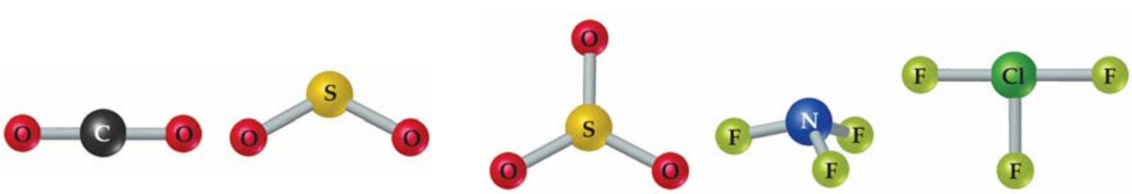
Chapter 9 Molecular Geometry and Bonding Theories

- molecular shapes
- the VSEPR model
- molecular shape and molecular polarity
- covalent bonding and orbital overlap
- hybrid orbitals
- multiple bonds

9.1 Molecular Shapes

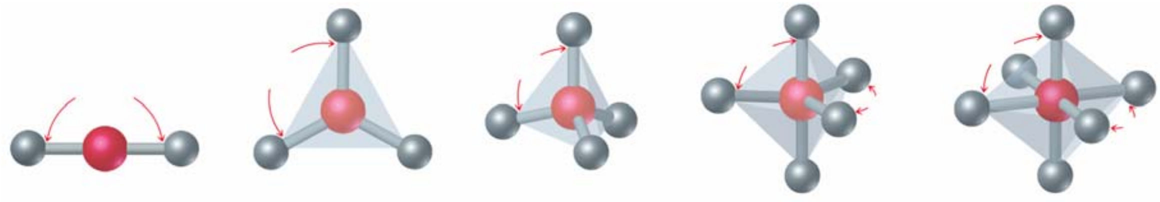
Lewis structures give atomic **connectivity** (which atoms are physically connected). The shape of a molecule is determined by its **bond angles**.

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

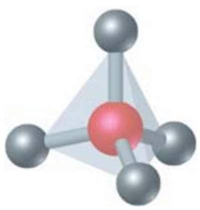


In order to predict molecular shape, we assume that the valence electrons repel each other.

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



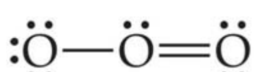
The shape of any particular AB_n molecule can usually be derived from one of these shapes. For example, starting from a tetrahedron:



9.2 The VSEPR Model

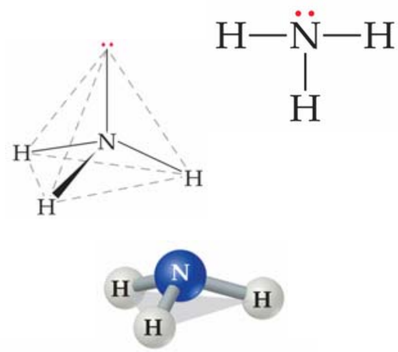
What determines the shape of a molecule? Electron pairs, whether bonding or nonbonding, repel each other. By assuming the electron pairs are placed as far as possible from each other, we can predict the shape of the molecule.

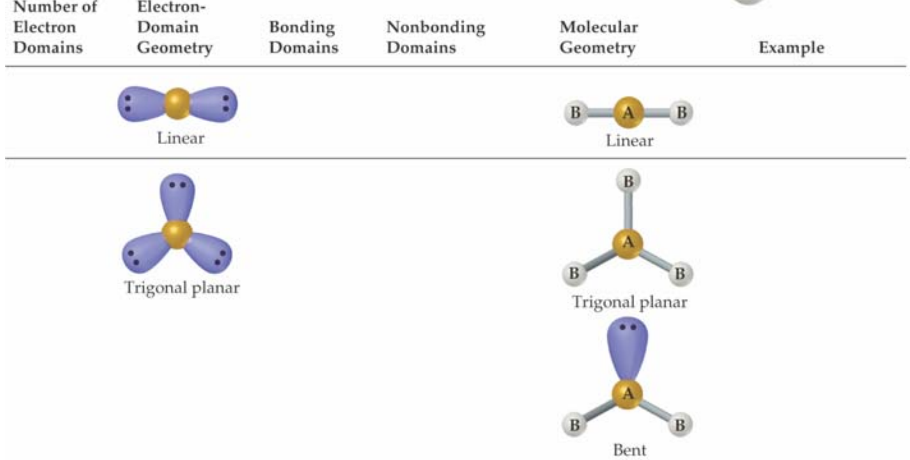
Each **nonbonding pair**, **single bond** or **multiple bond** produces an electron domain about the central atom.

