

MOLECULAR GEOMETRY AND BONDING THEORIES

The content in this topic is the basis for mastering Learning Objective 2.21 as found in the Curriculum Framework.

When you finish reviewing this topic, be sure you are able to:

- Know the difference between electron domain geometry and molecular geometry
- Apply VSEPR theory to both octet and non-octet Lewis structures of ions and molecules
- Predict molecular geometries and bond angles of molecules
- Distinguish between chemical species containing sp , sp^2 , and sp^3 hybridized orbitals
- Determine the polarity of molecules and their orbital hybridizations from geometries
- Visualize covalent bond formation as the overlap of atomic orbitals
- Distinguish between sigma and pi bonds
- Understand why sigma bonds have larger bond energies than pi bonds
- Use Lewis structures to identify formulas that have delocalized electrons

The VSEPR Model

Section 9.2

The **valence-shell electron-pair repulsion** (VSEPR) model is a way to use Lewis structures to determine the geometries of molecules. It is based on the natural repulsive forces that electron pairs exhibit within a molecule.

The **geometry** of a molecule refers to the arrangement of its atoms in three-dimensional space.

A **bond angle** is an angle made by the lines joining the nuclei of atoms in a molecule.

An **electron domain** is a region around an atom in which electrons will most likely be found. An electron domain is produced by a nonbonding pair, a single bond, a double bond, or a triple bond.

An **electron domain geometry** is the three-dimensional arrangement of electron domains around the central atom of a molecule.

A **molecular geometry** is the arrangement of only the atoms in the molecule.

Tables 9.1 and 9.2 show the common electron domain and molecular geometries of atoms.

Table 9.1 Electron domain geometries and molecular geometries for molecules with two, three, and four electron domains.



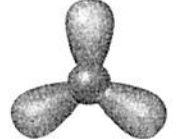
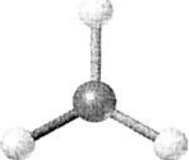
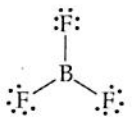
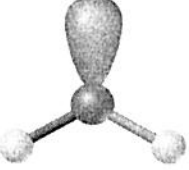
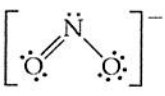
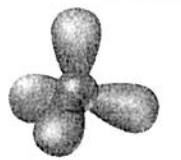
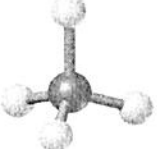
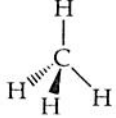
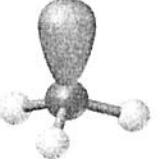

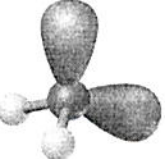

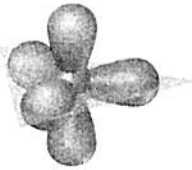


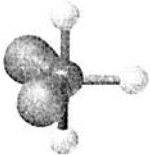
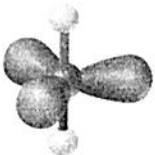
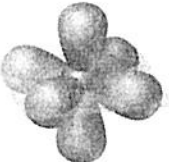


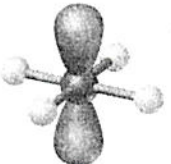
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

Table 9.2 Electron domain geometries and molecular geometries for molecules with five and six electron domains.

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

Rules for determining geometry from VSEPR theory are the following:

1. Draw the Lewis structure.
2. Count the number of electron domains around the central atom. Count each nonbonding pair, single bond, double bond, and triple bond as one domain.
3. Arrange the domains of electrons as far away in three-dimensional space as possible. Use the geometries in Tables 9.1 and 9.2 that correspond to the electron domains around the central atom. Examples are given in Table 9.3.

Table 9.3 Examples of geometries obtained from the VSEPR model. Notice that the existence of nonbonding electrons affects the name of the molecular geometry.

