Symmetry in Surface-Adsorbate Interaction - the wallpaper symmetry groups

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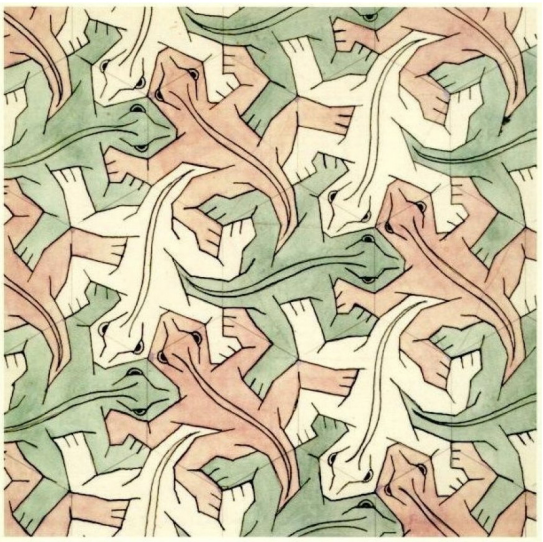


Aim of these notes is to discuss the symmetric properties of a potential energy surface for a molecule interacting with a surface. In particular the focus will be on the characterization of the group of symmetry of the translation parallel to the surface.

1 Symmetry and Degrees of freedom

We consider the Potential Energy Surface (PES) for a gas-surface reactive reactive process, *e.g.* the dissociative chemisorption of a molecule. As far as we are concerned with the symmetrical properties, we can schematically divide the set of coordinates on which the PES depend in three categories:

1. Reaction coordinates, usually the dissociating bond length (r) and the component of the center of mass along the normal to the surface (Z). Along these coordinates the potential does not show any symmetry.

2. Rotational degrees of freedom of the molecule. Along these coordinates the potential shows the symmetry of the isolated molecule, lowered by the interaction with the surface (and possibly by the internal degrees of freedom of the molecule taken into account). In particular, the operations of symmetry for which the potential is invariant are determined by the (X,Y) projections of the center of mass on the surface plane. In general, we can say that the group of these symmetry will be a subgroup of the point group of the molecule.

3. Translational degrees of freedom along the surface. The symmetry of the potential along these coordinates is entirely determined by the symmetry properties of the surface alone. As we will thoroughly discuss, the symmetry can be conveniently described in terms of the so-called *wallpaper* symmetry groups. Note that in case of molecule on surface, symmetry operations like rotations or translations on (X,Y) might results in a change of angular degrees of freedom as well, so that it is in general not possible to completely decouple the symmetrization in (X,Y) from the angular coordinates. [1]

In the following, we will describe the wallpaper groups and give some usuful group-theoretical characterization of the groups of symmetries which are more interesting for the description of molecule-surface interaction.

2 The wallpaper groups

The **wallpaper groups** are the 2D analogue of the more common crystallographic groups. As the crystallographic groups describe 3D periodic arrangements of atoms / molecules, the wallpaper groups are the appropriate way to describe surfaces and to take into account periodicity in 2 dimensions.

From a mathematical point of view, the 17 wallpaper groups are subgroups of ISO(2), *i.e.* the group of the isometries in the plane. This continuous group is the set of transformations of the plane which leave the euclidean distance invariant. The elements of

[1] We note that the translational symmetry can be broken when the motion of the surface atoms is taken into account. However two considerations make us think that the description in terms of plane symmetry group can still be useful:

- from a theoretical point of view, surface motion can be described in terms of surface phonons, that have well defined properties with respect to the symmetries of the ideal surface. In particular, they still span representation of the surface symmetry group (possibly non totally symmetric representation).
- from a practical point of view, even when considering surface atoms motion PES are computed in a supercell approach, in which by necessity translational symmetry is enforced.

ISO(2) are the combination of a rotation (proper or improper) and a translation. In an abstract setting, we will write isometries as

$$\mathbf{x}' = (\mathcal{O}, \tau)\,\mathbf{x} \qquad x \in \mathbb{R}^2 \quad \mathcal{O} \in O(2) \quad \tau \in T \tag{1}$$

where $O(2)$ is the orthogonal group in 2 dimensions (proper/improper rotations of the plane) and T is the group of translations in 2 dimensions. With the notation of Eq. 1, we will mean a transformation that in a cartesian reference can be written as

