

# Symmetry in Condensed Matter Physics

## *Group and representation theory Lectures 1-8*

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### Bibliography

- **Volker Heine** *Group Theory in Quantum Mechanics*, Dover Publication Press, 1993. A very popular book on the applications of group theory to quantum mechanics.
- **M.S. Dresselhaus, G. Dresselhaus and A. Jorio**, *Group Theory - Application to the Physics of Condensed Matter*, Springer-Verlag Berlin Heidelberg (2008). A recent book on irreducible representation theory and its application to a variety of physical problems. It should also be available on line free of charge from Oxford accounts.
- **T. Hahn**, ed., *International tables for crystallography*, vol. A (Kluwer Academic Publisher, Dordrecht: Holland/Boston: USA/ London: UK, 2002), 5th ed. The International Tables for Crystallography are an indispensable text for any condensed-matter physicist. It currently consists of 8 volumes. A selection of pages is provided on the web site. Additional sample pages can be found on <http://www.iucr.org/books/international-tables>.
- **J.F. Nye** *Physical properties of crystals*, Clarendon Press, Oxford 2004. A very complete book about physical properties and tensors. It employs a rather traditional formalism, but it is well worth reading and consulting.

#### *Additional texts*

- **C. Hammond** *The Basics of Crystallography and Diffraction*, Oxford University Press (from Blackwells). A well-established textbook for crystallography and diffraction.
- **Paolo G. Radaelli**, *Symmetry in Crystallography: Understanding the International Tables*, Oxford University Press (2011). An introduction to symmetry in the International Tables.
- **C. Giacovazzo**, H.L. Monaco, D. Viterbo, F. Scordari, G. Gilli, G. Zanotti and M. Catti, *Fundamentals of crystallography*, International Union of Crystallography, Oxford University Press Inc., New York. A very complete book on general crystallography.
- **"Visions of Symmetry: Notebooks, Periodic Drawings, and Related Work of M. C. Escher"**, W.H. Freeman and Company, 1990. A collection of symmetry drawings by M.C. Escher, also to be found here: <http://www.mcescher.com/Gallery/gallery-symmetry.htm>
- **A. Zee** *Group theory for physicists in a nutshell*, Princeton University Press, Princeton 2016. Quite a thick nut, but very complete and modern. Covers especially well continuous symmetries and Lie groups.

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# 1 Lecture 1: introduction to symmetry in CMP

## 1.1 The idea of symmetry

When we speak of symmetry informally we refer to *transformations that leave the state of affairs unchanged*. Crystals are often beautifully symmetric objects (the similarity between certain crystals and platonic solids has been recognised early on), and since the eighteenth century, symmetry has been used to classify the morphology of crystals. Later, with the development of X-ray diffraction, crystallography became a powerful tool not only to classify crystal structure in a much more systematic way using the 230 space groups, but also to determine precisely the positions of atoms and molecules in the crystals. Since crystals can be considered as rigid bodies with periodic properties in space, lattice translations, certain rotations and translation-rotation combinations *in ordinary space* turn out to be the most relevant transformations<sup>1</sup> for crystals and consequently for the branch of CMP that deals with crystalline materials.

Although knowing where atoms are is clearly necessary, the most important applications of symmetry in condensed matter physics are concerned with the determination of the symmetry of *fields* (functions of  $x$ ,  $y$ ,  $z$ , and  $t$ , although we will mostly consider static fields), which can be defined either on discrete points (e.g., the magnetic moments of atoms) or on the whole of space (e.g., electron density). These functions are usually solutions of a classical or quantum problems, and are defined over a set of points in real space, known in mathematics as the *domain* of the function. For example:

- In Schroedinger's description of quantum mechanics, the *wave function* is a complex scalar field defined over all the continuous domain of ordinary 3D space. *Electron density* is a real field derived from the many-body wave function. All descriptions based on discrete points (see here below) are useful approximations of continuous descriptions.
- A crystal lattice (an infinite but discrete set of points) can support, for example, a set of classical spins (magnetic structure) or a set of displacements (the displacements of phonon modes). These can be understood as real vector fields defined over the lattice domain.
- A *finite set of points*, for example, the atoms in a molecule, which again may support spins (if the atoms are magnetic), displacements etc. In this case, the domain of these vector functions is a discrete set of points.

**The theory of symmetry groups (including point groups and crystallographic space groups) can be employed to *classify* the symmetry not only of sets of atoms (described as points) but also of these more physics-related functions.** For example, the electron density in a crystal

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<sup>1</sup>Not the only ones — time reversal symmetry is also important for magnetism.

has the same symmetry of the crystal structure, which is described by one of the 230 crystallographic space groups.

There is generally a *hierarchy of symmetries*: the highest symmetry we need to consider is the symmetry of the set of points over which the fields are defined (i.e., the *domain*), because no function defined on a domain can have a symmetry higher than that of the domain itself. The Hamiltonian usually has lower symmetry than the domain, and the solution can have an even lower symmetry. As an example, we can consider the problem of single-particle electronic wave functions in a crystal (usually considered as infinite). Here, the domain is the continuous space within the crystal. The Hamiltonian is associated with the electrostatic potential generated by the atoms at the crystal lattice, and has lower translational/rotational symmetry than the free space. Finally, electronic eigenstates (especially excited states) usually have lower symmetry than the Hamiltonian.

## 1.2 Symmetry of the problem and symmetry of the solutions

One might argue that ‘classification by symmetry’ sounds too much like ‘stamp collecting’ for a serious physics student to be concerned with it. Nothing could be further from the truth, as **there is an intimate connection between the symmetry of the Hamiltonian (classical or quantum) and its spectral properties** (i.e., its energy levels and how degenerate they are).

To introduce this connection, let us consider the very familiar example of a planet orbiting a massive star. The energy of the system (Hamiltonian) is rotationally invariant, so the energy of the planet located at position  $\mathbf{r}$  and with momentum  $\mathbf{p}$  would be the same as at position  $R\mathbf{r}$  and momentum  $R\mathbf{p}$ , where  $R$  is any matrix describing a rotation or a reflection centred at the star. In fact, when expressed in appropriate form, the Hamiltonian is rotationally invariant *by inspection*:

$$H = \frac{|\mathbf{p}|^2}{2m} - G \frac{mM}{|\mathbf{r}|} \quad (1)$$

The Hamiltonian is also invariant by inversion (parity) and by any mirror reflection. By contrast, the *solutions* of the Hamilton equation (elliptical orbits) are clearly *not* rotationally invariant, although some of the original symmetry is nonetheless preserved (an elliptical orbit is still invariant by a reflection in the plane of the ellipse). Therefore, we find that a generic rotation *does* change the state of affairs, but *does not* change the energy. We conclude that, at least in this case, *the symmetry of the solutions is lower than the symmetry of the Hamiltonian*. We can, however, be assured that, if we transform one orbit by any rotation, reflection etc., we will find a new solution (orbit) that has the same energy (and in fact the same absolute value of the angular momentum) as the original one.

This simple example has myriads of analogies in solid-state physics. For

example, individual phonons or electronic excitations break all sorts of crystalline symmetries, but phonons related by symmetry have the same energy. Magnetic domains also break symmetry (including time-reversal symmetry), but symmetry-related domains are energetically equivalent.

### 1.3 Linear problems and linear (vector) spaces.

The example illustrated above shows that symmetry can be used to generate ‘by symmetry’ many equivalent solutions starting from one solution, which is convenient enough. We can however go a step further for problems where the equations of motion are *linear* in the dynamical variables<sup>2</sup>. Here we briefly illustrate the two most famous linear problems in physics — the harmonic oscillator problem and the Schroedinger equation. The equations of motion of the 1D harmonic oscillator are clearly linear in the dynamical variable, in that the equation:

$$m\ddot{x}(t) = -kx(t) \tag{2}$$

is linear in  $x(t)$ . If  $x_1(t)$  and  $x_2(t)$  are two solutions, then  $ax_1(t) + bx_2(t)$ , with  $a$  and  $b$  arbitrary constants, will also be a solution — this is known as the *superposition principle*. In fact, one may take  $x_1(t), x_2(t), a$  and  $b$  to be *complex* — e.g.,  $x_1(t) = |x_1|e^{i\omega t}$ , etc. — and recover the physical meaning of the solutions by taking the real part at the end of the process. This can be clearly generalised to any set of ‘balls and springs’ in 2D and 3D, giving rise to normal mode theory. In this case, the dynamical variables are the displacements of individual atoms, which form a vector field on a discrete domain.

Similarly, the Schroedinger equation

$$i\hbar\frac{\partial\psi(t)}{\partial t} = \hat{H}\psi(t) \tag{3}$$

is clearly *linear* in the wave function  $\psi(t)$  (a complex scalar field on a continuous domain), so that if two time-dependent solutions exist, say  $\psi_1(t)$  and  $\psi_2(t)$ , then  $a\psi_1(t) + b\psi_2(t)$ , with  $a$  and  $b$  arbitrary complex constants, will also be a solution, in complete analogy with the classical case.

It is instructive to note that, mathematically, linear problems of this kind can be reduced to the task of *diagonalising a symmetric/hermitian matrix*<sup>3</sup>, yielding

<sup>2</sup>This is not to say that symmetry does not have its uses for non-linear problems — it most certainly does, e.g., for the symmetry classification of phase transitions in the context of the Landau theory. However, even in these cases, there is usually an underlying linear theory; for example, *linear* normal modes theory underlies the classification of displacive phase transitions, where the free energy is non-linear in the order parameters.

<sup>3</sup>There are subtleties in the quantum case when dealing with the continuous spectrum, which we will ignore here.

the normal modes/normal frequencies and the eigenfunctions/eigenvalues in the two cases. The normal modes or eigenfunctions are part of a wider set of displacement patterns (classical) or wavefunctions (quantum) defined over the same domain, which are not solutions of the eigenvalue equation, but can still represent a ‘snapshot’ of the dynamical system. For want of a better word, we will call these functions/patterns ‘modes’ in the remainder.

What is it special about symmetry when the superposition principle applies? Consider a specific normal mode or eigenvector, with its time dependent phase factor, so that it define a particular solution of the dynamical equation, say  $\psi_1(t)$ . As we have seen, if we transform this solution by one of the symmetries of the Hamiltonian, we will obtain another solution with the same energy (eigenvalue), say  $\psi_2(t)$ . But, as we have just seen,  $a\psi_1(t) + b\psi_2(t)$  will also be an eigenfunction with the same eigenvalue. So, here, by applying one of the symmetries of the Hamiltonian, we have not only created a distinct solution (albeit with the same energy, as in the case of the planet orbits<sup>4</sup>), but we have generated an *entire space of degenerate eigenfunctions*.

We can now recall from our studies of quantum mechanics that the natural arena to discuss solutions of the Schrodinger equation is the so-called Hilbert space, which generalised the notion of Euclidean space, including the dot product, and extends it to infinite dimensions and to the complex field. An even more general definition is that of a *linear space* (also called a *vector space*), which may or may not have the definition of a dot product. We should also recall that any Hermitian operator defined on the Hilbert space (including, most importantly, the Hamiltonian) possess a complete set of *orthogonal eigenvectors*, which can be taken as a *basis* for the entire Hilbert space. The notion is completely analogous to the classical case, provided we replace ‘eigenvector(s)’ with ‘normal mode(s)’. What we have shown here is that, **in the presence of symmetry, eigenvectors or normal modes in general do not have distinct eigenvalues/frequencies, but form subspaces (of the original Hilbert space) of modes/eigenvectors with the same frequency/eigenvalues (multiplets)**. One important corollary is that, if symmetry is reduced, some of the multiplets split.

## 1.4 Physical consequences

The most obvious and historically important connection between between what we have been discussing and the experimental observation of the relevant phenomena is in the field of *optical spectroscopy* (and later *X-ray spectroscopy*). Even before the advent of quantum mechanics, it was well known than many prominent features in atomic spectra were in fact *multiplets*, i.e., sets of lines with very similar wavelengths. In addition to ‘natural’ multiplets, some individual lines can be split into a number of components in the presence of electric and magnetic field (the Stark and Zeeman effects, respectively — note that externally-applied  $\mathbf{E}$  and  $\mathbf{B}$  fields generally break some

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<sup>4</sup>It is worth remarking that a linear combination of two elliptical orbits is *not* an elliptical orbit.

symmetry), whereas others cannot. Other experimental effects and problems where symmetry plays a major roles are:

- **Determining the multiplet structure given the symmetry of the Hamiltonian.** For example the fact the the hydrogen levels have degeneracy  $2l + 1$  can be determined entirely from symmetry, regardless of the specific form of the central potential. Other applications are in the rotational/vibrational spectroscopy of molecules (IR, Raman and neutron spectroscopies).
- **Determining the symmetry and degeneracy of excitations** (particularly low-energy ones). For example, one can determine the degeneracy of phonon/magnon branches and of electronic excitations entirely from symmetry.
- **Determining the effect of symmetry breaking in the small-perturbation limit.** For example, lifting of degeneracy due to external magnetic or electric field, spin-orbit interaction, crystal-field effects, where the difference between the spectra of atoms in vacuum and in molecules or crystals can be explained by the reduced symmetry of their environment.
- **Determining the phase diagrams and the nature of the ordered phases** for structural and magnetic phase transitions.

One important point is that **linear algebra and group theory alone are not sufficient to understand these effects fully**: one needs additional tools which will be introduced in this course.

## 1.5 The tools of the trade

The most comprehensive understanding of the relation between the physical effects described above, which bewildered early spectroscopy, and symmetry is due to Hermann Weyl and Eugene Paul Wigner. In the 1930s, Hans Bethe and John Hasbrouck van Vleck developed crystal field theory using these principles.<sup>5</sup> This required the application a number of mathematical tools, which were well developed at the time of Wigner (see Fig. 1):

- *Linear algebra* deals with linear (vector) spaces (including ordinary Euclidean space and Hilbert spaces) and with linear operators acting on these spaces. Most physics courses introduce linear algebra in the first year. A good summary can be found in the lecture notes of the Oxford first-year ‘Vectors and matrices’ physics course. We will assume that the students are familiar, for example, with the concepts of *basis*

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<sup>5</sup>On the web one can find excellent interview with Hans Bethe, episode 15 of the series “Hans Bethe—Scientist”, about the early days of the application of group theory to crystal spectroscopy.

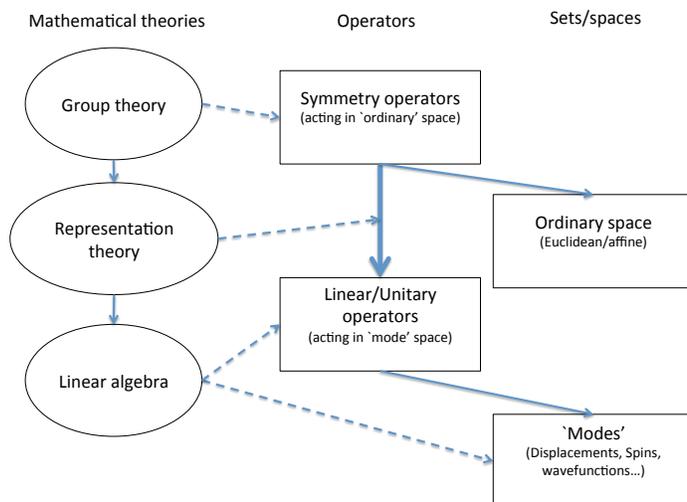


Figure 1: Spaces (**right**), operators (**middle**) and mathematical theories (**left**) relevant for the theory of symmetry.

vectors for a generalised linear space, dot products, etc., and can confidently manipulate simple matrices and arrays (i.e., elements of  $\mathbb{R}^n$ ). The useful concept of *projector operator* will be briefly introduced later in this lecture.

- *Group theory* is the best way to describe (among many other things) the transformations of ordinary space that form the basis of molecular and crystallographic symmetry. We will see very shortly why linear algebra is not sufficient for this task. Group theory is essential for modern physics, and it is a real pity that this important subject is not generally studied as part of the mathematical foundations of university physics. Here, we will introduce the main concepts of group theory very briefly and largely by examples.
- *Representation theory*. As we shall see shortly, every transformation (crystallographic or otherwise) of ordinary Euclidean space maps onto a *linear operator* acting on the space of *modes* defined onto the ordinary space.<sup>6</sup> The branch of mathematics that describes the mapping between a *group* (here, a particular group of symmetry operators) and a *set of linear operators* is called *representation theory*, and is the main focus of the present course.

<sup>6</sup>It is rather unfortunate that the word 'operator' is used for two rather different objects, but the word 'symmetry operator' is all too common to be replaced systematically with 'symmetry transformation'.

## 1.6 Isometric transformations of ordinary space and their link with linear operators

Here we are interested in transformations of an object, a pattern or a field that ‘take each point and move it elsewhere’ without changing the shape of the object (distances and angles). In mathematics, these transformations are a particular case of *active* or *alibi* transformations (from the Latin *alibi*, meaning *elsewhere*). We write this transformation generically as  $T(p)$ . Writing  $T(p_1) = p_2$  means that a point  $p_1$  is moved to a point  $p_2$ , in the sense that all the properties originally associated with  $p_1$  (e.g., the value of a function-field) will be found at  $p_2$  after the transformation. For an *alibi* transformation of this kind, the *inverse* transformation  $T^{-1}(p)$  is defined so that  $T^{-1}(p_2) = p_1$  for each point in the domain. In order for distances and angles in ordinary space to be preserved, the transformation must be a rotation, a reflection, a translation or a combination of these. If the ‘state of affairs’ is left unchanged after the *alibi* transformation, we say that the transformation is a *symmetry operator* of the object, pattern, function etc. *Alibi* transformations are distinct from coordinate transformations, also known as *passive* or *alias* transformations, which leave each point (and indeed everything else) where it is but create an *alias*, i.e., a different name for it. In this course, a ‘transformation’ is implicitly an *alibi* transformations — we will not refer to *alias* transformations at all.

An often unappreciated fact is that *alias* transformations leave all the ‘physics’ invariant, because they simply change the name of things. In particular, they leave all vectors invariant — this is accomplished by changing both the components and the basis vectors. All laws of physics remain valid after an *alias* transformation (remember, we are only changing the *names* of things!), but may not have the same form as with the original names...

### 1.6.1 *Alibi* transformations of points

If one employs Cartesian coordinates, a generic *alibi* transformation  $T[p]$  satisfying these properties is written as

$$\mathbf{x}_2 = \mathbf{t} + R\mathbf{x}_1 \quad (4)$$

where  $\mathbf{x}_1$  and  $\mathbf{x}_2$  are the coordinates of  $p_1$  and  $p_2$  (written as column arrays),  $\mathbf{t}$  is the translational part of the transformation and  $R$  is an orthogonal matrix, so that  $\det R = \pm 1$ , where the  $+/-$  sign is for proper/improper rotations, respectively. The inverse transformation will be obtained by replacing  $R$  with  $R^{-1}$  and  $\mathbf{t}$  with  $-R^{-1}\mathbf{t}$ . In fact, it is easy to verify that

$$\mathbf{x}_1 = -R^{-1}\mathbf{t} + R^{-1}\mathbf{x}_2 \quad (5)$$

It can be shown that the expressions for non-Cartesian crystallographic coordinates is identical, except that  $R$  is replaced by a non-orthogonal matrix  $D$

with  $\det D = \pm 1$ , but we will generally continue to use  $R$  in the remainder.

