Solid State Theory
Physics 545
Symmetry and Introduction to Group Theory

Symmetry is all around us and is a fundamental property of nature.
Symmetry and Introduction to Group Theory

The term *symmetry* is derived from the Greek word “symmetria” which means “measured together”. An object is symmetric if one part (e.g. one side) of it is the same* as all of the other parts. You know intuitively if something is symmetric but we require a precise method to describe how an object or molecule is symmetric.

*Group theory* is a very powerful mathematical tool that allows us to rationalize and simplify many problems in Chemistry. A group consists of a set of symmetry elements (and associated symmetry operations) that completely describe the symmetry of an object.

We will use some aspects of group theory to help us understand the bonding and spectroscopic features of molecules.
Crystallography is largely based Group Theory (symmetry).

Symmetry operations transform space into itself. Simplest symmetry operator is unity operator (=does nothing). (=Lattice is invariant with respect to symmetry operations)

Translation operator, \( T_R \), replaces radius vector of every point, \( r \), by \( r' = r + R \).
Symmetry

a state in which parts on opposite sides of a plane, line, or point display arrangements that are related to one another via a symmetry operation such as translation, rotation, reflection or inversion.
Divided into two parts by a plane

Mirror plane (symmetry element)

Have no symmetry remaining: Asymmetric units
Asymmetric unit

Recall that the unit cell of a crystal is the smallest 3-D geometric figure that can be stacked without rotation to form the lattice. The asymmetric unit is the smallest part of a crystal structure from which the complete structure can be built using space group symmetry. The asymmetric unit may consist of only a part of a molecule, or it can contain more than one molecule, if the molecules are not related by symmetry.

Protein Crystal Contacts
by Eric Martz, April 2001.
http://molvis.sdsc.edu/protexpl/xtlcon.htm
Group Theory

- mathematical method
- a molecule’s symmetry

information about its properties
(i.e., structure, spectra, polarity, chirality, etc…)

A-B-A is different from A-A-B.

However, important aspects of the symmetry of H$_2$O and CF$_2$Cl$_2$ are the same.
Symmetry and Point Groups

Point groups have symmetry about a single point at the center of mass of the system.

Symmetry elements are geometric entities about which a symmetry operation can be performed. In a point group, all symmetry elements must pass through the center of mass (the point). A symmetry operation is the action that produces an object identical to the initial object.

The symmetry elements and related operations that we will find in molecules are:

<table>
<thead>
<tr>
<th>Element</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation axis, $C_n$</td>
<td>$n$-fold rotation</td>
</tr>
<tr>
<td>Improper rotation axis, $S_n$</td>
<td>$n$-fold improper rotation</td>
</tr>
<tr>
<td>Plane of symmetry, $\sigma$</td>
<td>Reflection</td>
</tr>
<tr>
<td>Center of symmetry, $i$</td>
<td>Inversion</td>
</tr>
<tr>
<td></td>
<td>Identity, $E$</td>
</tr>
</tbody>
</table>

The Identity operation does nothing to the object – it is necessary for mathematical completeness, as we will see later.
There are two naming systems commonly used in describing symmetry elements

1. The Schoenflies notation used extensively by spectroscopists
2. The Hermann-Mauguin or international notation preferred by crystallographers
Symmetry Operations/Elements

A molecule or object is said to possess a particular operation if that operation when applied leaves the molecule unchanged.

Each operation is performed relative to a point, line, or plane - called a symmetry element.

There are 5 kinds of operations

1. Identity
2. n-Fold Rotations
3. Reflection
4. Inversion
5. Improper n-Fold Rotation
The 5 Symmetry Elements

Identity (C1 = E or 1)

Rotation by 360° around any randomly chosen axes through the molecule returns it to original position.

Any direction in any object is a C1 axis; rotation by 360° restores original orientation.

Schoenflies: C is the symbol given to a rotational axis

1 indicates rotation by 360°

Hermann-Mauguin: 1 for 1-fold rotation

Operation: act of rotating molecule through 360°

Element: axis of symmetry (i.e. the rotation axis).
Symmetry Elements

Rotation

turns all the points in the asymmetric unit around one point, the center of rotation. A rotation does not change the handedness of figures in the plane. The center of rotation is the only invariant point (point that maps onto itself).

