]^* \chi(C_k)^{\Gamma_{red}} \tag{45}$$

Example: let us look again at the example given on page 21 — the representation of 32 on the space of triangular distortions. This is a 6-dimensional *reducible* representation of 32. We have already found 3 *irreps* for 32 (see fig. 17), and we know that we cannot have more than 3, since 32 has 3 classes (eq. 41), so we can be confident we have found all the 32 *irreps*. We can also see that

$$\sum_j l_j^2 = 1^2 + 1^2 + 2^2 = 6 = h \tag{46}$$

The character array for Γ_{red} is (just take the trace of all matrices):

E	A	B	K	L	M
6	0	0	0	0	0

by applying eq. 44 we obtain

$$a_1 = 1;\ a_2 = 1;\ a_3 = 2 \tag{47}$$

We write:

$$\Gamma_{red} = \Gamma_1 + \Gamma_2 + 2\Gamma_3 \tag{48}$$

which means that Γ_1 and Γ_2 appear *once* in the decomposition of Γ_{red}, while Γ_3 appears *twice*.

3.4 Second WOT for characters and number of *irreps*

- We have seen that *rows* of the matrix:

$$\begin{gathered}
\left[\sqrt{\tfrac{N_1}{h}}\chi(C_1)^{\Gamma_1}, \sqrt{\tfrac{N_2}{h}}\chi(C_2)^{\Gamma_1}, \cdots \sqrt{\tfrac{N_n}{h}}\chi(C_n)^{\Gamma_1}\right] \\
\left[\sqrt{\tfrac{N_1}{h}}\chi(C_1)^{\Gamma_2}, \sqrt{\tfrac{N_2}{h}}\chi(C_2)^{\Gamma_2}, \cdots \sqrt{\tfrac{N_n}{h}}\chi(C_n)^{\Gamma_2}\right] \\
\cdots \\
\left[\sqrt{\tfrac{N_1}{h}}\chi(C_1)^{\Gamma_n}, \sqrt{\tfrac{N_2}{h}}\chi(C_2)^{\Gamma_n}, \cdots \sqrt{\tfrac{N_n}{h}}\chi(C_n)^{\Gamma_n}\right]
\end{gathered} \tag{49}$$

  are orthonormal arrays.

- It can also be easily proven (Dresselhaus, pp 36–37) that the *colums* of this matrix are orthonormal. This is the **second WOT for characters**, which can also be written as

$$\sum_i \chi(C_k)^{\Gamma_i} \left[\chi(C_{k'})^{\Gamma_i}\right]^* = \frac{h}{N_k}\delta_{kk'} \tag{50}$$

  This time, **the summation is over *irreps***, not over group elements as before.

- By using the second WOT for characters, we can prove that $N_{\textit{irreps}} = N_{classes}$. In fact, we have constructed $N_{classes}$ independent and orthonormal arrays of dimension $N_{\textit{irreps}}$, and in order to do this it must be $N_{\textit{irreps}} \geq N_{classes}$. However, we have already seen that $N_{\textit{irreps}} \leq N_{classes}$, which implies $N_{\textit{irreps}} = N_{classes}$.

3.5 * Construction of all the *irreps* for a finite group

- We illustrate one method to construct all *irreps* of a given group. This method is not the one employed in actual fact, but it is useful because is simple and enables us to prove that $\sum_j l_j^2 = h$.

- Let's consider the multiplication table of the group, as exemplified by fig. 5 for our usual group 32, and let's rearrange the order or rows and columns so that all the identity elements E fall on the diagonal, as in fig. 18. It is easy to see that this is always possible for any finite group.

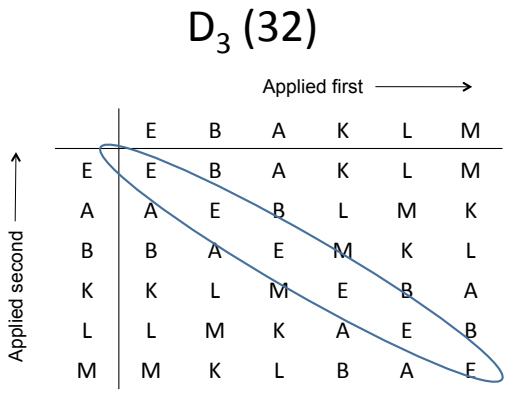


Figure 18: Multiplication table for the point group 32 (D_3), rearranged to contract the regular representation.

- We then construct the so-called **regular representation**, as follows: the matrix representative of group element g is obtained by replacing the g entries of the multiplications table with 1's and all the other entries with 0's. For example, in fig. 18, the representative matrix of element K is obtained by replacing all K's in the table with 1's and all the other letters with 0's.

- One can verify that the regular representation is in fact a representation — in particular it respects the composition – matrix multiplication relation.

- The regular representation has dimension h and is reducible. Its characters are h for the identity and 0 for all the other elements.

- By applying the decomposition formula we obtain:

$$a_j = \frac{1}{h} \sum_g \left[\chi(g)^{\Gamma_j}\right]^* \chi(g)^{\Gamma_{reg}} = l_j \tag{51}$$

since the character of the identity for a reducible or irreducible representation is equal to its dimension. In other words **each *irrep* is represented a number of times equal to its dimension in the regular representation**.

- It is therefore possible in principle to obtain all the *irreps* of a given group by block-diagonalising all the matrices of the regular representation (this is not what is done in practice).

- More usefully, since the dimension of Γ_{reg} is h, and the dimension of a reducible representation is the sum of the dimension of its *irreps* times the number of times they appear, it must be:

$$\sum_j l_j^2 = h \tag{52}$$

  as we set out to prove.

- All the *irreps* of the 32 crystallographic point groups have been determined many years ago, and can be found (including one standard setting for the matrices) at the following address: http://www.cryst.ehu.es/rep/point.html.

4 Lecture 4: Applications of representations to physics problems

4.1 Quantum mechanical problems: the symmetry of the Hamiltonian

- Let us first recall our definition of symmetry transformations for functions and their gradients from Section 1.2.1:

$$\begin{aligned} g[f(\boldsymbol{x})] &= f(\boldsymbol{R}^{-1}(g)\boldsymbol{x}) \\ g[\boldsymbol{\nabla} f(\boldsymbol{x})] &= (\boldsymbol{R}(g)\boldsymbol{\nabla})\, f(\boldsymbol{R}^{-1}(g)\boldsymbol{x}) \end{aligned} \tag{53}$$

  we have not proven explicitly the second line of eq. 53 , but its derivation is simple and completely general for **vector functions**.

- Since all transformations we are interested in here are isometric (i.e., preserve the norm) it also follows that

$$g[\nabla^2 f(\boldsymbol{x})] = \nabla^2 f(\boldsymbol{R}^{-1}(g)\boldsymbol{x}) \tag{54}$$

- As introduced in eq. 14, the mapping $g \to \hat{O}(g)\, \forall g \in G$ defines a *representation of the group* G onto the Hilbert space. The operators $\hat{O}(g)$ are *unitary*: therefore, they possess orthonormal eigenvectors with eigenvalues on the unit circle in complex space.

- Now we want to show explicitly that if the Hamiltonian is *invariant* by a transformation g as defined in eq. 53, then the operator $\hat{O}(g)$ *commutes* with the Hamiltonian:

$$\begin{aligned} \hat{O}(g)\hat{H}\psi(\boldsymbol{x}) &= \left(-\frac{\nabla^2}{2m} + U(\boldsymbol{R}^{-1}(g)\boldsymbol{x})\right)\psi(\boldsymbol{R}^{-1}(g)\boldsymbol{x}) \\ \hat{H}\hat{O}(g)\psi(\boldsymbol{x}) &= \left(-\frac{\nabla^2}{2m} + U(\boldsymbol{x})\right)\psi(\boldsymbol{R}^{-1}(g)\boldsymbol{x}) \end{aligned} \tag{55}$$

  so it is in fact necessary and sufficient for the *potential* to be invariant by the symmetry g to ensure that the Hamiltonian commutes with $\hat{O}(g)$. This relation between symmetry invariance and commutation is in general true for any quantum-mechanical Hermitian operator, not only for the Hamiltonian.

- Let us now assume that the Hamiltonian is invariant for *all* elements of the group G, i.e., that it commutes with all the operators $\hat{O}(g)\,\forall g \in G$. The following statements can be readily proven (they can in fact be extended to any Hermitian operator that has the symmetry of the group G):

  1. If $\phi(\boldsymbol{x})$ is an eigenstate of $\hat{H}$ with eigenvalue λ, then all $\hat{O}(g)\phi(\boldsymbol{x})$ are also eigenstates of $\hat{H}$ with the *same* eigenvalue λ, and this $\forall g \in G$. In fact,

$$\hat{H}\hat{O}(g)\phi(\boldsymbol{x}) = \hat{O}(g)\hat{H}\phi(\boldsymbol{x}) = \lambda\hat{O}(g)\phi(\boldsymbol{x}) \tag{56}$$

  2. If $\phi(\boldsymbol{x})$ is a ***non-degenerate*** **eigenstate** of $\hat{H}$, then the map $g \to \hat{O}(g)$ onto the one-dimensional subspace defined by $\phi(\boldsymbol{x})$ is a *one-dimensional irreducible representation of* G. In fact, since the eigenvector is non-degenerate, it must necessarily be $\hat{O}(g)\phi(\boldsymbol{x}) = c\phi(\boldsymbol{x})\,\forall g$, c being a *unitary constant*, and this is precisely the definition of a one-dimensional irreducible representation.
  3. If $\phi_1(\boldsymbol{x}) \ldots \phi_n(\boldsymbol{x})$ are ***degenerate*** **eigenstates** of $\hat{H}$ defining a subspace of the Hilbert space of dimension n, then the map $g \to \hat{O}(g)$ onto that subspace defines an n-dimensional representation of $\{g\}$ If the degeneracy is not accidental and there is no additional symmetry, then the representation is irreducible. In fact, since for every $\phi_i(\boldsymbol{x})$ of the degenerate subspace and for every g, $\hat{O}(g)\phi_i(\boldsymbol{x})$ is an eigenstate with the same eigenvalue, so

$$\hat{O}(g)\phi_i(\boldsymbol{x}) = \sum_j c_j\phi_j(\boldsymbol{x}) \tag{57}$$

Therefore the application of $\hat{O}(g)$ is *closed* within the $\phi_i(\boldsymbol{x})$ subspace, and is therefore a representation of the group G.

4. With regards to the question of whether this representation is reducible or irreducible, we will just give here some qualitative arguments. If the representation was reducible, then we could split the subspace defined by the $\phi_i(\boldsymbol{x})$ into two or more subspaces, each closed upon application of the operators $\hat{O}(g)$, but both with the same eigenvalues. If there is no additional symmetry, one can imagine changing the Hamiltonian adiabatically (and without altering its symmetry) in such a way that the eigenvalues of the two or more subspace become *different* — in other words, the degeneracy of the two subspaces would be accidental. On the other hand, if the Hamiltonian has additional symmetries, the reducible subspace by the first symmetry group may be irreducible by the *second* symmetry group, so that two or more irreducible representations of the first group may be "joined" together into multiplets (a classic case is that of the exchange multiplets in magnetism).

