From Solid State Chemistry to Heterogeneous Catalysis

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PREFACE

The development of heterogeneous catalysis as a scientific discipline with a well-established theoretical basis has been mostly possible thanks to the contribution of solid state chemistry and modern surface science. From a fundamental point of view, solid state chemistry is the starting point for designing a solid with optimal composition, structure and surface properties for practical applications including heterogeneous catalytic processes.

While some excellent books gathering general aspects of heterogeneous catalysis based on first principles are already available, this textbook provides fundamental insights into solid state chemistry in order to expand the horizons of heterogeneous catalysis as a central discipline laying at the frontier of chemistry, physics, engineering and materials science. Hence, we have covered an ample range of solid state concepts such as symmetry and diffraction techniques for structure elucidation and solids bonding as well as defects' formation and their implications in heterogeneous catalysis. Moreover, the last chapter emphasizes the importance of heterogeneous catalysis as a surface phenomenon and how solid surfaces are reconstructed during the chemical reaction.

This textbook is based on our own experience of many years delivering university lectures of key modules in inorganic chemistry, solid state chemistry, materials science and industrial and environmental catalysis for chemistry and engineering students. The genesis of this book is the lack of a comprehensive and contemporary academic textbook which unifies all the key aspects of solid state chemistry and their direct implications in surface chemistry and heterogeneous catalysis, including the most recent developments. At the end of the book, we have included a useful list of questions for every chapter as a handy tool to test the learning outcomes.

We gratefully appreciate the constructive suggestions provided by our colleagues in the research group “Surface Chemistry and Catalysis” at the Institute of Materials Science (CSIC-US) and the Inorganic Chemistry Department at University of Sevilla.

Sevilla, May 2021

The authors,
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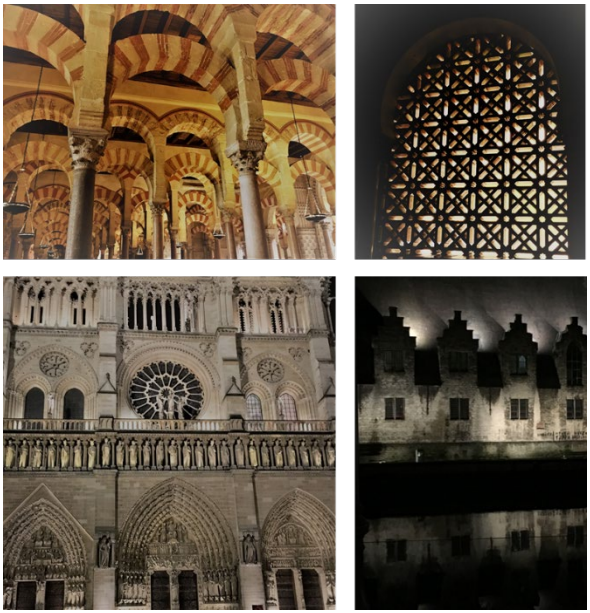
CHAPTER 1

SYMMETRY AND BASIC CONCEPTS

"The chief forms of beauty are order and symmetry and definiteness…"
Aristotle



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The word *symmetry* derives from the Greek *sun* ('with') and *metron* ('measure'), and usually relates to proportionality and beauty in their philosophical aspect. Beauty and symmetry are strictly related; humans and some other species find symmetrical patterns much more attractive than asymmetric patterns and their preference arises from the primary needs of

visualization and orientation, independently of biological signals. A sensory bias for symmetry exists and reflects the natural patterns of order and beauty which are repeated continuously in manufactured decorative and artistic patterns.

Before introducing the concepts of symmetry in solid state chemistry, it is worth briefly recalling and redefining crystal systems and Bravais lattices, together with some symmetry elements and related operations.

Crystal systems and Bravais lattices

In 1850, August Bravais defined his concept of crystalline lattices, *i.e.* group of parallelepipeds that fill up space, in pioneering work on the basis of geometrical and mathematical principles. This work, confirmed 60 years later using X-ray diffraction, provides the basis for classification of crystal systems and lattice unit cells. It is useful, in order to discuss the origin of the crystal systems and Bravais lattices, to first imagine an empty space structured by a set of vectors connecting an infinite array of discrete equivalent points (*Figure 1*).

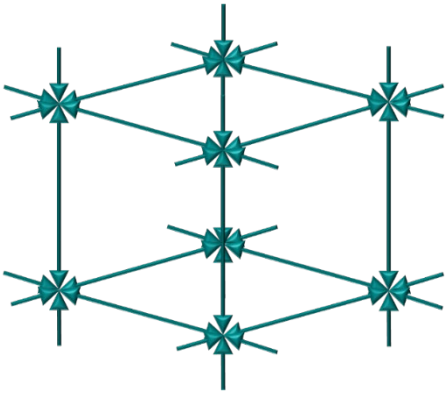


Figure 1. Definition of Bravais point array by position vectors.

The use of translation vectors fills up the space and an infinite number of equivalent points form a network. The application of the symmetry elements (translation included) over such a set of points produces crystal systems and Bravais lattices. Therefore, the set of points is defined by a position vector $\vec{R}$

$$\vec{R} = u\vec{a} + v\vec{b} + w\vec{c}$$

where $\vec{a}, \vec{b}$ and $\vec{c}$ are mutually non coplanar vectors and *u, v* and *w* any positive, negative (zero included) integer values.

Although the lattice is sufficiently defined by the three position vectors, in practice six parameters called ***lattice parameters*** are used, the magnitude of the vectors ***a***, ***b*** and ***c*** (lattice lengths) and the angles between them $\boldsymbol{\alpha}$ (between ***b*** and ***c***), $\boldsymbol{\beta}$ (between ***a*** and ***c***) and $\boldsymbol{\gamma}$ (between ***a*** and ***b***).

