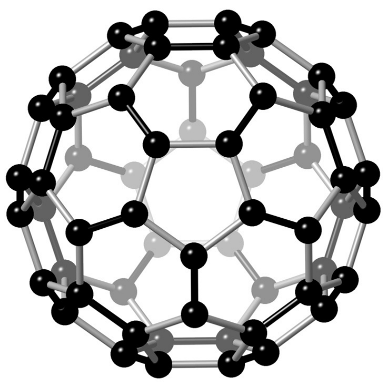
CHEMISTRY 673

Intro. to Symmetry and Group Theory in Chemistry



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- ★ This course is for 2 or 3 credits.
- ★ Lecture: 2 × 75 min/week; TTh 12:45 - 2:00, Room 2121
- ★ There will be three equally weighted exams. 2 credit students will take two exams, 3 credit students will take a “Final” worth the same as each of the first two.
- ★ 3 credit students will remain for the 3rd module of the course.

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- ★ Grades will be based on the homework (roughly 33%), midterm and final exams
- ★ Class web site: http://www.chem.tamu.edu/rgroup/hughbanks/courses/673/chem673.html

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Required Books, etc.

- ★ "Molecular Symmetry and Group Theory," by Carter, Wiley, 1998.
  - close to the right level but only loosely followed
  - early, my notes tend to follow Cotton, but I deviate from both in the 2nd half
- ★ "Symmetry and Spectroscopy; An Introduction...", by Harris & Bertolucci, Dover, 1989.
  - informal, supplies missing physical background (goes further than I will, useful for Chem 634)

Other Books

- ★ "Chemical Applications of Group Theory" by F. Albert Cotton.
  - An alternative textbook – level is similar to Carter; you can use this as long as you can occasionally get access to Carter's book
- ★ "Group Theory and Quantum Mechanics" by Tinkham. (A Dover book.)
  - More difficult than Cotton, but probably the most accessible of books written for physicists
  - Has a chapter on solids, band theory (**k**-space)

Prerequisites

- ★ Undergraduate chemistry courses, especially inorganic and physical chemistry
- ★ Usual math courses for scientists, especially linear algebra.
- ★ No linear algebra? Familiarity with vectors and matrices acquired elsewhere (handouts!) may suffice — don't wait to review these topics, do so this week! - *Minimum* background: Appendix in Cotton's text.

Reading

- ★ Please try to keep ahead in reading
- ★ This will allow me to avoid much mathematical detail in class. This is desirable because theorems and proofs become tedious - even when obvious!
- ★ Download and read the material on Determinants and Matrices from the web.

First Problem Sets

- The first two problem sets, #1a and #1b, are posted on the class web site.
- Problem Set 1a is math. I won't spend much time on it, but I'm willing to reserve a room for Thursday night to help out people who are feeling lost.
- The grading weights on the problem sets are anticipated to be: 1a: 3%, 1b – 5: 6% each, 33% total.

What is Group Theory?

★ A fairly "recent" branch of mathematics. Early principles were developed by Évariste Galois (killed in a duel in 1832 at age 20), and Niels Abel (died in 1829 at age 26 of TB).

★ First formal definition of a group was given by Cayley in 1854. Cayley, Hamilton, and Sylvester laid out fundamentals of matrices matrix groups.

★ Fedorov: application to crystallography.

Fedorov

★ 1890: Fedorov developed the mathematical technique for expressing combinations of symmetry operations; this led to his proof of 230 space groups.

★ Fedorov died in 1919 during the Russian civil war (revolution) of pneumonia/starvation.

Evgraf Stepanovich Fedorov
1853 - 1919

Schönflies

★ 1891: Independently of Fedorov, Schönflies used group theory to prove that there are exactly 230 space groups of symmetries governing crystal structures (in "Krystallsysteme and Krystallstruktur") and introduced the Schönflies symbols there.

Arthur Moritz Schönflies
1853 - 1928

... What's Beyond?

- ★ In 1873, Marius Sophus Lie began research into the theory of 'Lie groups' (continuous groups only peripherally alluded to in this course).
  - "At that time, mathematicians felt that they had finally invented something of no possible use to natural scientists. However..." Robert Gilmore, Lie Groups Lie Algebras and Some of Their Applications
- ★ Group Theory is the closest many chemists get to truly "modern" mathematics.

