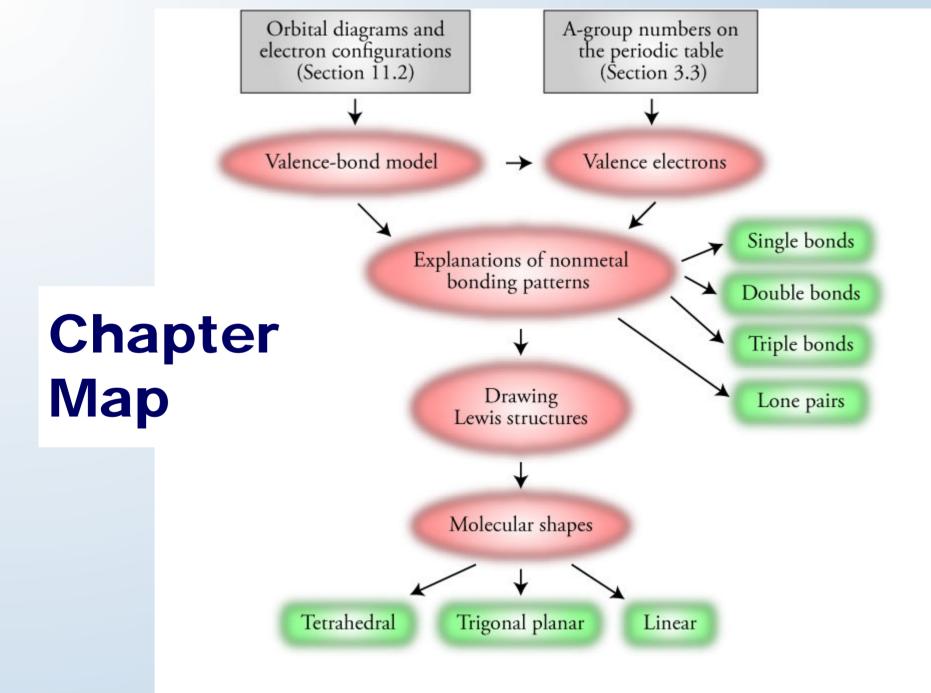
Chapter 12

Molecular Structure





Models - Advantages and Disadvantages (1)

- They help us to *visualize*, *explain*, and *predict* chemical changes.
- Because a model is a simplified version of what we think is true, the processes it depicts are sometimes described using the phrase as if. When you read, "It is as if an electron were promoted from one orbital to another," the phrase is a reminder that we do not necessarily think this is what really happens. We merely find it useful to talk about the process as if this is the way it happens.

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Models - Advantages and Disadvantages (2)

 One characteristic of models is that they change with time. Because our models are simplifications of what we think is real, we are not surprised when they sometimes fail to explain experimental observations. When this happens, the model is altered to fit the new observations.

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Assumptions of the Valence-Bond Model

 Only the highest energy electrons participate in bonding.

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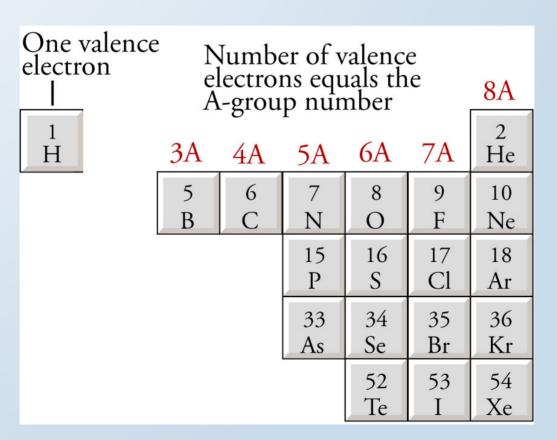
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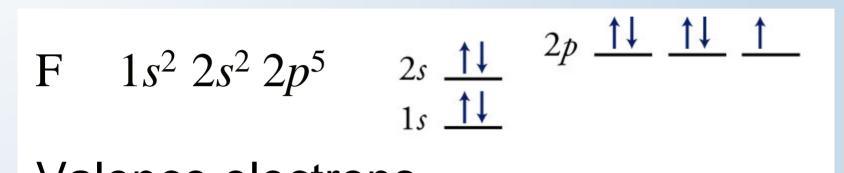
• Covalent bonds usually form to pair unpaired electrons.

