HYBRID ORBITALS/HYBRIDIZATION

With molecules such as CH4, VSEPR predicts a tetrahedral geometry with bond angles of 109.5° which implies the orbitals used to create these bonds must also lie at 109.5°. In CH4, the central C atom has 2s and 2p atomic orbitals (AO) available to form bonds with the 2p orbitals residing at 90° to one another. Therefore, the angles between the p-orbitals don’t align with the 109.5° molecular angles predicted by VSEPR. Hence, a model to explain the molecular bonding is needed. This model, Valence Bond Theory (VBT), combines atomic orbitals to form new hybridized orbitals (HO) with the new molecular bonds formed from the hybrid orbitals occurring at the appropriate angles.

<table>
<thead>
<tr>
<th>Tetrahedral (four domains)</th>
<th>Triangular Planar (three domains)</th>
<th>Linear (two domains)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Orbitals (AO)</td>
<td>Hybrid Orbitals (HO)</td>
<td>Hybrid Orbitals (HO)</td>
</tr>
<tr>
<td>C: 2s^2p^2</td>
<td>s + p + p + p</td>
<td>s + p + p + p</td>
</tr>
<tr>
<td></td>
<td>sp^3 + sp^3 + sp^3 + sp^3</td>
<td>sp^3 + sp^3 + sp^3</td>
</tr>
<tr>
<td></td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>p</td>
</tr>
</tbody>
</table>

Shown is a C atom with 4 valence electrons: 2s^2p^2. The four atomic orbitals (AO) (one s and three p orbitals) are combined to form four new sp^3 hybridized orbitals (HO). The electrons are then placed in the new HO. The images at the right show the AOs being combined to form the new HO. The bottom image shows all four HO around the C atom at 109.5°.

Shown is a C atom with 4 valence electrons: 2s^2p^2. Three of the four AO (one s and two p orbitals) are combined to form three new sp^2 hybridized orbitals (HO). The last electron is placed in the unhybridized p-orbital and will be used to form one π-bond. The images at the right show the AOs being combined to form the new HO. The bottom image shows the three HO around the C atom at 120°.

Shown is a C atom with 4 valence electrons: 2s^2p^2. Two of the four AO (one s and one p orbital) are combined to form two new sp HO. The last two electron are placed in two unhybridized p-orbitals and will be used to form two π-bonds. The images at the right show the AOs being combined to form the new HOs. The bottom image shows the two HO around the C atom at 180°.
Bonds are made from 2 electrons with opposite spins in two orbitals that overlap.

**Sigma (σ) Bonds:** The bonds/electrons *lie* on the internuclear axis directly between the nuclei of the two atoms. **All bonds (single, double, or triple) contain one σ bond.** Sigma (σ) bonds are commonly made from the overlap of two hybrid orbitals, HO–HO, (e.g., sp²–sp³) or 1s from H and a hybrid orbital, 1s–HO (e.g., H–C, 1s–sp³) when H is present. The H–H sigma (σ) bond in H₂ is described as 1s–1s. Sigma (σ) bonds can rotate, are symmetrical, and are stronger than pi (π) bonds.

[Note: Other sigma (σ) bonds involving halogen atoms can be described as being formed from atomic orbitals rather than hybrid orbitals. For example, the H–F bond can be described as atomic orbitals 1s–2p overlapping to form a sigma (σ) bond. Likewise, F–F bonds are described as atomic orbitals 2p–2p overlapping. Not all instructors present these non-HO sigma (σ) bonds: for instance, if all atoms are hybridized (except H which is never hybridized) then the H–F sigma (σ) bond could be described as 1s–sp³. Follow the approach presented by the instructor.]

**Pi (π) Bonds:** Bonds/electrons do not lie on the internuclear axis, and instead lie above and below the internuclear axis. Pi (π) bonds occur with double or triple bonds. One p-orbital from each atom is used to make the pi (π) bond; the π bonds are made from the side-to-side overlap of two p-atomic orbitals, p–p, as shown. The overlap region is the location of the pi (π) bond. Pi bonds cannot rotate as this would require the π bond to break.