Logically the most symmetrical situation occurs when all vectors present the same length and are mutually perpendicular. The cubic system is then generated with volume $\vec{a} \cdot (\vec{b} \times \vec{c})$. If this volume encloses only one lattice point the generated Bravais lattice is designated as **primitive**, **P** (*Figure 6*). Every vertex of the cubic **P** lattice is occupied by an equivalent point (represented by a sphere) and exactly 1/8 of this sphere lies within the limits of the cell resulting in one single point per lattice (8 vertex * 1/8 of a point = 1). For commodity, the point is placed at the origin and generates all other points by translation, the sum of the position and translation vectors.

A new Bravais lattice is created after adding a second point in the center of the cube: known as a cubic **I** lattice (**I** stands for *inner*). All points have eight-fold coordination and the resulting lattice is called **conventional**, as two points are necessary to describe the lattice. The coordinates of the points are (0,0,0) and (½, ½, ½). The added point belongs entirely to the cell (8 vertex * 1/8 + 1 = 2 points). This conventional cell usually contains a primitive cell but the conventional lattice parameters and the primitive cell parameters differ (*Figure 2*)

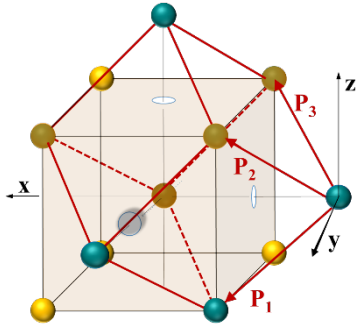


Figure 2. Conventional cubic **I** lattice and corresponding primitive (colors changed for clarity). P_1, P_2 and P_3 the new primitive vectors

We can add three more points to the (0, 0, 0) point to create new conventional **F** cubic lattice (**F** for *face-centered*), where every point has 12 neighbors and all additional points occupy the center of the cube faces. The new point coordinates are (½, 0, 0), (0, ½, 0) and (0, 0, ½,). Each added point counts as a half point for each cell as it is shared by two adjacent cells. A total of four points results from the 8 vertex * 1/8 points and 6 face centered * 1/2. Again, the resulting cell is conventional containing a new primitive cell (*Figure 3*).

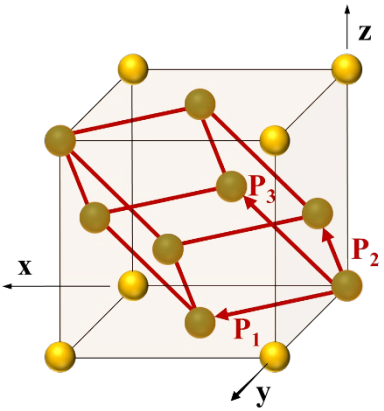


Figure 3. Conventional cubic **F** lattice and corresponding primitive. P_1, P_2 and P_3 the new primitive vectors

Problem I *Can we generate a new Bravais lattice adding points at the centers of the cube and on all faces?*

*No, the coordination of the **I**-centered atom is different from the **F**-centered one. By definition, the Bravais lattice only consists of equivalent points, which is not the case here. The resulting lattice is therefore not a Bravais lattice.*

After considering all possible combinations for the cubic Bravais lattices, the next logical step is to decrease the symmetry. If we maintain the mutually perpendicular vectors, but we change the length of one of them - *c*, for example, we can generate the tetragonal structure with a=b≠c and α=β=γ=90º. The symmetry change can be presented as stretching or compressing the cube along the *c* axis. The cubic **P** generates the tetragonal **P** lattice and the tetragonal **I** lattice arises from the cubic **I**. What happens when we stretch the cubic F lattice? It appears to be identical to a tetragonal **I** (*Figure 4*).

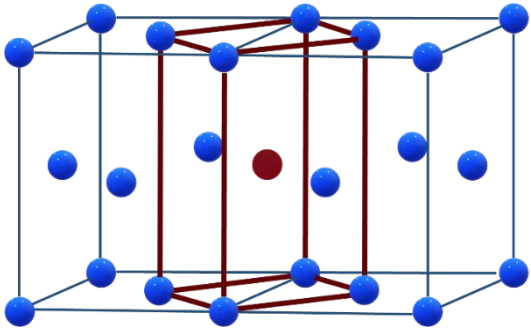


Figure 4. Tetragonal **I** creation after stretching the cubic **F** lattice

If we continue to lower the symmetry maintaining the orthogonality of the vectors and changing their lengths ($a \neq b \neq c$ and $\alpha=\beta=\gamma=90^{o}$), the result is an orthorhombic lattice. The distortion of tetragonal **P** along *a* or *b* results in an orthorhombic **P** lattice. However, if we stretch the tetragonal **P** lattice along the face diagonal, a new orthorhombic lattice centered on two opposite sides results, the orthorhombic **C** lattice where the *a*-*b* plane is centered. Correspondingly, the *b*-*c* plane is centered on the **A** centered lattice and **B** orthorhombic results from the *a*-*c* plane. If the originally distorted lattice is the tetragonal **I**, the orthorhombics **I** and **F** are obtained after axial and face diagonal distortions, respectively.

All remaining Bravais lattices are generated after angle distortions. The angle alteration of the orthorhombic **P** creates the monoclinic **P** lattice; the distorted angle being defined by convention as the one on the *a*-*c* plane always designated as β. The two opposite side centered orthorhombic lattices also generate the **P** monoclinic lattice, whereas the orthorhombic **I** and **F** transform to a monoclinic **C** lattice (*Figure 5*).

