

Crystal Symmetries and Space Groups

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1 Geometrical Symmetries

★ Many objects display geometrical symmetries which can be associated with a group of transformations that leaves the object invariant. For example, a five-pointed star is left unchanged by rotations of $360/5 = 72^\circ$, as well as by a reflection in a line passing from a point of the star through the center.

1.1 Linear molecules

★ This is also true at the microscopic level where, for example, a helium atom is spherically symmetrical—unchanged under all rotations and reflections of the group $O(3)$. Carbon monoxide, CO, is symmetrical under all rotations about the axis joining the carbon to the oxygen, and reflections in all planes that include this axis. Carbon dioxide, CO_2 , is linear and has the form O-C-O, with the carbon midway between the oxygens. Thus in addition to being invariant under the same rotations and reflections as CO, it is unchanged under a reflection in a plane through the center of the carbon and perpendicular to the axis, as well as by 2-fold (180°) rotations about any axis lying in this plane and passing through the carbon.

□ Exercise. Assume that the CO_2 molecular axis is the z axis, and C is at the center of coordinates. Describe the 3×3 matrices of $O(3)$ which constitute the different symmetry elements, and verify that they form a group.

□ Exercise. The H_2O molecule, unlike CO_2 , is not linear. The hydrogen atoms are equidistant from the oxygen, but the angle between them (seen from the center of the oxygen) is 104.5° instead of 180° . Assume the molecule lies in the x, z plane with O at the origin and the z axis midway between the hydrogens. Find the geometrical symmetries of this system including reflections as well as rotations. Show that the symmetry group is isomorphic to something well known.

1.2 Triangular prism

• An equilateral triangular prism with its 3-fold axis oriented along the z axis is shown schematically in Fig. 1. In parts (b) and (c) of the figure the fully symmetry has been reduced by placing arrows on some of the edges. Thus the reflection plane which interchanges the top and bottom of the prism is absent in (b), while the 2-fold rotations about an axis passing through the center of a rectangular face and the opposite vertical edge are absent in (c).

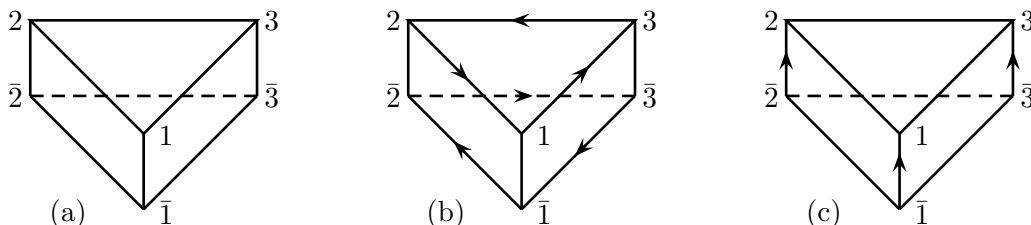


Figure 1: Triangular prism, where the dashed line indicates a hidden edge: (a) full symmetry D_{3h} , (b) reduced symmetry D_3 , (c) reduced symmetry C_{3v}

★ Let us start with Fig. 1(b) The symmetry elements are those of D_3 : a 3-fold axis with 3 2-fold axes perpendicular to it. Viewed as permutations on the labeled vertices the 2-fold rotations are

$$a = (1\bar{1})(\bar{2}3)(2\bar{3}), \quad b = (2\bar{2})(1\bar{3})(\bar{1}3), \quad c = (3\bar{3})(1\bar{2})(\bar{1}2), \quad (1)$$

while the rotations by 120° about the 3-fold axis are

$$r = (123)(\bar{1}\bar{2}\bar{3}), \quad s = r^2 = (132)(\bar{1}\bar{3}\bar{2}), \quad (2)$$

clockwise and counterclockwise when viewed from above. Along with the identity these operations give a group of order 6.

★ The full symmetry of the prism shown in Fig. 1(a) is a group D_{3h} obtained by adding to D_3 a horizontal reflection plane perpendicular to the 3-fold axis and passing through the geometrical

center of the prism. (This is the reason for the 'h' in D_{3h} .) The 6 new symmetries are obtained by multiplying each element in D_3 by this reflection,

$$h = (1\bar{1})(2\bar{2})(3\bar{3}). \quad (3)$$

This yields a set of 3 reflections in vertical planes passing through the z axis, which we label

$$\hat{a} = ha = (23)(\bar{2}\bar{3}), \quad \hat{b} = hb = (13)(\bar{1}\bar{3}), \quad \hat{c} = hc = (12)(\bar{1}\bar{2}) \quad (4)$$

and two screw reflections, the h reflection preceded or followed by one of the 3-fold rotations:

$$\hat{r} = hr = (1\bar{2}3\bar{1}2\bar{3}), \quad \hat{s} = hs = (1\bar{3}2\bar{1}3\bar{2}) \quad (5)$$

□ Exercise. Find the conjugate classes of D_{3h} . Show that D_3 and $\{e, h\}$ are normal subgroups of D_{3h} ; in particular, check that h commutes with every element of D_3 . Argue that D_{3h} is a direct product of D_3 and $\{e, h\}$.

□ Exercise. Find the 3×3 matrices in $O(3)$ that correspond to the symmetry elements of D_{3h} , with rows and columns in the order x, y, z , and axes chosen so that the $+y$ axis passes through the $1\bar{1}$ edge of the prism

★ The symmetry of the prism when decorated as in Fig. 1(c) is the group C_{3v} . The 2-fold axes are no longer symmetry elements, which is why D has been replaced by C . However, the 3 vertical reflection planes (the source of the 'v' in C_{3v}) indicated in (4) are present in C_{3v} , though absent from D_3 .

• The symmetry groups D_3 and C_{3v} are isomorphic as abstract groups, but do *not* denote the same set of crystal symmetries! No crystallographer will confuse quartz (D_3) with lithium sodium sulphate (C_{3v}).

□ Exercise. Exhibit the isomorphism between D_3 and C_{3v} , and show that it preserves group multiplication.

1.3 Tetrahedron

★ The molecule CH_4 has the symmetry of a tetrahedron, with the carbon at the center and the 4 hydrogens at the vertices. Figure 2 shows a tetrahedron oriented in such a way that one is looking down on the 13 edge, which is directly above the 24 edge shown as a dashed line.

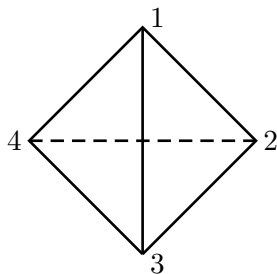


Figure 2: Tetrahedron

★ The tetrahedral group T is the subgroup of $SO(3)$, rotations but no reflections, that carries the tetrahedron into itself. The symmetry elements, indicated here as permutations, fall into four classes. The identity e , as always, is in a class by itself. There are 3 2-fold rotations about axes passing through the midpoints of opposite edges:

$$(12)(34), \quad (13)(24), \quad (14)(23). \quad (6)$$

Next come rotations by 120° about an axis passing through a vertex and the center of the opposite face. Perhaps somewhat surprisingly these fall into *two* classes, clockwise and counterclockwise when viewing the face:

$$\text{Clockwise: } (243), (134), (142), (123) \quad (7)$$

$$\text{Counterclockwise: } (234), (143), (124), (132) \quad (8)$$

- Total number of elements is $1 + 3 + 4 + 4 = 12$.
- Viewed in terms of permutations, T is isomorphic to A_4 , the alternating group on 4 letters.

