5.111 Lecture Summary #12 Friday, October 3, 2014

Readings for today: Section 3.1 – The Basic VSEPR Model, Section 3.2 – Molecules with Lone Pairs on the Central Atom. (Same sections in 5th and 4th ed.)
Read for Lecture #13: Section 3.8 – The Limitations of Lewis's Theory, Section 3.9 – 3.11 – Molecular Orbitals. (Same sections in 5th and 4th ed.)

Topics: **I.** The shapes of molecules: VSEPR theory
A. Molecules *without* lone pairs
B. Molecules *with* lone pairs

I. THE SHAPES OF MOLECULES: VSEPR THEORY

The shape (_______________) of molecules influences physical and chemical properties, including melting point, boiling point, and reactivity.

Shape is particularly important in biological systems where, for example, a molecule must fit precisely into the active site of an enzyme.

VALENCE **S**HELL **E**LECTRON **P**AIR **R**EPULSION (**VSEPR)** theory can be used to predict molecular geometry with high accuracy. The theory is based on Lewis structure and the principles that

- valence electron pairs ___________ each other.
- the geometry around the central atom will be such as to <u>minimize</u> the electron repulsion.

VSEPR nomenclature:

A = ______________ atom

X = ______________ atom

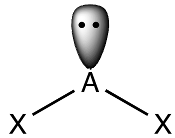
E = lone pair

General guidelines for the VSEPR model:

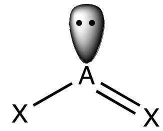
- ______________ number (SN) is used to predict geometries.

SN = (# of atoms bonded to central atom) + (# of lone pairs on central atom)

Note: When considering electron-pair repulsion, double bonds and triple bonds can be treated like single bonds. This approximation is valid for qualitative purposes.



AX_2E SN = ____



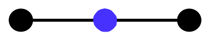
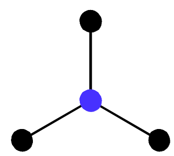
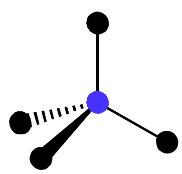
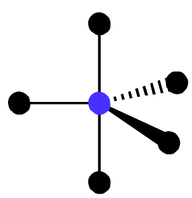
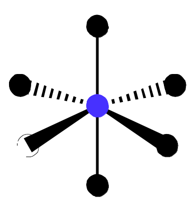
AX_2E SN = _____

Number of lone pairs and ______________ bonded to the central atom is important, not the BONDS to central atom.

- If a molecule has two or more resonance structures, the VSEPR model can be applied to any one of them.

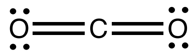
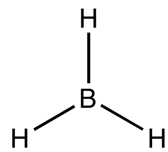
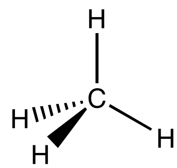
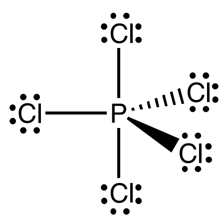
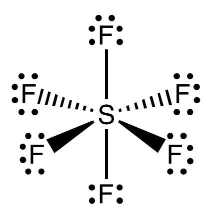
- If there is more than 1 central atom in a molecule, consider the bonding about each atom independently.

A. Molecules *without* lone pairs

Formula type	SN	Molecular shape	Geometry	Bond angle
AX_2	2		Linear	__________
AX_3	3		trigonal planar	__________
AX_4	4		tetrahedral	__________
AX_5	5		trigonal bipyramidal	__________ __________
AX_6	6		octahedral	__________

Note: Bonds into the paper are dashed, and bonds out of the paper are thick and triangular.

Examples of molecules *without* lone pairs:

	Formula type	SN	Lewis structure	Geometry	Bond angle
CO_2	AX_2	2		Linear	__________
BH_3	AX_3	3		______________	__________
CH_4	AX_4	4		______________	__________
PCl_5	AX_5	5		______________	__________ __________
SF_6	AX_6	6		______________	__________

B. Molecules *with* lone pairs
When lone pairs are involved, additional details must be considered.

Attractive forces exerted by the nuclei of the two bonded atoms hold electrons in a bond. These electrons have less "spatial distribution" than lone pairs, meaning

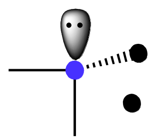
- electrons in bonds take up __________ space.
- lone-pair e$^-$s take up **more** space, and therefore experience ________ repulsion.

Thus, according to VSEPR, the repulsive forces decrease in the following order:

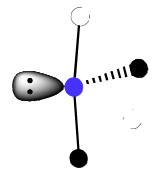
lone-pair/lone-pair repulsion > lone-pair/bonding-pair repulsion > bonding-pair/bonding-pair repulsion

Rationalization of <u>shapes</u> based on VSEPR theory

• AX_4E molecules have a seesaw shape. An axial lone pair would repel ____ bonding electron pairs strongly, whereas an equatorial lone pair repels only ____ strongly.



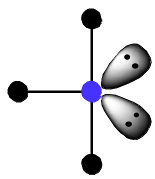
axial lone pair



equatorial lone pair

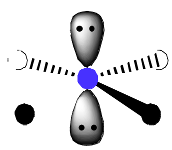
____

• AX_3E_2 molecules have a ____________. Lone pairs occupy two of the three equatorial positions, and these lone-pair electrons move away from each other slightly.