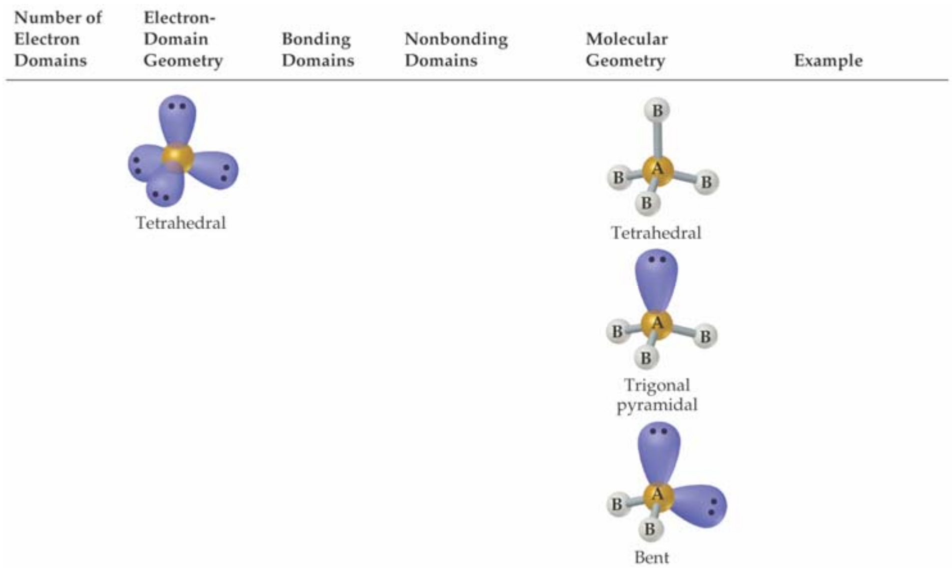


VSEPR predicts that "*the best arrangement of electron domains is the one that minimizes the repulsions among them*".

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

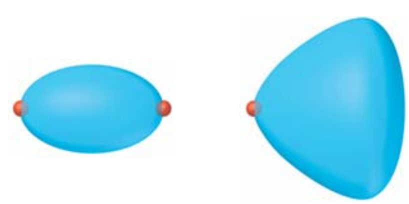




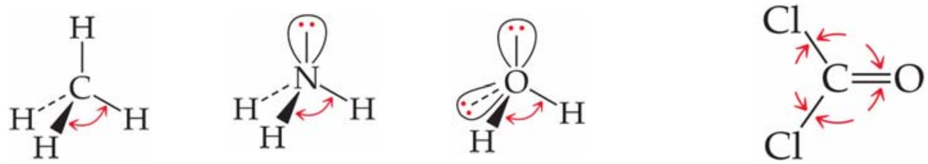


Effect of nonbonding electrons and multiple bonds on bond angles

Nonbonding pairs are physically larger than bonding pairs. Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.