Even when ordinary Euclidean space is treated as a linear space<sup>7</sup>, crystallographic transformations (symmetry operators) involving translations are *not* linear operators. In fact, if  $T$  represents a pure translation (i.e.,  $R = \mathbb{1}$ ), one can easily see that  $T(ar_1 + br_2) \neq aTr_1 + bTr_2$ . Consequently, linear algebra cannot be used in general to describe crystallographic transformations, and we have to employ the more general formalism of *group theory*<sup>8</sup>.

### 1.6.2 *Alibi* transformations of patterns and fields

As we mentioned at the beginning of the lecture, we are primarily interested in the symmetry properties of scalar and vector *fields* (complex- or real-valued, defined on a discrete or continuous domain). A useful and intuitive analogy here is provided by *alibi* transformations of patterns (think, for example, about the famous Escher symmetry drawings). For example, the colour originally found at point  $p_1$  will be found at point  $p_2$  after the transformation and so on. We can extend this concept to any *scalar field* (real or complex) defined on our ordinary space of points, say  $f(p)$ , in a straightforward way. The idea of a *vector pattern*, i.e., when points are ‘decorated’ with arrows, requires a bit more care, but is also quite intuitive if everything is done in Cartesian coordinates: if before the *alibi* transformation the vector  $\mathbf{v}_1$  is associated with point  $p_1$ , having coordinates  $\mathbf{x}_1$ , then after the transformation a vector  $\mathbf{v}_2 = R\mathbf{v}_1$ <sup>9</sup> will be associated with point  $p_2$  having coordinates  $\mathbf{x}_2 = \mathbf{t} + R\mathbf{x}_1$ . Again, this can be easily extended to any *vector function*, say  $\mathbf{f}(p)$ .

Regardless of the specific domain, the *alibi* transformation of a function  $f(p)$  under the *alibi* transformation  $T(p)$  has a simple general form:

$$f'(p) = T[f(p)] = f(T^{-1}[p]) \quad (6)$$

which, expressed in Cartesian or crystallographic coordinates, gives:

$$f'(\mathbf{x}) = T[f(\mathbf{x})] = f(R^{-1}\mathbf{x} - R^{-1}\mathbf{t}) \quad (7)$$

Let us analyse the rationale for this simple form. As we know,  $T(p_1) = p_2$  and also  $T^{-1}(p_2) = p_1$ . Therefore  $f'(p_2) = f(T^{-1}[p_2]) = f(p_1)$ , exactly as we wanted. For *vector* functions, following the general procedure to transform vectors, we will have  $\mathbf{f}'(p) = T[\mathbf{f}(p)] = R\mathbf{f}(T^{-1}[p])$  or, in Cartesian coordinates,

<sup>7</sup>In fact it is not! Points are not vectors, unless one introduces an arbitrary origin, but we can safely ignore this subtlety here.

<sup>8</sup>The exception to this are *point groups* (see below), for which there is a one-to-one correspondence between group elements and (proper and improper) rotation matrices.

<sup>9</sup>Strictly speaking, this form is correct only for a *polar* vector — see discussion in the remainder of this course.

$$\mathbf{f}' = T[\mathbf{f}(\mathbf{x})] = R\mathbf{f}(R^{-1}\mathbf{x} - R^{-1}\mathbf{t}) \quad (8)$$

which gives  $\mathbf{f}'(p_2) = R\mathbf{f}(T^{-1}[p_2]) = R\mathbf{f}(p_1)$  as expected.

Here is a more detailed recipe to transform a field:

- We want to transform a function  $f(x, y, z)$  with a given transformation, which is expressed as  $\mathbf{x}_2 = \mathbf{t} + R\mathbf{x}_1$  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 start by writing:

$$f'(x, y, z) = f(X(x, y, z), Y(x, y, z), Z(x, y, z)) \quad (9)$$

- In other words, we have replaced the arguments of  $f$  with formal arguments  $X, Y$  and  $Z$ , which are themselves functions of the variables  $x, y, z$ .
- The functions  $X, Y$  and  $Z$  are defined by *back-transforming*  $x, y, z$ , exactly as in eq. 5, as follows:

$$\begin{bmatrix} X(x, y, z) \\ Y(x, y, z) \\ Z(x, y, z) \end{bmatrix} = -R^{-1} \begin{bmatrix} t_x \\ t_y \\ t_z \end{bmatrix} + R^{-1} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (10)$$

### 1.6.3 Example of transformation on a function

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

$$\begin{aligned} f(x, y, z) &= R(x, y, z)Y(x, y, z) \\ R &= \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \\ Y &= \frac{1}{r^2} (x^2 - y^2) = \sin^2 \theta \cos 2\phi \end{aligned} \quad (11)$$

we want to apply to this function an *operator* that rotates it  $20^\circ$  *counter-clockwise* 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  $20^\circ$  *clockwise*:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \cos \phi_0 & -\sin \phi_0 & 0 \\ \sin \phi_0 & \cos \phi_0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (12)$$

where  $\phi_0 = -20^\circ$ . This yields:

$$\begin{aligned}
 T[f(x, y, z)] &= f(X, Y, Z) = R'(x, y, z)Y'(x, y, z) \\
 R' &= R = \left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \\
 Y' &= \frac{1}{r^2} (X^2 - Y^2) = \sin^2 \theta \cos 2(\phi + \phi_0) \quad (13)
 \end{aligned}$$

Fig. 2 shows the original function and the function rotated with this procedure.

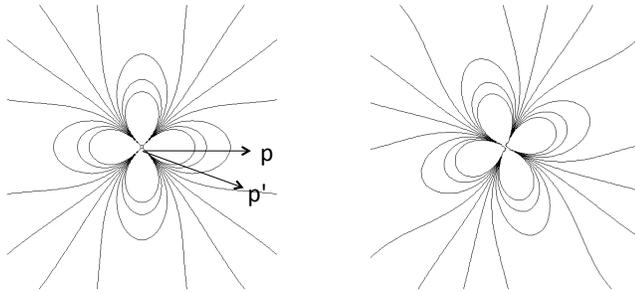


Figure 2: **Left:** the  $3d_{x^2-y^2}$  orbital: function. We want to rotate it by  $20^\circ$  counter-clockwise around the  $z$  axis, so that the “attributes” of point  $p'$  (here simply the value of the function) are transferred to point  $p$ . **Right:** the rotated function, constructed using the procedure in eq. 13.

#### 1.6.4 *Alibi* transformations of fields are linear in field (mode) space!

It is a very easy matter to see that, by our definition, *alibi* transformations of scalar/vector functions are *linear*. In fact, in the more general case of a vector function:

$$T[af_1(\mathbf{x}) + bf_2(\mathbf{x})] = R(af_1(\mathbf{x}') + bf_2(\mathbf{x}')) = aRf_1(\mathbf{x}') + bRf_2(\mathbf{x}') \quad (14)$$

with  $\mathbf{x}' = R^{-1}\mathbf{x} - R^{-1}\mathbf{t}$  as before. This may seem rather astonishing, because the original *alibi* transformation in ordinary space is generally not describable by a linear operator, but it is the basis for all subsequent developments.

### 1.6.5 *Alibi* transformations and linear spaces

The previous observation has clearly important implications for sets of functions that can be considered as elements of a *linear space* (e.g., the Hilbert space). Here the condition is clearly that if  $f_1(p)$  and  $f_2(p)$  must be members of the space, then  $af_1(p) + bf_2(p)$  must also be a member for  $a$  and  $b$  arbitrary real or complex numbers (depending on whether the linear space is defined over the real or complex field). To realise that this is not a trivial condition, let's immediately consider the counterexample of *electron density*. Since the density of electrons is a positively defined quantity, the set of all possible electron densities in a crystal *cannot form a linear space*. However, small deviations from an average density could be considered as forming a linear space. Other important examples of such linear spaces are:

- The displacements of atoms in a vibrating molecule.
- The spins on a lattice of magnetic atoms in a crystal.
- The set of wave-functions defined on ordinary space.

The implication is that each *alibi* transformation that is a symmetry of the domain *induces* a linear operator on the linear space of functions. As we have already mentioned, a map between group elements and linear operators is called a *representation*, and the one we just described will turn out to be a particular kind of representation (see the next lectures).

In most cases of interest, linear operators associated with isometric transformations are *unitary operators*, i.e., operators that preserve the dot product. This is straightforward to see for the Hilbert space. Remembering that the scalar dot product of two wave-functions  $f$  and  $g$ , written as  $\langle f|g \rangle$  in bra-ket notation, is

$$\langle f|g \rangle = \int f^*(\mathbf{x})g(\mathbf{x})d\mathbf{x} \quad (15)$$

then we will have

$$T(\langle f|g \rangle) = \int T(f^*(\mathbf{x}))g(\mathbf{x})d\mathbf{x} = \int g^*(R^{-1}\mathbf{x} - R^{-1}\mathbf{t})f(R^{-1}\mathbf{x} - R^{-1}\mathbf{t})d\mathbf{x} \quad (16)$$

defining  $\mathbf{x}' = R^{-1}\mathbf{x} - R^{-1}\mathbf{t}$ , changing variables and observing that the Jacobian of the transformation is simply  $R$ , we obtain:

$$T(\langle f|g \rangle) = \int T(f^*(\mathbf{x}))g(\mathbf{x})d\mathbf{x} = \int g^*(\mathbf{x}')f(\mathbf{x}')|\det(R)|d\mathbf{x}' = \langle f|g \rangle \quad (17)$$

### 1.6.6 Example: a simple *alibi* transformation

I provide here what is possibly the simplest example of an *alibi* transformation in the space of functions — a simple translation in 2D (no rotation). The general formulation of the 'recipe' for an *alibi* transformation is given in eq. 10:

$$\begin{bmatrix} X(x, y, z) \\ Y(x, y, z) \\ Z(x, y, z) \end{bmatrix} = -R^{-1} \begin{bmatrix} t_x \\ t_y \\ t_z \end{bmatrix} + R^{-1} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (18)$$

We want to limit ourselves to 2D. Given that  $R$  is the identity, the rule gives then:

$$\begin{aligned} X &= x - t_x \\ Y &= y - t_y \end{aligned} \quad (19)$$

Let us apply this transformation to a second-order polynomial in  $x$  and  $y$ , with generic expression:

$$f(x, y) = c_1 + c_2x + c_3y + c_4x^2 + c_5y^2 + c_6xy \quad (20)$$

By replacing  $x$  with  $X$  and  $y$  with  $Y$  in this expression, we obtain the polynomial translated by  $(t_x, t_y)$ :

$$\begin{aligned} T[f(x, y)] = f'(x, y) &= (c_1 - c_2t_x - c_3t_y + c_4t_x^2 + c_5t_y^2 + c_6t_xt_y) \\ &+ (c_2 - 2t_xc_4 - t_yc_6)x \\ &+ (c_3 - 2t_yc_5 - t_xc_6)y \\ &+ c_4x^2 \\ &+ c_5y^2 \\ &+ c_6xy \end{aligned} \quad (21)$$

It should be immediately clear that this is a *linear transformation* — this is in fact the case for *any alibi* transformation; in other words:

$$T[af_1(x, y) + bf_2(x, y)] = aT[(f_1(x, y))] + bT[(f_2(x, y))] \quad (22)$$

If so, one should be able to write it as a *matrix*, provided that a suitable basis is chosen. Conveniently, the polynomials are already expressed in the basis  $[1, x, y, x^2, y^2, xy]$ .

The transformation matrix can therefore be read out immediately from Equation 21:

$$M = \begin{bmatrix} 1 & -t_x & -t_y & t_x^2 & t_y^2 & t_xt_y \\ 0 & 1 & 0 & -2t_x & 0 & -t_y \\ 0 & 0 & 1 & 0 & -2t_y & -t_x \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \quad (23)$$

This result illustrates a very important and completely general point: **alibi transformations of functions are associated with *linear* operators.**

One can verify by direct multiplication that the two matrices  $M_1$  and  $M_2$ , corresponding to translations  $(t_{1x}, t_{1y})$  and  $(t_{2x}, t_{2y})$  **commute**, and that their product is the matrix corresponding to the translation  $(t_{1x} + t_{2x}, t_{1y} + t_{2y})$ , exactly as one should expect.

## 2 Lecture 2: Crystallographic point groups and group theory

### 2.1 A good place to start: crystallographic point groups in 2D

Before introducing the more formal aspects of group theory, it is useful to describe in some detail a set of examples. Crystallographic point groups in 2D are sufficiently simple to be grasped intuitively, yet sufficiently complex to illustrate most of the issues we will be concerned with. Moreover, crystallographic point groups describe the exact symmetry around all atoms and molecules in crystals, and of many free-standing molecules. The description can be easily extended to include molecules with non-crystallographic symmetry groups.

But what do we mean by 'crystallographic symmetry'? Essentially, a crystallographic symmetry operator is a transformation that leaves unaltered one of the 5 2D Bravais lattices or one of the 14 3D Bravais lattices. In addition to lattice translations, there is only a small number of such transformations:

#### In 2D

- Rotations of order 2, 3, 4 and 6 about an axis *normal* to the pattern (symbols 2, 3, 4 and 6 in the so-called Hermann-Mauguin notation).
- Reflection through a line in the plane of the pattern (symbol  $m$ ).

#### In 3D

- Rotations of order 2, 3, 4 and 6 about an axis as in the 2D case. These are called *proper* rotations, and are associated with matrices  $M$  having  $\det M = +1$
- Reflection through a point, i.e., *inversion* (symbol  $\bar{1}$ ). This is associated with minus the identity matrix ( $-\mathbb{1}$ , with  $\det -\mathbb{1} = -1$ )
- Combinations of proper rotations and the inversion (symbols  $m$ ,  $\bar{3}$ ,  $\bar{4}$  and  $\bar{6}$ ). These are called *improper* rotations, and are associated with matrices  $M$  having  $\det M = -1$

If one keeps at least one single point fixed, excluding therefore the possibility of translations, these symmetry operators can be combined to yield the 10 2-dimensional or the 32 3-dimensional point groups<sup>10</sup>, which are described in more details in Section 2.5.

In Cartesian coordinates, proper and improper rotations around the fixed point (origin) are associated with orthogonal matrices, which are clearly linear operators. This

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<sup>10</sup>Proving that there are only this number of point groups is a considerable task, which we will defer to more specialised textbooks.

seems to contradict what we just said about symmetry transformations not being linear operators. However, as soon as one introduces translations, this identification breaks down — this is why it is important to work in the more general framework of group theory.

### 2.1.1 Some important properties of operators

Operators can be applied one after the other, generating new operators, which are also part of the symmetry set. 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. 3.

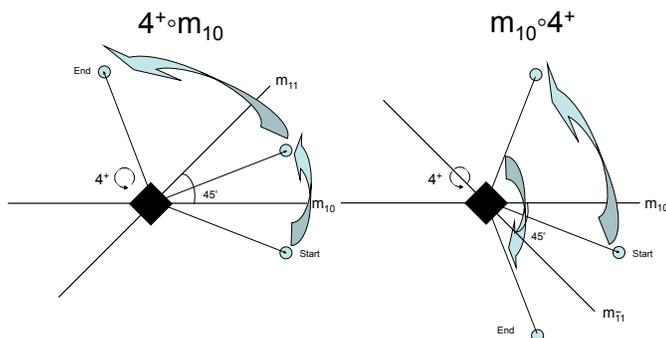


Figure 3: **Left:** A graphical illustration of the composition of the operators  $4^+$  and  $m_{10}$  to give  $4^+ \circ m_{10} = m_{11}$ . The fragment to be transformed (here a dot) is indicated with "start", and the two operators are applied in order one after the other (the rightmost first), until one reaches the "end" position. **Right:**  $4^+$  and  $m_{10}$  do not commute:  $m_{10} \circ 4^+ = m_{\bar{11}} \neq m_{11}$ .

As we see in fig. 3, some parts of the space are *left invariant* (transformed into themselves) by the application of a certain operator. For example,  $m_{10}$  leaves a horizontal plane invariant, whereas  $m_{11}$  leaves invariant a plane inclined by  $45^\circ$ . Parts of the space left invariant by a certain operator are called **symmetry elements** corresponding to that operator.

## 2.2 Introduction to group theory

The set of operators describing the symmetry of an object or pattern conforms to the mathematical structure of a **group**<sup>11</sup>. This is true in the case of the point groups but also in the more general case of space groups, which include translations. A group is a set of elements with a defined binary operation known as *composition* or *multiplication*, 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

$$f \circ (g \circ h) = (f \circ g) \circ h \quad (24)$$

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

$$g \circ E = E \circ g = g \quad (25)$$

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

$$g \circ g^{-1} = g^{-1} \circ g = E \quad (26)$$

- ◇ 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.

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<sup>11</sup>Leonard Euler (1707–1783) was responsible for developing the number-theory strand of group theory. In the 1830s, Evariste Galois was the first to employ groups to determine the solvability of polynomial equations. Arthur Cayley and Augustin Louis Cauchy pushed these investigations further by creating the theory of permutation groups. Felix Klein (1849–1925) used group theory to classify geometries

**Symmetry operators as elements of a group.** The important connection between symmetry operators and group elements is that **composing symmetry operator is equivalent to applying them one after another.** In line with the usual conventions in physics, when referring to symmetry operators the notation  $g \circ f$  means that  $f$  is applied *first*, followed by  $g$ . Groups of crystallographic symmetry operators can be constructed from a small number of *generators*, as explained above.

### 2.3 The point group $32$ ( $D_3$ ): a classic example

- Fig. 4 illustrates a classic example of a crystallographic group: the point group  $32$  (Hermann-Mauguin notation) or  $D_3$  (Schoenflies notation).

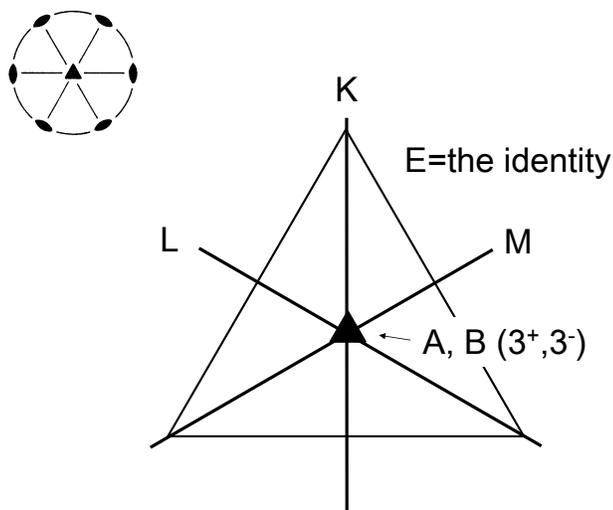


Figure 4: Schematic diagram for the the point group  $32$  (Hermann-Mauguin notation) or  $D_3$  (Schoenflies notation). This group has 6 elements (symmetry operators):  $E$  (identity),  $A$  and  $B$  (rotation by  $+120^\circ$  and  $-120^\circ$ , respectively),  $M$ ,  $K$ , and  $L$  (rotation by  $180^\circ$  around the dotted lines, as indicated). The graphical notation used in the International Tables is shown in the top left corner.

