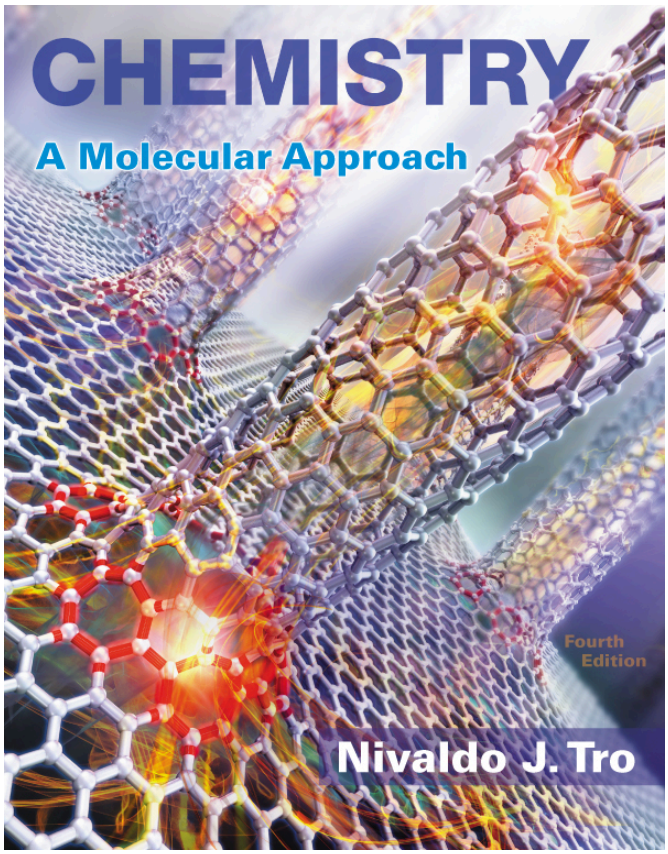


Lecture Presentation

Chapter 10 Chemical Bonding II: Molecular Shapes, Valence Bond Theory, and Molecular Orbital Theory

Taste

- The taste of a food depends on the interaction between the food molecules and taste cells on your tongue.
- The main factors that affect this interaction are the molecule's shape and charge distribution.
- The food molecule must fit snugly into the active site of specialized proteins on the surface of taste cells.
- When this happens, changes in the protein structure cause a nerve signal to transmit.

