Lecture 7 — Introduction to lattice modes and their symmetry.

1 Introduction

Up to this point, the focus of our course has been on understanding the *static* properties of crystals. In doing this, we have heavily exploited the *symmetry* of the crystals — in particular the *translational* symmetry, which is responsible for the characteristic features of crystalline diffraction patterns. Some dynamic features have been accommodated in this picture through the introduction of Debye-Waller factors. At this point, however, we have to abandon this "comfort zone", and deal with properties that distinctly *break* the symmetry. For example, a sound wave or, for metals, a conduction electron, may propagate in the crystal in a certain direction, and this "picks out" this direction over all the other, symmetry-equivalent directions. We may surmise (correctly) that the propagation along symmetry-equivalent directions would obey the same laws, but the fact remains that the propagation breaks the symmetry, since the electron or sound waves do not propagate along all the symmetry-equivalent directions *at the same time*. Perhaps more significantly, the **wavevector** of the propagating wave is, in general, **not in register with the crystal lattice**, so even **translational invariance is lost**. Another important class of problems involves **phase transitions**, where the crystal symmetry is reduced by atomic displacements (**structural phase transitions**), ordering of magnetic moments (**magnetic phase transitions**) etc. In this case also we have to be prepared to relinquish at least part of the symmetry that we enjoyed in the high-symmetry phase. Rather than "jettisoning" all the symmetry machinery we have so far employed, it would seem natural to attempt a step-by-step, **systematic lowering of the symmetry**, so as not to give up more than is needed. For example, one simple idea (that often works) is be to consider **group-subgroup relations**. In structural phase transitions, for example, the symmetry of the low-symmetry phase is often a subgroup of the high symmetry — an observation that can significantly help in solving the distorted structure. Even this approach, however, is clearly inadequate in the general case: when translational symmetry is lost, in general very little remains.

1.1 Symmetry approach to crystal dynamics: the general idea

Let's consider in general the solution ψ_1, either stationary or propagating, of a Hamiltonian or secular equation in a molecule or a crystal with a symmetry group $\{g\}$, e.g., a normal mode of vibration of the molecule, a phonon mode, an electronic wavefunction etc. When considering the symmetry of this solution (intended as a "pattern" of some kind in real space) there are three possibilities:

1. The solution ψ_2 is **completely invariant** by all the elements of the symmetry group $\{g\}$, i.e., $g[\psi_1] = \psi_1 \, \forall g \in \{g\}$.

2. The solution is *not* invariant for some elements of the group, but the transformed solution is proportional to the original one, i.e., $g[\psi_1] = c \, \psi_1$ for certain elements of the group. Because we are dealing with rotational symmetry, we can surmise that $|c| = 1$, i.e., $c = \pm 1$ if it is real. *Complex* values $c = e^{i\phi}$ are of course allowed for complex solutions (e.g., wavefunctions.

3. For certain elements of the group, the solution is *not* invariant and is *not* proportional to the original solution, i.e., $g[\psi_1] = \psi_2 \neq c\psi_1$.

In *all these cases*, it is completely intuitive that the transformed solutions are also solutions of the same equations with the same properties of the original one — this is obvious in the first two cases but not in the third. Moreover, if the equations are **linear** (e.g., harmonic oscillator, Schrodinger equation) and $\psi_2 \neq c\psi_1$, then $a\psi_1 + b\psi_2$ for generic a and b *will also be a solution with the same frequency or eigenvalue.* in other words **symmetry generates a subspace of degenerate modes or eigenvectors**. In the cases (1) and (2) here above, the eigenvectors are *non-degenerate*.

The key point here is that the *structure* of these subspaces (i.e., their dimensionality, which determines how many singlets, doublets, triplets etc. there are) *does not depend on the particular form of the potential*, but only by its **symmetry**.

> **The multiplet *structure* of a Hamiltonian is entirely determined by symmetry. Functions that uniquely transform with a certain symmetry are degenerate eigenfunctions of the Hamiltonian. In general, symmetry *does not* determine the energy of the levels.**

1.2   Inversion and parity

Inversion is in a sense a special symmetry operation: it commutes with all other rotations and forms a group of two elements with the identity. For this reasons, it is possible to show that in **centrosymmetric crystals** (i.e., those possessing the inversion as a symmetry element) **all solutions of the Schroedinger and normal-mode equations have a definite parity** — in other words, transform either into themselves (even-parity or "gerade" solutions) or into *minus* themselves (odd-parity or "gerade" solutions) by inversion. As we shall see, this is important in determining the Infrared and Raman selection rules.

1.3 Symmetry analysis

Given a certain "space of solutions" (e.g., the Hilbert space or a space of modes), how do we decompose it into the "multiplet spaces"? As we have seen, we can go a long way by just considering the symmetry, without any knowledge of the actual equations. To deal with this problem, mathematicians and physicists have, over the years, developed very powerful tools, all derived from the so-called **theory of the irreducible representations of symmetry groups**. Unfortunately, time does not allow us to describe in any detail the mathematical aspects of this theory, nor to learn the powerful "constructive" theorems required to solve meaningful problems. In the following sections, I aim to give a "flavour" of these methods, and to illustrate how their systematic use can simplify enormously the solution of a variety of problems in condensed-matter physics.

> **Our initial aim will be to find the normal mode of vibration of a 5-atom molecule — a problem that normally involves diagonalisation of a 10×10 matrix. As we shall see, with the help of symmetry we can do it with pen and paper. Later, we will extend the same concepts to *lattice* modes (phonons).**

2 Lattice fields and lattice "modes"

2.1 General definitions

What do the following concepts have in common?

1. Atomic displacements — static, as for a structural phase transition or dynamic, as for lattice vibrations.

2. Configurations of magnetic moments — static, as for magnetically-ordered phases or dynamic, as for "spin waves".

3. Electron density fluctuations from the "average" density.

4. Electronic wave-functions, for example, the solutions of the Schrodinger equation for the whole crystal.

The answer is: they (and many more quantities that are not mentioned here) are all represented by **lattice fields**, i.e., by quantities that have values either at *specific points* in the crystal (typically the location of ions, as for 1 and 2), or at *all points* within the crystal, as for 3 and 4. Beside this obvious difference (discrete vs continuous field), another important difference is represented by the **nature of the objects** that are defined at each point:

Atomic displacements are *polar vectors* i.e., **parity-odd** vectors. When each vector is considered in isolation, it changes sign upon inversion (parity). As it happens, atomic displacements are **time-reversal even**, i.e., they are insensitive to the arrow of time (velocities would be **time-reversal odd**).

Magnetic moments are *axial vectors*, i.e., **parity-even** vectors. When each vector is considered in isolation, it is unaffected by inversion. Parity-even and parity-odd vectors have the same behaviour upon proper rotations. Magnetic moments are **time-reversal odd**, since they represent circulating currents.

