Periodic Molecular Arrangements from Space Groups.

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We demonstrate, using examples from 2 and 3-dimensions, a systematic method of finding all possible periodic arrangements of a given molecule or molecules such that the arrangements have the symmetry of a given space group. The technique is based on work by Rabson et al. We give tables of generators which facilitate such work.

61.10.-i; 61.50.Em; 64.70.Kb

I. INTRODUCTION

The problem of determining all possible periodic arrangements of molecules within a given space group frequently arises in the study of structure using X-ray diffraction and elastic neutron scattering. The resolution of this issue needs a thorough understanding of space groups.

A new method of deriving and listing the crystallographic space groups, introduced by Rabson et al. and Mermin (RMRW) has simplified the derivation of space groups and made compact presentation possible. This has also unified the subjects of crystallography and quasicrystallography but, unfortunately, their techniques have not yet found widespread acceptance with researchers studying periodic structures in condensed matter physics. One reason for this may be that RMRW work in Fourier space while the arrangement of molecules is easier to visualize in real space. We will restate the algebraic relations used by RMRW in real space language and use their technique to list the crystallographic space groups compactly in real space.

We will then demonstrate our technique of using these algebraic relations to find molecular arrangements from these listings. Typically, the orientation of molecules at low temperature in a molecular crystal is determined by elastic diffraction, either of X-rays or of neutrons. If a large amount of high quality data is available, there may not be a problem in determining the crystal structure using standard computer programs to carry out the refinement. However, a more delicate approach, one that we used with reference to $C_{60}$ and which also has been used for other fullerene systems, is the following. For these systems, the orientationally disordered phase has been determined to be face-centered cubic (FCC). At the ordering temperature, new superlattice reflections appear indicating that the molecules develop long-range orientational order. From the outset, it was clear that the low temperature diffraction pattern had to be indexed with a simple cubic (SC) unit cell containing four orientationally inequivalent molecules. There was no suggestion that the centers of mass were no longer on an FCC lattice. To narrow down the possible structures, it was therefore sensible to ask the question: how can one arrange icosahedra on an FCC lattice such that the SC unit cell contains four molecules whose orientations are fixed? The determination of the allowed structures led to an easy identification of the space group of $C_{60}$. This structure has been identified by several groups. More recently, with the suggestion of a complicated (“2–a”) structure for $C_{60}$ (based on a still larger unit cell), a variant of the question arose, namely, how to arrange icosahedra on FCC lattice sites such that there are eight molecules per FCC unit cell. (In this case, the FCC unit cell would have a lattice constant twice as large as that of the orientationally disordered lattice.) However, it is now generally agreed\cite{1} that such a structure is not an equilibrium phase of $C_{60}$. The method we use\cite{2} in this work was, inelegant, however. It involved an explicit search through the listings of the crystallographic space groups in the International Tables of Crystallography (ITC)\cite{3}. The symmetries of all points in the unit cell are listed there, and, in principle, this information suffices to identify all allowed structures. However, a) such a direct consideration of all possibilities is tedious, b) in such an enumeration it is easy to overlook possible allowed space groups, and c) the tables themselves are not very easy to use without some background in crystallography. One advantage of the technique given here is that it is completely algebraic and the algorithm is a constructive one, rather than one of exhaustive enumeration. Also the method requires only an understanding of the symmetries of simple objects like the square, the cube, etc. In the course of this work, we have also become aware of some confusion concerning the proper formulation of this problem, associated with the question of what molecular distortions should or should not be considered in determining the allowed structures of molecular crystals.

This paper is organized as follows. In Sec. we define some terms and show how space groups can be specified compactly. In Sec. we state the relations we will be using. In Sec. we point out some basic properties that will be used in our technique. In Sec. we illustrate our technique by considering a hypothetical question concerning the
arrangement of hexagonal (benzene) and octagonal molecule on a square lattice. In Sec. [VI] we apply the technique to problem concerning 3-dimensions molecular crystal, in particular those of H$_2$ and C$_{60}$. A brief summary of our work is given in Sec. [VII]. In the course of this work it is helpful to relist all the cubic space groups in the RMRW language. (The similar list extended to all noncubic space groups is also available.)

II. SPACE GROUPS

In this and the next two sections we briefly review some of the basic facts concerning space groups and their characterization. In this we adapt the ideas of RMRW.

The set of symmetries of a periodic array is the space group of that array. There are only a finite number of distinct space groups (17 in 2-dimensions, 230 in 3-dimensions). We will see that to specify a space group it is necessary to specify the lattice, the point group, and the translations associated with the generators of the point group. The meaning of these terms will be clarified in the following paragraph.

In 2-dimensions, a Bravais lattice (henceforth just a lattice) is the set of points \( \{ \mathbf{r} \} \) defined by,

\[
\mathbf{r} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2,
\]

where \( \mathbf{a}_1, \mathbf{a}_2 \) comprise a linearly independent set of basis vectors and the \( n_i \) are integers. Such a vector \( \mathbf{r} \) is called a lattice vector. In \( d \)-dimensions there is a linearly independent set of \( d \) basis vectors. From the definition it is obvious that all lattices have inversion symmetry \( (n_i \rightarrow -n_i) \). The choice of basis vectors is not unique since any linearly independent set constructed from the \( \mathbf{a}_i \) can equally well be chosen as basis vectors. The obvious symmetries of any lattice are the translations by lattice vectors. The nontranslational symmetries, consisting of rotations, mirror planes, and combinations thereof, are the ones that specify a lattice uniquely. There are only a finite number of lattices with distinct symmetry, five in 2-dimensions and fourteen in 3 dimensions. For example, the square lattice of Fig. 3 is one of the five lattices in 2-d. Each of its points has the following symmetries in which the points itself remains fixed: \( M \), a mirror plane parallel to a crystallographic \((1,0)\) direction, \( M' \), a mirror plane parallel to a diagonal, and \( R_4 \), a 4-fold rotation about an axis perpendicular to the plane. There are a total of eight elements in the symmetry group of the point, \( E, M, R_4, M' = R_4M, R_4MR_4^{-1}, R_4M'R_4^{-1}, R_4^2 \) and \( R_4^4 \), where \( E \) is the identity and \( R_4^4 \) means a 4-fold rotation is applied \( n \) times. Any symmetry group can be completely specified by a few elements of the group called the generators. For example, the symmetry group of the square, denoted \( 4mm \), is completely specified by specifying the existence of the generators \( R_4, M \) and the generating relations \( R_4^4 = M^2 = E, (R_4M)^2 = E \).

In this paper we use the following conventions. Vectors are always specified by their components along the lattice vectors. With the symbols for vectors, a superscript represents the component of the vector and a subscript identifies a particular vector. For example, \( t^1_g \) is the component of vector \( t_g \) along the basis vector \( a_1 \). A superscript on the symbol for a symmetry element represents the number of times the operation is carried out. For example, applying the mirror \( m \) twice to any structure brings it back to its original state, or \( M^2 = E \). The symbol \( \equiv \) is used to signify that the vectors on both sides of the symbol differ from each other only by a lattice vector, for example \( \frac{1}{2} \mathbf{a}_1 \equiv \frac{3}{2} \mathbf{a}_1 \). Finally, to avoid confusion with the operations in three dimensions, we will denote point group operations in two dimensions by capital letters and those in three dimensions by small letters.

Any periodic structure can be considered to be a decoration of a lattice and the obvious symmetries of such a structure are the translations of the structure by a lattice vector. The decorations preserve some of the nontranslational symmetries of the lattice unchanged, while a few of these symmetries, of which say \( g \) is an example, require an additional non–lattice translation, say \( t_g \), to remain as symmetries. Some of the symmetries of the lattice may be completely lost. Specifying the unbroken symmetries of the lattice along with the required accompanying non–lattice translation completely specifies the symmetry of the space group. All the nontranslational symmetries of the lattice that are not lost form the point group of the space group. Obviously, if any \( t_g \) is nonzero, the point group is not actually a subgroup of the space group. In the literature such space groups are called nonsymmorphic.

Consider the square lattice shown in Fig. 3. Decorating it as shown in Fig. 3 (a) leads to all the symmetry elements of the lattice being preserved. Decorating the same square lattice with the pattern shown in Fig. 3 (b) leads to the mirror \( m \) requiring the translation \( t_M = (\frac{1}{2}, \frac{1}{2}) \) to follow it to get back the original structure. Since none of the symmetries are lost completely, the point group of both structures is \( 4mm \), the symmetry of the square. Decorating the lattice as shown in Fig. 3 (c) leads to the loss of mirror symmetries. The point group of this structure is now the point group with only the 4-fold rotations, \( C_4 \) or 4. These are the only distinct space groups with a square lattice. Table 1 lists the effect of the symmetry elements of a square on the point \((x, y)\). Table 1 lists all the space groups with a square lattice and point group \( 4mm \). These data will be used later.
III. THE ALGEBRAIC RELATIONS.