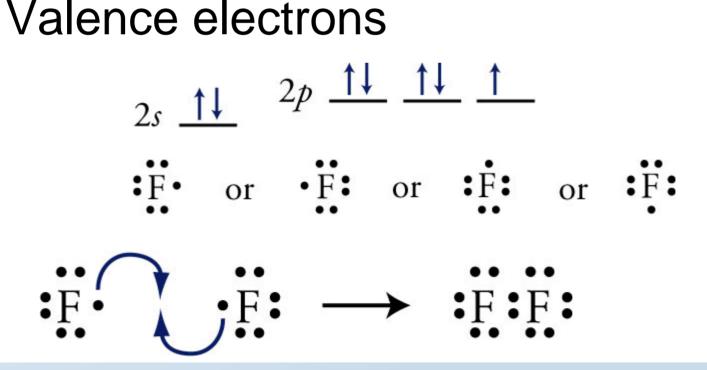
Valence Electrons

• Valence electrons are the highest-energy s and p electrons in an atom.



Fluorine



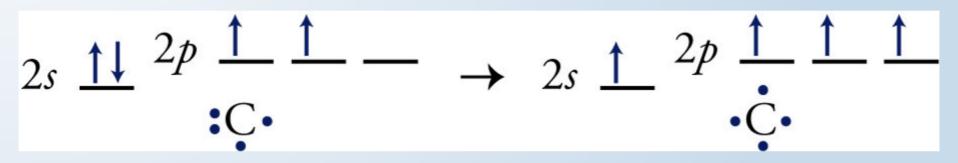


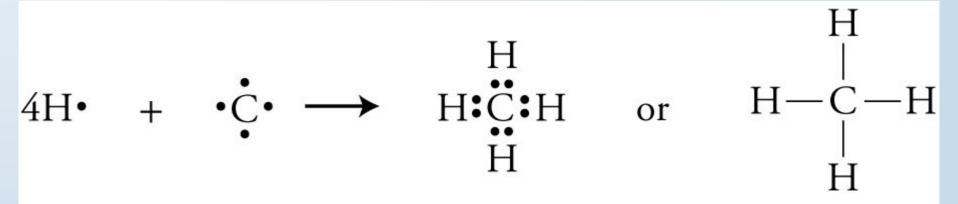
H₂ Formation

- The unpaired electron on a hydrogen atom makes the atom unstable.
- H• 1s <u>1</u>
 Two hydrogen atoms combine to form one hydrogen molecule.

$$H \rightarrow H:H$$
 or $H-H$

Carbon – 4 bonds





Carbon – Multiple Bonds

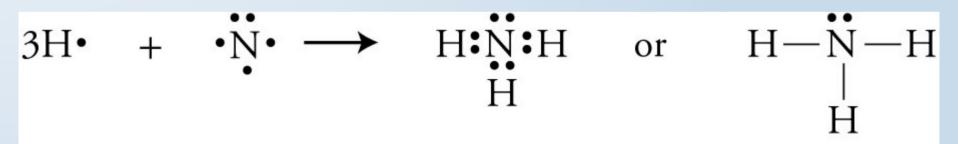
$$4H \cdot + 2 \cdot \dot{C} \cdot \longrightarrow H : C :: C : H \quad or \quad H - C = C - H \\ H \quad H \quad H$$

$$2H \cdot + 2 \cdot \dot{C} \cdot \longrightarrow H : C : C : H \quad or \quad H - C \equiv C - H$$

-

Nitrogen – 3 bonds & 1 lone pair

$$2s \stackrel{\uparrow \downarrow}{\underline{1}} 2p \stackrel{\uparrow}{\underline{1}} \stackrel{\uparrow}{\underline{1}} \stackrel{\uparrow}{\underline{1}} \stackrel{\bullet}{\underline{N}}$$



Nitrogen – 4 bonds

$$2s \stackrel{\uparrow \downarrow}{\longrightarrow} {2p \stackrel{\uparrow}{\longrightarrow}} {\frac{\uparrow}{N}} {\stackrel{\uparrow}{\longrightarrow}} {\frac{\uparrow}{\longrightarrow}} {\frac{-1e^-}{2s}} 2s \stackrel{\uparrow}{\longrightarrow} {2p \stackrel{\uparrow}{\longrightarrow}} {\frac{\uparrow}{N}} {\stackrel{\uparrow}{\longrightarrow}} {\frac{\uparrow}{N}} {\stackrel{\uparrow}{\longrightarrow}} {\frac{\uparrow}{N}} {\frac{\uparrow}{N}}$$

$$4H \bullet + \bullet \stackrel{\bullet}{N} \bullet \longrightarrow H \stackrel{\bullet}{H} \stackrel{\bullet}{N} H \text{ or } \begin{bmatrix} H \\ I \\ H - N - H \\ I \\ H \end{bmatrix}^{+}$$