Electron density fluctuations are **real scalar quantities**. Fluctuations from the average density can be positive and negative, whereas the density itself is positive-definite.

Electronic wave-functions are **complex scalar quantities**. Note that electronic wave-functions are not required to have the full symmetry of the crystal (probability densities do).

Importantly, all the aforementioned quantities can be thought of as **forming a linear space**. In fact, they can all be added, subtracted and multiplied by scalar quantities, whilst still yielding "valid" quantities (the dot product is not necessarily defined, though). In this sense, we could call them "vectors", but, to avoid confusion with the previous classification, we will use the general term **lattice modes**. We will call the linear space spanned by these modes **mode space**.

The **dimensionality** of mode space is clearly dependent on the specific field and on whether we are considering a finite lattice (or even a molecule) or an infinite lattice. Scalar modes defined on a N-node lattice have N degrees of freedom, which means that there are N linearly independent modes, whereas vector modes have 3N degrees of freedom. Generic continuous modes, in general, span infinite dimensions.

> There are clearly many different ways to select the basis vectors in mode space. The goal of the following paragraphs is to lean that some basis vectors are very special, and can simplify enormously the solution of a variety of problems involving modes.

2.2 Symmetry operations on lattice modes

Each lattice mode could be thought as defining a "pattern" on the crystal lattice, very much akin to the ones we have already encountered. Clearly, a generic mode will not obey the full symmetry of the crystal; consequently, if we apply what was previously a symmetry operator to a mode, in the form of an "active" transformation, we will in general get a **different mode**; we can, again, surmise that the new mode will largely behave as the old one because it is related to it by symmetry. It is easy to convince ourselves that these transformations **preserve the linearity of mode space**, so that, if g is an operator, $\mathbf{m}_1$ and $\mathbf{m}_2$ are modes and a and b are scalar constants

$$g[\mathrm{a}\mathbf{m}_1 + \mathrm{b}\mathbf{m}_2] = \mathrm{a}g\mathbf{m}_1 + \mathrm{b}g\mathbf{m}_2 \tag{1}$$

Therefore, **the symmetry operators of the crystal are linear operators in mode space**. Once a **suitable basis** is introduced in mode space **the symmetry operators can be *represented* by matrices**. We will not explore this further, but refer to appendix I (section 8.2) for a short introduction to matrix representations. A modern presentation of the theory of "irreducible representations" is given in [1].

2.3 An example of normal mode decomposition

Rather than describing in details the theory of irreducible representation, with all its theorems, lemmas and corollaries, we will here see a practical example in the form of a very simple set of displacement modes of for a hypothetical molecule with D_4 symmetry. **Our ultimate goal is to find the normal modes of vibration of the molecule**, but we will build up to this result by first considering the **possible displacements** of the atoms in the molecule. To further simplify the problem, we will consider only planar modes, so that the symmetry group to consider is the familiar $4mm$ 2-dimensional point group. Our molecule will have four atoms at the corners and one, of a different species, in the centre. We can start by counting the degrees of freedoms — two per atoms (x and y displacements), for a total of 10 degrees of freedom. We could consider each of these degrees of freedom as a *mode* — for instance, the displacement of atom 1 along the x axis (mode "[1x]") could be one of the modes (fig. 1 top left for the labelling). In this case, however, symmetry operations would mix all the modes; for instance, the 4^+ operator (90° counterclockwise rotation) would transform the mode $[1x]$ into a new mode whereby atom 2 would be displaced in the positive y direction, mode "[2y]" etc.

2.3.1 The "1D" modes of $4mm$

As an alternative to the simple modes like $[1x]$ and $[2y]$, let us consider the modes in fig. 1. For these modes, we use the labelling Γ_1, Γ_2, etc., which is widely used by physicists. It is very easy to understand that all these modes are either *symmetric* or *antisymmetric* (i.e, the mode is transformed into *minus itself*) under *all* symmetry operators of the $4mm$ point group. in particular (we remind that m_{10} is the mirror plane parallel to the x axis etc.:

- Mode Γ_1 is *symmetric* under *all* the symmetry operators of the group — we say that it transforms under the *totally symmetric mode*.

- Mode Γ_2 is *symmetric* under 1, 2, m_{10} and m_{01} and *antisymmetric* under 4^+, 4^-, m_{11} and $m_{1\bar{1}}$.

- Mode Γ_3 is *symmetric* under 1, 2, m_{11} and $m_{1\bar{1}}$ and *antisymmetric* under 4^+, 4^-, m_{10} and m_{01}.

- Mode Γ_4 is *symmetric* under 1, 2, 4^+ and 4^- and *antisymmetric* under m_{10}, m_{01}, m_{11} and $m_{1\bar{1}}$.

In general, we would say that "something that transforms like Γ_1 to mean that it has the same transformation rules.
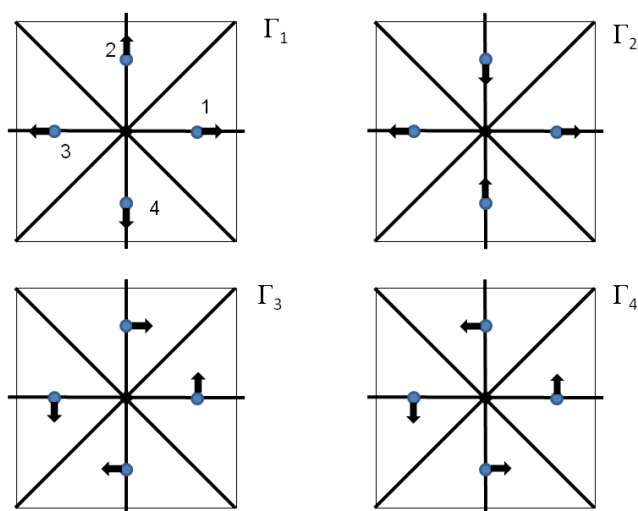

Figure 1: The four "1 dimensional modes" of the square molecule. These modes transform into either themselves (symmetric) or minus themselves (antisymmetric) upon all symmetries of the molecule.

Therefore, with this choice of modes the symmetry operators, $M(g)$ are "represented" by *numbers*. For the totally symmetric mode, every operator in $4mm$ is mapped to the number 1. For the others, operators are mapped onto 1 or -1, depending on whether the mode is symmetric or antisymmetric, respectively. For example (we enclose the modes in square brackets for clarity):

$$
\begin{aligned}
4^+\,[\Gamma 2] &= -1\,[\Gamma 2] \\
2\,[\Gamma 3] &= +1\,[\Gamma 3] \\
m_{11}\,[\Gamma 4] &= -1\,[\Gamma 4]
\end{aligned}
\tag{2}
$$

etcetera. With these modes, we have exhausted 4 of the 8 degrees of freedom of associated with the "corner" atoms. What about the other four?