Electron Domains, Nonbonding Pairs	Electron Domain Geometry	Molecular Geometry	Bond Angles	Orbital Hybridization	Examples
2,0	Linear	Linear	180°	sp	BeI_2 , CO_2 , HCN , OCN^-
3,0	Trigonal planar	Trigonal planar	120°	sp^2	BF_3 , SO_3 , PCl_3 , NO_3^- , CO_3^{2-}
3,1	Trigonal planar	Nonlinear	$<120^\circ$	sp^2	SO_2 , O_3 , NO_2^-
4,0	Tetrahedral	Tetrahedral	109.5°	sp^3	CH_4 , SO_4^{2-} , ClO_4^- , NH_4^+
4,1	Tetrahedral	Trigonal pyramidal	$<109^\circ$	sp^3	NH_3 , SO_3^{2-} , ClO_3^-
4,2	Tetrahedral	Nonlinear	$<109^\circ$	sp^3	H_2O , OF_2
5,0	Trigonal bipyramidal	Trigonal bipyramidal	90° 120°	—	PCl_5
5,1	Trigonal bipyramidal	See-saw	$<90^\circ$ $<180^\circ$	—	SF_4
5,2	Trigonal bipyramidal	T-shape	$<90^\circ$ $<120^\circ$	—	ClF_3
5,3	Trigonal bipyramidal	Linear	180°	—	I_3^- , XeF_2
6,0	Octahedral	Octahedral	90°	—	SF_6
6,1	Octahedral	Square pyramidal	$<90^\circ$ $<180^\circ$	—	BrF_5
6,2	Octahedral	Square planar	90° 180°	—	XeF_4

Common misconception: The vital and subtle difference between an electron domain geometry and a molecular geometry is the presence of one or more nonbonding pairs of electrons around the central atom. When no nonbonding pair is present, the electron domain geometry has the same name as the molecular geometry. When one or more nonbonding pairs exist on the central atom, the name changes for the molecular geometry to describe only the locations of the atoms and not the nonbonding pair(s).

Common misconception: Except for the 109.5° angles in tetrahedral geometries, most bond angles need not be memorized. Most bond angles can be deduced from the electron domain geometries using basic geometrical principles.



Any nonbonding pairs on a five electron domain geometry occupy the radial (or equatorial) positions, not the axial positions as seen in Figure 9.1. Because nonbonding pairs have greater repulsion, the radial positions offer fewer 90° interactions with other domains. In the axial position, a nonbonding pair experiences three 90° interactions. By contrast, the equatorial position offers only two 90° interactions.

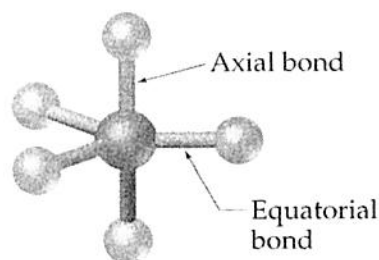


Figure 9.1 The trigonal bipyramidal geometry showing equatorial and axial bonds.

Examine Tables 9.1 and 9.2 and deduce the bond angles for the following electron domain geometries: linear, trigonal planar, trigonal bipyramidal, octahedral. Write your answers in the space provided.

Your Turn 9.1

Electron domains for nonbonding electron pairs and double bonds exert greater repulsive forces on adjacent domains and thus tend to compress the bond angles. Table 9.4 lists several examples of molecules having slightly smaller bond angles than predicted by VSEPR model.

Table 9.4 Molecules having smaller than normal bond angles because of nonbonding electron pairs or double bonds.

Molecule	Electron Domain Geometry	Molecular Geometry	Actual Bond Angle
NH_3	Tetrahedral	Trigonal pyramid	107°
H_2O	Tetrahedral	Nonlinear	104.5°
SF_4	Trigonal bipyramidal	Seesaw	116°
$\text{Cl}_2\text{C}=\text{O}$	Trigonal planar	Trigonal planar	111.4° (Cl–C–Cl)
SO_2	Trigonal planar	Nonlinear	116°

Section 9.3

Molecular Shape and Molecular Polarity

Bond polarity is a measure of how equally the electrons in a bond are shared between two atoms. The greater the difference in electronegativity of the bonded atoms, the more polar the bond.