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{bmatrix} \pm\cos\vartheta & \mp\sin\vartheta \\ \sin\vartheta & \cos\vartheta \end{bmatrix} \begin{pmatrix} x \\ y \end{pmatrix} + \begin{pmatrix} \tau_x \\ \tau_y \end{pmatrix}$$

where matrices with determinant equal to $+1$ or -1 are proper or improper rotations, respectively. For the sake of conveniency, in the following we will often make use of a non cartesian fractional reference. In the non-cartesian frame, the transformations of ISO(2) will still be given by a formula such as

$$\mathbf{x}' = \mathcal{O}\mathbf{x} + \tau \tag{2}$$

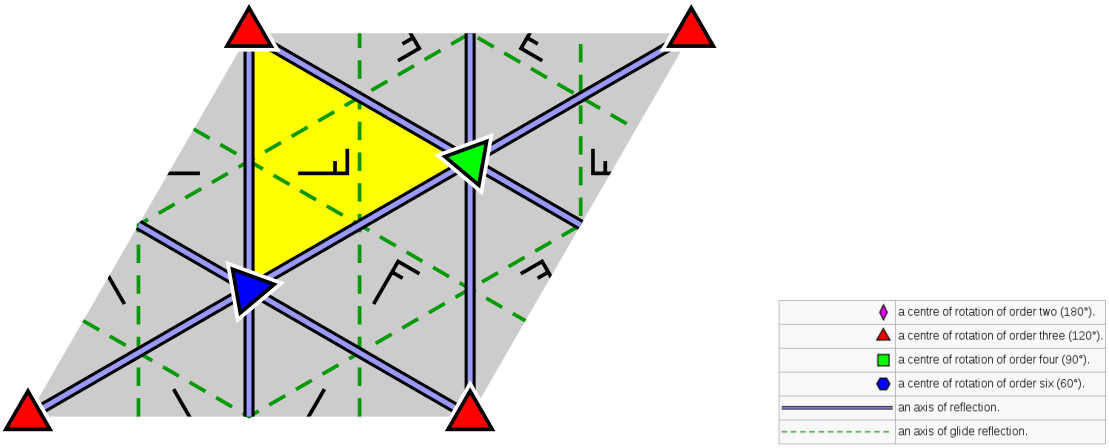
but the matrix $\mathcal{O}$ and the vector τ will have to be properly defined in the new reference system. The group of the isometries is non abelian: it is very easy to show, as an example, that a rotation and a translation do not in general commute. From a vector representation of the action of the group elements (such as 2) it can be easily shown that the group law is given by

$$(\mathcal{O}_2,\, \tau_2)(\mathcal{O}_1,\, \tau_1) = (\mathcal{O}_2\mathcal{O}_1,\, \tau_1 + \mathcal{O}_2\tau_1) \tag{3}$$

The wallpaper groups are subgroups of ISO(2) that include a finite number of proper/improper rotations and a discrete (but infinite) number of translations. It has been proven that there are just 17 types of wallpaper group, and this restriction comes from the compatibility of periodicity with rotations (a periodic arrangement of objects permits the presence of axis of rotations of order 2, 3, 4 and 6 only, the so-called crystallographic restriction theorem).

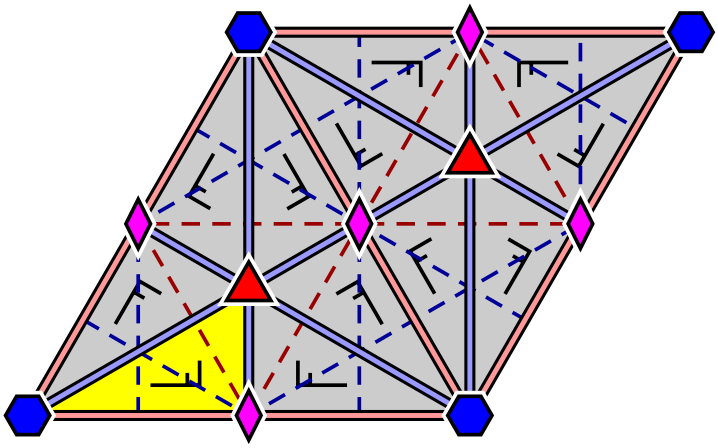
We now will briefly show the three wallpaper groups which are more related to metal surfaces:

- the group **p3m1**, that describes the symmetry of a (111) surface



The group p3m1 is characterized by a hexagonal lattice [2]. In a single unit cell there are 3 axis of rotations, each of order 3. Reflection axes lie on the lines connecting the nearest rotations. The three rotation centers are not related by any symmetry operations, and thus are independent points (for the (111) surface they are simply the TOP, the HCP and FCC sites).