Good introductory symmetry websites
http://mathforum.org/sum95/suzanne/symsusan.html
http://www.ucs.mun.ca/~mathed/Geometry/Transformations/symmetry.html
**Rotation axes (Cn or n)**

Rotations through angles other than 360°.

**Operation**: act of rotation

**Element**: rotation axis

*Symbol* for a symmetry element for which the operation is a rotation of 360°/n

\[
C_2 = 180°, \ C_3 = 120°, \ C_4 = 90°, \ C_5 = 72°, \ C_6 = 60° \text{ rotation, etc.}
\]

*Schoenflies*: Cn

*Hermann–Mauguin*: n.

The molecule has an *n-fold axis of symmetry*.

An object may possess several rotation axes and in such a case the one (or more) with the greatest value of *n* is called the **principal axes of rotation**.
**n-fold rotation** - a rotation of $360°/n$ about the $C_n$ axis ($n = 1$ to $\infty$)

In water there is a $C_2$ axis so we can perform a 2-fold ($180°$) rotation to get the identical arrangement of atoms.

In ammonia there is a $C_3$ axis so we can perform 3-fold ($120°$) rotations to get identical arrangement of atoms.
The *Principal axis* in an object is the highest order rotation axis. It is usually easy to identify the principle axis and this is typically assigned to the z-axis if we are using Cartesian coordinates.

Ethane, C$_2$H$_6$

The principal axis is the three-fold axis containing the C-C bond.

Benzene, C$_6$H$_6$

The principal axis is the six-fold axis through the center of the ring.

The principal axis in a tetrahedron is a three-fold axis going through one vertex and the center of the object.
Symmetry Elements

Reflection

flips all points in the asymmetric unit over a line, which is called the mirror, and thereby changes the handedness of any figures in the asymmetric unit. The points along the mirror line are all invariant points (points that map onto themselves) under a reflection.
**Mirror planes (h or m)**

Mirror reflection through a plane.

**Operation:** act of reflection

**Element:** mirror plane

Schoenflies notation:

*Horizontal* mirror plane (h): plane perpendicular to the principal rotation axis

*Vertical* mirror plane (v): plane includes principal rotation axis

*Diagonal* mirror plane (d): plane includes principal rotation axis and bisects the angle between a pair of 2-fold rotation axes that are normal (perpendicular) to principal rotation axis.

Schoenflies: h, v, d

Hermann–Mauguin: m
Reflection across a plane of symmetry, $\sigma$ (mirror plane)

These mirror planes are called “vertical” mirror planes, $\sigma_v$, because they contain the principal axis. The reflection illustrated in the top diagram is through a mirror plane perpendicular to the plane of the water molecule. The plane shown on the bottom is in the same plane as the water molecule. Handedness is changed by reflection!
Notes about reflection operations:
- A reflection operation exchanges one half of the object with the reflection of the other half.
- Reflection planes may be vertical, horizontal or dihedral (more on $\sigma_d$ later).
- Two successive reflections are equivalent to the identity operation (nothing is moved).

A “horizontal” mirror plane, $\sigma_h$, is perpendicular to the principal axis. This must be the xy-plane if the z-axis is the principal axis. In benzene, the $\sigma_h$ is in the plane of the molecule – it “reflects” each atom onto itself.

Vertical and dihedral mirror planes of geometric shapes.
Symmetry Elements

Inversion

every point on one side of a center of symmetry has a similar point at an equal distance on the opposite side of the center of symmetry.
Centres of inversion (centre of symmetry, i or $\bar{1}$)

**Operation:** inversion through this point

**Element:** point

Straight line drawn through centre of inversion from any point of the molecule will meet an equivalent point at an equal distance beyond the center.

*Schoenflies:* $i$

*Hermann–Mauguin:* $\bar{1}$

Molecules possessing a center of inversion are **centrosymmetric**
**Inversion** and centers of symmetry, $i$ (inversion centers)

In this operation, every part of the object is reflected through the inversion center, which must be at the center of mass of the object.

$$[x, y, z] \xrightarrow{i} [-x, -y, -z]$$

We will not consider the matrix approach to each of the symmetry operations in this course but it is particularly helpful for understanding what the inversion operation does. The inversion operation takes a point or object at $[x, y, z]$ to $[-x, -y, -z]$. 
Axes of rotary inversion (improper rotation Sn or $\bar{n}$)

Involves a combination or elements and operations

Schoenflies: Sn

Element: axis of rotatory reflection

The operation is a combination of rotation by $360°/n$ ($C_n$) followed by reflection in a plane normal ($\vec{h}$) to the $Sn$ axis.

