

# Writing Lewis Structures

Lewis structures show how valence electrons are arranged among atoms in a compound using dots to represent the valence electrons that are not shared in a covalent bond. To draw Lewis structures showing covalent bonds for elements in periods 1 and 2, do the following: [1] sum the valence electrons; [2] use a pair of electrons to form a bond (bonding electrons); and [3] arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for other elements (lone pairs).

Example:  $H_2O$

Step 1: sum the valence electrons

$$H=1, O=6 \quad 1+1+6=8$$

Step 2: use a pair of electrons per bond (each represented as a line)

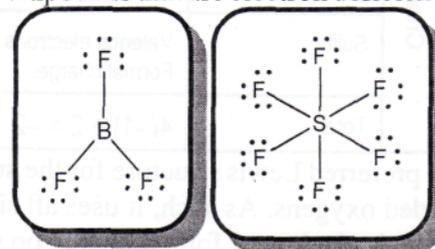


Step 3: distribute the remaining electrons



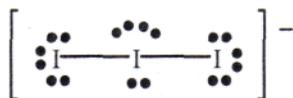
Step 4: check to see that the duet rule is satisfied for hydrogen and the octet rule is satisfied for all other atoms

There are exceptions to the octet rule. Boron and beryllium tend to form compounds that are electron deficient.



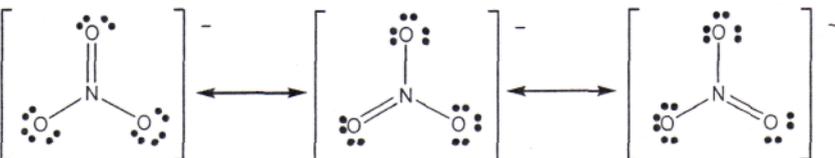
Elements in period 3 and beyond sometimes exceed the octet rule by using space in *d* orbitals to accommodate extra electrons. In  $SF_6$ , for example, S exceeds the octet rule.

When writing Lewis structures, satisfy the octet rule first; if extra electrons remain, place them on elements having available *d* orbitals; if one of several elements exceed the octet rule, assume the electrons are on the central atom.



There may be several valid *equivalent* Lewis structures for some molecules. This is called **resonance**.

The resonance structures for the polyatomic ion  $NO_3^-$  is pictured to the right. It does NOT have one double and two single bonds nor does it flip from one to the other structure as it appears. Rather it has 3 equivalent bonds. Resonance is represented by showing the possible Lewis structures with a double headed arrow indicating the actual structure is an average of the resonance structures.



When there are several nonequivalent Lewis structures for a molecule, it is possible to choose among them using formal charge. Formal charge is the difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule.

CONTINUED

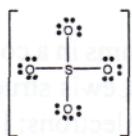
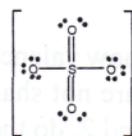
## Calculating Formal Charge

- lone pairs belong entirely to the atom in question
- shared electrons are divided equally among the sharing atoms  
 $\therefore (\text{Valence electrons})_{\text{assigned}} = (\text{number of lone pair electrons}) + \frac{1}{2}(\text{number of shared electrons})$

## Evaluating Lewis Structures with Formal Charge

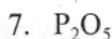
- atoms in molecules should have formal charges as close to zero as possible
- negative formal charges reside with the most electronegative element

**Example:  $\text{SO}_4^{2-}$**

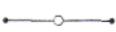
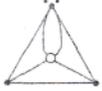
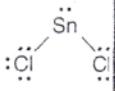
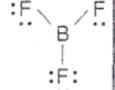
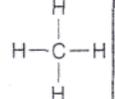
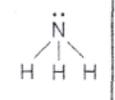
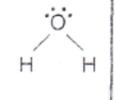
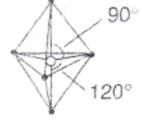
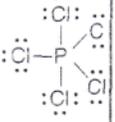
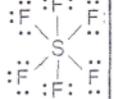
Structure		 32 valence electrons	 32 valence electrons
Formal Charge	Oxygen with single bonds	Valence electrons assigned: $6 + \frac{1}{2}(2) = 7$ Formal charge: $6 - 7 = -1$	Valence electrons assigned: $6 + \frac{1}{2}(2) = 7$ Formal charge: $6 - 7 = -1$
	Oxygen with double bonds	—	Valence electrons assigned: $4 + \frac{1}{2}(4) = 6$ Formal charge: $6 - 6 = 0$
	Sulfur	Valence electrons assigned: $0 + \frac{1}{2}(8) = 4$ Formal charge: $6 - 4 = 2$	Valence electrons assigned: $0 + \frac{1}{2}(12) = 6$ Formal charge: $6 - 6 = 0$
	Total	$4(-1) + 2 = -2$ ✗	$2(-1) + 2(0) + 0 = -2$ ✓

The preferred Lewis structure for the sulfate ion, as shown above, has two doubly bonded oxygens and two singly bonded oxygens. As such, it uses all six of sulfur's valence electrons to form bonds. This is preferred, because it results in the lowest formal charge on each atom.

