Chapter 3

3.1 General Remarks

What do we mean by the word "symmetry?" You have a qualitative feel for the term, but there is a more technical, quantitative measure as well. We'll begin with the question: which of the following drawings is most symmetrical?

It probably took you only a few seconds to select the first one. With this in mind, what is a good, non-mathematically based definition that would work here? I'll propose that symmetry is the presence of repeating patterns within an object or group of objects: the more repetition, the more symmetrical the object.

3.2 Symmetry Elements and Operations

A symmetry operation is the movement of an object such that the object before the operation is indistinguishable from it after the operation. For example, if a square is rotated 90º, 180º, or 270º about its center (in the plane it occupies) you couldn't tell the rotation occurred.

A symmetry element is the geometric entity about which the symmetry operation occurs. In the previous example, the symmetry element was a line perpendicular to the plane of the paper, passing through the center of the square.

Not surprisingly, symmetry elements and operations always occur together. For single objects, the element always passes through the center of the item. There are only 5 such element/operation pairings required to describe the symmetry of any object. The first is *E*, the identity element. The element is a point in the center of the molecule about which nothing is done.

3.3 Symmetry Planes and Reflections

A reflection through a symmetry plane transports everything on each side of the plane to the other side along its perpendicular to the plane. The distance from the plane is the same before and after the reflection. Objects in the plane do not move. A reflection is represented by the Greek letter σ. All planar molecules contain a symmetry plane.

Generalities

If a molecule contains a symmetry plane, there must be an even number of each type of atom/group not in the plane. Repeating a reflection regenerates the original molecule. This is the equivalent to *E*, the identity operation, in which molecule remains unchanged. If there is only one of any atom, then all planes for that molecule must pass through that atom.

How many planes do the following molecules possess? $HC\equiv CH$, H_2O, NH_3, CH_4, SF_6 Are the planes in any way related to one another? If so, how?

3.4 Inversion Center

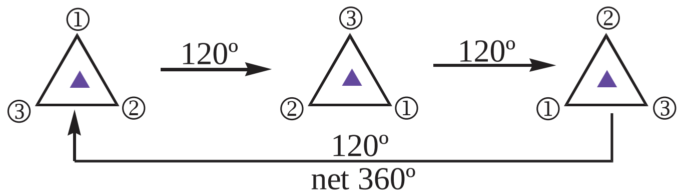
If each molecule in an atom were given Cartesian coordinates then inversion, *i*, would cause the following operation $(x, y, z) \rightarrow (-x, -y, -z)$.

Generalities:

Repeating an inversion regenerates the original molecule. (i.e. $i^2 = E$) Except for an atom at the center (an optional event), all atoms must come in pairs.

3.5 Proper Axes and Rotations

A proper (rotation) axis is a line passing through an object such that a rotation of the object about the line yields a form indistinguishable from the initial object. The book uses the equilateral triangle as an example. It is as good as any, and I'll use it as well. In the figure below, the blue triangle represents a C_3 rotation axis perpendicularly passing through the plane of the paper.

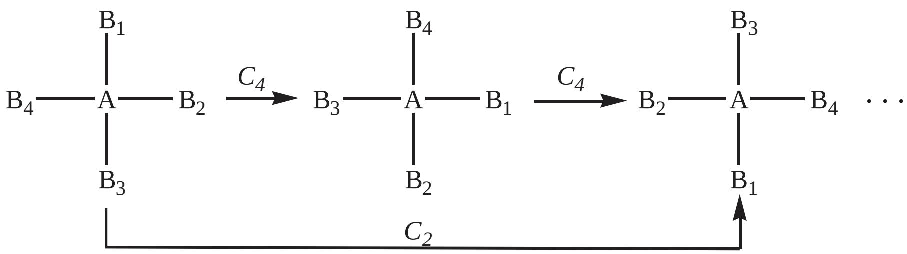


Rotation axes are designated by C_n, where n is the order of the axis. The book defines n as "the largest value of n such that rotation through $\frac{2\pi}{n}$ gives an equivalent configuration." The definition that I find more convenient to use is the minimum n to regenerate the original image. In the above example, 3 x 120º gives back the original image, so the axis is C_3.

The operations are represented as follows: 120º = C_3, 240º = C_3^2, 360º = $C_3^3 = E$. Thus, there are n operations associated with each C_n axis.

Species on a proper axis remain unchanged by a rotation. There must be n of each thing not on an axis for a C_n axis to exist. For example, in ammonia a C_3 axis passes through the lone pair and nitrogen atom. There are 3 identical hydrogen atoms equidistant from the axis and spatially equivalent.

By convention, operations of higher order are reduced when possible. The book works C_6 for you. I'll start with C_4. The operations possible for C_4 are C_4, C_4^2, C_4^3, and $C_4^4 = E$. But C_4^2 = C_2.



Thus, C_4, C_4^2, C_4^3, and C_4^4 becomes C_4, C_2, C_4^3, E.

Examples of other rotation axes include C_2 (H_2O, CH_2Cl_2), C_3 (NH_3, *mer*-$CrCl_3 \cdot 3H_2O$), C_4 ($PtCl_4^{2-}$), C_5 ($C_5H_5^-$), C_6 (C_6H_6), and C_∞ (CO_2). Locate the listed axis for each of these species.