Dipole moment is a quantitative measure of the charge separation in a molecule.

A **bond dipole** is the dipole moment for a particular bond in a molecule.

An **overall dipole moment** of a molecule is the vector sum of all of its bond dipoles. For a molecule that consists of more than two atoms, the dipole moment depends on both the polarities of the individual bonds and the geometry of the molecule. Figure 9.2 illustrates how bond polarity and geometry affect the polarity of a molecule.

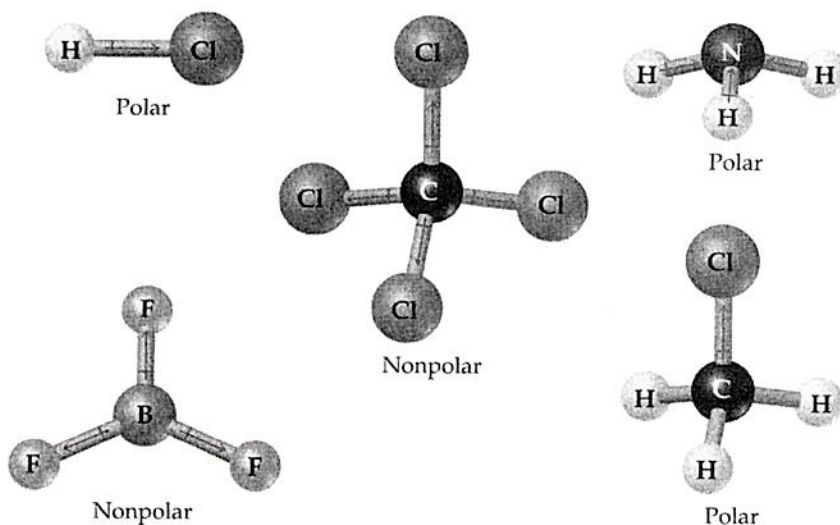


Figure 9.2 Geometry affects whether a molecule containing polar bonds will be polar.

Explain why the molecules shown in Figure 9.2 are polar or nonpolar. Write your answer in the space provided.

Your Turn 9.2

Hybrid Orbitals

Section 9.5

Valence-bond theory defines a covalent bond as an **overlap** of orbitals allowing two electrons of opposite spin to share a common region of space between the nuclei. Figure 9.3 illustrates bonding by orbital overlap in the molecules H_2 , HCl , and Cl_2 .

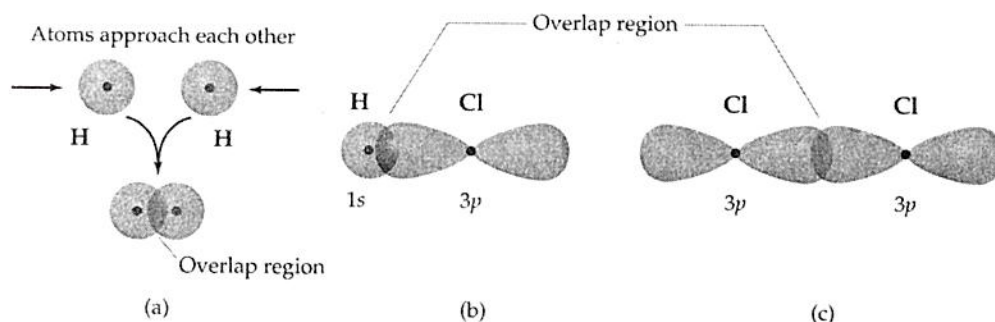


Figure 9.3 Orbitals overlap to form covalent bonds.

Hybrid orbitals result from the mathematical mixing of two or more atomic “unhybridized” atomic orbitals. The shape of any hybrid orbital is different from the shapes of the original unhybridized orbitals and explains the geometries of molecules. For example, the mixing of the valence $2s$ and $2p$ orbitals of carbon can result in sp^3 , sp^2 , or sp hybridized orbitals as shown in Figure 9.4.