We now show that specifying the translations associated with the generators of the point group is enough to specify the translations associated with all the other elements of the point group. If the symmetry of a periodic structure is of the form \((g, t_g), (h, t_h)\) etc., where \((g, t_g)\) means the action of the element \(g\) is followed by a nonlattice translation \(t_g\) and \(g, h\) etc. are the elements of the point group, then it is easy to show (See Appendix A) that

\[
t_{gh} \equiv g t_h + t_g,
\]

where \(t_{gh}\) is the translation associated with the element \(gh\). (The operation \(gh\) is the operation \(h\) followed by the operation \(g\).) This is called the Compatibility relation or the Frobenius relation. In view of Eq. \(3.1\) knowledge of the translations associated with the generators is enough to find the translations associated with all the elements of the point group. For example in Fig. 3 (b) we have \(t_{R_4} \equiv (0, 0),\ t_M \equiv (\frac{1}{2}, \frac{1}{2})\). Since \(M' = R_4 M\) we get from Eq. \(3.1\) \(t_{M'} \equiv t_{R_4 M} \equiv R_4 t_M + t_{R_4} \equiv (\frac{1}{2}, \frac{1}{2})\).

The symmetry axes of rotations and the mirror planes of a point group contain a point designated as the origin, which they leave invariant. In the space group operation, \((g, t_g)\), the translation, \(t_g\), associated with the element \(g\) of the point group is dependent on the choice, which is arbitrary, of the origin. For example, consider the structure shown in Fig. 3. Its point group is \(2\). Local symmetry groups, as shown by RMRW,\(1\) have a site symmetry with four elements and there are equivalent sites to each other, which means that any of these sites can be chosen as the origin for an equivalent description of the space group. The reason for the existence of these \(\epsilon\) equivalent sites is that there are \(\epsilon\) elements in \(P\) such that

\[
(P_1 S \cup P_2 S \cup \ldots \cup P_\epsilon S) = P.
\]

These sites are equivalent to each other, which means that any of these sites can be chosen as the origin for an equivalent description of the space group. The reason for the existence of these \(\epsilon\) equivalent sites is that there are \(\epsilon\) elements in \(P\) such that

\[
\epsilon = n_p / n_s .
\]
If we want to construct a structure using objects with symmetry group \( S \) so that it has the symmetry of the space group with point group \( P \), then each of the \( e \) equivalent sites must be occupied by one of the objects oriented such that the symmetry group \( S \) is preserved at the sites. Obviously, the objects that can be placed at these sites must have at least the site symmetry, but they are allowed extra symmetry. In general, this extra symmetry will not be preserved in the actual structure. The simplest example of this is illustrated by placing spheres on an SC lattice. The surface of the undistorted sphere is defined, of course, by \( r = R_0 \), where \( R_0 \) is the radius of the sphere and \( r \) is the distance from the center of the lattice point. When placed in the lattice the sphere will distort and its surface will have an expansion in terms of cubic harmonics: \( r = R_0 + \epsilon (\cos^4 \theta \sin^2 \phi + \sin^4 \theta \cos^4 \phi - 3/5) \ldots \), where \( \theta \) and \( \phi \) are the usual spherical angular coordinates. The size and sign of the amplitude \( \epsilon \) is determined by the elastic response of the sphere. We will refer back to this concept of molecular distortion frequently. In contrast, if one tries to put on a site an object which does not possess all the symmetry elements of the site, then the lattice must distort. For example, if the square lattice were to be decorated with, say, a rectangle (with principal axes along the crystal axes), then the crystal would spontaneously distort into a rectangular lattice.

V. THE TECHNIQUE: TWO DIMENSIONS.

Consider the following situation in which it is assumed known that benzene (or hexagonal) molecules are situated on a square lattice. We will demonstrate our technique by answering the following question: Is it possible to arrange molecules with fixed orientations so that the unit cell contains two molecules and that the point group of this structure is \( 4mm \)? For concreteness, one may think of this molecule as having extremely strong intramolecular bonds, so that it suffers at most an infinitesimal distortion when placed in the crystal. Our construction of allowed structures relies on Eq. \([11]\). If we want to have \( p \) molecules per unit cell, we look for a site having a site symmetry group which is a subgroup of the symmetry of the molecule and which has \( n_s = n_p/p \) elements, where we can then place the oriented molecule. In this case all molecules occupy sites which are equivalent in the sense mentioned after Eq. \([11]\). It is also possible to occupy more than one set of equivalent sites, providing the total number of sites in all sets of equivalents sites is \( p \). Having carried out a construction to obtain all such sites, it will be necessary to check a few constraints. First of all, since we imposed a condition on the locations of the centers of mass of the molecules, (i.e. that the centers form a square lattice), we must check that the proposed structures satisfy this condition. Less trivially, we must also check that the proposed structure does not have a higher symmetry than presupposed. Having higher symmetry can mean that the unit cell is smaller than desired. (We will see this when we later deal with octagonal molecules.) Alternatively, when we consider the three dimensional case, we will find structures in which the value of a structural parameter is not fixed by symmetry. In that case, it often happens that for a special value of that parameter additional symmetry elements appear, in which case the point group has higher symmetry than in the generic case.

We now determine the allowed arrangements of benzene molecules. The symmetry of benzene molecule belongs to the point group \( 6mm \). (In this notation, which is discussed in Appendix C, \( 6mm \) means that the molecule has a six–fold axis of symmetry perpendicular to its plane and it has two inequivalent mirror planes, the normals to which lie in the plane of the molecule. We treat the molecule as perfectly flat and thin, so that the additional mirror plane in the plane of the molecule is omitted as being irrelevant to the present discussion.) We have already discussed the 2-d space groups with square lattice and point group \( 4mm \) in the preceding discussion and the space groups are listed in Table \([H]\). \( 4mm \) has eight elements, so if we can find a site in the unit cell with a site symmetry group containing four elements, there must be two of them. This site symmetry group of four elements must also be a subgroup of the symmetry of the benzene molecule (\( 6mm \)) so that a molecule can be placed at each site without distorting the lattice.

Accordingly, we can only place hexagonal molecules on sites whose symmetry group is simultaneously a subgroup of that (\( 6mm \)) of the molecule and also a subgroup of the point group of the lattice. The symmetry group \( 2mm \), (the symmetry of a rectangle, generators \( R_2, M \), discussed in section \([H]\)) satisfies the requirement of being a group with four elements which is a subgroup of both \( 4mm \) and \( 6mm \). Thus the problem has been transformed to that of finding sites in the unit cell of the two space groups with \( 2mm \) symmetry. There are two distinct ways of getting the subgroup \( 2mm \) from \( 4mm \). We choose the 2-fold rotation, \( R_2 \), as one of the generators. For the other generator, we can choose either the mirror \( M \) or the mirror \( M' \). (Choosing \( M \) and \( M' \) as generators gives the full group \( 4mm \).)

We have two space groups with a square lattice and point group \( 4mm \) which we consider separately in the following subsections.
A. Space group $p4mm$: $t_{R_4} \equiv (0,0), t_M \equiv (0,0)$

From the compatibility relation, Eq. 3.1, we can find the translations associated with all the elements, given the translations for the generators. With the origin at point A in Fig. 3, $t_{R_4} \equiv (00)$ and $t_M \equiv (00)$. Then the translations associated with all the elements are zero. Thus, $t_{R_4} \equiv (0,0)$ and $t_M' \equiv (0,0)$.

The origin has $4mm$ symmetry. During the origin is shifted by $c \equiv (c_1,c_2)$, then the new values (indicated by primes) of the translations associated with the elements are obtained from Eq. (3.2) as

$$t'_{R_4} \equiv (-c_2 - c_1, c_1 - c_2) + t_{R_4} \equiv (-c_2 - c_1, c_1 - c_2)$$  \hspace{1cm} (5.1)
$$t'_M \equiv (0, -2c_2) + t_M \equiv (0, -2c_2)$$  \hspace{1cm} (5.2)
$$t'_{R_4} \equiv (-2c_1, -2c_2) + t_{R_2} \equiv (-2c_1, -2c_2)$$  \hspace{1cm} (5.3)
$$t'_M \equiv (c_2 - c_1, c_1 - c_2) + t_{M'} \equiv (c_2 - c_1, c_1 - c_2)$$  \hspace{1cm} (5.4)

We consider the two choices for $2mm$ separately.

