

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 σ -bond framework first.
 3. Add π -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 (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 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 BrF_3 ...

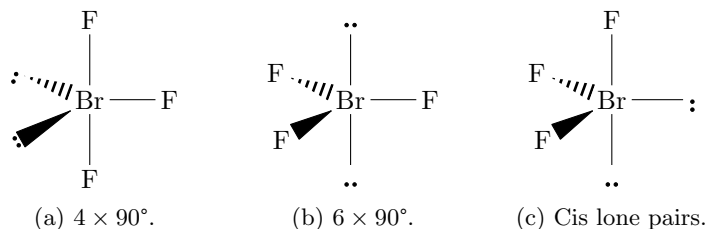
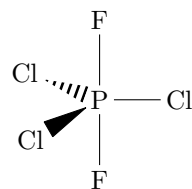


Figure I.1: VSEPR structure of BrF_3 .

- T-shaped \rightarrow Distorted T — $4 \times 90^\circ$ vs. $6 \times 90^\circ$ or lone pairs in cis-position.
- In ions such as ICl_4^- , we get square planar (D_{4h}).
- With mixed substituents (such as PF_2Cl_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 PF_2Cl_3 .

- **Electropositive** (species): A species that has relatively lower electronegativity than another.
- For molecules with multiple bonds, ignore π -bonds.
- Linear: $D_{\infty h}$.
- Problems with VSEPR:
 - 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 σ -bond exists in the latter species — it's all π -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).

I.3.1 Notes

- 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 BeF_2 , instead of getting the predicted double-bonded lewis structure, it forms a complex network with Be having coordination number 4.
 - 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 $\text{B}-\text{X}$ 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^[1] 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.

¹Eratta: "unlikely."

1/14:

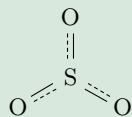
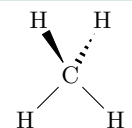
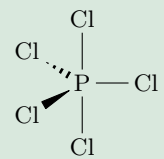
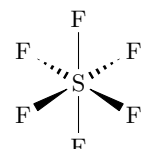
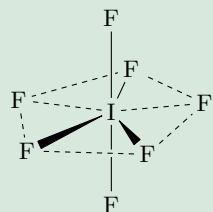
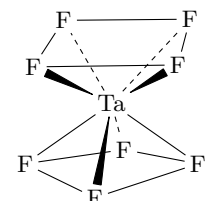
Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	CO ₂	180°	O=C=O
3	Trigonal (triangular)	SO ₃	120°	
4	Tetrahedral	CH ₄	109.5°	
5	Trigonal bipyramidal	PCl ₅	120°, 90°	
6	Octahedral	SF ₆	90°	
7	Pentagonal bipyramidal	IF ₇	72°, 90°	
8	Square antiprismatic	[TaF ₈] ³⁻	70.5°, 9.6°, 109.5°	

Table I.1: VSEPR predictions.

1/17:

- 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.
- “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.
 - 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.

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

Table I.2: Electronegativity and bond angles.

- Atomic size can also have effects on VSEPR predictions.
 - For example, the C–N–C angle in N(CF₃)₃ is larger than that of N(CH₃)₃ despite the prediction we'd make based on electronegativity alone. This is because F atoms are significantly larger than H atoms and 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 CH₃ and CF₃) 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 stands in contrast to 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 μ .*
 - This is calculated by measuring the dielectric constant at different temperatures.
 - SI unit: Coulomb meter; C m. Common unit: Debye; $1 \text{ D} = 3.335\,64 \times 10^{-30} \text{ C m}$.