

## 2.2: Day 10- Hybrid Orbitals; Molecular Geometry

9

### Day 10: Hybrid Orbitals; Molecular Geometry

Valence bond theory and hybrid orbitals were introduced in [Section D9.7](#). The ideas summarized here will be developed further in today's work:

- Hybrid orbitals are derived by combining two or more atomic orbitals from the valence shell of a single atom.
  - AOs are the most stable arrangement of electrons in isolated atoms.
  - Hybrid orbitals are important in molecules because they result in stronger  $\sigma$  bonding.
- Most  $\sigma$  bonds are formed from overlaps of hybrid orbitals. Most  $\pi$  bonds are formed from overlap of unhybridized AOs.
- The number of hybrid orbitals equals the number of valence AOs that were combined to produce the hybrid orbitals.
- The type of hybrid orbitals for each bonded atom in a molecule correlates with the local 3D geometry of that atom.
  - The type of hybrid orbitals for each atom can be determined from the Lewis structure (or resonance structures) of a molecule.
  - From the local 3D geometry of each atom, we can obtain the overall 3D geometry of the molecule.

### D10.1 Types of Hybrid Orbitals

#### *sp* Hybrid Orbitals

Combining the valence *s* AO with one of the valence *p* AOs yields two degenerate ***sp* hybrid orbitals**, as shown in Figure 1 for the case of 2*s* and 2*p* AOs. The two *sp* hybrid orbitals are oriented at 180° to each other—a **linear geometry**. After the hybridization, there are two unhybridized 2*p* AOs left on the atom.

Because these hybrid orbitals are formed from one *s* AO and one *p* AO, they have a 1:1 ratio of “*s*” and “*p*” characteristics, hence the name “*sp*”. One of the ways in which the hybrid orbitals exhibit their mixed “*s*” and “*p*” characteristics is in their energy. Specifically, the *sp* hybrid orbitals’ relative energies are about half-way between the 2*s* and 2*p* AOs, as illustrated in Figure 1.

**Figure 1.** Hybridization of the 2*s* and one of the 2*p* AOs forms two *sp* hybrid orbitals, oriented 180° with respect to each other; the two other 2*p* AOs remain unhybridized. (Move the slider to see the before/after of hybridization).

The hybridized orbitals are not energetically favorable for an isolated atom. For example, a beryllium atom is lower in energy with its two valence electrons in the 2*s* AO than if the electrons were in the two *sp* hybrid orbitals. However, in a covalent molecule, the one large lobe of each *sp* hybrid orbital gives greater overlap with another orbital from another atom, yielding  $\sigma$  bonds that lower the molecule’s energy.

#### *sp*<sup>2</sup> Hybridization

Combining one valence *s* AO and two valence *p* AOs produces three degenerate ***sp*<sup>2</sup> hybrid orbitals**, as shown in Figure 2 for the case of 2*s* and 2*p* AOs. The three *sp*<sup>2</sup> hybrid orbitals are oriented at 120° with respect to each other and are in the same plane—a **trigonal planar (or triangular planar) geometry**. Each hybrid orbital is pointed toward a different corner of an equilateral triangle. After hybridization, there is one unhybridized 2*p* AO left on the atom.