AX_3E_2 SN = 5

• AX_4E_2 molecules are <u>square planar</u>. The two lone pairs are farthest apart when they are on opposite sides of the central atom.

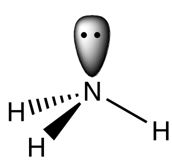


AX_4E_2 SN = 6

Rationalization of <u>angles</u> based on VSEPR theory

• In molecules with lone-pair e^-s, angles between bonded atoms tend to be __________ relative to the equivalent SN structures where only bonding electrons are present.

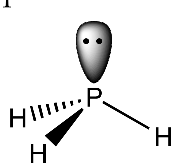
Example: NH_3 compared to CH_4



SN = 4 Instead of a H-C-H angle of 109.5° as in CH_4, the H-N-H angle is 106.7°.

• Atomic size _________________ down a column of the periodic table, and lone-pairs occupy **larger** spatial volumes. As a result, the angles between bonded atoms tend to be **even smaller** relative to the equivalent SN structures where only bonding electrons are present.

Example: compare PH_3 to NH_3.



SN = 4. Instead of an angle of 109.5° (as in CH_4), or 106.7° (as in NH_3), the H-P-H angle is ________°.

In their own words

MIT graduate student Stefanie Sydlik, from Tim Swager's research group, explains how her research on designing sensors for explosives depends on the principles of VSEPR theory.

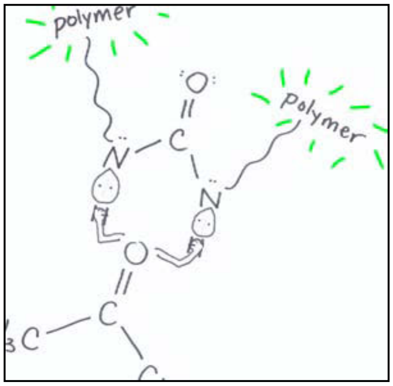
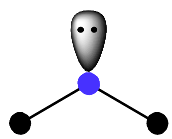
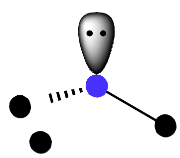
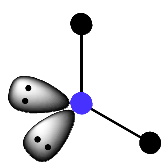
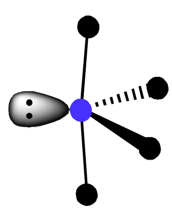
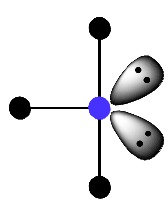
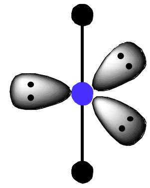
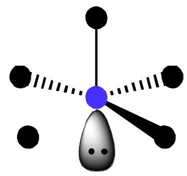
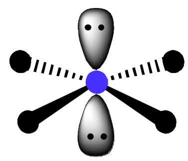
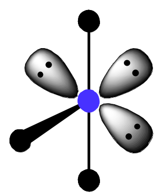
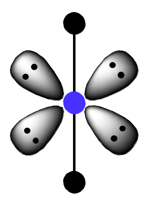


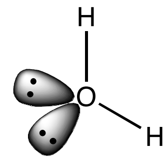
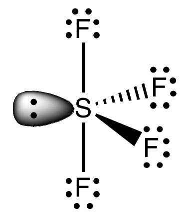
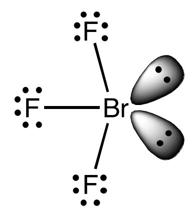
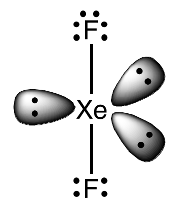
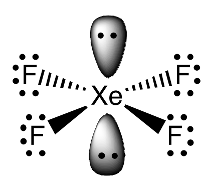
Image from "Behind the Scenes at MIT". The Drennan Education Laboratory. Licensed under a Creative Commons Attribution-NonCommercial-ShareAlike License.

In short, Stefanie's sensor is designed to amplify small-scale changes in bond angles following interaction with an analyte.

Formula type	**SN**	**Molecular shape**	**Geometry**	**Bond angle**
AX_2E	3		bent	__________
AX_3E	4		trigonal pyramidal	__________
AX_2E_2	4		bent	__________
AX_4E	5		see-saw	__________ __________
AX3E2	5		t-shaped	__________

Formula type	SN	Molecular shape	Geometry	Bond angle
AX_2E_3	5		__________	__________
AX_5E	6		square pyramidal	__________
AX_4E_2	6		square planar	__________
AX_3E_3	6		T-shaped	__________
AX_2E_4	6		__________	__________

Examples of molecules *with* lone pairs:

	Formula type	**SN**	**Lewis structure**	**Geometry**
H_2O	________	4		________
SF_4	________	___		________
BrF_3	AX_3E_2	5		________
XeF_2	AX_2E_3	5		________
XeF_4	AX_4E_2	6		________

The ideas of VSEPR make possible many predictions (or rationalizations) of molecular geometries about a central atom. There are very few incorrect predictions.

However, VSEPR provides no information about energies of bonds or about how multiple bonds affect structure.