★ The full tetrahedral group T_h is obtained by adding reflections such as (12) to the rotations comprising T . It is a group of order 24, isomorphic to the symmetric group S_4 .

• Note that while T is a normal subgroup of T_h , T_h is not (isomorphic to) a direct product of T and $T_h/T \cong Z_2$.

□ Exercise. Prove these assertions.

• When working out the 3×3 rotation or reflection matrices corresponding to the elements of T or T_h it is convenient to regard T as a subgroup of the group O of the cube (and T_h as a subgroup of O_h) by placing the tetrahedron inside a cube in such a way that the tetrahedron vertices coincide with 4 of the cube vertices, and the 6 edges of the tetrahedron are diagonals of the square faces of the cube. (It helps to draw a picture.)

1.4 Cube

★ The group O (O stands for “octahedron”) includes all the proper rotations, elements of $SO(3)$, that leave a cube invariant. These fall in a five classes, four in addition to the identity class, which can be described as follows, assuming that the faces of the cube are orthogonal to the x , y , and z axes.

- Six rotations of $\pm 90^\circ$ about a coordinate axis
- Three rotations by 180° about a coordinate axis
- Six rotations by 180° about an axis passing through the centers of two opposite edges of the cube
- Eight rotations of $\pm 120^\circ$ about axes connecting opposite cube vertices.
- It may come as a surprise, after considering the tetrahedral group T , that all the 90° rotations fall in a single class, and likewise all the 120° rotations, even though the symmetry group O does not include reflections. The reason is that in the case of the cube, unlike a tetrahedron, there is a proper (ordinary) rotation which interchanges the two ends of the relevant axis, thus interchanging clockwise and counterclockwise rotations.

• It is fairly easy to construct the 3×3 matrices for all the symmetry elements of O , since (with axes chosen normal to faces) the matrix elements are either 0 or ± 1 , and the determinant is always $+1$.

□ Exercise. Construct a matrix for one of the elements in each of the five classes, and explain how the matrices of the other elements in the class are related to it.

★ The symmetry group O_h of the cube *including reflections* has a total of 48 elements. It is a direct product of O with the the subgroup consisting of the identity and the inversion, the operation that reverses the sign of all of the coordinate axes.

• Since the inversion corresponds to the 3×3 matrix $J = -I$, where I is the identity, it is obvious that it commutes with all the matrices for O , and the additional 24 matrices that make

up O_h are obtained from those of O by multiplying each by -1 , hence changing the sign of the determinant.

★ Crystal symmetries are discussed extensively by Phillips, who gives a number of drawings of facets of different crystals. Hamermesh gives a somewhat shorter discussion in Ch. 2, and Tinkham a rather brief overview at the beginning of Ch. 4.

2 Space Groups

2.1 Introduction

★ Crystal symmetries were observed long before the internal structure of crystals was worked out, beginning around 1912, using X-ray diffraction. Observation of angles between the normals of different faces led to a systematic classification of crystal symmetries which was completed in the nineteenth century.

- For some notes on the historical development, see Koster, Sec. VI, and Phillips, Ch. I.

★ The 32 crystal symmetry groups or *classes*, each a subgroup of $O(3)$, rotations and reflections in 3 dimensions, are divided into 7 *systems* (monoclinic, cubic, etc.).

- Although they make no direct reference to internal structure, the fact that there are only 32 groups is nowadays understood to arise from the fact that crystals have a *periodic* internal structure, and periodic structures are only compatible with a rather small number of rotation and reflection symmetries. In particular, 5-fold axes, rotations by 72° , are incompatible with an internal periodicity.

- However, there are materials known as *quasicrystals* whose macroscopic symmetries fall outside the list of 32, and sometimes include 5-fold axes. While they do not possess an internal periodic structure in the same sense as a crystal, they nevertheless correspond to a fairly regular arrangement of atomic constituents. Their structure and properties have been the subject of intense study since their discovery in the 1980's. Quasicrystals lie outside the scope of these notes, which are only concerned with periodic crystals.

★ Space groups are used to describe the internal, microscopic symmetry of crystals. They include translations, corresponding to the periodic arrangement of atoms or molecules, and in addition various rotations and reflections.

- Each of the 32 possible macroscopic symmetry groups corresponds to a certain number of distinct periodic arrangements of elements in the crystal, the symmetries of which are distinguished by different space groups. There are a total of 230 space groups.

- Of these, 73 are symmorphic and 157 are nonsymmorphic, a distinction which will be discussed in Sec. 2.2.

★ Space groups are discussed by Dresselhaus, but I find the treatment in Koster a bit clearer. Phillips provides a fairly geometrical discussion with pictures. Tinkham, as well as much of the material in Dresselhaus, focuses on the representation of space groups, rather than on the groups as geometrical symmetries, which is the emphasis of these notes.

2.2 General Properties

★ Space groups can be defined for any n -dimensional space $\mathbb{R}^n$ with points of the form $\mathbf{r} = (r_1, r_2, \dots, r_n)$, and the square of the distance between two points defined by

$$|\mathbf{r} - \mathbf{r}'|^2 = \sum_{i=1}^n (r_i - r'_i)^2. \quad (9)$$

★ Transformations of $\mathbb{R}^n$ which leave the distance between any two points unchanged constitute the *Euclidean group* $E(n)$. Any such transformation can be denoted by a pair $(A|\mathbf{u})$, often written $\{A|\mathbf{u}\}$ using curly brackets, where $A \in O(n)$ and $\mathbf{u} \in \mathbb{R}^n$. It acts on $\mathbb{R}^n$ by mapping each point $\mathbf{r}$ to another point

$$(A|\mathbf{u})\mathbf{r} = \mathbf{r}' = \mathbf{u} + A\mathbf{r}, \quad (10)$$

where $A\mathbf{r}$ denotes the usual linear map or matrix multiplication applied to a vector.

◦ Note the order in (10): *first* A acts on $\mathbf{r}$ and only then is $\mathbf{u}$ added to the result. Adding $\mathbf{u}$ first and then applying A to the sum will in general give a different result.

★ One can use (10) to derive the rule for group multiplication:

$$(B|\mathbf{v})(A|\mathbf{u})\mathbf{r} = (B|\mathbf{v})(\mathbf{u} + A\mathbf{r}) = \mathbf{v} + B\mathbf{u} + BA\mathbf{r}. \quad (11)$$

From this it follows, again see (10), that the multiplication rule is

$$(B|\mathbf{v})(A|\mathbf{u}) = (BA|\mathbf{v} + B\mathbf{u}). \quad (12)$$

• The identity transformation $(I|\mathbf{0})$, where I is the identity operator of matrix and thus the identity of $O(n)$, leaves every point fixed, and is thus the group identity for $E(n)$. The operation $(A|\mathbf{0})$ is a rotation about the origin, or a reflection in a plane passing through the origin.