Since axes *a*, *b* and *c* are arbitrarily labeled, it is accepted that the resulting lattice is always **C**-centered and the same applies to the orthorhombic lattices.

The last-mentioned symmetry decrease generates the triclinic **P** lattice, the one with the lowest symmetry.

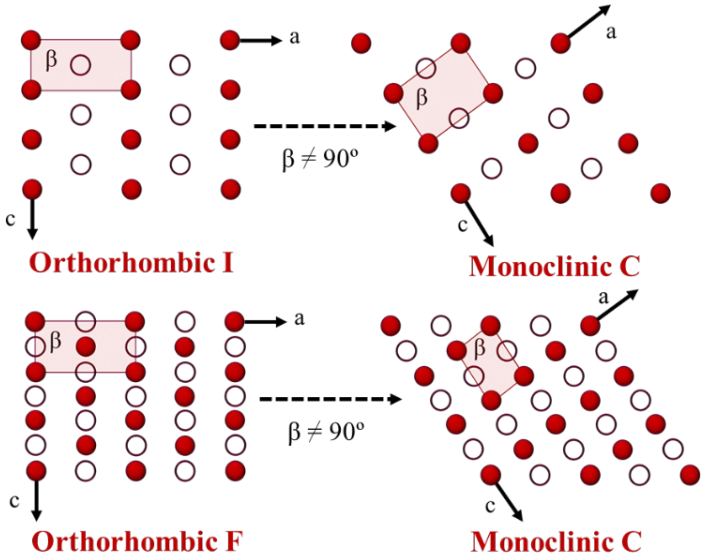
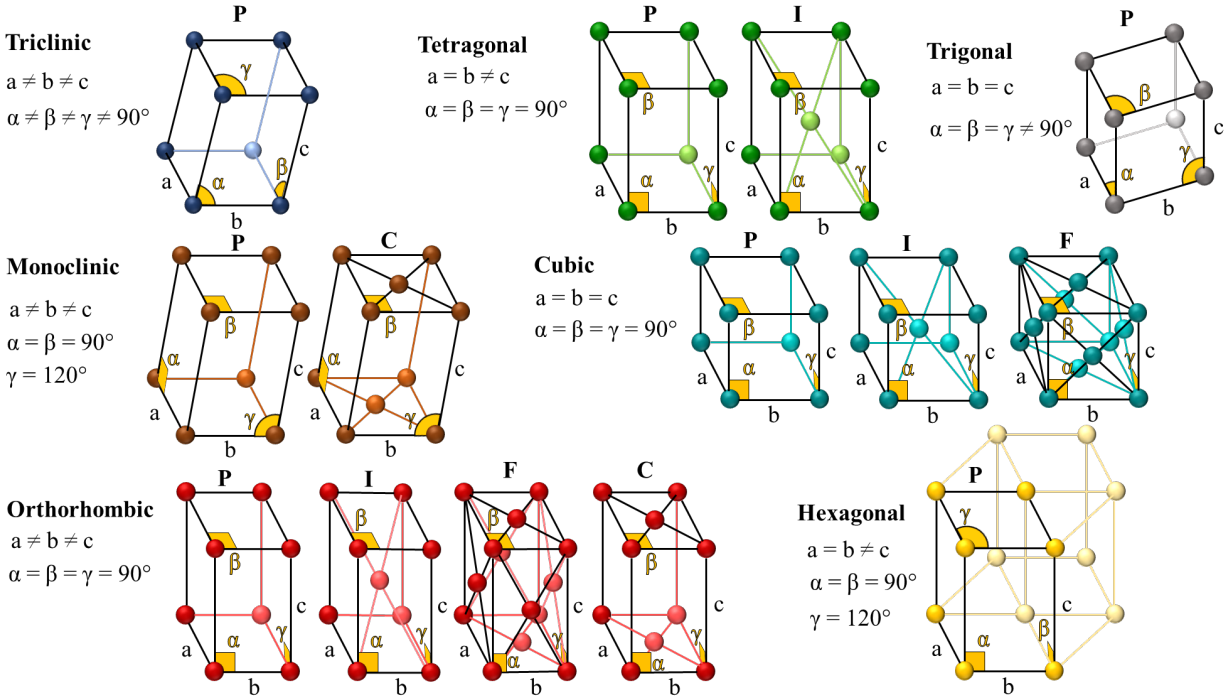


Figure 5. 2-D projection of the monoclinic lattices generated from the orthorhombic lattices. Empty symbols represent points at a ½ distance.

The final two Bravais lattices are the hexagonal **P** and trigonal **P** lattice, related closely to the first one and created by stretching the cube along its diagonal with a=b=c and $\alpha=\beta=\gamma\neq90^{o}$. A trigonal **P** lattice with a=b≠ c and $\gamma=120^{o}$ is a 1/3 part of the hexagonal P lattice. All 14 Bravais lattices are summarized in *Figure 6*.

Figure 6. The 14 Bravais lattices.



One half of the Bravais cells are primitive and the other half are conventional. We can define another special type of primitive cell: the Wigner-Seiz lattice. It is defined as a space around a point as close to that point as to any other lattice point. In real space it is a purely mathematical concept, constructed by drawing lines from a chosen point to all its nearest neighbors and then drawing a bisecting plane perpendicular to each of these planes. The 3 D construction results in a polyhedron which contains the original point (*Figure 7*).