2.3.2 The remaining four modes

Let us now consider the modes depicted in fig. 2. Here, the situation is clearly different. By applying one by one the symmetry operators (e.g, graphically) we can verify that:

- Certain symmetry operators **interchange the modes**. For example, the operator 4^+ transforms mode $[I]$ into mode $[II]$ and $[III]$ into mode $IV]$, etc.

- There is no way of decomposing these modes into "simpler" modes that transform as the previous group, i.e., as a multiplication by $+1$ or -1. **This is not immediately obvious but can be shown with a bit of work.**

- $[I]$ is *never* transformed into $[III]$ (or vice versa) and $[III]$ is *never* transformed into $[IV]$ (or vice versa). In other words, **the subspace of mode space spanned by $[I]$ and $[II]$ is *closed* with respect to the symmetry operators** (and likewise for $[III]$ and $[IV]$.

- The pairs $[I]$-$[II]$ and $[III]$-$[IV]$ **transform in the same way**. This becomes clear if we write the transformations in matrix form.
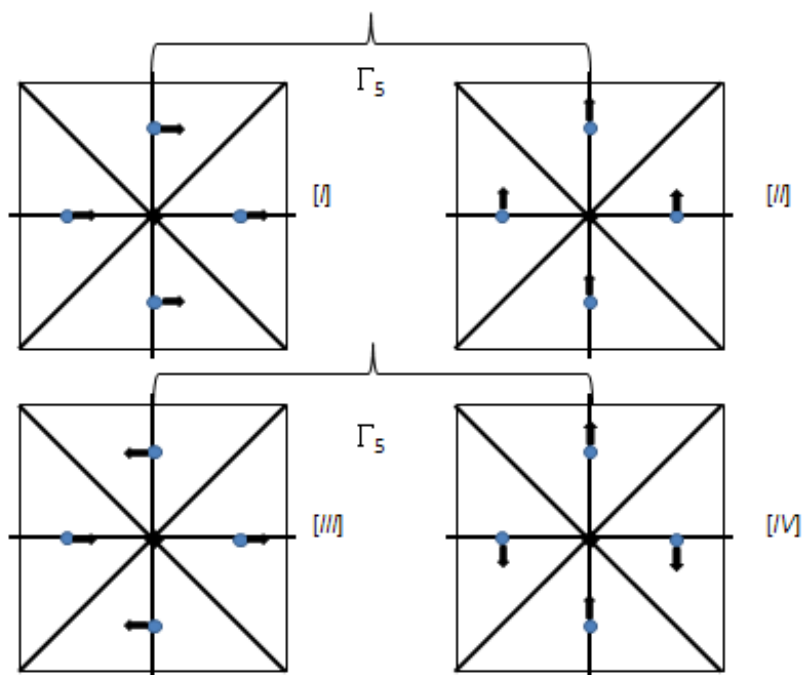

Figure 2: The four "2 dimensional modes" of the square molecule. These modes transform into either $\pm$ themselves (symmetric/antisymmetric) or *into each other in pairs* upon all symmetries of the molecule. Note that all these modes are *antisymmetric* upon 2-fold rotation.

2.3.3 Another example: the central atom

As a second example, we analyse the displacements of the central atom of our hypothetical molecule, located on the fourfold axis. This atom has two degrees of freedom, as shown in fig 3. It is a simple exercise, left to the students, to verify that the two corresponding modes **transform as** Γ_5.
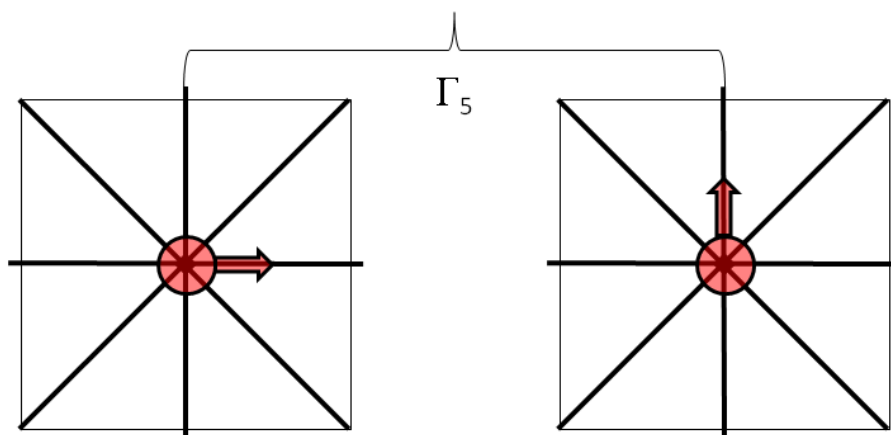

Figure 3: The two central-atom modes of the square molecule. One can verify that they transform as the "2-D" corner modes, i.e., with the representation Γ_5

3 Normal-mode analysis of molecular vibrations

In this section, we should (hopefully) see the point of all the hard work we put in decomposing the displacement modes into these special, symmetrised modes. In short, all the normal modes of vibration can be constructed by combining modes that transform in the same way. This enormously simplifies the problem of diagonalising the normal-mode matrix (see below), and will be come shortly even more significant, as we deal with dynamical matrices of infinite dimension (lattice modes.)

3.1 Normal-mode matrix

You should already be familiar with the material in this paragraph — if so, just skip it.

We start with the expression for the kinetic and potential energies in the limit of "small" displacements from the equilibrium position. In a somewhat short-hand notation, they are, respectively

$$\mathcal{E}_K = \frac{1}{2} \sum_i m_i \dot{x}^2$$

$$\mathcal{E}_P = \frac{1}{2} \sum_{i,j} \frac{\partial^2 V}{\partial x_i \partial x_j} x_i x_j \tag{3}$$

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

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

$$\xi_i = x_i \sqrt{m_i} \tag{4}$$

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

$$\mathcal{E}_K = \frac{1}{2} \sum_i \dot{\xi}^2$$

$$\mathcal{E}_P = \frac{1}{2} \sum_{i,j} \left(\frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial x_i \partial x_j} \right) \xi_i \xi_j \tag{5}$$

2. We write the equation of motion as:

$$\ddot{\xi}_i + \sum_j \left(\frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial x_i \partial x_j} \right) \xi_j = 0 \tag{6}$$

3. We seek solution of the form

$$\xi_i = q_i \, e^{i\omega t} \tag{7}$$

from which we derive the secular equation

$$\omega^2 q_i = \sum_j \left(\frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial x_i \partial x_j} \right) q_j \tag{8}$$

Eq. 8 is solved in the usual manner by diagonalising the matrix on the right-hand side.