◦ Henceforth I will replace $\mathbf{0}$, denoting the zero vector, by 0 .

• The inverse of $(A|\mathbf{u})$ is

$$(A|\mathbf{u})^{-1} = (A^{-1}|-A^{-1}\mathbf{u}). \quad (13)$$

□ Exercise. Check it.

★ A *space group* G is a subgroup of $E(n)$ with the property that the *translations*, defined by

$$\hat{T} = \{\mathbf{t} : (I|\mathbf{t}) \in G\}, \quad (14)$$

are of the form

$$\mathbf{t} = \sum_i n_i \mathbf{a}_i \quad (15)$$

where each n_i is some integer, and the *primitive translation vectors* $\mathbf{a}_1, \mathbf{a}_2, \dots, \mathbf{a}_n$ are linearly independent.

★ Sometimes it is convenient to think of “translations” as the collection of vectors in (14), and sometimes as the corresponding subgroup of G :

$$T = \{(I|\mathbf{t}) : \mathbf{t} \in \hat{T}\} \quad (16)$$

There would be little harm in using the same symbol for both, as the context will make clear which is meant.

★ In view of the multiplication rule (12), the elements A of that occur in G in the form $(A|\mathbf{u})$ must themselves form a subgroup of $O(n)$ known as the *point group*, and denoted here by P .

★ The translations T form a *normal* subgroup of G , as can be seen as follows. Conjugate $(I|\mathbf{t})$ by an arbitrary element of G :

$$(A|\mathbf{u})(I|\mathbf{t})(A^{-1}|-A^{-1}\mathbf{u}) = (I|A\mathbf{t}). \quad (17)$$

The right side is by definition an element of T . So $gTg = T$ for any $g \in G$, and thus T is normal.

★ In addition, (17) tells us that whenever $\mathbf{t}$ is in $\hat{T}$, so is $A\mathbf{t}$ for any A in the point group. In other words, since A is invertible,

$$A\hat{T} = \hat{T} \quad (18)$$

for every A in P .

- Since every A in P preserves the length of a vector, and since the primitive vectors $\mathbf{a}_j$ in (15) span $\mathbb{R}^n$, it is pretty obvious (though proving it could be a trifle tricky) that the point group P must be finite.

★ The *Bravais lattice* is the collection of points in $\mathbb{R}^n$ obtained by applying T to the origin, i.e., the set of points of the form $\sum_i n_i \mathbf{a}_i \in \mathbb{R}^n$ (compare (15)). It is convenient to think of it as a geometrical object, and as such it is mapped into itself by any member of T

- Defined in this way there is obviously a one-to-one correspondence between the Bravais lattice and the collection $\hat{T}$ of translations. Hence one sometimes thinks of, or refers to, the Bravais lattice as the collection of translations which represent *displacements* of $\mathbb{R}^n$ rather than as a collection of points in $\mathbb{R}^n$. No harm seems to arise from this ambiguous usage.

- When dealing with a particular crystal structure there will in general be good and bad choices for the origin of coordinates, which determines the Bravais lattice. This is a matter best dealt with using some examples, see Secs. 3 and 4.1.

- The point group of the Bravais lattice itself, (called the *holosymmetric* point group), may be larger than P ; again, this is best understood in terms of examples.

★ A *symmorphic* space group is one in which G contains an element $(A|0)$ for every element A in the point group P . Since elements of the type $(A|0)$ always form a subgroup of G , one can say that in this case G contains a subgroup isomorphic to P .

★ The point group P of a *nonsymmorphic* space group G contains certain elements F for which $(F|0)$ does *not* belong to G . That is, G contains $(F|\mathbf{u})$ for certain vectors $\mathbf{u}$ which are not in the collection $\hat{T}$ of translations.

★ If $(F|\mathbf{u})$ is in G , so is $(F|\mathbf{u} + \mathbf{t}) = (I|\mathbf{t})(F|\mathbf{u})$ for any $\mathbf{t}$ in $\hat{T}$. In addition, if $(F|\mathbf{u})$ and $(F|\mathbf{v})$ are both members of G , then so is

$$(F|\mathbf{u})(F|\mathbf{v})^{-1} = (F|\mathbf{u})(F^{-1}|\mathbf{v}) = (I|\mathbf{u} - \mathbf{v}). \quad (19)$$

Hence the *difference* $\mathbf{u} - \mathbf{v}$ must be in $\hat{T}$. Thus for a *particular* F in P , the collection of $\mathbf{u}$ vectors for which $(F|\mathbf{u})$ is a member of G is necessarily of the form

$$\mathbf{u}_F + \hat{T} = \{\mathbf{u}_F + \mathbf{t} : \mathbf{t} \in T\}. \quad (20)$$

In the symmorphic case we can choose $\mathbf{u}_F = 0$ for every $F \in P$, whereas in the nonsymmorphic case there are certain elements of P for which $\mathbf{u}_F$ cannot be 0.

- This needs to be made a bit more precise. For a given crystal structure there may be more than one sensible location for the origin of coordinates, as we shall see in examples. Naturally it makes sense to choose the origin so that as many as possible of the $\mathbf{u}_F$ in (20) can be set equal to 0. A nonsymmorphic space group is one in which no choice of origin allows one to simultaneously set $\mathbf{u}_F = 0$ for every F in P .

★ That $Q = G/T$ is isomorphic to P can be seen as follows. For each A in P define the A coset of T as $(A|\mathbf{u})T = T(A|\mathbf{u})$ using any $\mathbf{u}$ for which $(A|\mathbf{u})$ is in G . In view of the preceding discussion it does not matter which $\mathbf{u}$ we use, the result is always the same: all elements of G with A in front of the $|$. Clearly the cosets do not overlap, and G is equal to their union. In view of the multiplication rule (12) the product of the B and A cosets as sets yields the BA coset, which corresponds to the multiplication rule for P .

★ If G is a symmorphic space group it is a semidirect product of $P \cong G/T$ and T . This follows immediately from the product rule (12), where we can assume that $\mathbf{u}$ and $\mathbf{v}$, and therefore also $\mathbf{v} + B\mathbf{u}$, see (18), are members of $\hat{T}$. For a semidirect product one needs a collection of automorphisms of one of the groups, and in the present instance an appropriate automorphism is

$$(I|\mathbf{t}) \rightarrow (I|B\mathbf{t}) \quad (21)$$

for all $\mathbf{t}$ in $\hat{T}$, with B a fixed element of P . We leave the details as an exercise.

□ Exercise. Work out the details of the argument that a symmorphic space group G is a semidirect product of G/T and T . What prevents the same argument from working for a nonsymmorphic space group?

3 Space Groups in One Dimension

• Many of the principles that relate space groups to translation and point groups can be usefully explored in one or two dimensions, where things are easier to visualize than for three-dimensional crystals.