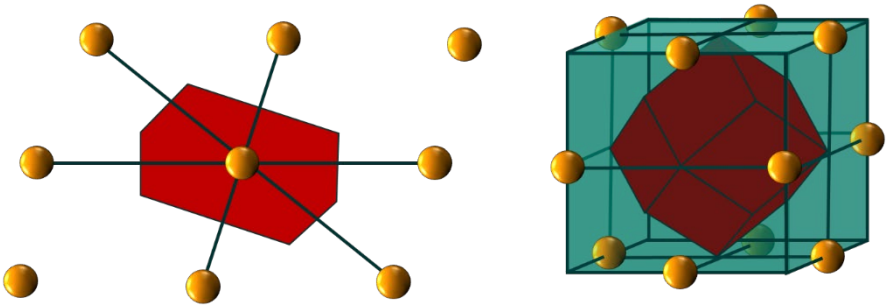


Figure 7. 2D construction of the Wigner-Seitz cell and 3D representation of the cell corresponding to the Cubic F Bravais cell.

In real space, the Wigner-Seitz cell remains a mathematical concept; however, in the reciprocal space the first Brillouin zone is defined as the Wigner-Seitz cell of the reciprocal space. The Brillouin zone allows us to understand the electronic energy bands and resulting electronic properties of the solids.

Symmetry elements

Rotational axis

An **axis of rotation**, as the name indicates, relates to the operation of rotation. An object presents an axis of rotation when a simple turn, by an angle of $2\pi/n$, results in an equivalent configuration. The n refers to the number of rotations after which the initial position is recovered. As an example, the initial position in a rectangle is obtained after four rotations at 90º, n being equal to 4, indicating a four-fold axis of rotation (*Figure 8*).

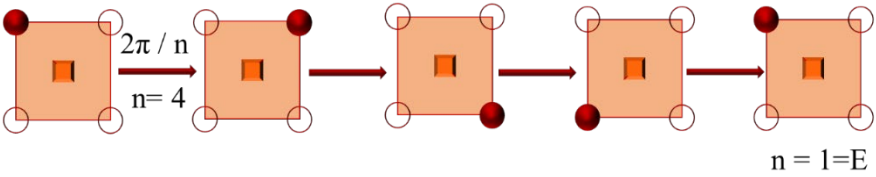


Figure 8. 4-fold rotation axis operations

n=1 corresponds to the identity operation (E) where the object remains unchanged. All objects present identity element E. By definition any type of ***n*** is possible, but only 2, 3, 4, 5 and 6 are found in 3-D space (although 5 is a very special case usually omitted).

One structure can contain multiple axes of rotation, the cube for example presents four, three and two-fold axes (*Figure 8*). However, the structures are classified by their highest order rotation axis, called the **principal axis of rotation**. All axes are represented graphically by a regular polygon, indicating an axis perpendicular to its base and with the same number of sides as the order of the axis (*Table 1*).

Table 1. Direct, inverse and helicoidal (screw) axis labeling

	Direct axes	**Inverse axes**	**Helicoidal axes**
Axes perpendicular to the plane of projection	2 3 4 6	$\bar{2}$ $\bar{3}$ $\bar{4}$ $\bar{6}$	2_1 3_1 3_2 4_1 4_2 4_3 6_1 6_2 6_3 6_4 6_5
Axes parallel to the plane of projection			

Two types of nomenclatures are usually employed to indicate the symmetry of the objects, i.e. Schönflies symbols for molecular symmetry operations and Hermann-Mauguin equivalents when considering solid classification. Both symbols reflect the highest symmetry elements (or a combination of a few elements generating the point and space groups' classification). Thus, for an object with a 4-fold axis of rotation, the Schönflies symbol is C_4, and the equivalent in the Hermann-Mauguin nomenclature is 4 (see Annex I for more equivalents).

As an example, three successive rotations at a rotation angle of $2\pi/4=90^{o}$ on the 4-fold axis will generate three equivalent points and the fourth one will coincide with the identity operation. Two successive operations (notated C_4^2 for molecules and 4 for solids) will rotate the molecule/lattice at 180º.

Finding the rotation axes for more complicated structures can be more complex and a basic approach is usually applied. In the case of a lattice, the highest order axis is first identified, and then all other elements, using for that purpose a bare polyhedron (a geometrical figure without counting atoms or considering their chemical nature). The rotation axes of a cube are presented in *Figure 9*.

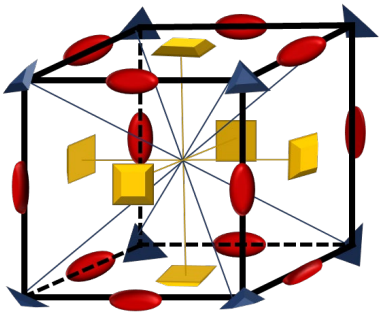
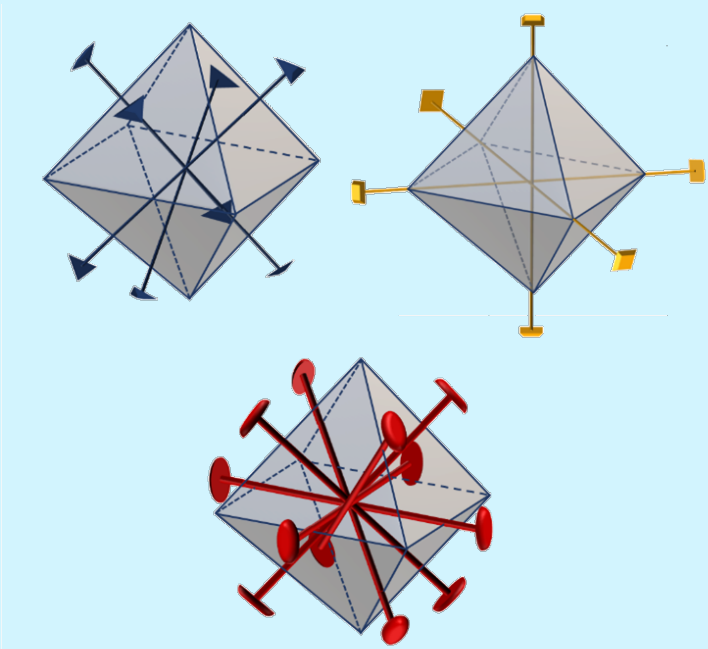


Figure 9. Rotational axes of a cube.