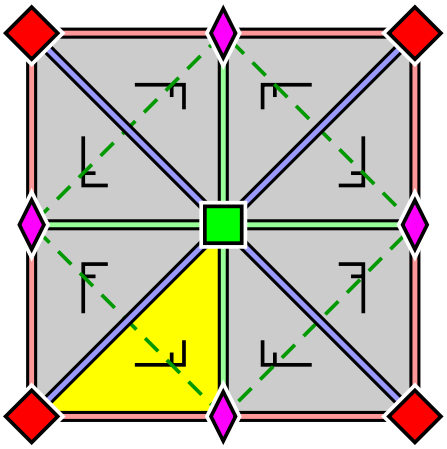
- the group **p6m**, that describes the symmetry of a (111) surface with the approximation that the hollow sites are equivalent (even if in the true (111) surface they are not for the difference in the 2nd and 3rd layer)



Like p3m1 (which is a subgroup of this group), p6m has an hexagonal lattice. The difference with respect to p3m1 is in one of the rotation axis, that now has order 6, and in the presence of reflection axes along the sides of the unit cell (as represented in figure). The additional order 2 axes are the composition of the perpendicular intersection of reflection axes. Note that in this case the order 3 rotation centers are related by symmetry (and in fact they corresponds to the hollow sites, that are now equivalent for the approximation fcc = hcp)

[2] rigorously, the lattice is the set of points related to the origin by the pure translations of the group

- the group **p4m**, describing the symmetry of a (100) surface



This group has a square unit cell, with two inequivalent axis of order 4 and symmetry axis along the sides, the diagonals and the perpendiculars in the midpoints of the sides. Rotation axis of order 2 arise at the perpendicular intersection of symmetry axis. Note that in case the 4-fold rotations axes are the top and hollow sites, while the 2-fold rotation axis is on the bridge site.

3 Wallpaper groups as semi-direct product of groups

In this section we want to introduce the notion of semidirect product of groups (which is precisely defined in Appendix A) with the aim of easily characterize all the elements of a wallpaper group. In some way, this discussion will let us distinguish the "translational part" of a group from everything else.

First, we need to introduce the **point group** G_0 of a wallpaper group G. We define in this way the set of those elements of the wallpaper group that do not include a translation, *i.e.* those elements r in the form $(\mathcal{O}, 0)$ where 0 is the zero vector. As can be easily shown, this set is a subgroup of the wallpaper group, since the composition of two such elements does still belong to the subgroup. Intuitively, the point group is the set of symmetry operations at the origin of the lattice.

In the case of p3m1, the point group is D_3 (the planar analogue of C_{3v}) which includes the identity, two rotations of $^{2\pi}/_3$ and $^{4\pi}/_3$ around the origin and three symmetry axis at angles $^{2\pi}/_3$ one with each other. In the case of p6m, the point group is D_6 (analogue of C_{6v}) with identity, 5 rotations of $n^{2\pi}/_6$ and 6 reflections. In the case of p4m, the point group is D_4 (C_{4v}) with identity, 3 rotations of $n^{\pi}/_2$ and 4 reflections.

The second ingredient we need is the **lattice group** T. The lattice group is the set of all the elements t of the wallpaper group in the form $(1, \tau)$ where 1 is the identity of O(2). Again, since the composition of two pure translations is still a translation, this a subgroup of the wallpaper group.

We could feel tempted to say that any element of the wallpaper group is a combination of an element of the point group and an element of the lattice group. In general this is

not true, and does not hold for those group which are represented with a glide reflection (the combination of a translation of half cell and a reflection) passing through the origin. In fact in this case there will be symmetry elements in the form $(\mathcal{O}, \sigma)$ - with σ being a translation that do not belong to the lattice group - that cannot be represented as composition of a rotation of G_0 and a translation of T.

The groups that not require the introduction of these glide reflections are called symmorphic or split groups. The three cases of our interest are all symmorphic groups. Hence if we focus on those groups, we are allowed to write any the elements of the wallpaper group as

$$(\mathcal{O}, \tau) \qquad \mathcal{O} \in G_0 \; \tau \in T$$

With the definitions of T and G_0 we can see that three properties hold:

1. the only common element between the point group and the lattice group is the identity $T \cap G_0 = \{e\}$
2. T is a normal subgroup if G, i.e. for any $g \in G$ and any $t_1 \in T$, $g^{-1} t_1 g = t_2$ (which can be proven directly with the composition Eq. 3)
3. any group element g can be obtained as a product of a $r \in G_0$ and a $t \in T$, which is formally written as $TG_0 = G$ - meaning with TG_0 the set of all the products rt with $r \in G_0$ and a $t \in T$ (just for symmorphic groups)

These properties are the axioms that allow us to write the wallpaper group as semi-direct product of G_0 and T

$$G = T \ltimes G_0$$

Among the properties of the semi-direct product (see Appendix A), one particularly interesting for our purposes is the fact that an element of G can be **uniquely** written as product of a rotation of the rotation group and a translation of the lattice group

$$g = t\, r$$

4 Totally symmetric projector

We now focus on the totally symmetric representation of the wallpaper group, with the aim of writing the totally symmetric projector.