1. 2mm with the generators $R_2, M$

The problem for this case boils down to this. Is it possible to choose $c_1, c_2$ such that $t_{R_4}' \neq (00)$ but $t_{R_2}' \equiv t'_M \equiv (00)$? If the answer is yes, then we have found sites whose symmetry group is $2mm$, with generators $R_2, M$.

Clearly, we may restrict $c_1$ and $c_2$ to satisfy $0 \leq c_i < 1$. Then to get $t_{R_2}' = 0$, we must have $c_1 = 0$ or $c_1 = 1/2$ and $c_2 = 0$ or $c_2 = 1/2$. To get $t_{R_4}' \neq 0$ restricts us to the two possibilities: $c_1 = 1/2, c_2 = 0$ or $c_1 = 0, c_2 = 1/2$. First consider the choice $c = (1/2,0)$. This site has the desired symmetry; therefore we may place a benzene molecule here. Since $t_{R_4}' = 0$, the molecule has symmetry with respect to a mirror along the $x$-axis. There are two choices (which lead to equivalent structures), one of which is shown in Fig. 5a. [The other choice is obtained by applying a $90^\circ$ rotation to the hexagon at $(1/2,0).]$ Having made the selection as in Fig. 5 for the molecule at $(1/2,0)$ the orientation of the other molecule may be determined by applying the space group operation $(R_4, t_{R_4}')$. Thereby we see that the orientation of the second molecule in the unit cell is as shown in Fig. 5. One can check that an equivalent structure is obtained by the choice $c = (0,1/2)$.

2. 2mm with generators, $R_2, M'$

In this case we try to make $t_{R_2}' \equiv t'_M \equiv (0,0)$ and $t_{R_4}' \neq (0,0)$. It is easy to see in this case, $t_{R_2}' \equiv t'_M \equiv (0,0)$ implies that $t_{R_4}' \equiv (0,0)$. Thus it is impossible to find a structure satisfying our requirements. This means that the structure in Fig. 3(a) is the only one allowed in this space group with 2 benzenes per unit cell.

B. Space group $p4gm$: $t_{R_4} \equiv (0,0), t_M \equiv (1/2,1/2)$

We follow the same procedures used for the previous space group, except here we have to do a little more work to find the translations associated with the elements of $4mm$.

From Eq. 3.1 and the fact that $R_2^2 = R_2$ we have $t_{R_2} \equiv (0,0)$. Using Eq. 3.1 and the fact that $M' = R_4 M$, we find that $t_{M'} \equiv (1/2,1/2)$. Both these values pertain to the origin as shown in Fig. 1. Thus for this space group, Eqs. (5.2), (5.4) become, respectively,

$$t'_M = \left(\frac{1}{2}, \frac{1}{2} - 2c_2\right)$$  \hspace{1cm} (5.5)

$$t'_{M'} = \left(\frac{1}{2} + c_2 - c_1, \frac{1}{2} + c_1 - c_2\right)$$  \hspace{1cm} (5.6)

Since $t_{R_4}' \equiv t_{R_2} \equiv (0,0)$, Eqs. (5.4) and (5.3) also hold for this space group.
1. 2mm with the generators $R_2, M$.

Here we try to make $t'_{R_2} \equiv t_M \equiv (0,0)$. But from Eq. (5.3) it is obvious that it is impossible to make $t^1_M \equiv (0,0)$. Thus it is not possible to have a structure with two hexagons per unit cell that preserves $M$ as a local site symmetry.

2. 2mm with the generators $R_2, M'$.

We now try to find sites with 2mm symmetry using $R_2, M'$ as the generators. Using the relations Eqs. (5.3), (5.4) and (6.0) one may verify that choosing either $c \equiv (\frac{1}{2}, 0)$ or $(0, \frac{1}{2})$ makes $t_M' \equiv t_{R_2} \equiv (0,0)$ and makes $t_{R_4} \neq (0,0)$.

The structure, shown in Fig. 5(b), is constructed for the case $c \equiv (\frac{1}{2}, 0)$ following the procedure outlined in the previous case. The other choice, $c \equiv (0, \frac{1}{2})$, gives the same structure rotated by 90 degrees about the 2-fold axis through the origin ‘O’.

C. Inequivalent sites

The procedures detailed above considered only the case when the molecules are placed in equivalent sites, defined in Sec. IV. In fact, in the above example it was not possible to place two hexagons on a square lattice on inequivalent sites. From an algebraic point of view, that would have required finding a group of 8 elements which was simultaneously a subgroup of the point group of the molecule and of the point group of the crystal. One may also see by inspection that the above solutions do not work. To visualize inequivalent sites, imagine painting the hexagons different colors, say, red and blue. In the above solutions, such a difference causes the $x$ and $y$ axes in Fig. 4a to differ and the $(1,1)$ and $(1,-1)$ directions in Fig. 4b to differ. (In the first case, one axis is parallel to a mirror line passing through the vertices of a blue hexagon, and the other axis is parallel to a mirror line passing through the vertices of a red hexagon.) So in this case, the lattice will distort into a rectangular lattice. Which axis becomes elongated depends on which color hexagon is easier to squash.

To illustrate an arrangement involving inequivalent sites, consider putting two octagonal molecules per unit cell on a square lattice. In the most general case, which we will discuss later, we will allow the molecules to distort in response to their environment in the crystal. However, at first, we first consider the molecules to be perfectly rigid.

We start by looking for arrangements of rigid octagons on equivalent sites on a square lattice. For this purpose we follow the procedure we used to place oriented hexagons: we look for sites which have a symmetry group having four elements and which is a subgroup of both 4mm (the point group of the lattice) and 8mm (the point group of the molecule). Following exactly the analysis for benzene, we have to determine the orientations of octagons which have mirror planes along the $x$ and $y$-directions. There are two such orientations: one, used in panel (a), in which the mirror planes cut the faces at their midpoints and (b) another in which the mirrors pass through a vertex. Using this information we obtain the structures shown in panels (a) and (b) of Fig. 6. But since these structures index to a smaller unit cell, we reject them. Note that, as in Fig. 5, the orientations of the two molecules were assumed to be related by a symmetry operation.

Now we consider the possibility of occupying two inequivalent sites in the unit cell with oriented octagons. In this case we look for sites which have a symmetry group which is a subgroup of both 4mm and 8mm which contains eight elements. We will need two such sites, because according to Eq. (4.1) each site in this case has only a single response to their environment in the crystal. However, at first, we first consider the molecules to be perfectly rigid.

