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 $[\text{Ar}]4s^2 3d^8$ 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.
    - Talapin 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.

  - For molecules with multiple bonds, ignore π bonds.

- VSEPR is ok but it doesn't capture reality too well.

- Consider trimethyl boron (BMe_3).

  - Trigonal planar (D_{3h}).

- There also exist octahedral (O_h) and bent (C_{2v}) geometries. More on these symbols/shorthands later.

- **Order of the repulsive forces**: lone pair - lone pair > lone pair - bonding pair > bonding pair - bonding pair.

- We now investigate how electron-pair geometry determines structure in several molecules.

- In SF_4 (see-saw), will the lone pair be axial or equatorial?

  - Equatorial — $2 \times 120°$ and $2 \times 90°$ vs. $3 \times 90°$.

- In BrF_3:

(a) $4 \times 90°$.   (b) $6 \times 90°$.   (c) *cis*-lone pairs.

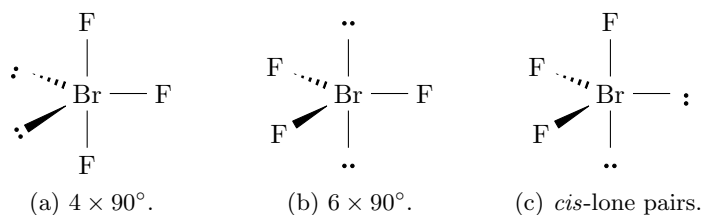Figure I.1: VSEPR structure of BrF_3.

  - T-shaped $\rightarrow$ Distorted T — $4 \times 90°$ vs. $6 \times 90°$ 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 $3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{z^2}^1$ 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.
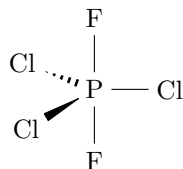
Figure I.2: Lewis structure of PF_2Cl_3.

- ■ To reiterate: By Bent's rule, *pd* hybrid orbitals more readily share electron density. Thus, atoms that are more greedy for electrons (i.e., more electronegative) will preferentially bond to these *pd* orbitals. In our example, fluorine is more electronegative than chlorine, so it will preferentially bond to the *pd* hybrid orbitals, which happen to be located axially in this case. Therefore, the fluorines bond axially. The chlorines fill the remaining vacant positions.
  - ■ We can also approach this problem from the perspective of the *s* orbitals and chlorines. Indeed, orbitals with greater *s* character are greedier/want more electron density. Thus, they will attract groups that more readily give up their electron density. In our specific example, chlorine gives up its electron density more readily than fluorine, so it will be attracted to the equatorial sp^2 hybrid orbitals.
  - – 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.

- • 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 $14\,\mathrm{e}^-$ systems).
  - – Heavy main group elements with no hybridization.
    - ■ $H-C\equiv C-H$ is linear, but $H-Si\equiv Si-H$ 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).

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 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 $B-X$ bonds and the **ligand-close packing** (LCP) model account for the observed shorter bond length.
  - – Boron trihalides also act as Lewis acids.

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 bipyrimidal	PCl_5	$120°, 90°$	
6	Octahedral	SF_6	$90°$	
7	Pentagonal bipyrimidal	IF_7	$72°, 90°$	
8	Square antiprismatic	$[TaF_8]^{3-}$	$70.5°, 9.6°, 109.5°$	

Table I.1: VSEPR predictions.

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.

- 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).

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[1]Errata: "unlikely."

- 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.

Molecule	$X-P-X$ Angle (°)	Molecule	Bond Angle (°)
PF_3	97.8	H_2O	104.5
PCl_3	100.3	H_2S	92.1
PBr_3	101.0	H_2Se	90.6

Table I.2: Electronegativity and bond angles.

  - For instance, electronegative outer atoms pull electrons away from the central atom (electron domains become more conical), allowing lone pairs to further push together such atoms.
  - Electronegative central atoms pull electrons toward the central atom (electron domains become more cylindrical), pushing bonding pairs farther apart.

- Atomic size can also have effects on VSEPR predictions.

  - For example, the $C-N-C$ angle in $N(CF_3)_3$ is larger than that of $N(CH_3)_3$ 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_3 and CF_3) 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* $\boldsymbol{\mu}$.

  - This is calculated by measuring the dielectric constant at different temperatures.
  - SI unit: Coulomb meter; C m. Common unit: Debye; $1\,D = 3.335\,64 \times 10^{-30}\,C\,m$.