From the theory of finite group representation, once we have established the action of our transformation group on a linear space, we know that a projector on a 1D representation is given by

$$P\,|\varphi\rangle = \frac{1}{|G|} \sum_{g \in G} \chi(g)\; g \cdot |\varphi\rangle \tag{4}$$

where $\chi(g)$ is the character of the element g for the desired representation. In our case we have an infinite group, but we can make it finite with Born-Von Karman periodic boundary conditions (see Appendix B).

Thanks to the semi-direct product structure, we can greatly simplify the enumeration of all the elements of the wallpaper group. A sum over the elements of a semi-direct product, in fact can be written as product of sum over the elements over the subgroups. Suppose $G = T \ltimes G_0$ and consider the expression

$$\sum_{r \in G_0} \sum_{t \in T} f(rt)$$

Since $G_0 T = G$ (for a symmorphic group) the expression then include all the elements of G. Furthermore, since the decomposition rt is unique, we can conclude that all the elements of G are included in the summation just one time. We can thus identify

$$\sum_{r \in G_0} \sum_{t \in T} f(rt) = \sum_{g \in G} f(g) \tag{5}$$

Using this identity in the projector Eq. 4, we get

$$P\,|\varphi\rangle = \frac{1}{|T||G_0|} \sum_{r \in G_0} \sum_{t \in T} \chi(rt)\; rt \cdot |\varphi\rangle$$

The character of a product of elements is the product of the characters of the elements, and then

$$P\,|\varphi\rangle = \left(\frac{1}{|G_0|} \sum_{r \in G_0} \chi(r)\; r \right) \left(\frac{1}{|T|} \sum_{t \in T} \chi(t)\; t \right) \cdot |\varphi\rangle \tag{6}$$

We can recognize in parentheses the projectors over the lattice group and the point group. The characters here are the characters of the representation of G_0 "induced" by the representation of G (and equivalently for T), in other words the trivial restriction of the representation of G to the elements of its subgroup.

Eq. 6 proves in a rigourous way one reasonable fact: we can symmetrize a function by first symmetrizing with respect to translational symmetry, and then to point group symmetry (we can also invert the order, still building a proper symmetrized state).

Following the same key idea of converting a sum over the entire group in two sums over the subgroups, the procedure can be easily generalized in case of representations that are not one dimensional.

5 Irreps of the wallpaper groups

A general procedure exists to build the representation of a semi-direct product group from its factor groups. Due to the complexity of this procedure, we will just describe the result for the wallpaper groups in two extreme cases.

The main idea of this procedure is to start from the irreps of the lattice group (see Appendix B for a brief overview of the irreps of a group of translations only). We can "symmetry adapt" the irreps of the translation by building the set of representation that are related by the action of the symmetry operations included in the point group G_0.

As en example, starting from a representation $\exp(-\imath\mathbf{k}\cdot\mathbf{t})$ we can obtain the related represention $\exp(-\imath\mathbf{k}\cdot(g\mathbf{t}))$ where g is a symmetry operation in G_0. Each representation $\exp(-\imath\mathbf{k}\cdot(g\mathbf{t}))$ can be equivalently expressed with another k-vector $\mathbf{k}'$ as $\exp(-\imath\mathbf{k}'\cdot\mathbf{t})$. The set of vectors $\mathbf{k}$ that are related by the symmetry operations of G_0 form a so-called **star** of k vectors.

A star contains at most a number of vectors equal to $|G_0|$, the number of elements of G_0. Note however that a star might contain less than $|G_0|$ k-points. Generally speaking, this will happen for high symmetry points of the reciprocal space. As an example, let $\mathbf{k}$ be equal to the gamma point, $\mathbf{k}=\mathbf{0}$. Any transformation of G_0 will relate the gamma point to itself. Hence the star of the gamma point is made by the gamma point alone. We will now describe the irreps obtained in the two cases in which we start from a non symmetric k-point (hence with a star of dimension $|G_0|$) or when we start from the most symmetric k-point, i.e. the gamma point.