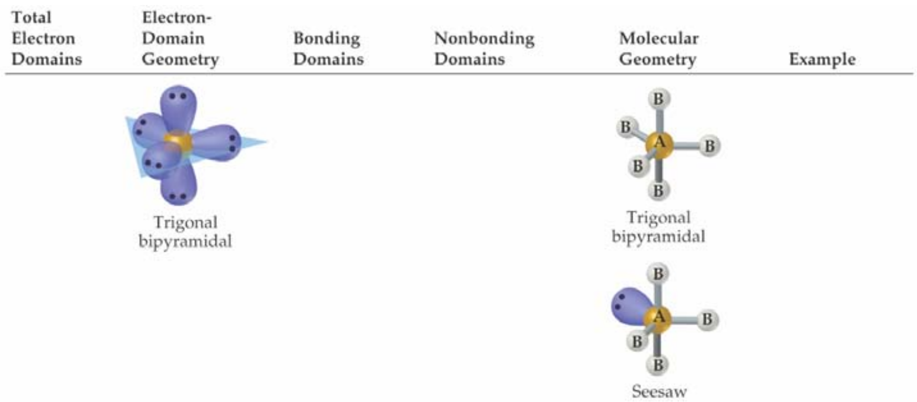


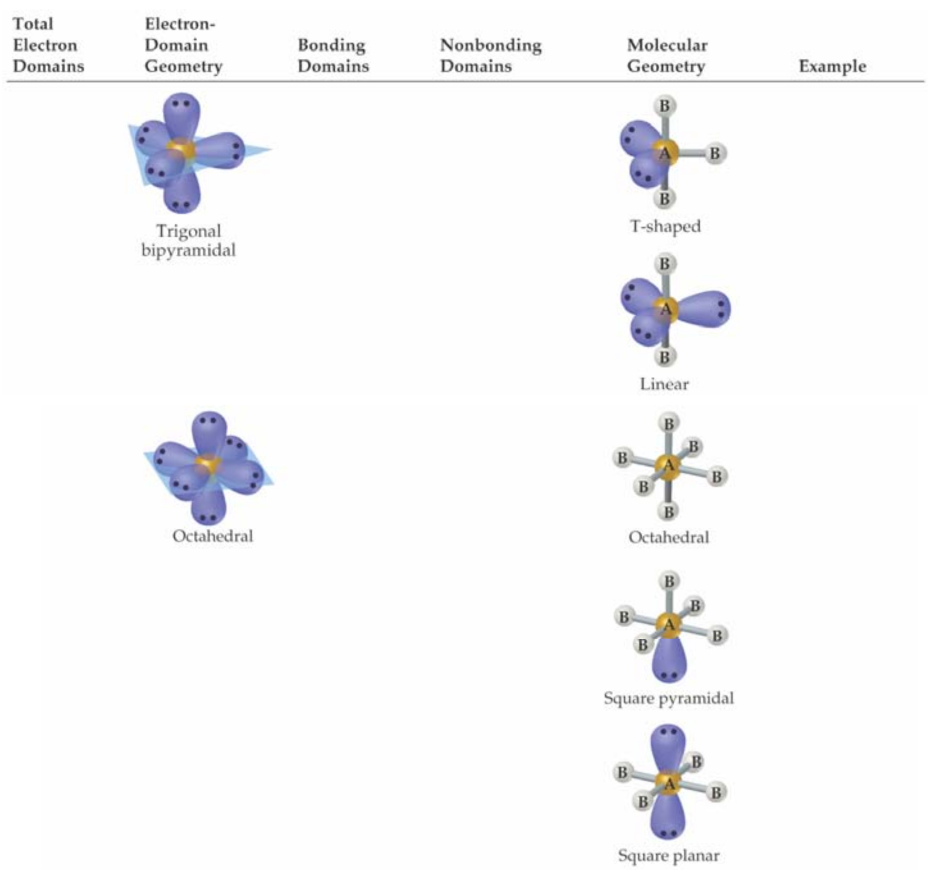
Electrons in nonbonding pairs and in multiple bonds repel **more** than electrons in single bonds:



Molecules with Expanded Valence Shells

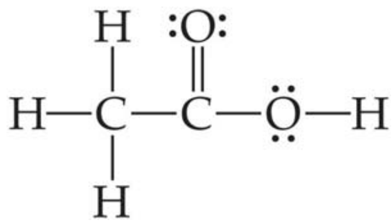
Atoms that have expanded octets have five electron domains (*trigonal bipyramidal*) or six electron domains (*octahedral*) electron-domain geometries.