- We conclude that, in general, **the complete orthogonal basis set of eigenstates of the Hamiltonian fully reduces the representation $g \to \hat{O}(g)$ of the symmetry group of the Hamiltonian.**

- It is important to note that **the reverse is *not* true** — in other words, a basis set that fully reduces the representation $g \to \hat{O}(g)$ is *not necessarily* a set of eigenstates for the Hamiltonian. The problem arises when a particular irreducible representation Γ of the group $\{g\}$ **appears more than once** in the decomposition of the representation $g \to \hat{O}(g)$.

Example; let's consider two sets of eigenstates, $\phi_1(\boldsymbol{x}) \ldots \phi_n(\boldsymbol{x})$ with eigenvalue λ_1 and $\psi_1(\boldsymbol{x}) \ldots \psi_n(\boldsymbol{x})$, with eigenvalue λ_2. Let us also assume that both sets transform with the *same* irreducible matrix representation Γ_i, which would therefore appear more than once in the decomposition of $g \to \hat{O}(g)$. It is easy to see that the set $a\phi_1(\boldsymbol{x}) + b\psi_1(\boldsymbol{x}) \ldots a\phi_n(\boldsymbol{x}) + b\psi_n(\boldsymbol{x})$ (a and b being complex constants) also transforms with the same irreducible representation — in fact with the same matrices as the original two sets. However, it is also clear that the new basis set is not a set of eigenstates of $\hat{H}$.

- Therefore, in the presence of irreducible representations that appear more than once, more work is required to extract eigenstates from basis functions of irreducible representations (which can be obtained by the application of the projection operator — see below).

- Nevertheless, structuring the Hilbert space in terms of invariant subspaces by the *irreps* of the symmetry group of the Hamiltonian provides an enormous simplification to the solution of the Schroedinger equation, and defined a natural connection between problems having different potentials but the same symmetry group.

4.2 * Classical eigenvalue problems: coupled harmonic oscillators

- The same techniques can be applied with hardly any modifications to **classical eigenvalue problems**, since the mathematical formalism is identical to that of the quantum case. Classical eigenvalue problems are relevant to many CMP systems, for example, molecular vibrations, phonons in crystals, but also classical spin waves.

- As an example, we present the case of molecular vibrations. We start with the expression for the kinetic and potential energies in the limit of "small" displacements from the equilibrium position.

$$\begin{aligned} \mathcal{E}_K &= \frac{1}{2}\sum_i m_i \dot{x}^2 \\ \mathcal{E}_P &= \frac{1}{2}\sum_{i,j} \frac{\partial^2 U}{\partial x_i \partial x_j} x_i x_j \end{aligned} \tag{58}$$

Here, the x_i's are the displacement coordinates of ion i and m_i are their mass. The sum runs over *both* ions *and* components. The analysis proceeds in the following steps:

1. We perform a transformation to the **reduced coordinates**:

$$\xi_i = x_i \sqrt{m_i} \tag{59}$$

This has the effect of eliminating the masses from the kinetic energy expression:

$$\begin{aligned} \mathcal{E}_K &= \frac{1}{2}\sum_i \dot{\xi}^2 \\ \mathcal{E}_P &= \frac{1}{2}\sum_{i,j} \left(\frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 U}{\partial x_i \partial x_j} \right) \xi_i \xi_j \end{aligned} \tag{60}$$

2. We write the equation of motion as:

$$\ddot{\xi}_i + \sum_j \left(\frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 U}{\partial x_i \partial x_j} \right) \xi_j = 0 \tag{61}$$

3. We seek solution of the form

$$\xi_i = q_i \, e^{i\omega t} \tag{62}$$

from which we derive the secular equation

$$\omega^2 q_i = \sum_j \left(\frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 U}{\partial x_i \partial x_j} \right) q_j = \sum_j V_{ij} q_j \tag{63}$$

Eq. 63 is usually solved by diagonalising the matrix V_{ij} on the right-hand side.

- We want to show that symmetry analysis simplifies the solution of this problem very significantly.
- First of all, we define our **vector space** as the space of all **modes**, defined as $[q_{1x}, q_{1y}, q_{1z}, q_{2x} \cdots]$. The dimension of the space is mD, where m is the number of atoms in the molecule and D is the dimension of the (ordinary) space.
- We can define a (reducible) representation Γ of the symmetry group of the potential energy U onto this vector space as the symmetry transformation of the modes, involving both a change of the atom labelling and of the components. This is completely analogous to the example in section 2.4 (representation of the group 32 onto the space of distortions of a triangle).
- One can show explicitly that the invariance of U by the symmetry group G implies that V_{ij} **commutes with all the representative matrices**.
- From here onward, we can follow the quantum derivation step by step. In particular, we conclude that the **eigenvectors of** V_{ij} provide an irreducible decomposition of Γ in terms of the *irreps* of G. In particular, **the multiplet structure of the solution is deduced entirely by symmetry**. If an *irrep* Γ_i appears more than once in the decomposition of Γ, the eigenvectors of V_{ij} will not be determined entirely by symmetry, but one will have to diagonalise a much smaller matrix to find them.

4.3 Extended example: normal modes of the square molecule

- We illustrate these concepts with the concrete example of a square harmonic molecule, illustrate in fig.19 . Note that, in general, the exact solution of this problem require terms higher than the quadratic term, even if all the springs are perfectly harmonic. He will only address the problem in the limit of small displacements.

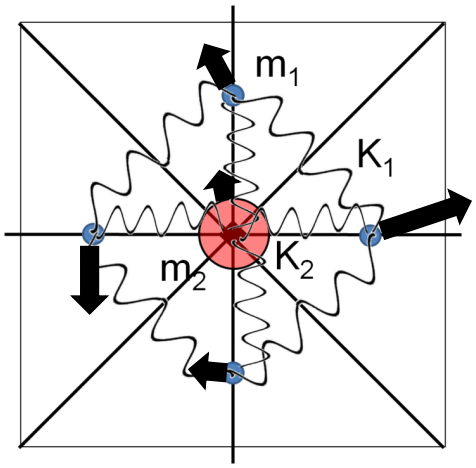


Figure 19: A snapshot of a vibrating square molecule, with the arrows represent a generic *mode*. This can be obtained as a linear combination of basis modes.

- The space of modes (i.e., of possible solution of the dynamical equations) is 10-dimensional (D=2, m=5). The 10 basis modes used in the original secular equation (eq. eq. 63) are illustrated in fig. 20. The order of the modes and in some case their sign has been altered, to show that the representation is *reducible*. In fact, one can see that all symmetry operators convert block-A modes into block-A modes, Block-B modes into block-B modes and block-C modes into block-C modes. Therefore, with this basis, the matrix representation is made up of 3 blocks (of dimensions 4, 4 and 2).

- It is also possible to determine the characters of the reducible representation Γ without constructing all the matrices.

  - ◇ The character of the identity is *always* equal to the dimension of Γ — in this case 10.
  - ◇ There is no mode in fig. 20 that is transformed into itself (or minus itself) by a 4-fold rotation or a diagonal -fold rotation. Therefore, the characters of the $4^+/4^-$ and $2_{xy}/2_{x\bar{y}}$ class are zero.

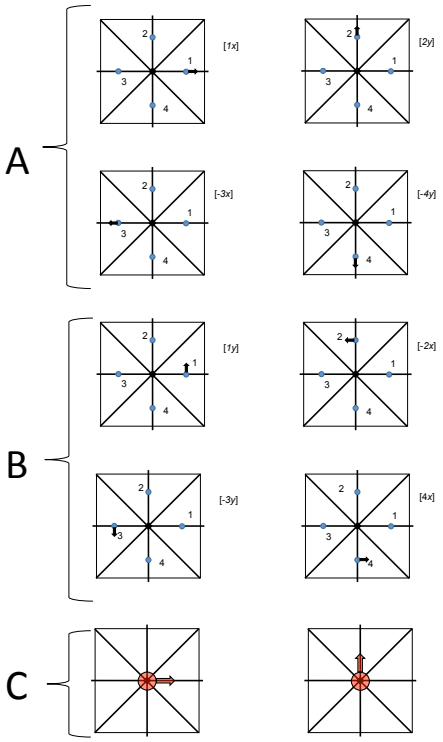


Figure 20: The 10 modes in the square molecule dynamical matrix, slightly rearranged to show that the representation can be reduced.

- ◇ Some modes are transformed into themselves or minus themselves by the in-plane 2-fold axes. For example the two right-hands modes in block A are invariant by 2_y, while those on the left side are invariant by 2_x. Likewise, modes in block B are multiplied by -1 by the same transformation. However, since $+1$ and -1 always appear in pairs along the diagonal of the representative matrices, their trace is zero.
- ◇ Modes in blocks A and B are never transformed into themselves (or minus themselves) by 2_z. However, modes in block C are always transformed into minus themselves. Therefore the trace of the matrix representation of 2_z is -2.
- ◇ The character table of Γ is therefore:

E	2_z	$2(4^+)$	$2(2_x)$	$2(2_{xy})$
10	-2	0	0	0

- Point group 422 has 5 classes and 5 *irreps*. Their dimensions are 1, 1, 1, 1 and 2, since$1^2 + 1^2 + 1^2 + 1^2 + 1^2 + 2^2 = 8 = h$.
- The character table can be constructed, for example, from fig. 16:

	E	2_z	$2(4^+)$	$2(2_x)$	$2(2_{xy})$
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
Γ_3	1	1	-1	1	-1
Γ_4	1	1	-1	-1	1
Γ_5	2	-2	0	0	0

- By applying eq. 45 or simply by inspection, one can decompose Γ into its irreducible components:

$$\Gamma = \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 3\Gamma_5 \tag{64}$$

- As one can see, 1-dimensional *irreps* Γ_1, Γ_2, Γ_3 and Γ_4 only appear once in the decomposition. **Modes that transform according to these *irreps* will therefore be automatically *normal modes*, regardless to the exact form of the potential matrix**.

- These modes are easy to construct by hand, without using the projectors. They are shown in fig. 21 .

- Mode Γ_4 has clear zero frequency (is a pure rotation in the limit of small displacements). The frequency of the other modes can be obtained by equating the **potential energy at maximum stretch** with the **kinetic energy at zero stretch**, both proportional to the square of the amplitude of the mode in the small-displacement limit.

- The remaining 6 normal modes all transform in pairs according to Γ_5. One of the pairs is made up of pure translation of the molecule, and has zero frequency. The other two modes have non-zero frequencies, and have the form shown in fig. 24.

- One can see that these are generic linear combinations of the modes shown in fig. 22 and 23, with the further constraint that the centre-of-mass motion can be set to zero. The problem has been therefore reduced to 2 coupled equations, as opposed to the original 10.