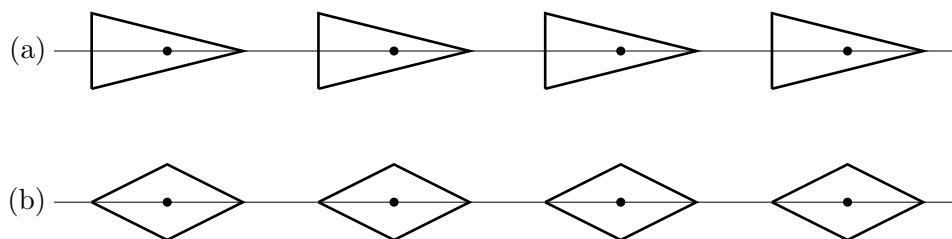


Figure 3: One dimensional crystal with (a) no symmetry apart from translation, (b) an additional reflection symmetry

• In one dimension there are only two space groups, corresponding to the symmetries of the two “crystals” in Fig. 3

★ In (a) there is no symmetry apart from translation, and the space group G is the same as the translation group T , with all translations multiples of the period $a > 0$. The Bravais lattice is indicated by a series of dots. The choice of the position of the dot relative to one of the “molecules” is arbitrary; it could be placed anywhere. Of course, once one dot is fixed the rest of the Bravais lattice is fixed. By convention the origin $x = 0$ is a point on the Bravais lattice, and for this symmetry group the choice of origin, relative to the crystal structure, makes no difference.

• The region between two points on the Bravais lattice constitutes a “primitive cell”: the entire periodic structure can be made up by taking a single primitive cell and translating by all possible translation vectors. These images of the primitive cell do not overlap, and their union is the entire “crystal.” Obviously the choice of primitive cell is not unique.

★ In Fig. 3(b) the situation is different from (a) in that there is a reflection symmetry in addition to the translational symmetry. The point group P is then $\{I, J\}$, where $Ix = x$ and $Jx = -x$, a reflection through the origin. The group consists of all the elements $(I|m)$ and $(J|n)$, where for convenience we assume that the lattice constant a is equal to 1, and thus m and n are integers.

• Note that the choice of origin of the Bravais lattice is no longer altogether arbitrary. In order for the crystal to be invariant under $(J|0)$ we place the origin at one of the points of reflection symmetry. One possibility is that indicated in Fig. 3(b). However, we could also have arranged the

Bravais lattice so as to have the points midway between the molecules. The fact that we seem to have not one but two types of reflection by no means accidental, and follows from the mathematics, as we shall see.

◦ The definition of a primitive cell is exactly the same as for the less symmetric situation in part (a) of the figure. However, one may wish to choose the primitive cell in some way that reflects the structure of the underlying crystal, in which case there are two obvious choices: an interval that begins and ends on a Bravais lattice point, or begins and ends midway between two such points.

- The multiplication table for G is relatively simple:

$$\begin{aligned}(I|m)(I|n) &= (I|m+n), & (J|m)(J|n) &= (I|m-n), \\ (I|m)(J|n) &= (J|m+n), & (J|m)(I|n) &= (J|m-n),\end{aligned}\tag{22}$$

• Note that $(J|m)$ is its own inverse, and multiplication is not commutative, so the space group is nonabelian, even though the point group is abelian.

★ The geometrical interpretation of $(I|m)$ is straightforward, but that of $(J|m)$ is less so. To understand what is going on note that the action of $(J|m)$ on $\mathbb{R}$ is given by

$$(J|m)x = m - x,\tag{23}$$

and this leaves the point $x = m/2$ fixed. Thus $(J|m)$ is a reflection about the point $m/2$, corresponding in Fig. 3(b) to a reflection about a point on the Bravais lattice when m is even, and a point midway between points on the Bravais lattice when m is odd. While both of these are reflections, we feel intuitively that they are in some sense different.

- The difference just mentioned is confirmed by an analysis of the conjugacy classes. Thus

$$(I|n)(J|m)(I|-n) = (J|m+2n), \quad (J|n)(J|m)(J|n) = (J|2n-m)\tag{24}$$

are elements conjugate to $(J|m)$, and it is at once evident that that they change m to a new value m' which is even if m is even, and odd when m is odd. Thus the even-odd character of the reflections is preserved under conjugacy.

□ Exercise. Complete the analysis of conjugate classes in G by finding the elements conjugate to $(I|m)$.

★ The translations T , i.e., all the elements $(I|m)$, are obviously a normal subgroup—in agreement with the general argument given earlier, see (17)—since the only other coset consists of precisely the elements $(J|m)$. The quotient group is $Q = G/T \cong Z_2$, but G is obviously not the direct product of T and Q .

□ Exercise. Why is it obvious?

• In fact G is (isomorphic to) the semidirect product of Q and T , using the identity and the $m \rightarrow -m$ automorphisms of $Z \cong T$.

□ Exercise. Work out the details.

4 Space Groups in Two Dimensions

4.1 Introduction

★ In two dimension there are 10 different point groups or crystal classes divided into 4 distinct systems. Associated with these are a total of 17 space groups. For complete descriptions see ITC. We shall only look at a few examples in order to get the general idea.

- The four systems are: oblique (2), rectangular (2), square (2), hexagonal (4), where the numbers in parentheses indicate the number of distinct point groups associated with the system. The classification up to this point makes no essential reference to the internal structure of the two-dimensional crystal. However, the limited number of point groups results from restrictions encountered when combining them with a periodic structure.

4.2 Oblique system

- There are two point groups, each with an associated space group, associated with the oblique system. The name “oblique” refers to the fact that there is no particular relationship between the primitive translation vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, or, on the macroscopic level, between crystal facets, in contrast to the other systems. We will describe both space groups

★ One should think of the periodic array in Fig. 4 as extending off to infinity. The “molecules” have no particular symmetry associated with them, but lie in a periodic array on top of which is superimposed a Bravais lattice with light lines connecting the lattice points. The origin of the lattice is arbitrary. The primitive translation vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ have no particular relationship with each other, and their choice is not unique even when the Bravais lattice is given. One searches in vain for any sort of rotation or reflection which will carry the structure onto itself, and consequently the point group is the trivial $\{I\}$

- One of the small parallelograms between lines connecting points on the Bravais lattice can serve as a primitive cell: something which will cover the entire crystal when shifted by all of the translations in T .

- Notice that in this case the Bravais lattice (think of it as the collection of points that are at the intersections of the straight lines) has a higher symmetry than the crystal, as it is invariant under a set of 2-fold rotations discussed in the next example.

□ Exercise. Why are the primitive translations $\mathbf{a}_1$ and $\mathbf{a}_2$ not unique? An obvious choice is to make them two sides of one of the parallelograms in the figure, and of course one can reverse the direction of either, e.g., $\mathbf{a}_1 \rightarrow -\mathbf{a}_1$. But is there more freedom than this? Are there other choices that will produce the same Bravais lattice?

★ A more interesting example is provided by the crystal in Fig. 5. The molecules are no more symmetrical than those in Fig. 4, but by arranging them with appropriate positions and orientations one arrives at a higher symmetry for the overall structure. Inspection shows that each Bravais lattice point, at the intersection of two of the light straight lines, is a 2-fold rotation axis. In addition there are other distinct kinds of 2-fold axes (or points).

□ Exercise. How many distinct kinds of 2-fold rotations can you spot before reading further?