- 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  $A \circ M$  is a 2-fold axis rotated *counter-clockwise* by half the angle of rotation of  $A$ , i.e., the operator  $K$ .
  - ◊ 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 2-fold axes and in the direction defined by  $M \times K$ , i.e., the operator  $A$ .
- Fig. 6 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

$D_3 (32)$

		Applied first $\longrightarrow$					
		E	A	B	K	L	M
Applied second $\longrightarrow$	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 5: Multiplication table for the point group 32 ( $D_3$ ).

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 $\longrightarrow$					
		123	312	231	321	132	213
Applied second $\longrightarrow$	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 6: Multiplication table for the 3-element permutation group.

## 2.4 Conjugation

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

$$f = h \circ g \circ h^{-1} \tag{27}$$

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

- Conjugation has the following properties:

- ◇ It is **reflexive**:  $g \sim g$

$$g = E \circ g \circ E^{-1} \quad (28)$$

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

$$f = h \circ g \circ h^{-1} \Leftrightarrow h^{-1} \circ f \circ h = g \Leftrightarrow g = h^{-1} \circ f \circ (h^{-1})^{-1} \quad (29)$$

- ◇ 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.

#### 2.4.1 Example: the classes of the point group $422$ ( $D_4$ )

- The crystallographic point group  $422$  and its multiplication table are illustrated in fig. 7 and fig. 8.
- 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.
- Once can observe the following important relation: **graphs of conjugated operators are related to each other by symmetry**.

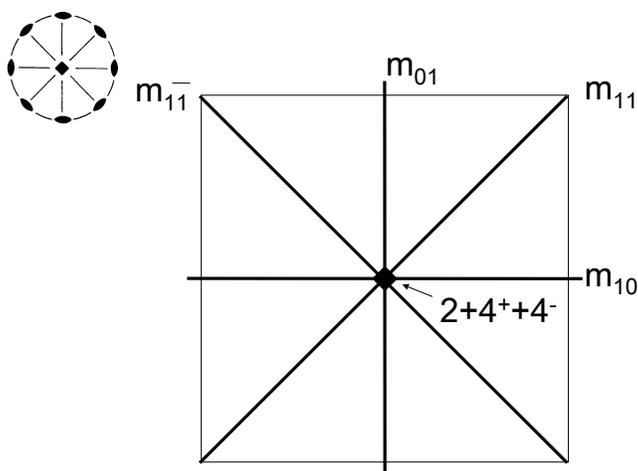


Figure 7: Schematic diagram for the the point group  $422$  (Hermann-Mauguin notation) or  $D_4$  (Schoenflies notation). This group has 8 elements (symmetry operators):  $E$  (identity),  $4^+$  and  $4^-$  (rotation by  $+90^\circ$  and  $-90^\circ$ , respectively),  $2_z$  (rotation by  $180^\circ$  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  $\longrightarrow$

	$E$	$2_z$	$4^+$	$4^-$	$m_{10}$	$m_{01}$	$m_{11}$	$m_{1\bar{1}}$
$\uparrow$ Applied second	$E$	$2_z$	$4^+$	$4^-$	$m_{10}$	$m_{01}$	$m_{11}$	$m_{1\bar{1}}$
	$2_z$	$2_z$	$4^-$	$4^+$	$m_{01}$	$m_{10}$	$m_{1\bar{1}}$	$m_{11}$
	$4^+$	$4^+$	$4^-$	$2_z$	$E$	$m_{11}$	$m_{1\bar{1}}$	$m_{01}$
	$4^-$	$4^-$	$4^+$	$E$	$2_z$	$m_{1\bar{1}}$	$m_{11}$	$m_{10}$
	$m_{10}$	$m_{10}$	$m_{01}$	$m_{1\bar{1}}$	$m_{11}$	$E$	$2_z$	$4^-$
	$m_{01}$	$m_{01}$	$m_{10}$	$m_{11}$	$m_{1\bar{1}}$	$2_z$	$E$	$4^+$
	$m_{11}$	$m_{11}$	$m_{1\bar{1}}$	$m_{10}$	$m_{01}$	$4^+$	$4^-$	$E$
	$m_{1\bar{1}}$	$m_{1\bar{1}}$	$m_{11}$	$m_{01}$	$m_{10}$	$4^-$	$4^+$	$2_z$
								$E$

Figure 8: Multiplication table for the point group  $422$  ( $D_4$ ).

## 2.5 Appendix: 2D point group tables in the ITC

The 10 2D point groups are listed in ITC-Volume A on pages 768–769 (Table 10.1.2.1 therein, see Fig. 9). We have not introduced all the notation at this point, but it is worth examining the entries in some details, as the principles of the notation will be largely the same throughout the ITC.

- **Reference frame:** All point groups are represented on a circle with thin lines

10. POINT GROUPS AND CRYSTAL CLASSES

Table 10.1.2.1. *The ten two-dimensional crystallographic point groups*

General, special and limiting edge forms and *point forms* (italics), oriented edge and site symmetries, and Miller indices ( $hk$ ) of equivalent edges [for hexagonal groups Bravais-Miller indices ( $hki$ ) are used if referred to hexagonal axes]; for point coordinates see text.

<b>OBLIQUE SYSTEM</b>				
<b>1</b>				
1	<i>a</i>	1	Single edge Single point ( <i>a</i> )	( $hk$ )
<b>2</b>				
2	<i>a</i>	1	Pair of parallel edges Line segment through origin ( <i>e</i> )	( $hk$ ) ( $\bar{h}\bar{k}$ )
<b>RECTANGULAR SYSTEM</b>				
<b><i>m</i></b>				
2	<i>b</i>	1	Pair of edges Line segment ( <i>c</i> )	( $hk$ ) ( $\bar{h}\bar{k}$ )
1	<i>a</i>	<i>.m</i>	Pair of parallel edges Line segment through origin	(10) ( $\bar{1}0$ )
			Single edge Single point ( <i>a</i> )	(01) or ( $0\bar{1}$ )
<b>2mm</b>				
4	<i>c</i>	1	Rhomb Rectangle ( <i>i</i> )	( $hk$ ) ( $\bar{h}\bar{k}$ ) ( $\bar{h}k$ ) ( $h\bar{k}$ )
2	<i>b</i>	<i>.m</i>	Pair of parallel edges Line segment through origin ( <i>g</i> )	(01) ( $0\bar{1}$ )
2	<i>a</i>	<i>.m</i>	Pair of parallel edges Line segment through origin ( <i>e</i> )	(10) ( $\bar{1}0$ )
<b>SQUARE SYSTEM</b>				
<b>4</b>				
4	<i>a</i>	1	Square Square ( <i>d</i> )	( $hk$ ) ( $\bar{h}\bar{k}$ ) ( $\bar{k}h$ ) ( $k\bar{h}$ )
<b>4mm</b>				
8	<i>c</i>	1	Ditetragon Truncated square ( <i>g</i> )	( $hk$ ) ( $\bar{h}\bar{k}$ ) ( $\bar{k}h$ ) ( $k\bar{h}$ ) ( $\bar{h}k$ ) ( $h\bar{k}$ ) ( $kh$ ) ( $\bar{k}\bar{h}$ )
4	<i>b</i>	<i>.m</i>	Square Square ( <i>f</i> )	(11) ( $\bar{1}\bar{1}$ ) ( $\bar{1}1$ ) ( $1\bar{1}$ )
4	<i>a</i>	<i>.m</i>	Square Square ( <i>d</i> )	(10) ( $\bar{1}0$ ) (01) ( $0\bar{1}$ )

10.1. CRYSTALLOGRAPHIC AND NONCRYSTALLOGRAPHIC POINT GROUPS

Table 10.1.2.1. The ten two-dimensional crystallographic point groups (cont.)

HEXAGONAL SYSTEM				
3				
3	<i>a</i>	1	Trigon Trigon ( <i>d</i> )	
				$(hki) \quad (ihk) \quad (kih)$
<b>3m1</b>				
6	<i>b</i>	1	Ditrigon Truncated trigon ( <i>e</i> )	
			Hexagon Hexagon	$(hki) \quad (ihk) \quad (kih)$ $(khi) \quad (ikh) \quad (hik)$
3	<i>a</i>	<i>.m</i>	Trigon Trigon ( <i>d</i> )	$(11\bar{2}) \quad (\bar{2}11) \quad (1\bar{2}1)$ $(\bar{1}12) \quad (211) \quad (121)$
				or $(10\bar{1}) \quad (\bar{1}10) \quad (0\bar{1}1)$ $(\bar{1}01) \quad (110) \quad (011)$
<b>31m</b>				
6	<i>b</i>	1	Ditrigon Truncated trigon ( <i>d</i> )	
			Hexagon Hexagon	$(hki) \quad (ihk) \quad (kih)$ $(khi) \quad (ikh) \quad (hik)$
3	<i>a</i>	<i>.m</i>	Trigon Trigon ( <i>c</i> )	$(10\bar{1}) \quad (\bar{1}10) \quad (0\bar{1}1)$ $(\bar{1}01) \quad (110) \quad (011)$
				or $(11\bar{2}) \quad (\bar{2}11) \quad (1\bar{2}1)$ $(\bar{1}12) \quad (211) \quad (121)$
<b>6</b>				
6	<i>a</i>	1	Hexagon Hexagon ( <i>d</i> )	
				$(hki) \quad (ihk) \quad (kih)$ $(\bar{h}\bar{k}\bar{i}) \quad (\bar{i}\bar{h}\bar{k}) \quad (\bar{k}\bar{i}\bar{h})$
<b>6mm</b>				
12	<i>c</i>	1	Dihexagon Truncated hexagon ( <i>f</i> )	$(hki) \quad (ihk) \quad (kih)$ $(\bar{h}\bar{k}\bar{i}) \quad (\bar{i}\bar{h}\bar{k}) \quad (\bar{k}\bar{i}\bar{h})$ $(\bar{k}\bar{h}\bar{i}) \quad (\bar{i}\bar{k}\bar{h}) \quad (\bar{h}\bar{i}\bar{k})$ $(khi) \quad (ikh) \quad (hik)$
6	<i>b</i>	<i>.m</i>	Hexagon Hexagon ( <i>e</i> )	$(10\bar{1}) \quad (\bar{1}10) \quad (0\bar{1}1)$ $(\bar{1}01) \quad (110) \quad (011)$
6	<i>a</i>	<i>.m</i>	Hexagon Hexagon ( <i>d</i> )	$(11\bar{2}) \quad (\bar{2}11) \quad (1\bar{2}1)$ $(\bar{1}12) \quad (211) \quad (121)$

Figure 9: 2-Dimensional point groups: a reproduction of Pages 768–769 of the ITC

through it. The fixed point is at the center of the circle. All symmetry-related points are at the same distance from the center (remember that symmetry operators are isometries), so the circle around the center locates symmetry-related points. The thin lines represent possible systems of coordinate axes (*crystal axes*) to locate the points. We have not introduced axes at this point, but we will note that the lines have the same symmetry of the pattern.

- **System:** Once again, this refers to the type of axes and choice of the unit length. The classification is straightforward.
- **Point group symbol:** It is listed in the top left corner, and it generally consists of 3 characters: a number followed by two letters (such as  $6mm$ ). When there is no symmetry along a particular direction (see below), the symbol is omitted, but it could also be replaced by a "1". For example, the point group  $m$  can be also written as  $1m1$ . The first symbol stands for one of the allowed rotation axes perpendicular to the sheet (the "primary symmetry direction"). Each of the other two symbols represent elements defined by *inequivalent* symmetry directions, known as "secondary" and "tertiary", respectively. In this case, they are *sets of mirror lines that are equivalent by rotational symmetry* or, in short, different conjugation classes. The lines associated with each symbol are not symmetry-equivalent (so they belong to different conjugation classes). For example, in the point group  $4mm$ , the first  $m$  stands for two orthogonal mirror lines. The second  $m$  stands for two other (symmetry-inequivalent) orthogonal mirror lines rotated by  $45^\circ$  with respect to the first set. Note that all the symmetry directions are equivalent for the three-fold axis 3, so either the primary or the secondary direction must carry a "1" (see below).
- **General and special positions:** Below the point group symbol, we find a list of general and special positions (points), the latter lying on a symmetry element, and therefore having fewer "equivalent points". Note that the unique point at the center is always omitted. From left to right, we find:

**Column 1** The **multiplicity**, i.e., the number of equivalent points.

**Column 2** The **Wickoff letter**, starting with  $a$  from the bottom up. Symmetry-inequivalent points with the same symmetry (i.e., lying on symmetry elements of the same type) are assigned different letters.

**Column 3** The **site symmetry**, i.e., the symmetry element (always a mirror line for 2D) on which the point lies. The site symmetry of a given point can also be thought as the **point group leaving that point invariant**. Dots are used to indicate which symmetry element in the point group symbol one refers to. For example, site  $b$  of point group  $4mm$  has symmetry  $..m$ , i.e., lies on the *second* set of mirror lines, at  $45^\circ$  from the first set.

**Column 4** Name of crystal and *point* forms (the latter in italic) and their "limiting" (or degenerate) forms. Point forms are easily understood as the polygon (or later polyhedron) defined by sets of equivalent points with a given site symmetry. Crystal forms are historically more important, because they are related to *crystal shapes*. They represent the polygon (or polyhedron) with sides (or faces) passing through a given point of symmetry and orthogonal to the radius of the circle (sphere). We shall not be further concerned with forms.

**Column 5** Miller indices. For point groups, Miller indices are best understood as related to crystal forms, and represent the inverse intercepts along the crystal axes. By the well-known "law of rational indices", real crystal faces are represented by integral Miller indices. We also note that for the hexagonal system 3 Miller indices (and 3 crystal axes) are shown, although naturally only two are needed to define coordinates.

- **Projections:** For each point group, two diagrams are shown. It is worth noting that for 3D point groups, these diagrams are *stereographic projections* of systems of equivalent points. The diagram on the **left** shows the projection circle, the crystal axes as thin lines, and a set of equivalent general positions, shown as dots. The diagram on the **right** shows the symmetry elements, using the same notation we have already introduced.
- **Settings** We note that one of the 10 2D point groups is shown twice with a different notation,  $3m1$  and  $31m$ . By inspecting the diagram, it is clear that the two only differ for the position of the crystal axes with respect of the symmetry elements. In other words, the difference is entirely conventional, and refers to the choice of axes. We refer this situation, which reoccurs throughout the ITC, as two different *settings* of the same point group.
- Unlike the case of other groups, the **group-subgroup relations** are not listed in the group entries but in a separate table.

### 3 Lecture 3: Introduction to the theory of representations

Having learned a bit about the general theory of groups, he can now hopefully make the connection with linear operators and the theory of representations:

- Each symmetry operator is an element of a group.
- When applied to *functions* (scalar or vector), the symmetry operator is linear, in the sense explained in Section 1.6.4.
- If the functions in question form a linear space, then symmetry operator *induces* a linear operator onto that space.

#### 3.1 Formal definition of a representation

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

$$g \rightarrow \hat{O}(g) \forall g \in G. \quad (30)$$

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

- Physically, the **linear space** will represent the set of all possible solutions of our problem, i.e., generally, a set of scalar or vector functions defined on a certain domain (Lecture 1).
- More abstractly, a **linear space** is a set formed by a collection of elements, (sometimes 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 remainder.
- To be a representation, the map must obey the rules:

$$\begin{aligned} \hat{O}(g \circ f) &= \hat{O}(g)\hat{O}(f) \\ \hat{O}(E) &= \hat{E} \\ \hat{O}(g^{-1}) &= \hat{O}^{-1}(g) \end{aligned} \quad (31)$$

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  $\mathfrak{32}$  onto a set of  $2 \times 2$  matrices:

$$\begin{aligned}
E &\rightarrow \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & A &\rightarrow \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \\
B &\rightarrow \begin{bmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} & K &\rightarrow \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \\
L &\rightarrow \begin{bmatrix} +\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} & M &\rightarrow \begin{bmatrix} +\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}
\end{aligned} \tag{32}$$

This is a simple case of **matrix representation**. Here, the matrices are linear operators onto the linear 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:

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{33}$$

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:

$$\hat{O}(\mathbf{t}) \left[ \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \right] = e^{-i\mathbf{k}\cdot\mathbf{t}} \left[ \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \right] \tag{34}$$

and

$$\hat{O}(\mathbf{t})\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{t}} \left[ \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \right] = \psi(\mathbf{r} - \mathbf{t}) \tag{35}$$

### 3.2 Basis sets for the linear space and matrix representations

- If the linear space in question has finite dimension, we can always introduce a finite **basis set** for it, which we shall call  $[\mathbf{a}_\mu]$ .<sup>12</sup> Each element  $\mathbf{v}$  can be written as:

<sup>12</sup>The notation here can seem rather cumbersome, due to the proliferation of subscripts and superscripts. We will use *greek lowercase letters* such as  $\mu$  and  $\nu$  to indicate elements in an array. Roman subscripts will be used to label representations (see below).

$$\begin{aligned}\mathbf{v} &= \sum_{\mu} v_{\mu} \mathbf{a}_{\mu} \\ \hat{O}(g)\mathbf{v} &= \sum_{\mu} v_{\mu} \hat{O}(g)\mathbf{a}_{\mu}\end{aligned}\quad (36)$$

Writing

$$\hat{O}(g)\mathbf{a}_{\mu} = \sum_{\nu} D_{\mu\nu}(g)\mathbf{a}_{\nu}\quad (37)$$

we obtain

$$\begin{aligned}\hat{O}(g)\mathbf{v} &= \sum_{\mu,\nu} D_{\mu\nu}(g)v_{\mu}\mathbf{a}_{\nu} \\ \left[\hat{O}(g)\mathbf{v}\right]_{\nu} &= \sum_{\mu} D_{\mu\nu}(g)v_{\mu}\end{aligned}\quad (38)$$

- $D_{\mu\nu}(g)$  is clearly a matrix. The map  $g \rightarrow D_{\mu\nu}(g)$  is called the **matrix representation** of the original representation  $g \rightarrow \hat{O}(g)$  **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**.

### 3.2.1 Abstract representations and matrix representations

- As we have just seen, all the matrix representations of the same representation onto a *given* linear space are related by a similarity transformation. Since all linear spaces with the same dimension are isomorphic, we can extend this definition to different linear 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 linear space they operate on.

**Notation:** we indicate such abstract representations with the greek letter  $\Gamma$ .  $\Gamma_1, \Gamma_2$ , 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  $D_{\mu\nu}^{\Gamma}(g)$ .

### 3.2.2 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 linear space. Tables 1 and 2 show the two matrix representations for Cartesian basis  $[\hat{i}, \hat{j}, \hat{k}]$  and  $[\hat{i} + \hat{j}, -\hat{i} + \hat{j}, \hat{k}]$ , 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  $[\hat{i}, \hat{j}, \hat{k}]$ .