5 Lecture 5: Projectors, subduction and group product

In this section, we will finally answer question 6 on page 28, by constructing the **projection operators** (*projectors*), which will enable us to generate the

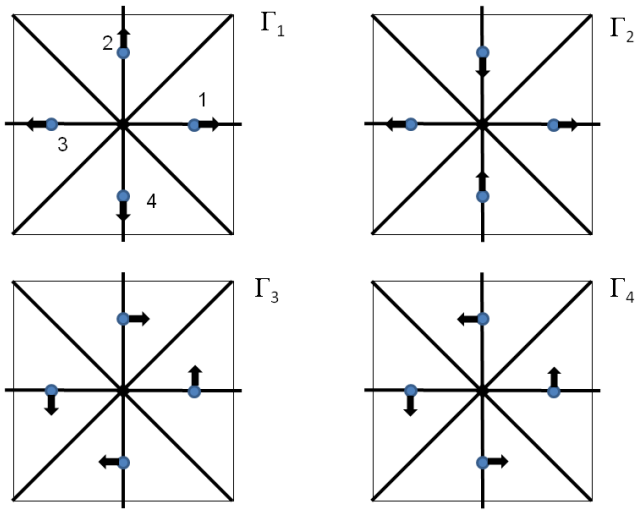


Figure 21: The four "1 dimensional modes" of the square molecule. These modes transform into either themselves (symmetric) or minus themselves (antisymmetric) upon all symmetries of the molecule.

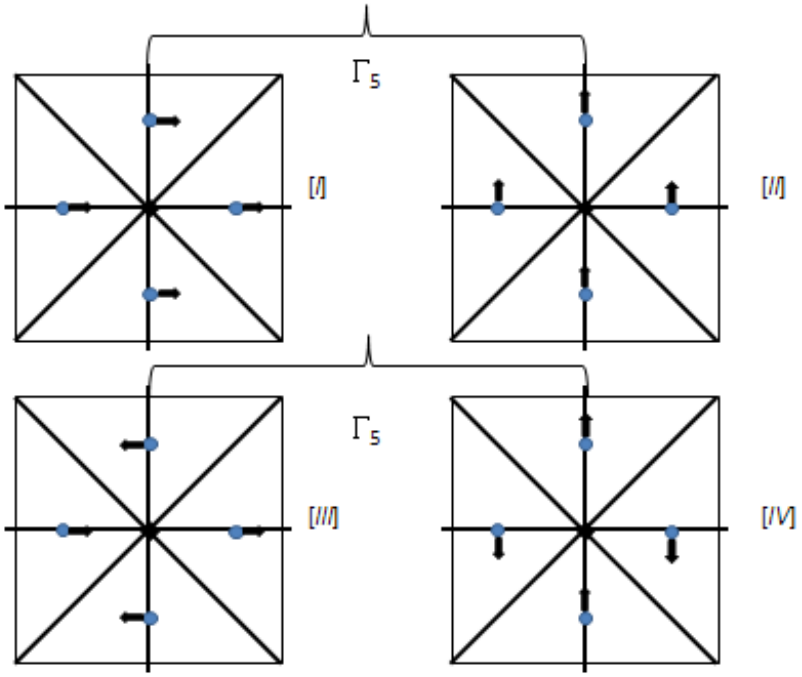


Figure 22: The four "2 dimensional modes" of the square molecule for the corner atoms. These modes transform into either $\pm$ themselves (symmetric/antisymmetric) or *into each other in pairs* upon all symmetries of the molecule. Note that all these modes are *antisymmetric* upon 2-fold rotation.

basis vectors for a given matrix representation of an *irrep*. We will also learn a number of techniques (**subduction**, **direct product of groups**), which will

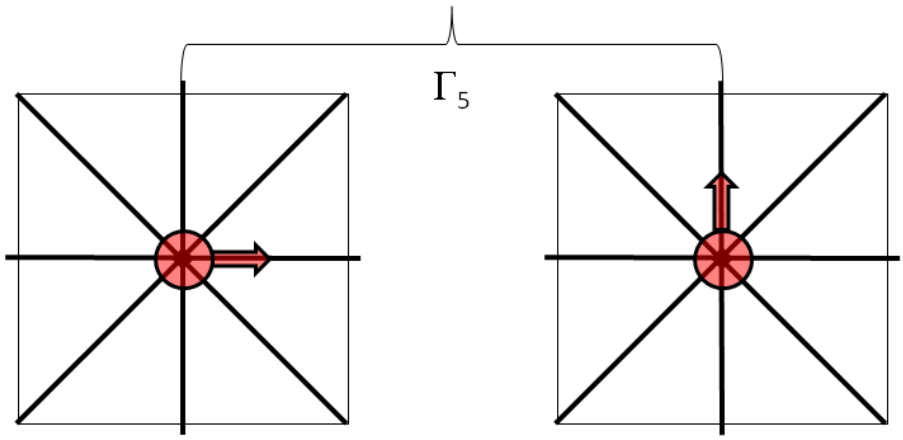


Figure 23: The two central-atom modes of the square molecule. One can verify that they transform as the "2-D" corner modes, i.e., with the representation Γ_5

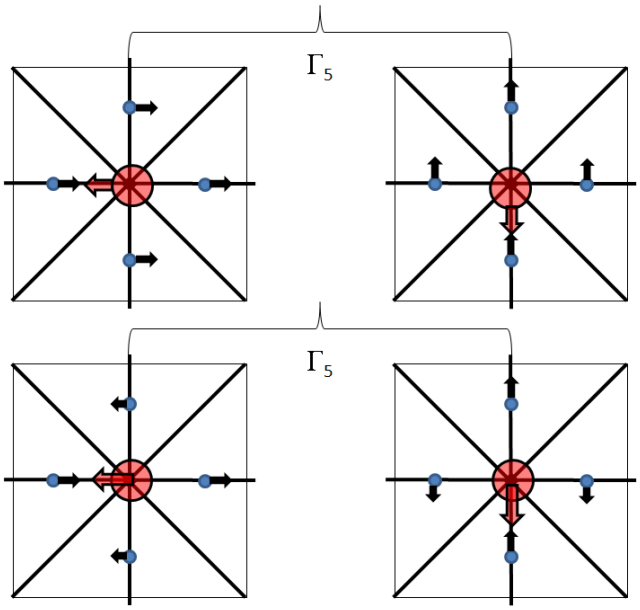


Figure 24: Examples of non-zero-frequency normal modes of Γ_5 symmetry involving two-atom displacements. The exact mixing coefficient depend on the mass and spring constant parameters.

help to construct representations and decompose them into *irreps* for several physically relevant problems.

5.1 Projectors

- As the name suggests, projectors project an arbitrary element of the vector space onto the basis vectors of a given matrix representation of an *irrep*.
- Because of this, projectors depend on the particular choice of matrix representation, and one therefore needs the full matrix (not just the characters) to construct them.
- Projectors are *operators* (not matrices). In fact they are linear combinations of the operators $\hat{O}(g)$ for all the elements of the group.
- The coefficient of the linear combination are related to the matrix elements $D^{\Gamma_i}_{\mu\nu}(g)$, in other words, the matrix elements of a specific matrix representation of the *irrep* Γ_i. More precisely:

$$\hat{P}^{\Gamma_i}_{\mu\nu} = \frac{l_i}{h} \sum_g \left[D^{\Gamma_i}_{\mu\nu}(g)\right]^* \hat{O}(g) \tag{65}$$

- Note that there will be l_j^2 projectors for an *irrep* of dimension l_j, so there is a lot of redundancy in the way projectors can be constructed.
- By employing the WOT, one can find out how projectors work. Let

$$\mathbf{v} = \sum_{\substack{i=1,\cdots n \\ \kappa=1,\cdots l_i}} a_{i\kappa}\mathbf{v}_{i\kappa} \tag{66}$$

be a generic vector in the vector space. The sum over j runs over the *irreps*, while the sum over κ runs over the different basis vector of a given *irrep* and matrix representation. If each *irrep* is represented no more than once in the decomposition, one can show that

$$\hat{P}^{\Gamma_i}_{\mu\nu}\mathbf{v} = a_{i\nu}\mathbf{v}_{i\mu} \tag{67}$$

In the case of multiple instances of the same *irrep*, the formula is

$$\hat{P}^{\Gamma_i}_{\mu\nu}\mathbf{v} = \sum_p a^p_{i\nu}\mathbf{v}^p_{i\mu} \tag{68}$$

where the sum over p is over the multiple instances of Γ_i.

- Let us verify this latest result explicitly. Let

$$\mathbf{v} = \sum_{j,p,\kappa} a^p_{j\kappa} \mathbf{v}^p_{j\kappa} \tag{69}$$

Where $\sum_j$ is over the *irreps*, $\sum_p$ is over the instances of the same *irrep* and $\sum_\kappa$ is over the basis vectors of that *irrep*. Since

$$\hat{O}(g)\mathbf{v}^p_{j\kappa} = \sum_\lambda D^{\Gamma_j}_{\lambda\kappa}(g)\mathbf{v}^p_{j\lambda} \tag{70}$$

the application of the projector to $\mathbf{v}$ yields:

$$\begin{aligned}
\hat{P}^{\Gamma_i}_{\mu\nu}\mathbf{v} &= \frac{l_i}{h}\sum_g \left[D^{\Gamma_i}_{\mu\nu}(g)\right]^* \sum_{j,p,\kappa} a^p_{j\kappa} \sum_\lambda D^{\Gamma_j}_{\lambda\kappa}(g)\mathbf{v}^p_{j\lambda} \\
&= \sum_{j,p,\kappa,\lambda} \left\{ \frac{l_i}{h}\sum_g \left[D^{\Gamma_i}_{\mu\nu}(g)\right]^* D^{\Gamma_j}_{\lambda\kappa}(g) \right\} a^p_{j\kappa}\mathbf{v}^p_{j\lambda} \\
&= \sum_{j,p,\kappa,\lambda} \{\delta_{\mu\lambda}\delta_{\nu\kappa}\delta_{ij}\}\, a^p_{j\kappa}\mathbf{v}^p_{j\lambda} \\
&= \sum_p a^p_{i\nu}\mathbf{v}^p_{i\mu}
\end{aligned} \tag{71}$$

where the last line of 71 is identical to 68. The delta functions in the curly brackets are from the WOT.

- In all cases, $\hat{P}^{\Gamma_i}_{\mu\nu}\mathbf{v}$ is an element of the invariant subspace of Γ_i. It can, however, be **zero**, if the vector $\mathbf{v}$ has no component on the subspace spanned by Γ_i.

- If they are non-zero, these $\hat{P}^{\Gamma_i}_{\mu\nu}\mathbf{v}$ for *fixed* ν and *different* μ (i.e., for matrix elements of the same columns) represent *unnormalised* basis functions for Γ_i. We can verify this explicitly:

$$\begin{aligned}
\hat{O}(g)\left[\sum_p a^p_{i\nu}\mathbf{v}^p_{i\mu}\right] &= \sum_p a^p_{i\nu}\sum_\lambda D^{\Gamma_j}_{\lambda\mu}(g)\mathbf{v}^p_{j\lambda} \\
&= \sum_\lambda D^{\Gamma_j}_{\lambda\mu}(g)\left[\sum_p a^p_{i\nu}\mathbf{v}^p_{j\lambda}\right]
\end{aligned} \tag{72}$$

so the term in square brackets transforms like the original basis vector $\mathbf{v}^p_{j\mu}$ in eq. 70.