Mirror planes

The **mirror planes** introduce the operation of reflection. An object presents a mirror plane when a reflection on this plane results in an equivalent specular image. To specify the plane, the σ symbol is used for molecule and **m** for solids. This operation converts the right-hand object into a left-hand one and each object moves across the plane perpendicularly to a new position as far from the plane as the original one. A position with coordinates (x,y,z) is converted into (x, y, $\bar{z}$) when the reflection occurs in *x-z* plane. The use of the bar symbol over z instead of –z indicates that the position of this point is at coordinate (1-z) and enters within the defined cell.

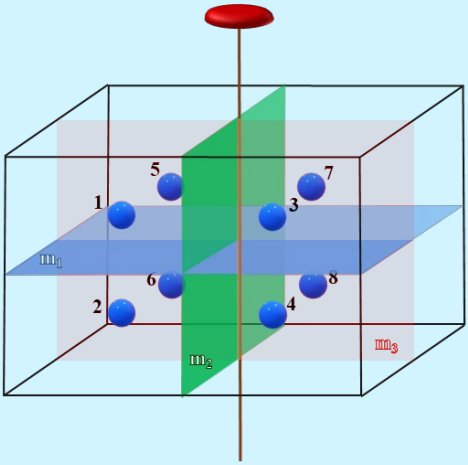
Problem II. *Find the rotation axes of an octahedron.*



A way to reduce the complexity of the symmetry operations is to associate the rotation features with geometrical elements. Thus, if we consider the vertices (6 in total) and axes passing through two opposite vertices, it is evident that the octahedron contains three 4-fold rotation axes and three coincident 2-fold axes. Now, if we switch to the faces, we have 8 equilateral triangular faces, and a set of four 3-fold axes appears (with the axis crossing the mid-points of a pair of triangular faces on the opposite sides of the octahedron). With the edges now left (12 in total), six C_2 axes are crossing every pair of opposite edges. These axes are perpendicular to C_2, coincident with the highest order axis, and adopt a prime symbol (C_2'). There are two possible directions of rotation for the sets of C_3 and C_4 axes: clockwise and anticlockwise, which doubles the sets, and the rotational symmetry operations for an octahedron are: **E, $8C_3$, $6C_4$, $3C_2$, $6C_2$'** a set of 24 operations.

Problem III. *Compare the rotational axes of cube and octahedron.*

Problem IV. *Find all equivalent positions upon reflection for the polyhedron indicated in the figure and starting point 1.*



For an orthogonal parallelepiped with three perpendicular mirrors, we can generate multiple positions from the initial position **1**. The reflection in plane m_1 generates point **2**, and the operation through m_2 produces **3** and **4** from the positions **1** and **2**, respectively. The last operation m_3 generates **5**, **6**, **7** and **8** from **1**, **2**, **3** and **4**. There are eight equivalent positions of point **1**. However, if the initial point is situated on one of the planes, only four positions are generated and if it is placed at the intersection of them all, only one position is available.

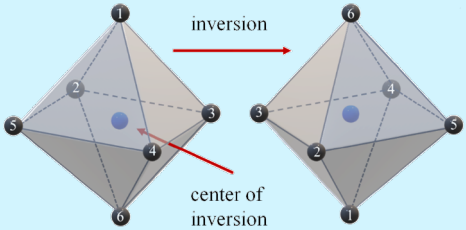
For every set of symmetry operations, the number of all resulting equivalent positions depends on the position of the starting point.

We can apply another operator to pass from one equivalent position to another. Positions **1** and **2** generate positions **7** and **8** in the presence of a 2-fold axis in the plane m_2. The same operation will generate **5** and **6** from **3** and **4**.

Symmetry center

Problem V. *Which point is generated from position 1 in the presence of the center of symmetry of the octahedron.*

The squares, rectangles, parallelepipeds (orthogonal or not) and octahedra present a center of symmetry unlike the triangles and the tetrahedra.



A more complex symmetry operation is **inversion**, a new position is generated through a center at an opposite position to the starting point, as far from the center as the original point. This operation is designated with ***i*** for molecules and with a bar over a symbol ($\bar{1}$), indicating the presence of the center of symmetry for the solids. Similar to the mirror plane operation, the positions generated with the inversion operator are of different chirality. The presence of a symmetry center in the origin inverts the (*x,y,z*) point to (*-x,- y,-z*).

All equivalent positions of a point with coordinates (*x,y,z*) generated after proper symmetry operations such as rotation, reflection and inversion through a center of symmetry are summarized in *Figure 10*.

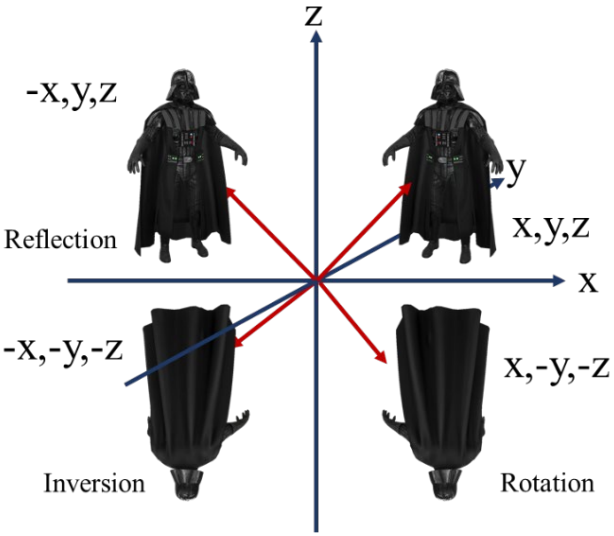


Figure 10. Equivalent positions generated after proper symmetry operations over a given (*x,y,z*) point.