We wish to emphasize that there is no physical requirement that identical molecules should occupy crystallographically equivalent sites. So we now turn to a brief discussion of orientational potentials which give rise to a structure such as (c) of Fig. 6 which involve inequivalent sites. For simplicity this discussion is carried out for a two dimensional system, but the conclusions hold for three dimensional systems also. To obtain the symmetry of the orientational potential, it is convenient to imagine the molecules interacting via an atom–atom potential, $\Phi(I, J)$, where $I$ and $J$ label molecules and
\[ \Phi(I, J) = \sum_{i \in I} \sum_{j \in J} \phi(R_i - R_j), \]  
\[ \text{where } i \text{ and } j \text{ label atoms, } i \in I \text{ indicates that atom } i \text{ is in molecule } I, \text{ and } \phi \text{ is a generic atom–atom potential. To discuss the symmetry of } \Phi(I, J) \text{ we consider expanding it in powers of } r_i \equiv R_i - R_J, \text{ where } R_J \text{ is the position of the center of molecule } I. \text{ Atomic coordinates will appear in the combinations} \]
\[ r_i^m e^{im\phi}(1 + a_2 r_i^2 + a_4 r_i^4 + \ldots), \]
\[ \text{where } r_i e^{i\phi_j} = x_j + iy_j \text{ and } a_{2n} \text{ depends on the details of the potential } \phi. \text{ To discuss questions of symmetry, we may ignore terms involving } a_2, a_4, \text{ etc. Then} \]
\[ \Phi(I, J) = \sum_{M=-\infty}^{\infty} \sum_{N=-\infty}^{\infty} a(M, N)\sigma_M(I)\sigma_N(J)e^{-i(M+N)\phi_{IJ}}, \]
\[ \text{the coefficients } a(M, N) \text{ depend on } R_{I,J} \text{ and } R_{I,J} e^{i\phi_{IJ}} = X_{I,J} + iY_{I,J}, \text{ where } R_{I,J} = R_I - R_J, \text{ etc. Also} \]
\[ \sigma_M(I) = \sum_{i \in I} r_i^M e^{iM\phi_i}. \]
\[ \text{For completely rigid octagons } \sigma_M \text{ is only nonzero when } M \text{ is divisible by } 8. \text{ If we specify the orientation of an octagon by the angle, } \theta, \text{ the line joining its center to a vertex makes with a nearest neighbor direction, then one sees that} \]
\[ \sigma_M \propto e^{iM\theta}. \text{ For our purposes, it suffices to consider the following intermolecular potential for rigid octagons:} \]
\[ V(\{\theta_i\}) = A \sum_i V_0 \cos(8\theta_i) + B \sum_{\langle ij \rangle} \cos(8\theta_i) \cos(8\theta_j), \]
\[ \text{where } \langle ij \rangle \text{ indicates that the sum is over pairs of nearest neighbors. Then the structures in Fig. 1 correspond to choices of signs of the parameters in the potential as indicated in the figure caption. Within the approximation of completely rigid molecules there is thus only one way to arrange octagons on a square lattice (see panel c of Fig. 1) so that they belong to a space group having } (4mm) \text{ point group symmetry and have two molecules per unit cell. This example is important because it shows explicitly that there is no requirement that two identical molecules should remain equivalent when placed in the crystal. To reach this case merely requires that } B > 0 \text{ in Eq. (5.11) and that } A \text{ plays no role in determining the structure (} A = 0, \text{ for example).} \]
\[ \text{Now let us see what happens when we relax the assumption that the molecules are perfectly rigid. We therefore consider the limit when all the intramolecular force constants are arbitrarily large, but are not actually infinite. It is clear that in this limit the } \text{th molecule will distort in response to the crystal field, } V_c, \text{ of the square lattice. To see this analytically, we look at terms in the multipole expansion of Eq. (5.13) with } M = 4 \text{ and } N = 0. \text{ Denoting this term for molecule } I \text{ by } V_c^{(4)}(I), \text{ we have} \]
\[ V_c^{(4)}(I) = A \sum_j \sum_{i \in I} r_i^4 \cos(4\phi_i - 4\phi_{IJ}), \]
\[ \text{where the constant } A \text{ depends on the details of the potential. Considering only nearest neighbor interactions, we may write} \]
\[ V_c^{(4)}(I) = A \sum_{i \in I} r_i^4 \cos(4\phi_i). \]
\[ \text{Now we allow for a distortion of the molecule by setting} \]
\[ r_m = r[1 + (-1)^m \epsilon], \quad \phi_m = \theta + (m \pi/4) - (-1)^m \delta, \]
\[ \text{where the atoms in the octagon are numbered sequentially from 1 to 8. To leading order in } \epsilon \text{ and } \delta \text{ we have} \]
\[ V_c^{(4)}(I) = B_\epsilon \epsilon \cos(4\theta) + B_\delta \delta \sin(4\theta), \]
\[ \text{where the } B's \text{ are constant dependent on the details of the potential. Since the intramolecular interactions give rise to a energy for such distortions of the form} \]
it is clear that in the generic case, (i.e., barring an accidental vanishing of $B_\epsilon$ or $B_\delta$) the molecule will be distorted in the crystal. The distortions are illustrated for the cases $\theta = 0$ and $\theta = \pi/4$ in Fig. 7.

In contrast, one may ask whether it is possible for the structures of panels (a) and (b) of Fig. 8, which we rejected as giving rise to a smaller unit cell, to lead to acceptable structures when given inequivalent distortions, as in Fig. 8. Of course, such a structure is possible. But it involves an additional removal of degeneracy. Analytically, the situation is as follows. We have already seen the existence of terms in the energy of the form

$$E = \frac{1}{2}C_\epsilon \epsilon^2 + \frac{1}{2}C_\delta \delta^2,$$

(5.16)

where $\delta(I)$ and $\epsilon(I)$ are the distortions in molecule $I$. To get inequivalent distortions (As in the right panel of Fig. 8) we need to invoke the term with $M = \pm 4, N = \pm 4$ from Eq. (5.9), which gives rise to an energy involving $\epsilon(I)$ of the form

$$E = -D_\epsilon \sum_{<I,J>} \epsilon(I)\epsilon(J),$$

(5.17)

where $D_\epsilon$ is a constant. As the temperature is lowered to reach the orientationally ordered phase, one may ask about the role of this interaction. Clearly $D_\epsilon$ has to exceed a critical strength in order for there to be an instability towards $\epsilon(I)$ becoming nonzero at nonzero wavevector, before orientational ordering of octagons occurs. In other words, since this requires $D_\epsilon/C_\epsilon$ to exceed a critical threshold value, this is not the generic case.

The situation is only simple in the limit when the molecules are nearly infinitely rigid. In this limit, the only distortions which are allowed are those which involve linear coupling, as in Eq. (5.13). If one considers such cooperative distortions, then, at least in principle, one should allow for arbitrary rearrangements of the atoms, even rearrangements totally unrelated to the structure of the original molecule. In that case, essentially anything is possible. So the only meaningful question to ask is how do nearly perfectly rigid molecules orient within a given space group or class of space groups. The group theoretical method described here enables a treatment of perfectly rigid molecules. Then to take nonrigidity into account, one can allow distortion due to linear interactions with the crystal field as outlined above.

VI. THE TECHNIQUE: THREE DIMENSIONS

We will now discuss arrangements in 3-dimensions using the example of icosahedral $C_{60}$ molecules (symmetry group $Y_6$) in a cubic lattice. At high temperatures it is known that the molecules are on an FCC lattice. Each site on this lattice is occupied by a molecule that is randomly reorienting and hence each site has the full symmetry of the FCC lattice. At about 250K there is a first order phase transition to an SC lattice. Evidence from NMR shows that the molecules are no longer randomly reorienting. The obvious conclusion is that the molecules are now orientationally ordered.

Concerning the placement of icosahedra there are two scenarios: we either find all four sites equivalent to each other or we find sites that are inequivalent, in which case the molecules at different sites are not related to each other through some symmetry operation. The inequivalent sites can be partitioned as $(1 + 3)$, where there is one site with the full symmetry of the point group and three other sites equivalent to each other, $(2 + 2), (1 + 1 + 2)$ and $(1 + 1 + 1 + 1)$. Note that these are 

$$E = \sum_i \left( \frac{1}{2}C_\epsilon \epsilon^2(I)^2 + B_\epsilon \epsilon(I) + \frac{1}{2}C_\delta \delta^2(I) + B_\delta \delta(I) \right),$$

(5.17)

where $\delta(I)$ and $\epsilon(I)$ are the distortions in molecule $I$. To get inequivalent distortions (As in the right panel of Fig. 8) we need to invoke the term with $M = \pm 4, N = \pm 4$ from Eq. (5.9), which gives rise to an energy involving $\epsilon(I)$ of the form

$$E = -D_\epsilon \sum_{<I,J>} \epsilon(I)\epsilon(J),$$

(5.18)

where $D_\epsilon$ is a constant. As the temperature is lowered to reach the orientationally ordered phase, one may ask about the role of this interaction. Clearly $D_\epsilon$ has to exceed a critical strength in order for there to be an instability towards $\epsilon(I)$ becoming nonzero at nonzero wavevector, before orientational ordering of octagons occurs. In other words, since this requires $D_\epsilon/C_\epsilon$ to exceed a critical threshold value, this is not the generic case.

The situation is only simple in the limit when the molecules are nearly infinitely rigid. In this limit, the only distortions which are allowed are those which involve linear coupling, as in Eq. (5.13). If one considers such cooperative distortions, then, at least in principle, one should allow for arbitrary rearrangements of the atoms, even rearrangements totally unrelated to the structure of the original molecule. In that case, essentially anything is possible. So the only meaningful question to ask is how do nearly perfectly rigid molecules orient within a given space group or class of space groups. The group theoretical method described here enables a treatment of perfectly rigid molecules. Then to take nonrigidity into account, one can allow distortion due to linear interactions with the crystal field as outlined above.
A. Icosahedral symmetry

The isolated C_{60} molecule (bucky ball) forms a truncated icosahedron. The symmetry of the structure is the same as that of an icosahedron, Y_h, which is the highest possible non-axial symmetry group, with 60 elements. Fig. [10] shows a icosahedron and its relation to the symmetries of a cube. It is not a crystallographic symmetry group. The crystallographic subgroups of Y_h can be classified under three classes, as can be seen from Fig. [10].

1) T_h and its subgroups. (generators = \tau_3 and \tau'_2)
2) 3m and its subgroups. (generators = \tau_3 and a mirror passing through a vertex of the icosahedron and containing the 3-fold rotoinversion axis.)
3) mmn and its subgroups. (generators = the mirrors along the xy, yz, and z axes)

In what follows we use the tables [V], [V1] and [V2]

B. Simple Cubic O_h space groups.

We first consider 4 equivalent sites. Since O_h has 48 elements we need to find a subgroup of Y_h and O_h with 12 elements. There are two possibilities, T and 3m.