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

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

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

- 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. ,  $[\hat{O}(g)] [\hat{O}(g)]^\dagger = 1$ ). 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 1.6.2 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:  $dx dy dz = dX dY dZ$ . We can therefore conclude that  $\hat{O}^\dagger \hat{O}$  is the identity, so  $\hat{O}$  is unitary if it is linear.

$$\forall \psi, \langle \psi | \hat{O}^\dagger \hat{O} | \psi \rangle = \langle \psi | \psi \rangle \Rightarrow \hat{O}^\dagger \hat{O} = \hat{E} \quad (39)$$

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

### 3.2.3 Traces and determinants: characters of a representation

- We remind the following properties of the trace and determinant of a square matrix:
  - ◊  $\text{tr}(A + B) = \text{tr}(A) + \text{tr}(B)$ ;  $\text{tr}(cA) = c \text{tr}(A)$ ;  $\text{tr}(AB) = \text{tr}(BA)$ ;  
 $\text{tr}(A^T) = \text{tr}(A)$ ;  $\text{tr}(PAP^{-1}) = \text{tr}(A)$ .
  - ◊  $\det(A^T) = \det(A)$ ;  $\det(A^{-1}) = 1/\det(A)$ ;  $\det(AB) = \det(A) \det(B)$ ;  
 $\det(PAP^{-1}) = \det(A)$ .
- 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.



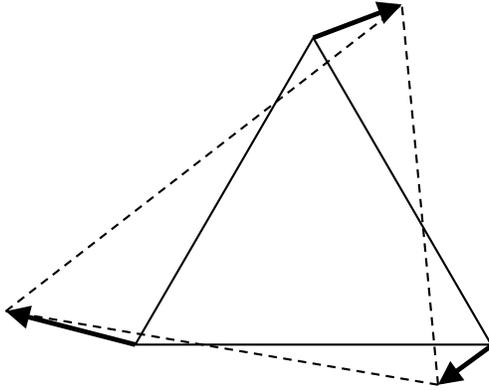


Figure 10: . A generic mode in the space of all possible configurations of polar vectors at the corners of a triangle. Modes such as this in general lose all the symmetry of the original pattern.

$$a |1\rangle + b |2\rangle + c |5\rangle = \begin{bmatrix} a \\ b \\ \cdot \\ \cdot \\ c \\ \cdot \end{bmatrix} \quad (41)$$

**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):

$$\begin{aligned}
[A] &= \begin{bmatrix} \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot \end{bmatrix} & [K] &= \begin{bmatrix} \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & -1 \\ \cdot & \cdot & \cdot & \cdot & -1 & \cdot \\ \cdot & \cdot & \cdot & -1 & \cdot & \cdot \end{bmatrix} \\
[B] &= \begin{bmatrix} \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot \end{bmatrix} & [L] &= \begin{bmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & -1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & -1 \\ \cdot & \cdot & \cdot & \cdot & -1 & \cdot \end{bmatrix} \\
[E] &= \begin{bmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{bmatrix} & [M] &= \begin{bmatrix} \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & -1 & \cdot \\ \cdot & \cdot & \cdot & -1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & -1 \end{bmatrix}
\end{aligned}
\tag{42}$$

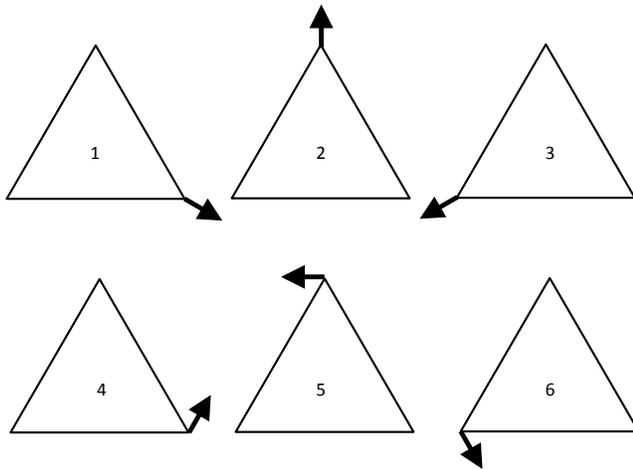


Figure 11: . A simple basis set for the space of all possible configurations of polar vectors at the corners of a triangle.

- These arrays are already in block-diagonal form (two  $3 \times 3$  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.
- Fig. 12 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).

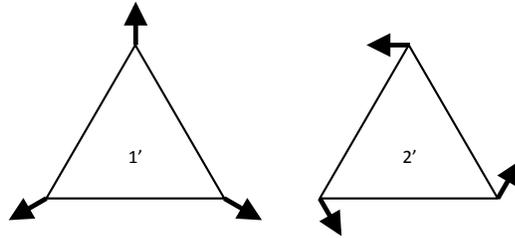


Figure 12: . Two  $3_2$  modes retaining a higher degree of symmetry. Mode  $m'_1$  is totally symmetric with respect to all symmetry operators. Mode  $m'_2$  is symmetric by the two 3-fold rotations (and the identity) and antisymmetric by the 2-fold rotations.

### 3.5 Example: representation of the cyclic group $3$ onto the space of quadratic polynomials

**The group:** the cyclic group  $3$  is a sub-group of  $3_2$ , and has only 3 elements:  $E, A, B$ . Unlike  $3_2$ ,  $3$  is an Abelian group.

**The linear 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:

$$f_1 = x^2; f_2 = y^2; f_3 = z^2; f_4 = xy; f_5 = xz; f_6 = yz \quad (43)$$

**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:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \frac{1}{2}(-x + \sqrt{3}y) \\ \frac{1}{2}(-\sqrt{3}x - y) \\ z \end{bmatrix} \quad (44)$$

this produced the following set of rotated basis functions:

$$\begin{aligned}
 f'_1 &= \frac{1}{4} (x^2 + 3y^2 - 2\sqrt{3}xy) \\
 f'_2 &= \frac{1}{4} (3x^2 + y^2 + 2\sqrt{3}xy) \\
 f'_3 &= z^2 \\
 f'_4 &= \frac{1}{4} (\sqrt{3}x^2 - \sqrt{3}y^2 - 2xy) \\
 f'_5 &= \frac{1}{2} (-xz + \sqrt{3}yz) \\
 f'_6 &= \frac{1}{2} (-\sqrt{3}xz - yz)
 \end{aligned} \tag{45}$$

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

$$\begin{bmatrix}
 \frac{1}{4} & \frac{3}{4} & 0 & \frac{\sqrt{3}}{4} & 0 & 0 \\
 \frac{3}{4} & \frac{1}{4} & 0 & -\frac{\sqrt{3}}{4} & 0 & 0 \\
 0 & 0 & 1 & 0 & 0 & 0 \\
 -\frac{\sqrt{3}}{2} & \frac{\sqrt{3}}{2} & 0 & -\frac{1}{2} & 0 & 0 \\
 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\
 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2}
 \end{bmatrix} \tag{46}$$

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

$$\begin{bmatrix}
 \frac{1}{4} & \frac{3}{4} & \frac{\sqrt{3}}{4} & 0 & 0 & 0 \\
 \frac{3}{4} & \frac{1}{4} & -\frac{\sqrt{3}}{4} & 0 & 0 & 0 \\
 -\frac{\sqrt{3}}{2} & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 \\
 0 & 0 & 0 & 1 & 0 & 0 \\
 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\
 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2}
 \end{bmatrix} \tag{47}$$

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.

### 3.6 \* 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 linear 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. 13, where + and - indicates +1 and -1.

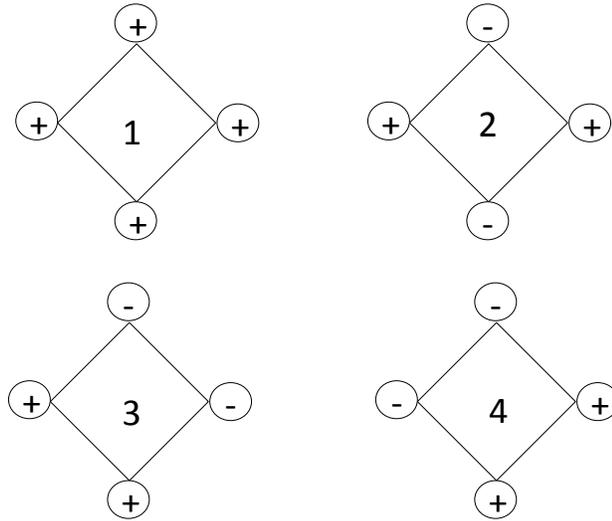


Figure 13: . A basis set for the space of scalar functions on a square.

**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  $4 \times 4$  matrix representation. Modes  $|3\rangle$  and  $|4\rangle$  are transformed either into themselves or into each other. This is illustrated in tab. 3.

- 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. 14. 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.

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
$\begin{bmatrix}  3\rangle \\  4\rangle \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$

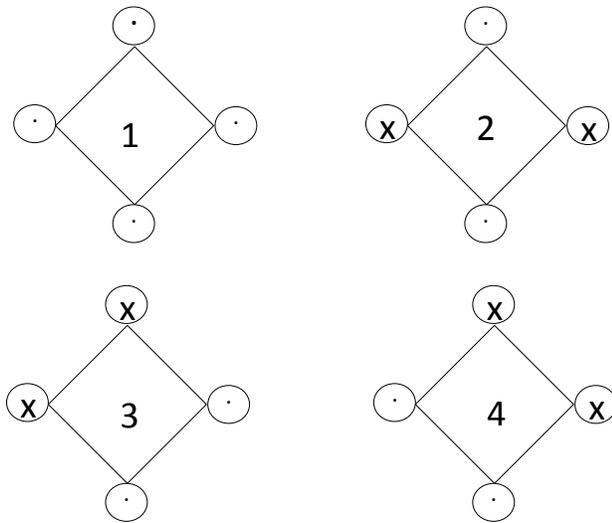


Figure 14: . A basis set for the space of  $z$ -vector functions on a square.

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

## 4 Lecture 4: 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
$\Gamma_1$	1	1	1	1	1	1
$\Gamma_2$	1	1	1	-1	-1	-1
$\Gamma_3$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} +\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} +\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$



Figure 15: . A matrix representation for 3 *irreps* of for the point group 32 . The modes in fig. 12 are basis vectors for  $\Gamma_1$  and  $\Gamma_2$ . The appropriate basis vectors for  $\Gamma_3$  in the space of ordinary 2D vectors are indicated.

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
$\Gamma_1$	1	1	1	1	1	1
$\Gamma_2$	1	1	1	-1	-1	-1
$\Gamma_3$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} +\frac{\sqrt{3}}{2} & +\frac{1}{2} \\ +\frac{1}{2} & -\frac{\sqrt{3}}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{\sqrt{3}}{2} & +\frac{1}{2} \\ +\frac{1}{2} & +\frac{\sqrt{3}}{2} \end{pmatrix}$



Figure 16: . Same as fig. 15, but with a different set of basis vector and matrix representation for  $\Gamma_3$ . The transformation matrix from the basis in fig. 15 is indicated.

Point group 32 – variant 3

$$U = \frac{\sqrt{2}}{3} \begin{pmatrix} \frac{\sqrt{3}}{2}(1-e^{-i\omega}) & -\frac{1}{2}(1+e^{-i\omega})+e^{+i\omega} \\ \frac{\sqrt{3}}{2}(1-e^{+i\omega}) & -\frac{1}{2}(1+e^{+i\omega})+e^{-i\omega} \end{pmatrix}$$

$UMU^{-1}$

	E	A	B	K	L	M
$\Gamma_1$	1	1	1	1	1	1
$\Gamma_2$	1	1	1	-1	-1	-1
$\Gamma_3$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2}+\frac{\sqrt{3}}{2} & 0 \\ 0 & -\frac{1}{2}-\frac{\sqrt{3}}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2}-\frac{\sqrt{3}}{2} & 0 \\ 0 & -\frac{1}{2}+\frac{\sqrt{3}}{2} \end{pmatrix}$	$\begin{pmatrix} 0 & -\frac{1}{2}-\frac{\sqrt{3}}{2} \\ -\frac{1}{2}+\frac{\sqrt{3}}{2} & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -\frac{1}{2}+\frac{\sqrt{3}}{2} \\ -\frac{1}{2}-\frac{\sqrt{3}}{2} & 0 \end{pmatrix}$

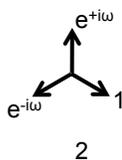
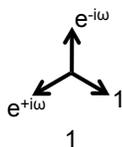


Figure 17: . Same as fig. 15 and 16 , but with a different set of (complex) basis vector and matrix representation for  $\Gamma_3$ . The transformation matrix from the basis in fig. 15 is indicated.

- To start answering these questions, let us look at 3 *irreps* of the point group 32 we have already encountered (see figs 15, 16 and 17). The modes

in fig. 12 are basis vectors for  $\Gamma_1$  and  $\Gamma_2$ , which are obviously irreducible since they are 1-dimensional.  $\Gamma_3$  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 15, 16 and 17 show 3 different matrix representations (and basis vectors) for  $\Gamma_3$ .

- 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* 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  $\Gamma_1$ ,  $-1$  for  $\Gamma_2$  and 0 for  $\Gamma_3$ . As already mentioned, we call this trace the **character** of the *irrep* for a given class<sup>14</sup>. 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*  $\Gamma_1$  and  $\Gamma_2$  and one of the 4 elements of the representative matrices for the 2D *irrep*  $\Gamma_3$ . For example, for the table in fig. 15 we get the following 6 arrays:

$$\begin{array}{cccccc}
 1 & 1 & 1 & 1 & 1 & 1 \\
 1 & 1 & 1 & -1 & -1 & -1 \\
 1 & -\frac{1}{2} & -\frac{1}{2} & -1 & +\frac{1}{2} & +\frac{1}{2} \\
 0 & -\frac{\sqrt{3}}{2} & +\frac{\sqrt{3}}{2} & 0 & -\frac{\sqrt{3}}{2} & +\frac{\sqrt{3}}{2} \\
 0 & +\frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 & -\frac{\sqrt{3}}{2} & +\frac{\sqrt{3}}{2} \\
 1 & -\frac{1}{2} & -\frac{1}{2} & 1 & -\frac{1}{2} & -\frac{1}{2}
 \end{array} \quad (48)$$

- ◊ 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  $\Gamma_1$  and  $\Gamma_2$  and  $\sqrt{3}$  for  $\Gamma_3$ , 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 16, although the arrays for  $\Gamma_3$  are clearly different.
- We can also verify that the same properties apply to the table in fig 18, which contains 5 *irreps* of the point group 422.

<sup>14</sup>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.

- The table in figs 17, is slightly different, because the matrix elements are complex<sup>15</sup>. The 6 arrays are:

$$\begin{array}{cccccc}
 1 & 1 & 1 & 1 & 1 & 1 \\
 1 & 1 & 1 & -1 & -1 & -1 \\
 1 & -\frac{1}{2} + i\frac{\sqrt{3}}{2} & -\frac{1}{2} - i\frac{\sqrt{3}}{2} & 0 & 0 & 0 \\
 0 & 0 & 0 & -\frac{1}{2} - i\frac{\sqrt{3}}{2} & 1 & -\frac{1}{2} + i\frac{\sqrt{3}}{2} \\
 0 & 0 & 0 & -\frac{1}{2} + i\frac{\sqrt{3}}{2} & 1 & -\frac{1}{2} - i\frac{\sqrt{3}}{2} \\
 1 & -\frac{1}{2} - i\frac{\sqrt{3}}{2} & -\frac{1}{2} + i\frac{\sqrt{3}}{2} & 0 & 0 & 0
 \end{array} \quad (49)$$

- 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**:

$$\sum_g D(g)_{\mu\nu}^{\Gamma_i} D^*(g)_{\mu'\nu'}^{\Gamma_j} = \frac{h}{l_i} \delta_{ij} \delta_{\mu\mu'} \delta_{\nu\nu'} \quad (50)$$

Point group 422 (one of the variants)

	$E$	$2_z$	$4^+$	$4^-$	$2_x$	$2_y$	$2_{xy}$	$2_{x\bar{y}}$
$\Gamma_1$	1	1	1	1	1	1	1	1
$\Gamma_2$	1	1	1	1	-1	-1	-1	-1
$\Gamma_3$	1	1	-1	-1	1	1	-1	-1
$\Gamma_4$	1	1	-1	-1	-1	-1	1	1
$\Gamma_5$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$

Figure 18: . A matrix representation for 5 *irreps* of for the point group 422 .

<sup>15</sup>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  $g = g^{-1}$ .

- The *orthogonality* relation in eq. 50 can be easily converted into an *orthonormality relation* by normalising all the arrays with the coefficient  $\sqrt{l_j/h}$ .

#### 4.1 The Wonderful Orthogonality Theorem and its implications

- Amazingly, eq. 50 **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)<sup>16</sup>, 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:

$$\sum_j l_j^2 \leq h \quad (51)$$

As we will see later it is the strict = sign that holds in eq. 51.

#### 4.2 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. 19.

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<sup>16</sup>The general relation valid for non-orthogonal matrices is  $\sum_g D(g)_{\mu\nu}^i D(g^{-1})_{\nu'\mu'}^j = (h/l_i)\delta_{ij}\delta_{\mu\mu'}\delta_{\nu\nu'}$

Point group 32 – Character Table (full group)

	E	A	B	K	L	M
$\Gamma_1$	1	1	1	1	1	1
$\Gamma_2$	1	1	1	-1	-1	-1
$\Gamma_3$	2	-1	-1	0	0	0

Point group 32 – Character Table(classes)

	E	2A	3K
$\Gamma_1$	1	1	1
$\Gamma_2$	1	1	-1
$\Gamma_3$	2	-1	0

Figure 19: 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.

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

$$tr(D(g)^{\Gamma_i}) = \sum_{\mu} D(g)_{\mu\mu}^{\Gamma_i} \quad (52)$$

- 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  $\Gamma_3$  is:

$$\begin{aligned} [ 2 \quad -1 \quad -1 \quad 0 \quad 0 \quad 0 ] &= [ 1 \quad -\frac{1}{2} \quad -\frac{1}{2} \quad -1 \quad +\frac{1}{2} \quad +\frac{1}{2} ] \\ &+ [ 1 \quad -\frac{1}{2} \quad -\frac{1}{2} \quad +1 \quad -\frac{1}{2} \quad -\frac{1}{2} ] \quad (53) \end{aligned}$$

the arrays to the right of the = sign being arrays 3 and 6 in eq. 48. Since these are orthogonal to all the other arrays in eq. 48, 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*  $\Gamma_i$ , we obtain the following **WOT for characters - full group version**.

$$\sum_g \chi(g)^{\Gamma_i} \chi^*(g)^{\Gamma_j} = h \delta_{ij} \quad (54)$$

- This can be easily modified for application to the class version of the character table, e.g., fig. 19 (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. 19 — bottom panel), eq. 54 becomes the **WOT for characters - classes version**:

$$\sum_k N_k \chi(C_k)^{\Gamma_i} \chi^*(C_k)^{\Gamma_j} = h \delta_{ij} \quad (55)$$

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

$$\left[ \sqrt{\frac{N_1}{h}} \chi(C_1)^{\Gamma_i}, \sqrt{\frac{N_2}{h}} \chi(C_2)^{\Gamma_i}, \dots, \sqrt{\frac{N_n}{h}} \chi(C_n)^{\Gamma_i} \right] \quad (56)$$

are orthonormal for different  $i$ 's.