Hermann-Mauguin: $\bar{n}$

Element: axis of rotatory inversion.

The operation is a combination of rotation by $360°/n$ ($n$) followed by inversion through a point (1).
n-fold improper rotation, $S_n^m$ (associated with an improper rotation axis or a rotation-reflection axis) This operation involves a rotation of $360°/n$ followed by a reflection perpendicular to the axis. It is a single operation and is labeled in the same manner as “proper” rotations.

Note that: $S_1 = \sigma$, $S_2 = i$, and sometimes $S_{2n} = C_n$ (e.g. in box) this makes more sense when you examine the matrices that describe the operations.
Symmetry Elements in Arrays

Translational symmetry elements

Screw axis

: general symbol for a screw axis is $N_n^*$, where $N$ is the order (2, 3, 4 or 6) of the axis

(a) A twofold screw axis, $2_1$

(b) A fourfold screw axis, $4_1$

: Screw axes are very common in protein structures

Glide plane (c)

: combination of a mirror plane and a translation operation parallel to it
Symmetry Elements

Glide reflections

reflects the asymmetric unit across a mirror line and then translates parallel to the mirror. A glide reflection changes the handedness of figures in the asymmetric unit. There are no invariant points (points that map onto themselves) under a glide reflection.
Symmetry Elements

Screw axes

rotation about the axis of symmetry by 360°/n, followed by a translation parallel to the axis by r/n of the unit cell length in that direction.

Diagram from:
http://www-structure.llnl.gov/xray/101index.html
Symmetry Elements

Translation

moves all the points in the asymmetric unit the same distance in the same direction. This has no effect on the handedness of figures in the plane. There are no invariant points (points that map onto themselves) under a translation.
A lesson in symmetry from M. C. Escher
To be a group several conditions must be met:

1. The group multiplication table must be closed.
   Consider $\text{H}_2\text{O}$ which has $E, C_2$, and $2 \sigma_v$'s.

\[ \overset{\text{C}_2}{\text{C}_2} \sigma_v \equiv \sigma_v \]

i.e.,

of course

etc…

The group multiplication table obtained is therefore:

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$C_2$</td>
<td>$\sigma_v$</td>
<td>$\sigma'_v$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$C_2$</td>
<td>$E$</td>
<td>$\sigma'_v$</td>
<td>$\sigma_v$</td>
</tr>
<tr>
<td>$\sigma_v$</td>
<td>$\sigma_v$</td>
<td>$\sigma'_v$</td>
<td>$E$</td>
<td>$C_2$</td>
</tr>
<tr>
<td>$\sigma'_v$</td>
<td>$\sigma'_v$</td>
<td>$\sigma_v$</td>
<td>$C_2$</td>
<td>$E$</td>
</tr>
</tbody>
</table>
To be a group several conditions must be met:

2. Must have an identity \((\hat{E})\).

3. All elements must have an inverse.

i.e., for a given operation \((\hat{A})\) there must exist an operation \((\hat{B})\) such that \(\hat{A}\hat{B} = \hat{E}\)
Point group  \textit{(point symmetry)}

: All molecules characterized by 32 different combinations of symmetry elements

Space group  \textit{(point \& translational symmetry)}

: There are 230 possible arrangements of symmetry elements in the solid state. Any crystal must belong to one (and only one) space group.