- It is worth noting that in this example the symmetry of the crystal is exactly the same as the symmetry of the Bravais lattice, obtained by throwing away the molecules in Fig. 5 and retaining only the straight lines (or, to be more precise, their intersections).

★ The space group is generated by two types of operation: $(I|\mathbf{t})$ and $(J|\mathbf{t})$, where J is the 2-fold rotation that carries x, y into $-x, -y$, the element of $O(2)$ represented by the matrix $-I$.

- It will be convenient to represent points in $\mathbb{R}^2$ using the nonorthogonal coordinates system provided by $\mathbf{a}_1$ and $\mathbf{a}_2$, and to write

$$\mathbf{r} = \xi \mathbf{a}_1 + \eta \mathbf{a}_2 = (\xi, \eta), \quad (J|\mathbf{r}) = (J|\xi, \eta), \quad (I|\mathbf{r}) = (I|\xi, \eta). \quad (25)$$

The Bravais lattice itself corresponds to ξ and η taking integer values, and the other points of interest to us turn out to be simple fractions. The elements of G are of the form $(I|m, n)$ and $(J|m, n)$, where m and n are integers.

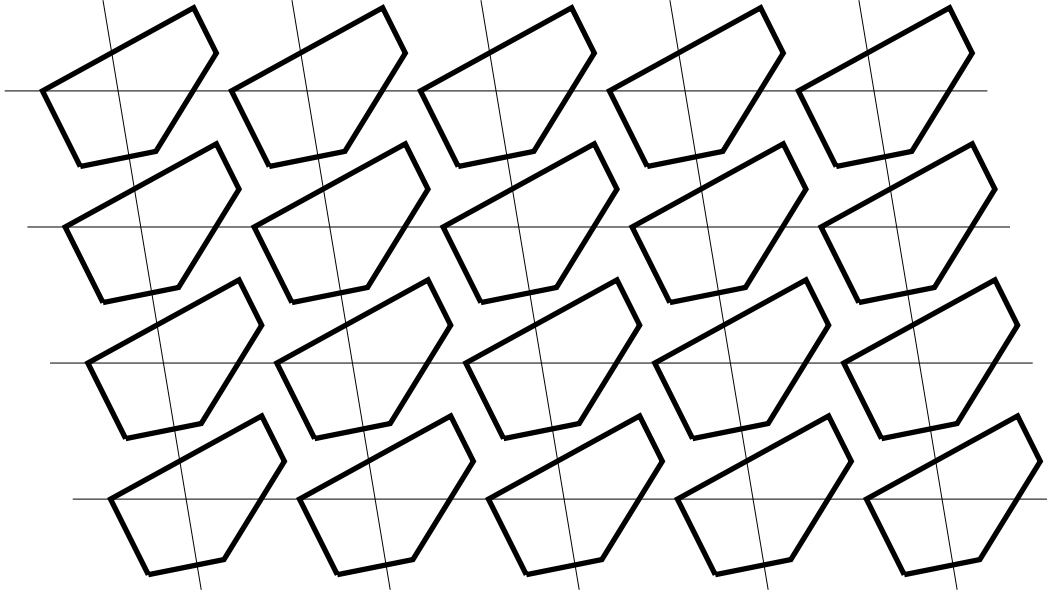


Figure 4: Crystal in 2 dimensions with no symmetry except translation

★ The group multiplication table is easily seen to be

$$\begin{aligned} (I|m, n)(I|m', n') &= (I|m + m', n + n'), & (J|m, n)(J|m', n') &= (I|m - m', n - n'), \\ (I|m, n)(J|m', n') &= (J|m + m', n + n'), & (J|m, n)(I|m', n') &= (J|m - m', n - n'), \end{aligned} \quad (26)$$

which bears a suspicious resemblance to (22).

★ To give $(J|m, n)$ a geometrical interpretation, we note that when acting on $\mathbb{R}^2$,

$$(J|m, n)(\xi, \eta) = (m - \xi, n - \eta) \quad (27)$$

has a fixed point at

$$\xi = m/2, \quad \eta = n/2. \quad (28)$$

• Thus the situation is analogous to the 1-dimensional case studied earlier in Sec. 3: we expect to find four different types of 2-fold rotation: (i) both m and n even, (ii) m even and n odd, (iii) m odd and n even, (iv) m and n both odd.

□ Exercise. Identify the location of one instance of each of these types in Fig. 5, assuming that $\mathbf{a}_1$ points horizontally to the right and $\mathbf{a}_2$ upwards and slightly to the left.

□ Exercise. Find the conjugacy classes of G . Check that the four types of 2-fold rotation just discussed fall in four distinct conjugacy classes. How are the translations divided up into conjugacy classes?

★ Since the point group $\{I, J\}$ is obviously isomorphic to $Q = G/T$, the discussion about the relationship of G to Q and T at the end of Sec. 3 applies almost word for word to the present situation.

□ Exercise. Confirm that this is so

• Again, one of the small parallelograms constitutes a primitive cell. Note that each type of 2-fold rotation occurs precisely once in a primitive cell if one shifts it slightly so that no rotation point lies on a boundary.

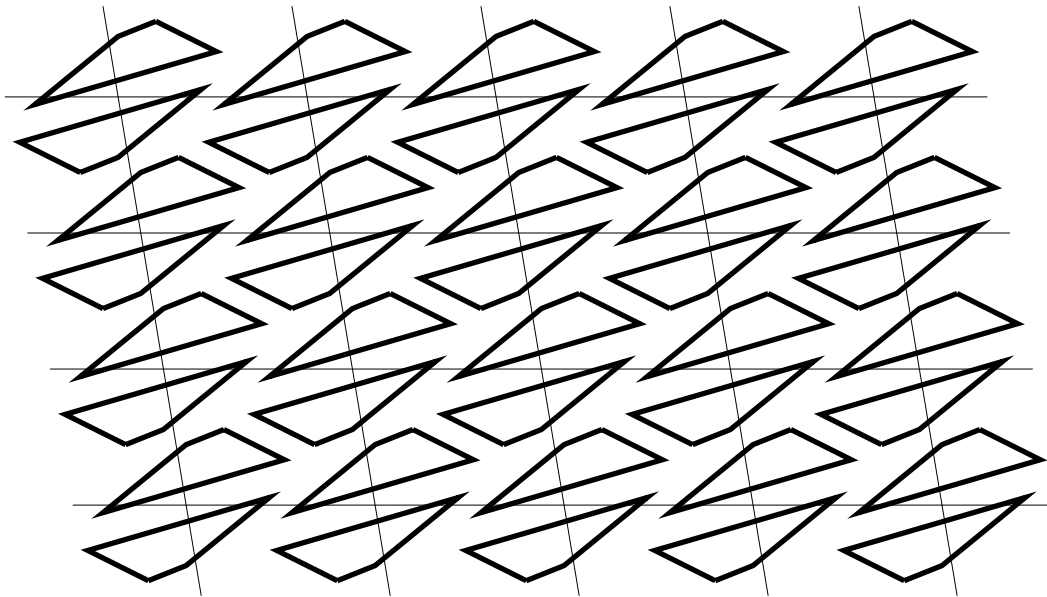


Figure 5:

4.3 Rectangular system: glide lines

- There are two point groups associated with the rectangular system, which takes its name from the fact that the unit cell may be taken to be a rectangle. Each point group has several space groups associated with it, for a total of 7 space groups for this system. We discuss one of them here, and a second below.