Sugar and Artificial Sweeteners

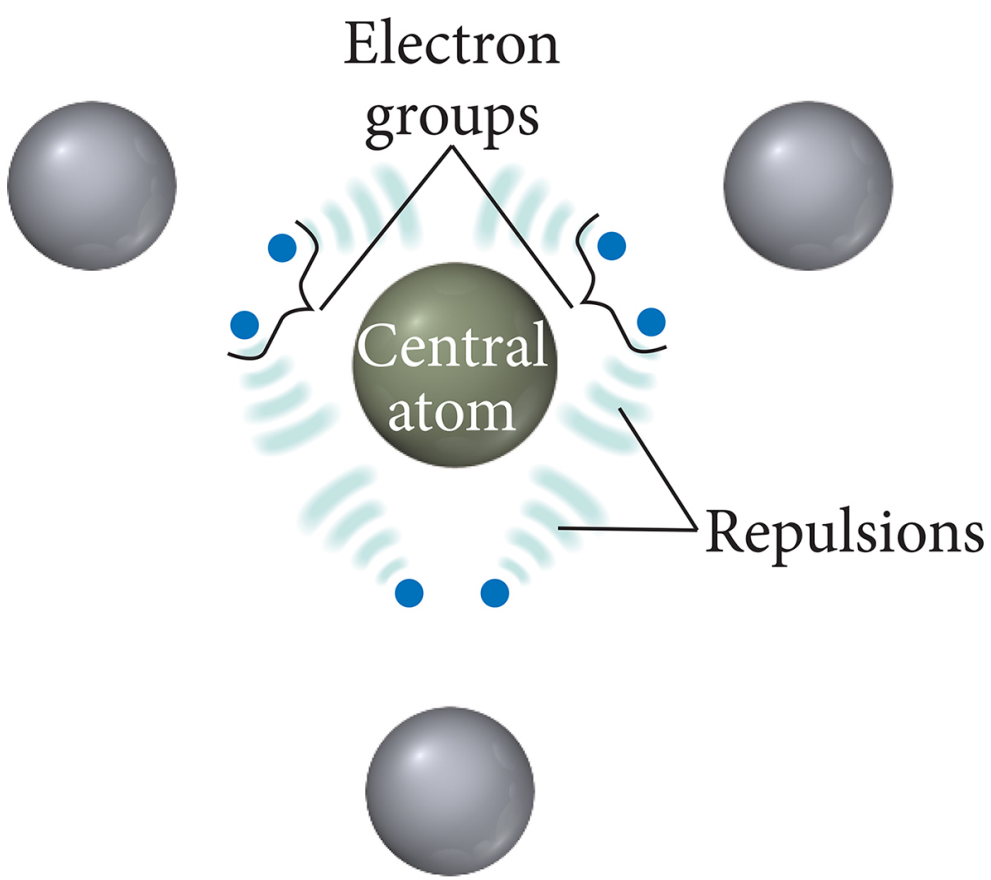
- Sugar molecules fit into the active site of taste cell receptors called T1r3 receptor proteins.
- When the sugar molecule (the key) enters the active site (the lock), the different subunits of the T1r3 protein split apart.
- This split causes ion channels in the cell membrane to open, resulting in nerve signal transmission.
- Artificial sweeteners also fit into the T1r3 receptor, sometimes binding to it even stronger than sugar, making them “sweeter” than sugar.

Valence Shell Electron Pair Repulsion Theory

- Properties of molecular substances depend on the structure of the molecule.
- **Valence shell electron pair repulsion (VSEPR) theory** is a simple model that allows us to account for molecular shape.
- **Electron groups** are defined as lone pairs, single bonds, double bonds, and triple bonds.
- VSEPR is based on the idea that electron groups repel one another through coulombic forces.

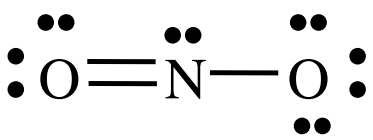
VSEPR Theory

- Electron groups around the central atom will be most stable when they are as far apart as possible. We call this **VSEPR** theory.
  - Because electrons are negatively charged, they should be most stable when they are separated as much as possible.
- The resulting geometric arrangement will allow us to predict the shapes and bond angles in the molecule.



Electron Groups

- The Lewis structure predicts the number of valence electron pairs around the central atom(s).
- Each lone pair of electrons constitutes one electron group on a central atom.
- Each bond constitutes one electron group on a central atom, regardless of whether it is single, double, or triple.



There are three electron groups on N:

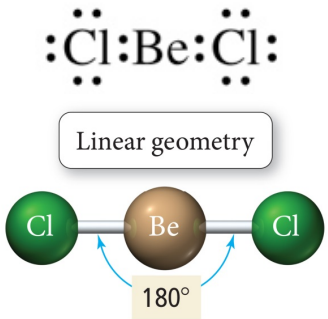
- Three lone pair
- One single bond
- One double bond

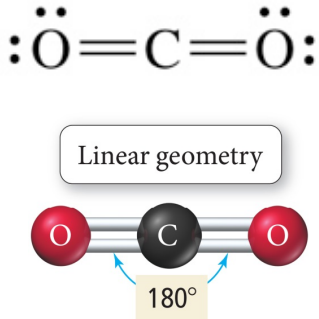
Electron Group Geometry

- There are five basic arrangements of electron groups around a central atom.
  - Based on a maximum of six bonding electron groups
    - Though there may be more than six on very large atoms, it is very rare.
- Each of these five basic arrangements results in five different basic electron geometries.
  - In order for the molecular shape and bond angles to be a “perfect” geometric figure, all the electron groups must be bonds, and all the bonds must be equivalent.
- For molecules that exhibit resonance, it doesn’t matter which resonance form you use since the electron geometry will be the same.