**Summary: How to make bonds (Chem 103)**

- **σ bonds:** HO–HO, (e.g., sp²–sp³) or 1s–HO (e.g., 1s–sp³)
  
  (sometimes specific bonds can be described in a different manner; for instance: H–F: 1s–2p; F–F: 2p–2p; see above.)

- **π bonds:** p–p (two p-atomic orbitals always)

**Single bond = 1σ bond; Double bond = 1σ bond + 1π bond; Triple bond = 1σ bond + 2π bonds**

**GEOMETRIC ISOMERS:** cis and trans configuration; no rotation around the double bond because of the π bond

<table>
<thead>
<tr>
<th>Type of bond</th>
<th>Characteristic</th>
<th>Total Domains</th>
<th>Electron pair geometry</th>
<th>Angles</th>
<th>HO</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ bond</td>
<td>e⁻ lie on the internuclear axis</td>
<td>2</td>
<td>Linear</td>
<td>180⁰</td>
<td>sp</td>
</tr>
<tr>
<td>π bond</td>
<td>e⁻ lie above and below the internuclear axis</td>
<td>3</td>
<td>Trigonal planar</td>
<td>120⁰</td>
<td>sp²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>Tetrahedral</td>
<td>109.5⁰</td>
<td>sp³</td>
</tr>
</tbody>
</table>

**Summary**

- Single bond: σ
- Double bond: σ + π
- Triple bond: σ + π

- Orbits used to create bond
  - σ bond: 1s–HO or HO–HO
  - π bond: p–p
**Example 1:** a. Draw the Lewis dot structure for CF₂=CH₂. b. Identify the hybridization for each atom. c. Identify what orbitals make up each bond.  

**Answer 1:**

![Lewis structure of CF₂=CH₂](image)

**Example 2:** Draw the hybrid orbital picture for the above molecule showing all hybrid and atomic orbitals, label these orbitals, label the σ and π bonds, and add electrons. *(Note: This type of question is usually not asked but is still useful to do as it helps coalesce one’s understanding.)*

**Answer 2:** The answer is shown below, and below the answer is the step-by-step process to build the hybrid orbital diagram of this molecule.

<table>
<thead>
<tr>
<th>Step 1: The 2 F atoms are sp³ hybridized. Draw in the 4 sp³ HO (blue) in a tetrahedral arrangement around each F atom with 1 sp³ HO pointing toward the C atom and label each HO drawn.</th>
<th>Step 2: Add the lone pairs of electrons (2e⁻) to 3 of the sp³ HO on each F atom (matching the Lewis dot structure), and add 1 e⁻ to each of the sp³ HO pointing towards the C atom. This takes care of the 7 valence e⁻ each F atom has.</th>
<th>Step 3: The 2 C atoms are sp² hybridized. Draw in the 3 sp² HO (green) in a triangular planar arrangement around each C atom and label each HO drawn. For the C on the left, the 3 sp² HO should point towards the F, F, and C atoms. For the C on the right, the 3 sp² HO should point towards C, H, and H atoms.</th>
<th>Step 4: Add 1 e⁻ to each sp² HO pointing towards the F, C, and H atoms.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Step 1 Diagram" /></td>
<td><img src="image" alt="Step 2 Diagram" /></td>
<td><img src="image" alt="Step 3 Diagram" /></td>
<td><img src="image" alt="Step 4 Diagram" /></td>
</tr>
</tbody>
</table>

**Step 5:** H is never hybridized and stays as a 1s atomic orbital (AO). Draw in the 1s AO (red) around each H atom, label each AO drawn, and add 1 e⁻ to each 1s AO. This takes care of the 1 valence e⁻ each H atom has.

**Step 6:** Label the bonds between the F–C, C–C, and C–H atoms as sigma (σ) bonds.

**Step 7:** A double bond (σ + π bond) exists between the 2 C atoms. The σ bond was created with 2 HO. Each C atom still has a 2p atomic orbital remaining. Draw in the one 2p AO on each C atom (purple), label each AO drawn, and add 1 e⁻ to each p-orbital. This takes care of the 4 valence e⁻ each C has (in 3 sp² HO and 1 in the p-orbital). “Overlap” the p-orbitals to make a π bond—the curved line between the two p-orbitals represents this overlap—and label the bond a π bond. (Below is the π bond drawn separately for clarity.)