★ The pattern shown in Fig. 6(a), next page, has very little symmetry, but if one inspects it closely one sees that the dashed lines, placed as a guide to the eye, are actually reflection lines provided that the reflection is accompanied by a shift of $1/2$ of a primitive translation in the horizontal direction. There are no rotation axes

- Part (b) of the figure shows a Bravais lattice superimposed on the pattern, and also shows the rectangular unit cell. The horizontal origin of coordinates is arbitrary, whereas the vertical is chosen in such a way that the Bravais lattice falls on glide reflection lines.

★ If x and y are measured in units of the width (a) and height (b) of the unit cell, respectively, the group elements can be written in the form $(I|m, n)$ and $(B|m + 1/2, n)$, where m and n in each case are arbitrary integers, and B is the point operation consisting of reflection in the x axis, thus $y \rightarrow -y$.

- As there is no way to choose the coordinate system in order to make $(B|0, 0)$ a member of G , this is an example of a nonsymmorphic group—see the discussion at the end of Sec. 2.2, and further remarks in Sec. 5

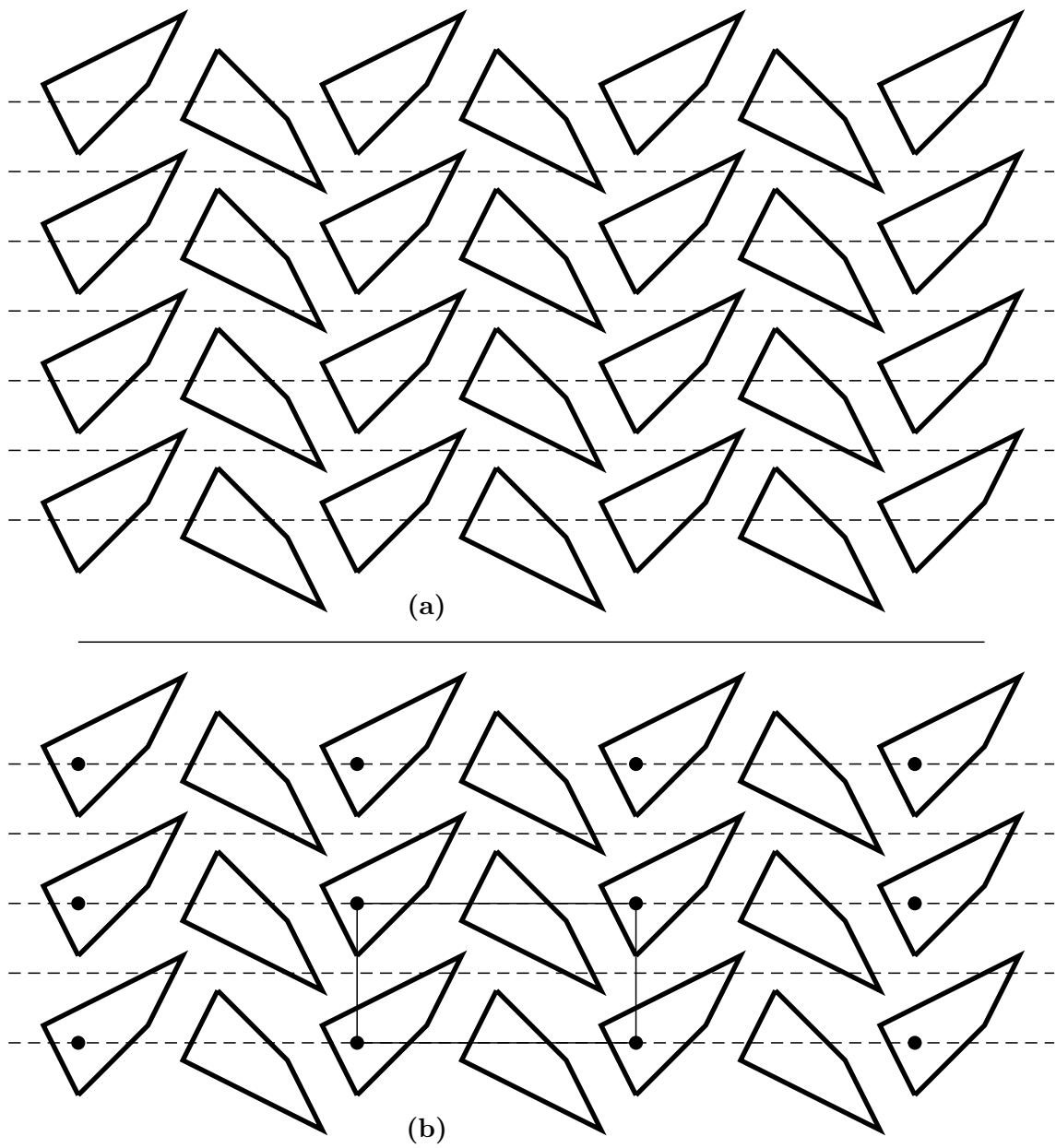


Figure 6: (a) Pattern with glide reflection symmetry indicated by dashed lines. (b) Bravais lattice and unit cell for this pattern shown in (b).