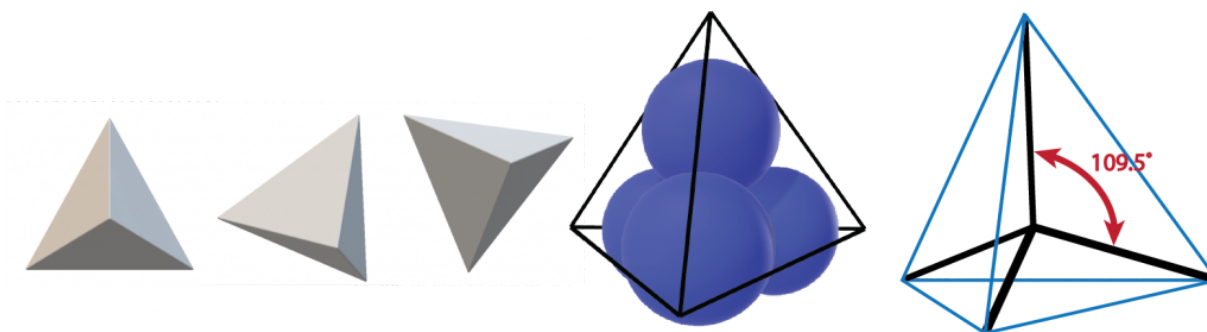
The *sp*<sup>2</sup> hybrid orbitals have twice as much “*p*” character as “*s*” character; this is indicated by the superscript “2” in *sp*<sup>2</sup>. Energetically, *sp*<sup>2</sup> hybrid orbitals lie closer to the *p* AO than the *s* AO, as illustrated in Figure 2 (the *sp*<sup>2</sup> hybrid orbitals are higher in energy than the *sp* hybrid orbitals).

**Figure 2.** Hybridization of the 2*s* and two of the 2*p* AOs forms three *sp*<sup>2</sup> hybrid orbitals, oriented 120° with respect to each other in the same plane; one of the 2*p* AOs remain unhybridized (move the slider around to see the before/after of hybridization).

#### *sp*<sup>3</sup> Hybridization

Combining one valence *s* AO and all three valence *p* AOs produces four degenerate ***sp*<sup>3</sup> hybridized orbitals**, as shown in Figure 4 for the case of 2*s* and 2*p* AOs. The four *sp*<sup>3</sup> hybridized orbitals are oriented at 109.5° with respect to each other, each pointing toward a different corner of a tetrahedron—a **tetrahedral geometry**.

A **tetrahedron** is a three-dimensional object that has four equilateral triangular faces and four apexes (corners). All four corners are equivalent. See Figure 3.



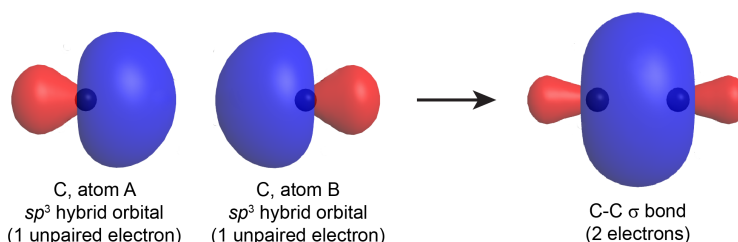
**Figure 3.** A tetrahedron has four equilateral triangular sides and four apexes (corners). Three views of a tetrahedron are shown at left. Four  $sp^3$  hybridized orbitals point from the tetrahedron's center toward the four corners. These hybrid orbitals form four bonds that point toward each corner of a tetrahedron. The angle between any two bonds is 109.5 degrees.

An  $sp^3$  hybrid orbital has 75% “p” character and 25% “s” character, a 3:1 ratio, hence the superscript “3” in its name. The  $sp^3$  hybrid orbitals are higher in energy than the  $sp^2$  hybrid orbitals, as illustrated in Figure 4.

**Figure 4.** Hybridization of the 2s and all three 2p AOs forms four  $sp^3$  hybrid orbitals, oriented 109.5° with respect to each other (move the slider around to see the before/after of hybridization).

### Formation of a $\sigma$ bond

When a  $\sigma$  bond forms between two atoms, a hybrid orbital with one unpaired electron from one atom overlaps with a hybrid orbital with one unpaired electron from the other atom. The resulting  $\sigma$  bond is an orbital that contains a pair of electrons (just as a line in a Lewis structure represents two electrons in a  $\sigma$  bond). For example, Figure 5 shows the formation of a C-C  $\sigma$  bond from two  $sp^3$  hybridized carbon atoms.



**Figure 5.** An  $sp^3$  hybrid orbital from carbon<sub>A</sub> overlaps with an  $sp^3$  hybrid orbital from carbon<sub>B</sub>, resulting in the formation of a C-C  $\sigma$  bond (in, for example,  $H_3C-CH_3$ ).

