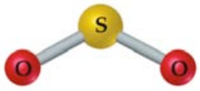
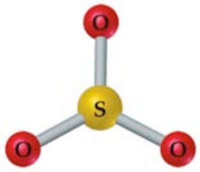
Chapter 9 Molecular Geometry and Bonding Theories

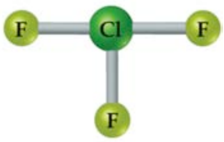
9.1 Molecular Shapes

Lewis structures give atomic **connectivity** (which atoms are physically connected).

By noting the number of bonding and nonbonding electron pairs we can easily predict the shape of the molecule

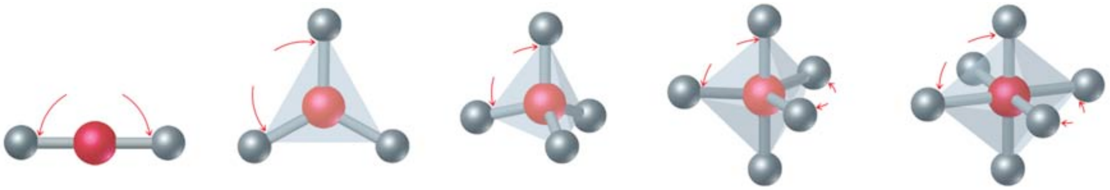




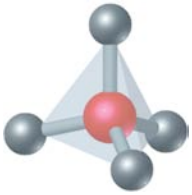


In order to predict molecular shape, we assume that the valence electrons repel each other.

For molecules of the general form **AB_n** there are 5 fundamental shapes:



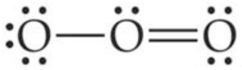
The shape of any particular AB_n molecule can usually be derived from one of these shapes. For example, starting from a tetrahedron:



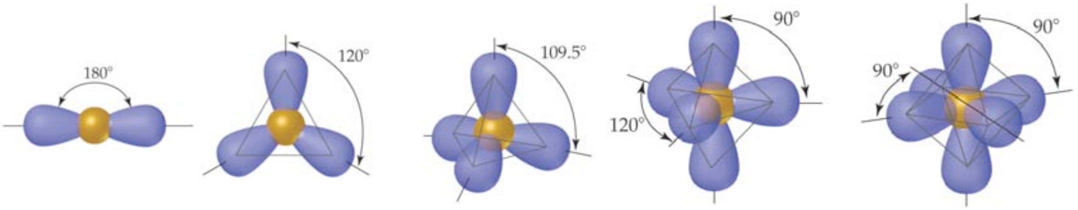
9.2 The VSEPR Model

What determines the shape of a molecule? Electron pairs, whether bonding or nonbonding, repel each other.

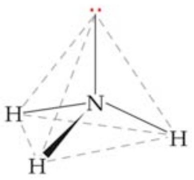
Each **nonbonding pair**, **single bond** or **multiple bond** produces an electron domain about the central atom.

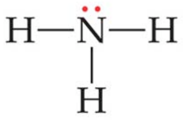


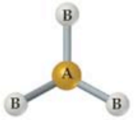
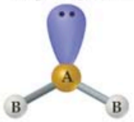
VSEPR predicts that

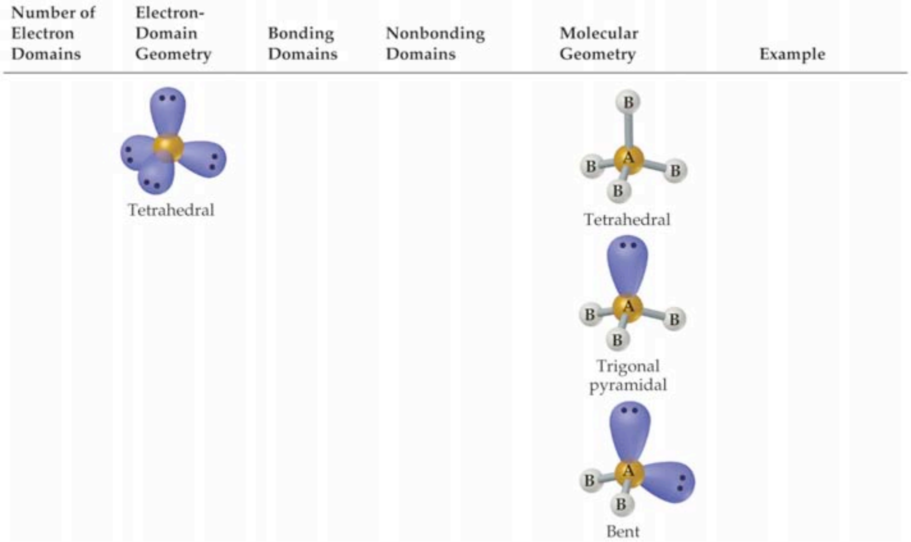


We use the electron-domain geometry to help us predict the molecular geometry.