$|G_0|$-dimensional star In this case, we obtain just a single wallpaper group irrep, of dimension equal to $N=|G_0|$. The representation can be generated by a vector composed by all the functions composing a star. We build a N elements vector

$$\begin{pmatrix} \exp(-\imath\mathbf{k}_1\cdot\mathbf{t}) \\ \exp(-\imath\mathbf{k}_2\cdot\mathbf{t}) \\ \cdots \\ \exp(-\imath\mathbf{k}_N\cdot\mathbf{t}) \end{pmatrix}$$

with the set of k-vectors $\mathbf{k}$ composing the star and we see how it transforms under the action of a transformation of the wallpaper group.

In particular, the representation of a lattice translation τ will be a diagonal matrix of the form

$$\begin{bmatrix} \exp(-\imath\mathbf{k}_1\cdot\tau) & 0 & 0 & \\ 0 & \exp(-\imath\mathbf{k}_2\cdot\tau) & 0 & \\ 0 & 0 & \cdots & 0 \\ & & 0 & \exp(-\imath\mathbf{k}_3\cdot\tau) \end{bmatrix}$$

where $g_1, g_2 ... g_N$ are the elements of G_0.

On the contrary the representations of the elements of G_0 will not be diagonal, since the action of $g\in G_0$ in general brings a given k-vector to another k-vector of the star.

1 dimensional star In the case of a symmetric k-point, the representation built as in the general case explained above can be reduced. In particular for the gamma point, we get a set of irreps which is exactly the set of irreps of the point group G_0 itself. In this case, the representation of a pure translations is a unit matrix with dimension equal to the dimension of the representation. The representation of the elements of G_0 are simply given by the corresponding representation of G_0 alone. The representation of all the other elements, can be build as product given the decomposition of the element on the semi-direct product space.

We remark that since among the irreps of G_0 there will be the totally symmetric one, the totally symmetric irrep of the wallpaper group will be obtained in the representation of the gamma point star.

6 An example: the (111) surface

We now consider the (111) surface and we try to apply some ideas related to what discussed above.

Fractional coordinates and reciprocal lattice To deal with periodicity, it is often convenient to define a frame of reference in which the translations are expressed as vectors of integer components. This reference is obtained by choosing the axes along two independent directions of translation and scaling the coordinates by the unit cell dimensions. In the case of the (111) surface, we can fix the origin on one of the 1st layer lattice atoms, we choose two axis at 60° directed along other 1st layer atoms and we scale the coordinates by the lattice constant. With this choice, the unit cell vectors will be given (in cartesian coordinates) by

$$\mathbf{a}_1 = a(1,0) \qquad \mathbf{a}_2 = a(\frac{1}{2}, \frac{\sqrt{3}}{2})$$

The transformation from a cartesian reference to a fractional reference will be

$$C \; : \; \begin{pmatrix} u \\ v \end{pmatrix} = \begin{bmatrix} 1/a & -1/a\sqrt{3} \\ 0 & 2/a\sqrt{3} \end{bmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

whereas the inverse transformation will be

$$C^{-1} \; : \; \begin{pmatrix} x \\ y \end{pmatrix} = \begin{bmatrix} a & a/2 \\ 0 & a\sqrt{3}/2 \end{bmatrix} \begin{pmatrix} u \\ v \end{pmatrix}$$

The reciprocal lattice unit vectors obtained from $\mathbf{a}_1$ and $\mathbf{a}_2$ are (in cartesian coordinates)

$$\mathbf{b}_1 = \frac{2\pi}{a}(1, -\frac{1}{\sqrt{3}}) \qquad \mathbf{a}_2 = \frac{2\pi}{a}(0, \frac{2}{\sqrt{3}})$$

and give raise to an hexagonal lattice.

Symmetry group of (111) surface As discussed above, the (111) surface has symmetry p3m1. All the elements of this group can be generated as composition of a translation of the lattice and a proper/improper rotation of the point group D_3

In fractional coordinates, all the translations are very easily expressed by vectors with integer components:

$$\mathbf{r}' = T\,\mathbf{r} \iff \begin{cases} u' = & u + n_1 \\ v' = & v + n_2 \end{cases}$$

The action of the elements of D_3 can be found from the rotation in cartesian coordinates with the coordinate transformation

$$\mathcal{R}_{fractional} = C^{-1}\,\mathcal{R}_{cartesian}\,C$$

where C is the coordinate transformation from fractional to cartesian. In this way, we can easily find the expression of the symmetry transformation in fractional coordinates:

- identity

$$\mathbf{r}' = 1\,\mathbf{r} \quad \Longleftrightarrow \begin{cases} u' = & u \\ v' = & v \end{cases} \qquad \begin{bmatrix} +1 & 0 \\ 0 & +1 \end{bmatrix}$$