Oxygen – 2 bonds & 2 lone pairs

$$2s \stackrel{\uparrow \downarrow}{\underline{1}} 2p \stackrel{\uparrow \downarrow}{\underline{1}} \stackrel{\uparrow}{\underline{1}} \stackrel{\uparrow}{\underline{1}} \stackrel{\uparrow}{\underline{1}} \stackrel{\uparrow}{\underline{1}} \stackrel{\bullet}{\underline{1}}$$

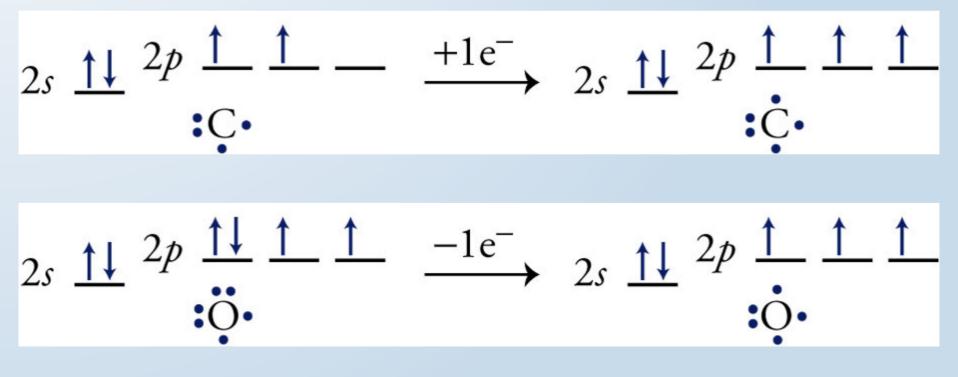
Oxygen – 1 bond & 3 lone pairs

$$2s \underbrace{\uparrow \downarrow}_{O} 2p \underbrace{\uparrow \downarrow}_{O} \uparrow \underbrace{\uparrow}_{O} \uparrow \underbrace{+1e^{-}}_{2s} 2s \underbrace{\uparrow \downarrow}_{O} 2p \underbrace{\uparrow \downarrow}_{O} \uparrow \underbrace{\uparrow \downarrow}_{O} \uparrow \underbrace{\uparrow}_{O} \uparrow \underbrace{\downarrow}_{O} \uparrow \underbrace{\uparrow}_{O} \uparrow \underbrace{\uparrow}_{O} \uparrow \underbrace{\uparrow}_{O} \uparrow \underbrace{\downarrow}_{O} \uparrow \underbrace{\uparrow}_{O} \uparrow \underbrace{\uparrow}_{O} \uparrow \underbrace{\downarrow}_{O} \uparrow \underbrace{\uparrow}_{O} \downarrow \underbrace{\uparrow}_{O} \downarrow \underbrace{\uparrow}_{O} \downarrow \underbrace{\uparrow}_{O} \downarrow \underbrace{\downarrow}_{O} \downarrow \underbrace{\uparrow}_{O} \bullet \underbrace{\downarrow}_{O} \downarrow \underbrace{\downarrow}_{O} \downarrow \underbrace{\downarrow}_{O} \downarrow \underbrace{\downarrow}_{O} \bullet \underbrace{\downarrow}_{O}$$

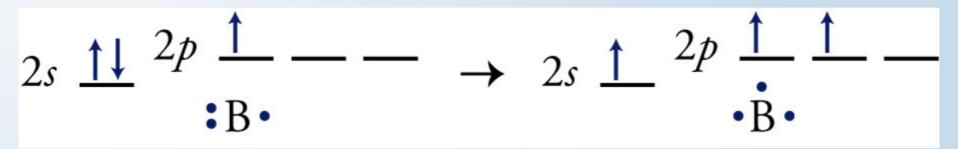
$$H \cdot + : \Theta \cdot \longrightarrow : \Theta \cdot H \quad or \quad \left[: \Theta - H \right]^{-}$$