T has the generators r_3, r'_2. Also we can see that \((e + r_4 + \tau_4 + i)T = O_h \). Thus we need to have the translations associated with r_3, r'_2 be zero while the translations associated with r_4, \tau_4, i have to be non-zero so that the site has T symmetry.

We will now present arguments to prove that it is impossible to have sites with only T symmetry in the O_h simple cubic space groups. Of course, this can be easily verified by going through the algebra.

Let us assume there exist four sites in a unit cell with T symmetry. Consider a tetrahedron at the origin. The three other sites must have tetrahedra related to the one at the origin by the the operations r_4, \tau_4 and i respectively.

Symmetry elements of T, applied at the origin, must be symmetries of the whole crystal. This means they should either leave the other three molecules invariant or exchange their sites and orientations. The rotation about the 3-fold along the 111 axis leaves all the molecules invariant which means, to leave their positions invariant they must all lie on the 111 axis, but applying the 3-fold along say 111 would want the molecules to lie along this axis, which would not be compatible. So we have a proof by contradiction.

Let us now consider 3m with generators \tau_3, m'''. Arguments given above do not prevent the occurrence of sites with 3m symmetry and do occur as shown below. We see that \((e + r_4 + r'_2 + r_4')3m = O_h \). So we need to find a space group that has \(t_{r_4} \equiv (000) \equiv t_{m'''} \) and \(t_{r_4} \) nonzero. From \(m''' = r_3 m'' r'_2 \) and \(m = r_4 \tau_3 \) and the compatibility relations, we get for the four O_h simple cubic space groups listed in Table [V].

\[
t_{r_4} = \begin{pmatrix} (0,0,0) \\ (0,0,1) \\ (0,1,1) \\ (1,0,1) \\ (1,1,0) \end{pmatrix} \quad t_{m'''} = \begin{pmatrix} (0,0,0) \\ (1,0,0) \\ (1,1,1) \end{pmatrix}
\]

Since all the space groups already have \(t_{r_3} \equiv (000) \) we are restricted to c \( \equiv \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{pmatrix} \). This will not change any of the \(t_g\), since gc = c for any g \in O_h is zero. So we need to find a space group that has the required symmetry at the origin.

The only suitable space group with 3m as site symmetry is the one with \(t_{r_3} \equiv (000), t_{r_4} \equiv \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{pmatrix} \). This is space group \(Pn\overline{3}m \). In this structure a C_{60} molecule is placed at the origin with one of its \(\overline{3}\) axis along the 111 axis and rotated about this axis till the mirror of the molecule containing the 3-fold axis is along the mirror \(m'' \) of the lattice. Applying the operation \(r_4 \) to this creates a molecule pointing in the (11T) direction and since \(t_{r_4} \equiv \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{pmatrix} \), the molecule is placed at \(\begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{pmatrix} \). The other two molecules in the unit cell can be placed by noting that repeated application of the 3-folding rotation about the (111) direction should be a symmetry and hence there are two more molecules at \(0, \frac{1}{2}, \frac{1}{2} \) pointing in the (111) direction and at \(\frac{1}{2}, 0, \frac{1}{2} \) pointing in the (111) direction.

**Inequivalent sites**

The (1+3), (1+1+2) and (1+1+1+1) partitions are easily excluded since the unique site must have O_h symmetry which is not a symmetry of the molecule under consideration. If we restrict attention to the FCC sites then \((2+2)\) is also excluded since the two equivalent sites must necessarily lie on the (111) axis and be separated by \(\begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{pmatrix} \) if the cubic symmetry of the lattice is to be preserved. This reasoning will exclude the consideration of this partition from all the following point groups. Actually we need only consider the (1+3) partition in the following examples.
C. Simple Cubic $T_h$ space groups.

$T_h$ has 24 elements. For four equivalent sites the only subgroup of $Y_h$ and $T_h$ with 6 elements is 3, whose generator is $T_3$.

Since all the $T_h$ simple cubic space groups are listed with $t_{T_3} = (000)$, we are again restricted to $c = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ which leaves all the translations unaltered. Hence we are again reduced to finding a space group whose origin has the required symmetry. All space groups with $t_{T_3} = (000)$ and non-zero $t_{m'}$ can be used and hence there are two possibilities.

1) $t_{T_3} = (000), t_{c'} = (\frac{1}{2}, 0, \frac{1}{2})$ [Pn$\bar{3}$]

This structure is identical to the one found in the $O_h$ case above except for the fact that the molecule can be rotated an arbitrary angle about the local 3-fold. If this angle is such that a mirror plane of the molecule coincides with a crystal (110) direction, then the crystal has an additional mirror symmetry and the structure should be classified under the higher symmetry $O_h$ space group, which we found already.

2) $t_{T_3} = (000), t_{c'} = (0, 0, 0)$ [Pa$3$]

By arguments similar to those used above we find that four molecules are at

i) (000) with a three-fold axis in the (111) direction.

ii) $(\frac{1}{2}, \frac{1}{2}, 0)$ with a three-fold axis in the (311) direction.

iii) $(0, \frac{1}{2}, \frac{1}{2})$ with a three-fold axis in the (311) direction.

iv) $(\frac{1}{2}, 0, \frac{1}{2})$ with a three-fold axis in the (311) direction.

Applying the 2-fold rotation about the 110 axis gives us the other possible realization of this space group with $t_{T_3} = (000), t_{c'} = (0, \frac{1}{2}, \frac{1}{2})$.

Inequivalent Sites: We have already discussed why we need consider only the (1 + 3) partition. The unique site must have $T_h$ symmetry, which automatically restricts us to considering only the space group with $t_{c'} = (000)$ since all the other space groups with $T_h$ point group cannot have a site with full $T_h$ symmetry. The 3 equivalent sites must have $mmm$ (8 elements) symmetry with the translation associated with the 3-fold rotation nonzero at these sites. Let the three mirrors along the $xyz$, $yz$ and $zx$ planes be labeled $m'_2, m'_c, m'$. The translations associated with all three of them are zero at the origin. Under an origin translation we have $\Delta t_{m'} = (0, -2c_2, 0)$, $\Delta t_{m'_c} = (0, 0, -2c_3), \Delta t_{m'_3} = (-2c_1, 0, 0)$ and $\Delta t_{c} = (c_3 - c_1, c_1 - c_2, c_2 - c_3)$. There are two choices, the first of which is $c = (\frac{1}{2}, 0, 0)$ and its cyclic permutations, all of which lead to icosahedra being placed at the edge centers with mirrors along the mirrors of the lattice. Since the molecules do not form an FCC lattice, we reject this choice. The second choice is $c = (\frac{1}{2}, 0, 0)$ and its cyclic permutations, which lead to icosahedra placed at the face centers. This choice, which yields a structure of space group Pm$\bar{3}$, does satisfy our requirements.

D. Other Simple Cubic Space Groups.

The other cubic point groups, $O$, $T$, and $T_d$, lack inversion symmetry. Since we have required the molecules to be placed on an FCC lattice, allowed structures must have inversion symmetry. (In a moment, we will discuss the extent to which this restriction can be relaxed.) So, unless we allow a molecular distortion which removes inversion symmetry, there are no allowable structures of these cubic point groups.

Now we address the question as to whether inversion symmetry should actually be required. We argue that removal of inversion symmetry requires a breaking of symmetry analogous to that we discussed in conjunction with Eq. (5.18). If we place molecules on an FCC lattice, there is no generic loss of inversion symmetry. For nearly infinitely rigid molecules, a loss of inversion symmetry is not expected. When one considers the related problem of alkali metal doped C$_{60}$, the situation is different. There one has a reason why generically inversion symmetry could be broken, and consideration of space groups without inversion symmetry is reasonable.

We now discuss briefly, without derivation, structures which can occur if we relax the condition that the molecule has inversion symmetry. First we consider the case when all four sites are equivalent. Each of the structures found requiring inversion symmetry has a counterpart without inversion symmetry, as one would expect, since one can easily envision a small perturbation which breaks inversion symmetry. Thus the Pn$\bar{3}m$ structure of the $O_h$ point group becomes the P4$_3$32 structure of $O$ point group symmetry. In this case, a loss of inversion symmetry does not cause any displacement of the molecules from their FCC lattice sites. In the case of the Pn$\bar{3}$ and Pa$\bar{3}$ structures, loss of inversion symmetry implies a displacement of the molecules away from their positions when there is inversion symmetry. (Of course, this is the generic case. One can imagine the accidental case when this displacement is zero.) In both cases, this displacement is such that the center of mass of the molecule is translated along the three-fold axis. Thus the analog of Pn$\bar{3}$ is P23 and that of Pa$\bar{3}$ is P213. Presumably, if this displacement is small enough, it could be consistent with the experimental determination that the centers of mass of the molecules form an FCC lattice. In any
event, the loss of inversion symmetry is NOT generic and requires either noninfinitesimal distortion of the molecule or an external perturbation, like doping.

