

# Topic I

## Review of VSEPR Theory

### I.1 Module 1: Course Logistics and History

- 1/11:
- Homework questions will be similar to exam questions, so although you probably *can* find answers online, you shouldn't.
  - Submit Psets to chem201hw@gmail.com.
  - Watch modules before office hours and bring questions.
  - If you have a question outside of office hours, post it on Slack.
  - It's a difficult class, but he is open to and welcomes our feedback (via Slack, again).
  - You do need to read from Miessler et al. (2014), too; his class is not a replacement for this textbook.
    - He is a big fan of Cotton (1990).
    - There is an extra, new textbook to look for!
  - Convince yourself not to be afraid of time-independent quantum mechanics (we won't go too deep, but know wave functions and the like).
  - Exams will probably be open book/open note.
  - Inorganic chemistry contains too much information to rationalize empirically, so we need a system (the development of this system will be the focus of this course).
  - Reviews history of chemistry from Miessler et al. (2014) Chapter 1.
  - What is Nickel's electron configuration?
    - When Nickel is a free atom, the  $[\text{Ar}]4s^23d^8$  electron configuration is the lowest energy.
    - When Nickel is chemically bound, the  $[\text{Ar}]3d^{10}$  electron configuration is the lowest energy because it is energetically unfavorable to have a large 4s orbital pushing the bounds of the atom.
    - What is a **term symbol**?
  - Homework: Refresh Chapter 2 in Miessler et al. (2014).
  - **Covalent bond**: The sharing of pairs of electrons...?
  - G. N. Lewis predicts in 1916 (before Rutherford) that the atom has a positive **kernel** surrounded by a shell containing up to 8 electrons.
    - Also orbital penetration.
    - He recommends that we read the full paper: Lewis (1916).

## I.2 Module 2: Molecular Geometries and VSEPR

- The easiest way to approach a new Lewis structure:
  1. Draw a valid Lewis structure for a molecule.
  2. Place electron pairs in the valence shell as far away from each other as possible. Use the  $\sigma$ -bond framework first.
  3. Add  $\pi$ -bonds to complete the molecule.
- Through the VSEPR approach, think of a molecule as arranged around a central atom  $A$  by  $m$  atoms or groups of atoms  $X$  and  $n$  lone electron pairs  $E$ .
- **Steric number:** The sum  $n + m$  of groups and electron pairs around the central atom.
- Steric numbers correspond to geometries.
- VSEPR is ok but it doesn't capture reality too well.
- Consider trimethyl boron ( $\text{BMe}_3$ ).
  - Trigonal planar ( $D_{3h}$ ).
- Octahedral:  $O_h$ .
- Bent:  $C_{2v}$ .
- **Order of the repulsive forces:** lone pair - lone pair  $>$  lone pair - bonding pair  $>$  bonding pair - bonding pair.
- In  $\text{SF}_4$  (see-saw), will the lone pair be axial or equatorial?
  - Equatorial —  $2 \times 120^\circ$  and  $2 \times 90^\circ$  vs.  $3 \times 90^\circ$ .
- In  $\text{BrF}_3 \dots$

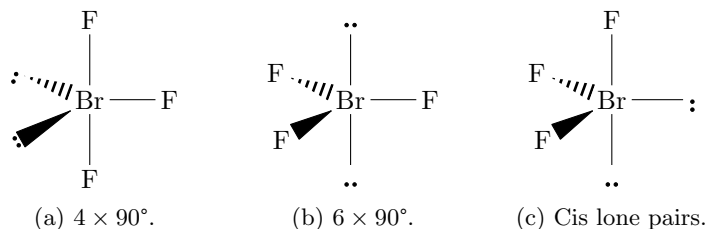
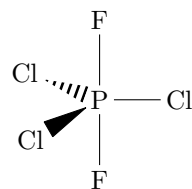


Figure I.1: VSEPR structure of  $\text{BrF}_3$ .

- T-shaped —  $4 \times 90^\circ$  vs.  $6 \times 90^\circ$  or lone pairs in cis-position.
- In ions such as  $\text{ICl}_4^-$ , we get square planar ( $D_{4h}$ ).
- With mixed substituents (such as  $\text{PF}_2\text{Cl}_3$ )...
  - We need **Bent's rule**, which tells us that atoms share electrons from  $p$ - or  $d$ -orbitals to a greater extent than they do from  $s$ -orbitals.
  - Thus, when phosphorous excites  $3s^2 3p^3$  to  $3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{z^2}^2$  and then rehybridizes to create three  $sp^2$  orbitals (each composed of  $s + p_x + p_y$ ) and two " $pd$ " hybrid orbitals (each composed of  $p_z + d_{z^2}$ ), the equatorial  $sp^2$  orbitals bond to the more **electropositive** chlorines and the axial " $pd$ " hybrid orbitals bond to the remaining more electronegative fluorines.
- **Bent's rule:** Atomic  $s$ -character concentrates in orbitals directed toward electropositive substituents.

Figure I.2: Lewis structure of  $\text{PF}_2\text{Cl}_3$ .

- **Electropositive** (species): A species that has relatively lower electronegativity than another.
- For molecules with multiple bonds, ignore  $\pi$ -bonds.
- Linear:  $D_{\infty h}$ .
- Problems with VSEPR:
  - $\text{XeF}_6$  with 14 bonding electrons (7 pairs) is supposed to be pentagonal bipyramidal, but is actually octahedral (a known problem for  $14e^-$  systems).
  - Heavy main group elements with no hybridization.
    - $\text{H}-\text{C}\equiv\text{C}-\text{H}$  is linear, but  $\text{H}-\text{Si}\equiv\text{Si}-\text{H}$  is not.
    - No  $\sigma$ -bond exists in the latter species — it's all  $\pi$ -bonding interactions.
- You maybe don't have to watch the modules and textbook *and* attend class.