3.2 Solution of the dynamical problem for our hypothetical molecule

The corner atoms are linked to their neighbours by a spring with constant K_1 and to the central atom with a spring with constant K_2 (fig. 4). In considering the vibration modes of a molecule, we can exclude the ones that give rise to translations (2) and rotations (1) of the *whole* molecule, so we are left with 7 degrees of freedom in total. The normal-mode equation, nevertheless, will entail the diagonalisation of a 10×10 matrix, whilst we expect that three of the resulting modes will have zero frequency.
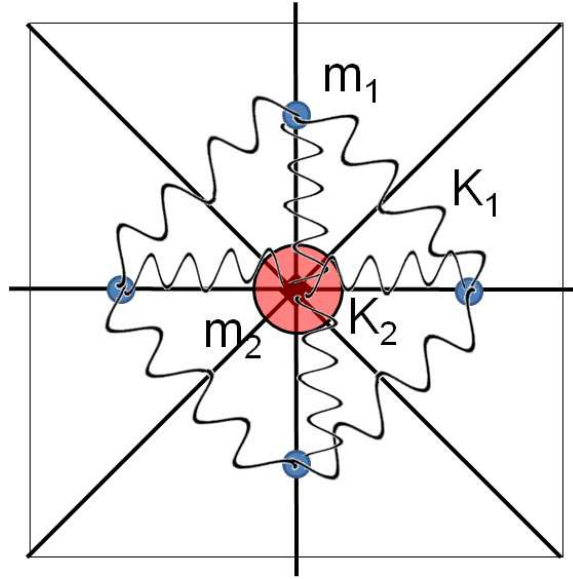

Figure 4: The masses and spring constants used to solve the dynamical problem of our molecule.

We can, however, dramatically simplify the problem by exploiting symmetry. Let us consider a normal mode Q_i so that

$$Q_i = \sum_j a_{ij} \, q_j \tag{9}$$

and let us assume that Q_i is **non-degenerate**, so that it uniquely satisfies the secular equation with a frequency ω_i. We can simply use physical intuition to conclude that **all the modes related by symmetry to Q_i, such as $(g\,[Q_i])$ must also be eigenvectors with the same frequency**. However, we just assumed that Q_i is **non-degenerate**, so it must necessarily follow that

$$g\,[Q_i] = cQ_i \tag{10}$$

where c is a **constant** (in fact, a *unitary constant*, here, ± 1). We reach therefore the following surprising conclusion:

The non-degenerate modes of our molecule must transform as one of the four modes Γ_1–Γ_4. Since there are no other modes with these transormation properties, Γ_1–Γ_4 must be normal modes!

In particular, we know that for these modes we should not invoke displacements of the central atom, because

Modes can only "mix" with other modes of the same symmetry.

3.2.1 Frequencies of the Γ_1–Γ_4 modes

We can immediately find out their frequency by equating the potential and kinetic energy terms (conservation of energy). For example, if mode Γ_1 has amplitude δ, the "stretch" of each K_1 spring is $\sqrt{2}\delta$, whereas that of each K_2 spring is δ. Equating potential and kinetic energy per ion (we omit a factor of 4 in each) we get:

$$\frac{1}{2}\left(2K_1 + K_2\right) = \frac{1}{2}m_1\omega_1^2 \tag{11}$$

whence (and likewise for the other modes):

$$
\begin{aligned}
\omega_1 &= \left(\frac{2K_1 + K_2}{m_1}\right)^{1/2} \\
\omega_2 &= \left(\frac{K_2}{m_1}\right)^{1/2} \\
\omega_3 &= \left(\frac{2K_1}{m_1}\right)^{1/2} \\
\omega_4 &= 0
\end{aligned}
\tag{12}
$$

3.2.2 Frequencies of the other modes

We can repeat the same argument we made regarding non-degenerate eigenvectors to **degenerate eigenvectors**, and reach a very similar conclusion:

The degenerate eigenvectors with degeneracy d transform in such a way as to span a subspace of dimension d (unless the degeneracy is accidental). This follows from the fact that $g[Q_i]$ is an eigenvector with the same frequency, and must be either the same mode or a degenerate mode.

In our problem, we have 6 modes with the same Γ_5 transformation properties, transforming in

pair into each other. How do we combine them to get degenerate normal modes? In principle, they can all mix, since they have identical transformation properties. Therefore, it would seem that the complexity of the problem has only been slightly reduced. However, we can get much closer to the solution by considering that:

- If $K_2 = 0$, the Γ_5 modes listed above are the normal modes of the problem. In particular, modes $[I]$ and $[II]$ and the central atom modes have zero frequency.

- If $K_2 \neq 0$, the new normal modes can only be admixtures of *collinear* modes (e.g., $[I]$, $[III]$ and the x-displacement of the central atom). We could assume this as physical intuition, but formally this comes about because the part of the dynamical matrix containing K_2 is diagonal, and cannot mix components.

- Even if $K_2 \neq 0$, two of the normal modes remain at zero frequency: they correspond to rigid displacements of the whole molecule in the x and y direction.

Therefore, the problem reduces to finding the eigenvectors of a zero-determinant 3×3 matrix - a quadratic equation that has a simple analytic solution (see Appendix II).
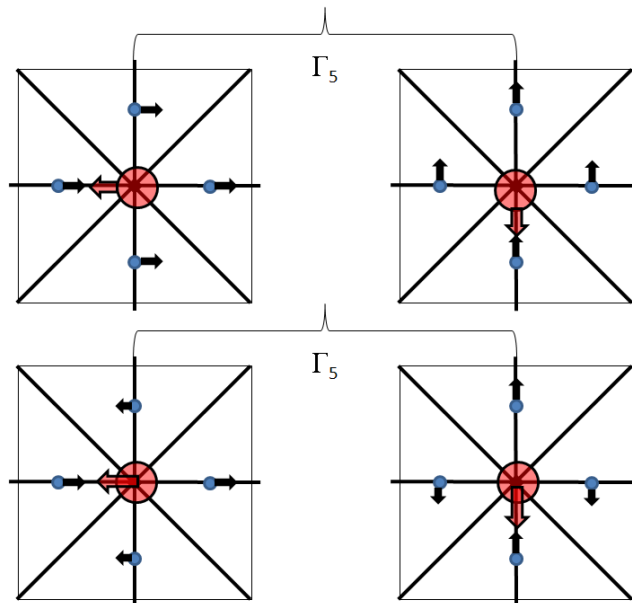

Figure 5: Examples of non-zero-frequency normal modes of Γ_5 symmetry involving two-atom displacements. The exact mixing coefficient depend on the mass and spring constant parameters.