**Step 8:** The π bond has now been added to the σ bond scaffolding. Note how this hybrid orbital picture:
- matches the Lewis dot structure,
- has the correct number of bonds,
- all valence e⁻ are accounted for,
- each bond made was created with 2 orbitals overlapping + 2 e⁻ one coming from each atom,
- each σ bond lies directly between the 2 atoms on the internuclear axis,
- the π bond lies above/below the internuclear axis.
Resonance Hybrid (not all instructors cover this topic)

Example: A Lewis dot structure for NO\textsubscript{2}\textsuperscript{-} including both resonance structures looks as follows:

\[
\begin{align*}
\text{O} &\equiv \text{N} \longrightarrow \text{O} \\
\text{O} &\equiv \text{N} \longrightarrow \text{O} \\
\end{align*}
\]

Hybrid orbitals from the above Lewis dot structure would be assigned as follows:

\[
\begin{align*}
\text{sp}\textsuperscript{2} &\quad \text{sp}\textsuperscript{2} &\quad \text{sp}\textsuperscript{3} &\quad \text{sp}\textsuperscript{3} &\quad \text{sp}\textsuperscript{3} &\quad \text{sp}\textsuperscript{3}
\end{align*}
\]

Though these hybrid orbital assignments look reasonable, a hybrid orbital diagram drawn for the left structure would generate a static hybrid orbital diagram:

\[
\text{Static hybrid orbital diagram: resonance not permitted}
\]

In the above diagram, there is no mechanism for the \(\pi\)-bond to jump from the O–N bond on the left side of the molecule to the N–O bond on the right side as this requires a p-orbital on the right O atom to create the \(\pi\)-bond. Since the left Lewis dot structure above has the right O atom hybridized as a sp\textsuperscript{3} hybrid orbital there are no p-orbitals left on the O atom to create a \(\pi\)-bond. Here the creation of the hybrid orbitals are shown with a sp\textsuperscript{3} hybridized O atom (note: no p-orbitals remain):

\[
\begin{align*}
\text{O atom hybridized as a sp}\textsuperscript{3} \\
\text{Atomic Orbitals (AO)} &\quad \text{Hybrid Orbitals (HO)}
\end{align*}
\]

To resolve this and allow the \(\pi\)-bond to jump to the other N–O bond, the hybrid orbital assignments when there is a resonance structure present is to have both O atoms assigned as sp\textsuperscript{2} hybridized:

\[
\begin{align*}
\text{sp}\textsuperscript{2} &\quad \text{sp}\textsuperscript{2} &\quad \text{sp}\textsuperscript{2} &\quad \text{sp}\textsuperscript{2} &\quad \text{sp}\textsuperscript{2} &\quad \text{sp}\textsuperscript{2}
\end{align*}
\]

By assigning both O atoms as sp\textsuperscript{2} hybridized, each O atom now has a p-orbital available to create the \(\pi\)-bonding resonance and allow the electron to “jump” back and forth between the p-orbitals and create a resonance \(\pi\) structure. In essence, an electron p-orbitals highway has been created. Here is creation of the sp\textsuperscript{2} hybrid orbitals for the O atoms (note: the available p-orbital):

\[
\begin{align*}
\text{O atom hybridized as a sp}\textsuperscript{2} \\
\text{Atomic Orbitals (AO)} &\quad \text{Hybrid Orbitals (HO)}
\end{align*}
\]

The revised \(\sigma\)-bonding and \(\pi\)-bonding hybrid orbital diagrams would look as follows:

\[
\text{Note the O atom on the right has three sp}\textsuperscript{2} hybrid orbitals rather than four sp}\textsuperscript{3} hybrid orbitals:}

\[
\begin{align*}
\text{Sigma (\(\sigma\)) bonds only} &\quad \text{Pi (\(\pi\)) bonds only}
\end{align*}
\]

Note how one O atom as a lone pair of electrons residing in the p-orbital rather than a sp\textsuperscript{3} hybrid orbital while the other O atom has one electron in the p-orbital used to create the \(\pi\)-bond with the N atom. Only one electron needs to move from one O atom to the other to allow the \(\pi\)-bond to resonate.
1. For each molecule below, determine the electron pair geometry and hybridization around the central atom.
   a. \(\text{CO}_3^{2-}\)  b. \(\text{SO}_2\)  c. \(\text{SO}_3^{2-}\)  d. \(\text{BCl}_3\)

2. I. a. For the molecule, \(\text{C}_2\text{H}_4\), what orbitals are used to make the two \(\text{C} = \text{C}\) bonds?  
   (Hint: Draw the Lewis dot structure first.)
   b. What orbitals are used to make the \(\text{C} - \text{H}\) bonds?