- rotation of $\frac{2\pi}{3}$

$$\mathbf{r}' = C(\frac{2\pi}{3})\,\mathbf{r} \quad \Longleftrightarrow \begin{cases} u' = & -u-v \\ v' = & u \end{cases} \qquad \begin{bmatrix} -1 & -1 \\ +1 & 0 \end{bmatrix}$$

- rotation of $\frac{4\pi}{3}$

$$\mathbf{r}' = C(\frac{4\pi}{3})\,\mathbf{r} \quad \Longleftrightarrow \begin{cases} u' = & v \\ v' = & -u-v \end{cases} \qquad \begin{bmatrix} 0 & +1 \\ -1 & -1 \end{bmatrix}$$

- reflection 1

$$\mathbf{r}' = \sigma\,\mathbf{r} \quad \Longleftrightarrow \begin{cases} u' = & v \\ v' = & u \end{cases} \qquad \begin{bmatrix} 0 & +1 \\ +1 & 0 \end{bmatrix}$$

- reflection 2

$$\mathbf{r}' = \sigma C(\frac{2\pi}{3})\,\mathbf{r} \Longleftrightarrow \begin{cases} u' = & u \\ v' = & -u-v \end{cases} \qquad \begin{bmatrix} +1 & 0 \\ -1 & -1 \end{bmatrix}$$

- reflection 3

$$\mathbf{r}' = \sigma C(\frac{4\pi}{3})\,\mathbf{r} \Longleftrightarrow \begin{cases} u' = & -u-v \\ v' = & v \end{cases} \qquad \begin{bmatrix} -1 & -1 \\ 0 & +1 \end{bmatrix}$$

The semi-direct product decomposition of p3m1 in terms of its point group D_3 and its lattice group assure us that any element of the group can be uniquely written as

$$\mathbf{r}' = \mathcal{R}T\,\mathbf{r} \Longleftrightarrow \begin{pmatrix} u \\ v \end{pmatrix} = \mathcal{R}\begin{pmatrix} u \\ v \end{pmatrix} + \begin{pmatrix} n_1 \\ n_2 \end{pmatrix}$$

where $\mathcal{R}$ is one of the D_3 operation described above.

Symmetry of the k-space The action of the operators of D_3 on the k vectors can be found by transforming the expression of a generic exponential of a direct lattice - reciprocal lattice product representation

$$\exp\left(-\imath\mathbf{k}\cdot\mathbf{r}\right) = \exp\left(-2\pi\imath(k_1u + k_2v)\right)$$

By using the coordinates transformation reported above, we find

$$\exp\left(-\imath\mathbf{k}\cdot 1\mathbf{r}\right) = \exp\left(-2\pi\imath(k_1u + k_2v)\right)$$

$$\exp\left(-\imath\mathbf{k}\cdot C(\frac{2\pi}{3})\mathbf{r}\right) = \exp\left(-2\pi\imath k_1(-u-v) + -2\pi\imath k_2u)\right) = \exp\left(-2\pi\imath(k_2-k_1)u - 2\pi\imath(-k_1)u)\right)$$

and analogous relation for the other transformation. So the k points transform according to the following relations

$$1 \Longleftrightarrow \mathbf{k} = \mathbf{k}$$

$$C(\frac{2\pi}{3}) \Longleftrightarrow \begin{cases} k_1' = & k_2 - k_1 \\ k_2' = & -k_1 \end{cases}$$

$$C(\frac{4\pi}{3}) \Longleftrightarrow \begin{cases} k_1' = & -k_2 \\ k_2' = & k_1 - k_2 \end{cases}$$

$$\sigma \Longleftrightarrow \begin{cases} k_1' = & k_2 \\ k_2' = & k_1 \end{cases}$$

$$\sigma(\frac{2\pi}{3}) \Longleftrightarrow \begin{cases} k_1' = & k_1 - k_2 \\ k_2' = & -k_2 \end{cases}$$

$$\sigma C(\frac{4\pi}{3}) \Longleftrightarrow \begin{cases} k_1' = & -k_1 \\ k_2' = & k_2 - k_1 \end{cases}$$

when these points are represented on the reciprocal lattice for a given k_1 k_2, it becomes evident that they are related by the same transformation of D_3 but performed on the reciprocal lattice instead of the direct lattice. As an example, a rotation of $\frac{2\pi}{3}$ in the direct lattice results in a rotation of $-\frac{2\pi}{3}$ in the reciprocal lattice.

With the transformation rules obtained above, we can build stars of k points and find irreducible representation for p3m1. In particular, the irreps build with the star of the gamma point will simply be the irreps of the D_3 group (that can be simply found in the character table of the isomorphic C_{3v} group).