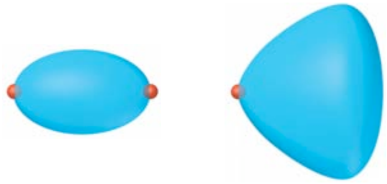


Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
	 Linear			 Linear	
	 Trigonal planar			 Trigonal planar	
				 Bent	



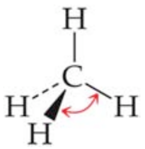
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
	Tetrahedral			Tetrahedral	
				Trigonal pyramidal	
				Bent	

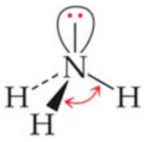
Effect of nonbonding electrons and multiple bonds on bond angles

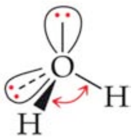


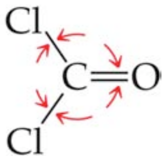
Nonbonding pairs are physically larger than bonding pairs.

Electrons in nonbonding pairs and in multiple bonds repel **more** than electrons in single bonds:



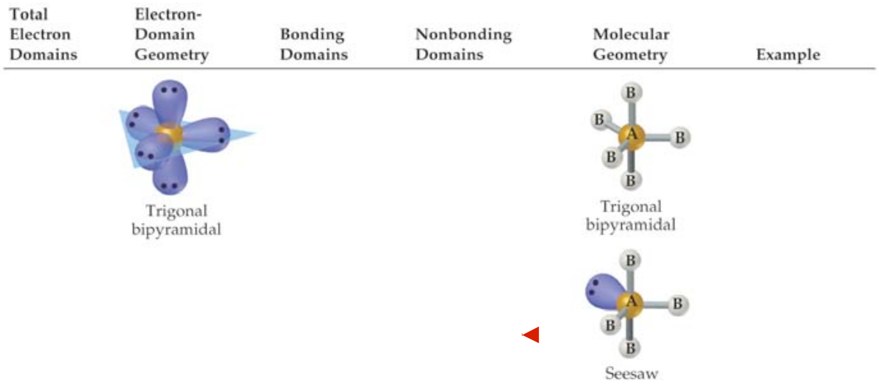




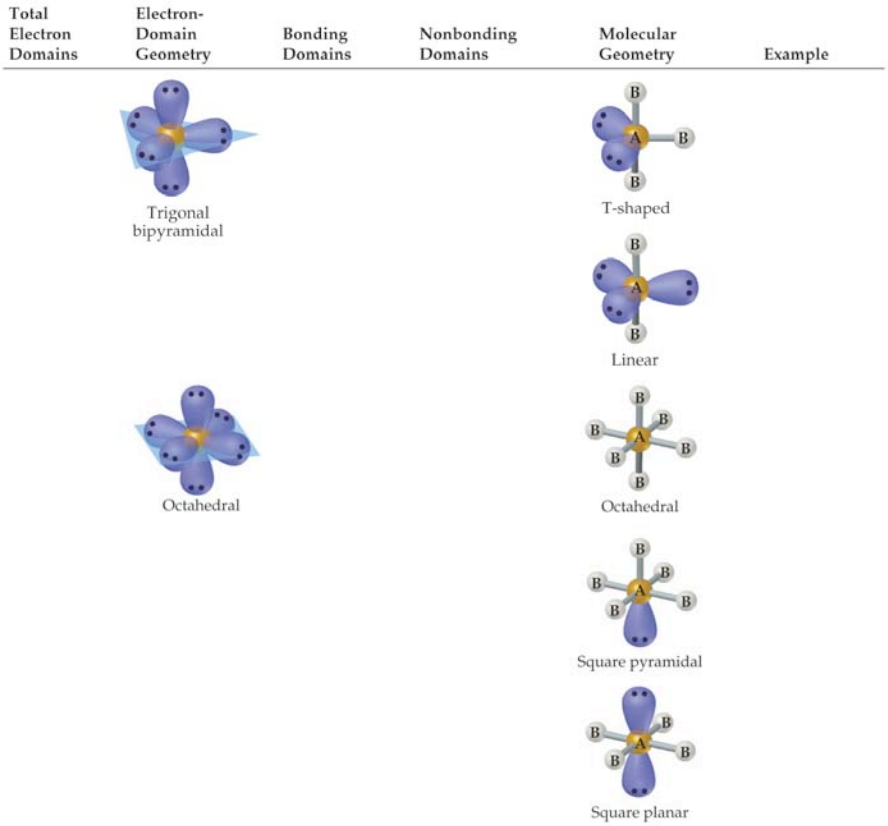


Molecules with Expanded Valence Shells