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4 Extended lattices: phonons and the Bloch theorem

Up to this point, we have only considered an isolated molecule with point-group symmetry. How will the concepts that we learned apply to space groups, which, as we have seen, have infinite dimension? The answer is that all of the symmetry machinery — particularly representation analysis — still applies. The demonstration is much beyond the scope of this course (a good reference, again, is [1]). We will instead proceed as follows: we will prove a very simple but far-reaching result, known as the **Bloch theorem**

The Bloch theorem: **The lattice modes *fully symmetrised* with respect to the translation group are constructed by defining an arbitrary mode $[u(0)]$ in the first unit cell and repeating in all the other unit cells with origin R_i the *same pattern* multiplied by a phase factor, as**

$$[u(\boldsymbol{R}_i)] = [u(0)]e^{i\boldsymbol{k}\cdot\boldsymbol{R}_i} \tag{13}$$

The vector k is known as the *propagation vector* of the mode, and can be restricted to the *first Brillouin zone*. This is clear from the fact that an arbitrary propagation vector k can be written as

$$\boldsymbol{k} = \boldsymbol{\tau} + \boldsymbol{k}' \tag{14}$$

Where τ is a RL vector. However, τ can always be omitted since $R_i \cdot \tau = 2\pi n$
The proof of the Bloch theorem is very simple: one shows that if one applies the lattice translation t (with translation vector t) to the mode in eq. 13, one obtains

$$t\,[u(\boldsymbol{R}_i)] = e^{-i\boldsymbol{k}\cdot\boldsymbol{t}}[u(\boldsymbol{R}_i)] \tag{15}$$

This is shown graphically in fig. 6. Because this mode transforms upon translation by multiplication with a constant, *it must be fully symmetrised*.

It is necessary to emphasise that the arbitrary Bloch modes we just described are in general fully symmetrised *with respect to the translation group* but **not** fully symmetrised *with respect to the other symmetry elements of the space group*. Considerably more effort is required to achieve full symmetrisation.

All eigenfunctions of a Hamiltonian with a translational periodicity are Bloch waves or linear combinations of Bloch waves with symmetry-related propagation vectors.

4.1 A simple case: symmorphic groups

A considerable simplification of the problem occurs when the space group is **symmorphic**, i.e., as we will remember, it contains a point with site symmetry equivalent to the crystal class. We must also require that the propagation vector k obeys the same symmetry. In this case, we can apply the following recipe:
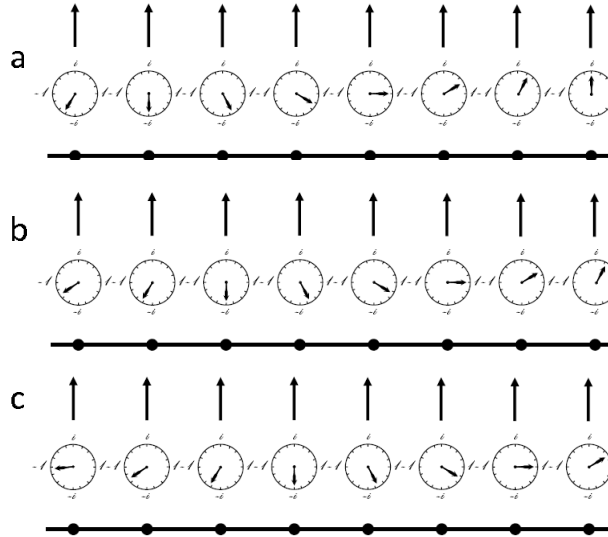
Figure 6: A simple example of a vector Bloch mode to illustrate the transformation properties of these modes upon translation. The arrows represent the *amplitude* of the mode (here a constant vector), while the clocks represent the *phases*. Mode (b) and (c) are the same as mode (a) translated by one or two unit cells to the *right*. However, they can also by obtained *multiplying* mode (a) by $exp(ikR)$ where R is one or two lattice spacings for (b) and (c), respectively, and k is the **propagation or Bloch vector of the mode.**

1. Consider all the atom in the unit cell centred around the high-symmetry point as a "molecule" and construct the appropriate point-group modes.

2. Propagate the modes using the Bloch construction (eq. 13).

We can see the implications of this by examining once again the modes of our square molecule, and trying to imagine how they will propagate in an extended lattice, for example, with space-group symmetry P4mm. To comply with our requirements, the propagation vector must be along the c axis. We can see that:

- The three zero-frequency modes will give rise to **acoustic modes**. All the other modes will be **optical**.

- If no other spring constants are introduced, the energy of the modes will be unchanged. Springs *between* the "molecules" in different unit cells, will give rise to *dispersion*, i.e., the energy will depend on **k**.

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5 Experimental techniques using light as a probe: "Infra-Red" and "Raman"

Optical techniques are extremely useful to determine vibration frequencies in molecules, as well as phonon frequencies in solids. Here, we will briefly introduce two techniques — Infrared (IR) absorption/reflection and Raman scattering. As we shall see, these techniques have opposite and complementary selection rules, and must be used in combination to measure all frequencies. Inelastic neutron scattering (see below) does not suffer from selection rules, and is able to measure all vibration modes at the same time. As the name suggests, IR spectroscopy is performed by measuring the *absorption* or *reflection* of infra-red radiation (the latter exploiting the fact that reflectivity contains information about absorption). In the more "direct" absorption process, a photon is completely absorbed and a *phonon* is created instead (fig. 7 **a**). Raman scattering is a "photon-in-photon-out" technique, where one measures the *wavelength change of visible light* as a phonon is created or annihilated (fig. 7 **b**). Typical values of the incident energy and wave-vector are:

$$
\begin{aligned}
\text{IR} \qquad & \hbar\omega \sim 10 - 100\,\text{meV} \\
& \frac{1}{\lambda} \sim 10^3\,\text{cm}^{-1} \\
\text{Raman} \qquad & \hbar\omega \sim 1 - 10\,\text{eV} \\
& \frac{1}{\lambda} \sim 10^5\,\text{cm}^{-1}
\end{aligned}
\tag{16}
$$

5.1 IR absorption and reflection

We know from the theory of optics that the dielectric constant acquires an anomalous component with both real and imaginary parts near a resonance of the material. In particular (you will have seen this in more details in the "Optical Properties of Solids" part of the C3 course. We defer to this part for the detailed mathematical treatment). The following results can be obtained by analysing the *Classical Dipole Oscillator Model*:

- The reflectivity R of a material contains information about both refractive index n and absorption coefficient α.

- Near a resonance, both R and n become **anomalous**, and show a **peak** at the resonant energy.