**Draw the Lewis structures for each of the following using the procedures described above.**



## Summary of Molecular Shapes

Type of Molecule	Molecular Shape	Atoms Bonded to Central Atom	Lone Pairs of Electrons	Formula Example	Lewis Structure
Linear		2	0	BeF <sub>2</sub>	
Bent		2	1	SnCl <sub>2</sub>	
Trigonal-planar		3	0	BF <sub>3</sub>	
Tetrahedral		4	0	CH <sub>4</sub>	
Trigonal-pyramidal		3	1	NH <sub>3</sub>	
Bent		2	2	H <sub>2</sub> O	
Trigonal-bipyramidal		5	0	PCl <sub>5</sub>	
Octahedral		6	0	SF <sub>6</sub>	

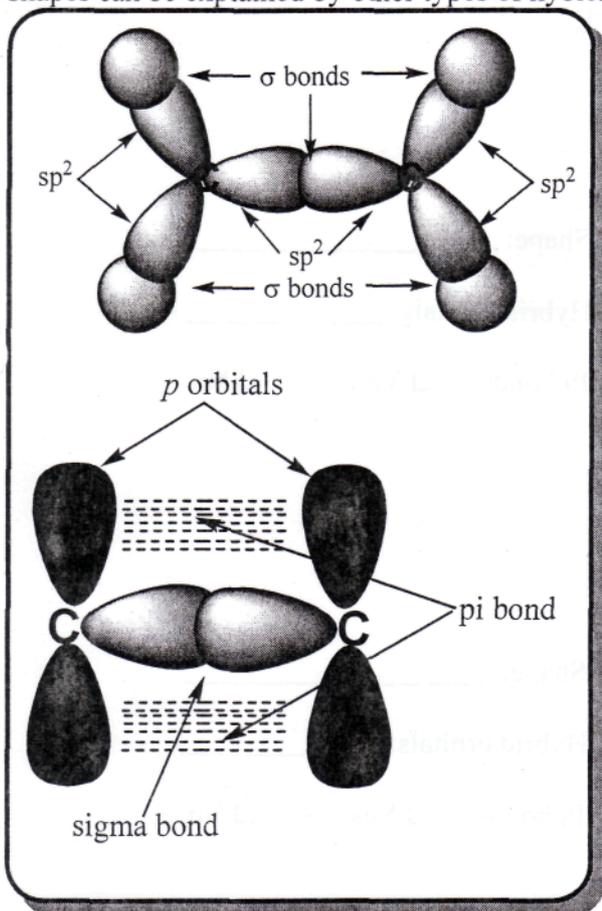
## Summary of Hybridization

Number of Bonds	Number of Unused Electron Pairs	Type of Hybrid Orbital	Angle Between Bonded Atoms	Geometry	Example
2	0	<i>sp</i>	180°	Linear	BeF <sub>2</sub>
3	0	<i>sp<sup>2</sup></i>	120°	Trigonal-planar	BF <sub>3</sub>
4	0	<i>sp<sup>3</sup></i>	109.5°	Tetrahedral	CH <sub>4</sub>
3	1	<i>sp<sup>3</sup></i>	90° to 109.5°	Pyramidal	NH <sub>3</sub>
2	2	<i>sp<sup>3</sup></i>	90° to 109.5°	Angular	H <sub>2</sub> O
6	0	<i>sp<sup>3</sup>d<sup>2</sup></i>	90°	Octahedral	SF <sub>6</sub>