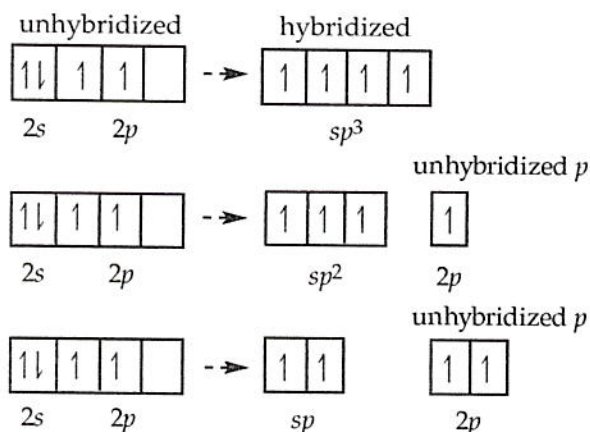


Figure 9.4 Mixing one s and three p orbitals results in an sp^3 hybrid. Mixing one s and two p orbitals creates an sp^2 hybrid. Mixing one s and one p orbital yields an sp hybrid.



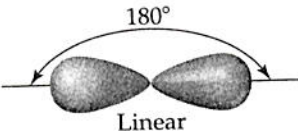
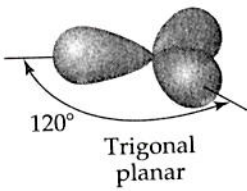
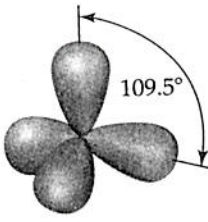
Common misconception: Remember that the number of orbitals mixed always equals the number of hybrid orbitals produced. Leftover orbitals that are unhybridized often take part in bonding, especially with double and triple bonds.

Your Turn 9.3

Use a diagram like that in Figure 9.4 to show the valence unhybridized and sp^3 hybridized orbitals of the oxygen atom. Write your answer in the space provided.

Table 9.5 illustrates the various geometrical arrangements associated with hybrid orbitals.

Table 9.5 Geometric arrangements characteristic of hybrid orbital sets.

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s, p	Two sp	 Linear	$\text{BeF}_2, \text{HgCl}_2$
s, p, p	Three sp^2	 Trigonal planar	BF_3, SO_3
s, p, p, p	Four sp^3	 Tetrahedral	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$

Multiple Bonds

Section 9.6

A **sigma (σ) bond** is formed by the **end-to-end overlap** of orbitals. All single bonds are sigma bonds.

A **pi (π) bond** results from a **side-to-side overlap** of orbitals. A double bond consists of one sigma and one pi bond. A triple bond results from one sigma and two pi bonds.

Sigma bonds are stronger than pi bonds. Sigma bonds have most of their electron density concentrated between and, therefore, closer to the nuclei of the bonded atoms. The pi bond sideways orientation of p orbitals does not produce as effective overlap as the sigma orientation, so sigma bonds are stronger.

Figure 9.5 illustrates the difference between a sigma and a pi bond.

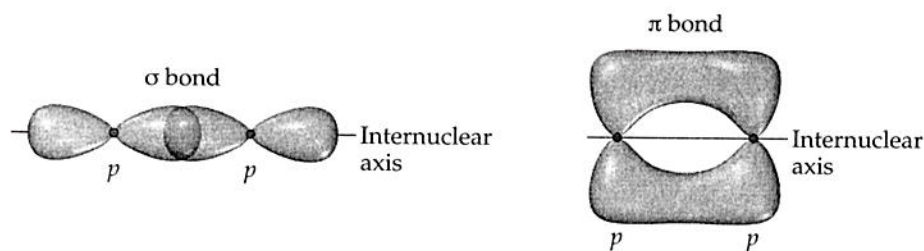


Figure 9.5 Comparison of a sigma and a pi bond. Note that the two regions of overlap in the pi bond, above and below the internuclear axis, constitute a single pi bond.

