5.111 Lecture Summary #13

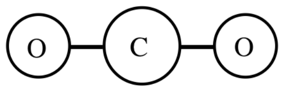
Readings for today: Section 3.1 (*3rd* or *4th ed*) – The Basic VSEPR Model, Section 3.2 (*3rd* or *4th ed*) – Molecules with Lone Pairs on the Central Atom.
Read for Lecture #14: Section 3.8 (3.9 in *3rd ed*) – The Limitations of Lewis's Theory, Section 3.9 (3.10 in *3rd ed*) – Molecular Orbitals, Section 3.10 (3.11 in *3rd ed*) – The Electron Configuration of Diatomic Molecules, Section 3.11 (3.12 in *3rd ed*) – Bonding in Heteronuclear Diatomic Molecules.

Topics: **I.** Polar covalent bonds and polar molecules (continued from Lecture #12)
II. The shapes of molecules: VSEPR theory
- **A.** Molecules *without* lone pairs
- **B.** Molecules *with* lone pairs

I. POLAR COVALENT BONDS/POLAR MOLECULES (continued from Lect. #12)

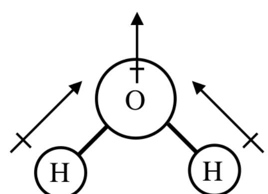
A polar covalent bond is an **unequal sharing** of e^-s between two atoms with different electronegativities (χ). In general, a bond between two atoms with an χ difference of > _____ and < _____ (on the Pauling scale) is considered polar covalent.

Polar molecules have a non-zero net dipole moment.



CO_2

______________ molecule



H_2O

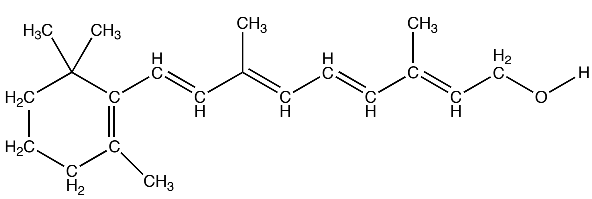
______________ molecule

$\chi_H = 2.2$
$\chi_C = 2.6$
$\chi_N = 3.0$
$\chi_O = 3.4$

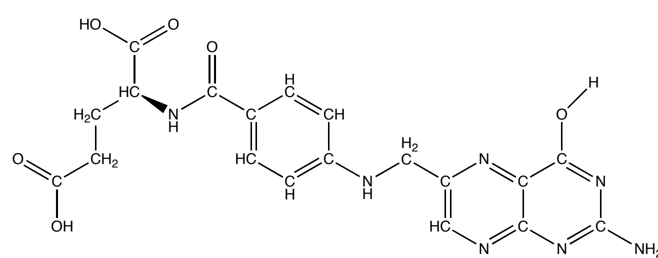
In large organic molecules and in biomolecules, such as proteins, we often consider the number of polar groups within the molecule.

For example, let's compare vitamin A to vitamin B9

Which vitamin contains a higher number of polar bonds? vitamin ________



Vitamin A



Vitamin B9 (________________________)

__________________ soluble

__________________ soluble

II. THE SHAPES OF MOLECULES: VALENCE SHELL ELECTRON PAIR REPULSION (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.

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 minimize the electron repulsion.

VSEPR nomenclature:

A = ______________ atom

X = ______________ atom

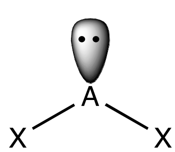
E = lone pair

General guidelines for the VSEPR model:

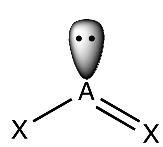
- ______________ number (SN) is used to predict geometries.

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 = ____

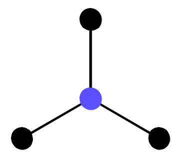
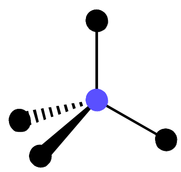
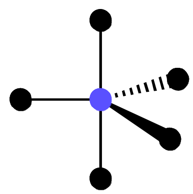
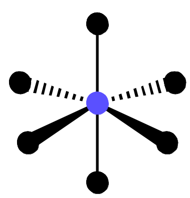


AX_2E SN = 3

This means the number of ______________ bonded to the central atom is important, not the BONDS to central atom.

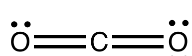
- If a molecule has two or more resonance structures, the VSEPR model can be applied to any one of them.
- If there is more than 1 central atom in a molecule, consider the bonding about each atom independently.