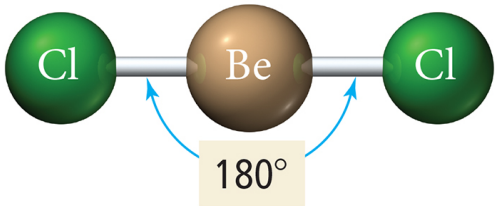
Two Electron Groups: Linear Electron Geometry

- When there are two electron groups around the central atom, they will occupy positions on opposite sides of the central atom.
- This results in the electron groups taking a **linear geometry**.
- The bond angle is 180°.





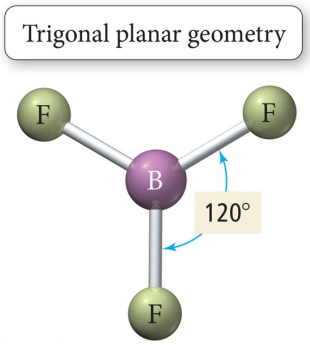
Linear Geometry



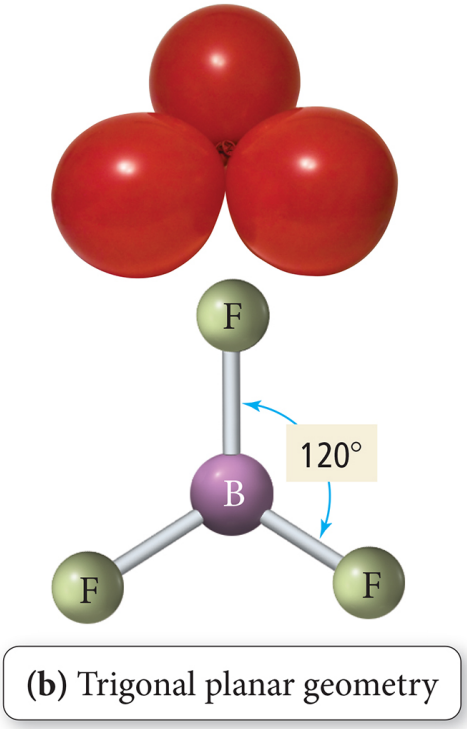
(a) Linear geometry

Three Electron Groups: Trigonal Planar Electron Geometry

- When there are three electron groups around the central atom, they will occupy positions in the shape of a triangle around the central atom.
- This results in the electron groups taking a **trigonal planar geometry**.
- The bond angle is 120°.

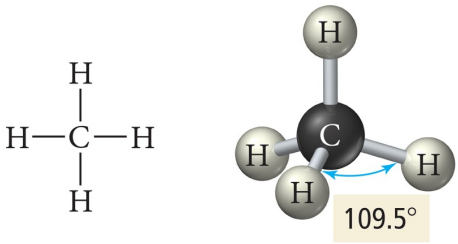


Trigonal Planar Geometry



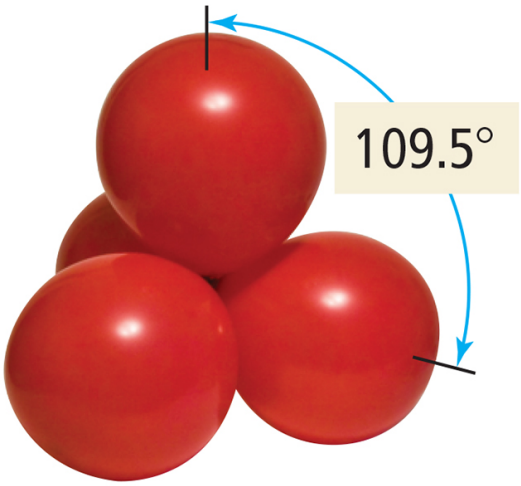
Four Electron Groups: Tetrahedral Electron Geometry

- When there are four electron groups around the central atom, they will occupy positions in the shape of a tetrahedron around the central atom.
- This results in the electron groups taking a **tetrahedral geometry**.
- The bond angle is 109.5°.