The  $\sigma$  bond thus formed by two hybrid orbitals (valence bond theory) is similar to a  $\sigma$  bond formed in a diatomic molecule as described by MO theory (Section D5.5). In polyatomic molecules with more than three atoms, the MOs are not localized between two atoms like this, but in valence bond theory, the bonds are described individually, between each pair of bonded atoms. Notice that in either MO or valence bond theory, the  $\sigma$  bond has a cylindrical symmetry with respect to the bonding axis.

If a hybridized orbital on an atom in a molecule has two electrons but is not pointing at another atom, the filled hybrid orbital is not involved in bonding. This corresponds to a lone pair on an atom in a Lewis structure.

## D10.2 Predicting the Geometry of Bonds Around an Atom

Once you have drawn the best Lewis structure (or a set of resonance structures) for a molecule, you can use the structure(s) to assign hybridization to each atom, predict the geometric arrangement of bonds around each atom, and then predict the 3D structure for the molecule. This and the next few sections explain how this works.

For each atom in a molecule, determine the number of AOs that are hybridized,  $n_{\text{hyb}}$ , and use this value to predict hybridization.

- Count the number of  $\sigma$  bonds ( $n_\sigma$ ) the atom forms.
  - A double (or triple) bond contains 1  $\sigma$  bond and 1 (or 2)  $\pi$  bond(s).
- Are there any lone pairs on the atom?

- If yes:  $n_{\text{hyb}} = n_{\sigma} + 1$
- If no:  $n_{\text{hyb}} = n_{\sigma}$
- Is an atom's  $n_{\text{hyb}}$  different in one resonance structure from another?
  - If yes, use the smaller  $n_{\text{hyb}}$  to determine hybridization.
- Use the value of  $n_{\text{hyb}}$  to determine the number of AOs combined and hence the type of hybridization:
  - For  $n_{\text{hyb}} = 2$ , the atom is  $sp$  hybridized (two AOs are combined);
  - for  $n_{\text{hyb}} = 3$ , the atom is  $sp^2$  hybridized (three AOs are combined);
  - for  $n_{\text{hyb}} = 4$ , the atom is  $sp^3$  hybridized (four AOs are combined);
  - An H atom in a molecule has  $n_{\text{hyb}} = 1$ . It is not hybridized; its electron is in the 1s AO when forming a  $\sigma$  bond.

These rules derive from the idea that hybridized orbitals form stronger  $\sigma$  bonds. Therefore, the more  $\sigma$  bonds to an atom, the more atomic orbitals are combined to form hybrid orbitals.

#### Activity 1: Molecular geometry of BeCl<sub>2</sub>

#### Activity 2: Molecular geometry of BF<sub>3</sub>

### D10.3 Three-dimensional Bond Geometry

The two examples so far were a linear (one-dimensional) molecule, BeCl<sub>2</sub>, and a planar (two-dimensional) molecule, BF<sub>3</sub>. What happens when a molecule is three dimensional?

#### Activity 3: Molecular geometry of CH<sub>4</sub>

#### Activity 4: Molecular geometry of NH<sub>3</sub>

#### Wedge-dash Notation

The Lewis structures in the activities above are drawn using **wedge and dash notation**. *Straight lines represent bonds in the plane of the page/screen, solid wedges represent bonds coming toward you out of the plane, and dashed wedges represent bonds going away from you behind the plane.*

Examine this [3D model of NH<sub>3</sub>](#) and rotate it until it looks like the Lewis structure drawn in the answer in Activity 4. The NH<sub>3</sub> molecule has trigonal pyramidal geometry because the lone pair on nitrogen occupies one of the corners of a tetrahedron, leaving the three N-H bonds occupying the other three corners; this gives a three-cornered pyramid.

Redraw the Lewis structure you drew for ammonia in Activity 4 using wedge-dash notation. Then, rotate the 3D model until it matches your drawing. If you can find an orientation that matches, your wedge-dash Lewis structure is probably correct; if you cannot find a match, your Lewis structure is probably incorrect.

For simplicity, a wedge-dash Lewis structure draws as many as possible of a molecule's bonds in a plane. However, as is the case with CH<sub>4</sub> and NH<sub>3</sub>, most molecules do not have all bonds in the same plane.