- Eq. 55 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

$$N_{irreps} \leq N_{classes} \quad (57)$$

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

### 4.3 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  $\Gamma_{red}$ :

$$[\chi(g_1)^{\Gamma_{red}}, \chi(g_2)^{\Gamma_{red}}, \dots, \chi(g_h)^{\Gamma_{red}}] = \sum_i a_i [\chi(g_1)^{\Gamma_i}, \chi(g_2)^{\Gamma_i}, \dots, \chi(g_h)^{\Gamma_i}] \quad (58)$$

or

$$[\chi(C_1)^{\Gamma_{red}}, \chi(C_2)^{\Gamma_{red}}, \dots, \chi(C_n)^{\Gamma_{red}}] = \sum_i a_i [\chi(C_1)^{\Gamma_i}, \chi(C_2)^{\Gamma_i}, \dots, \chi(C_n)^{\Gamma_i}] \quad (59)$$

- The coefficients  $a_i$  are integers indicating the **number of times irrep  $\Gamma_i$  appears in the decomposition of reducible representation  $\Gamma$**  — in other words, the number of identical (or better similar) diagonal blocks corresponding to *irrep*  $\Gamma_i$  along the diagonal, once  $\Gamma$  is fully decomposed.
- Eq. 58 can be inverted exploiting the orthonormality relation, to find the coefficients:

$$a_j = \frac{1}{h} \sum_g [\chi(g)^{\Gamma_j}]^* \chi(g)^{\Gamma_{red}} \quad (60)$$

or, for classes

$$a_j = \sum_k \frac{N_k}{h} [\chi(C_k)^{\Gamma_j}]^* \chi(C_k)^{\Gamma_{red}} \quad (61)$$

**Example:** let us look again at the example given on page 35 — 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. 19), and we know that we cannot have more than 3, since 32 has 3 classes (eq. 57), so we can be confident we have found all the 32 *irreps*. We can also see that

$$\sum_j l_j^2 = 1^2 + 1^2 + 2^2 = 6 = h \quad (62)$$

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

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

by applying eq. 60 we obtain

$$a_1 = 1; a_2 = 1; a_3 = 2 \quad (63)$$

We write:

$$\Gamma_{red} = \Gamma_1 + \Gamma_2 + 2\Gamma_3 \quad (64)$$

which means that  $\Gamma_1$  and  $\Gamma_2$  appear *once* in the decomposition of  $\Gamma_{red}$ , while  $\Gamma_3$  appears *twice*.

#### 4.4 Second WOT for characters and number of *irreps*

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

$$\begin{bmatrix} \sqrt{\frac{N_1}{h}} \chi(C_1)^{r_1}, \sqrt{\frac{N_2}{h}} \chi(C_2)^{r_1}, \dots, \sqrt{\frac{N_n}{h}} \chi(C_n)^{r_1} \\ \sqrt{\frac{N_1}{h}} \chi(C_1)^{r_2}, \sqrt{\frac{N_2}{h}} \chi(C_2)^{r_2}, \dots, \sqrt{\frac{N_n}{h}} \chi(C_n)^{r_2} \\ \dots \\ \sqrt{\frac{N_1}{h}} \chi(C_1)^{r_n}, \sqrt{\frac{N_2}{h}} \chi(C_2)^{r_n}, \dots, \sqrt{\frac{N_n}{h}} \chi(C_n)^{r_n} \end{bmatrix} \quad (65)$$

are orthonormal arrays.

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

$$\sum_i \chi(C_k)^{r_i} [\chi(C_{k'})^{r_i}]^* = \frac{h}{N_k} \delta_{kk'} \quad (66)$$

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

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

#### 4.5 \* 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. 6 for our usual group  $32$ , and let's rearrange the order of rows and columns so that all the identity elements  $E$  fall on the diagonal, as in fig. 20. It is easy to see that this is always possible for any finite group.
- 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. 20, 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.

$D_3 (32)$

		Applied first →					
		E	B	A	K	L	M
↑ Applied second	E	E	B	A	K	L	M
	A	A	E	B	L	M	K
	B	B	A	E	M	K	L
	K	K	L	M	E	B	A
	L	L	M	K	A	E	B
	M	M	K	L	B	A	E

Figure 20: Multiplication table for the point group  $32 (D_3)$ , rearranged to contract the regular representation.

- 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:

$$a_j = \frac{1}{h} \sum_g [\chi(g)^{\Gamma_j}]^* \chi(g)^{\Gamma_{reg}} = l_j \quad (67)$$

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  $\Gamma_{reg}$  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:

$$\sum_j l_j^2 = h \quad (68)$$

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>.

## 5 Lecture 5: Applications of representations to physics problems

### 5.1 Quantum mechanical problems: the symmetry of the Hamiltonian

- Let us first recall our definition of symmetry transformations for functions and their gradients from Section 1.6.2:

$$\begin{aligned} T_g[f(\mathbf{x})] &= f(R^{-1}(g)\mathbf{x} - R^{-1}(g)\mathbf{t}) \\ T_g[\nabla f(\mathbf{x})] &= (R(g)\nabla) f(R^{-1}(g)\mathbf{x} - R^{-1}(g)\mathbf{t}) \end{aligned} \quad (69)$$

where  $T_g[\ ]$  is the alibi transformation associated with group element  $g$ . We have not proven explicitly the second line of eq. 69, but its derivation is simple and completely analogous to the general transformation for **vector functions**.

- Since all transformations we are interested in here are isometric (i.e., preserve the norm), and noting that  $\nabla^2 = \nabla \cdot \nabla$ , it also follows that

$$T_g[\nabla^2 f(\mathbf{x})] = \nabla^2 f(R^{-1}(g)\mathbf{x} - R^{-1}(g)\mathbf{t}) = \nabla^2 T_g[f(\mathbf{x})] \quad (70)$$

- As introduced in eq. 30, the mapping  $g \rightarrow \hat{O}(g) \forall g \in G$  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. 69, then the operator  $\hat{O}(g)$  *commutes* with the Hamiltonian:

$$\begin{aligned} \hat{O}(g)\hat{H}\psi(\mathbf{x}) &= \left( -\frac{\nabla^2}{2m} + U(R^{-1}(g)\mathbf{x} - R^{-1}(g)\mathbf{t}) \right) \psi(R^{-1}(g)\mathbf{x} - R^{-1}(g)\mathbf{t}) \\ \hat{H}\hat{O}(g)\psi(\mathbf{x}) &= \left( -\frac{\nabla^2}{2m} + U(\mathbf{x}) \right) \psi(R^{-1}(g)\mathbf{x} - R^{-1}(g)\mathbf{t}) \end{aligned} \quad (71)$$

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

$$\hat{H}\hat{O}(g)\phi(\mathbf{x}) = \hat{O}(g)\hat{H}\phi(\mathbf{x}) = \lambda\hat{O}(g)\phi(\mathbf{x}) \quad (72)$$

2. If  $\phi(\mathbf{x})$  is a **non-degenerate eigenstate** of  $\hat{H}$ , then the map  $g \rightarrow \hat{O}(g)$  onto the one-dimensional subspace defined by  $\phi(\mathbf{x})$  is a *one-dimensional irreducible representation of  $G$* . In fact, since the eigenvector is non-degenerate, it must necessarily be  $\hat{O}(g)\phi(\mathbf{x}) = c\phi(\mathbf{x}) \forall g$ ,  $c$  being a *unitary constant*, and this is precisely the definition of a one-dimensional irreducible representation.
3. If  $\phi_1(\mathbf{x}) \dots \phi_n(\mathbf{x})$  are **degenerate eigenstates** of  $\hat{H}$  defining a subspace of the Hilbert space of dimension  $n$ , then the map  $g \rightarrow \hat{O}(g)$  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  $\phi_i(\mathbf{x})$  of the degenerate subspace and for every  $g$ ,  $\hat{O}(g)\phi_i(\mathbf{x})$  is an eigenstate with the same eigenvalue, so

$$\hat{O}(g)\phi_i(\mathbf{x}) = \sum_j c_j \phi_j(\mathbf{x}) \quad (73)$$

Therefore the application of  $\hat{O}(g)$  is *closed* within the  $\phi_i(\mathbf{x})$  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  $\phi_i(\mathbf{x})$  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  $g \rightarrow \hat{O}(g)$  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  $g \rightarrow \hat{O}(g)$  is *not necessarily*

a set of eigenstates for the Hamiltonian. The problem arises when a particular irreducible representation  $\Gamma$  of the group  $\{g\}$  **appears more than once** in the decomposition of the representation  $g \rightarrow \hat{O}(g)$ .

- Note that if  $\xi_1(\mathbf{x}) \dots \xi_n(\mathbf{x})$  are a basis set for a certain  $n$ -dimensional irrep, then  $\hat{H}\xi_1(\mathbf{x}) \dots \hat{H}\xi_n(\mathbf{x})$  are a basis set of the same irrep *with the same matrices*. This follows straightforwardly from commutativity between  $\hat{H}$  and  $\hat{O}$  and linearity of the two operators. If the irrep is contained only once in the total representation, then the two spaces generated by the two sets of basis vectors must necessarily coincide.

**Example;** let's consider two sets of eigenstates,  $\phi_1(\mathbf{x}) \dots \phi_n(\mathbf{x})$  with eigenvalue  $\lambda_1$  and  $\psi_1(\mathbf{x}) \dots \psi_n(\mathbf{x})$ , with eigenvalue  $\lambda_2$ . Let us also assume that both sets transform with the *same* irreducible matrix representation  $\Gamma_i$ , which would therefore appear more than once in the decomposition of  $g \rightarrow \hat{O}(g)$ . It is easy to see that the set  $a\phi_1(\mathbf{x}) + b\psi_1(\mathbf{x}) \dots a\phi_n(\mathbf{x}) + b\psi_n(\mathbf{x})$  ( $a$  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.

## 5.2 \* 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.

$$\begin{aligned}\mathcal{E}_K &= \frac{1}{2} \sum_i m_i \dot{x}_i^2 \\ \mathcal{E}_P &= \frac{1}{2} \sum_{i,j} \frac{\partial^2 U}{\partial x_i \partial x_j} x_i x_j\end{aligned}\quad (74)$$

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**:

$$\xi_i = x_i \sqrt{m_i} \quad (75)$$

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

$$\begin{aligned}\mathcal{E}_K &= \frac{1}{2} \sum_i \dot{\xi}_i^2 \\ \mathcal{E}_P &= \frac{1}{2} \sum_{i,j} \left( \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 U}{\partial x_i \partial x_j} \right) \xi_i \xi_j\end{aligned}\quad (76)$$

2. We write the equation of motion as:

$$\ddot{\xi}_i + \sum_j \left( \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 U}{\partial x_i \partial x_j} \right) \xi_j = 0 \quad (77)$$

3. We seek solution of the form

$$\xi_i = q_i e^{i\omega t} \quad (78)$$

from which we derive the secular equation

$$\omega^2 q_i = \sum_j \left( \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 U}{\partial x_i \partial x_j} \right) q_j = \sum_j V_{ij} q_j \quad (79)$$

Eq. 79 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 **linear space** as the space of all **modes**, defined as  $[q_{1x}, q_{1y}, q_{1z}, q_{2x} \dots]$ . 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  $\Gamma$  of the symmetry group of the potential energy  $U$  onto this linear 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 3.4 (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  $\Gamma$  in terms of the *irreps* of  $G$ . In particular, **the multiplet structure of the solution is deduced entirely by symmetry**. If an *irrep*  $\Gamma_i$  appears more than once in the decomposition of  $\Gamma$ , 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.

### 5.3 Extended example: normal modes of the square molecule

- We illustrate these concepts with the concrete example of a square harmonic molecule, illustrate in fig.21 . 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.

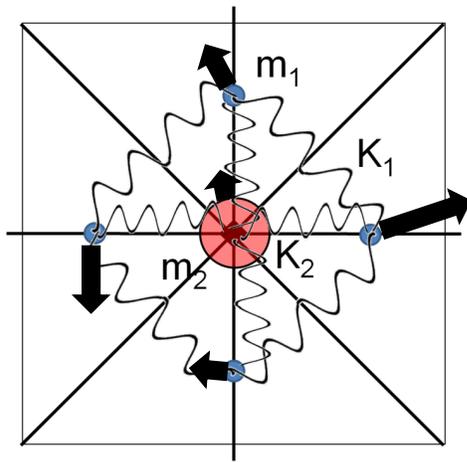


Figure 21: A snapshot of a vibrating square molecule, with the arrows represent a generic mode. This can be obtained as a linear combination of basis modes.

- 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. 79) are illustrated in fig. 22. 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).

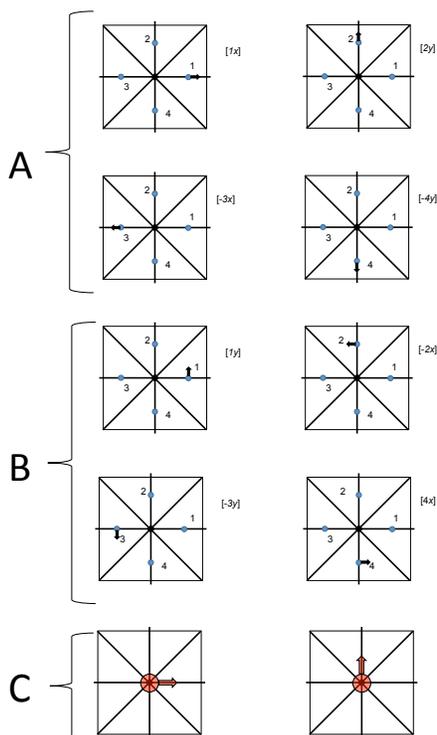


Figure 22: The 10 modes in the square molecule dynamical matrix, slightly rearranged to show that the representation can be reduced.

- It is also possible to determine the characters of the reducible representation  $\Gamma$  without constructing all the matrices.
  - ◊ The character of the identity is *always* equal to the dimension of  $\Gamma$  — in this case 10.
  - ◊ There is no mode in fig. 22 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.
  - ◊ 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  $\Gamma$  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  $1^2 + 1^2 + 1^2 + 1^2 + 2^2 = 8 = h$ .
- The character table can be constructed, for example, from fig. 18:

	E	$2_z$	$2(4^+)$	$2(2_x)$	$2(2_{xy})$
$\Gamma_1$	1	1	1	1	1
$\Gamma_2$	1	1	1	-1	-1
$\Gamma_3$	1	1	-1	1	-1
$\Gamma_4$	1	1	-1	-1	1
$\Gamma_5$	2	-2	0	0	0

- By applying eq. 61 or simply by inspection, one can decompose  $\Gamma$  into its irreducible components:

$$\Gamma = \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 3\Gamma_5 \quad (80)$$

- As one can see, 1-dimensional *irreps*  $\Gamma_1$ ,  $\Gamma_2$ ,  $\Gamma_3$  and  $\Gamma_4$  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. 23 .
- Mode  $\Gamma_4$  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  $\Gamma_5$ . 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. 26.
- One can see that these are generic linear combinations of the modes shown in fig. 24 and 25, 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.

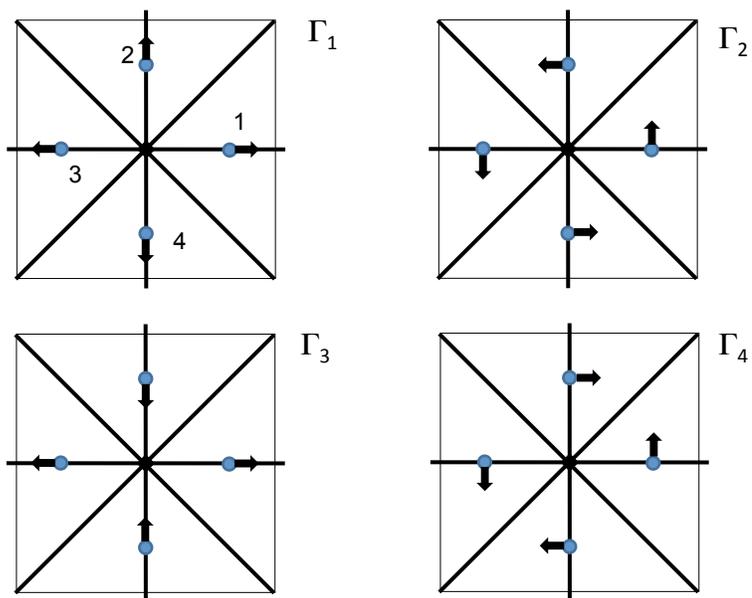


Figure 23: The four “1 dimensional modes” of the square molecule. These modes transform into either themselves (symmetric) or minus themselves (antisymmetric) upon all symmetries of the molecule.

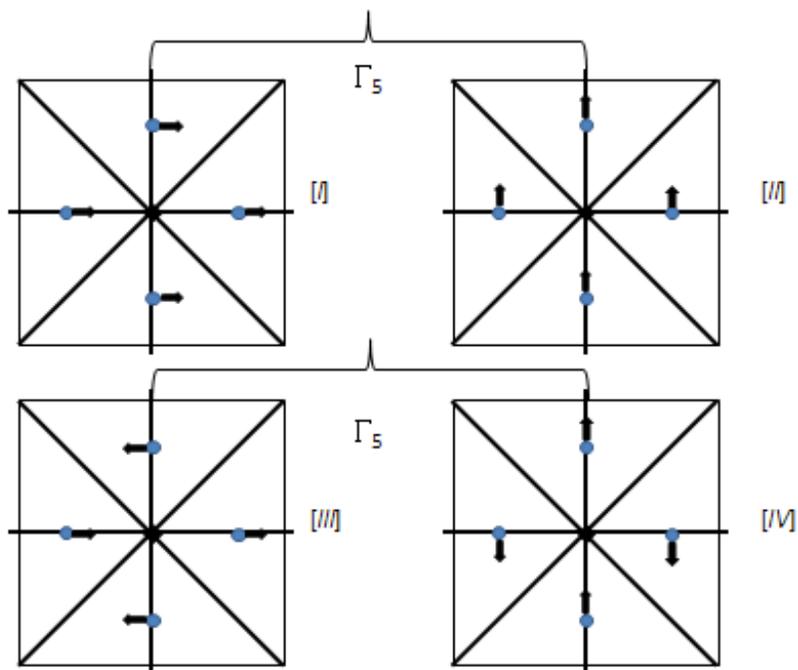


Figure 24: The four “2 dimensional modes” of the square molecule for the corner atoms. These modes transform into either  $\pm$  themselves (symmetric/antisymmetric) or *into each other in pairs* upon all symmetries of the molecule. Note that all these modes are *antisymmetric* upon 2-fold rotation.