- The width of the peak is related to the width (sharpness) of the resonance (the "γ" coefficient, which you might have encountered already).
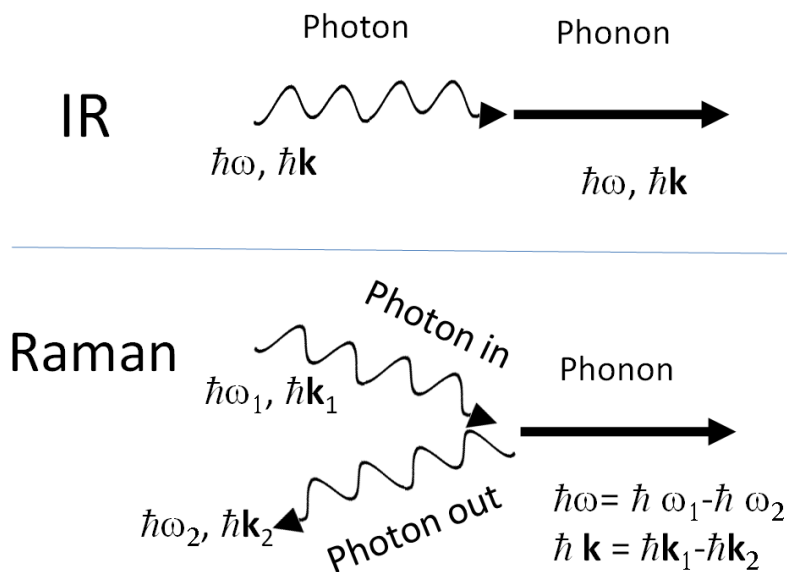
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Figure 7: Diagrammatic representation of the IR and Raman scattering processes in a crystalline material, illustrating the energy and momentum conservation. For a molecule, the recoil of the molecule itself ensures conservation of momentum.

An example of an absorption spectrum for a the Vanillin molecule is shown in fig 8.
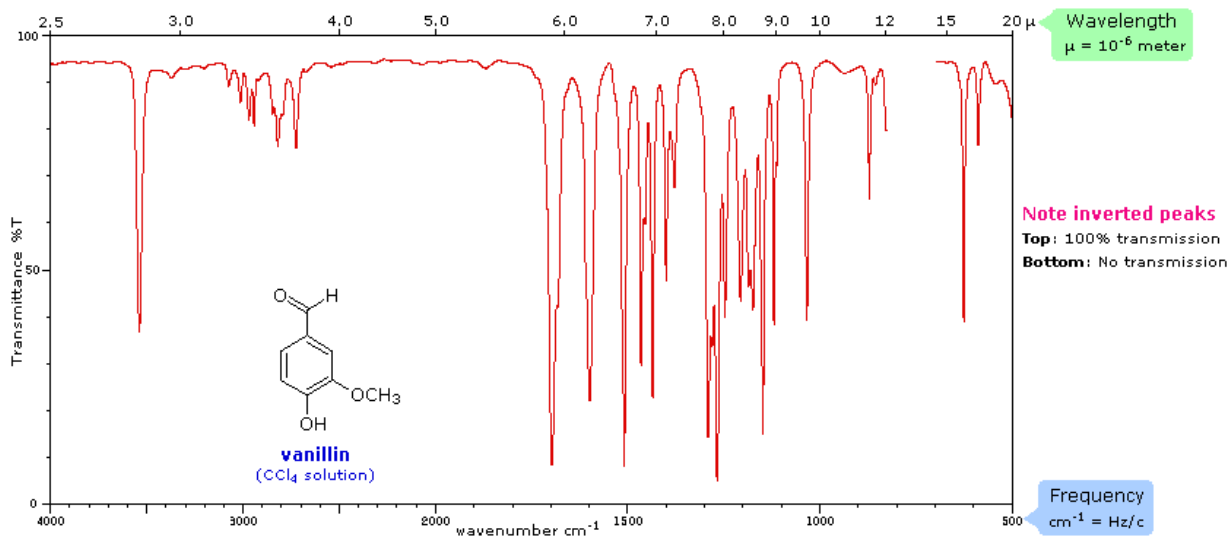

Figure 8: The IR transmission (1/absorption) spectrum of the vanillin molecule. Note the sharp peaks where the IR light is strongly absorbed by the molecular vibration modes.

> **Typical vibration frequencies in molecules and *optical* phonon frequencies in solids (see here below) are of the order of several THz ($1000 \text{ cm}^{-1} = 30$ THz), which falls in the IR region of the electromagnetic spectrum. For our purpose, it is important to stress two things:**
>
> - **It is the displacement of oscillating charges that causes the polarisation. In other words, in order for a resonance to cause a IR anomaly, the vibration of phonon modes *must generate oscillating electrical dipoles*.**
>
> - **The momentum of the electromagnetic radiation, $h\nu/c$, is much smaller than that of typical phonons, except for phonons very near the zone centre. On the other hand, the frequency of near-zone-centre *acoustic* phonons is much too low to be accessed with this method. Therefore, in extended solids, IR spectroscopy *essentially probes zone-centre optical phonons*.**

With this introduction, we can look back at the vibration modes of our molecule, and ask ourselves which ones will be visible by IR. The answer, once again, is obtained from symmetry considerations:

> **Since a dipole moment is parity-odd (i.e., it change sign upon inversion) only parity-odd modes (i.e., modes that are antisymmetric by inversion) can be "IR active". The same selection rules apply to *centrosymmetric crystals* where phonons can also be classified as parity-even and parity-odd.**

Since we only considered 2-dimensional modes, we can identify inversion and 2-fold rotation and look at the symmetry-antisymmetry properties of our normal modes. Referring to section 2.3.1 and to fig. 1 and 5, we can easily see that modes Γ_1–Γ_4 are *symmetric* upon 2-fold rotation, whereas all the Γ_5 modes are *antisymmetric*. It follows that only the modes in 5 (degenerate in pairs) will be IR-active — all the rest are *IR-silent*. The IR spectrum of this molecule (excluding "overtones"= higher harmonics) will only contain 2 peaks.

5.2   Raman scattering

The second important optical spectroscopy technique is **inelastic light scattering**. In extended solids, this technique can be used to measure both *acoustic* and *optical* phonons. Inelastic light scattering via acoustic phonons is known as **Brillouin scattering** — a technique that is perhaps more often applied to liquids. Inelastic light scattering via molecular vibrations or optical phonons is known as **Raman scattering** In both cases, the previous consideration apply and the phonon probed optically are those very near the zone centre.

In the case, of Brillouin scattering however, acoustic phonons can be probed because their frequency is equal to the frequency *change* $\omega_1 - \omega_2$, which can be a small fraction of ω_1. Note that the shift can be positive (phonon *creation*) or negative(phonon *annihilation*), so, in general, two
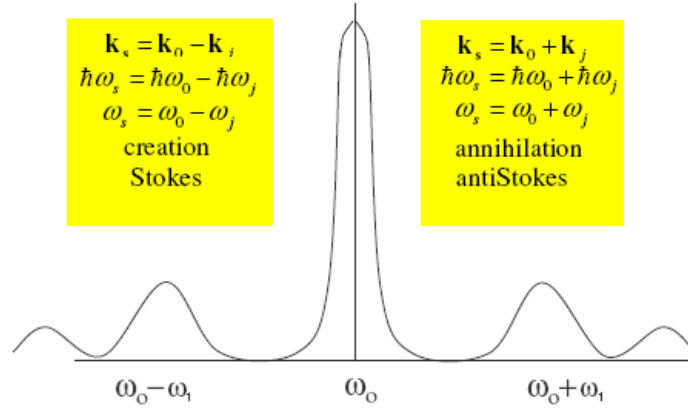
peaks are observed (fir 9.