D_3	E	$2C_3$	3σ
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Totally symmetric Fourier series Suppose now we want to symmetrize a Fourier series for a (111) surface. We start from an expresssion of the 2D Fourier series with the proper translational symmetry. The basis function f_{mn} will be

$$f_{mn} = \exp\left(2\pi\imath \mathbf{k}_{mn} \cdot \mathbf{r}\right)$$

where the vectors $\mathbf{k}_{mn}$ are the vectors of the reciprocal lattice. Expressing $\mathbf{r}$ in fractional coordinates, we can conveniently write

$$f_{mn} = \exp\left(2\pi\imath \left(mu + nv\right)\right)$$

As explained above, the totally symmetric projection can be done by first applying the totally symmetric projection for the lattice group, and then the totally symmetric projection for the point group. However, the fouries series already spans the totally symmetric representation of the lattice group. Hence we can simply obtained the symmetry adapted Fourier series by applying the operations of the point group

$$f_{mn}^{(p3m1)} = \frac{1}{|D_3|} \sum_{\mathcal{R} \in D_3} \mathcal{R} \exp\left(2\pi\imath \mathbf{k}_{mn} \cdot \mathbf{r}\right) = \frac{1}{6} \sum_{\mathcal{R} \in D_3} \exp\left(2\pi\imath \mathbf{k}_{mn} \cdot \mathcal{R}\mathbf{r}\right)$$

I have previously shown that such an expression can be related to a sum over the points of a k-star. Hence the sum becomes

$$f_{mn}^{(p3m1)} = \frac{1}{n} \sum_{i=1}^{n} \exp\left(2\pi\imath \mathbf{k}_{mn}^{i} \cdot \mathbf{r}\right)$$

where the sum goes over the n elements of the star generated from the $\mathbf{k}_{mn}$ vector. The elements might be less then 6 in case the point $\mathbf{k}_{mn}$ is invariant under some symmetry operations of D_3 (in the reciprocal space).

When we build the fouries series, we do not need to include all the possible k point corresponding to integer m, n. In fact we need only to include the different stars generated by the k points. This can be very easily achieved by summing over the m, n values that lie in a symmetry "unique" portion of the k space that can generate the whole k space with the transformation of D_3.

A Semi-direct product of groups

Before introducing the semi-direct product of groups, we recall some basic definitions of group theory.

Definition: Group A *group* is a set of elements $G = \{g\}$ with a composition law $G \times G \to G$ (called in different ways depending on the context, *i.e.* "group addition" or "group multiplication" or "group law"), that satisfy the following axioms

1. the composition is associative $(g_1 \cdot g_2) \cdot g_3 = g_1 \cdot (g_2 \cdot g_3) = g_3 \cdot g_2 \cdot g_3$

2. the identity belongs to the group $\exists e \in G \,:\, g \cdot e = e \cdot g = g \, \forall g \in G$

3. for each element, its inverse is in the group $\forall g \in G \, \exists g^{-1} \in G \,:\, g \cdot g^{-1} = g^{-1} \cdot g = e$

A *subgroup* is a subset of a group that still meet the group axioms with the same composition law.

Definition: Normal Subgroup A subgroup H of a group G is said to be *normal* when $\forall g \in G$ and $\forall h \in H$ we have that $ghg^{-1} \in H$.

If we write the set of elements obtained multiplying g and all the elements of H as $gH = \{gh, \forall h \in H\}$, we can equivalently write that a subgroup is normal when $gHg^{-1} = H$

Now we have all the necessary definitions to introduce the notion of semi-direct product of subgroups.

Definition: Semi-Direct Product Let G be a group with subgroups H and Q. H is a normal subgroup of G. We say that G is the *semi-direct product* of H and Q (we write $G = H \ltimes Q$) if:

1. $HQ = G$, *i.e.* any element of G can be written as a product of an element of H and an element of Q

2. the identity is the only element that belongs both to H and to Q, $H \cap Q = \{e\}$.

The importance of this notion, lies in the fact that it allows a unique decomposition of each group element. This is essentialy the meaning of the following theorem.