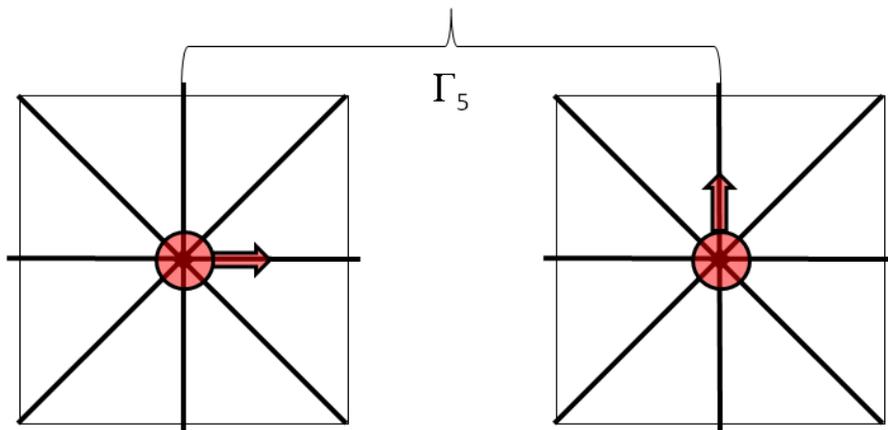


Figure 25: The two central-atom modes of the square molecule. One can verify that they transform as the "2-D" corner modes, i.e., with the representation  $\Gamma_5$

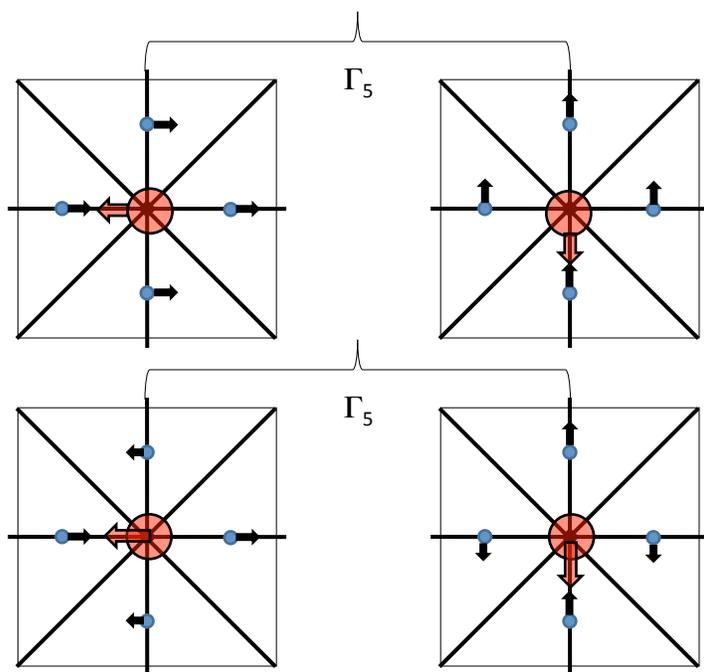


Figure 26: Examples of non-zero-frequency normal modes of  $\Gamma_5$  symmetry involving two-atom displacements. The exact mixing coefficient depend on the mass and spring constant parameters.

## 6 Lecture 6: Projectors, subduction and group product

In this section, we will finally answer question 6 on page 41, by constructing the **projection operators** (*projectors*), which will enable us to generate the 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 help to construct representations and decompose them into *irreps* for several physically relevant problems.

### 6.1 Projectors

- As the name suggests, projectors project an arbitrary element of the linear 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  $D_{\mu\nu}^{\Gamma_i}(g)$ , in other words, the matrix elements of a specific matrix representation of the *irrep*  $\Gamma_i$ . More precisely:

$$\hat{P}_{\mu\nu}^{\Gamma_i} = \frac{l_i}{h} \sum_g [D_{\mu\nu}^{\Gamma_i}(g)]^* \hat{O}(g) \quad (81)$$

- 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

$$\mathbf{v} = \sum_{\substack{i=1, \dots, n \\ \kappa=1, \dots, l_i}} a_{i\kappa} \mathbf{v}_{i\kappa} \quad (82)$$

be a generic vector in the linear space. The sum over  $j$  runs over the *irreps*, while the sum over  $\kappa$  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

$$\hat{P}_{\mu\nu}^{\Gamma_i} \mathbf{v} = a_{i\nu} \mathbf{v}_{i\mu} \quad (83)$$

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

$$\hat{P}_{\mu\nu}^{\Gamma_i} \mathbf{v} = \sum_p a_{i\nu}^p \mathbf{v}_{i\mu}^p \quad (84)$$

where the sum over  $p$  is over the multiple instances of  $\Gamma_i$ .

- Let us verify this latest result explicitly. Let

$$\mathbf{v} = \sum_{j,p,\kappa} a_{j\kappa}^p \mathbf{v}_{j\kappa}^p \quad (85)$$

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

$$\hat{O}(g) \mathbf{v}_{j\kappa}^p = \sum_\lambda D_{\lambda\kappa}^{\Gamma_j}(g) \mathbf{v}_{j\lambda}^p \quad (86)$$

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

$$\begin{aligned} \hat{P}_{\mu\nu}^{\Gamma_i} \mathbf{v} &= \frac{l_i}{h} \sum_g [D_{\mu\nu}^{\Gamma_i}(g)]^* \sum_{j,p,\kappa} a_{j\kappa}^p \sum_\lambda D_{\lambda\kappa}^{\Gamma_j}(g) \mathbf{v}_{j\lambda}^p \\ &= \sum_{j,p,\kappa,\lambda} \left\{ \frac{l_i}{h} \sum_g [D_{\mu\nu}^{\Gamma_i}(g)]^* D_{\lambda\kappa}^{\Gamma_j}(g) \right\} a_{j\kappa}^p \mathbf{v}_{j\lambda}^p \\ &= \sum_{j,p,\kappa,\lambda} \{ \delta_{\mu\lambda} \delta_{\nu\kappa} \delta_{ij} \} a_{j\kappa}^p \mathbf{v}_{j\lambda}^p \\ &= \sum_p a_{i\nu}^p \mathbf{v}_{i\mu}^p \end{aligned} \quad (87)$$

where the last line of 87 is identical to 84. The delta functions in the curly brackets are from the WOT.

- In all cases,  $\hat{P}_{\mu\nu}^{\Gamma_i} \mathbf{v}$  is an element of the invariant subspace of  $\Gamma_i$ . It can, however, be **zero**, if the vector  $\mathbf{v}$  has no component on the subspace spanned by  $\Gamma_i$ .
- If they are non-zero, these  $\hat{P}_{\mu\nu}^{\Gamma_i} \mathbf{v}$  for *fixed*  $\nu$  and *different*  $\mu$  (i.e., for matrix elements of the same columns) represent *unnormalised* basis functions for  $\Gamma_i$ . We can verify this explicitly:

$$\begin{aligned} \hat{O}(g) \left[ \sum_p a_{i\nu}^p \mathbf{v}_{i\mu}^p \right] &= \sum_p a_{i\nu}^p \sum_\lambda D_{\lambda\mu}^{\Gamma_i}(g) \mathbf{v}_{j\lambda}^p \\ &= \sum_\lambda D_{\lambda\mu}^{\Gamma_i}(g) \left[ \sum_p a_{i\nu}^p \mathbf{v}_{j\lambda}^p \right] \end{aligned} \quad (88)$$

so the term in square brackets transforms like the original basis vector  $v_{j\mu}^p$  in eq. 86.

## 6.2 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  $116.8^\circ$ . 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. 11 page 36, 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. 42 page 36. We have already decomposed the reducible representation into *irreps* as  $\Gamma_{red} = \Gamma_1 + \Gamma_2 + 2\Gamma_3$  (eq. 64 page 48). The two basis vectors for the 1-dimensional *irreps* were found by trial and error, and are shown in fig. 12 page 37. We will indicate these two modes as  $|\Gamma_1\rangle$  and  $|\Gamma_2\rangle$ . Finally, we have several variants of the matrix representations (figs 15, 16, 17 ) but we will only employ Variant 1 for the projectors (fig. 15 page 41). The character table is on fig. 19 page 46.
- We will start by applying  $\hat{P}^{\Gamma_1}$  to modes  $|1\rangle \cdots |6\rangle$ . There is only one projector for  $\Gamma_1$ , since the *irrep* is 1-dimensional, and all the coefficients in eq. 81 are 1, since this is the *totally symmetric representation*. It is easy to show that

$$\begin{aligned}\hat{P}^{\Gamma_1} |1\rangle &= \hat{P}^{\Gamma_1} |2\rangle = \hat{P}^{\Gamma_1} |3\rangle = \frac{1}{3} |\Gamma_1\rangle \\ \hat{P}^{\Gamma_1} |4\rangle &= \hat{P}^{\Gamma_1} |5\rangle = \hat{P}^{\Gamma_1} |6\rangle = 0\end{aligned}\quad (89)$$

Likewise

$$\begin{aligned}\hat{P}^{\Gamma_2} |1\rangle &= \hat{P}^{\Gamma_2} |2\rangle = \hat{P}^{\Gamma_2} |3\rangle = 0 \\ \hat{P}^{\Gamma_2} |4\rangle &= \hat{P}^{\Gamma_2} |5\rangle = \hat{P}^{\Gamma_2} |6\rangle = \frac{1}{3} |\Gamma_2\rangle\end{aligned}\quad (90)$$

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**.  $\Gamma_2$  represents a pure rotation and has zero frequency.

- The situation is somewhat more complicated for  $\Gamma_3$ : 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. 15 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,  $\hat{P}_{\mu\nu}^{\Gamma_3} \mathbf{v}$  **projects onto mode  $\mu$  with the coefficient of mode  $\nu$  in the decomposition of  $\mathbf{v}$** . Since  $|2\rangle$  is symmetric, there will be no antisymmetric component in its decomposition, so

$$\begin{aligned}\hat{P}_{11}^{\Gamma_3} |2\rangle &= \hat{P}_{21}^{\Gamma_3} |2\rangle = 0 \\ \hat{P}_{12}^{\Gamma_3} |5\rangle &= \hat{P}_{22}^{\Gamma_3} |5\rangle = 0\end{aligned}\tag{91}$$

- The modes generated by application of the projectors to modes  $|2\rangle$  and  $|5\rangle$  are shown in fig. 27. In particular, one can verify directly the relations in eq. 91 and

$$\begin{aligned}\hat{P}_{11}^{\Gamma_3} |5\rangle &= \frac{1}{3} |m_1\rangle \\ \hat{P}_{12}^{\Gamma_3} |2\rangle &= \frac{1}{3} |m'_1\rangle \\ \hat{P}_{21}^{\Gamma_3} |5\rangle &= \frac{1}{3} |m_2\rangle \\ \hat{P}_{22}^{\Gamma_3} |2\rangle &= \frac{1}{3} |m'_2\rangle\end{aligned}\tag{92}$$

- Modes  $|m_1\rangle$  and  $|m_2\rangle$  form a basis set for the chosen matrix representation of  $\Gamma_3$ , and so do modes  $|m'_1\rangle$  and  $|m'_2\rangle$ . This is consistent with the general rule that  $\hat{P}_{\mu\nu}^{\Gamma_i} \mathbf{v}$  for *fixed*  $\nu$  and *different*  $\mu$  represent unnormalised basis functions for  $\Gamma_i$ .
- 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  $|m_1\rangle$ ,  $|m_2\rangle$ ,  $|m'_1\rangle$  and  $|m'_2\rangle$ , intended as vibration modes, do not conserve the centre of mass, one can try the following linear combinations:

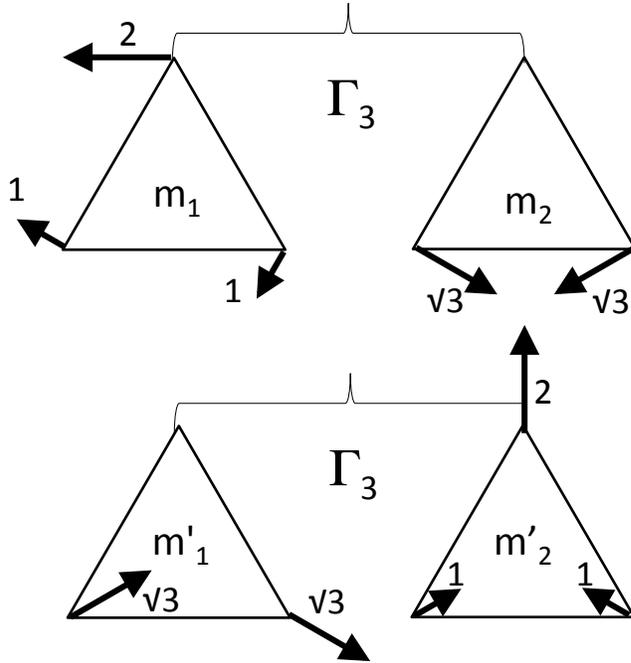


Figure 27: Modes generated by  $|2\rangle$  and  $|5\rangle$  through the application of the projectors. The length of the arrows is indicated.

$$\begin{aligned}
 |n_1\rangle &= \frac{|m_1\rangle - |m'_1\rangle}{2} \\
 |n_2\rangle &= \frac{|m_2\rangle - |m'_2\rangle}{2} \\
 |n'_1\rangle &= \frac{|m_1\rangle + |m'_1\rangle}{2} \\
 |n'_2\rangle &= \frac{|m_2\rangle + |m'_2\rangle}{2}
 \end{aligned} \tag{93}$$

These modes are shown in fig. 28, and are in fact the remaining **normal modes** of the triangular molecule. Modes  $|n_1\rangle$  and  $|n_2\rangle$  are pure translations, and have zero frequency.

### 6.3 Subduction

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

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1 \tag{94}$$

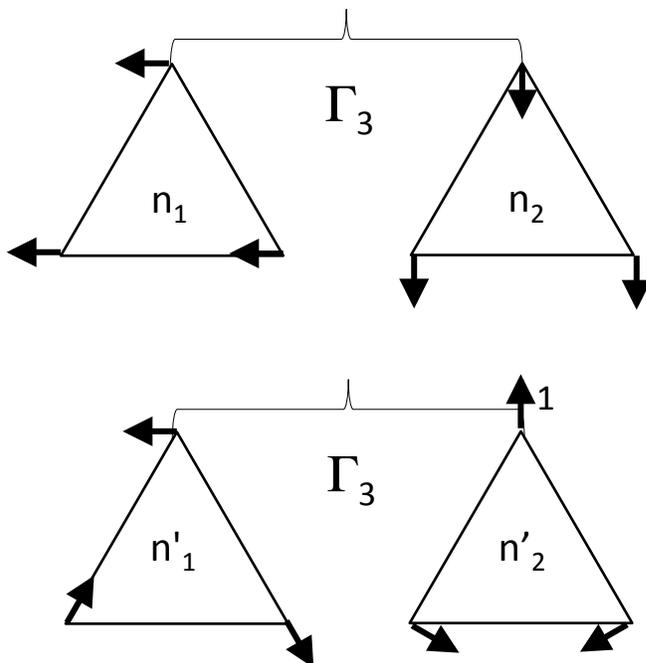


Figure 28: The  $\Gamma_3$  normal modes of the triangulate molecule. The relation between these modes and those in fig. 27 is shown in eq. 93.

where  $\lambda$  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  $\lambda$  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:  $E$ ,  $2_z$ ,  $4^+/4^-$ ,  $2_x/2_y$  and  $2_{xy}/2_{x\bar{y}}$ . Its proper subgroup 222 has *four* classes:  $E$ ,  $2_z$ ,  $2_x$  and  $2_y$ , all of one element each since 222 is Abelian.  $4^+/4^-$  and  $2_{xy}/2_{x\bar{y}}$  are suppressed, while  $2_x/2_y$  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. 61) 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*  $\Gamma_i$  of  $G_0$ , the decomposition of the subduced representation  $sub(\Gamma_i)$  will determine how the  $\Gamma_i$  multiplet will split.

**Example 1** Fig. 29 shows the character table of point group 622 ( $D_6$ ). 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.

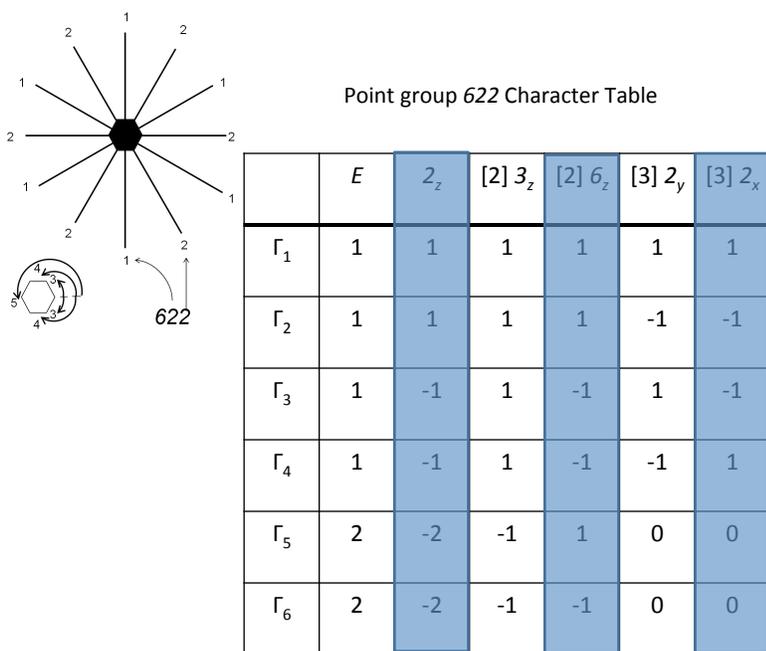


Figure 29: . The character table of point group 622 and the subduction of its *irreps* into its subgroup 32.

the subduction is as follows:

$$\begin{aligned}
\Gamma_1^{622} &\rightarrow \Gamma_1^{32} \\
\Gamma_2^{622} &\rightarrow \Gamma_2^{32} \\
\Gamma_3^{622} &\rightarrow \Gamma_1^{32} \\
\Gamma_4^{622} &\rightarrow \Gamma_2^{32} \\
\Gamma_5^{622} &\rightarrow \Gamma_3^{32} \\
\Gamma_6^{622} &\rightarrow \Gamma_3^{32}
\end{aligned}
\tag{95}$$

(note that  $\Gamma_1$  always subduces to  $\Gamma_1$ .)

**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. 30 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 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.

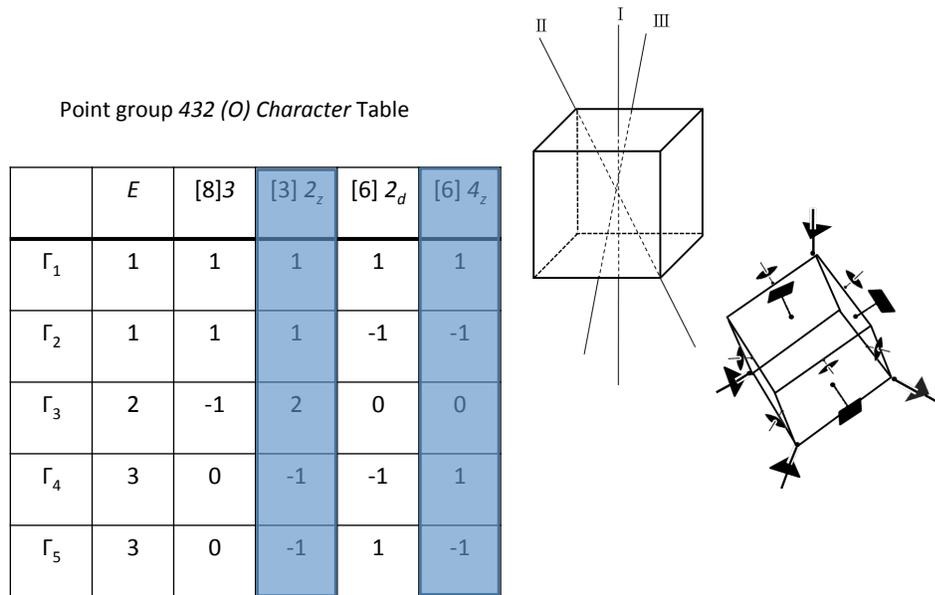


Figure 30: . The character table of point group 432 (cubic) and the subduction of its *irreps* into its subgroup 32.

the subduction is as follows:

$$\begin{aligned}
\Gamma_1^{432} &\rightarrow \Gamma_1^{32} \\
\Gamma_2^{432} &\rightarrow \Gamma_2^{32} \\
\Gamma_3^{432} &\rightarrow \Gamma_3^{32} \\
\Gamma_4^{432} &\rightarrow \Gamma_3^{32} + \Gamma_2^{32} \\
\Gamma_5^{432} &\rightarrow \Gamma_3^{32} + \Gamma_1^{32}
\end{aligned} \tag{96}$$

**Conclusion:**

- ◇  $\Gamma_1^{432}$  and  $\Gamma_2^{432}$  are **singlets**. They subduce into *irreps* of 32 and are not split
- ◇  $\Gamma_3^{432}$  is a **doublet**. It subduces into an *irreps* of 32 ( $\Gamma_3^{32}$ , also a doublet) and is not split.
- ◇  $\Gamma_4^{432}$  and  $\Gamma_5^{432}$  are **triplets**. They subduce into a **doublet**  $\Gamma_3^{32}$  and a **singlet** ( $\Gamma_2^{32}$  or  $\Gamma_1^{32}$ ). There will be a corresponding splitting of the energy levels upon lowering of the symmetry.