When we consider inequivalent sites, we find that the only possibility occurs within $T$ point group symmetry. Starting from $Pm\bar{3}$, one can remove inversion symmetry. In this case, the molecules are not displaced from their position in the presence of inversion symmetry. But, as in the case of equivalent sites, this removal of inversion symmetry does require either a noninfinitesimal distortion of the molecule, or a perturbation to break inversion symmetry, and thus is NOT generic.

VII. CONCLUSIONS

We have demonstrated a constructive algorithm for finding orientations of molecules whose centers of mass are at or infinitesimally near specified locations. In this algorithm one obtains candidate structures from which one eliminates structures which are unacceptable because they do not have molecules at the specified locations. Also, in classifying structures one has to take care to identify additional symmetries that may be introduced in the construction, especially when structural parameters whose values are not fixed by symmetry, are assigned special values. In addition, we have given an extensive discussion of the role of symmetry breaking in which the molecule spontaneously distorts or its center of mass spontaneously is displaced from the assigned position. Unless there is some external perturbation (like doping) such spontaneous symmetry breaking is not the generic case which applies when the ratio of force constants associated with intramolecular bonds to those associated with intermolecular interactions is arbitrarily large. If such spontaneous symmetry breaking is allowed, the problem becomes poorly formulated in that molecular and atomic positions arbitrarily far from those desired become permissible.

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APPENDIX A: DERIVATION OF THE COMPATIBILITY RELATION.

Let $g$, $h$, $k = gh$ etc. be the elements of the point group of a periodic structure. Let the symmetries of the structure be $(g, t_g)$, $(h, t_h)$, $(k, t_k)$ etc. The compound operation, $(h, t_h)$ followed by $(g, t_g)$, is a symmetry of the structure. Thus,

$$ (g(h, t_h), t_g) = gh + g t_h + t_g $$

But $(k, t_k)$ is a symmetry of the structure, so comparing this with Eq. A1 gives,

$$ t_k = t_{gh} = g t_h + t_g. $$

APPENDIX B: DERIVATION OF THE ORIGIN SHIFT RELATION.

Let $(g, t_g)$ be a symmetry of a periodic structure. If we apply this symmetry operation to the structure then the coordinates $x$ of a point $A$ in the structure transforms to $x'$ given by

$$ x' = g x + t_g. $$

In a new coordinate system, which is obtained by translating the original system by $c$, the coordinates of $A$ are given by $x_n$, where

$$ x_n = x - c. $$

Using this relation in Eq. B1 we get,

$$ x'_n + c = g(x_n + c) + t_g $$
which gives us
\[ x'_n = gx_n + t_g + gc - c. \]  
(B4)

This means in the new frame,
\[ (t_g)_{\text{new frame}} = (t_g)_{\text{old frame}} + \Delta t_g, \]  
(B5)

where
\[ \Delta t_g = gc - c. \]  
(B6)

APPENDIX C: AXIAL POINT GROUPS

Axial point groups are those with a unique axis of high symmetry. Obviously the symmetry groups of the five regular Platonic solids (cube, tetrahedron etc.) don’t qualify as axial point groups. In this paper an \textit{n-fold rotation} is \( r_n \), that is, a rotation by \( \frac{2\pi}{n} \) radians. The \textit{n-fold rotoinversion} is \( \tau_n \), which is defined by,
\[ \tau_n = r_n i, \]  
(C1)

where \( i \) is the \textit{inversion}. A \textit{dihedral axis}, \( d \), is a 2-fold rotation axis perpendicular to the high symmetry axis. \( m \) is a \textit{mirror containing} the high symmetry axis. \( h \) is a \textit{mirror perpendicular} to the high symmetry axis. The following are a few properties of these point groups.

i) Since
\[ r_2h = i, \]  
(C2)

if any two of the three elements exist the third also exists.

ii) If two mirrors \( m_1 \) and \( m_2 \) exist at an angle \( \frac{2\pi}{n} \) with respect to each other, then the line of intersection of the mirrors is an \( r_n \) axis. There will be \( n \) mirrors in such a point group, which are in two distinct conjugate classes if \( n \) is even and in the same class if \( n \) is odd. Two elements \( g_1, g_2 \) of a point group belong to the same conjugate class if
\[ hg_1h^{-1} = g_2, \]  
where \( h \) is also an element of the point group. A special case is when the two mirrors are perpendicular to each other in which case the line of intersection is \( r_2 \). Obviously, if a mirror contains an \( r_n \) axis, then there are \( n \) mirrors which all intersect at \( r_n \) and are at an angle \( \frac{\pi}{n} \) to each other. The new mirrors can be generated using
\[ r_n m = m'. \]  
(C3)

Similar statements can be made for dihedrals, in which case the line perpendicular to the axes at the intersection point of the two dihedrals forms the \( r_n \) axis.

iii) \( \tau_n \) exists, in which case we can have three cases,
\[ a) \text{ If } n = 2p + 1, \text{ then } \tau_n^0 = i, \tau_n^{p+1} = r_n \text{ and } \tau_n^{2m} = e. \]
\[ b) \text{ If } n = 2p, \text{ } p \text{ is odd, then } \tau_n^0 = h, \tau_n^{p} = r_p \text{ and } \tau_n^{m} = e. \]
\[ c) \text{ If } n = 2p, \text{ } p \text{ is even, then } \tau_n^0 = r_2, \tau_n^{p} = r_p \text{ and } \tau_n^{m} = e. \]

iv) \( \tau_n \) and \( m \) exist. In this case,
\[ \tau_n m = ir_n m = im' = d', \]  
(C4)

which means that there always exists a dihedral axis perpendicular to each mirror. Thus this case is the same as \( \tau_n \) occurring with \( d \). Again three cases to be considered separately following the discussion of the previous case,
\[ a) \text{ If } n = 2p + 1, \text{ then, since } r_n \text{ and } i \text{ exist we have } n \text{ mirrors at } \frac{\pi}{n} \text{ from each other and } n \text{ dihedrals bisecting the angle between the mirrors.} \]
\[ b) \text{ If } n = 2p, \text{ } p \text{ is odd, then } r_p \text{ and } h \text{ exist and thus there are } p \text{ mirrors are } \frac{\pi}{p} \text{ with respect to each other and } p \text{ dihedrals parallel to } m. \]
\[ c) \text{ If } n = 2p, \text{ } p \text{ is even, then only } r_p \text{ exists, no } h \text{ or } i \text{ and thus there are } p \text{ mirrors at } \frac{\pi}{p} \text{ with respect to each other and } p \text{ dihedrals bisecting the angle between the mirrors.} \]

**Notations**: Two conventions of naming point groups are prevalent, Schoenflies and International. Tables [IV] and [V] list all the kinds of point groups in both notations.
In the Schoenflies convention, capital letters are used to designate the class of the point group and subscripts of small letters and numbers are used to specify the point group completely. For example in $D_{4d}$, $D$ says that the point group is a dihedral group, that is it has dihedral axes, the 4 says it has a 4-fold axis and $d$ says that it has diagonal mirrors, that is the mirrors bisect the angle between the dihedrals. Another example is $C_{4h}$, where the point group has a 4-fold axis and a horizontal mirror, that is the mirror is perpendicular to the $r_4$ axis.

In the International convention, small letters and numbers specify the point group. For example $2mm$ means the point group has a 2-fold axis and the two $m$’s specify that there are two classes of mirrors. $4/mmm$ means that there is a 4-fold axis and three classes of mirrors with one of them perpendicular to the 4-fold axis.

APPENDIX D: NON-AXIAL POINT GROUPS

There are only five non-axial crystallographic point groups $O_h$, $T_h$, $O$, $T_d$ and $T$. They are related to each other as follows, $T \subset T_d \subset O_h$, $T \subset T_h \subset O_h$ and $T \subset O \subset O_h$. ($e + r_4)T = T_d$, ($e + r_4)T_d = O_h$, ($e + i)O = O_h$, ($e + i)T = T_h$ and ($e + r_4)T_h = O_h$. The main axial subgroups of each of these groups are listed below, with their generators given in brackets.