Delocalized electrons are spread out over a number of atoms in a molecule rather than localized between a pair of atoms. Delocalized pi bonding electrons are characteristic of molecules that have resonance structures involving double bonds. For example, benzene, C_6H_6 , is a ring of six carbons, each bonded to the next by a sigma bond. Delocalized pi bonds blend the two resonance structures into a single structure as shown in Figure 9.6.

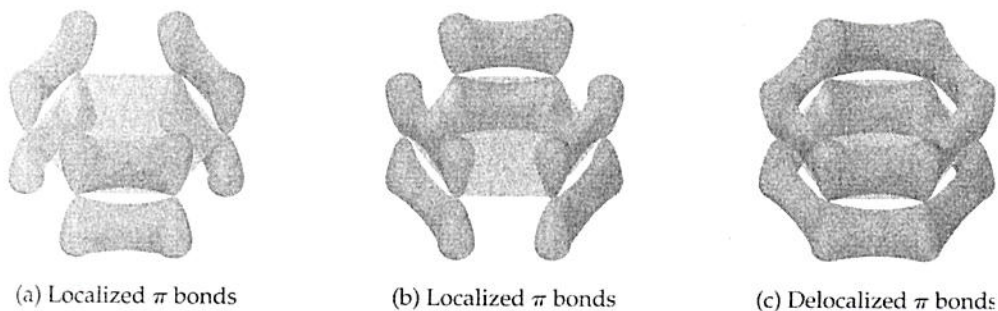


Figure 9.6 Two resonance structures of benzene (a and b) showing localized pi bonds differ from a more accurate representation (c) showing delocalized pi bonds.

Section 9.7

Molecular Orbitals

Molecular orbital (MO) theory is a more sophisticated model that explains bonding systems that valence bond theory or Lewis structures cannot. For example, MO theory explains the excited states of molecules and why they absorb light. In its simplest form MO theory states that whenever two atomic orbitals overlap, two MOs form. For instance, two overlapping 1s hydrogen orbitals form two MOs, one bonding orbital and one antibonding orbital as shown in Figure 9.7.

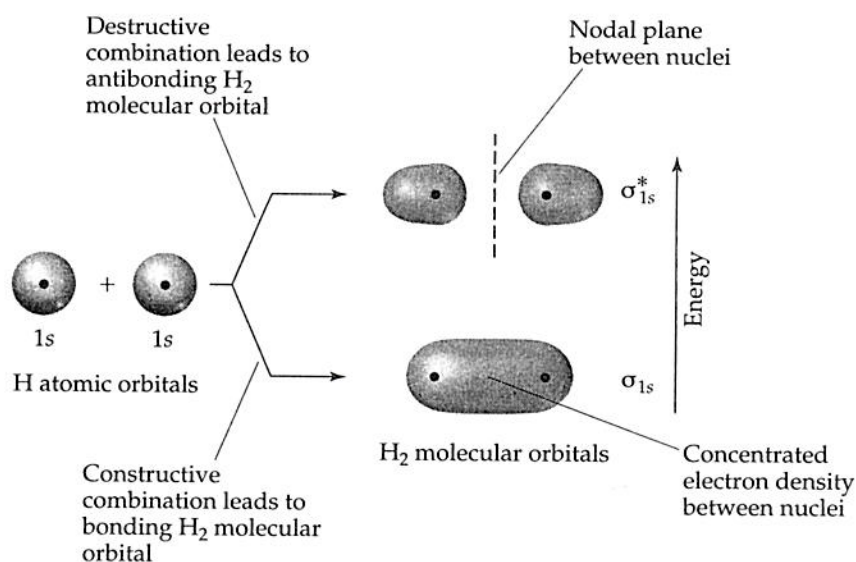


Figure 9.7 The two MOs of H₂, one a bonding MO and one an antibonding MO.

In the ground state, the two electrons, one from each hydrogen atom, occupy the bonding orbital and constitute a sigma bond. When the hydrogen molecule absorbs light, an electron can be excited into the antibonding orbital.