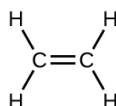
### D10.4 Molecules with More Than One Central Atom

Larger molecules have more than one “central” atom with several other atoms bonded to it. The arrangement of bonds for each central atom can be predicted as described in the preceding sections. The way these local structures are oriented with respect to each other influences the overall molecular shape.

#### Activity 5: Molecules with Several Central Atoms

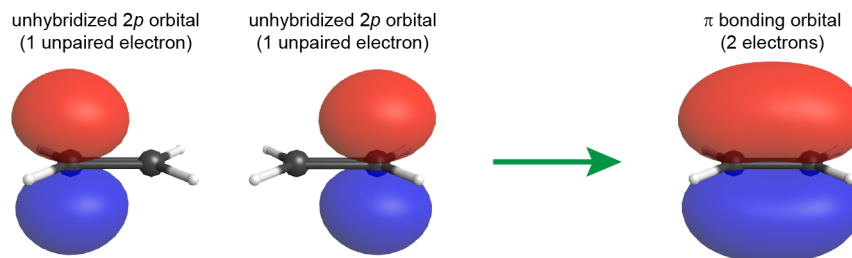
#### Double and Triple Bonds

The Lewis structure of ethene, C<sub>2</sub>H<sub>4</sub>, shows that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms:



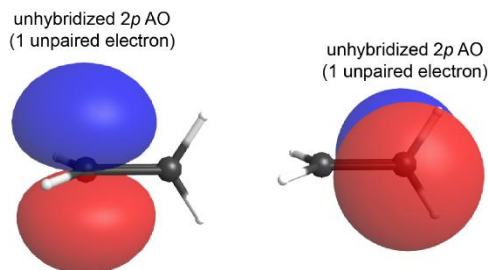
Each carbon atom has  $n_{\text{hyb}} = 3$  and therefore is  $sp^2$  hybridized. Around each C atom there are three bonds in a plane. Two of the  $sp^2$  orbitals form two C–H  $\sigma$  bonds and the third  $sp^2$  orbital forms a C–C  $\sigma$  bond.

The double bond between the two C atoms contains a  $\pi$  bond as well as a  $\sigma$  bond. The  $\pi$  bond results from overlap of the unhybridized 2p AO on each carbon atom. The unhybridized 2p AO is perpendicular to the plane of the  $sp^2$  hybrid orbitals (Figure 6). Thus when the 2p AOs overlap in a side-by-side fashion to form a  $\pi$  bond, the electron densities in the  $\pi$  bond are above and below the plane of the molecule (the plane containing the  $\sigma$  bonds).



**Figure 6.** The ball-and-stick model of  $C_2H_4$  is planar and roughly perpendicular to the plane of the page. The  $\sigma$  bonds are formed by overlap of  $sp^2$  hybrid orbitals on each C atom with two H 1s orbitals and an  $sp^2$  orbital on the other C atom. The unhybridized 2p AOs on the two C atoms (left) overlap side by side to form the  $\pi$  bond in  $C_2H_4$  (right). Click on the image for a rotatable view of the  $\pi$  bond.

If the plane containing the  $sp^2$  hybrid orbitals of one carbon atom were rotated  $90^\circ$  relative to the other carbon, the two 2p AOs would also be rotated  $90^\circ$  to each other (Figure 7). The 2p AOs would no longer be able to overlap and the  $\pi$  bond cannot form.



**Figure 7.** If one of the carbon in  $C_2H_4$  is rotated relative to the other one, by  $90^\circ$ , the two 2p AOs are now perpendicular to each other, and the  $\pi$  bond can no longer be formed.

This is a significant difference between  $\sigma$  and  $\pi$  bonds: one atom rotating around the internuclear axis with respect to the other atom does not change the extent to which the  $\sigma$  bonding orbitals overlap because the  $\sigma$  bond is cylindrically symmetric about the bond axis (see Figure 5); in contrast, rotation by  $90^\circ$  about the internuclear axis breaks the  $\pi$  bond entirely because the p orbitals can no longer overlap.