- $T$ - $3(r_3)$, $222(r_2' and its partners along the $x$ and $z$ axis).
- $T_d$ - $2mm(m, m'')$, $\overline{3}m(m, r_2')$, $\overline{3}(r_4)$.
- $O$ - $422(r_2, r_2')$, $222(r_2, r_2'')$, $32(r_3, r_2'')$.
- $T_h$ - $\overline{3}(r_3)$, $mmm$ (mirrors along the coordinate planes).
- $O_h$ - $3m(r_3, m'')$, $4/mmm(i, m, m')$.

| Operation | $e$ | $m$ | $m' = r_4m$ | $r_2$ | $r_4$ | $r_2'$ | $r_2''$ | $m''$ | $r_2' = r_3r_2'$ | $r_2'' = r_2'r_2''$ | $m'' = r_3m''$ |
|-----------|-----|-----|--------------|------|------|--------|--------|-------|----------------|------------------|----------------|
| Image     | $xy$ | $xy$ | $yx$         | $yx$ | $yx$ | $yx$   | $yx$   | $yx$   | $yx$          | $yx$             | $yx$           |

TABLE II. The space groups with square lattice and point group $4mm$. The origin is assumed to be at a lattice point (point A in Fig. 1).

| Point group | generators | ITC number | translations |
|-------------|------------|------------|--------------|
| $4mm$       | $r_4, m$   | $11(p4mm)$ | $t_{r_4} \equiv (0,0), t_m \equiv (0,0)$ |
|             |            | $12(p4gm)$ | $t_{r_4} \equiv (0,0), t_m \equiv (\frac{1}{2}, \frac{1}{2})$ |

TABLE III. Images of $(x, y, z)$ due to various symmetry operations of the cube.

| Operation | $e$ | $i$ | $m = r_4r_3$ | $r_2 = im$ | $r_2' = r_2^2$ | $r_4$ | $r_3$ | $r_3' = r_3r_2'$ | $r_2'' = r_3r_2''$ | $m'' = r_3m''$ |
|-----------|-----|-----|--------------|------------|---------------|------|------|----------------|------------------|----------------|
| Image     | $xy$ | $xy$ | $yx$         | $yx$       | $yx$          | $yx$ | $yx$ | $yx$          | $yx$             | $yx$           |

TABLE IV. The Non-Axial Point Groups.
### TABLE V. The Axial Point Groups.\(^a\)

| Generators | Schoenflies International | \# of elements | Generating relations | Crystallographic Realizations |
|------------|----------------------------|-----------------|----------------------|-----------------------------|
| 1 \(r_n\) | \(C_n(n)\) | \(n\) | \(r_n^n = e\) | \(n = 1, 2, 3, 4, 6\) |
| 2 \(\tau_n\) | \(S_{2n}(\tau); n = 2p + 1\) | \(2n\) | \(\tau_n^2 = i, \tau_n^{2n} = e\) | \(n = 1, 3\) |
| | \(C_{ph}(\tau); n = 2p; p odd\) | \(n\) | \(\tau_n^p = r_p, \tau_n^{2p} = h\) | \(n = 2, 6\) |
| | \(S_h(\tau); n = 2p; p even\) | \(n\) | \(\tau_n^p = e, \tau_n^{2p} = r_2\) | \(S_4(4)\) |
| 3 \(r_n, d\) | \(D_n(n2); n = 2p + 1\) | \(2n\) | \(r_n^2 = e, d^2\) | \(D_3(32)\) |
| | \(D_n(n22); n = 2p\) | \(2n\) | \(r_n^2 = r_2; d^2 = e\) | \(n = 2, 4, 6\) |
| 4 \(r_n, m\) | \(C_{nv}(nm); n = 2p + 1\) | \(2n\) | \(r_n^2 = e, m^2\) | \(C_{3v}(3m)\) |
| | \(C_{nv}(nmn); n = 2p\) | \(r_n^2 = r_2; m^2 = e\) | \(n = 2, 4, 6\) |
| 5 \(r_n, h\) | \(C_{sh}(2n); n = 2p + 1\) | \(2n\) | \(r_n^2 = e, h^2\) | \(n = 1, 3\) |
| | \(C_{sh}(m/n); n = 2p\) | \(2n\) | \(r_n^2 = r_2; m^2 = e = h^2\) | \(n = 2, 4, 6\) |
| 6 \(r_n, m, h\) | \(D_{nh}(2n2m); n = 2p + 1\) | \(4n\) | \(r_n^2 = e, h^2 = m^2\) | \(D_{3h}(62m)\) |
| | \(D_{nh}(nmmm); n = 2p\) | \(4n\) | \(r_n^2 = r_2; m^2 = e = h^2\) | \(n = 2, 4, 6\) |
| 7 \(\tau_n, m\) | \(D_{nd}(\bar{m}m); n = 2p + 1\) | \(4n\) | \(\tau_n^2 = i, \tau_n^{2n} = e = m^2\) | \(D_{3d}(3m)\) |
| | \(D_{ph}(\bar{m}2m); n = 2p; p odd\) | \(2n\) | \(\tau_n^p = r_p, \tau_n^{2p} = h\) | \(D_{3h}(62m)\) |
| | \(D_{pd}(\bar{m}2m); n = 2p; p even\) | \(2n\) | \(\tau_n^p = e, \tau_n^{2p} = r_2\) | \(D_{3d}(42m)\) |

\(a\) Note that \(C_{1h}(\bar{2}), C_{3h}(\bar{5})\), and \(D_{3h}(\bar{2}2m)\) each appear twice in this listing, also technically, \(r_n\) with \(n = 2\) should be classified separately.

### TABLE VI. The Simple Cubic Space Groups.
TABLE VII. The Face-Centered Cubic Space Groups listed using the same bases as in the simple cubic space groups. Thus, for every site in this list add three more at $(0,\ 1/2,\ 1/2)$ and its cyclic permutations. Note that translations by these vectors are now identities. This allows the use of Table II without any changes. The natural bases for this lattice are $a_1 = \frac{1}{2}(0,\ 1,\ 1)$ and its cyclic permutations.

| Point group | generators | ITC number | translations |
|-------------|------------|------------|--------------|
| $O_h$       | $\overline{3}$, $r_4$ | $221(Pm\overline{3}m)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_4} = (0,0,0)$ |
|             |            | $222(Pm3n)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_4} = (0,0,\frac{1}{2})$ |
|             |            | $224(Pm\overline{3}m)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_4} = (\frac{1}{2},\frac{1}{2},0)$ |
|             |            | $223(Pm3n)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_4} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ |
| $T_h$       | $\overline{3}, r_2'$ | $200(Pm\overline{3}m)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_2'} = (0,0,0)$ |
|             |            | $201(Pm3)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_2'} = (\frac{1}{2},0,\frac{1}{2})$ |
|             |            | $205(Pa\overline{3})$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_2'} = (\frac{1}{2},\frac{1}{2},0)$ |

TABLE VIII. The Body-Centered Cubic Space Groups listed using the same bases as in the simple cubic space groups. Thus, for every site in this list add one more at $(\frac{1}{2},\ 1/2,\ 1/2)$. Note that translations by this vector is now an identity. This allows the use of Table II without any changes. The natural bases for this lattice are $a_1 = \frac{1}{2}(1,\ 1,\ 1)$ and its cyclic permutations.