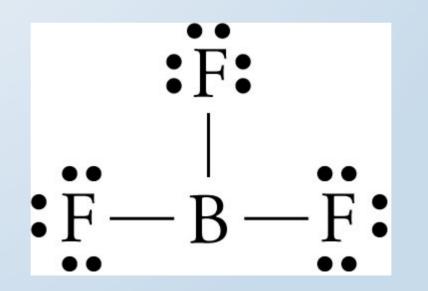
Carbon – 3 bonds & 1 lone pair Oxygen – 3 bonds & 1 lone pair

C≡O:



Boron – 3 bonds





Halogens – 1 bond & 3 lone pairs

$$ns \stackrel{\uparrow\downarrow}{\underline{1}} np \stackrel{\uparrow\downarrow}{\underline{1}} \stackrel{\uparrow\downarrow}{\underline{1}} \stackrel{\uparrow}{\underline{1}} \bullet \overset{\bullet}{X}^{\bullet}$$

$$H \bullet + \bullet X \coloneqq \longrightarrow H \bullet X \coloneqq$$
 or $H - X \coloneqq X = F$, Cl, Br, or I

Drawing Lewis Structures (1)

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- **Step 1:** Determine the total number of valence electrons for the molecule or polyatomic ion.
- For uncharged molecules, the total number of valence electrons is the sum of the valence electrons of each atom.
- For polyatomic cations, the total number of valence electrons is the sum of the valence electrons for each atom minus the charge.
 - For polyatomic anions, the total number of valence electrons is the sum of the valence electrons for each atom plus the charge.

Drawing Lewis Structures (2)

- **Step 2:** Draw a reasonable skeletal structure, using single bonds to join all the atoms.
 - Try to arrange the atoms to yield the most typical number of bonds for each atom.
 - Apply the following guidelines in deciding what element belongs in the center of your structure.
 - Hydrogen and fluorine atoms are never in the center.
 - Oxygen atoms are rarely in the center.

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- The element with the fewest atoms in the formula is often in the center.
- The atom that is capable of making the most bonds is often in the center.
- Oxygen atoms rarely bond to other oxygen atoms.
- The molecular formula often reflects the molecular structure.
- Carbon atoms commonly bond to other carbon atoms.

Drawing Lewis Structures (3)

 Step 3: Subtract 2 electrons from the total for each of the single bonds (lines) described in Step 2.



Drawing Lewis Structures (4)

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- **Step 4:** Try to distribute the remaining electrons as lone pairs to obtain a total of eight electrons around each atom except hydrogen and boron.
 - In a reasonable Lewis structure, carbon, nitrogen, oxygen, and fluorine always have eight electrons around them.
 - Hydrogen will always have a total of two electrons from its one bond.
 - Boron can have fewer than eight electrons but never more than eight.
 - The nonmetallic elements in periods beyond the second period (P, S, Cl, Se, Br, and I) usually have eight electrons around them, but they can have more.
 - The bonding properties of the metalloids arsenic, As, and tellurium, Te, are similar to those of phosphorus, P, and sulfur, S, so they usually have eight electrons around them but can have more.

Drawing Lewis Structures (5)

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Step 5: Do one of the following.