4.4 Rectangular system: bricks

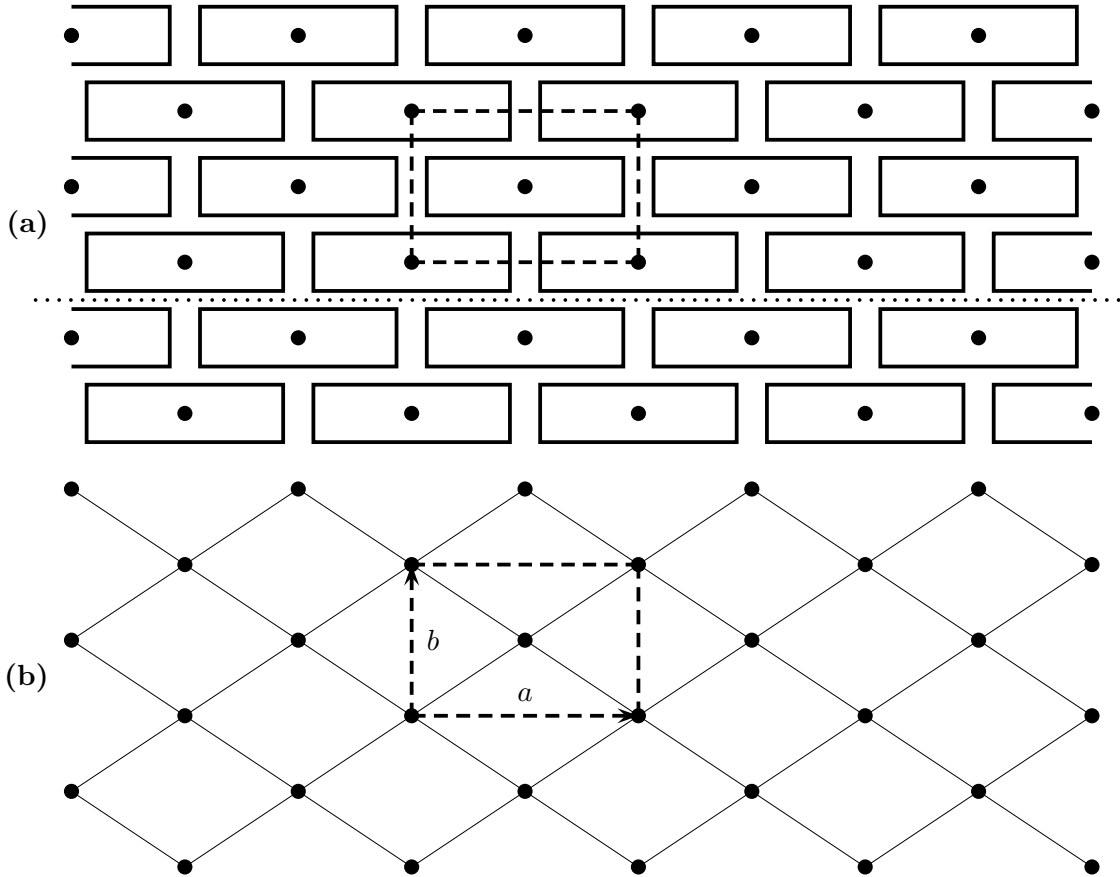


Figure 7: (a) A two-dimensional “brick” lattice. (b) The Bravais lattice with the bricks removed. The dashed lines indicate the rectangular unit cell.

★ The “brick lattice” in Fig. 7(a) illustrates the sort of symmetry which might arise from a molecule of a rectangular shape. We have chosen the points on the Bravais lattice to lie at the centers of the bricks, and Fig. 7(b) shows the lattice itself without the bricks so as to make its geometrical character more apparent. The obvious choice for primitive translation vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are those on two sides of a rhombus. However, they form a nonorthogonal coordinate system, and certain calculations become a bit easier if one adopts a rectangular coordinate system given by the perpendicular vectors $\mathbf{a}$ and $\mathbf{b}$, with

$$\mathbf{r} = \xi \mathbf{a} + \eta \mathbf{b} = (\xi, \eta). \quad (29)$$

- A disadvantage of this coordinate system is that the points on the Bravais lattice occur not only when ξ and η are both integers, but also when both are half integers (i.e., half of an odd integer). We shall call the latter “half-integer” points. Note that so far as crystal symmetry is concerned there is no difference between integer and half-integer points on the Bravais lattice: the crystal looks exactly the same from either. Instead, this slight peculiarity arises from our choice to use a rectangular coordinate system.

- A single rectangle with edges a and b is referred to as a *unit cell*, and has twice the area of a *primitive cell*, such as one of the rhombuses in Fig. 7(b).

★ By looking at Fig. 7 it is evident that there are no n -fold axes with n larger than 2. However, one can see various horizontal and vertical reflection lines. Hence the point group now consists of $\{I, J, A, B\}$ where A will denote a reflection in the y axis and B a reflection in the x axis. In other words,

$$A(\xi, \eta) = (\xi, -\eta), \quad B(\xi, \eta) = (-\xi, \eta), \quad J(\xi, \eta) = (-\xi, -\eta). \quad (30)$$

Since the square of any of these is I , and the product of any two of them is the third, the point group is isomorphic to the four group V or $Z_2 \times Z_2$.

- By using (30) one can work out the multiplication table for the space group. For example

$$(B|\mu', \nu')(A|\mu, \nu) = (J|\mu' - \mu, \nu' + \nu). \quad (31)$$

Note that in the pair (μ, ν) , either both μ and ν are integers, or they are both half integers, and this is preserved on the right side, where both $\mu' - \mu$ and $\nu' + \nu$ will both be integers or half integers. Working out the entire table is a trifle tedious, so we will simply evaluate the products we need as we go along.

★ Inspection of Fig. 7 reveals various symmetry elements of the following sorts. (i) Various 2-fold rotations about different points. (ii) Reflections in various vertical lines, including some cases in which a reflection is accompanied by a translation (not belonging to the Bravais lattice) parallel to this line. See, for example, the vertical line located at $\xi = 1/4$. (iii) Reflections in horizontal lines, including some accompanied by translations parallel to the line.

★ We know that $(J|\mu, \nu)$ is a two-fold rotation, and, following the analysis in Sec. 4.2, the rotation axis is located at $\xi = \mu/2, \eta = \nu/2$. Setting μ, ν equal to $0, 0$, $0, 1$ and $1/2, 1/2$ we see that there will be 2-fold axes at $0, 0$, $0, 1/2$ and $1/4, 1/4$. Other possible locations in the unit cell are actually obtained from these three by symmetry operations. Thus $1/2, 0$ is of the same type as $0, 1/2$ since $1/2, -1/2$ is in the Bravais lattice. A less obvious case is that of $3/4, 1/4$ which is the same type as $1/4, 1/4$ if one employs a suitable reflection.

□ Exercise. Show that elements of the group G of the form $(J|\mathbf{t})$ fall into exactly three conjugate classes corresponding to the three types of 2-fold rotation just discussed.

□ Exercise. Can you explain why there are only three kinds of 2-fold rotation in this case rather than four as in the example in Sec. 4.2? How has the additional symmetry made one kind disappear?

★ Elements of G of the form $(A|\mu, \nu)$ represent reflections in a horizontal axis accompanied by some sort of translation parallel to the axis. Since

$$(A|\mu, \nu)(\xi, \eta) = (\mu + \xi, \nu - \eta) \quad (32)$$

it is evident that a horizontal line at $\eta = \nu/2$ will be mapped to itself, and there will be a corresponding horizontal translation by μ . If μ and ν are both integers, this horizontal line passes through points on the Bravais lattice and the horizontal translation is an integer multiple of the distance between two successive points, so the result is indistinguishable from a simple reflection in this line. On the other hand, when μ and ν are both half integers, the horizontal line passes midway between two rows of Bravais lattice points, and since the corresponding translation is by half an odd integer, the reflection in the line must be accompanied by a shift or glide of $a/2$ to bring the pattern back on itself. The dotted line in Fig. 7(a) is the glide reflection line.

- Note that in this case, in contrast with the example discussed earlier in Sec. 4.3, $(A|0, 0)$ belongs to G , so this space group is symmorphic, see the remarks in Sec. 2.2.

- Elements of G of the form $(B|\mu, \nu)$ can be discussed in exactly the same way, with reflections in vertical lines replacing reflections in horizontal lines.

□ Exercise. Find a vertical glide reflection line in Fig. 7(a) and identify the corresponding μ and ν , one of which is, of course, not unique, assuming the origin is the left lower corner of the dashed unit cell.

4.5 Other systems in two dimensions

★ The two systems of crystal symmetries in two dimensions not yet discussed are the square and the hexagonal systems. See ITC for a full discussion of the different possibilities. An example of the square system is the pattern shown in Fig. 8, and of the hexagonal system the pattern shown in Fig. 9. Working out the properties is left as exercises.