There are two naming systems commonly used in describing symmetry elements

1. The Schoenflies notation used extensively by spectroscopists
2. The Hermann-Mauguin or international notation preferred by crystallographers
Typical space group symbols are: \( P\bar{1}, C2/m, Ibca, \bar{R}3, Fm3m, P2_12_12_1. \)

\( P \) means \textit{primitive},

\( A, B, \) or \( C \) means \textit{centred on the face perpendicular to the a, b or c axis},

\( F \) means \textit{centred on all the faces},

\( I \) means \textit{body centred -- centred in the middle of the cell --}

\( R \) means \textit{rhombohedral},
Reflection
a) Mirror plane

n-Fold Rotations
b) two-fold axis
c) two-fold axis + mirror planes

d) three-fold axis

Inversion
e) Center of symmetry

f) four-fold inversion axis
The symmetry classification of molecules

The groups $C_1$, $C_i$ and $Cs$

$C_1$ : no element other than the identity

$C_i$ : identity and inversion alone

$Cs$ : identity and a mirror plane alone

The groups $C_n$, $C_{nv}$ and $C_{nh}$

$C_n$ : n-fold rotation axis

$C_{nv}$ : identity, $C_n$ axis plus $n$ vertical mirror planes $\int_v$

$C_{nh}$ : identity and an $n$-fold rotation principal axis plus a horizontal mirror plane $\int_h$
The groups $Dn$, $Dnh$ and $Dnd$

$Dn$ : $n$-fold principal axis and $n$ two-fold axes perpendicular to $Cn$

$Dnh$ : molecule also possesses a horizontal mirror plane

$Dnd$ : in addition to the elements of $Dn$ possesses $n$ dihedral mirror planes $d$
The cubic groups

*Td* and *Oh*: groups of the regular tetrahedron (e.g. CH4) and regular octahedron (e.g. SF6), respectively.

*T* or *O*: object possesses the rotational symmetry of the tetrahedron or the octahedron, but none of their planes of reflection

*Th*: based on *T* but also contains a center of inversion

The full rotation group

*R3*: consists of an infinite number of rotation axes with all possible values of *n*.

A sphere and an atom belong to *R3*, but no molecule does.

The groups *Sn*

*Sn*: Molecules not already classified possessing one *Sn* axis

*S2 α Ci*
## 32 Point Groups

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>Triclinic</strong></td>
<td>1*</td>
<td>-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Monoclinic</strong></td>
<td>2*</td>
<td>m*</td>
<td>2/m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Orthorhombic</strong></td>
<td>222</td>
<td>mm2*</td>
<td>mmm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tetragonal</strong></td>
<td>4*</td>
<td>-4</td>
<td>4/m</td>
<td>422</td>
<td>4mm*</td>
<td>-42m</td>
<td>4/mmm</td>
</tr>
<tr>
<td><strong>Trigonal</strong></td>
<td>3*</td>
<td>-3</td>
<td>32</td>
<td>3m*</td>
<td>-3m</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Hexagonal</strong></td>
<td>6*</td>
<td>-6</td>
<td>6/m</td>
<td>622</td>
<td>6mm*</td>
<td>-62m</td>
<td>6/mmm</td>
</tr>
<tr>
<td><strong>Cubic</strong></td>
<td>23</td>
<td>m-3</td>
<td>432</td>
<td>-43m</td>
<td>m-3m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The 11 centrosymmetric point groups are shown in **red**, the 11 enantiomorphic point groups are shown in **green**, and the 10 polar point groups are shown with an asterisk *. (Note that in the above table, inversion axes are written with a minus sign in front of the axis symbol.)
230 space groups

1-2 : Triclinic, classes 1 and -1
3-15 : Monoclinic, classes 2, m and 2/m
16-24 : Orthorhombic, class 222
25-46 : Orthorhombic, class mm2
47-74 : Orthorhombic, class mmm
75-82 : Tetragonal, classes 4 and -4
83-88 : Tetragonal, class 4/m
89-98 : Tetragonal, class 422
99-110 : Tetragonal, class 4mm
111-122 : Tetragonal, class 42m
123-142 : Tetragonal, class 4/mmm
143-148 : Trigonal, classes 3 and -3
149-155 : Trigonal, class 32
156-161 : Trigonal, class 3m
162-167 : Trigonal, class -3m
168-176 : Hexagonal, classes 6, -6 and 6/m
177-186 : Hexagonal, classes 622 and 6mm
187-194 : Hexagonal, classes -6m2 and 6/mmm
195-206 : Cubic, classes 23 and m-3
206-230 : Cubic, classes 432, -43m and m-3m
Triclinic system