Figure 9: Phonon creation ("Stokes" process) and phonon annihilation ("antiStokes" process) in Brillouin scattering. in Raman scattering, only the "Stokes" process is usually observed at room temperature, because the optical phonon modes have low populations.

The mechanism giving rise to Raman scattering involves a **change in the polarisability** of the molecule or crystal as it vibrates, which generates alternative selection rules to the IR process. Again, this can be seen classically as follows: the polarisation vector inside the material at a given position r and time t can be written as:

$$
\begin{aligned}
\boldsymbol{P}(t, \boldsymbol{r}) &= \overline{\overline{\boldsymbol{\alpha}}} \boldsymbol{E} e^{i(\boldsymbol{k}_0 \boldsymbol{r} - \omega_0 t)} + c.c. \\
\overline{\overline{\boldsymbol{\alpha}}} &= \overline{\overline{\boldsymbol{\alpha}_0}} + \sum_i \overline{\overline{\boldsymbol{\alpha}_i}} Q_i \, e^{i(\boldsymbol{k}_i \boldsymbol{r} - \omega_i t)} + \ldots + c.c.
\end{aligned}
\tag{17}
$$

In eq. 17 $\boldsymbol{k}_0$ and ω_0 are the wavevector and frequency of the electric field and $\boldsymbol{k}_i$ and ω_i are the values for normal mode i having amplitude Q_i. The quantities $\overline{\overline{\boldsymbol{\alpha}_0}}$ and $\overline{\overline{\boldsymbol{\alpha}_i}}$ are components of the **polarisability tensor**, since, in general, $\boldsymbol{P}$ is not parallel to $\boldsymbol{E}$. Importantly, all the $\overline{\overline{\boldsymbol{\alpha}}}$'s are **properties of the crystal, and must have the full symmetry of the crystal**.

By combining the two expression in eq. 17 we obtain

$$
\boldsymbol{P}(t, \boldsymbol{r}) = \overline{\overline{\boldsymbol{\alpha}_0}} \boldsymbol{E} e^{i(\boldsymbol{k}_0 \boldsymbol{r} - \omega_0 t)} + \sum_i \overline{\overline{\boldsymbol{\alpha}_i}} Q_i \boldsymbol{E} \, e^{i[(\boldsymbol{k}_0 \pm \boldsymbol{k}_i) \boldsymbol{r} - (\omega_0 \pm \omega_i) t)]} + \ldots + c.c.
\tag{18}
$$

We can see from eq. 18 that the polarisation vibrates with three distinct frequencies: that of the original photon and those shifted upwards or downwards by the phonon frequency. A full quantum-mechanical analysis is required in order to obtain the relative height of the "Stokes" and "antiStokes" peaks (see, again, fig. 9.

Here, we are principally interested in the symmetry selection rules. Let us have another look at eq. 18 in the case of a **centrosymmetric molecule or crystal**. Once again, we remind that the $\overline{\overline{\alpha}}$'s **must have the full symmetry of the molecule or crystal — in particular, they must be parity-even for a centrosymmetric system**. Both P and E are parity-odd, so **the phonon or vibration must be parity-even** (This is strictly true only if one ignores the small amount of momentum carried by the photon). In the case of our molecule, this condition is satisfied by modes Γ_1-Γ_4, which are therefore **Raman active**.

6   Inelastic neutron scattering

Inelastic neutron scattering (INS) is another powerful technique to measure molecular and lattice vibrations. In this case, the probe is a thermal neutron, and one measures the change in energy and momentum of the scattered neutron. This process is illustrated in diagrammatic form in fig. 10 for a crystal. For a molecule, as in the case or IR and Raman scattering, conservation of momentum is ensured by the recoil motion of the molecule itself.
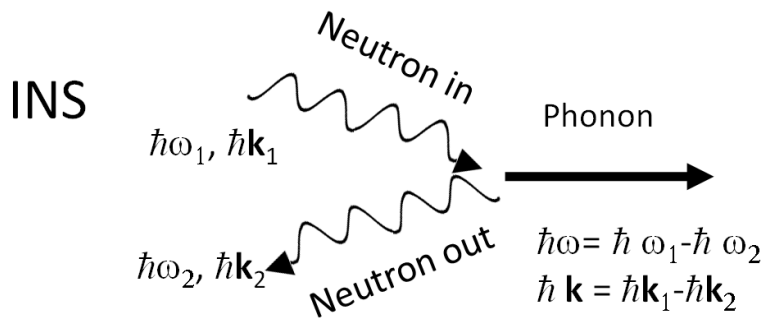

Figure 10: Diagrammatic representation of the inelastic neutron scattering process (INS) in a crystalline material, illustrating the energy and momentum conservation. For a molecule, the recoil of the molecule itself ensures conservation of momentum.

Typical neutron parameters employed for INS are

$$
\begin{aligned}
\text{INS} \quad & \hbar\omega \sim 10 - 400\,\text{meV} \\
& \frac{1}{\lambda} \sim 10^7 - 10^9\,\text{cm}^{-1}
\end{aligned}
$$

(19)

As we can see, the neutron and IR energies are comparable, but the **neutron wavenumber (momentum) is much larger**, enabling one to access several Brillouin zones

The main advantages of INS over IR and Raman are in fact

- The range and momentum is much extended.

- There are no selection rules, so all phonon modes can be accessed at the same time.

The most popular neutron instrument used to measure phonons in crystal is known as a **triple-axis spectrometer** (fig. 11). By varying the monochromator, sample, analysed and detector angle one can explore a vast say of the energy-momentum space.
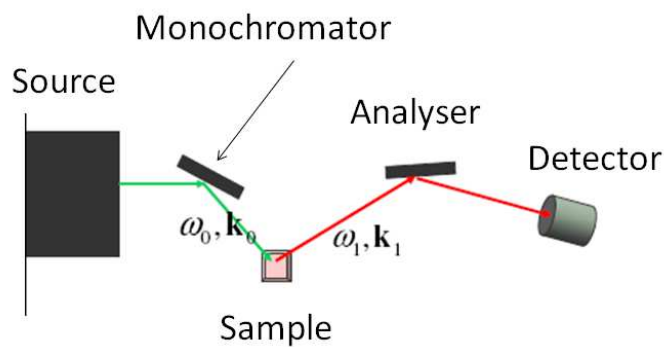

Figure 11: Schematic drawing of a "triple-axis" spectrometer.