Rotoinversion

The improper rotation (rotoinversion), labelled *Sn* for molecules and $\bar{n}$ for solids, is a combination of two operations, rotation at 2π/n and inversion through a center of inversion (*Figure 11*).

The rotoinversion of a point (*x,y,z*) along the $\bar{2}$ axis transforms its position at a given ($x,y,\bar{z}$) point via temporary positions ($\bar{x},\bar{y},\bar{z}$) or ($\bar{x},\bar{y},z$), as a function of the primary operation, inversion or rotation, respectively. The geometrical symbol for the improper axis is the same as for the proper one, but with a white/black circle inside (*Table 1* inverse axis symbols).

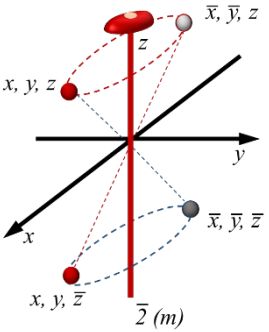


Figure 11. Operation of rotoinversion.

If we consider a tetrahedron (T_d), usually not presenting 4-fold axis or symmetry center, its four vertices are related through the $\bar{4}$ axis. Each axis crosses two opposite T_d edges and, if we draw the tetrahedra within a cube (*Figure 12*), it will be located along the perpendiculars to the opposite faces of the cube diagonals. The first rotation at 90º and inversion generates a similar tetrahedron, but with different relative position of its vertex (in a different color for clarity). The first $\bar{4}$ (z) and second $[\bar{4}\ (z)]^2$ operations are related to the third $[\bar{4}\ (z)]^3$ and fourth $[\bar{4}\ (z)]^4$ by a 2-fold axis with the same orientation as the $\bar{4}$ axis.

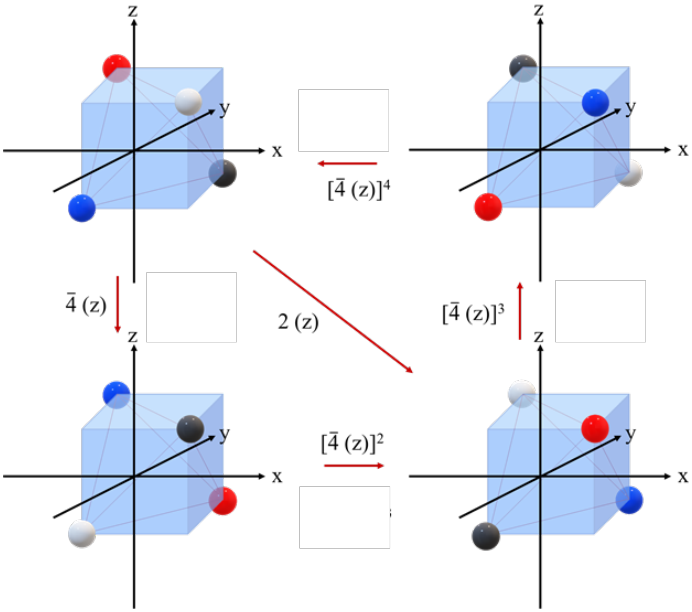
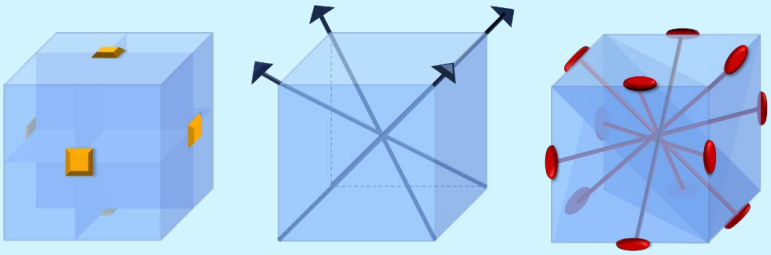


Figure 12. $\bar{4}$ axis operation in tetrahedron.

All symmetry elements discussed so far are point symmetry elements and every molecule or polyhedron of finite size possesses a set of symmetry operations that upon combination could describe the whole molecule or a finite part of a solid. Such a set of symmetry elements is known as a **point group** and the symbols that describe it correspond to the principal elements of symmetry for finite objects. To label the point groups, first we have to find the principal axis of rotation and afterwards all perpendicular mirror planes to that axis, if any. The mirror planes (*m*) perpendicular to the principal axis that is established are indicated by a bar symbol / (**4/m**, for example).

Problem VI. *Use cube symmetry elements to deduce the symmetry elements, their corresponding Hermann-Mauguin symbols and point groups.*

Thus, a cube presents three mutually perpendicular 4-fold axes and two perpendicular mirror planes (4/m), four 3-fold axes situated on cube diagonals (3), and six 2-fold axes perpendicular to the opposite edges and the corresponding perpendicular mirror planes situated along the face diagonals (2/m).