Shapes of larger molecules

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

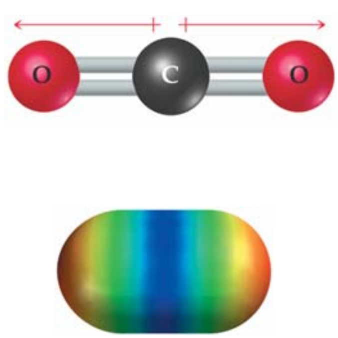


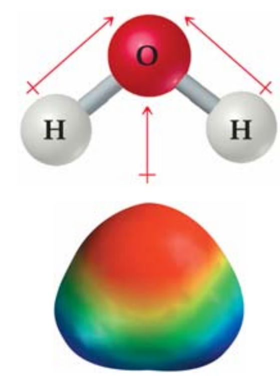
Blackboard examples

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^-.

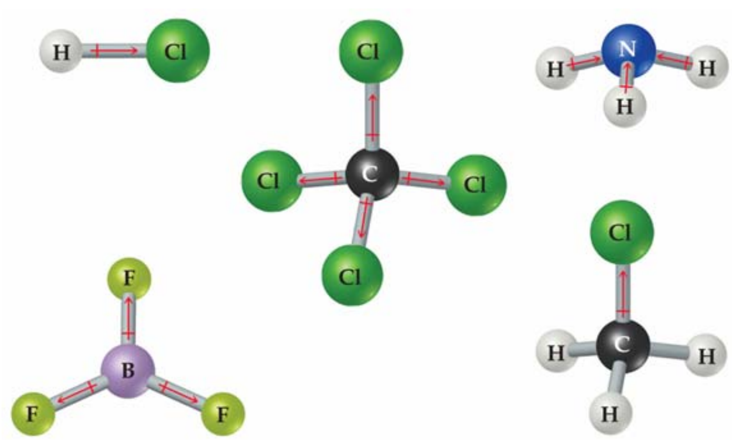
9.3 Molecular Shape and Molecular Polarity

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



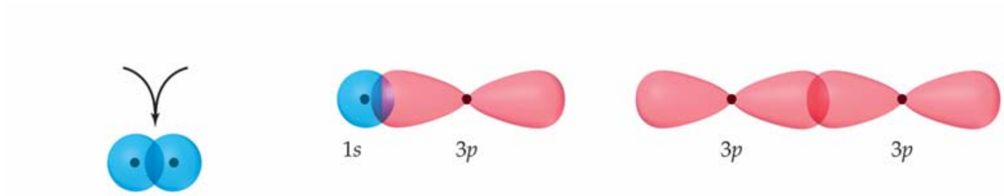


The orientation of the individual dipole moments determines whether a molecule has an overall dipole moment.

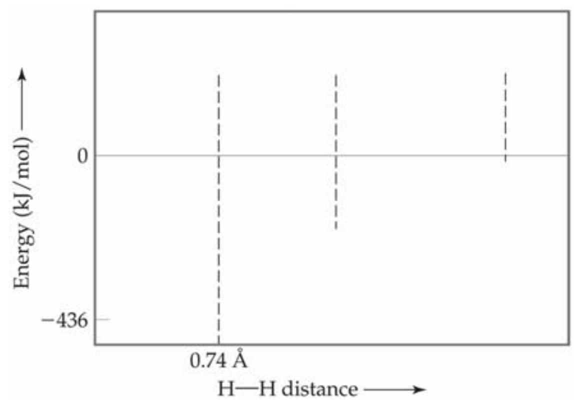


9.4 Covalent Bonding and Orbital Overlap

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:

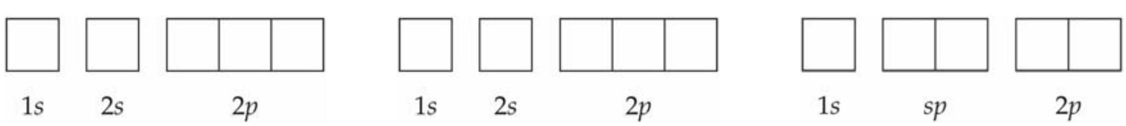


9.5 Hybrid Orbitals

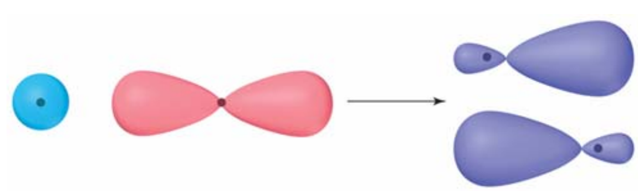
To apply the ideas of orbital overlap and valence-bond theory to polyatomic molecules, we need to introduce the concept of **hybrid orbitals**.

sp hybrid orbitals

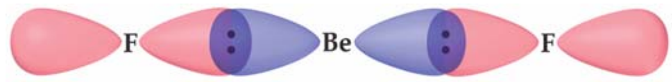
Consider beryllium: in its ground electronic state, it would not be able to form bonds because it has no singly-occupied orbitals:



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

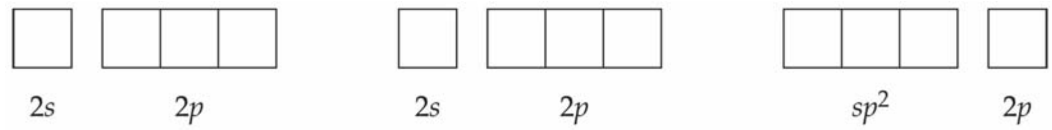


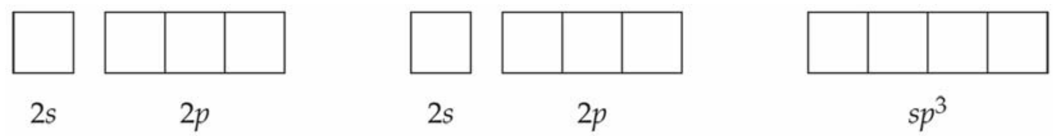
These two degenerate orbitals align themselves 180° from each other, and 90° from the two remaining unhybridized *p* orbitals.

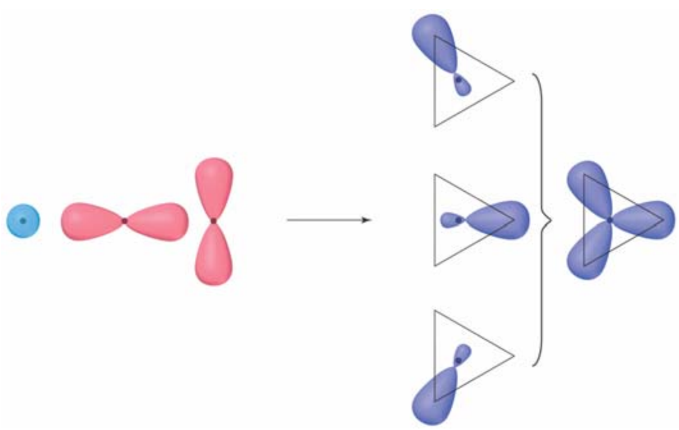


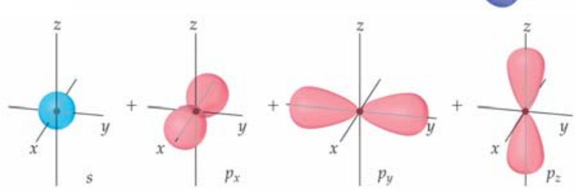
*sp*² and *sp*³ hybrid orbitals

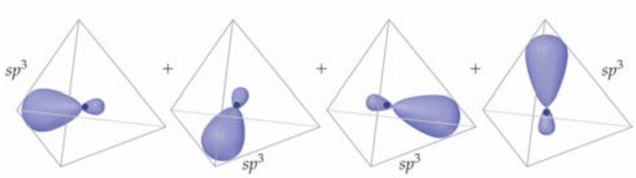
Three *sp*² hybrid orbitals are formed from hybridization of one *s* and two *p* orbitals; four *sp*³ hybrid orbitals are formed from hybridization of one *s* and three *p* orbitals.