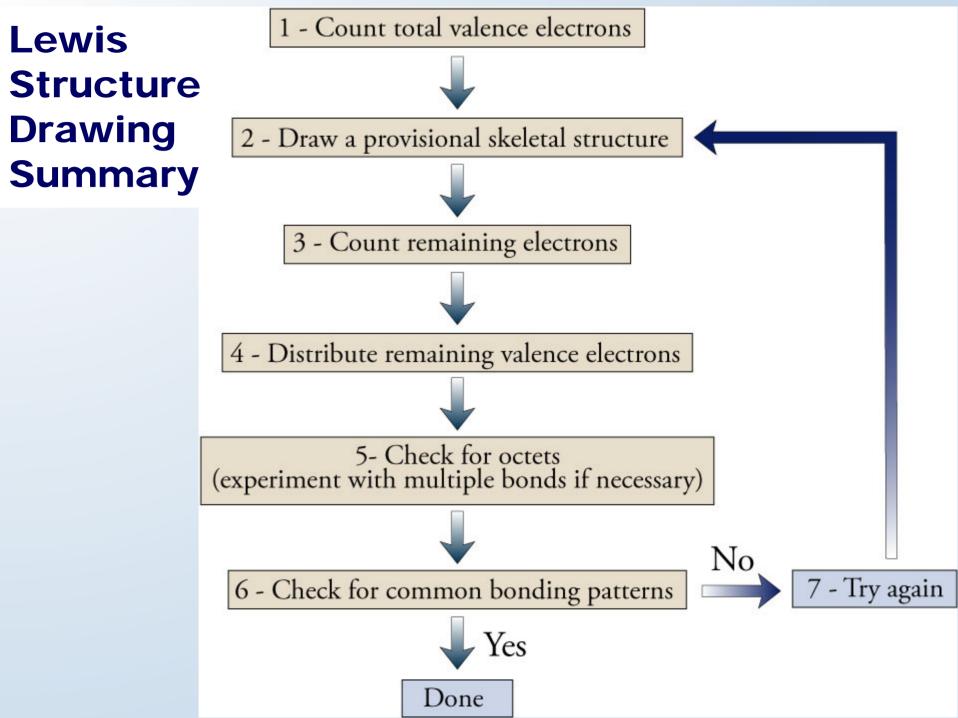
- If in Step 4 you were able to obtain an octet of electrons around each atom other than hydrogen and boron, and if you used all of the remaining valence electrons, go to Step 6.
 - If you have electrons remaining after each of the atoms other than hydrogen and boron have their octet, you can put more than eight electrons around elements in periods beyond the second period. (You will not need to use this procedure for any of the structures in this text, but if you take more advanced chemistry courses, it will be useful.)
 - If you do not have enough electrons to obtain octets of electrons around each atom (other than hydrogen and boron), convert one lone pair into a multiple bond for each two electrons that you are short.

Drawing Lewis Structures (6 & 7)

- Step 6: Check your structure to see if all of the atoms have their most common bonding pattern.
- Step 7: If necessary, try to rearrange your structure to give each atom its most common bonding pattern. One way to do this is to return to Step 2 and try another skeleton. (This step is unnecessary if all of the atoms in your structure have their most common bonding pattern.)

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Resonance

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 We can view certain molecules and polyatomic ions as if they were able to resonate-to switch back and forth-between two or more different structures. Each of these structures is called a *resonance* structure. The hypothetical switching from one resonance structure to another is called resonance.

To draw Resonance Forms

It is as if this ...pushing the electrons lone pair forms in this bond off to form a second bond... $x = Y = Z \iff x = Y = Z$

Resonance Hybrid

- To blend the resonance structures into a single resonance hybrid:
 - Step 1: Draw the skeletal structure, using solid lines for the bonds that are found in all of the resonance structures.
 - Step 2: Where there is sometimes a bond and sometimes not, draw a dotted line.

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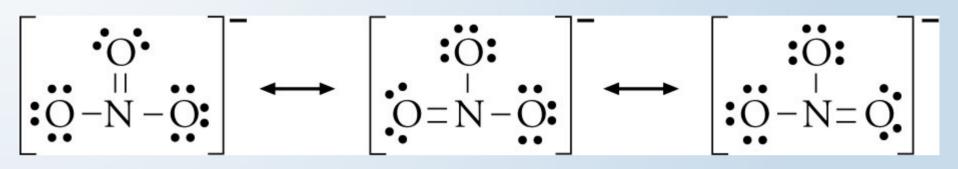
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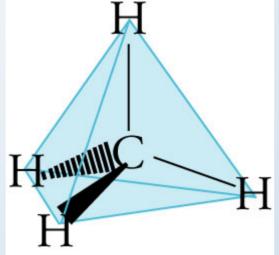
 Step 3: Draw only those lone pairs that are found on every one of the resonance structures. (Leave off the lone pairs that are on one or more resonance structure but not on all of them.)