Multiple Choice Questions

1. Which of these molecules is not polar?
 - A) H_2O
 - B) CO_2
 - C) NO_2
 - D) SO_2
 - E) NH_3
2. Which species contains a central atom with sp^2 hybridization?
 - A) C_2H_2
 - B) SO_3^{2-}
 - C) O_3
 - D) BrI_3
 - E) NH_3
3. For ClF_3 , the electron domain geometry of Cl and the molecular geometry are, respectively,
 - A) trigonal planar and trigonal planar.
 - B) trigonal planar and trigonal bipyramidal.
 - C) trigonal bipyramidal and trigonal planar.
 - D) trigonal bipyramidal and T-shaped.
 - E) trigonal planar and T-shaped.
4. The size of the H-N-H bond angles of the following species increases in which order?
 - A) $NH_3 < NH_4^+ < NH_2^-$
 - B) $NH_3 < NH_2^- < NH_4^+$
 - C) $NH_2^- < NH_3 < NH_4^+$
 - D) $NH_2^- < NH_4^+ < NH_3$
 - E) $NH_4^+ < NH_3 < NH_2^-$
5. What is the molecular geometry and polarity of the BF_3 molecule?
 - A) trigonal pyramidal and polar
 - B) trigonal pyramidal and nonpolar
 - C) trigonal planar and polar
 - D) trigonal planar and nonpolar
 - E) T-shaped and polar

6. In which species is the F-X-F bond angle the smallest?
- A) NF_3
 - B) BF_3
 - C) CF_4
 - D) BrF_3
 - E) OF_2
7. Which set does not contain a linear species?
- A) $\text{CO}_2, \text{SO}_2, \text{NO}_2$
 - B) $\text{H}_2\text{O}, \text{HCN}, \text{BeI}_2$
 - C) $\text{OCN}^-, \text{C}_2\text{H}_2, \text{OF}_2$
 - D) $\text{I}_3^-, \text{BrF}_3, \text{SCN}^-$
 - E) $\text{H}_2\text{S}, \text{ClO}_2^-, \text{NH}_2^-$
8. The hybrid orbitals of nitrogen in N_2O_4 are
- A) sp .
 - B) sp^2 .
 - C) sp^3 .
 - D) sp and sp^3 .
 - E) sp^2 and sp^3 .
9. How many sigma and pi bonds are in
- $$\begin{array}{c} \text{O} \\ || \\ \text{CH}_2 = \text{CHCH}_2\text{CCH}_3 \end{array}?$$
- A) five sigma and two pi
 - B) eight sigma and four pi
 - C) eleven sigma and two pi
 - D) eleven sigma and four pi
 - E) thirteen sigma and two pi
10. What is the best estimate of the H-O-H bond angle in H_3O^+ ?
- A) 109.5°
 - B) 107°
 - C) 104.5°
 - D) 116°
 - E) 120°

Free Response Questions

1. Consider the chemical species IF_5 and IF_4^+ .
 - a. Draw the Lewis structure and make a rough three-dimensional sketch of each species.
 - b. Identify the electron domain geometry and the molecular geometry of each structure.
 - c. Identify the approximate bond angles of each species.
 - d. Predict which, if any, is a polar species. Justify your answer.
 - e. Predict the most probable oxidation number of the iodine atom in each species. Give an example of another chemical species with iodine having the same oxidation number as IF_4^+ .
 - f. Would you expect the conversion of IF_5 to IF_4^+ to be exothermic or endothermic? Explain.
2. Consider each of these molecules: C_3H_4 , C_3H_6 , and C_3H_8 .
 - a. Draw the Lewis structure for each molecule and identify the orbital hybridization of each carbon atom.
 - b. Specify the geometry of each central carbon atom.
 - c. Write a balanced chemical equation for the complete combustion of each molecule.
 - d. Use the following bond enthalpies to determine the heat of combustion of each molecule. Specify your answer in kJ/mol.

Bond	kJ/mol	Bond	kJ/mol
$C-H$	413	$O-H$	463
$C-C$	348	O_2	495
$C=C$	614	$C=O$	799
$C\equiv C$	839	$C-O$	358