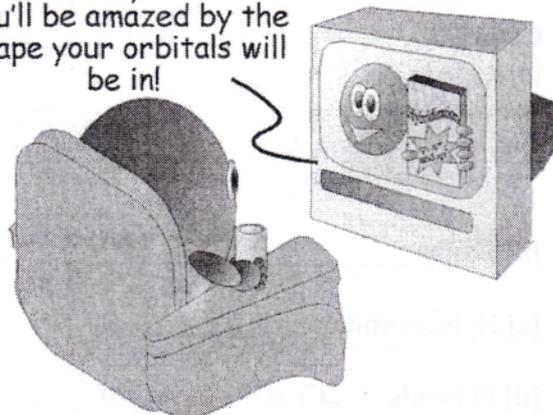
# Understanding Hybrid Orbitals

The native orbitals found in an atom in the free state cannot always account for the geometry of the compounds formed from the atom. Atomic orbitals that provide for minimum energy in the free state, are often different from those in a molecule. Mixing of native atomic orbitals to allow bonding to occur is known as **hybridization**.

Methane ( $\text{CH}_4$ ) illustrates how hybridization explains observed molecular structure. Methane has four equivalent bonds with a tetrahedral arrangement. The valence structure of carbon ( $2s^2 2p^2$ ) does not fit this structure because  $s$  orbitals are nondirectional,  $p$  orbitals are at right angles, and  $s$  and  $p$  orbitals don't form equivalent bonds. When methane forms, one  $s$  orbital combines with three  $p$  orbitals to form four equivalent  $sp^3$  hybrid orbitals.  $sp^3$  hybrid orbitals are tetrahedral. Other molecular shapes can be explained by other types of hybrid orbitals:



Try **new molecular hybridization formula**, now with  $sp$  factor. You'll be amazed by the shape your orbitals will be in!



- Whenever an atom is surrounded by three effective electron pairs to form a trigonal planar molecule, a set of  $sp^2$  hybrid orbitals is required.. Combination of one  $s$  orbital and two  $p$  orbitals to form an  $sp^2$  hybrid gives the appropriate  $120^\circ$  angle. In forming the  $sp^2$  orbital, one  $p$  orbital is not used, and is oriented perpendicular to the plane of the  $sp^2$  orbitals each of the three  $sp^2$  orbitals forms bonds by sharing a pair of electrons in an area centered on a line between the two atoms. These are called sigma ( $\sigma$ ) bonds. The double bond is formed in the space above and below the  $\sigma$  bond by the  $p$  orbital perpendicular to the  $sp^2$  orbitals. This is called a pi ( $\pi$ ) bond.
- $sp$  hybridization enables two effective pairs of electrons to bond at  $180^\circ$ . One  $s$  and one  $p$  are hybridized to form two  $sp$  hybrid orbitals at a  $180^\circ$  angle. Two  $p$  orbitals remain. The hybrid orbitals form sigma bonds and the  $p$  orbitals form pi bonds.
- $dsp^3$  hybridization enables a trigonal bipyramidal arrangement for five pairs of electrons surrounding a central atom, while  $d^2sp^3$  hybridization enables an octahedral arrangement for six pairs of electrons surrounding a central atom.

CONTINUED 

For each of the formulas below, do the following: [a] Draw the Lewis structure; [b] state the shape (*Linear*, *Trigonal planar*, *Tetrahedral*, *Trigonal bipyramidal*, *Octahedral*, *Pyramidal*, or *Bent*); [c] identify the type of hybrid orbitals present ( $sp^3$ ,  $sp^2$ ,  $sp$ ,  $dsp^3$  or  $d^2sp^3$ ); and [d] indicate whether or not there are any  $\pi$  bonds.

1.  $\text{CO}_2$   
[a]

[b] Shape: \_\_\_\_\_

[c] Hybrid orbitals: \_\_\_\_\_

[d]  $\pi$  bonds  Yes  No

4.  $\text{PCl}_5$   
[a]

[b] Shape: \_\_\_\_\_

[c] Hybrid orbitals: \_\_\_\_\_

[d]  $\pi$  bonds  Yes  No

2.  $\text{C}_2\text{F}_4$   
[a]

[b] Shape: \_\_\_\_\_

[c] Hybrid orbitals: \_\_\_\_\_

[d]  $\pi$  bonds  Yes  No

5.  $\text{C}_6\text{H}_6$   
[a]

[b] Shape: \_\_\_\_\_

[c] Hybrid orbitals: \_\_\_\_\_

[d]  $\pi$  bonds  Yes  No

3.  $\text{H}_2\text{O}$   
[a]

[b] Shape: \_\_\_\_\_

[c] Hybrid orbitals: \_\_\_\_\_

[d]  $\pi$  bonds  Yes  No

6.  $\text{XeF}_4$   
[a]