The symbols of the cube's point group should be 4/m32/m which we can simplify, by only considering the mirror planes, as all their intersections are defined by one axis. So, the point group notation for a cube becomes *m*3*m*

Problem VII. *Repeat the operation for a tetrahedron.*

A new question arises: *how many point groups are possible?* Usually, the number of point groups originated by all possible combinations of

symmetry operations is very large. However, only the point groups compatible with the lattice translation vectors (Bravais lattice vectors) count for crystals. Thus, the number of groups, known as **crystallographic point groups**, is limited to **32**.

Point groups

A simple rotation through an angle, with the condition $n\alpha=2\pi$, where *n* is an integer number equal to 1, 2, 3, 4 and 6, will generate 5 corresponding singular point groups (*Figure 13*). This figure represents the point groups' 2D projection where all equivalent positions obtained after applying the symmetry operators are indicated.

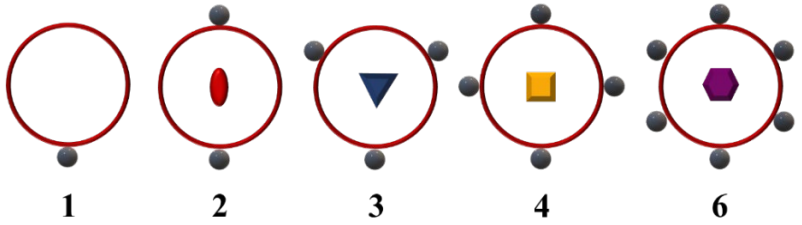


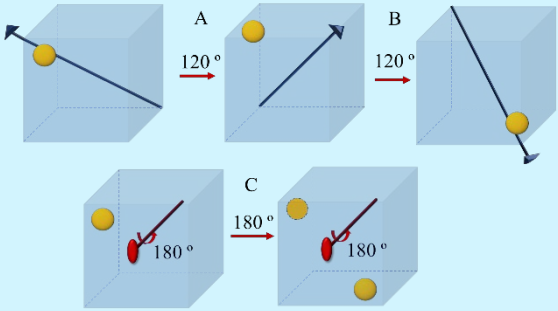
Figure 13. 2-D projection of simple rotational point groups.

Upon combination of those proper rotations, only the groups formed upon the condition that any effect produced by a combination of two operations is equal to a third one (A•B=C) are defined as point groups.

Problem VIII. *Consider a cube and three symmetry operations:* ***A*** *3-fold axis rotation around the body diagonal;* ***B*** *3-fold axis rotation around the other body diagonal; and,* ***C*** *2-fold axis on any line passing through the centers of the cube's faces. Determine the compatibility of the rotation operations with the condition A•B=C.*

If compatibility is to be tested, we have to be sure that A, B and C comply with the group properties: i) the successive application of two operators originates another which is a part of the same group A•B=C; ii) the composition of any two operators is associative (A•B)C =A(B•C); iii) an identity operator exists and A•E= E•A=A; and, iv) every operator presents an inverse one and their combination results in the identity operator $A \bullet A^{-1} = A^{-1} \bullet A = E$.

It is clear that the application of A and B has the same effect as C.



An alternative way to determine the compatibility of the rotation is to use the Euler equations relating the angles of rotation (α, β ,γ) with the angles between the rotation axes (A, B, C).

$$\cos(A \wedge B) = \frac{\cos(\gamma/2) + \cos(\alpha/2)\cos(\beta/2)}{\sin(\alpha/2)\sin(\beta/2)}$$

$$\cos(A \wedge C) = \frac{\cos(\beta/2) + \cos(\alpha/2)\cos(\gamma/2)}{\sin(\alpha/2)\sin(\gamma/2)}$$

$$\cos(B \Lambda C) = \frac{\cos(\alpha/2) + \cos(\beta/2)\cos(\gamma/2)}{\sin(\beta/2)\sin(\gamma/2)}$$

If the substitution of rotation angles results in acceptable values of intra-rotational angles the group meets the condition A•B=C

Such groups are summarized in *Table 2* and *Figure 14*.

Table 2. Compatibility of the rotational combinations.

A	**B**	**C**	**ABC**	**A∧B**	**A∧C**	**B∧C**
2	2	2	222	90º	90º	90º
3	2	2	32	90º	90º	60º
4	2	2	422	90º	90º	45º
6	2	2	622	90º	90º	30º
4	3	2	432	54º44’	45º	35º16’
2	3	3	23	54º44’	54º44’	70º32’

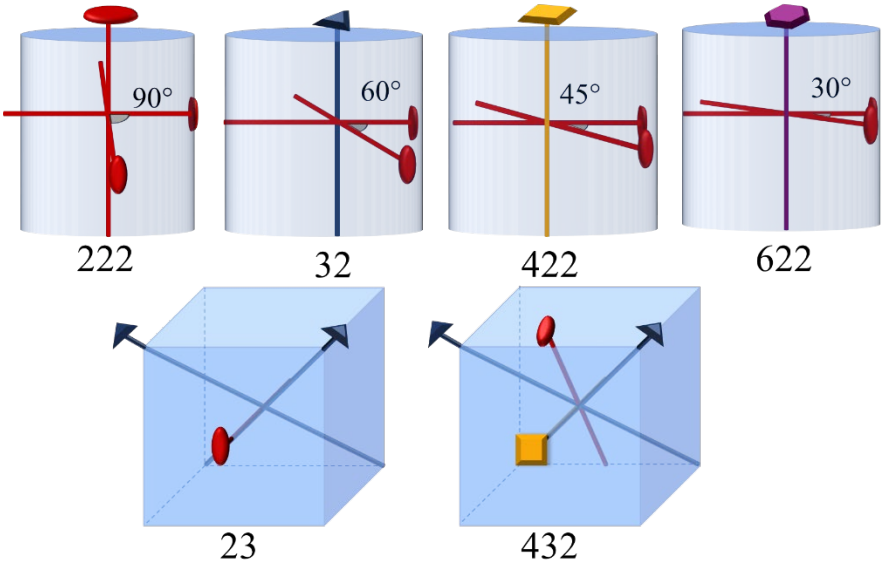


Figure 14. Point groups originated following rotational combinations.

