

## Week 1

# A Rigorous Definition of Symmetry

### 1.1 Symmetry: Symmetry Elements and Operations

- 9/28:
- Dr. Anna Wuttig (AH-nuh WUH-tig).
    - Teaches exclusively on the blackboard.
    - Will record lectures, however; if there is a technical error, she will upload last year's lecture.
  - Syllabus.
    - PSets graded on completion, not accuracy.
    - Two exams: One on the first half of the course; one on the second half of the course.
      - Cumulativeness: You'll need to understand the first half to do the second half, but there won't be questions specifically targeted to first-half material.
    - No final.
    - Participation. Showing up to class and working in groups.
  - Chris, Dan, Amy, Matt, Jintong, Yibin, Ben, Sara, Ryan, Joe, Owen, Isabella, Pierce are the people.
    - People come from a diversity of chemistry subfields (physical, inorganic, organic, materials, biological).
  - Every day will have a handout that we will write on (in pencil).
  - Study the learning objectives!
  - (Local) symmetry of a molecule helps us predict and describe bonding, spectroscopic properties, and reactivity.
    - We describe symmetry with group theory.
  - **Symmetry operation:** An operation which moves a molecule into a new orientation equivalent to its original one (geometrically indistinguishable).
    - Symmetry operations that can be applied to an object always form a **group**.
  - **Symmetry element:** A point, line, or plane about which a symmetry operation is applied.
  - Symmetry operations.
    1. Identity operation ( $E$ ): Do nothing; null operation.
    2. Reflection through a plane ( $\sigma$ ): Subdivided into...

- $\sigma_d$ : dihedral mirror planes, which contain the principle  $C_n$  axis and bisect the angles formed between adjacent  $C_2$  axes;
  - $\sigma_h$ : horizontal mirror planes, in which the mirror plane is perpendicular to the principal  $C_n$  axis;
  - $\sigma_v$ : vertical mirror planes, which contain the  $C_n$  axis and are not dihedral mirror planes.
3. Rotation about an axis ( $C_n$ ): A clockwise<sup>[1]</sup> rotation about the  $C_n$  axis.
  4. Improper rotation ( $S_n$ ): A two-step symmetry operation consisting of a  $C_n$  followed by a  $\sigma$  that is perpendicular to  $C_n$  (i.e.,  $\sigma_h$ ).
  5. Inversion ( $i$ ): Take any point with coordinates  $(x, y, z)$  to  $(-x, -y, -z)$ .
- To describe the operations, we'll introduce **stereographic projections**.



Table 1.1: Symbols for stereographic projections.

- We have a working area (the plane of the page is the  $xy$ -plane). It is useful to draw quadrants.
- We describe a general point which experiences our symmetry operation.
  - When the point reflects through the working area, we denote the image with an “X” instead of a circle.
- We need a gear symbol in the middle for rotations and improper rotations (see Table 1.1).
  - Must stereographic projections be drawn one at a time because it seems that the squares should not be in a reflection?
  - No — the symbols are to help us and should be included somewhere, but there are no hard-and-fast rules.
- Stereographic projections for each of the five elementary symmetry operations.

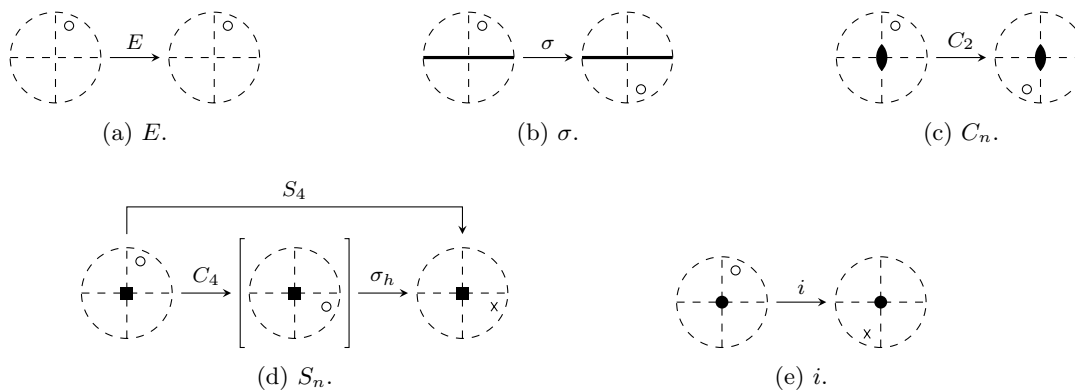


Figure 1.1: Stereographic projections of the elementary symmetry operations.

- Principal  $C_n$  axis: The  $C_n$  axis for which  $n$  is the highest.
  - In a stereographic projection, the  $C_n$  axis is the one that is perpendicular to the working area (goes in/out of the page).

<sup>1</sup>Really?

- Example: Give the symmetry elements of  $\text{NH}_3$ .
  - $C_3$  axis, 3  $\sigma_v$  mirror planes (denoted  $\sigma_v$ ,  $\sigma'_v$ , and  $\sigma''_v$ ).
  - The symmetry operations are  $E$ ,  $C_3$ ,  $C_3^2$ ,  $\sigma_v$ ,  $\sigma'_v$ , and  $\sigma''_v$ . These operations form the  $C_{3v}$  point group.
- Direct products of symmetry operations:  $YX = Z$  means “operation  $X$  is carried out first and then operation  $Y$ ,” giving the same net effect as would the carrying out of the single operation  $Z$ .
  - If  $YX = XY = Z$ , then the two operations  $Y$  and  $X$  commute.
- What is the direct product of  $C_2$  and  $\sigma_h$ ?
  - $\sigma_h C_2 = S_2 = i$ . They do commute.
- Do  $C_4$  and  $\sigma_{x,z}$  commute? Take the plane of this page as  $xy$ .
  - They do not (determine by drawing out both sets of stereographic projections).
- Don't get careless, Steven. This is easy, but it's also easy to make easy mistakes.
- New symmetry operations *of your group* are generated by taking the direct product of two.

## 1.2 Point Groups

9/30:

- The symmetry operations that apply to a given molecule collectively possess the properties of a mathematical **group**.
- **Group**: A set of symmetry operations that satisfy the following conditions.
  - *Closure*: All binary products must be in the group, i.e., the product of any two operators must also be a member of the group.
  - *Identity*: Must contain an identity, i.e.,  $E$  must be part of the group.
  - *Inverse*: All elements must have an inverse in the group, and they must commute with their inverse.
  - *Associativity*: The associative law  $(A \cdot B) \cdot C = A \cdot (B \cdot C)$  must hold.
- **Abelian** (group): A group in which all direct products commute.
  - Not all groups are Abelian.
- Question: Do  $C_3$  and  $\sigma_v$  form a group?
  - No: No identity (for example).
  - Wuttig draws out a stereographic projection for  $C_3 \cdot \sigma_v$  and overlays the first and last picture, showing that  $C_3 \cdot \sigma_v$  is a reflection over a new mirror plane  $\sigma'_v$ .
  - $C_3$  and  $\sigma_v$  do **generate** the set of operations  $E, C_3, C_3^2, \sigma_v, \sigma'_v, \sigma''_v$ , which collectively form the **point group  $C_{3v}$** .
- To prove something on a pset or exam, it's probably a good idea to do it in terms of stereographic projections!
- **Point group**: A group such that at least one point in space is invariant to all operations in the group.
- **Group order**: The number of symmetry operations in the group. *Denoted by  $h$* .
- Table activity: Finding  $E$ , principal  $C_n$ ,  $\sigma$ ,  $C_2 \perp C_n$ ,  $C_n$  position relative to  $\sigma$  (collinear or perpendicular), and  $i$  for various point groups.

- These properties are the ones that distinguish each point group from every other point group.
- Notes on the pedagogy: Animations and/or tangible models should be used to discuss this stuff. PowerPoint slides are definitely the way to go — far more tangible tools; blackboard should be a supplement. It is key to be careful what you say (*element* and *operation* must be consistently used). Dr. Wuttig glides over several things (like naming point groups).
- Developing a flow chart that distinguishes between  $D_{nh}$ ,  $D_{nd}$ ,  $D_n$ ,  $C_{nh}$ ,  $C_{nv}$ ,  $C_n$ , and  $S_n$ .