As the discussion above shows, molecules may have more than one type of axis. In the C_4 example, a C_2 and C_4 were coincident, but this need not be the case. For example, in benzene, there are coincident C_6, C_3, and C_2 axes, but also 6 C_2 axes perpendicular to the first group. Try to find them.

An interesting aside is that a molecule may not possess only two C_2 axes, but more or fewer are possible. (see p. 30 of the book or p. 7 of the notes)

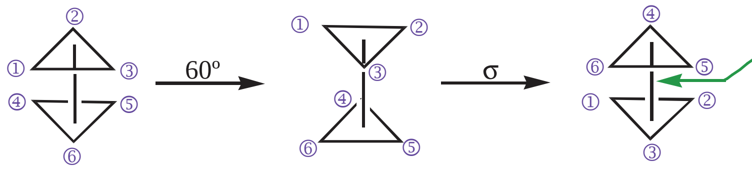
On page 26 the book describes, at great length, the interrelationship of planes and proper axes. Generally, these things may be found by inspection and after some practice become intuitive. Personally, I find these rules cumbersome. Use them if you wish, and ask about them in class.

3.6 <u>Improper Axes and Improper Rotations</u>

An <u>improper rotation</u> axis is one about which an object is rotated then reflected through a plane perpendicular to the rotation axis (or vice-versa, the order does not matter). It is designated S_n, where n carries a similar meaning to n in C_n. Note that S_n may exist where C_n

and/or σ do not.

Let's use the example in the book.



The S_3 in this example is coincident with a C_3. This occurs frequently. A good place to look for an S_n axis is overlapping a C_n axis. As you'll see shortly, all even S_n axes have coincident $C_{n/2}$ axes.

An improper axis generates operations S_n, S_n^2, S_n^3, …, S_n^n. These can frequently be reduced to other operations. For example, every other operation the σ planes cancel each other. There are two scenarios for S_n. n = even or odd. Unique (ie. non-convertible) S_n axes appear in blue.

<u>*n* even</u>

Let n = 6 then S_6, S_6^2, S_6^3, S_6^4, S_6^5, and S_6^6

S_6= turn 60º and reflect = unique

S_6^2 = turn 120º and reflect twice = turn 120º = C_3

S_6^3 = turn 180º and reflect 3 times = i = S_2

S_6^4 = turn 240º and reflect 4 times = C_3^2

S_6^5 = turn 300º and reflect 5 times = unique

S_6^6 = turn 360º and reflect 6 times = E

Thus for S_n (n = even), there will always be a $C_{n/2}$ axis. (Recall the previous example.)

n = odd

Let n = 5 then S_5, S_5^2, S_5^3, S_5^4, and S_5^5

S_5 = rotate 72º and reflect once = unique

S_5^2 = rotate 144º and reflect 2 times = C_5^2

S_5^3 = rotate 216º and reflect 3 times = unique

S_5^4 = rotate 288º and reflect 4 times = C_5^4

S_5^5 = rotate 360º and reflect 5 times = σ

This means that if S_n (n = odd) exists C_n and σ must also exist independently. Note that S_5^7 and S_5^9 are also important and unique.

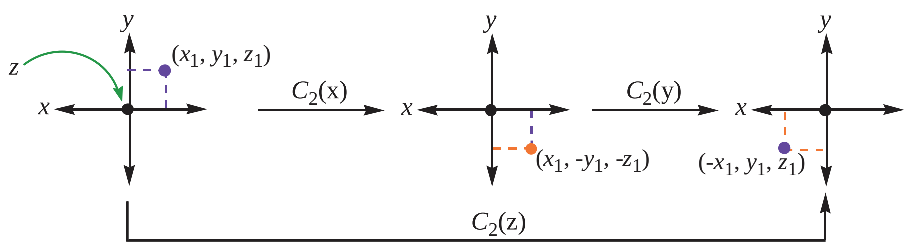
3.7 Products of Symmetry Operations

We just finished discussing the physical operations and elements necessary for describing the symmetry of everything: E, σ, i, C_n, S_n. The last element provides a nice lead-in to this section.

S_n results from the consecutive application of two symmetry operations: C_n then σ (or the reverse). This can be expressed as $\sigma C_n = S_n$ where C_n is carried out first. In general, YX = Z means carry out X, then Y, which is the same as Z. **In general, the order of the operations matters.** The consecutive application of operations is called a product, and if the order of application doesn't matter, they are said to commute.

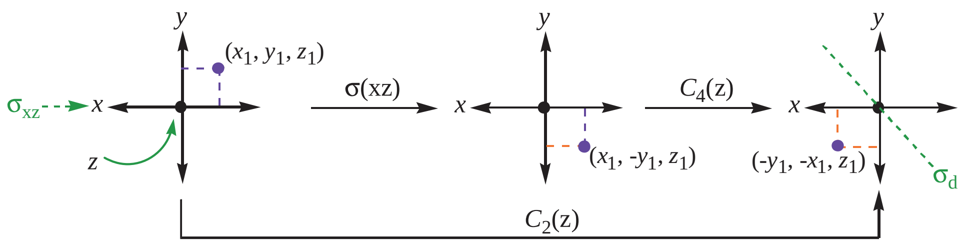
As you saw some products of C_n and σ led to other symmetry elements such as *i*. Your book works several examples using coordinates. An important consequence of these examples is the demonstration that, typically, the product of two operations is a third, different operations. I'll work a couple of the examples pictorially (blue denotes a positive coordinate, red is negative).