Properties of Groups

- ★ Closure: "product" of any two group elements (operations) is a group element (operation), including squares
- ★ One element, the identity, commutes with all others
- ★ Associative property holds (commutative property does not necessarily hold)
- ★ Every element (operation) has an inverse — which is also a group element (operation)

Simple Examples

- ★ The integers, under the operation of addition?
- ★ The integers, under the operation of multiplication?
- ★ Relevant Example: A simple symmetry group, C_{2v}
  - what are the elements (operations)?
  - how do we define a product?

Another Relevant Example: Rotation Matrices

- Claim: The set of all 2×2 matrices of the form

$$\begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

forms an continuous, infinite-order group, where the product is assumed to be defined by the usual definition of matrix multiplication.

- Proof ? Geometric Interpretation?
- The group is called $SO(2)$, the *S*pecial *O*rthogonal Group of order 2

Symmetry Elements vs. Operations

- ★ Mathematically, the members of a group are called "elements"
- ★ In symmetry groups these "elements" are called "operations" - the term "element" is reserved for something else:
- ★ The term "symmetry element" refers to a geometrical entity (a point, a line or axis, or a plane) about which the operation is defined.

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The Symmetry Operations

★ Reflection (in a *plane*)	σ
★ Inversion (through a *point*)	i
★ Rotation (about a *proper axis*)	C_n
- through an angle $2\pi/n$	
★ Improper Rotation	S_n
(about an *improper axis*)	
★ Identity (do nothing)	E

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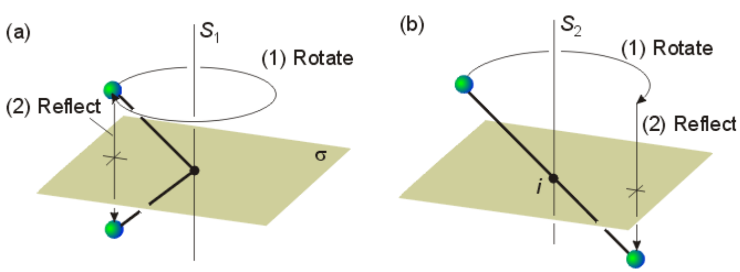
S_1 , S_2 are just σ and i



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Defining Properties

- ★ The product of any two elements in the group and the square of each element must be an element in the group.
- ★ One element in the group must commute with all others and leave them unchanged.
- ★ The associative law of multiplication must hold

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Defining Properties, cont.

- Every element must have a reciprocal, which is also an element of the group.
- The reciprocal of a product of two or more elements is equal to the product of the reciprocals, in reverse order.

$$(\mathcal{AB})^{-1} = \mathcal{B}^{-1}\mathcal{A}^{-1}$$
$$(\mathcal{ABC})^{-1} = \mathcal{C}^{-1}\mathcal{B}^{-1}\mathcal{A}^{-1}$$

$$(\mathcal{AB})\mathcal{B}^{-1}\mathcal{A}^{-1}$$
$$\mathcal{A}(\mathcal{BB}^{-1})\mathcal{A}^{-1}$$
$$= \mathcal{AA}^{-1} = E$$

Multiplication Tables, Rearrangement Theorem

- Each row and each column in the group multiplication table lists each of the group elements once and only once. (Why must this be true?) From this, it follows that no two rows may be identical. Thus each row and each column is a rearranged list of the group elements.

Subgroups

- A subgroup is a "group within another group"- a subset of group elements. A supergroup is a group obtained by adding new elements to a group (to give a larger group).
- The order of any subgroup g of a group of order h must be a divisor of h:

$$h/g = k \quad \text{where } k \text{ is an integer}$$

Similarity Transforms, Classes

- $\mathcal{A}$ is said to be **conjugate** with $\mathcal{B}$, if there exists any element of the group, $\mathcal{X}$, such that

$$\mathcal{A} = \mathcal{X}^{-1}\mathcal{B}\mathcal{X}$$

(i) Every element is conjugate with itself.

(ii) If $\mathcal{A}$ is conjugate with $\mathcal{B}$, then $\mathcal{B}$ is conjugate with $\mathcal{A}$.

(iii) If $\mathcal{A}$ is conjugate with $\mathcal{B}$ and $\mathcal{C}$, then $\mathcal{B}$ and $\mathcal{C}$ are conjugate with each other.

Classes, cont.

- A complete set of elements that are conjugate to one another within a group is called a *class* of the group. The number of elements in a class is called its *order*.
- The orders of all classes must be integral factors of the order of the group.