5.2 Example of use of the projectors: distortions on a triangles (the "ozone" molecule)

- We can put these concepts into practice by examining a problem we have already encountered multiple times — that of the distortions (vibrations) of a triangle. This is often dubbed the "ozone molecule" problem, although the actual ozone (O_3) molecule is an isosceles triangle with the obtuse angle equal to 116.8°. The formalism is, however, suitable to study actual molecules such as SO_3 and BF_3. We will only consider the displacements of the external atoms, which form a perfect equilateral triangle in the ground state.

- We have essentially all the elements already in place to discuss this problem. The basis vectors of the *reducible* representation, shown in fig. 9 page 23, span a 6-dimensional space. Hereafter, we will indicate these modes with $|1\rangle \cdots |6\rangle$. The full matrices on these basis vectors are displayed in eq. 26 page 22. We have already decomposed the reducible representation into *irreps* as $\Gamma_{red} = \Gamma_1 + \Gamma_2 + 2\Gamma_3$ (eq. 48 page 36). The two basis vectors for the 1-dimensional *irreps* were found by trial and error, and are shown in fig. 10 page 23. We will indicate these two modes as $|\Gamma_1\rangle$ and $|\Gamma_2\rangle$. Finally, we have several variants of the matrix representations (figs 13, 14, 15) but we will only employ Variant 1 for the projectors (fig. 13 page 28). The character table is on fig. 17 page 33.

- We will start by applying $\hat{P}^{\Gamma_1}$ to modes $|1\rangle \cdots |6\rangle$. There is only one projector for Γ_1, since the *irrep* is 1-dimensional, and all the coefficients in eq. 65 are 1, since this is the *totally symmetric representation*. It is easy to show that

$$\begin{aligned} \hat{P}^{\Gamma_1}|1\rangle &= \hat{P}^{\Gamma_1}|2\rangle = \hat{P}^{\Gamma_1}|3\rangle = \frac{1}{3}|\Gamma_1\rangle \\ \hat{P}^{\Gamma_1}|4\rangle &= \hat{P}^{\Gamma_1}|5\rangle = \hat{P}^{\Gamma_1}|6\rangle = 0 \end{aligned} \tag{73}$$

  Likewise

$$\begin{aligned} \hat{P}^{\Gamma_2}|1\rangle &= \hat{P}^{\Gamma_2}|2\rangle = \hat{P}^{\Gamma_2}|3\rangle = 0 \\ \hat{P}^{\Gamma_2}|4\rangle &= \hat{P}^{\Gamma_2}|5\rangle = \hat{P}^{\Gamma_2}|6\rangle = \frac{1}{3}|\Gamma_2\rangle \end{aligned} \tag{74}$$

So we have easily obtained the basis vectors of the to 1-dimensional *irreps* by projection. As in the previous cases, these are automatically **normal modes**. Γ_2 represents a pure rotation and has zero frequency.

- The situation is somewhat more complicated for Γ_3: this *irrep* is 2-dimensional (so we have 4 projectors), it appears twice in the decomposition and we do not know the answers in advance. To simplify the problem slightly, we can look the full matrix *irrep* in fig. 13 and note that the matrix for operator K is diagonal, with the first mode being *antisymmetric* and the second *symmetric*. Since mode $|2\rangle$ and $|5\rangle$ are also symmetric and antisymmetric by K , respectively, projecting these two modes will result in a simpler combination of modes. In fact, $\hat{P}^{\Gamma_3}_{\mu\nu}\mathbf{v}$ **projects onto mode μ with the coefficient of mode ν in the decomposition of $\mathbf{v}$.** Since $|2\rangle$ is symmetric, there will be no antisymmetric component in its decomposition, so

$$\begin{aligned} \hat{P}^{\Gamma_3}_{11}|2\rangle &= \hat{P}^{\Gamma_3}_{21}|2\rangle = 0 \\ \hat{P}^{\Gamma_3}_{12}|5\rangle &= \hat{P}^{\Gamma_3}_{22}|5\rangle = 0 \end{aligned} \tag{75}$$

- The modes generated by application of the projectors to modes $|2\rangle$ and $|5\rangle$ are shown in fig. 25. In particular, one can verify directly the relations in eq. 75 and

$$\begin{aligned} \hat{P}^{\Gamma_3}_{11}|5\rangle &= \frac{1}{3}|m_1\rangle \\ \hat{P}^{\Gamma_3}_{12}|2\rangle &= \frac{1}{3}|m'_1\rangle \\ \hat{P}^{\Gamma_3}_{21}|5\rangle &= \frac{1}{3}|m_2\rangle \\ \hat{P}^{\Gamma_3}_{22}|5\rangle &= \frac{1}{3}|m'_2\rangle \end{aligned} \tag{76}$$

- Modes $|m_1\rangle$ and $|m_2\rangle$ form a basis set for the chosen matrix representation of Γ_3, and so do modes $|m'_1\rangle$ and $|m'_2\rangle$. This is consistent with the general rule that $\hat{P}^{\Gamma_i}_{\mu\nu}\mathbf{v}$ for *fixed* ν and *different* μ represent unnormalised basis functions for Γ_i.

- This is as much as one can say by employing symmetry considerations. It is not possible to make more progress towards determining the normal modes without employing some physical considerations. Since modes

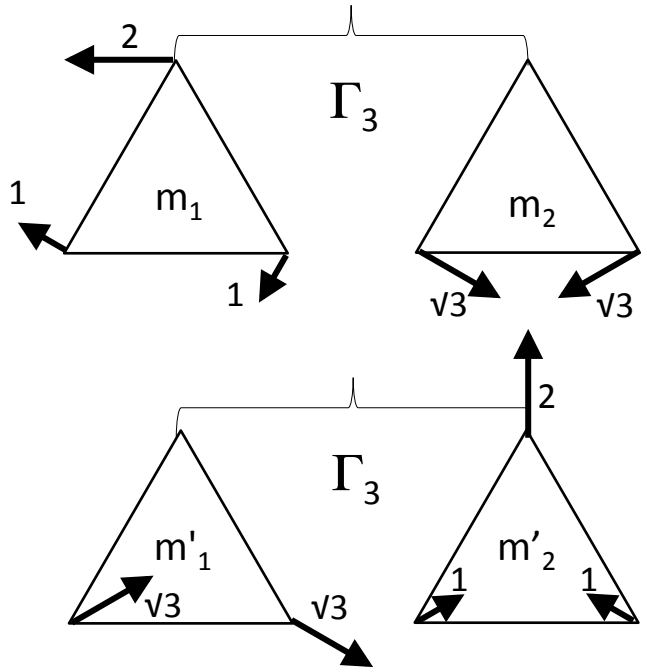


Figure 25: Modes generated by $|2\rangle$ and $|5\rangle$ through the application of the projectors. The length of the arrows is indicated.

$|m_1\rangle$, $|m_2\rangle$, $|m_1'\rangle$ and $|m_2'\rangle$, intended as vibration modes, do not conserve the centre of mass, one can try the following linear combinations:

$$\begin{aligned} |n_1\rangle &= \frac{|m_1\rangle - |m_1'\rangle}{2} \\ |n_2\rangle &= \frac{|m_2\rangle - |m_2'\rangle}{2} \\ |n_1'\rangle &= \frac{|m_1\rangle + |m_1'\rangle}{2} \\ |n_2'\rangle &= \frac{|m_2\rangle + |m_2'\rangle}{2} \end{aligned} \tag{77}$$

These modes are shown in fig. 26, and are in fact the remaining **normal modes** of the triangular molecule. Modes $|n_1\rangle$ and $|n_2\rangle$ the are pure translations, and have zero frequency.

5.3 Subduction

- One of the most useful application of the theory of representations is in the study of spectroscopic splittings. Let 's imagine a Hamiltonian of the form:

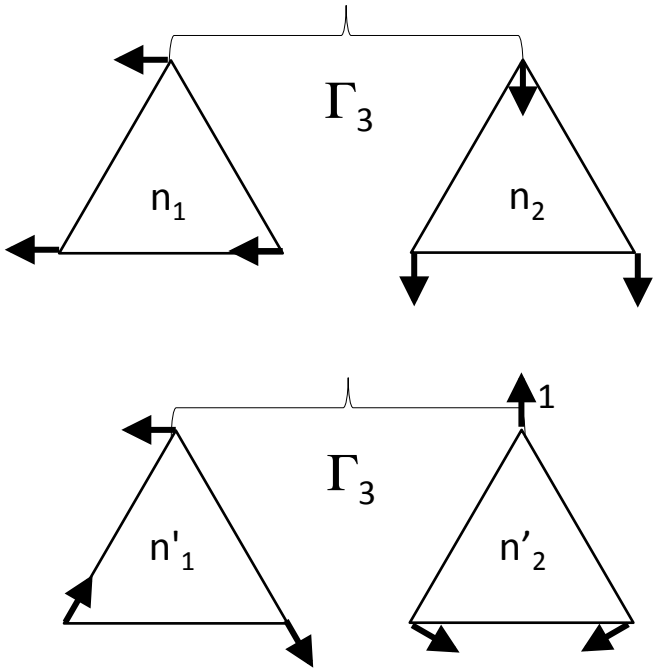


Figure 26: The Γ_3 normal modes of the triangulate molecule. The relation between these modes and those in fig. 25 is shown in eq. 77.

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1 \tag{78}$$

where λ is a small parameter, $\hat{H}_0$ has symmetry group G_0, while $\hat{H}_1$ (and therefore $\hat{H}$) have symmetry group $G_1 \subset G_0$, i.e., G_1 is a proper **subgroup** of G_0. Since λ is *small*, the energy levels of $\hat{H}_0$ will not be changed by much by the presence of $\hat{H}_1$. However, each $\hat{H}_1$ multiplet will in general be **split** due to the reduction in symmetry. Except for the actually energy splitting, which requires knowledge of $\hat{H}_1$, we can characterise the sub-multiplet structure of $\hat{H}$ by employing the so-called **subduction method**.

- The starting point is to recognise that each element of G_1 is also in G_0, so we can construct the full character table of G_1 from that of G_0 by eliminating the columns corresponding to group elements that are in G_0 but not in G_1.

- The character table expressed in term of *classes* requires a bit more care. Entire classes in G_0 may be eliminated in G_1, but some new classes can appear by splitting classes in G_0. **Example:** 422 has 5 classes: E, 2_z, $4^+/4^-$, $2_x/2y$ and $2_{xy}/2x\bar{y}$. Its proper subgroup 222 has *four* classes: E, 2_z, 2_x and $2y$, all of one element each since 222 is Abelian. $4^+/4^-$

and $2_{xy}/2x\bar{y}$ are suppressed, while $2_x/2y$ is split into 2 classes.