The point groups resulting from the combination of rotational axes are named over the participants starting with the principal axis; two digits are sufficient to indicate the point group. However, in some cases a third one appears for additional clarification of the crystal system.

The presence of rotoinversion generates another 5-point groups where only one pattern is produced and cannot be generated by another simple operation or combination of more symmetry elements. The 2-D projection must indicate all equivalent positions, but in this case negative coordinates and specular images appear. The symbols ’ and – are therefore used whenever the equivalent position is chiral and with negative *z* coordinates. The presence of mirror planes in the plane of the paper are indicated with crossed black lines in the right corner of the sketch (*Figure 15*).

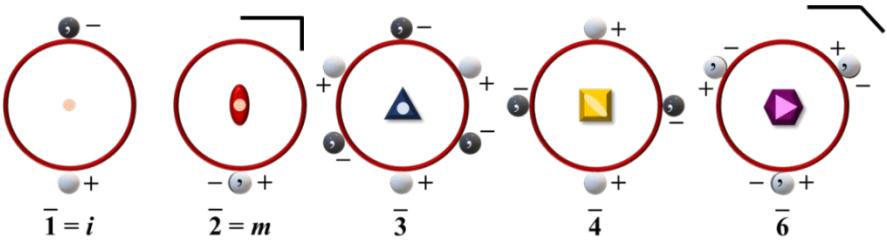


Figure 15. 2D projections of the inverted axis point groups

The inversion 2-fold axis, $\bar{2}$, is always written as *m* (mirror plane). The $\bar{6}$ group can also be denoted 3/m, as the same result is obtained after successive 3-fold axis rotation and reflection through a mirror plane perpendicular to that axis.

Operations producing left-handed objects can be combined to produce right-handed objects. There are 16 groups that contain improper axes deriving from groups with the proper rotation axis, *n*. The improper axis, $\bar{n}$, either substitutes the proper one or is parallel to it. The combination of both is indicated as a fraction, n/$\bar{n}$. Simplifying the labeling, we use n/m (instead of n/$\bar{n}$) when *n* is an even number and $\bar{n}$ implies a mirror plane. For *n* odd numbers the *n*/$\bar{n}$ is denoted as $\bar{n}$. Nevertheless, $\bar{2}$ is always *m*, and a group such as $\bar{2}\bar{2}2$ converts into *mm*2. Some examples are shown in *Figure 16* and all 16 groups are summarized in *Table 3*.

Table 3. 16 point groups generated by a combination of proper/improper rotation axes and mirror planes.

2/m	**2mm**		
mmm			
4/m	**$\bar{4}$2m**	**4mm**	**4/mmm**
3m	**$\bar{3}$m**		
6/m	**6mm**	**$\bar{6}$m2**	**6/mmm**
m3	**$\bar{4}$3m**	**m3m**	

The red colored groups correspond to a combination of an even order principal axis and inversion center (center of symmetry), the groups in blue correspond to an axis and a plane that contains the axis, and all the others correspond to three axes and a center of symmetry.

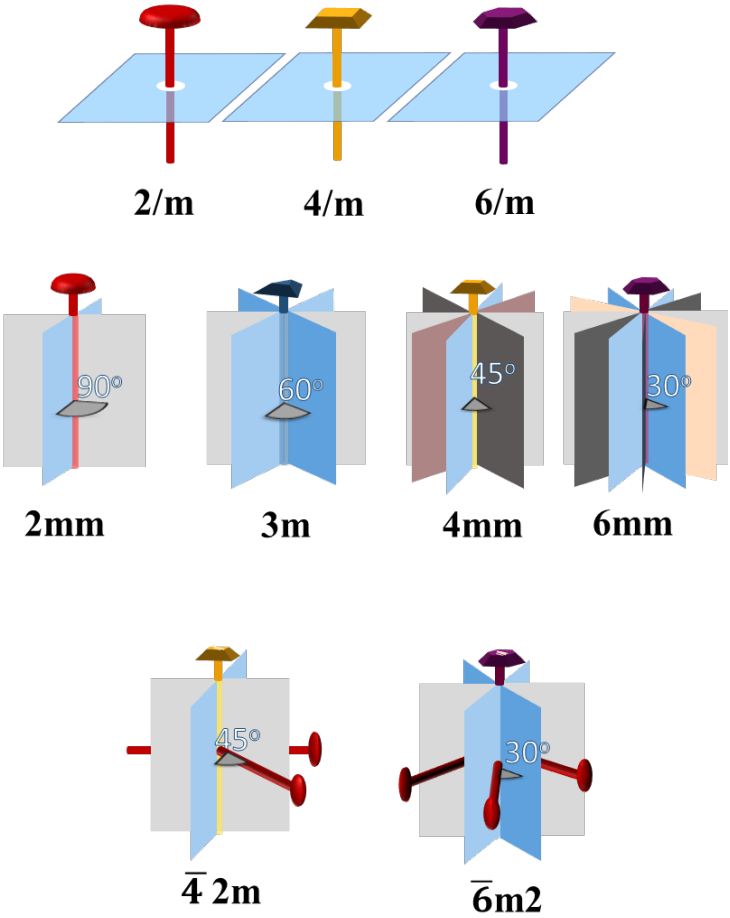


Figure 16. Examples of rotational axis and combinations of mirror plane point groups.