7 Bibliography

M. Dresselhaus [1] A very new 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.

References

[1] M.S. Dresselhaus, G. Dresselhaus and A. Jorio, *Group Theory - Application to the Physics of Condensed Matter*, Springer-Verlag Berlin Heidelberg (2008).

8   Appendix I: Representations and matrices

8.1   Matrix representation of generic modes

Let us imagine that we want to describe a generic displacement pattern as a *linear superposition* of the generic modes in which only one atom is displaced, as

$$
a[1x] + b[1y] + c[2x] + d[2x] + \ldots \rightarrow
\begin{pmatrix}
a \\
b \\
c \\
d \\
\vdots
\end{pmatrix}
\tag{20}
$$

Since, as we just said, symmetry operations mix all the modes, **the *matrix representation* of a generic symmetry operator will contain non-zero off-diagonal elements.**

For example, the matrix representation of the operator 4^+ on this basis will be:

$$
4^+ \rightarrow
\begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0
\end{pmatrix}
\tag{21}
$$

> The "special modes" we are seeking are the ones in which the representative matrices are "as diagonal as possible".

8.2   Representations

The matrices associated with a given group also form a group, where the composition is replaced by **matrix multiplication**. If $M(g)$ is the matrix associated with g, it is rather straightforward to prove the following:

$$
\begin{aligned}
M(g \circ f) &= M(g)M(f) \\
M(g^{-1}) &= M^{-1}(g) \\
M(E) &= \mathbb{1}
\end{aligned}
\tag{22}
$$

where $\mathbb{1}$ is the identity matrix. A mapping (not necessarily bijective) of a group $\{g\}$ into a set of matrices $\{\mathrm{M}\}$ obeying the identities in eq. 22 is known as a **representation** of the group (a bijective mapping is known as a *faithful* representation). Note that from eq. 22 follows that all matrices have non-zero determinant.

8.2.1 The "2D" modes in matrix form

Let us consider the set of displacements that are **linear combinations** of modes $[I]$ and $[II]$ — in other words, all the displacements of the type

$$a[I] + b[II] \rightarrow \begin{pmatrix} a \\ b \end{pmatrix} \tag{23}$$

where the **array notation** in eq. 24 should be obvious. An alternative phrasing is that we are considering the **subspace** spanned by modes $[I]$ and $[II]$. The transformations can now be expressed in **matrix form**, as illustrated in tab. 1.

Table 1: Matrix representation of the transformations of point group $4mm$ on the subspace spanned by modes $[I]$ and $[II]$

1	2	4^+	4^-
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$

m_{10}	m_{01}	m_{11}	$m_{1\bar{1}}$
$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$

By repeating the same operation on the subspace spanned by modes $[III]$ and $[IV]$ as

$$c[III] + d[IV] \rightarrow \begin{pmatrix} c \\ d \end{pmatrix} \tag{24}$$

we discover that **the matrix expressions of the symmetry operators in this subspace are exactly the same**. As stated before, the pairs $[I]$-$[II]$ and $[III]$-$[IV]$ **transform in the same way**. We call Γ_5 this matrix representation of the group (in the two subspaces).

8.2.2 The full matrix representation

We are now in the position of replacing the "off-diagonal" matrices like the one in eq. 21 with "almost diagonal" matrices. We say "almost" because the fact that Γ_5 cannot be further "reduced" means that some of its matrices will always contain off-diagonal elements. Let us re-write the matric representation of 4^+ (as for eq. 21) in terms of the new basis vectors Γ_1–Γ_4 and $[I]$–$[IV]$ — the latter related to Γ_5, so that

$$a[\Gamma_1] + b[\Gamma_2] + c[\Gamma_3] + d[\Gamma_4] + e[I] + f[II] + g[III] + h[IV] \rightarrow \begin{pmatrix} a \\ b \\ c \\ d \\ \vdots \end{pmatrix} \qquad (25)$$

With this basis, the matrix representation of 4^+ will be.

$$4^+ \rightarrow \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \qquad (26)$$

> **When we express it in term of the new, "symmetrised" modes, the matrix representation of all the operators is *block-diagonal*, and it has the same shape for all the operators. We can also note that the two blocks on the bottom-right corner are the same for all the operator, indicating that the transformation of the associated basis vectors is the same.**

8.2.3 Irreducible representations

> **All the concepts in this section are important and should be remembered. We can see that the statements are true for the specific example. General proofs are presented in [?], chapters 1-3.**

- The matrix representations of the group into the **individual subspaces** spanned by the symmetrised modes are called **Irreducible Representations** (*irreps* in the remainder)

- The *irreps* are a unique property of the **group**, not of the specific system of modes under investigation. For example, point group $4mm$ has always 5 *irreps*.

- It is always possible to choose **unitary matrices** (real or complex) for a given representation. In the case we showed, the matrices are all real and orthogonal.

- Their matrix representation is also unique, except for a **unitary transformation** of the matrices. This is equivalent to a change in the basis vectors within each subspace.

- **1-dimensional representations**, i.e., with matrices that reduce to a single number (like Γ_1–Γ_4 above) are **uniquely defined**.

- For multi-dimensional representations, the **trace** of the matrices (known as the **character**) is also uniquely defined, as it is left invariant by unitary transformations.

- The representation of any system of lattice modes can be **uniquely decomposed in *irreps***. For example, in our case, we would use the shorthand notation:

$$\Gamma_{full} = \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 \tag{27}$$

  where Γ_{full} is the full matrix representation of the $4mm$ group upon the system of modes. Note that Γ_5 appears twice. As we will see shortly, not all *irreps* have to be present.

A series of powerful theorems (which, unfortunately, we do not have the time to study) enables one to perform the decomposition into *irreps* and to construct the relevant basis vector.

8.2.4   Representation decomposition for the central atom

Based on what we showed in the text, it is easy to understand that the full representation of the central atom displacements contains only Γ_5, so

$$\Gamma_{full} = 2\Gamma_5 \tag{28}$$

9   Appendix II: Frequencies of the compound modes

As explained in the text, we are working in the subspace of 3 collinear modes, say mode $[I]$, $[III]$ and the central atom displacement along x. Using this basis set, the reduced dynamical matrix can be written as:

$$\frac{K_1}{m_1} \begin{bmatrix} 2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \frac{K_2}{m_1} \begin{bmatrix} 1/2 & 1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \frac{K_2}{\sqrt{m_1 m_2}} \begin{bmatrix} 0 & 0 & -1/2 \\ 0 & 0 & -1/2 \\ -2 & -2 & 0 \end{bmatrix}$$

$$+ \frac{K_2}{m_2} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2 \end{bmatrix} \tag{29}$$

This matrix has zero determinant for every value of the parameters. The eigenvalue equation is therefore quadratic, and can be solved analytically.