In acetylene,  $H-C\equiv C-H$ , each carbon atom has  $n_{\text{hyb}} = 2$  and therefore is  $sp$  hybridized with two unhybridized 2p orbitals. One  $sp$  hybrid orbital from each C atom overlaps to form a C–C  $\sigma$  bond, the other  $sp$  hybrid orbital forms a C–H  $\sigma$  bond with a hydrogen atom. The unhybridized 2p AOs overlap to form two *perpendicular* C–C  $\pi$  bonds (Figure 8). The two carbon atoms of acetylene are thus bound together by one  $\sigma$  bond and two  $\pi$  bonds, giving a triple bond.

**Figure 8.** In the  $C_2H_2$  molecule, there are two C–H  $\sigma$  bonds and a  $C\equiv C$  triple bond. the triple bond involves one  $\sigma$  bond and two  $\pi$  bonds. The two  $\pi$  bonds are perpendicular to each other. Slide back and forth to see all the bonds; the molecule is fixed in the same perspective throughout.

Because  $\pi$  bonds are formed from unhybridized p AOs, an atom that is involved in  $\pi$  bonding cannot be  $sp^3$  hybridized.

## Activity 6: Predicting Structure of a Molecule with Several Central Atoms

### D10.5 Hybridization and Bond Angles

Think back to the example molecules  $CH_4$  and  $NH_3$  in Section D9.4. Both involve  $sp^3$  hybridized orbitals on the central atom. In the case of  $CH_4$ , a 1s orbital on each of the four H atoms overlaps with each of the four  $sp^3$  hybrid orbitals to form four bonds. All angles between pairs of C–H bonds are  $109.5^\circ$ . In  $NH_3$  the situation is different in that there are only three H atoms. Three of the four  $sp^3$  hybrid orbitals form three bonds to H atoms, but the fourth  $sp^3$  hybrid orbital contains the lone pair. The lone pair is different from the H atoms, and this is important.

In earlier sections we described each of a set of four  $sp^3$  hybridized orbitals as having  $\frac{1}{4}$   $s$  character and  $\frac{3}{4}$   $p$  character. This is what happens in  $\text{CH}_4$ . Each of the four C–H bonds involves a hybrid orbital that is  $\frac{1}{4}$   $s$  and  $\frac{3}{4}$   $p$ . Summing over the four bonds gives  $4 \times \frac{1}{4} = 1$   $s$  orbital and  $4 \times \frac{3}{4} = 3$   $p$  orbitals—exactly the number and type of AOs from which the hybrid orbitals were formed.

In  $\text{NH}_3$ , however, three of the four  $sp^3$  hybrids form bonds to H atoms and the fourth involves a lone pair. In this and similar situations, the partial  $s$  and  $p$  characters must still sum to 1 and 3 but each hybrid orbital does not have to be the same as all the others. That is, a hybrid orbital forming an N–H bond could have more  $p$  character (and less  $s$  character) compared to the hybrid orbital involving the lone pair. The only requirement is that the total  $s$  character and the total  $p$  character, summed over all four hybrid orbitals, must be one  $s$  and three  $p$ .

A different ratio of  $s$  character and  $p$  character gives a different bond angle. For example, in  $sp^2$  hybridized orbitals (with one-third  $s$  character and two-thirds  $p$  character) the angle between bonds is  $120^\circ$ , whereas, for  $sp^3$  the angle is  $109.5^\circ$ . More  $p$  character results in a smaller bond angle. (This makes sense, because for the maximum  $p$  character, that is, for two unhybridized  $p$  orbitals, the bond angle would be  $90^\circ$  because the  $p$  orbitals are at  $90^\circ$ .)

How can you tell how much  $s$  character and how much  $p$  character is in a specific hybrid orbital? A MO-theory calculation can provide this information, but, for our purposes, a qualitative rule that indicates where there will be more  $p$  character is sufficient. **Bent's rule** says that *a hybrid orbital on a central atom has greater  $p$  character the greater the electronegativity of the other atom forming a bond*. A lone pair is assigned zero electronegativity because there is no atom attracting electrons in the bond away from the central atom.