This is shown schematically in fig. 31. 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  $H_1$ .

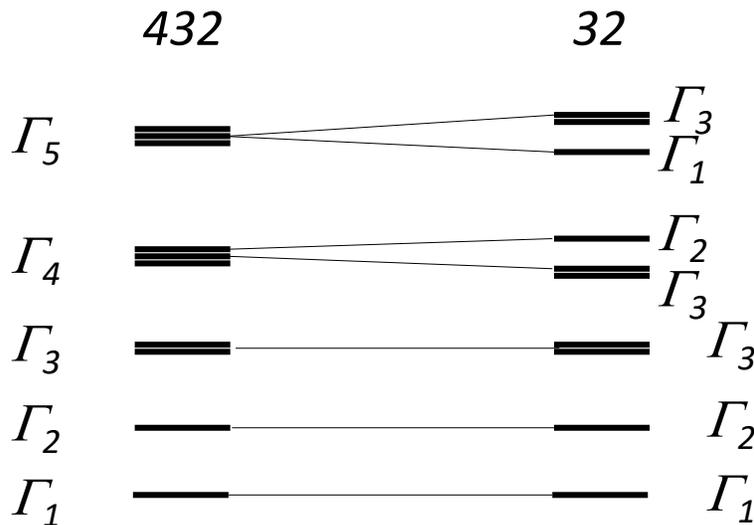


Figure 31: Schematic representation of the energy level splitting by lowering the symmetry from 432 to 32.

## 6.4 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-translations and pure translations.

**N.B.** Some groups contain both proper and improper elements, but **cannot be written as direct products**, since they do not contain the inversion  $I$ .

**Another counter-example** <sup>422</sup> 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
$\Gamma_1$	1	1
$\Gamma_2$	1	-1

- $G$  has **twice as many classes** as  $F$ .<sup>17</sup>
- 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 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  $I \circ f$ .

---

<sup>17</sup>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  $I \circ C_k$ .

- ◇ For each  $\Gamma_i$  of  $F$  we get two irreps of  $G$ :  $\Gamma_{ig}$  and  $\Gamma_{iu}$ .
- ◇ For the g- or gerade (even) irreps, we get:

$$\begin{aligned}\chi^{\Gamma_{ig}}(fC_k) &= +\chi^{\Gamma_i}(C_k) \\ \chi^{\Gamma_{ig}}(I \circ C_k) &= +\chi^{\Gamma_i}(C_k)\end{aligned}\tag{97}$$

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

$$\begin{aligned}\chi^{\Gamma_{iu}}(C_k) &= +\chi^{\Gamma_i}(C_k) \\ \chi^{\Gamma_{iu}}(I \circ C_k) &= -\chi^{\Gamma_i}(C_k)\end{aligned}\tag{98}$$

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

	$E$	$C_1$	$C_2$	$\dots$	$C_n$
$\Gamma_1$	$\chi_1(E)$	$\chi_1(C_1)$	$\chi_1(C_2)$	$\dots$	$\chi_1(C_n)$
$\Gamma_2$	$\chi_2(E)$	$\chi_2(C_1)$	$\chi_2(C_2)$	$\dots$	$\chi_2(C_n)$
$\vdots$	$\dots$	$\dots$	$\dots$	$\dots$	$\dots$
$\Gamma_n$	$\chi_n(E)$	$\chi_n(C_1)$	$\chi_n(C_2)$	$\dots$	$\chi_n(C_n)$

we obtain the character table of  $G$ :

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

## 7 Lecture 7: Tensors and tensor products of representations

### 7.1 Tensors: an overview

Tensors are ubiquitous in the description of physical phenomena, and find applications in particular in equilibrium properties (e.g., the dielectric tensor), optical properties (e.g., the magneto-optical tensor) and transport properties (e.g., the conductivity and Hall effect tensors). We can think of tensors in two related ways:

1. As objects extending the concepts of vectors and their dot products. Whereas the dot product takes two vectors as input and outputs a scalar, the equivalent operations in ‘tensor world’ are considerably more elaborate: We can use two vectors and a rank-2 tensor to produce a scalar, or a single vector and a rank-2 tensor to produce another vector — all by extension of the ordinary dot product (see here below).
2. As elements of a new linear space in their own right, which are used to describe ‘composite objects’, such as an ensemble of several electrons with their spins and orbital degrees of freedom. Examples of this second function will be given in the remainder.

### 7.2 Tensor product of linear spaces

- Given two linear spaces  $V$  and  $W$ , one can define their **tensor product**  $V \otimes W$ , a new **linear 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

$$[(\mathbf{a}_1 | \mathbf{b}_1), (\mathbf{a}_1 | \mathbf{b}_2), \dots, (\mathbf{a}_1 | \mathbf{b}_m), (\mathbf{a}_2 | \mathbf{b}_1), \dots, (\mathbf{a}_n | \mathbf{b}_m)] \quad (99)$$

It is therefore natural to write an element of this new linear space as:

$$\mathbf{T} = \sum_{ij} T_{ij} [(\mathbf{a}_i | \mathbf{b}_j)] \quad (100)$$

This can be extended to composite bases made of any number of elements, such as

$$\mathbf{T} = \sum_{ijk} T_{ijk} [(\mathbf{a}_i | \mathbf{b}_j | \mathbf{c}_k)] \quad (101)$$

etc., where the number of indices is known as the *rank of the tensor*.

- This formalism is directly related to the use of tensors to extend the dot product (see point 1. above). For example, let us consider the relation between the dielectric displacement vector and the electric field vector through the electrical permittivity tensor, which is usually written in component form:

$$D_i = \sum_j \epsilon_{ij} E_j \quad (102)$$

we can expand this notation to include the basis vectors:

$$\epsilon \odot \mathbf{E} = \sum_{ij} \epsilon_{ij} [(\mathbf{a}_i | \mathbf{b}_j)] \odot \sum_k E_k \mathbf{b}_k \quad (103)$$

where  $\odot$  is the equivalent of the dot product. If we use Cartesian bases:

$$[(\mathbf{a}_i | \mathbf{b}_j)] \odot \mathbf{b}_k = \mathbf{a}_i \delta_{jk} \quad (104)$$

whence:

$$\epsilon \odot \mathbf{E} = \sum_{ij} \mathbf{a}_i \epsilon_{ij} E_j = \sum_i D_i \mathbf{a}_i = \mathbf{D} \quad (105)$$

where the dielectric displacement has the usual definition in eq. 102. All this complexity may seem unnecessary, but is useful to guarantee explicitly that all our 'objects' are invariant by coordinate transformations, which affect both the basis vectors and the components.

- If, under the action of a group  $G$ , the elements of  $V$  transform with a certain representation  $\Gamma$  (not necessarily irreducible) with matrix representation  $A(g)$  on the given basis  $\mathbf{a}_i$ , while those of  $W$  transform with representation  $\Delta$  and matrix representation  $B(g)$ , one can define the **tensor product representation**  $\Gamma \otimes \Delta^B$  so that the tensor components transform as:

$$g[T_{ij}] = \sum_{lm} A_{il} B_{jm} T_{lm} \quad (106)$$

- By reordering the elements of  $T_{ij}$  as a single column, one can easily find out that the matrix representation of  $\Gamma \otimes \Delta$  on the 'compound basis' is the **Kronecker product** (or tensor product)  $A \otimes B$  of the two matrices, where:

$$A \otimes B = \left[ \begin{array}{c|c|c|c} a_{11}B & a_{12}B & \cdots & a_{1n}B \\ \hline a_{21}B & a_{22}B & \cdots & a_{2m}B \\ \hline \vdots & \vdots & \vdots & \vdots \\ \hline a_{n1}B & a_{n2}B & \cdots & a_{nn}B \end{array} \right] \quad (107)$$

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:  $tr(A \otimes B) = tr(A) tr(B)$ .

### 7.3 Characters of the tensor product of representations

- As we have seen, the matrix representatives of  $\Gamma \otimes \Delta$  are the **Kronecker product or matrix representatives for  $\Gamma$  and  $\Delta$** , as

$$D^{\Gamma \otimes \Delta}(g) = D^{\Gamma}(g) \otimes D^{\Delta}(g) \quad (108)$$

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

$$\chi^{\Gamma \otimes \Delta}(g) = \chi^{\Gamma}(g) \chi^{\Delta}(g) \quad (109)$$

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.

### 7.4 Symmetrised and anti-symmetrised tensor spaces

- In many physically relevant cases, it is important to consider tensors  $T_{ijk\dots}$  that are either **symmetric** or **antisymmetric** by exchange of some or all the indices. When one considers the tensor product of a linear space by itself  $V \otimes V$  (or more generally of two linear spaces having the same dimension), 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:

$$[(\mathbf{a}_1|\mathbf{a}_1), (\mathbf{a}_1|\mathbf{a}_2), \dots, (\mathbf{a}_1|\mathbf{a}_n), (\mathbf{a}_2|\mathbf{a}_1), \dots, (\mathbf{a}_n|\mathbf{a}_n)] \quad (110)$$

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:

$$\left[ (\mathbf{a}_1|\mathbf{a}_1), \frac{1}{2}(\mathbf{a}_1|\mathbf{a}_2) + \frac{1}{2}(\mathbf{a}_2|\mathbf{a}_1), \dots, \frac{1}{2}(\mathbf{a}_1|\mathbf{a}_n) + \frac{1}{2}(\mathbf{a}_n|\mathbf{a}_1), \dots, (\mathbf{a}_n|\mathbf{a}_n) \right] \quad (111)$$

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

$$\left[ \left( \frac{1}{2}(\mathbf{a}_1|\mathbf{a}_2) - \frac{1}{2}(\mathbf{a}_2|\mathbf{a}_1), \dots, \frac{1}{2}(\mathbf{a}_1|\mathbf{a}_n) - \frac{1}{2}(\mathbf{a}_n|\mathbf{a}_1), \dots, \frac{1}{2}(\mathbf{a}_{n-1}|\mathbf{a}_n) - \frac{1}{2}(\mathbf{a}_n|\mathbf{a}_{n-1}) \right) \right] \quad (112)$$

- There is a very useful formula for the **characters** of the symmetric and antisymmetric subspaces, which we present without proof <sup>18</sup>:

$$\begin{aligned} \chi_{[\Gamma \otimes \Gamma]}(g) &= \frac{1}{2} [\chi_{\Gamma}^2(g) + \chi_{\Gamma}(g^2)] \\ \chi_{\{\Gamma \otimes \Gamma\}}(g) &= \frac{1}{2} [\chi_{\Gamma}^2(g) - \chi_{\Gamma}(g^2)] \end{aligned} \quad (113)$$

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

## 7.5 Spin and orbital states of 2-electron $p$ orbital

This example requires the determination of the characters of the *irreps* of the group  $SO(3)$  of continuous rotations in 3D, which we have not discussed in this course. However, the application of the tensor product of representations is so powerful in this case that it is worth discussing it anyway. Ordinary representations of  $SO(3)$  have odd dimensions, and are parametrised by the equivalent of the angular momentum quantum number  $l$ .

$$\begin{aligned} \chi^0(\alpha) &= 1 \\ \chi^1(\alpha) &= 2 \cos \alpha + 1 \\ \chi^2(\alpha) &= 4 \cos^2 \alpha + 2 \cos \alpha - 1 \\ \chi^3(\alpha) &= 8 \cos^3 \alpha + 4 \cos^2 \alpha - 4 \cos \alpha - 1 \end{aligned} \quad (114)$$

We will also need the characters of the spinor representation, which has dimension 2:

$$\chi^{\frac{1}{2}}(\alpha) = 2 \cos \frac{\alpha}{2} \quad (115)$$

<sup>18</sup>Eq. 113 is only valid if the two representations in the tensor product we are symmetrising are not only the same, but have the same *matrices*. Otherwise, the term  $\chi_{\Gamma}(g^2)$  should be replaced by  $\text{Tr} [M_1^{\Gamma}(g)M_2^{\Gamma}(g)]$ , where the two (distinct) matrix representatives  $M_1^{\Gamma}(g)$  and  $M_2^{\Gamma}(g)$  are multiplied with the usual matrix product.

we begin by constructing the one-electron states as the tensor product of the orbital and spin states with  $l = 1$  and  $s = 1/2$ . The space of possible states has 6 dimensions and the character of the tensor product representation is:

$$\chi_{1el} = 2 \cos \frac{\alpha}{2} (2 \cos \alpha + 1) \quad (116)$$

The representation of the 2-electron states is the *antisymmetric* part of the tensor product of the one electron state with itself. By using the formula we find:

$$\begin{aligned} \chi_{2el} &= \frac{1}{2} \left[ 4 \cos^2 \frac{\alpha}{2} (1 + 2 \cos \alpha)^2 - 2 \cos \alpha (1 + 2 \cos 2\alpha) \right] \\ &= 8 \cos^2 \alpha + 6 \cos \alpha + 1 = 2\chi^2(\alpha) + \chi^1(\alpha) + 2\chi^0(\alpha) \quad (117) \end{aligned}$$

(see proof here below). In other words, the full representation decomposes in two quintets ( $J = 2$ ), one triplet ( $J = 1$ ) and two singlets ( $J = 0$ ). In a situation in which the total angular momentum is conserved,  $J$  is a good quantum number, so the decomposition in  $J$  multiplet corresponds to a decomposition in multiplets of the Hamiltonian.

PROOF: using eq. 113, we get:

$$\begin{aligned} \{\chi_{1el} \otimes \chi_{1el}\} &= \frac{1}{2} \left[ \left( 2 \cos \frac{\alpha}{2} (2 \cos \alpha + 1) \right)^2 \right. \\ &\quad \left. - 2 \cos \alpha (2 \cos 2\alpha + 1) \right] \quad (118) \end{aligned}$$

Since

$$\begin{aligned} \left( \cos \frac{\alpha}{2} \right)^2 &= \frac{1}{2} (\cos \alpha + 1) \\ \cos 2\alpha &= 2 \cos^2 \alpha - 1 \quad (119) \end{aligned}$$

we obtain

$$\{\chi_{1el} \otimes \chi_{1el}\} = \frac{1}{2} (16 \cos^2 \alpha + 12 \cos \alpha + 2) \quad (120)$$

which yield the result above.

## 7.6 \* Decomposition into S and L states

We can further decompose the  $J$  multiplets in the spirit of the  $\mathbf{L} \cdot \mathbf{S}$  coupling scheme. This is done by considering separately the multiplets

of  $S$  and those of  $L$ . For 2 electrons, it can be either  $S = 0$  (singlet, antisymmetric in the spin variables) or  $S = 1$  (triplet, symmetric in the spin variables). The corresponding orbital parts are the *symmetric* and *antisymmetric* tensor products of the 1-electron orbital wavefunctions. The characters of the orbital representations are in the two cases

$$\begin{aligned}
 \chi_{o-2el}^{S=0} &= \frac{1}{2} [(1 + 2 \cos \alpha)^2 + (1 + 2 \cos 2\alpha)] \\
 &= 4 \cos^2 \alpha + 2 \cos \alpha = \chi^2(\alpha) + \chi^0(\alpha) \\
 \chi_{o-2el}^{S=1} &= \frac{1}{2} [(1 + 2 \cos \alpha)^2 - (1 + 2 \cos 2\alpha)] \\
 &= 2 \cos \alpha + 1 = \chi^1(\alpha)
 \end{aligned} \tag{121}$$

Therefore the orbital part decomposes in a quintet and a singlet for  $S = 0$  and is a triplet for  $S = 1$ . In the  $S = 0$  case,  $J = L$  and the symbols are therefore  ${}^1D_2 + {}^1S_0$ . In the  $S = 1$  case, the  $J$  can be recovered by the tensor products of the spins and orbital sectors:

$$\begin{aligned}
 \chi_{2el}^{S=1} &= \chi_{o-2el}^{S=1} \chi_{spin}^{S=1} = (2 \cos \alpha + 1)^2 \\
 &= 4 \cos^2 \alpha + 4 \cos \alpha + 1 = \chi^2(\alpha) + \chi^1(\alpha) + \chi^0(\alpha)
 \end{aligned} \tag{122}$$

corresponding to the three values of  $J = 2, 1, 0$  (all the values between  $J = L + S$  and  $J = |L - S|$ ). The full decomposition therefore reads:

$$\Gamma_{2el} = {}^1D_2 + {}^1S_0 + {}^3P_2 + {}^3P_1 + {}^3P_0 \tag{123}$$

According to the Hund's rules, the ground state for less-than-half filled shells is  ${}^3P_0$ , i.e.,  $J = |L - S|$ , with the  ${}^3P$  multiplet being split by the spin-orbit coupling  $\mathbf{L} \cdot \mathbf{S}$ .