$C_2(\mathrm{x})C_2(\mathrm{y}) = C_2(\mathrm{z})$



This proves that if two C_2 exist in an object, a third C_2 must also exist (*cf*. bottom of p. 24 of the book, p. 4 of the notes).

$C_4(\mathrm{z})\sigma(\mathrm{xz}) = \sigma_\mathrm{d}$

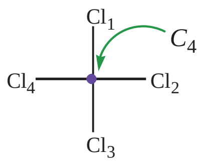


On p. 31 the book suggests trying $C_4(\mathrm{z})C_2(\mathrm{y}) = C_2(\mathrm{xy}) = C_2'$. Try it with pictures if you have trouble.

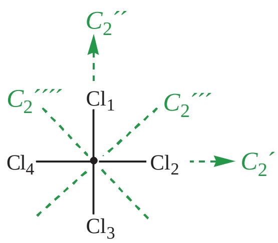
3.8 Equivalent Symmetry Elements and Equivalent Atoms

Equivalent symmetry elements or atoms are those that may be carried into each other by (other) symmetry elements in the molecule. The book's language may be a little hard to follow, and examples may be a better way to explain this. Consider O_2. Chemically the oxygen atoms are identical. Rotating the molecule 180º about a perpendicular axis passing through the bond midpoint causes the atoms to exchange positions. The atoms are thus equivalent by symmetry. In the same way, if the operations/elements in a molecule are displayed, any that can be moved to overlay another using other symmetry operations are equivalent. A couple of examples are shown below.

Consider $PtCl_4^{2-}$:



The C_4 will interconvert all 4 chlorine ions, so all are equivalent.



C_4 also interconverts C_2' and C_2'' so these operations are equivalent, as are C_2''' and C_2'''', but the first two operations are <u>not</u> equivalent to the second two.

3.9 General Relations among Symmetry Elements/Operations

Read on your own. These probably aren't worth committing to memory.

3.10 Symmetry Elements and Optical Isomerism

At this point your book gives a definition worth noting. You are used to thinking of chiral molecules as asymmetric. This is not always the case however (a spiral for example). Thus the definitions:

<u>dissymmetric</u> – molecules not superimposable on their mirror images.

<u>asymmetric</u> – having no symmetry (only the operation *E* is present)

A molecule having no improper axis, inversion center, or symmetry plane is dissymmetric (chiral). The book goes into great detail about this, but all you really need to remember is this rule.

3.11 Symmetry Point Groups

This section begins by demonstrating that the symmetry elements/operations found within molecules actually do form a group and then goes on to describe the different types of point groups, building up from those with only the identity to those with increasingly large numbers of elements. It will be important for you to know the various point groups, but you can see the same information laid out more succinctly in Appendix IIA (in the book and the insert in the back cover).

One useful assignment that both the book and I recommend is to take a group (say D_{3h} (ethane eclipsed) or D_{3d} (ethane staggered)) and show how elements interchange.

3.12 Symmetry with Higher Order Multiple Axes

All of the groups discussed in the previous section share in common that there is, at most, one unique C_n axis where n > 2. It turns out there are only 5 shapes, the Platonic solids, that allow multiple higher-order C_n axes. These are the only polyhedra that can be formed from sides made of only 1 regular polygon (e.g. equilateral triangle). The book provides a simple proof of this. From these shapes, one can derive 3 high order, high symmetry groups, and 4 somewhat lower order/symmetry groups. These all have multiple, non-coincident axes that are C_3 and higher.

There are 3 point groups based on the tetrahedron T_d, T_n, and T (decreasing symmetry). Two are based on the octahedron (O_h , O) and one on the icosahedron (I_h, I). The book does a nice job of taking you through how they are made.

3.13 Classes of Symmetry Operations

In order for 2 elements to be members of the same class they must be the same type of element, e.g. C_n or σ or S_n, etc. To be in the same class those elements must be equivalent (i.e.

interchangeable by a 3rd operation). The book works an example on page 52. Some general points include (i) only C_n , S_n, σ_v can be in classes with multiple elements, (ii) axes will tend to pair in classes, and (iii) there may be more than two σ planes in a class (e.g. in C_{3v}). The importance of this occurs in character tables (the tables appearing in Appendix IIA) where operations in the same class are grouped together. That is, instead of listing them separately, they are preceded by a coefficient (e.g. in the point group C_{3v} instead of C_3 and C_3^2 one finds $2C_3$).

3.14 A Systematic Procedure for Symmetry Classification of Molecules

There is a narrative here, but make sure you go over and learn the flow chart on p. 56.

3.15 Illustrative Examples:

Make sure you go over these.