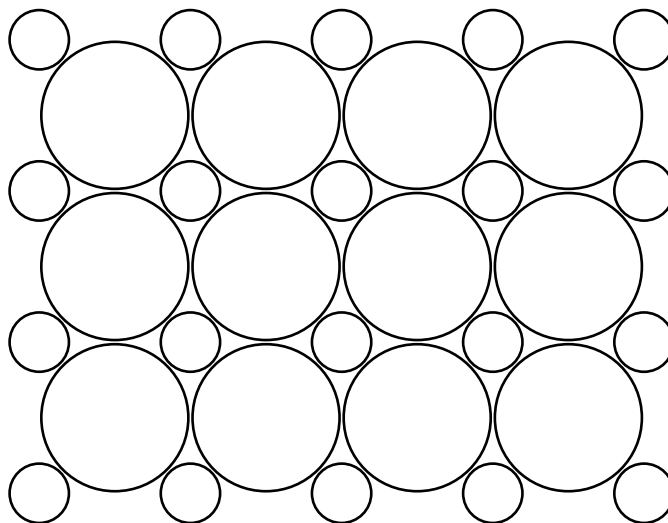


Figure 8: Structure forming a square lattice

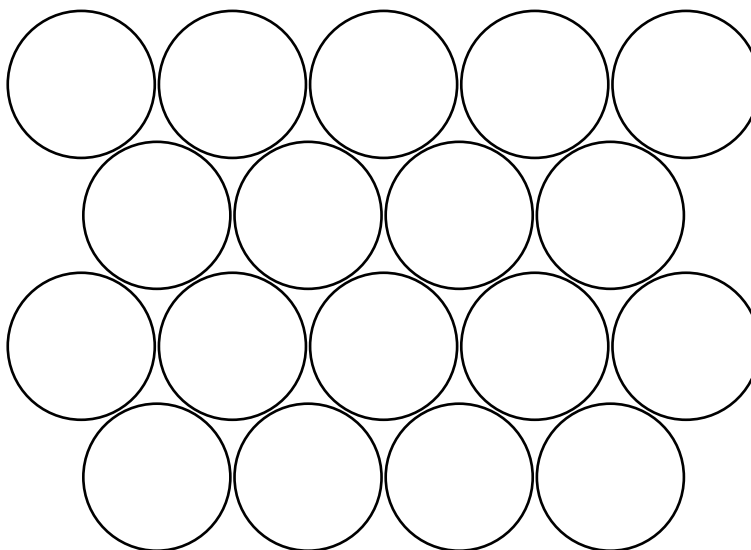


Figure 9: Structure forming a triangular lattice

□ Exercise. Construct a Bravais lattice for the pattern in Fig. 8. Identify the different symmetry elements including translations, rotations, reflections. Classify them into different conjugacy classes. Are there some glide lines? When finished (or before you finish, in case you get stuck) consult the

ITC tables to check your results. In the Hermann-Mauguin notation used by the ITC tables what is the symbol ('p' followed by something) for this space group?

□ Exercise. Same for the pattern in Fig. 8. Note that in this case the crystallographers do not seem to prefer a rectangular unit cell, at least if the ITC tables are a guide.

5 Nonsymmorphic Space Groups

5.1 Introduction

★ The study of space groups is rendered more complicated (or more interesting, depending on one's perspective) by the possible presence of certain symmetry elements which combine operations from the point group with translations that do *not* belong to the Bravais lattice. See the remarks on nonsymmorphic groups at the end of Sec. 2.2.

- In two dimensions the new element is a glide reflection line, as in the example in Sec. 4.3
- In three dimensions these elements are of two kinds. A *screw axis* is a rotation by $2\pi/n$ around some axis accompanied by a shift in the direction of this axis by some vector $\mathbf{u}$ not in T . A *glide plane* is a reflection in a plane accompanied by a translation parallel to the plane by a vector $\mathbf{u}$ not in T .

• As noted in Sec. 2.2, a nonsymmorphic space group arises when it is impossible to choose the origin of the coordinate system in such a way that $(A|0)$ is a member of G for every A in the point group P . This, rather than the presence of screw axes or glide planes as such, is what distinguishes nonsymmorphic space groups from symmorphic space groups. The latter may contain screw axes or glide planes that arise “naturally” when operations in the point group are combined with translations in the Bravais lattice; a two-dimensional example was discussed in Sec. 4.4.

5.2 Simple example

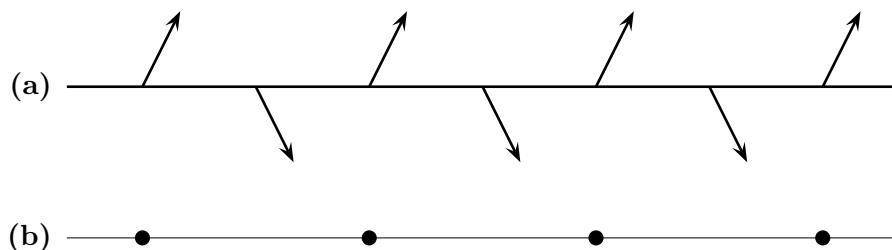


Figure 10: Branching pattern (a) and corresponding Bravais lattice (b)

★ A one-dimensional example illustrating some of the features of a nonsymmorphic space group is shown in Fig. 10, and is closely analogous to the pattern discussed in Sec. 4.3. The branching structure shows an obvious symmetry when translated to the right by half the lattice constant, assumed for simplicity to be 1, but only if it is rotated about, or reflected in, the horizontal line. Thus the space group consists of elements of the form $(I|m)$ and $(F|n + 1/2)$, where m and n are any integers, and F represents the rotation (or reflection) operation. There is no way to eliminate the $1/2$ by shifting the origin of the coordinate system.

• The point group, which is $\{I, F\}$, is obviously isomorphic to G/T , but in this case we cannot express G as a semidirect product of G/T and T , but must use a more general extension.

□ Exercise. Show that G cannot be reconstituted from G/T and T using a semidirect product. Hint: See the corresponding exercise in Sec. 3. What are the possible automorphisms of Z ?

□ Exercise. Construct G as an extension of $\{I, F\}$ by T .

6 Site symmetries

★ In applications of space groups to solid state physics one often finds that atoms in a crystal are located at particular sites where the symmetry is higher than at a general point in the primitive or unit cell, and this additional symmetry can be used to make inferences about energy levels of such atoms, or the behavior of nuclei undergoing magnetic resonance.

- A special site at point $\mathbf{r}_0$ is characterized by the fact that in addition to $(I|0)$ at least one element of the space group leaves $\mathbf{r}_0$ invariant:

$$(A|\mathbf{u})\mathbf{r}_0 = \mathbf{u} + A\mathbf{r}_0 = \mathbf{r}_0; \quad (A|\mathbf{u})(\mathbf{r}_0 + \Delta\mathbf{r}) = \mathbf{r}_0 + A\Delta\mathbf{r}. \quad (33)$$

for some A other than I in the point group P . The collection of elements of G of this type form a subgroup, the *stabilizer* of $\mathbf{r}$, and the corresponding subgroup of P defines the site symmetry.

- The ITC tables give locations of special sites and the corresponding point symmetry for each of the space groups in two and three dimensions.