- The *irreps* of G_0 will create, or **subduce**, new representations in G_1. This is easiest to understand in terms of matrix representations — the subduced representation in G_1 has exactly the same matrices as the original *irrep*, but only for the group elements in G_1.

- The subduced representations, however, **are not necessarily *irreps* of** G_1. It is clear that they cannot always be so, since the number of classes in G_1 is usually smaller than in G_0. One can apply the usual formula (eq. 45) to establish whether the subduced representation is reducible and, if so, its decomposition in terms of *irreps* of G_1.

- If a certain energy level of $\hat{H}_0$ corresponded to a certain *irrep* Γ_i of G_0, the decomposition of the subduced representation $sub(\Gamma_i)$ will determine how the Γ_i multiplet will split.

Example 1 Fig. 27 shows the character table of point group 622 ($D6$). This group has 12 elements in 6 classes (shows also in the diagram). Note that the in-plane 2-fold axes form two distinct classes (this is a general property of even-n dihedral groups — see below). In the subgroup 32, the 2_z axis (one element, one class), the 6-fold axes (two elements, one class) and one of the sets of in-plane 2-fold axes (three elements, one class) are suppressed, as indicated by the darker columns.

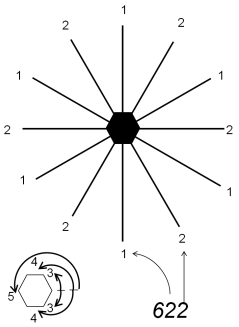
the subduction is as follows:

$$\begin{aligned}
\Gamma_1^{622} &\rightarrow \Gamma_1^{32} \\
\Gamma_2^{622} &\rightarrow \Gamma_2^{32} \\
\Gamma_3^{622} &\rightarrow \Gamma_1^{32} \\
\Gamma_4^{622} &\rightarrow \Gamma_2^{32} \\
\Gamma_5^{622} &\rightarrow \Gamma_3^{32} \\
\Gamma_6^{622} &\rightarrow \Gamma_3^{32}
\end{aligned} \tag{79}$$

(note that Γ_1 *always* subduces to Γ_1.)

Conclusion: each *irrep* of 622 subduces to an *irrep* of 32, so there is no spectroscopic splitting upon lowering the symmetry from 622 to 32.

Example 2 Fig. 28 shows the character table of cubic point group 432 (O). 432 has 24 elements in 5 classes. In its proper subgroup 32, two of the 8 3-fold axes survive (clockwise and counterclockwise rotations around a single cubic diagonal). The 2-fold and 4-fold axes through the cube



Point group *622* Character Table

	E	2_z	[2] 3_z	[2] 6_z	[3] 2_y	[3] 2_x
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	1	-1	-1
Γ_3	1	-1	1	-1	1	-1
Γ_4	1	-1	1	-1	-1	1
Γ_5	2	-2	-1	1	0	0
Γ_6	2	-2	-1	-1	0	0

Figure 27: . The character table of point group 622 and the subduction of its *irreps* into its subgroup 32.

faces disappear, and only 3 of the 6 diagonal 2-fold axes survive, forming the in-plane 2-fold rotations K, L and M of 32.

the subduction is as follows:

$$\begin{aligned}
\Gamma_1^{432} &\rightarrow \Gamma_1^{32} \\
\Gamma_2^{432} &\rightarrow \Gamma_2^{32} \\
\Gamma_3^{432} &\rightarrow \Gamma_3^{32} \\
\Gamma_4^{432} &\rightarrow \Gamma_3^{32} + \Gamma_2^{32} \\
\Gamma_5^{432} &\rightarrow \Gamma_3^{32} + \Gamma_1^{32}
\end{aligned} \tag{80}$$

Conclusion:

- Γ_1^{432} and Γ_2^{432} are **singlets**. They subduce into *irreps* of 32 and are not split
- Γ_3^{432} is a **doublet**. It subduces into an *irreps* of 32 (Γ_3^{32}, also a doublet) and is not split.
- Γ_4^{432} and Γ_5^{432} are **triplets**. They subduce into a **doublet** Γ_3^{32} and a **singlet** (Γ_2^{32} or Γ_1^{32}). There will be a corresponding splitting of the energy levels upon lowering of the symmetry.

Point group *432 (O) Character* Table

	E	[8]*3*	[3] 2_z	[6] 2_d	[6] 4_z
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
Γ_3	2	-1	2	0	0
Γ_4	3	0	-1	-1	1
Γ_5	3	0	-1	1	-1

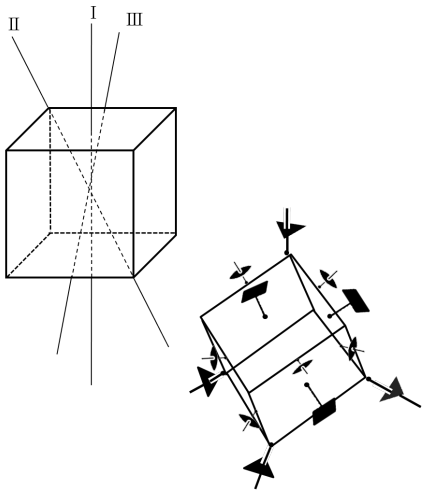


Figure 28: . The character table of point group 432 (cubic) and the subduction of its *irreps* into its subgroup 32.

This is shown schematically in fig. 29. Note that the relative position of the levels in 432 and the energy splitting in 32 are **not determined by symmetry**, but rather by the exact form of H_0 and H_1.

5.4 Direct product of groups

Definition: a group G is said to be the **direct product** of two (sub)groups, say F and H, if each element $g \in G$ can be written as $g = f \circ h = h \circ f$, $f \in F$, $h \in H$. Importantly, elements of F *must commute* with all elements of H .

- The classic case of direct product, and basically the only important one, is when $H = \{E, I\}$, the 2-element group composed of **the identity and the inversion** (which both commute with all other operators).

- Any point or space group containing the inversion is a **direct product group**, since the conditions of our definition are clearly fulfilled. The group G can be written as $G = F \times \{E, I\}$, where F contains only proper rotations, roto-translatons and pure translations.

N.B. Some groups contain both proper and improper elements, but **cannot**

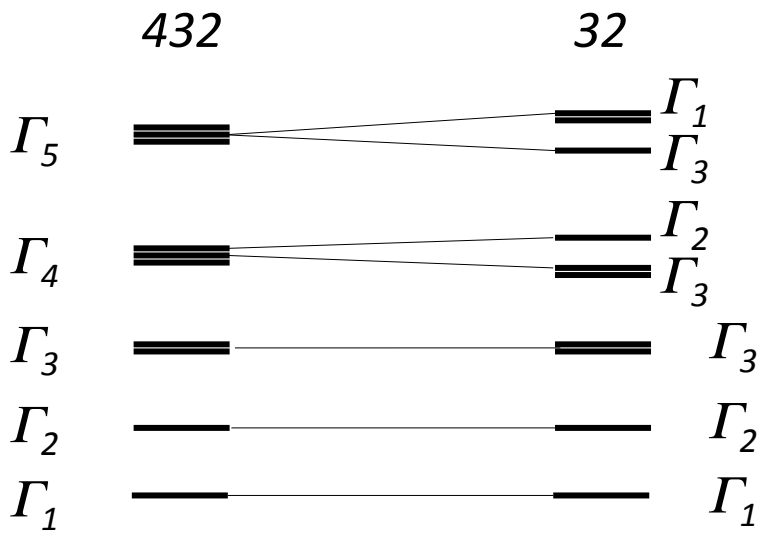


Figure 29: Schematic representation of the energy level splitting by lowering the symmetry from 432 to 32.

be written as direct products, since they do not contain the inversion I.

Another counter-example 422 contains a subgroup that commutes with all the other operators — the group $\{E, 2_z\}$, but is *not* a direct product group, because the remaining operators **do not form a group**, since $2_x \circ 2_y = 2_z$.

- The group $\{E, I\}$ is Abelian and has 2 classes and two *irreps*. Its character table is:

	E	I
Γ_1	1	1
Γ_2	1	-1

- G has **twice as many classes** as F.[5]

- It also follows that G has **twice as many *irreps* as** F. One can see how this can be generalised to direct products of groups with more than two

[5]Here is the somewhat technical proof: if $\tilde{g} = h \circ (I \circ f) \circ h^{-1}$, $h \in G$, then it is either $h \in F$, in which case $\tilde{g} = I \circ (h \circ f \circ h^{-1})$ or $h = I \circ h'$, $h' \in F$ in which case $\tilde{g} = I \circ (I \circ h' \circ f \circ h'^{-1} \circ I) = I \circ (h' \circ f \circ h'^{-1})$, so all the classes in G are either the same classes C_k in F or entire classes in F multiplied by the inversion, as $I \circ C_k$.

elements, and the importance of the commutation of all elements of F with all elements of H. In the general case, the number of classes in G is the product of the classes in F times the classes in H.

- All the *irreps* of $G = F \times \{E, I\}$ can be obtained as follows:
  - ◇ Start from the character table of F.
  - ◇ Double the number of columns (classes). For each class C_k of F containing the element f, there will be a new class $I \circ C_k$ containing the element $I \circ f$.
  - ◇ For each Γ_i of F we get *two irreps* of G: Γ_{ig} and Γ_{iu}.
  - ◇ For the g- or *gerade* (even) *irreps*, we get:

$$\begin{aligned} \chi^{\Gamma_{ig}}(fC_k &= +\chi^{\Gamma_i}(C_k) \\ \chi^{\Gamma_{ig}}(I \circ C_k) &= +\chi^{\Gamma_i}(C_k) \end{aligned} \tag{81}$$

  - ◇ For the g- or *ungerade* (odd) *irreps*, we get:

$$\begin{aligned} \chi^{\Gamma_{iu}}(C_k) &= +\chi^{\Gamma_i}(C_k) \\ \chi^{\Gamma_{iu}}(I \circ C_k) &= -\chi^{\Gamma_i}(C_k) \end{aligned} \tag{82}$$

- This procedure is illustrated in the two tables here below. From the character table of F

	E	C_1	C_2	$\cdots$	C_n
Γ_1	$\chi_1(E)$	$\chi_1(C_1)$	$\chi_1(C_2)$	$\cdots$	$\chi_1(C_n)$
Γ_2	$\chi_2(E)$	$\chi_2(C_1)$	$\chi_2(C_2)$	$\cdots$	$\chi_2(C_n)$
$\vdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$
Γ_n	$\chi_n(E)$	$\chi_n(C_1)$	$\chi_n(C_2)$	$\cdots$	$\chi_n(C_n)$

we obtain the character table of G:

	E	C_1	C_2	$\cdots$	C_n	I	$I \circ C_1$	$I \circ C_2$	$\cdots$	$I \circ C_n$
Γ_{1g}	$\chi_1(E)$	$\chi_1(C_1)$	$\chi_1(C_2)$	$\cdots$	$\chi_1(C_n)$	$+\chi_1(E)$	$+\chi_1(C_1)$	$+\chi_1(C_2)$	$\cdots$	$+\chi_1(C_n)$
Γ_{2g}	$\chi_2(E)$	$\chi_2(C_1)$	$\chi_2(C_2)$	$\cdots$	$\chi_2(C_n)$	$+\chi_2(E)$	$+\chi_2(C_1)$	$+\chi_2(C_2)$	$\cdots$	$+\chi_2(C_n)$
$\vdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$
Γ_{ng}	$\chi_n(E)$	$\chi_n(C_1)$	$\chi_n(C_2)$	$\cdots$	$\chi_n(C_n)$	$+\chi_n(E)$	$+\chi_n(C_1)$	$+\chi_n(C_2)$	$\cdots$	$+\chi_n(C_n)$
Γ_{1u}	$\chi_1(E)$	$\chi_1(C_1)$	$\chi_1(C_2)$	$\cdots$	$\chi_1(C_n)$	$-\chi_1(E)$	$-\chi_1(C_1)$	$-\chi_1(C_2)$	$\cdots$	$-\chi_1(C_n)$
Γ_{2u}	$\chi_2(E)$	$\chi_2(C_1)$	$\chi_2(C_2)$	$\cdots$	$\chi_2(C_n)$	$-\chi_2(E)$	$-\chi_2(C_1)$	$-\chi_2(C_2)$	$\cdots$	$-\chi_2(C_n)$
$\vdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$
Γ_{nu}	$\chi_n(E)$	$\chi_n(C_1)$	$\chi_n(C_2)$	$\cdots$	$\chi_n(C_n)$	$-\chi_n(E)$	$-\chi_n(C_1)$	$-\chi_n(C_2)$	$\cdots$	$-\chi_n(C_n)$

6 Lecture 6: Tensors and tensor products of representations

6.1 Tensor product of vector spaces

- Given two vector spaces V and W, one can define their **tensor product** $V \otimes W$, a new **vector space**, as the set of linear combination of **ordered pairs** of basis vectors of V and W. Essentially, one defines the basis vectors of $V \otimes W$ as $(\mathbf{a}_i|\mathbf{b}_j)$, $\mathbf{a}_i \in V$, $\mathbf{b}_j \in W$. The elements of $V \otimes W$ are linear combinations of $(\mathbf{a}_i|\mathbf{b}_j)$. Clearly, the dimension of $V \otimes W$ is $\dim V \times \dim W$.

- The basis vectors of $V \otimes W$ can be ordered in a *single array* as

$$[(\mathbf{a}_1|\mathbf{b}_1)(,\mathbf{a}_1|\mathbf{b}_2), \cdots, (\mathbf{a}_1|\mathbf{b}_m), (\mathbf{a}_2|\mathbf{b}_1), \cdots (\mathbf{a}_n|\mathbf{b}_m)] \tag{83}$$

- If the elements of V transform according to matrix A and those of W according to matrix B, then the elements of $V \otimes W$ will transform according to the **Kronecker product** (or tensor product) $A \otimes B$ of the two matrices, where:

$$A \otimes B = \left[\begin{array}{c|c|c|c} a_{11}B & a_{12}B & \cdots & a_{1n}B \\ \hline a_{21}B & a_{22}B & \cdots & a_{2m}B \\ \hline \vdots & \vdots & \vdots & \vdots \\ \hline a_{n1}B & a_{n2}B & \cdots & a_{nn}B \end{array}\right] \tag{84}$$

  The new matrix $A \otimes B$ has dimensions $nm \times nm$.

- We can immediately see that the **trace** of $A \otimes B$ is the product of the two traces: $tr(A \otimes B) = tr(A)\, tr(B)$.

6.2 Tensor product of representations

- Let's assume that the elements of V transform according to a representation Γ (reducible or irreducible) and the elements of W according to a representation Δ. Elements of the tensor product space $V \otimes W$ will transform according to representation $\Gamma \otimes \Delta$ — the **tensor product of the two representations**.

- The matrix representatives of $\Gamma \otimes \Delta$ are the **Kronecker product or matrix representatives for Γ and Δ**, as

$$D^{\Gamma\otimes\Delta}(g) = D^{\Gamma}(g) \otimes D^{\Delta}(g) \tag{85}$$

- A very important result on the **characters** of $\Gamma \otimes \Delta$ follows immediately:

$$\chi^{\Gamma\otimes\Delta}(g) = \chi^{\Gamma}(g)\,\chi^{\Delta}(g) \tag{86}$$

  Therefore, **to determine the characters of a representation in the tensor product space, one simply multiplies the characters of the representations in the constituent spaces**.

- This is an extremely important and powerful result: if we know the representations of the constituent spaces, we can immediately find the characters of the tensor product representation and decompose it into *irreps*. This can be repeated many times, giving rise to representations and decomposition of extremely complex tensor spaces with very little work.

6.3 * Extended example: vibrational spectra of planar molecules with symmetry D_n

- We have already seen examples for $D3$ (32, section 5.2, page 50) and for D_4(422, section 4.3, page 43). Armed with the knowledge of tensor product, we can now solve the problem for any n.

- We can consider the space of the modes as the **tensor product** of two spaces: V is the space of scalar functions on the regular polygon with n sides, and W is the space of ordinary vectors in 2D. The basis functions of V can be taken as arrays of n numbers, all of them 0 except for a 1 corresponding to one of the vertices. The space of ordinary vectors has its usual basis functions (e.g.,$\hat{\mathbf{i}}, \hat{\mathbf{j}}$). For example, the top-left mode in block A of fig. 20 can be written in tensor notation as $([1,0,0,0]|\hat{\mathbf{i}})$.

- Let us consider independently the representations of D_n onto the two spaces V and W — call them Γ and Δ as before.

- Γ is the so-called **permutational representation**, although D_n is not in general the full permutation group of the n-polygon. We can deduce its characters as follows:

  - ◇ The character of the identity E is n
  - ◇ C_n (the group of pure rotations around z) is a subgroup of D_n. The elements of C_n will generate several classes in D_n — for example, we know that in D_4 there are two classes of this kind, 2_z and

$4^+/4^-$. However, no basis function of V is ever conserved by these transformation, so the characters of Γ on all these classes are 0.

◇ The in-plane two-fold axes form **two classes** for n even and **one class** for n odd. For n even, the 2-fold axes can cut either through two sides or two vertices of the n-polygon, while for n odd they always cut through one vertex and one side (fig. 30). Consequently, the characters of Γ will be 2 (for the vertex axes) or 0 (for the side axes) for n even and 1 for n odd.

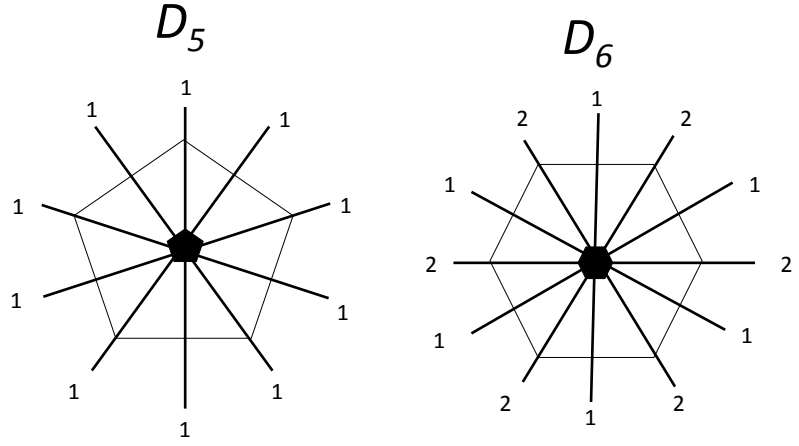


Figure 30: Two examples of dihedral groups of odd order (D_5) and even order (D_6). For n odd, there is a single class of in-plane 2-fold axes, while for n even there are two classes.

- Δ is the transformation of ordinary vectors by D_n. It is a 2-dimensional representation, and its characters can be found as follows:
  - ◇ The character of the identity E is 2
  - ◇ The character of the 2_z (only present for n even) is -2, since both basis vectors are reversed by 2_z.
  - ◇ The characters of the z axis rotations are $2\cos\theta$, θ being the rotation axis (they are just the sum of the diagonal elements of the rotation matrix).
  - ◇ The character of 2_x is 0. In fact $\hat{\mathbf{i}}$ is unchanged, while $\hat{\mathbf{j}}$ is reversed.
  - ◇ The character of 2_y (a representative element of the other class of in-plane two-fold axes) is also zero. Although 2_y is not necessarily

perpendicular to 2_x (e.g., in the case of $n = 8$), its matrix representative is still related by a similarity transformation to the matrix representative of 2_x, the the characters remain the same.

- We can also easily add a central atom. Its modes represent an additional subspace and transform like Δ, so its characters are simply added to the tensor product characters. This can be summarised as follows: for n **even**

	E	2_z	$2C_z^1$	$2C_z^2$	$\cdots$	$(n/2)2_x$	$(n/2)2_y$
χ^{Γ}	n	0	0	0	$\cdots$	2	0
χ^{Δ}	2	-2	$2\cos\theta$	$2\cos 2\theta$	$\cdots$	0	0
$\chi^{\Gamma\otimes\Delta}$	$2n$	0	0	0	$\cdots$	0	0
$\chi^{\Gamma\otimes\Delta+\Delta}$	$2n+2$	-2	$2\cos\theta$	$2\cos 2\theta$	$\cdots$	0	0

for n **odd**

	E	$2C_z^1$	$2C_z^2$	$\cdots$	$n2_x$
χ^{Γ}	n	0	0	$\cdots$	1
χ^{Δ}	2	$2\cos\theta$	$2\cos 2\theta$	$\cdots$	0
$\chi^{\Gamma\otimes\Delta}$	$2n$	0	0	$\cdots$	0
$\chi^{\Gamma\otimes\Delta+\Delta}$	$2n+2$	$2\cos\theta$	$2\cos 2\theta$	$\cdots$	0

- We can see that our result is in agreement with our previous findings for D_3 (eq. 48 page 36) and D_4 (page 44).

- Let us try with D_6 (622). The *irrep* character table is in fig. 27. The characters are:

	E	2_z	$2\,6_z$	$2\,3_z$	$3\,2_x$	$3\,2_y$
$\chi^{\Gamma\otimes\Delta}$	12	0	0	0	0	0
$\chi^{\Gamma\otimes\Delta+\Delta}$	14	-2	1	-1	0	0

By applying eq. 45 we obtain:

$$\begin{aligned} \Gamma\otimes\Delta &= \Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4+2\Gamma_5+2\Gamma_6 \\ \Gamma\otimes\Delta+\Delta &= \Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4+3\Gamma_5+2\Gamma_6 \end{aligned} \tag{87}$$

- The central atom modes clearly transform as Γ_5 ($\equiv\ \Delta$, characters $2|-2|1|-1$), and so will the pure translations of the whole molecule (which are also ordinary vectors). One of the 1-dim modes must correspond to a pure rotation of the molecule. It is easy to see that this must be Γ_2, since this mode must be invariant by all z-axis rotations. Therefore the set of non-zero-frequency normal modes is:

$$\begin{aligned} \Gamma\otimes\Delta-\Gamma_2-\Gamma_5 &= \Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5+2\Gamma_6 \\ \Gamma\otimes\Delta+\Delta-\Gamma_2-\Gamma_5 &= \Gamma_1+\Gamma_3+\Gamma_4+2\Gamma_5+2\Gamma_6 \end{aligned} \tag{88}$$

three singlets and three doublets or three singlets and four doublets without or with the central atom, respectively.

