# **Shapes of Molecules and Hybridization**

# A. Molecular Geometry

• Lewis structures provide us with the number and types of bonds around a central atom, as well as any NB electron pairs. They do not tell us the 3-D structure of the molecule.

 $CH_4$  as drawn conveys no 3-D information (bonds appear like they are 90° apart)

- The Valence Shell Electron Pair Repulsion Theory (**VSEPR**), developed in part by Ron Gillespie at McMaster in 1957, allows us to predict 3-D shape. This important Canadian innovation is found worldwide in any intro chem course.
- VSEPR theory has four assumptions
  - 1. Electrons, in pairs, are placed in the valence shell of the central atom
  - 2. Both bonding and non-bonding (NB) pairs are included
  - 3. Electron pairs repel each other  $\rightarrow$  maximum separation.
  - 4. NB pairs repel more strongly than bonding pairs, because the NB pairs are attracted to only one nucleus
- To be able to use VSEPR theory to predict shapes, the molecule first needs to be drawn in its Lewis structure.

 VSEPR theory uses the AXE notation (m and n are integers), where m + n = number of regions of electron density (sometimes also called number of charge clouds).



#### 1. Molecules with no NB pairs and only single bonds

- We will first consider molecules that do not have multiple bonds nor NB pairs around the central atom (n = 0).
- Example: BeCl<sub>2</sub>

• Molecule is linear (180°)

• Example: BF<sub>3</sub>

• Molecule is **trigonal (or triangular) planar** (120°)

• Example: CH<sub>4</sub>

• Molecule is tetrahedral (109.5°)

• Example: PF<sub>5</sub>

- Molecule is trigonal bipyramidal (90° and 120°). There are three X atoms in a planar triangle and two axial atoms, one above and one below the central atom.
- Example: SF<sub>6</sub>

Molecule is octahedral (all 90°)

#### **2**. Molecules with $\geq$ 1 NB pairs and only single bonds

- The geometry of the *regions of electron density* is roughly the same as what we see when no NB pairs are involved.
- However, the shape of the molecule is determined by looking at only the bonding pairs, NOT the non-bonding pairs.
- Example: NH<sub>3</sub>

- There are four regions of electron density (m + n = 4), and the electronic arrangement is still tetrahedral.
- Yet, the shape of the molecule (look at bonding pairs only) is trigonal pyramidal. Angles < 109.5° (why?)</li>
- Example: H<sub>2</sub>O

Electronic arrangement is tetrahedral.
 Shape of molecule = bent

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• Example: NF

Electronic arrangement is trigonal planar.
 Shape of molecule = linear

• Example: SF<sub>4</sub>

- Electronic arrangement is trigonal bipyramidal.
  Shape of molecule = see saw
- Example: XeF<sub>3</sub><sup>+</sup>

Electronic arrangement is trigonal bipyramidal.
 Shape of molecule = **T-shaped**

• Example: XeF<sub>5</sub><sup>+</sup>

- Electronic arrangement is octahedral.
  Shape of molecule = Square pyramidal
- Example: ICl<sub>4</sub><sup>-</sup>

- Electronic arrangement is octahedral.
  Shape of molecule = Square planar
- Example: the amino acid alanine
  - o There can be more than one "central atom"

#### **3. Molecules with double or triple bonds**

- These are quite simple: treat them as single bonds, and the AXE system still works. *i.e.* a multiple bond is still considered to be one region of electron density.
- Examples: predict the shapes of CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and NO<sub>2</sub><sup>-</sup>

### **B.** Molecular Polarity

• Recall that electronegativity is a relative measurement of an atom's ability to attract a bonding electron pair to itself.



- Differences in electronegativity between two covalently bonded atoms result in a polar covalent bond, and atoms have a partial negative or partial positive charge.
- These bonds are said to have dipole moments, which can be experimentally quantified. If placed in an electric field, the molecule will rotate and line up to the field.
- The greater the bond polarity, the greater the dipole moment. However, can we say that a molecule with a polar bond must also be a polar molecule? Not necessarily!

- Note: The overall polarity of a molecule depends on its geometry and the presence of polar bonds.
  - The presence of polar bonds does not necessarily imply that the molecule is polar. This is because the bond dipole moments can cancel out (no net dipole moment).
  - Think of the bond dipoles as vectors, and if the sum of all of the vectors is zero, the molecule is not polar.

H<sub>2</sub>O

• Examples:

CO<sub>2</sub>

 $NH_3$ 

 $CCI_4$ 

CFCI<sub>3</sub>

- Notice that non-polar molecules are highly symmetrical, allowing the bond dipole moments to cancel out.
- In a set of resonance structures, the overall polarity is averaged out over the resonance structures. For example, CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> are non-polar (no net dipole moment).