Atoms that have expanded octets have **five** electron domains (*trigonal bipyramidal*) or **six** electron domains (*octahedral*) electron-domain geometries.

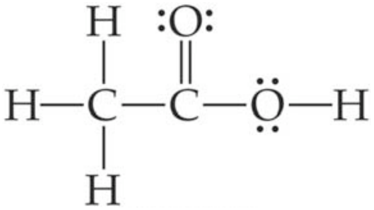


Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
	Trigonal bipyramidal			Trigonal bipyramidal	
				Seesaw	



Shapes of larger molecules

The interior atoms of more complicated molecules can be dealt with in turn using the VSEPR model.

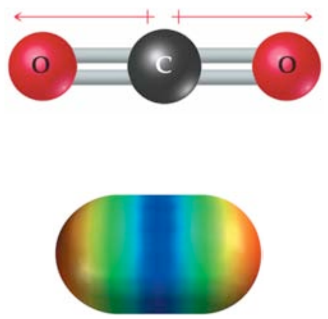


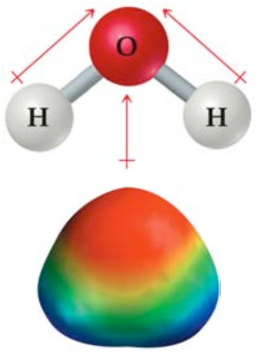
Blackboard examples

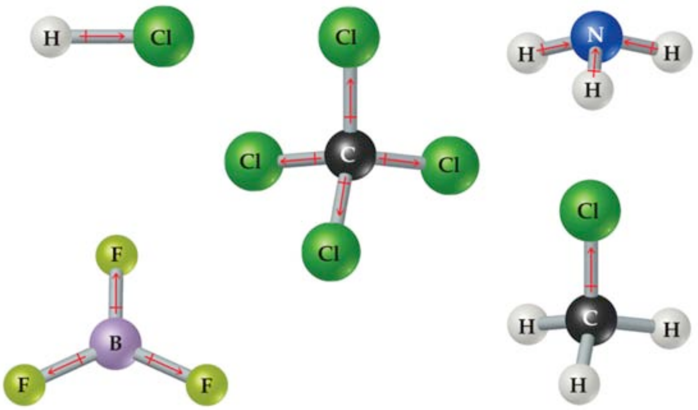
1. Give the electron-domain and molecular geometries for the following molecules and ions: (a) HCN, (b) SO_3^{2-}, (c) SeF_4, (d) PF_6^-, (e) BF_4^-, (f) N_3^-.

9.3 Molecular Shape and Molecular Polarity

Polar molecules interact with electric fields. Binary compounds are polar if their centers of negative and positive charge **do not** coincide.