One can do a similar derivation in the  **$\mathbf{j} \cdot \mathbf{j}$  coupling scheme**. Considering that the character of the  $j = 3/2$  spinor representation is  $4 \cos \frac{\alpha}{2} \cos \alpha$ , and by taking appropriate antisymmetrised products (for equal  $j$ 's) and normal tensor product (for unequal  $j$ 's) one obtains:

$$\begin{aligned}
 \chi_{\frac{1}{2}, \frac{1}{2}} &= \chi^0(\alpha) \\
 \chi_{\frac{1}{2}, \frac{3}{2}} &= \chi^2(\alpha) + \chi^1(\alpha) \\
 \chi_{\frac{3}{2}, \frac{3}{2}} &= \chi^2(\alpha) + \chi^0(\alpha)
 \end{aligned} \tag{124}$$

## 7.7 \* Extended example: vibrational spectra of planar molecules with symmetry $D_n$

- We have already seen examples for  $D_3$  (32, section 6.2, page 63) and for  $D_4$  (422, section 5.3, page 56). 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.,  $\hat{i}, \hat{j}$ ). For example, the top-left mode in block A of fig. 22 can be written in tensor notation as  $([1, 0, 0, 0]|\hat{i})$ .
- Let us consider independently the representations of  $D_n$  onto the two spaces  $V$  and  $W$  — call them  $\Gamma$  and  $\Delta$  as before.
- $\Gamma$  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  $\Gamma$  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. 32). Consequently, the characters of  $\Gamma$  will be 2 (for the vertex axes) or 0 (for the side axes) for  $n$  even and 1 for  $n$  odd.
- $\Delta$  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  $2 \cos \theta$ ,  $\theta$  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  $\hat{i}$  is unchanged, while  $\hat{j}$  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

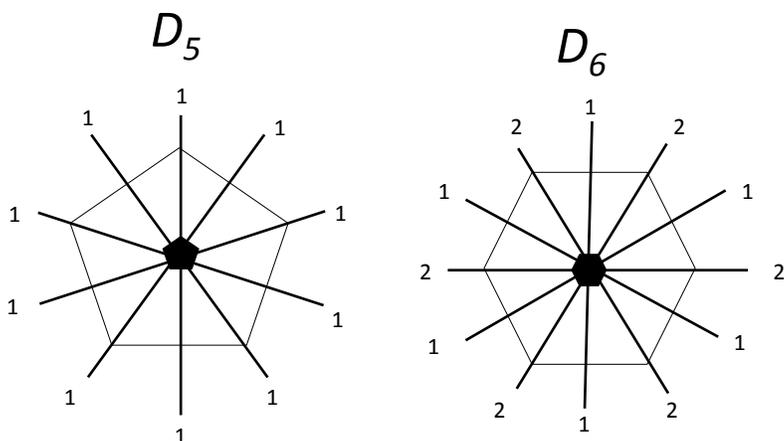


Figure 32: Two examples of dihedral groups of odd order ( $D_5$ ) and even order ( $D_6$ ). For  $n$  odd, there is a single class of in-plane 2-fold axes, while for  $n$  even there are two classes.

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  $\Delta$ , so its characters are simply added to the tensor product characters. This can be summarised as follows: for  $n$  **even**

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

for  $n$  **odd**

	$E$	$2C_z^1$	$2C_z^2$	$\dots$	$n2_x$
$\chi^{\Gamma}$	$n$	0	0	$\dots$	1
$\chi^{\Delta}$	2	$2 \cos \theta$	$2 \cos 2\theta$	$\dots$	0
$\chi^{\Gamma \otimes \Delta}$	$2n$	0	0	$\dots$	0
$\chi^{\Gamma \otimes \Delta + \Delta}$	$2n + 2$	$2 \cos \theta$	$2 \cos 2\theta$	$\dots$	0

- We can see that our result is in agreement with our previous findings for  $D_3$  (eq. 64 page 48) and  $D_4$  (page 58).
- Let us try with  $D_6$  (622). The *irrep* character table is in fig. 29. The characters are:

	$E$	$2_z$	$2\delta_z$	$2\beta_z$	$3\alpha_x$	$3\alpha_y$
$\chi^{\Gamma \otimes \Delta}$	12	0	0	0	0	0
$\chi^{\Gamma \otimes \Delta + \Delta}$	14	-2	1	-1	0	0

By applying eq. 61 we obtain:

$$\begin{aligned} \Gamma \otimes \Delta &= \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 + 2\Gamma_6 \\ \Gamma \otimes \Delta + \Delta &= \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 3\Gamma_5 + 2\Gamma_6 \end{aligned} \quad (125)$$

- The central atom modes clearly transform as  $\Gamma_5$  ( $\equiv \Delta$ , 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  $\Gamma_2$ , since this mode must be invariant by all  $z$ -axis rotations. Therefore the set of non-zero-frequency normal modes is:

$$\begin{aligned} \Gamma \otimes \Delta - \Gamma_2 - \Gamma_5 &= \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5 + 2\Gamma_6 \\ \Gamma \otimes \Delta + \Delta - \Gamma_2 - \Gamma_5 &= \Gamma_1 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 + 2\Gamma_6 \end{aligned} \quad (126)$$

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

- $\Gamma_1$  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,  $\Gamma_2$  will give rise to Raman-active *phonon* modes.

## 8 Lecture 8: “Physical” tensors

### 8.1 Introduction to tensors in physics

- What we have just introduced is a rather abstract definition of tensors, and we have applied it to linear 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  $\Gamma_u$ . Axial vectors, forming a space  $A$ , transform under the corresponding *gerade irrep*  $\Gamma_g$ .
- We define **polar tensors** and **axial tensors of different ranks as follows**:

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

- ◊ The tensor product representation is *gerade* if it contains an even number of  $\Gamma_u$ , *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:

$$D_i = \epsilon_{ij} E_j \quad (127)$$

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

$$P_i = \mu_{ij} B_j \quad (128)$$

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

## 8.2 Matrix transformations of ordinary 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 product is not of practical application. The transformation of ordinary tensors in a specific case of the more general transformation in eq. 106. We should observe that the matrix representatives of the elements of the rotation group onto the space of ordinary vectors are:
  - **For polar vectors:** the ordinary proper or improper rotation matrices associated with group element  $g$ .
  - **For axial vectors:** The corresponding proper rotation matrix, which is obtained by multiplying the rotation matrix by the factor  $(-1)^{p(g)}$ , where  $p(g)$  is the parity of the operation  $g$  ( $=$  *even* for proper rotations,  $=$  *odd* for improper rotations).

Consider, for example, a mirror plane  $m_z$  perpendicular to  $z$ , which is parity-odd ( $p = 1$ ). The corresponding matrix will be:

$$m_z \rightarrow M(m_z) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad (129)$$

with  $\det(M(m_z)) = -1$ . *Polar* vectors transform with  $M(m_z)$ , while *axial* vectors transform with

$$(-1)^1 M(m_z) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (130)$$

which is the corresponding proper rotation (a 2-fold axis).

To extend this to polar and axial *tensors*, we can once again write the elements of a tensor space as

$$\mathcal{T} = \sum_{i,j,k,\dots} T_{i,j,k,\dots} (\mathbf{a}_i | \mathbf{b}_j | \mathbf{c}_k | \dots) \quad (131)$$

where  $\mathbf{a}_i, \mathbf{b}_j, \mathbf{c}_k$  etc. are basis sets for ordinary vectors. With this notation, the transformation upon *proper* operations is:

$$\begin{aligned}
\hat{O}(g)\mathbf{T} &= \sum_{l,m,n,\dots} T_{l,m,n,\dots} \sum_{i,j,k,\dots} R_{li}(g)\mathbf{a}_i R_{mj}(g)\mathbf{b}_j R_{nk}(g)\mathbf{c}_k \dots \\
&= \sum_{i,j,k,\dots} \left( \sum_{l,m,n,\dots} T_{l,m,n,\dots} R_{li}(g)R_{mj}(g)R_{nk}(g) \right) (\mathbf{a}_i|\mathbf{b}_j|\mathbf{c}_k|\dots)
\end{aligned} \tag{132}$$

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  $g$ :

$$\begin{aligned}
\hat{O}(g)T_{ijk\dots} &= \sum_{l,m,n,\dots} T_{l,m,n,\dots} R_{li}(g)R_{mj}(g)R_{nk}(g) \dots \text{ (polar tensors)} \\
\hat{O}(g)T_{ijk\dots} &= (-1)^{p(g)} \sum_{l,m,n,\dots} T_{l,m,n,\dots} R_{li}(g)R_{mj}(g)R_{nk}(g) \dots \text{ (axial tensors)}
\end{aligned} \tag{133}$$

### 8.3 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:

$$\begin{aligned}
P_i &= -\frac{\partial F}{\partial E_i} \\
\epsilon_{ij} &= -\frac{\partial^2 F}{\partial E_i \partial E_j}
\end{aligned} \tag{134}$$

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

**Counter-example:** Magnetoelectric tensor:

$$\begin{aligned}
P_i &= \mu_{ij}B_j \\
\mu_{ij} &= -\frac{\partial^2 F}{\partial E_i \partial B_j}
\end{aligned} \tag{135}$$

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

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

$$P_i = d_{i\alpha\beta}\sigma_{\alpha\beta} \quad (136)$$

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).

#### 8.4 Application of the formula for symmetric and antisymmetric tensors

- In the previous lecture, we have stated a formula to construct the characters of the symmetric and antisymmetric part of a tensor product representation. 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. 113, if one knows the characters of  $\Gamma$ .
- 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. 136. It is a 3<sup>rd</sup>-rank polar tensor that is symmetric in the last two indices, so it transforms according to representation  $\Gamma \otimes [\Gamma \otimes \Gamma]$ .  $\Gamma$  is the ordinary vectors transformation by 32. As we already know,  $\Gamma = \Gamma_2 + \Gamma_3$ . The character table for  $\Gamma$  is therefore:

E	2A	3K
3	0	-1

Let's employ eq. 113 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:

$$\begin{aligned}
\chi_{[\Gamma \otimes \Gamma]}(E) &= \frac{1}{2} [\chi_{\Gamma}^2(E) + \chi_{\Gamma}(E^2)] = 6 \\
\chi_{[\Gamma \otimes \Gamma]}(A) &= \frac{1}{2} [\chi_{\Gamma}^2(A) + \chi_{\Gamma}(A^2)] = 0 \\
\chi_{[\Gamma \otimes \Gamma]}(K) &= \frac{1}{2} [\chi_{\Gamma}^2(K) + \chi_{\Gamma}(K^2)] = 2
\end{aligned} \tag{137}$$

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

E	2A	3K
18	0	-2

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

## 8.5 “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:  $\Gamma_1$  or  $\Gamma_{1g}$  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:

$$\sigma_{ij} = c_{ijkl}\epsilon_{kl} \quad (138)$$

or its converse

$$\epsilon_{ij} = s_{ijkl}\sigma_{kl} \quad (139)$$

- ◇  $\sigma_{ij}$  is the **applied stress tensor** — a field tensor
- ◇  $\epsilon_{kl}$  is the **induced strain tensor** — a field tensor
- ◇  $c_{ijkl}$  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).

## 8.6 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 84. 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  $\Gamma_1$  or ( $\Gamma_{1g}$  for centrosymmetric groups) appears in the decomposition.
  - ◇ If  $\Gamma_1$  appears 0 times, then the physical properties described by this tensor is forbidden in that particular symmetry group.
  - ◇ If  $\Gamma_1$  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 81), 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,  $\Gamma_{1g}$  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  $\Gamma_1$ :  
for **polar tensors**:

$$\tilde{T}_{ijk} = \frac{1}{h} \sum_g \sum_{lmn} T_{lmn} R_{li}(g) R_{mj}(g) R_{nk}(g) \quad (140)$$

while for **axial tensors**:

$$\tilde{T}_{ijk} = \frac{1}{h} \sum_g (-1)^{p(g)} \sum_{lmn} T_{lmn} R_{li}(g) R_{mj}(g) R_{nk}(g) \quad (141)$$

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

## 8.7 A practical way to symmetrise tensors

Most crystallographic coordinates are not Cartesian, but, conveniently, tensors are always expressed in suitable Cartesian coordinates in all point groups. The rule to construct these auxiliary coordinates is the following:

1. The Cartesian versor  $\hat{i}$  is always parallel to the crystallographic basis vector  $a$ , and has dimensionless length 1 (unlike  $a$ ).
2. The Cartesian unit versor  $\hat{j}$  is perpendicular to  $\hat{i}$  and is in the plane defined by the crystallographic basis vectors  $a$  and  $b$ .
3. The Cartesian unit versor  $\hat{k}$  is perpendicular to the other two, i.e.,  $\hat{k} = \hat{i} \times \hat{j}$

Although this may seem straightforward, coordinate conventions are often a source of confusion (see piezoelectric tensor example here below).

Once the appropriate coordinates are chosen, we can then apply the rotation matrices as per 140 and 141. The programs TENSOR and MTENSOR within the Bilbao Crystallographic Suite provide fully symmetrised tensors for most common physical properties.

Finally, it is important to remember that certain tensors are expressed in a variety of non-standard notations. This is true particularly for partially symmetrised tensors of higher rank, where a rectangular matrix notation is often used (again, see piezoelectric tensor example here below).

## 8.8 Example: explicit form of the piezoelectric tensor in 32.

- Following on from the determination of the number of independent elements (see above), 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. 32.  $\tilde{d}_{i\alpha\beta}$  is a polar tensor with symmetric indices  $\alpha$  and  $\beta$ . We therefore start from a generic symmetric tensor

We will use the projection formula as per eq. 140 to symmetrise the tensor.

$$\tilde{d}_{i\mu\nu} = \frac{1}{h} \sum_g \sum_{l\kappa\lambda} d_{l\kappa\lambda} R_{il}(g) R_{\mu\kappa}(g) R_{\nu\lambda}(g) \quad (142)$$

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

- Since we will be comparing the result of our calculations with standard table from the Bilbao server, it is important to become acquainted with the **rectangular notation for the piezoelectric tensor**. This tensor has 18 components, and it is often written as a  $3 \times 6$  array as follows:

$$d_{ij} = \begin{bmatrix} d_{111} & d_{122} & d_{133} & 2d_{123} & 2d_{113} & 2d_{112} \\ d_{211} & d_{222} & d_{233} & 2d_{223} & 2d_{213} & 2d_{212} \\ d_{311} & d_{322} & d_{333} & 2d_{323} & 2d_{313} & 2d_{312} \end{bmatrix} \quad (143)$$

The factor of 2 in front of the off-diagonal elements is due to the fact that the stress-polarisation relation is written as:

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} d_{111} & d_{122} & d_{133} & 2d_{123} & 2d_{113} & 2d_{112} \\ d_{211} & d_{222} & d_{233} & 2d_{223} & 2d_{213} & 2d_{212} \\ d_{311} & d_{322} & d_{333} & 2d_{323} & 2d_{313} & 2d_{312} \end{bmatrix} \begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{bmatrix} \quad (144)$$

which requires a factor of 2 in the piezoelectric matrix<sup>19</sup>.

In fig. 33, we report the output from the TENSOR program as part of the Bilbao Suite. Note that the Bilbao convention (and more generally the crystallographic convention) is to choose the  $x$  axis *parallel* to a 2-fold axis, while we have so far assumed that the  $y$  axis is *parallel* to a 2-fold axis (K). This will need to be taken into account when comparing this result with our calculation.

**Table of tensor components**

$d_{ij}$		j					
		1	2	3	4	5	6
i	1	$d_{11}$	$-d_{11}$	0	$d_{14}$	0	0
	2	0	0	0	0	$-d_{14}$	$-2d_{11}$
	3	0	0	0	0	0	0

**Number of independent coefficients: 2**

Figure 33: The form of the piezoelectric tensor (in 2-index notation) for point group symmetry 32 (output of the TENSOR program, part of the Bilbao Crystallographic Suite).

## 8.9 The piezoelectric tensor in 32: explicit calculations

As we already stated, the procedure involves symmetrising the most general form of the piezoelectric tensor using equation 142. The following code in *Mathematica* as been used to symmetrise the piezoelectric tensor explicitly. We have employed the Variant 1 matrices of the  $T_3$  representation to construct the full (3D) vector representation (matrices  $ME$ ,  $MA$ ,  $MB$ , etc. here below).

```
ME = {{1, 0, 0}, {0, 1, 0}, {0, 0, 1}}
MA = {{-1/2, -Sqrt[3]/2, 0}, {Sqrt[3]/2, -1/2, 0}, {0, 0, 1}}
MB = Transpose[MA]
MK = {{-1, 0, 0}, {0, 1, 0}, {0, 0, -1}}
ML = MB.MK.MA
MM = MA.MK.MB
```

<sup>19</sup>Bizarrely, the alternative form of the piezoelectric tensor  $e_{ij}$  that relates the polarisation to the strain tensor  $\epsilon_j$  (expressed in vector form as  $\sigma_j$  here above) does not have the factor of 2, because this is included *by convention* in the strain.

```

pz = {{{d11, d16, d15}, {d16, d12, d14}, {d15, d14, d13}}, {{d21,
  d26, d25}, {d26, d22, d24}, {d25, d24, d23}}, {{d31, d36,
  d35}, {d36, d32, d34}, {d35, d34, d33}}}

pzsym = Simplify[
  1/6 (Table[
    Sum[pz[[i, j, k]] ME[[1, i]] ME[[m, j]] ME[[n, k]], {i, 3}, {j,
      3}, {k, 3}], {1, 1, 3}, {m, 1, 3}, {n, 1, 3}] +
    Table[Sum[
      pz[[i, j, k]] MA[[1, i]] MA[[m, j]] MA[[n, k]], {i, 3}, {j,
        3}, {k, 3}], {1, 1, 3}, {m, 1, 3}, {n, 1, 3}] +
    Table[Sum[
      pz[[i, j, k]] MB[[1, i]] MB[[m, j]] MB[[n, k]], {i, 3}, {j,
        3}, {k, 3}], {1, 1, 3}, {m, 1, 3}, {n, 1, 3}] +
    Table[Sum[
      pz[[i, j, k]] MK[[1, i]] MK[[m, j]] MK[[n, k]], {i, 3}, {j,
        3}, {k, 3}], {1, 1, 3}, {m, 1, 3}, {n, 1, 3}] +
    Table[Sum[
      pz[[i, j, k]] ML[[1, i]] ML[[m, j]] ML[[n, k]], {i, 3}, {j,
        3}, {k, 3}], {1, 1, 3}, {m, 1, 3}, {n, 1, 3}] +
    Table[Sum[
      pz[[i, j, k]] MM[[1, i]] MM[[m, j]] MM[[n, k]], {i, 3}, {j,
        3}, {k, 3}], {1, 1, 3}, {m, 1, 3}, {n, 1, 3}]]])

pzthreebysix = {{pzsym[[1, 1, 1]], pzsym[[1, 2, 2]],
  pzsym[[1, 3, 3]], 2 pzsym[[1, 2, 3]], 2 pzsym[[1, 1, 3]],
  2 pzsym[[1, 1, 2]]}, {pzsym[[2, 1, 1]], pzsym[[2, 2, 2]],
  pzsym[[2, 3, 3]], 2 pzsym[[2, 2, 3]], 2 pzsym[[2, 1, 3]],
  2 pzsym[[2, 1, 2]]}, {pzsym[[3, 1, 1]], pzsym[[3, 2, 2]],
  pzsym[[3, 3, 3]], 2 pzsym[[3, 2, 3]], 2 pzsym[[3, 1, 3]],
  2 pzsym[[3, 1, 2]]}

MatrixForm[%]

```

The output of *Mathematica* is the following:

$$\tilde{d}_{ij} = \begin{bmatrix} 0 & 0 & 0 & -A & 0 & -2B \\ -B & B & 0 & 0 & A & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (145)$$

with  $A = d_{25} - d_{14}$  and  $B = -\frac{1}{4}(2d_{16} + d_{21} - d_{22})$ . 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  $\Gamma_1$  is contained in  $\Gamma \otimes [\Gamma \otimes \Gamma]$ .

Note that we can re-obtain the result in in fig. 33 by exchanging the axes  $x$  and  $y$ , i.e., swapping row  $\tilde{d}_{1j}$  with row  $\tilde{d}_{2j}$  and then exchanging  $\tilde{d}_{i1} \leftrightarrow \tilde{d}_{i2}$  and  $\tilde{d}_{i4} \leftrightarrow \tilde{d}_{i5}$ .