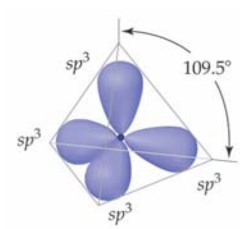




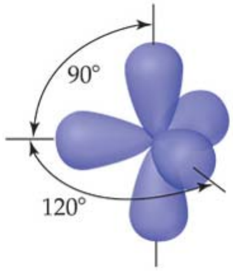


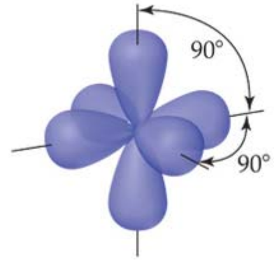






For geometries involving expanded octets on the central atom, we use *d* orbitals in our hybrids:



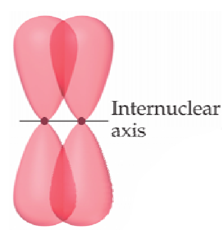


Once you know the electron-domain geometry, you know the hybridization state of the atom

9.6 Multiple Bonds

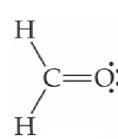
The covalent bonds we have seen so far are **sigma** (σ) bonds, characterized by:

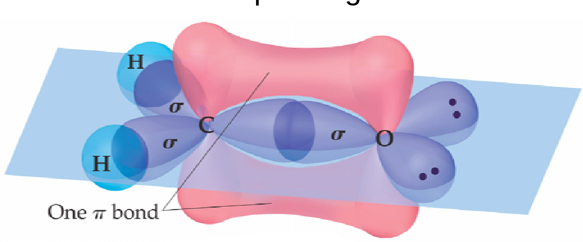
To describe multiple bonding, we must invoke **pi** (π) bonds, characterized by:



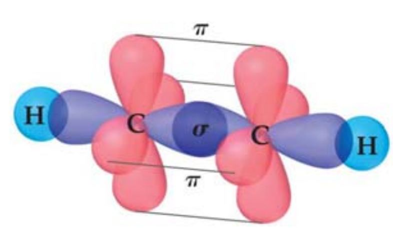
Single bonds are ***always*** σ bonds, because σ overlap is greater, resulting in a stronger bond and more energy lowering.

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



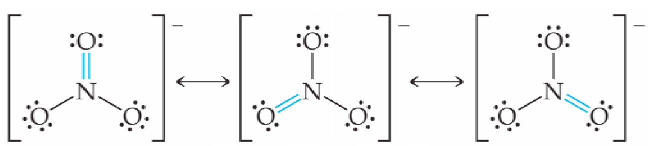


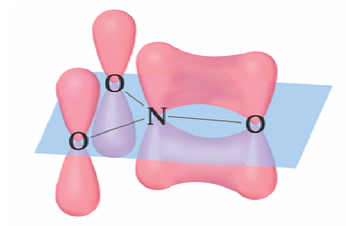
In triple bonds, as in acetylene, two *sp* orbitals form a σ bond between the carbons, and two pairs of *p* orbitals overlap in π fashion to form the two π bonds.

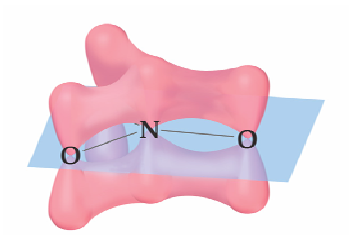


Delocalized π Bonding

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

The organic molecule benzene has six σ bonds and a *p* orbital on each carbon atom