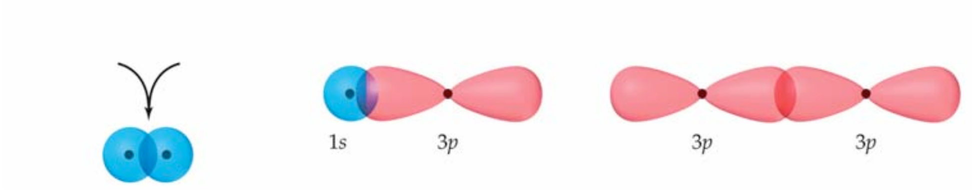




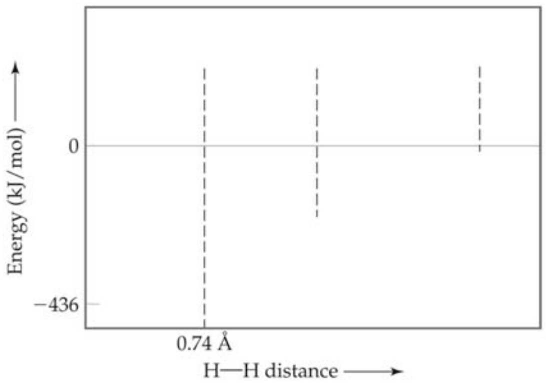


9.4 Covalent Bonding and Orbital Overlap

Covalent bonds form through sharing of electrons by adjacent atoms.



The change in potential energy as two hydrogen atoms combine to form the H_2 molecule:

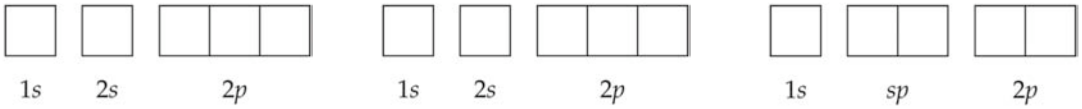


9.5 Hybrid Orbitals

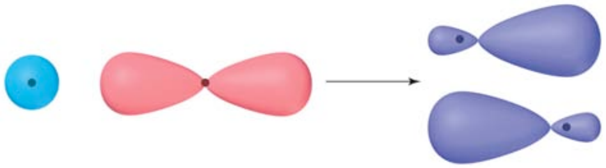
To apply the ideas of orbital overlap and valence-bond theory to polyatomic molecules, we need to introduce the concept of **hybrid orbitals**.

sp hybrid orbitals

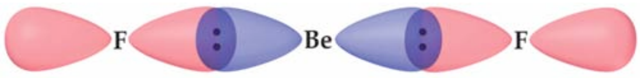
Consider beryllium: in its ground electronic state, it would not be able to form bonds because it has no singly-occupied orbitals:



Mixing the *s* and *p* orbitals yields two degenerate orbitals

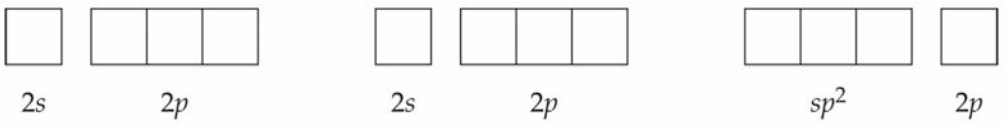


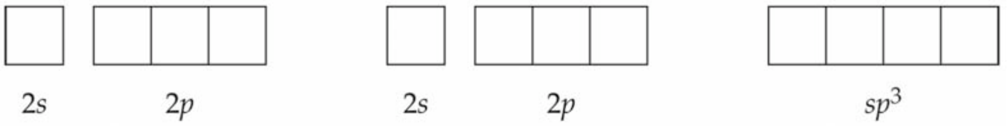
These two degenerate orbitals align themselves 180° from each other, and 90° from the two remaining unhybridized *p* orbitals.