- Γ_1 is the only Raman-active mode (in 2D, the 2-fold axis corresponds to the inversion in 3D). All other modes are IR-active. in a molecular crystal, Γ_2 will give rise to Raman-active *phonon* modes.

6.4 "Ordinary" tensors

- What we have just introduced is a rather abstract definition of tensors, and we have applied it to vector spaces that do not look anything like the more familiar tensors in physics.
- "Ordinary" tensors are actually closely related to the ones we just introduced. They are **tensor products of spaces or ordinary (polar) vectors or axial vectors.**
- In free space, ordinary **polar vectors** and **axial vectors** transform in the same way under proper rotations, i.e., according to a 3-dimensional irreducible representation of the continuous group of proper rotations. If one includes improper rotations, polar vectors, forming a space that we will call V, transform as an *ungerade* irreducible representation of the continuous group of proper and improper rotations, which we shall call Γ_u. Axial vectors, forming a space A, transform under the corresponding *gerade irrep* Γ_g.
- We define **polar tensors** and **axial tensors of different ranks as follows**:

Rank	0	1	2	3	4	$\cdots$
Polar tensors — space	scalars	V	$V \otimes V = V^2$	V^3	V^4	$\cdots$
Polar tensors — representation	Γ_{1g}	Γ_u	$\Gamma_u \otimes \Gamma_u = \left[\Gamma_u^2\right]_g$	$\left[\Gamma_u^3\right]_u$	$\left[\Gamma_u^4\right]_g$	$\cdots$
Axial tensors — space	pseudo-scalars	A	$A \otimes V$	A^3	$A^3 \otimes V$	$\cdots$
Axial tensors — representation	Γ_{1u}	Γ_g	$\left[\Gamma_g \otimes \Gamma_u\right]_u$	$\left[\Gamma_g^3\right]_g$	$\left[\Gamma_g^3 \otimes \Gamma_v\right]_u$	$\cdots$

  - ◇ The tensor product representation is *gerade* if it contains an even number of Γ_u, *ungerade* otherwise. We have indicated this as $[]_g$ or $[]_u$
  - ◇ There are many different combinations of spaces that give the same transformation rules, and are therefore isomorphic (symbol $\cong$). For example, $A \otimes A \cong V \otimes V$ and $A^3 \cong V^2 \otimes A$.
  - ◇ We have also introduced the rank-zero tensors, known as **scalars** and **pseudo-scalars**. They transform like the totally symmetrical representation of the proper rotation group SO(3), but are *gerade* and *ungerade*, respectively.

- **Polar tensors of odd rank are parity-odd. Polar tensors of even rank are parity even**.
- **Axial tensors of odd rank are parity-even. Axial tensors of even rank are parity odd**.

Example of polar tensor: The **permittivity tensor** is a rank-2 polar tensor, defined by the formula:

$$D_i = \epsilon_{ij} E_j \tag{89}$$

Example of axial tensor: The **linear magneto electric tensor** is a rank-2 axial tensor, defined by the formula:

$$P_i = \mu_{ij} B_j \tag{90}$$

in fact, the electrical polarisation P_i an ordinary vector, whereas the magnetic field B_j is an axial vector.

6.5 "Materials" tensors vs. "Field" tensors

- A distinction can be made between tensors that describe intrinsic properties or spontaneous effects of the crystals — so-called **materials tensors**, and tensors that describe external forces or the reaction of the materials to those forces — so-called **field tensors**.

Materials tensors representing macroscopic properties **must have the full point-group symmetry of the crystal**. This is another way to state the famous Neumann's principle: "The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal". It is applicable to any physical observable measured with a probe that is insensitive to lattice periodicity. In the language of *irreps*, **materials tensors must transform like the totally symmetric *irrep* of the crystal class: Γ_1 or Γ_{1g} for acentric and centric classes, respectively**. **Examples** of materials tensors are: permittivity tensor, permeability tensor, conductivity tensor, piezoelectricity tensor, magneto-electricity tensor, spontaneous strain tensor, elastic tensor.

Field tensors can have any symmetry — in fact they usually define they own symmetry. For example, the applied electric field (an ordinary polar vector) will have a continuous rotational symmetry around its own direction

and it is clearly parity-odd (*ungerade*). However, there can be other restrictions on the elements of a field tensor (see here below). **Examples** of field tensors, in addition to the usual fields, are: stress tensor, induced strain tensor.

Example: Hooke's law in materials In tensor form, Hooke's law of elasticity is expressed as:

$$\sigma_{ij} = c_{ijkl}\epsilon_{kl} \tag{91}$$

or its converse

$$\epsilon_{ij} = s_{ijkl}\sigma_{kl} \tag{92}$$

- $\diamond$ σ_{ij} is the **applied stress tensor** — a field tensor
- $\diamond$ ϵ_{kl} is the **induced strain tensor** — a field tensor
- $\diamond$ c_{ijkl} and s_{ijkl} are the **stiffness tensor** and the **elastic tensor**, respectively —both materials tensors. They are *doubly symmetric* tensors in ij and kl separately, so they have 36 elements (see here below for an explanation).

6.6 Internal symmetry of tensor elements

- In addition to the crystal symmetry properties of materials tensors, which we just described, many tensors are **symmetric by exchange of some of their indices** (as hinted here above).
- Some tensors reflect **equilibrium properties of the crystal, for example under an applied external field**, and can be obtained by differentiation of the free energy. If the differentiation occurs twice with respect to the same quantity, the tensor is symmetric.

Example: Permittivity tensor:

$$\begin{aligned} P_i &= -\frac{\partial F}{\partial E_i} \\ \epsilon_{ij} &= -\frac{\partial^2 F}{\partial E_i \partial E_j} \end{aligned} \tag{93}$$

so the permittivity tensor is clearly symmetric by exchange of its indices.

Counter-example: Magnetoelectric tensor:

$$\begin{aligned} P_i &= \mu_{ij} B_j \\ \mu_{ij} &= -\frac{\partial^2 F}{\partial E_i \partial B_j} \end{aligned} \tag{94}$$

so the magneto electric tensor is *not* a symmetric tensor.

- Some field tensors are symmetric by construction – for example, the stress tensor σ_{ij} is symmetric because it excludes any torque component. As a consequence, the piezoelectric tensor $d_{i\alpha\beta}$, defined as

$$P_i = d_{i\alpha\beta}\sigma_{\alpha\beta} \tag{95}$$

is *symmetric* in $\alpha\beta$ (but the symmetry does not involve the first index i).

- Some materials tensor describing non-equilibrium steady-state properties, such as the conductivity tensor, are also symmetric. The symmetry properties of such tensors are expressed by the so-called Onsager reciprocity principle (see book by J.F. Nye).

6.7 Symmetrised and anti-symmetrised tensor spaces

- As we had just seen, certain tensors are symmetric by exchange of one or more pairs of indices. It is also useful in some cases to consider **antisymmetric** tensors by exchange of indices. When one considers the tensor product of a vector space by itself, $V \otimes V$, one can see how the definition of symmetric and antisymmetric tensors naturally arises. If the basis vectors of $V \otimes V$ (with dimension n^2) are:

$$[(\mathbf{a}_1|\mathbf{a}_1)(,\mathbf{a}_1|\mathbf{a}_2),\cdots,(\mathbf{a}_1|\mathbf{a}_n),(\mathbf{a}_2|\mathbf{a}_1),\cdots(\mathbf{a}_n|\mathbf{a}_n)] \tag{96}$$

then one can consider two subspaces of $V \otimes V$: the **symmetric subspace** $[V \otimes V]$, with dimension $\frac{1}{2}n(n+1)$ and basis vectors:

$$\left[(\mathbf{a}_1|\mathbf{a}_1), \frac{1}{2}(\mathbf{a}_1|\mathbf{a}_2)+\frac{1}{2}(\mathbf{a}_2|\mathbf{a}_1),\cdots,\frac{1}{2}(\mathbf{a}_1|\mathbf{a}_n)+\frac{1}{2}(\mathbf{a}_n|\mathbf{a}_1),\cdots,(\mathbf{a}_n|\mathbf{a}_n)\right] \tag{97}$$

and the the **anti-symmetric subspace** $\{V \otimes V\}$, with with dimension $\frac{1}{2}n(n-1)$ and basis vectors:

$$\left[(\frac{1}{2}(\mathbf{a}_1|\mathbf{a}_2)-\frac{1}{2}(\mathbf{a}_2|\mathbf{a}_1),\cdots,\frac{1}{2}(\mathbf{a}_1|\mathbf{a}_n)-\frac{1}{2}(\mathbf{a}_n|\mathbf{a}_1),\cdots,\frac{1}{2}(\mathbf{a}_{n-1}|\mathbf{a}_n)-\frac{1}{2}(\mathbf{a}_n|\mathbf{a}_{n-1})\right] \tag{98}$$

- There is a very useful formula for the **characters** of the symmetric and antisymmetric subspaces, which we present without proof:

$$\begin{aligned}\chi_{[\Gamma\otimes\Gamma]}(g) &= \frac{1}{2}\left[\chi_\Gamma^2(g)+\chi_\Gamma(g^2)\right]\\ \chi_{\{\Gamma\otimes\Gamma\}}(g) &= \frac{1}{2}\left[\chi_\Gamma^2(g)-\chi_\Gamma(g^2)\right]\end{aligned} \tag{99}$$

  where $g^2 = g \circ g$.

- This rule enables us to construct the transformation properties of very complex tensors. For example, the doubly symmetric elastic tensor s_{ijkl} transforms like the doubly symmetric tensor representation $[\Gamma\otimes\Gamma]\otimes[\Gamma\otimes\Gamma]$, and its characters are easily determined from eq. 99, if one knows the characters of Γ.

- Note that many relevant decompositions of tensor representations can be found on the Bilbao Crystallographic Server http://www.cryst.ehu.es/rep/point.html.