Monoclinic system
Trigonal system
### 32 Point Groups

<table>
<thead>
<tr>
<th></th>
<th>Triclinic</th>
<th>Monoclinic</th>
<th>Tetragonal</th>
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<td>$x$</td>
<td><img src="image1" alt="Diagram" /></td>
<td><img src="image2" alt="Diagram" /></td>
<td><img src="image3" alt="Diagram" /></td>
</tr>
<tr>
<td>$\overline{x}$</td>
<td><img src="image4" alt="Diagram" /></td>
<td><img src="image5" alt="Diagram" /></td>
<td><img src="image6" alt="Diagram" /></td>
</tr>
<tr>
<td>$x+T$</td>
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<td><img src="image8" alt="Diagram" /></td>
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<tr>
<td>$x2$</td>
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<td><img src="image11" alt="Diagram" /></td>
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<td>$xm$</td>
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<td><img src="image15" alt="Diagram" /></td>
</tr>
<tr>
<td>$\overline{x}m$</td>
<td><img src="image16" alt="Diagram" /></td>
<td><img src="image17" alt="Diagram" /></td>
<td><img src="image18" alt="Diagram" /></td>
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<tr>
<td>$x2+\overline{T}$</td>
<td><img src="image19" alt="Diagram" /></td>
<td><img src="image20" alt="Diagram" /></td>
<td><img src="image21" alt="Diagram" /></td>
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<tr>
<td>Trigonal</td>
<td>Hexagonal</td>
<td>Cubic</td>
<td></td>
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<td>-------</td>
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<td><img src="image" alt="Trigonal 3" /></td>
<td><img src="image" alt="Hexagonal 6" /></td>
<td><img src="image" alt="Cubic 23" /></td>
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<tr>
<td><img src="image" alt="Trigonal 3" /></td>
<td><img src="image" alt="Hexagonal 6" /></td>
<td><img src="image" alt="Cubic -" /></td>
<td></td>
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<tr>
<td><img src="image" alt="Trigonal -" /></td>
<td><img src="image" alt="Hexagonal 6/m" /></td>
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<td><img src="image" alt="Trigonal 32" /></td>
<td><img src="image" alt="Hexagonal 622" /></td>
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<td><img src="image" alt="Trigonal 3m" /></td>
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</table>
7 Crystal Systems

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>External Minimum Symmetry</th>
<th>Unit Cell Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>None</td>
<td>a, b, c, al, be, ga,</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>One 2-fold axis,</td>
<td></td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>Three perpendicular 2-folds</td>
<td>a, b, c, 90, 90, 90</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>One 4-fold axis, parallel c</td>
<td>a, a, c, 90, 90, 90</td>
</tr>
<tr>
<td>Trigonal</td>
<td>One 3-fold axis</td>
<td>a, a, c, 90, 90, 120</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>One 6-fold axis</td>
<td>a, a, c, 90, 90, 120</td>
</tr>
<tr>
<td>Cubic</td>
<td>Four 3-folds along space diagonal</td>
<td>a, a, a, 90, 90, 90</td>
</tr>
</tbody>
</table>
The combination of all available symmetry operations (point groups plus glides and screws) within the seven crystal systems equals 230 combinations, called the 230 Space Groups. The International Tables list those by symbol and number, together with symmetry operators, origins, reflection conditions, and space group projection diagrams.

Inversion symmetry elements are not allowed when dealing with protein crystals (all amino acids present in proteins have the L stereochemical configuration; the inverse, the D configuration, can’t be found in proteins.) Therefore, the number of space groups is reduced from 230 for small molecules to 65 for proteins.
Identification of the Space Group is called **indexing** the crystal. The International Tables for X-ray Crystallography tell us a huge amount of information about any given space group. For instance, if we look up space group P2, we find it has a 2-fold rotation axis and the following symmetry equivalent positions:

\[
\begin{align*}
&x, y, z \\
&-x, y, -z
\end{align*}
\]

and an asymmetric unit defined by:

\[
\begin{align*}
&0 \leq x \leq 1 \\
&0 \leq y \leq 1 \\
&0 \leq z \leq 1/2
\end{align*}
\]

An interactive tutorial on Space Groups can be found on-line in Bernhard Rupp’s Crystallography 101 Course: [http://www-structure.llnl.gov/Xray/tutorial/spcgrps.htm](http://www-structure.llnl.gov/Xray/tutorial/spcgrps.htm)