# C. Hybridization (Compounds with Single Bonds)

- How does molecular shape relate to the orbitals in the valence shell?
- Consider methane,  $CH_4$ , which uses the valence electrons in the 2s,  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals. These electrons must become unpaired prior to making bonds with H.

• Recall the shapes of the *s* and *p* orbitals.

- If we used these orbitals to bond with the H atoms, we would get this structure. Yet, we know that the proper structure from VSEPR theory is tetrahedral. This structure shown is clearly incorrect!
- How do we explain this?

Before bonding to H atoms, the one 2s and three 2p atomic orbitals are mixed and rearranged to give a new set of four equivalent (same energy) "hybrid" atomic orbitals (sp<sup>3</sup>) arranged at tetrahedral angles of 109.5°.



The single bond formed by the *direct, head-on overlap* of orbitals is a sigma bond (σ).

- Note: hybrid orbitals can also contain NB pairs, for example, in ammonia and water. These also have tetrahedral electronic arrangements and are sp<sup>3</sup>.
- NH<sub>3</sub>, which has a tetrahedral electronic arrangement, contains three σ bonds. Its shape is trigonal pyramidal.



 sp<sup>3</sup> hybridization is just one possibility. Five major hybridization types form the VSEPR structures, and these types are summarized in this table (details follow).

Regions of e <sup>−</sup> density	Atomic orbitals	Hybrid orbitals	Electronic arrangement
2	one s, one p	two <i>sp</i>	linear
3	one <i>s</i> , two <i>p</i>	three <i>sp</i> <sup>2</sup>	trigonal planar
4	one s, three p	four <i>sp</i> <sup>3</sup>	tetrahedral
5	one <i>s</i> , three <i>p,</i> one <i>d</i>	five <i>sp</i> <sup>3</sup> d	trigonal bipyramidal
6	one <i>s</i> , three <i>p,</i> one <i>d</i>	six sp³d²	octahedral

- *Regions of electron density*: an NB pair, a single bond, or a multiple bond each constitute one region.
- *Electronic arrangement* may not equate to molecular shape if there is at least an NB pair present.

#### 1. *sp* hybridization

• The combination of one *s* and one *p* results in the formation of two *sp* orbitals. These two hybrid orbitals are 180° apart.



- Where we have used only one of the *p* orbitals, there must be two *p* orbitals remaining. (Recall there are three *p* orbitals).
   We'll see later on that these leftover orbitals are used when there is multiple bonding.
- The two leftover p are 90° to each other and the sp hybrids.

### **2**. $sp^2$ hybridization

• One s + two p = three  $sp^2$  orbitals 120° apart.



• There is one leftover *p* orbital remaining, since we started with three *p* orbitals and used two of them for hybridization.

### 3. *sp*<sup>3</sup> hybridization

- One *s* + three p = four  $sp^3$  orbitals 109.5° apart.
- There are no leftover *p* orbitals. Also see diagram on p. 12.



#### 4. Others: $sp^3d$ and $sp^3d^2$ hybridization

- One *s* + three *p* + one *d* = five  $sp^3d$  orbitals
- One s + three p + two d = six  $sp^3d^2$  orbitals





IF<sub>5</sub> (sq. pyramidal)

# D. Hybridization (Compounds with Multiple Bonds)

- How do we assign hybridization to compounds containing multiple bonds? The same way! We still examine the number of regions of electron density (table on page 13).
- Consider ethene. Each carbon has an AX<sub>3</sub>
  configuration (*sp*<sup>2</sup>-hybridized). Remember to count double bonds as one region. Each C also H has a remaining *p* orbital (see p. 15).
- Recall that  $\sigma$  bonds are formed by the direct overlap of orbitals, which result in single bonds. Where do double bonds come from?
  - $\circ$  The first bond in the double bond comes from a regular single bond caused by direct overlap (*i.e.* a  $\sigma$  bond)



• The second bond comes from the *sideways overlap* of the leftover *p* orbitals to give a pi ( $\pi$ ) bond. This is 90° to the plane defined by the trigonal-planar  $\sigma$  bonds. The  $\pi$ bond is both above and below the plane (2 lobes).



• The structure therefore appears like this... note that  $\pi$  bonds involve a sideways overlap, so bond rotation is not possible.



- How about a triple bond? Example: acetylene H—C≡C—H
  - Carbon atoms are *sp*-hybridized, and each has two remaining *p* orbitals 90° to each other (see p. 14)
  - $\circ\,$  The first bond in the triple bond originates from the direct overlap of *sp* orbitals ( $\sigma\,$  bond)
  - Both the second and the third bonds in the triple bond are  $\pi$  bonds originating from the sideways overlap of the remaining *p* orbitals. These two  $\pi$  bonds are 90° apart.



• Example: assign the hybridizations and the number of  $\pi$  bonds present in the molecule acetone