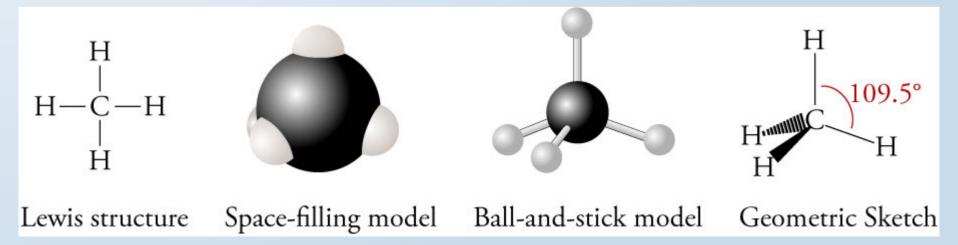
Nitrate Resonance



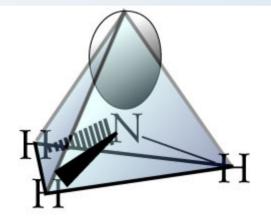
A bond found in all A bond found in all A bond found in all the resonance structures



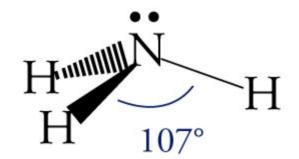




Ammonia, NH₃, Geometry

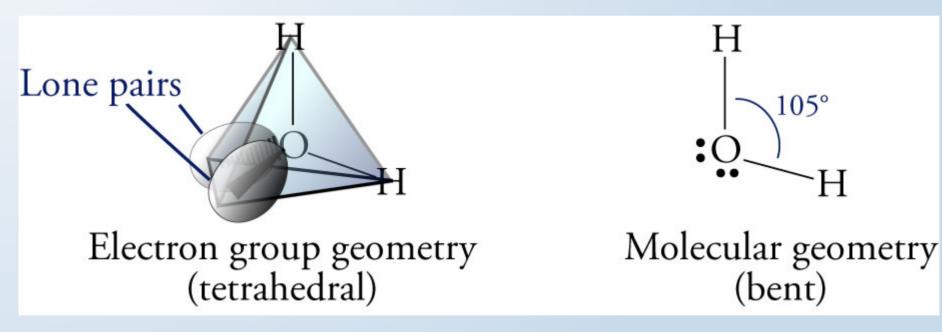


Electron group geometry (tetrahedral)

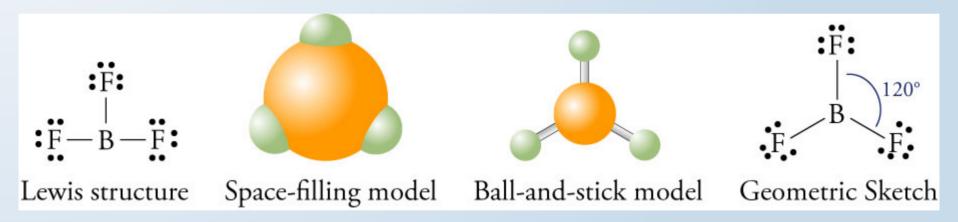


Molecular geometry (trigonal pyramid)

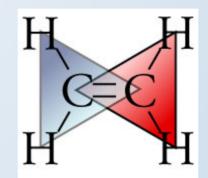
Water, H₂O, Geometry



Trigonal Planar Geometry – BF₃



Ethene (ethylene)

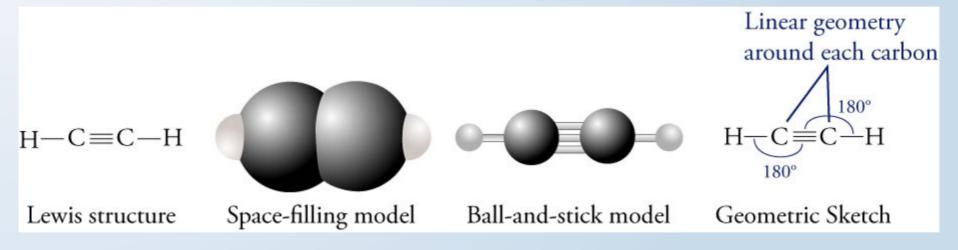


Trigonal planar
geometry around
each carbon

$$H - C = C - H$$

Lewis structure Space-filling model Ball-and-stick model Geometric Sketch

Ethyne (acetylene), C₂H₂



Steps for Molecular Geometry

- Step 1: To determine the name of the electron group geometry around each atom that is attached to two or more atoms, count the number of electron groups around each atom and apply the guidelines found on Table 12.3.
- Step 2: Use one or more of the geometric sketches shown on Table 12.3 for the geometric sketch of your molecule.

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Steps for Molecular Geometry (cont.)

 Step 3: To determine the name of the molecular geometry around each atom that has two or more atoms attached to it, count the number of bond groups and lone pairs, and then apply the guidelines found on Table 12.3.

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