   II. a. For the molecule, \(\text{Cl}_2\text{CO}\), what orbitals are used to make the two \(\text{C} = \text{O}\) bonds?  
   (Hint: Draw the Lewis dot structure first.)
   b. What orbitals are used to make the \(\text{C} - \text{Cl}\) bonds?

3. a. Draw in the lone pairs in the structure that are missing.
   b. What is the hybridization on the \(\text{N}\) labeled “b”?
   c. What is the angle for the \(\text{H} - \text{C} - \text{C}\) atoms labeled “c”?
   d. What is the electron pair geometry for the \(\text{O}\) atom labeled “f”?
   e. What orbitals overlap to form the bond labeled “e”?
   f. How many \(\sigma\) and \(\pi\) bonds are in the molecule below?
   g. What is the molecular geometry around the \(\text{N}\) labeled “b”?
   h. What orbitals overlap to form the \(\sigma\) bond labeled “d”? What orbitals are used to form the \(\pi\) bond labeled “d”?
   i. What is the bond order for the carbon-carbon bond labeled “a”?

4. Use the structure to answer the questions below about the structure and bonding in this molecule.
   a. What is the angle between the \(\text{H} - \text{C} - \text{H}\) atoms labeled “c”?
   b. What is the electron pair geometry around the carbon atom labeled “b”?
   c. What is the hybridization of the carbon atom labeled “a”?
   d. What bonds make up the triple bond between carbon atoms labeled “d”?
   e. What orbitals overlap to make the bonds between the \(\text{C}\) atoms labeled “d”?
   f. How many \(\sigma\) and \(\pi\) bonds are there in the molecule?

5. How many \(\pi\) and \(\sigma\) bonds does the molecule below have?
   \[\text{HO} - \text{C} \equiv \text{C} - \text{C} \equiv \text{C} - \text{C} \equiv \text{C} - \text{C} - \text{NH}_2\]
   a. 16\(\sigma\), 5\(\pi\)  b. 16\(\sigma\), 3\(\pi\)  c. 16\(\sigma\), 4\(\pi\)  d. 19\(\sigma\), 5\(\pi\)  e. 19\(\sigma\), 4\(\pi\)

6. (Skip if geometric isomers are not covered) Which of these molecules can have geometric isomers? Not a multiple choice question; there may be more than one molecule.
   a.  
   b.  
   c.  
   d.  
   e.  
7. (This type of question is not always asked but is useful to coalesce one’s understanding.) For each molecule below, draw the hybrid orbital picture. Draw all HO or AO and label them, draw all valence electrons, show orbital overlap by drawing a bond between the atoms, and label the bonds σ or π. (Hint: Draw in the lone pairs of electrons in the Lewis dot structures and build octets before drawing the hybrid orbital picture!)

a. H₂O
b. H₂N→H
c. H₂C→H
d. O=C=O

8. (Drawing resonance hybrid orbital pictures is often not asked.) Draw the resonance hybrid orbital pictures for the molecules shown below. The structures shown do not include lone pairs of electrons, and the negative charge on NO₃⁻ is also not included.

a. O=O → O=O
b. N=O → N=O → N=O

ANSWERS

1. a. triangular planar, sp² { O⁻→O⁻→O⁻ (has resonance structures-not needed here); 3 atoms + 0 lone pairs = 3 → triangular planar and sp²}
b. triangular planar, sp² { O⁻→O⁻→O⁻ (has resonance structures-not needed here); 2 atoms + 1 lone pairs = 3 → triangular planar and sp²}
c. tetrahedral, sp³ { O⁻→O⁻→O⁻; 3 atoms + 1 lone pair = 4 → tetrahedral and sp³}
d. triangular planar, sp² { O⁻→O⁻→O⁻; 3 atoms + 0 lone pairs = 3 → triangular planar and sp²}

