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 (σ): Subdivided into...

    - σ_d: dihedral mirror planes, which contain the principle C_n axis and bisect the angles formed between adjacent C_2 axes;
    - σ_h: horizontal mirror planes, in which the mirror plane is perpendicular to the principal C_n axis;
    - σ_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[1] rotation about the C_n axis.
4. Improper rotation (S_n): A two-step symmetry operation consisting of a C_n followed by a σ that is perpendicular to C_n (i.e., σ_h).
5. Inversion (i): Take any point with coordinates (x, y, z) to $(-x, -y, -z)$.

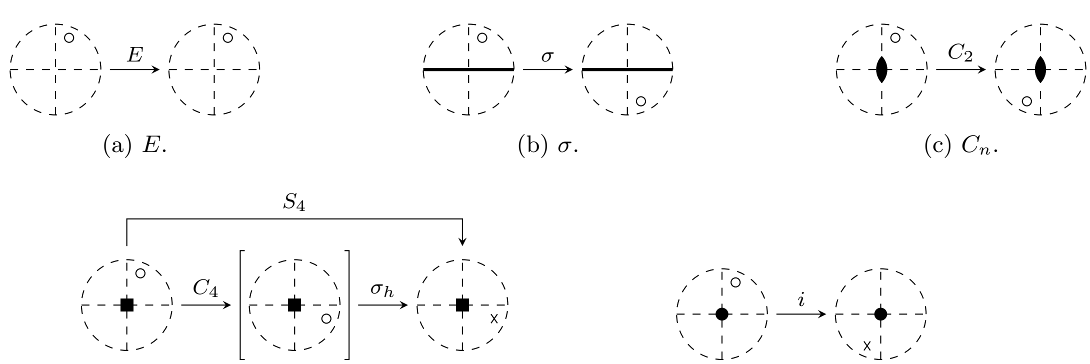
- To describe the operations, we'll introduce **stereographic projections**.

(a) Rotations. (b) Improper rotations.

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.



(a) E. (b) σ. (c) C_n. (d) S_n. (e) i.

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).

[1] Really?

- Example: Give the symmetry elements of NH_3.
  - C_3 axis, 3 σ_v mirror planes (denoted σ_v, σ_v', and σ_v'').
  - The symmetry operations are E, C_3, C_3^2, σ_v, σ_v', and σ_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 σ_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 σ_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 σ_v'.
  - C_3 and σ_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 $\boldsymbol{C_{3v}}$**.
- 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. *Given by $\boldsymbol{h}$.*
- Table activity: Finding E, principal C_n, σ, $C_2 \perp C_n$, C_n position relative to σ (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 is skipping a lot of key points (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.