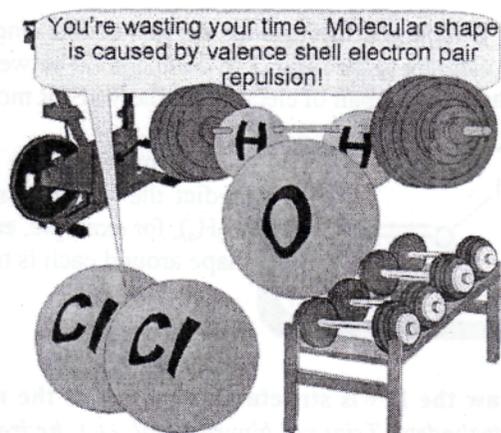
[b] Shape: \_\_\_\_\_

[c] Hybrid orbitals: \_\_\_\_\_

[d]  $\pi$  bonds  Yes  No

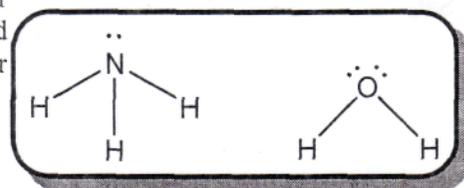
# Predicting Molecular Shapes

One approach to predicting molecular shape is the valence shell electron repulsion model (VSEPR). According to VSEPR theory, repulsion between sets of valence shell electrons causes them to be as far apart as possible. Taking this repulsion into account, the shape of a molecule depends upon how many pairs of valence electrons surround the central atom, the number of lone pairs of electrons, and the presence of multiple bonds (double bonds or triple bonds). Two pairs of valence electrons will be at  $180^\circ$  to each other producing a linear molecule, three pairs will be at  $120^\circ$  to each other in a single plane producing a trigonal planar molecule, and four pairs will be at  $109.5^\circ$  to each other producing a tetrahedral molecule, a three sided pyramid with a triangular base. The central atom is in the center of the pyramid and the attached atoms are at the four apices. Five pairs of valence electrons around the central atom produces a trigonal bipyramidal, a molecule with a trigonal planar portion having bond angles of  $120^\circ$  and two bonding sites above and below the plane at  $90^\circ$  to it. Six pairs of valence electrons around the central atom produces an octahedral molecule with  $90^\circ$  angles in all six directions. See below.



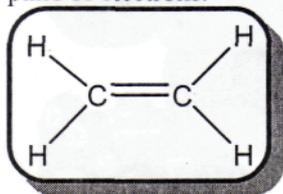
Number of Electron Pairs	Shape	Arrangement of Electron Pairs	
2	Linear		
3	Trigonal planar		
4	Tetrahedral		
5	Trigonal bipyramidal		
6	Octahedral		

If the central atom has a full octet of valence electrons, but some of them are lone pairs, the bond angle changes from the standard  $109.5^\circ$  tetrahedral angle. Lone pairs of electrons increase the repulsion reducing the angle between bonded pairs. The shape of the molecule includes only the bonded atoms and not the lone pair electrons. As a result, ammonia ( $\text{NH}_3$ ) is pyramidal with a bond angle of  $107^\circ$ , and water ( $\text{H}_2\text{O}$ ) is bent with a bond angle of  $105^\circ$ . The bond angle is smaller in water than in ammonia because it has two lone pairs of electrons instead of one.

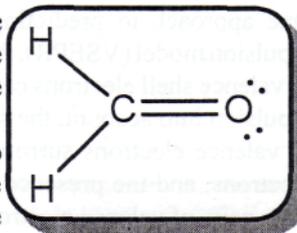


(CONTINUED )

Double and triple bonds are treated like single bonds. As a result,  $\text{CH}_2\text{O}$  is trigonal planar. See the diagram to the right. The double bond between the oxygen and the carbon behaves like a single bond with one pair of electrons in the VSEPR model. This means that carbon has only three effective pairs of electrons.



For molecules in which there is no central atom, it is possible to predict the shape of sections of the molecule. In the molecule ethene ( $\text{C}_2\text{H}_4$ ), for example, each of the carbons behaves like a central atom. The shape around each is trigonal planar. See the diagram to the left.



Draw the Lewis structures for each of the molecules below, and predict whether each is *Linear*, *Trigonal planar*, *Tetrahedral*, *Trigonal bipyramidal*, *Octahedral*, *Pyramidal*, or *Bent*.