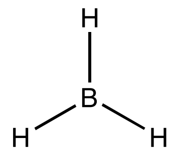
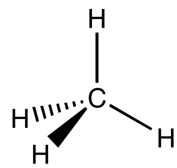
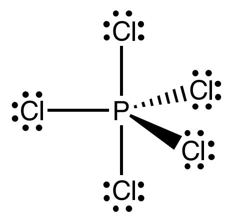
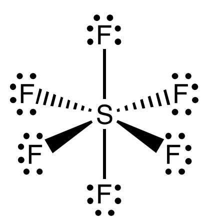
A. Molecules *without* lone pairs

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	__________

	Formula type	SN	Lewis structure	Geometry	Bond angle
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

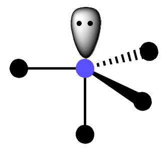
- electrons in bonds take up ___________ space.
- lone-pair e^-s take up more space, and therefore experience ________ repulsion.

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

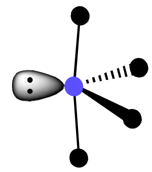
lone-pair/lone-pair repulsion > lone-pair/bonding-pair repulsion > bonding-pair/bonding-pair repulsion

Rationalization of shapes 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.

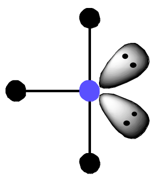


axial lone pair



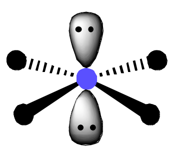
equatorial lone pair

• 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

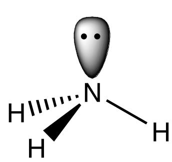
• AX_4E_2 molecules are square planar. The two lone pairs are farthest apart when they are on opposite sides of the central atom.



AX_4E_2 SN = 6

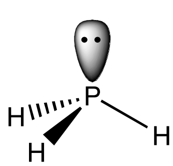
• In molecules with lone-pair e^-s, angles between bonded atoms tend to be _________ relative to the equivalent SN structures where only bonding electrons are present.

Example: NH_3



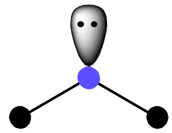
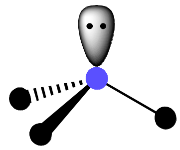
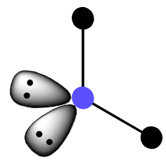
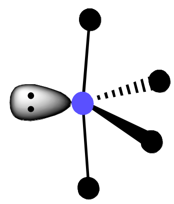
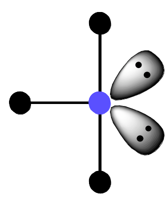
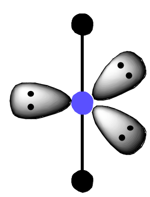
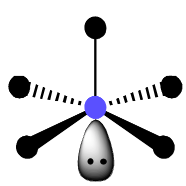
SN = 4 Instead of an angle of 109.5° (as in CH_4), the angle is 106.7°.

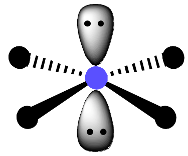
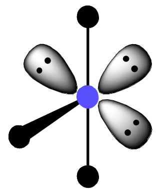
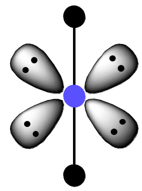
• Atomic size _____________ down a column of the periodic table.
Therefore, lone-pairs occupy larger spatial volumes as one moves down a column, and the angles between bonded atoms tend to be even smaller relative to the equivalent SN structures where only bonding electrons are present.



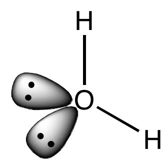
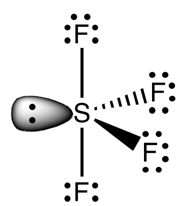
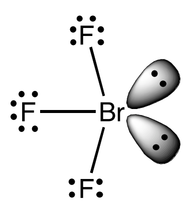
Example: compare PH_3 to NH_3.

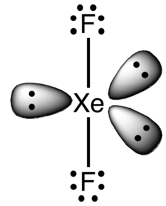
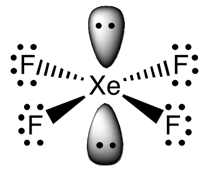
SN = 4. Instead of an angle of 109.5° (as in CH_4), or 106.7° (as in NH_3), the angle is _______°.

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	__________ __________
AX_3E_2	5		t-shaped	__________
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	______	5		______
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.