Applying Bent's rule to  $\text{NH}_3$ , the three bonded H atoms have higher electronegativity than the lone pair (no atom) so we expect more  $p$  character in the hybrid orbitals that form the bond pairs. Thus, the angle between any two N–H bonds should be less than the tetrahedral angle. The experimentally measured angle is  $106.7^\circ$ , a bit less than the expected  $109.5^\circ$ .

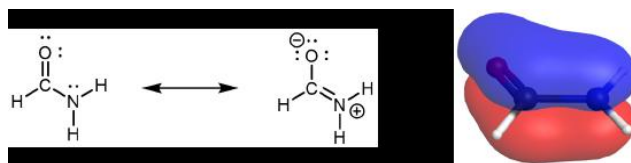
### Activity 7: Molecular geometry of H<sub>2</sub>O

In the  $\text{H}_2\text{O}$  molecule, two of the O's  $sp^2$  hybrid orbitals are involved in forming the O–H  $\sigma$  bonds. One of O lone pairs is in the other  $sp^2$  hybrid orbital; the other O lone pair is in the unhybridized  $2p$  AO. The overall molecular geometry is bent. If O had perfect  $sp^2$  hybridization, the H–O–H angle would be  $120^\circ$ , but because the three hybrid orbitals are not equivalent, the angle deviates from ideal. To obtain an accurate bond angle requires an experiment or a high-level MO calculation.

## D10.6 Hybridization in Resonance Hybrids

The assignment of hybridization and molecular geometry for molecules that have two or more major resonance structures is similar to the process discussed above, but remember that a set of resonance structures describes a single molecule. Hence the hybridization (and molecular geometry) assigned to one resonance structure must be the same as all other resonance structures in the set. Hence, when assigning hybridization, you should consider all the major resonance structures.

Consider Figure 9:



**Figure 9.** The two major contributing resonance structures of formamide are shown on the left. The delocalized  $\pi$  MO of formamide is shown on the right. Click on the image to see a rotatable 3D structure.

The delocalized  $\pi$  MO extends over the oxygen, carbon, and nitrogen atoms. One of the three AOs contributing to this  $\pi$  MO is an unhybridized  $2p$  AO on the N atom. This is also described by the set of resonance structures, where there is double-bond character between O and C and between C and N. Therefore the nitrogen atom must have  $sp^2$  hybridization (it forms three  $\sigma$  bonds) and a trigonal planar local geometry. This is more obvious when looking at the right resonance structure. When looking at the left resonance structure, you might be tempted to assign  $sp^3$  hybridization to N given its similarity to ammonia ( $\text{NH}_3$ ). However, this is a resonance structure; the set of resonance structures describes a molecule that cannot be described correctly by a single Lewis structure. Hence, the lone pair on N in the left resonance structure is in an unhybridized  $2p$  AO.

All atoms must remain in the same positions from one resonance structure to another in a set of resonance structures. There cannot be a N atom that is trigonal pyramidal in one resonance structure and trigonal planar in another resonance structure, because the

atoms attached to the N would have to change positions. Experimental evidence and high-level MO calculations show that formamide is a planar molecule.

### Day 10 Pre-class Podia Problem: Three-dimensional Models and Lewis Structures

Here are three links to 3-D models of molecules. For each molecule rotate the model to observe the structure. Then draw *three* 3-D Lewis structures of each molecule, using wedge and dash notation. Each wedge-dash structure should be viewed from a *different* perspective. If there are any lone pairs and/or formal charges, be sure to include them.

[Glycine](#) is an amino acid, a component of protein molecules.

[Acrolein](#) is used to kill algae and weeds in irrigation ditches and other natural waters.

[Methyl formate](#) is used mainly in the manufacture of other chemicals.

*Two days before the next whole-class session, this Podia question will become live on [Podia](#), where you can submit your answer.*

**Comments.** If you found any inconsistencies, errors, or other things you would like to report about this module, please use [this link](#) to report them. A similar link will be included in each day's material. We appreciate your comments.

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