2. I. a. σ bond = sp²(C)–sp²(C); π bond = p(C)–p(C)
   b. σ bond: sp²(C)–1s(H)
   II. a. σ bond = sp²(C)–sp²(O); π bond = p(C)–p(O)
   b. σ bond = sp²(C)–sp³(Cl)
3. a. See figure right.

b. \( \text{sp}^3 \) \{3 atoms + 1 lone pair = 4 \( \rightarrow \) \( \text{sp}^3 \)\}

c. \( 120^\circ \) \{at the vertice C: HO = \( \text{sp}^2 \) \( \rightarrow \) triangular planar = \( 120^\circ \)\}

d. tetrahedral \{2 atoms + 2 lone pairs = 4 \( \rightarrow \) tetrahedral\}

e. 1s(H)\(-\text{sp(C)}\) \{C has 2 atoms + 0 lone pairs = 2 \( \rightarrow \) \( \text{sp} \)\}

f. 21\( \sigma \) bonds; 6\( \pi \) bonds \{single, double, and triple bond has a \( \sigma \) bond; double bond has 1 \( \pi \) bond; triple bond has 2 \( \pi \) bonds\}

g. triangular pyramid \{3 atoms + 1 lone pair = 4; EDG = tetrahedral; MG = triangular pyramid\}

h. \( \sigma \): \( \text{sp}^2(C)\)–\( \text{sp}^2(C) \); \( \pi \): \( \text{p(C)}\)–\( \text{p(C)} \) \{each C atom has 3 atoms + 0 lone pairs = 3 \( \rightarrow \) \( \text{sp}^2 \); \( \sigma \) bond = HO–HO = \( \text{sp}^2 \)–\( \text{sp}^2 \); the double bond means there is also a \( \pi \) bond; \( \pi \) bond = \( \text{p} \)–\( \text{p} \)\}

i. 1.5 \{benzene ring has resonance; BO\( _{C–C} = 1.5 \)\}

4. a. 109.5\(^\circ \) \{at the vertex C there are 4 atoms + 0 lone pairs = 4 \( \rightarrow \) tetrahedral \( \rightarrow 109.5^\circ \)\}

b. linear \{2 atoms + 0 lone pairs = 2 \( \rightarrow \) linear\}

c. \( \text{sp}^2 \) \{C atom has 3 atoms + 0 lone pairs = 3 \( \rightarrow \) triangular planar \( \rightarrow \) \( \text{sp}^2 \)\}

d. 1\( \sigma \) + 2\( \pi \) \{every triple bond has 1 \( \sigma \) bond and 2 \( \pi \) bonds\}

e. \( \sigma \) bond: \( \text{sp(C)}\)–\( \text{sp(C)} \); \( \pi \) bond: \( \text{p(C)}\)–\( \text{p(C)} \); \( \pi \) bond: \( \text{p(C)}\)–\( \text{p(C)} \)

\{since each C atom has 2 atoms + 0 lone pairs = 2 \( \rightarrow \) linear \( \rightarrow \) \( \text{sp} \)\}

f. 22\( \sigma \), 5\( \pi \) \{every single, double, and triple bond has a \( \sigma \) bond; every double bond has 1 \( \pi \) bond; every triple bond has 2 \( \pi \) bonds\}

5. d \{\( \pi \) bonds: each double bond = 1\( \pi \) bond; each triple bond = 2\( \pi \) bonds; \( \pi \) bonds = 1 + 1 + 1 + 2 = 5\( \pi \) bonds; each bond (single, double, or triple) has 1\( \sigma \) bond; be careful not to miss the O–H single bond (1\( \sigma \) bond) and the 2 N–H single bonds (2\( \sigma \) bonds)\}

6. b, d, e \{“a”: has duplicate groups on each C atom:

duplicate

“c”: has duplicate groups on each C atom:

duplicate

duplicate

duplicate

duplicate

duplicate

duplicate

duplicate

duplicate
7. a. σ bonds:

b. σ bonds:

c. entire drawing; just σ bonds;

d. entire drawing; just σ bonds:

just π bonds:

8. a. σ bonds; π bonds/resonance:

b. σ bonds:

note how the π bonds and resonance: