

# Topic I

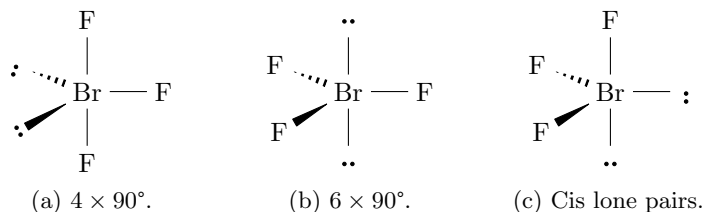
## Review of VSEPR Theory

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

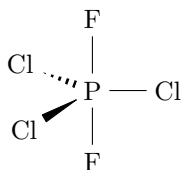
- 1/11:
- Homework questions will be similar to exam questions, so although you probably *can* find answers online, you shouldn't.
  - Submit Psets to chem201hw@gmail.com.
  - Watch modules before office hours and bring questions.
  - If you have a question outside of office hours, post it on Slack.
  - 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  $\rightarrow$  Distorted T —  $4 \times 90^\circ$  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  $\text{PF}_2\text{Cl}_3$ )...

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

- 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  $3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{z^2}^1$  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.
- There is also sometimes a tendency for symmetry.
- **Bent’s rule**: Atomic  $s$ -character concentrates in orbitals directed toward electropositive substituents.
- **Electropositive** (species): A species that has relatively lower electronegativity than another.
- For molecules with multiple bonds, ignore  $\pi$ -bonds.
- 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.

### I.3 Chapter 3: Simple Bonding Theory

From Miessler et al. (2014).

- 1/14:
- **Hypervalent** (central atom): A central atom that has an electron count greater than the atom’s usual requirement.
  - There are rarely more than 18 electrons around a central atom (2 for  $s$ , 6 for  $p$ , 10 for  $d$ ). Even heavier atoms with energetically accessible  $f$  orbitals usually don’t have more surrounding electrons because of crowding.
  - With  $\text{BeF}_2$ , instead of getting the predicted double-bonded Lewis structure, it forms a complex network with Be having coordination number 4.
    - $\text{BeCl}_2$  dimerizes to a 3-coordinate structure in the vapor phase.
  - Boron trihalides exhibit partial double bond character.
    - It is also possible that the high polarity of B–X bonds and the **ligand-close packing** (LCP) model account for the observed shorter bond length.
    - Boron trihalides also act as Lewis acids.
- 1/17:
- The variety of structures means that one unified VSEPR theory will not likely<sup>[1]</sup> work.
  - **Not stereochemically active** (lone pair): “A lone pair that appears in the Lewis-dot structure but has no apparent effect on the molecular geometry” (Miessler et al., 2014, p. 54).
  - Double and triple bonds have slightly greater repulsive effects than single bonds in the VSEPR model.
  - Multiple bonds tend to occupy the same positions as lone pairs.
  - Electronegativity varies for a given atom based on the neighboring atom to which it is bonded.

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<sup>1</sup>Eratta: “unlikely.”

1/14:

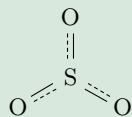
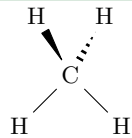
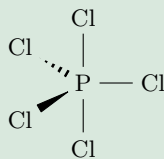
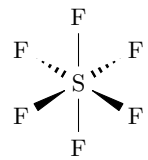
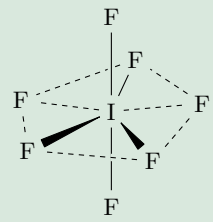
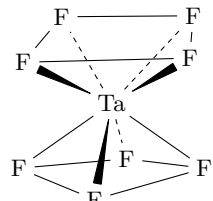
Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	CO <sub>2</sub>	180°	O = C = O
3	Trigonal (triangular)	SO <sub>3</sub>	120°	
4	Tetrahedral	CH <sub>4</sub>	109.5°	
5	Trigonal bipyramidal	PCl <sub>5</sub>	120°, 90°	
6	Octahedral	SF <sub>6</sub>	90°	
7	Pentagonal bipyramidal	IF <sub>7</sub>	72°, 90°	
8	Square antiprismatic	[TaF <sub>8</sub> ] <sup>3-</sup>	70.5°, 9.6°, 109.5°	

Table I.1: VSEPR predictions.

1/17:

- “With the exception of helium and neon, which have large calculated electronegativities and no known stable compounds, fluorine has the largest value” (Miessler et al., 2014, p. 59).
- Although usually classified with Group 1, hydrogen’s chemistry is distinct from that of the alkali metals and actually all of the groups.
- Some bond angle trends can be explained by electronegativity (see Table I.2).
  - For instance, electronegative outer atoms pull electrons away from the central atom, allowing lone pairs to further push together such atoms.
  - Electronegative central atoms pull electrons toward the central atom, pushing bonding pairs farther apart.
- Atomic size can also have effects on VSEPR predictions.

Molecule	X–P–X Angle (°)	Molecule	Bond Angle (°)
PF <sub>3</sub>	97.8	H <sub>2</sub> O	104.5
PCl <sub>3</sub>	100.3	H <sub>2</sub> S	92.1
PBr <sub>3</sub>	101.0	H <sub>2</sub> Se	90.6

Table I.2: Electronegativity and bond angles.

- For example, the C–N–C angle in N(CF<sub>3</sub>)<sub>3</sub> is larger than that of N(CH<sub>3</sub>)<sub>3</sub> despite the prediction we'd make based on electronegativity alone. This is because F atoms are significantly larger than H atoms so we get some steric hindrance.
- In molecules with steric number 5, axial bond length is greater than equatorial.
- Symmetric structures are often preferred.
- Groups (such as CH<sub>3</sub> and CF<sub>3</sub>) have the ability to attract electrons, too — thus, they are also assigned electronegativities.
- **Ligand close-packing:** A model that uses the distances between outer atoms in molecules as a guide to molecular shapes. *Also known as LCP.*
  - Works off of the observation that the nonbonded distances between outer atoms are consistent across molecules with the same central atom, but the bond angles and lengths change.
  - This contrasts with VSEPR theory's concern with the central atom, as opposed to the ligands.
- **Dielectric constant:** “The ratio of the capacitance of a cell filled with the substance to be measured to the capacitance of the same cell with a vacuum between the electrodes” (Miessler et al., 2014, p. 66).
  - This is measured to experimentally determine the polarity of molecules.
- **Dipole moment:** The product  $Qr$  of the distance  $r$  between two charges' centers and the difference  $Q$  between the charges. *Also known as  $\mu$ .*
  - This is calculated by measuring the dielectric constant at different temperatures.
  - SI unit: Coulomb meter; C m. Common unit: Debye;  $1\text{ D} = 3.335\,64 \times 10^{-30}\text{ C m}$ .