Theorem Let G be a group with subgroups H and Q. Let H be a normal subgroup. Then the following statements are equivalent

1. G is the semi-direct product of H and Q, $G = H \ltimes Q$

2. any element $g \in G$ can be *uniquely* written as $h \cdot q$ with $h \in H$ and $q \in Q$

3. any element $g \in G$ can be *uniquely* written as $q \cdot h$ with $h \in H$ and $q \in Q$

Proof From 1. to 2. : From the definition of semi-direct product, we know $G = HQ$ and then g can be written as hq. Suppose it can also be written as $h'q'$. Then $hq = h'q'$ so $h'^{-1}h = q'q^{-1} \in H \cap Q = \{1_G\}$. Therefore $h = h'$ and $q = q'$ $\square$

From 2. to 1. : From the hypotheses, it is obvious that $HQ = G$. Furthermore, suppose that an element $\tilde{g}$ belongs both to H and Q. Then we can write it as $\tilde{g} \cdot e$, with $\tilde{g} \in H$ and $e \in Q$, and we can write it as $e \cdot \tilde{g}$, with $e \in H$ and $\tilde{g} \in Q$. For the unicity of the representation, we conclude that $\tilde{g} = e$. $\square$

From 2. to 3. and *viceversa* : An element g can be written uniquely as hq, $g = hq$. Introducing the identity $e = qq^{-1}$ in the right hand side, we get $g = qq^{-1}hq$. Since H

is a normal subgroup, we know that $h' = q^{-1}hq$ is still an element of H. Thus g can be written uniquely as $g = qh'$, with $h' = q^{-1}hq$. The inverse can be proved with an analogous argument.□

B Irreps of a group of sole translations

A group of translations $\{T\}$ is an abelian group, generated by repeated application of a number of "minimum" translations $\{A_i\}_{i=1}^{D}$ equal to the number of dimensions of the geometrical space on which the transformation act. For example, a group of translation in 3 dimension can be generated by the three translations A_1,A_2, A_3 corresponding to the three vectors of the first unit cell $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$.

Starting from these very basic properties, it can be shown that the group has only 1D representations (as any abelian groups), that can be conveniently represented in terms of vectors of the reciprocal lattice. In particular, for any vector of the first brillouin zone of the reciprocal lattice, there exist a representation of the group

$$D^{\mathbf{k}}(T) = \exp(-\imath \mathbf{k} \cdot \mathbf{t}) \tag{7}$$

where T is a translation of vector $\mathbf{t}$ in a geometrical space and $\mathbf{k}$ is a vector of the reciprocal lattice associated with the direct lattice generated by the translations. It is easy to check from the properties of the complex exponential that each $D^{\mathbf{k}}(T)$ is indeed a representation of the group of the translation (*i.e.* $D^{\mathbf{k}}(T_1 \cdot T_2) = D^{\mathbf{k}}(T_1)D^{\mathbf{k}}(T_2)$) and that representations corresponding to $\mathbf{k}$ vectors that differ by a reciprocal lattice vector are equivalent.

We choose a convenient system of reference for the direct lattice $\{\mathbf{a}_i\}_{i=1}^{D}$ with the D vectors defining the first unit cell. Consequently, we can define the reciprocal system of reference with the vectors $\{\mathbf{b}_j\}_{j=1}^{D}$ obtained by the condition

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\, \delta_{ij} \tag{8}$$

Since a translation vector will have integer components in the system of reference $\{\mathbf{a}_i\}$, we easily obtain that the representation will be given by the formula

$$D^{\mathbf{k}}(T) = \exp(-\imath \sum k_i N_i) \tag{9}$$

where k_i are the components of the first brillouin zone in the system of reference of the reciprocal lattice and N_i are the integer components of the translation $T = \Pi_i A_i^{N_i}$.

The group of translation is in principle infinite. For the sake of semplicity, in problems with translational symmetry it is often convenient to apply the particular Periodic Boundary Conditions (PBC) that in solid-state physics are commonly known as Born-Von Karman PBC.

In a group-theoretical framework, these conditions are equivalent to the assumption that the translation group is cyclic, *i.e.* there exists a large integer number n such that $T^n = E$, where E is the identity. As an example, we can fix a large integer N and set

$$A_i^N = E \quad i = 1,\, D \tag{10}$$

for the translations defining the first unit cell. In this way, we can consider the group of translation a large but finite dimensional set, and we can apply the standard techniques of the theory of representation of finite groups without any relevant approximation.

Born-Von Karman conditions also have consequences on the allowed group representation. If the conditions of Eq. 10 are imposed, we have to force the representations of A_i to be complex N-roots of the unit

$$D^{\mathbf{k}}(A_i) = \exp(-2\pi\imath \sum \frac{n_j^{(i)}}{N}) \qquad\qquad n_j = 0, \ldots, N-1 \tag{11}$$

so that $D^{\mathbf{k}}(E) = D^{\mathbf{k}}(A_i^N) = \left[D^{\mathbf{k}}(A_i)\right]^N = 1$. Since we can choose an integer number $n_j^{(i)}$ for each of the D indipendent translation of the first unit cell, we have N^D possible representation of the group. As expected for a finite group, the number of representation equals the cardinality of the group (*i.e.* its number of elements).