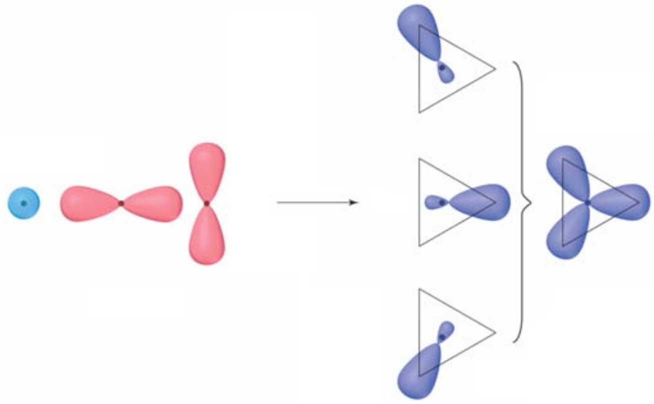


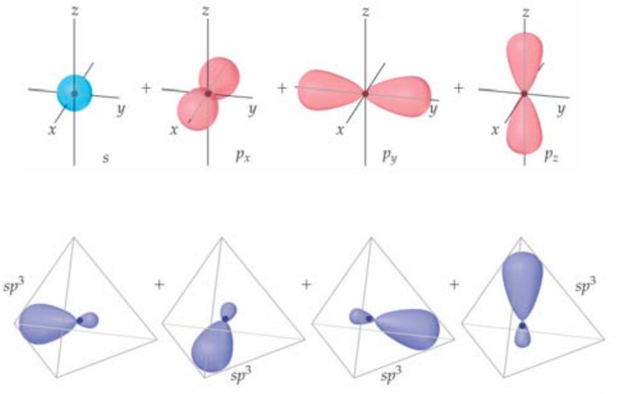
*sp*² and *sp*³ hybrid orbitals

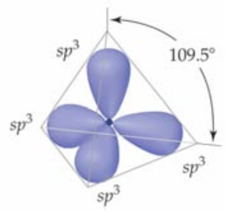
Three sp^2 hybrid orbitals are formed from hybridization of one *s* and two *p* orbitals;



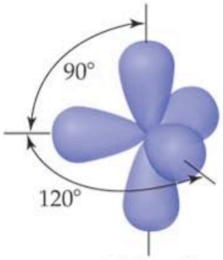


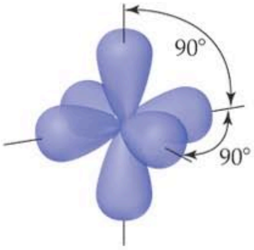






For geometries involving expanded octets on the central atom, we use *d* orbitals in our hybrids:





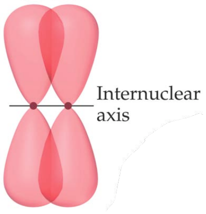
Once you know the electron-domain geometry, you know the hybridization state of the atom

9.6 Multiple Bonds

The covalent bonds we have seen so far are **sigma** (σ) bonds, characterized by:

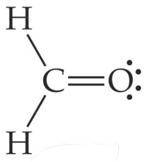
To describe multiple bonding, we must invoke **pi** (π) bonds.

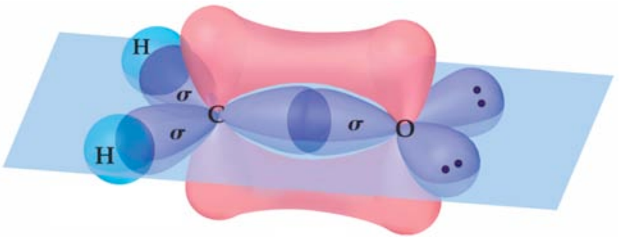
Pi (π) bonds are characterized by:



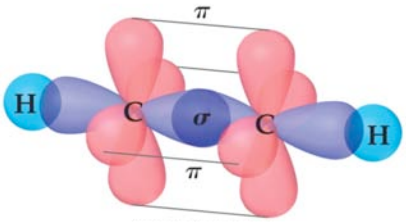
Single bonds are ***always*** σ bonds, because σ overlap is greater, resulting in a stronger bond and more energy lowering.

In a molecule like formaldehyde an sp^2 orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.



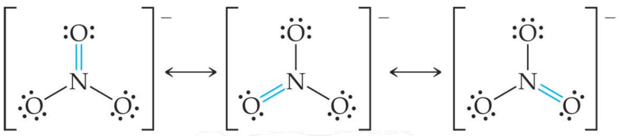


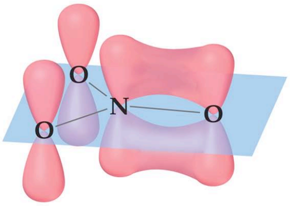
In triple bonds, e.g. acetylene, two *sp* orbitals form a σ bond between the carbons

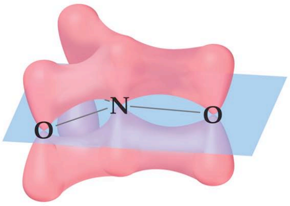


Delocalized π Bonding

When writing Lewis structures for species like the nitrate ion, we draw resonance structures to more accurately reflect the structure of the molecule or ion







The *p* orbitals on all three oxygens overlap with the *p* orbital on the central nitrogen