Example: transformation properties of the piezoelectric tensor in the point group 32.
The definition of the piezoelectric tensor $d_{i\alpha\beta}$ is in eq. 95. It is a 3^{rd}-rank polar tensor that is symmetric in the last two indices, so it transforms according to representation $\Gamma\otimes[\Gamma\otimes\Gamma]$. Γ is the ordinary vectors transformation by 32. As we already know, $\Gamma=\Gamma_2+\Gamma_3$. The character table for Γ is therefore:

E	2A	3K
3	0	-1

Let's employ eq. 99 to determine the characters of $[\Gamma\otimes\Gamma]$. For the identity and the 2-fold axes, $g^2=E$, whereas for the 3-fold rotations $A^2=B$. Therefore:

$$\begin{aligned}\chi_{[\Gamma\otimes\Gamma]}(E) &= \frac{1}{2}\left[\chi_\Gamma^2(E)+\chi_\Gamma(E^2)\right]=6\\ \chi_{[\Gamma\otimes\Gamma]}(A) &= \frac{1}{2}\left[\chi_\Gamma^2(A)+\chi_\Gamma(A^2)\right]=0\\ \chi_{[\Gamma\otimes\Gamma]}(K) &= \frac{1}{2}\left[\chi_\Gamma^2(K)+\chi_\Gamma(K^2)\right]=2\end{aligned} \tag{100}$$

Therefore $[\Gamma \otimes \Gamma] = 2\Gamma_1 + 2\Gamma_3$. Multiplying by Γ again we obtain the character table for $\Gamma \otimes [\Gamma \otimes \Gamma]$:

E	2A	3K
18	0	-2

This decomposes into $\Gamma \otimes [\Gamma \otimes \Gamma] = 2\Gamma_1 + 4\Gamma_2 + 6\Gamma_3$. However, the piezoelectric tensor is a materials property tensor, and it has therefore to transform according to the totally symmetric *irrep* Γ_1. All the other components must correspond to zero elements of the tensor matrix. Γ_1 appears twice in the decomposition. Therefore, the matrix elements of $d_{i\alpha\beta}$ are described by only **two independent parameters**.

6.8 Matrix transformations of tensors

- Up to this point, we have employed the powerful machinery of representation theory to describe the transformation properties of tensors. However, in order to perform calculations, we need the actual matrix form of the tensors, which of course depends on the choice of coordinates, Cartesian, spherical and crystallographic being possible choices. Also, we need another explicit form of transformation rules, since the Kronecker form is not of practical application.

- The matrix form of the tensor arises from writing the elements of a tensor space as

$$\boldsymbol{T} = \sum_{i,j,k,\cdots} T_{i,j,k,\cdots} \left(\boldsymbol{a}_i|\boldsymbol{b}_j|\boldsymbol{c}_k|\cdots\right) \tag{101}$$

where $\boldsymbol{a}_i$,$\boldsymbol{b}_j$, $\boldsymbol{c}$ etc. are basis sets for ordinary vectors. With this notation:

$$\begin{aligned} \hat{O}(g)\boldsymbol{T} &= \sum_{l,m,n,\cdots} T_{l,m,n,\cdots} \sum_{i,j,k,\cdots} R_{li}(g)\mathbf{a}_i R_{mj}(g)\mathbf{b}_j R_{nk}(g)\mathbf{c}_k \cdots \\ &= \sum_{i,j,k,\cdots} \left(\sum_{l,m,n,\cdots} T_{l,m,n,\cdots} R_{li}(g) R_{mj}(g) R_{nk}(g) \right) \left(\mathbf{a}_i|\mathbf{b}_j|\mathbf{c}_k|\cdots\right) \end{aligned} \tag{102}$$

where the $R_{li}(g)$ are the ordinary *proper* rotation matrices, i.e., the matrix representative of the group elements on the space of ordinary vectors. In the case of improper rotations, one has to take into account

whether the tensor is polar or axial. This can be summarised in the following formula, where $p(g)$ is the parity of g:

$$\begin{aligned}\hat{O}(g)T_{ijk\cdots} &= \sum_{l,m,n,\cdots} T_{l,m,n,\cdots}R_{li}(g)R_{mj}(g)R_{nk}(g)\cdots \text{ (polar tensors)} \\ \hat{O}(g)T_{ijk\cdots} &= (-1)^{p(g)}\sum_{l,m,n,\cdots} T_{l,m,n,\cdots}R_{li}(g)R_{mj}(g)R_{nk}(g)\cdots \text{ (axial tensors)}\end{aligned} \tag{103}$$

6.9 Allowed physical properties and materials tensors elements

- Two central questions about physical properties described by materials tensors are:

  1. **which physical properties are allowed in certain crystal symmetries, and how many independent parameters are needed to describe them?**
  2. **what is the explicit form of the tensors in a given coordinate system?**

  these questions can be answered exclusively by use of symmetry arguments.

- The first question can be fully addressed by employing character decomposition, as we have seen in the piezoelectricity tensor example on page 67. One determines the characters of the tensor representation (in that case $\Gamma \otimes [\Gamma \otimes \Gamma]$), decomposes the resulting character table into *irreps* and considers the number of times Γ_1 or (Γ_{1g} for centrosymmetric groups) appears in the decomposition.

  - ◇ If Γ_1 appears 0 times, then the physical properties described by this tensor is forbidden in that particular symmetry group.
  - ◇ If Γ_1 appears $n > 0$ times, then the physical properties described by this tensor are spanned by n independent parameters in that particular symmetry group, meaning that the variability of that properties in all molecules or crystals with that symmetry is described by n parameters.

- From the parity classification of polar and axial tensors (page 63), it follows immediately that **physical properties described by polar tensors of odd rank and axial tensors of even rank cannot exist in systems**

having centrosymmetric symmetry groups. In fact, Γ_{1g} can never appear in the decomposition of an *ungerade* representation.

- Therefore, for example, piezoelectricity and ferroelectricity are only restricted to non-centrosymmetric groups.

- Further restrictions can be found by actually applying the decomposition formula. For example, ferroelectricity and pyroelectricity are restricted to only 10 point groups (out of the 21 non-centrosymmetric point groups): 1, 2, m, $2mm$, 4, $4mm$, 3, $3m$, 6 and $6mm$. Every non-centrosymmetric point group is piezoelectric, except 432.

- To find the explicit form of the tensors in a given coordinate system, one can employ the **projector operators**. One simply takes non-symmetry-specific form of the tensor, with appropriately symmetrised indices if necessary, and projects it onto the totally symmetric representation Γ_1:

$$\tilde{T}_{ijk} = \frac{1}{h} \sum_g \sum_{lmn} T_{lmn} R_{li}(g) R_{mj}(g) R_{nk}(g) \tag{104}$$

  where, again, one can see that the symmetrised tensor will be zero for parity-odd tensors in centro-symmetric groups.

6.10 *Example: explicit form of the piezoelectric tensor in 32.

- Following on from the previous example, we will now determine the explicit form of this tensor in Cartesian coordinates. The non-symmetry-specific tensor has 18 independent components, and the transformation matrices are in eq. 16. The form in 3D is obtained by setting $R_{31} = R_{32} = R_{13} = R_{23} = 0$. $R_{33} = 1$ for E, A, and B and -1 for K, L and M. We will use the projection formula:

$$\tilde{d}_{i\mu\nu} = \frac{1}{h} \sum_g \sum_{l\kappa\lambda} d_{l\kappa\lambda} R_{li}(g) R_{\kappa\mu}(g) R_{\lambda\nu}(g) \tag{105}$$

  where we use the Greek letter to label the symmetric indices.

  - ◇ We start by calculating $1/h \sum_g$ over the 6 elements of the group for all the different combinations of matrices, which we will indicate with the notation:

$$(1\underline{1})(1\underline{2})(3\underline{3}) = \frac{1}{6} \sum_g R_{11}(g) R_{12}(g) R_{33}(g) \tag{106}$$

the order of the matrices clearly does not matter. This calculation is further simplified by the fact that all matrix elements containing a "3" (13, 23, 31, 32) are *zero* except for 33. We can find all the non-zero elements with the help of a spreadsheet:

$$\begin{aligned}
(1\underline{1})(2\underline{2})(3\underline{3}) &= (1\underline{1})(3\underline{3})(2\underline{2}) = (2\underline{2})(1\underline{1})(3\underline{3}) = \frac{1}{2} \\
(2\underline{2})(3\underline{3})(1\underline{1}) &= (3\underline{3})(1\underline{1})(2\underline{2}) = (3\underline{3})(2\underline{2})(1\underline{1}) = \frac{1}{2} \\
(1\underline{2})(2\underline{1})(3\underline{3}) &= (1\underline{2})(3\underline{3})(2\underline{1}) = (2\underline{1})(1\underline{2})(3\underline{3}) = -\frac{1}{2} \\
(2\underline{1})(3\underline{3})(1\underline{2}) &= (3\underline{3})(1\underline{2})(2\underline{1}) = (3\underline{3})(2\underline{1})(1\underline{2}) = -\frac{1}{2} \\
(1\underline{1})(1\underline{1})(2\underline{2}) &= (1\underline{1})(2\underline{2})(1\underline{1}) = (2\underline{2})(1\underline{1})(1\underline{1}) = \frac{1}{4} \\
(1\underline{1})(1\underline{2})(2\underline{1}) &= (1\underline{1})(2\underline{1})(1\underline{2}) = (1\underline{2})(1\underline{1})(2\underline{1})\frac{1}{4} \\
(2\underline{1})(1\underline{1})(1\underline{2}) &= (1\underline{2})(2\underline{1})(1\underline{1}) = (2\underline{1})(1\underline{2})(1\underline{1}) = \frac{1}{4} \\
(2\underline{2})(2\underline{2})(2\underline{2}) &= \frac{1}{4} \\
(1\underline{2})(1\underline{2})(2\underline{2}) &= (1\underline{2})(2\underline{2})(1\underline{2}) = (2\underline{2})(1\underline{2})(1\underline{2}) = -\frac{1}{4} \\
(2\underline{1})(2\underline{1})(2\underline{2}) &= (2\underline{1})(2\underline{2})(2\underline{1}) = (2\underline{2})(2\underline{1})(2\underline{1}) = -\frac{1}{4} \qquad (107)
\end{aligned}$$

◇ We now consider the summation $\sum_{l\kappa\lambda}$ in (eq. 105). One can notice that the *second* index in each rotation matrix (the one we underlined) determines which symmetrised tensor element that matrix will contribute to, so, for example in our notation, the term $(2\underline{1})(1\underline{2})(3\underline{3})$ will provide a contribution $-\frac{1}{2}d_{213}$ to $\tilde{d}_{123}$. With a bit of bookkeeping, one gets the following:

$$\begin{aligned}
\tilde{d}_{123} &= \tilde{d}_{132} = A \\
\tilde{d}_{213} &= \tilde{d}_{213} = -A \\
\tilde{d}_{112} &= \tilde{d}_{121} = \tilde{d}_{211} = B \\
\tilde{d}_{222} &= -B \qquad (108)
\end{aligned}$$

where

$$\begin{aligned}
A &= \frac{1}{2}\left[d_{123} - d213\right] \\
B &= \frac{1}{4}\left[2d_{112} + d_{211} - d_{222}\right] \qquad (109)
\end{aligned}$$

All the other elements of the tensor are *zero*.

As we had predicted using *irrep* analysis, the piezoelectric tensor has 2 free parameters in 32 (A and B), corresponding to the number of times Γ_1 is contained in $\Gamma \otimes [\Gamma \otimes \Gamma]$.