| Point group | generators | ITC number | translations |
|-------------|------------|------------|--------------|
| $O_h$       | $\overline{3}$, $r_4$ | $225(F4/m\overline{3}m)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_4} = (0,0,0)$ |
|             |            | $226(F4/m\overline{3}2m)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_4} = (0,0,\frac{1}{2})$ |
|             |            | $227(F41/d\overline{3}2m)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_4} = (\frac{1}{2},\frac{1}{2},0)$ |
|             |            | $228(F41/d\overline{3}2c)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_4} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ |
| $T_h$       | $\overline{3}, r_2'$ | $202(F2/m\overline{3})$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_2'} = (0,0,0)$ |
|             |            | $203(F2/d\overline{3})$ | $t_{\overline{3}} = (\frac{1}{2},\frac{1}{2},0)$, $t_{r_2'} = (\frac{1}{2},0,\frac{1}{2})$ |
|             |            | $210(F41/d\overline{3}2c)$ | $t_{\overline{3}} = (0,0,0)$, $t_{r_2'} = (0,0,0)$ |
| $O$         | $r_3, r_4$ | $209(F432)$ | $t_{r_3} = (0,0,0)$, $t_{r_4} = (0,0,0)$ |
|             |            | $210(F41/32)$ | $t_{r_3} = (0,0,0)$, $t_{r_4} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ |
| $T_d$       | $r_3, \overline{3}$ | $216(F43\overline{3}m)$ | $t_{r_3} = (0,0,0)$, $t_{\overline{3}} = (0,0,0)$ |
|             |            | $219(F4\overline{3}c)$ | $t_{r_3} = (0,0,0)$, $t_{\overline{3}} = (0,0,0)$ |
| $T$         | $r_3, r_2'$ | $196(F23)$ | $t_{r_3} = (0,0,0)$, $t_{r_2'} = (0,0,0)$ |
| Point group | generators | ITC number | translations |
|------------|------------|------------|--------------|
| $O_h$      | $\mathbf{3}, r_4$ | 229($I4/m32/m$) | $t_{\mathbf{3}} \equiv (0,0,0), t_{r_4} \equiv (0,0,0)$ |
|            |            | 230($I4_1/a32/d$) | $t_{\mathbf{3}} \equiv (0,0,0), t_{r_4} \equiv (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ |
| $T_h$      | $\mathbf{3}, r'_2$ | 204($I2/m3$) | $t_{\mathbf{3}} \equiv (0,0,0), t_{r'_2} \equiv (0,0,0)$ |
|            |            | 206($I2_1/a3$) | $t_{\mathbf{3}} \equiv (0,0,0), t_{r'_2} \equiv (\frac{1}{2}, 0, 0)$ |
| $O$        | $r_3, r_4$ | 211($I432$) | $t_{r_3} \equiv (0,0,0), t_{r_4} \equiv (0,0,0)$ |
|            |            | 214($I4_132$) | $t_{r_3} \equiv (0,0,0), t_{r_4} \equiv (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ |
| $T_d$      | $r_3, \overline{r}_4$ | 217($I43m$) | $t_{r_3} \equiv (0,0,0), t_{\overline{r}_4} \equiv (0,0,0)$ |
|            |            | 220($I43d$) | $t_{r_3} \equiv (0,0,0), t_{\overline{r}_4} \equiv (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ |
| $T$        | $r_3, r'_2$ | 197($I23$) | $t_{r_3} \equiv (0,0,0), t_{r'_2} \equiv (0,0,0)$ |
|            |            | 199($I2_13$) | $t_{r_3} \equiv (0,0,0), t_{r'_2} \equiv (0,0,0)$ |

TABLE IX. The Space Groups for 4 $C_{60}$ Molecules at equivalent FCC Sites.

| Space group | Site | FCC | Inversion |
|-------------|------|-----|-----------|
| $O_h$       | $t_{r_3} \equiv (\frac{1}{2}, \frac{1}{2}, 0), Pn3m$ | 3m | Y | Y |
| $T_h$       | $t_{r'_2} \equiv (0,0,0), Pn3$ | 3 | Y | Y |
| $O$         | $t_{r_4} \equiv (\frac{1}{2}, \frac{1}{2}, 0), Pa3$ | 3 | Y | Y |
| $T_d$       | $t_{r_3} \equiv (0,0,0), t_{\overline{r}_4} \equiv (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ | 32 | Y | N |
| $T$         | $t_{r'_2} \equiv (0,0,0), P23$ | 3 | $N^a$ | N |

TABLE X. Space Groups for 4 $C_{60}$ Molecules at Inequivalent FCC Sites.

| Space group | Site | FCC | Inversion |
|-------------|------|-----|-----------|
| $O_h$       | $t_{r_3} \equiv (\frac{1}{2}, \frac{1}{2}, 0), Pn3m$ | 3m | Y | Y |
| $T_h$       | $t_{r'_2} \equiv (0,0,0), Pn3$ | 3 | Y | Y |
| $O$         | $t_{r_4} \equiv (\frac{1}{2}, \frac{1}{2}, 0), Pa3$ | 3 | Y | Y |
| $T_d$       | $t_{r_3} \equiv (0,0,0), t_{\overline{r}_4} \equiv (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ | 32 | Y | N |
| $T$         | $t_{r'_2} \equiv (0,0,0), P23$ | 3 | $N^a$ | N |

$N^a$ means that, as discussed in the text, in the generic case the structure is not FCC, but involves a nonzero displacement of the molecules such that the lattice is still SC, but the molecule do not quite sit on FCC lattice sites.
|     | Space group          | Site | FCC | Inversion |
|-----|----------------------|------|-----|-----------|
| 1   | $T_h(t_{15}^r \equiv (0,0,0), Pm3\bar{3})$ | $T_h + 3(mmm)$ | Y   | Y         |
| 2   | $T(t_{15}^r \equiv (0,0,0), P23)$ | $T + 3(222)$ | Y   | N         |

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FIG. 1. The structure in (a) has rectangular lattice, point group $2mm$. For the origin chosen $t_R \equiv (0, 0)$, $t_M \equiv t_{M'} \equiv (\frac{1}{2}, 0)$. (b) shows the same structure with a different choice of origin. For the origin here, $t_R \equiv (\frac{1}{2}, 0) \equiv t_M$, $t_{M'} \equiv (0, 0)$.

FIG. 2. The symmetries of a square.
FIG. 3. (a) shows a decoration of the square lattice. The structure has point group $4mm$ and $t_{R_4} \equiv t_M \equiv (0,0)$. (b) shows a decoration of the square lattice with a symmetry distinct from (a). The structure has point group $4mm$ and $t_{R_4} \equiv (0,0)$, $t_M \equiv (\frac{1}{2}, \frac{1}{2})$.

FIG. 4. A decoration that leads to only the 4-fold rotation symmetry being preserved.

FIG. 5. (a) shows hexagons in space group $p4mm$ on a square lattice with point group $4mm$ and translations $t_{R_4} \equiv (0,0)$, $t_M \equiv (0,0)$ defined with respect to origin $A$. The choice of origin here (O) makes $t_{R_4} \equiv (\frac{1}{2}, \frac{1}{2}) \equiv t_M'$, $t_M \equiv t_{R_2} \equiv (0,0)$. (b) shows hexagons in space group $p4gm$ for the same lattice and point group but the translations are $t_{R_4} \equiv (0,0)$. One of the hexagons has sides parallel to the $(1,0)$ axis and the other has sides parallel to the $(0,1)$ axis. $t_M \equiv (\frac{1}{2}, \frac{1}{2})$ defined with respect to the origin $A$. The choice of origin here (O) makes $t_{R_4} \equiv (\frac{1}{2}, \frac{1}{2}) \equiv t_M$, $t_M' \equiv t_{R_2} \equiv (0,0)$.

One of the hexagons has sides parallel to the $(1,1)$ direction and the other has sides parallel to the $(1, -1)$ direction.
FIG. 6. Placement of perfectly rigid octahedrons on a square lattice. In panels a), b), and c) we show structures corresponding to taking $A > 0$ and $B < 0$, $A < 0$, $B < 0$, and $A = 0$, $B > 0$, respectively (See Eq. 5.11). Because of the high symmetry of the octagon, the structures in panels a) and b) yield a square lattice whose lattice constant is smaller than the original lattice by $\sqrt{2}$. If our aim is to obtain a diffraction pattern in which indexing is according to the square lattice shown, these structures are not acceptable. Structure c), which is similar to an antiferromagnet, is acceptable. The effect of molecular distortions is shown in Fig. 7 and 8.

FIG. 7. Placement of nonrigid octahedrons on a square lattice. The left-hand structure corresponds to $A > 0$ and $B < 0$ in Eq. (5.11) and the right-hand one to $A < 0$ and $B < 0$. These are the structures one must obtain in the limit when the molecules are almost perfectly rigid. (In this limit one can imagine the molecule held together by springs whose force constants are arbitrarily large.) Whether, compared to the free molecule, the nearest-neighbor faces (vertex angles) become smaller, as shown, or larger depends on the nature of the intermolecular interactions. The left panel corresponds to Eq. (5.14) with $\epsilon = 0$ and $\delta \sin(4\theta) > 0$ and the right panel to $\delta = 0$ and $\epsilon \cos(4\theta) > 0$. In both cases all molecules remain equivalent and the unit cell is smaller by $\sqrt{2}$ than that shown.
FIG. 8. Placement of nonrigid octahedrons on a square lattice. The left-hand structure corresponds to $A > 0$ and $B < 0$ in Eq. (5.11) and the right-hand one to $A < 0$ and $B < 0$. In this case the molecules are inequivalent by reason of having different distortions. However, to reach this state the spring constants of the molecule cannot be arbitrarily large, but have to be smaller than some critical value dependent on the intermolecular interactions.

FIG. 9. The symmetries of a cube.

FIG. 10. An Icosahedron bounded by a cube. The edges $AB CD$ etc. are on the face of the cube and the ratio of the length of the edges of the icosahedron and the edge of the cube is the golden mean. Each vertex of the icosahedron is a 5-fold axis of symmetry.