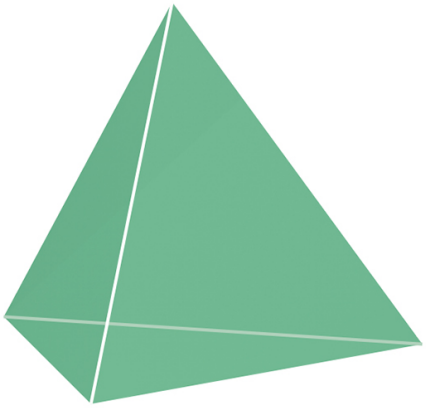


Tetrahedral geometry

Tetrahedral Geometry



Tetrahedral geometry



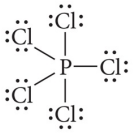
Tetrahedron

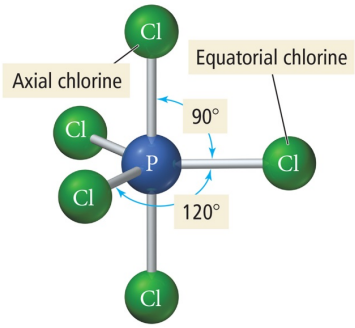
Five Electron Groups: Trigonal Bipyramidal Electron Geometry

- When there are five electron groups around the central atom, they will occupy positions in the shape of two tetrahedra that are base to base with the central atom in the center of the shared bases.
- This results in the electron groups taking a **trigonal bipyramidal geometry**.

Five Electron Groups: Trigonal Bipyramidal Electron Geometry

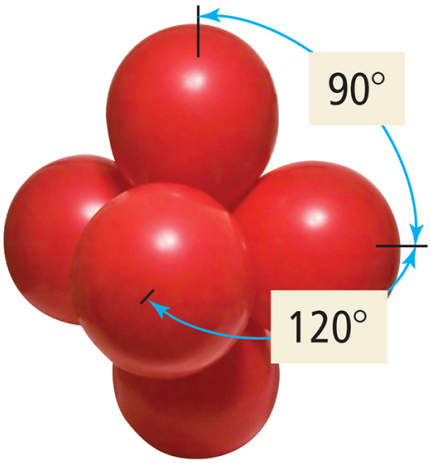
- The positions above and below the central atom are called the **axial** positions.
- The positions in the same base plane as the central atom are called the **equatorial** positions.
- The bond angle between equatorial positions is 120°.
- The bond angle between axial and equatorial positions is 90°.



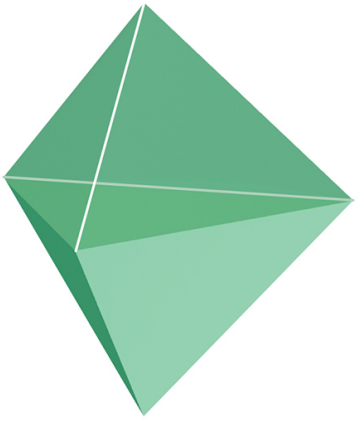


Trigonal bipyramidal geometry

Trigonal Bipyramidal



Trigonal bipyramidal geometry

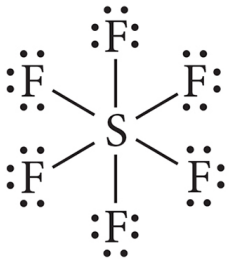


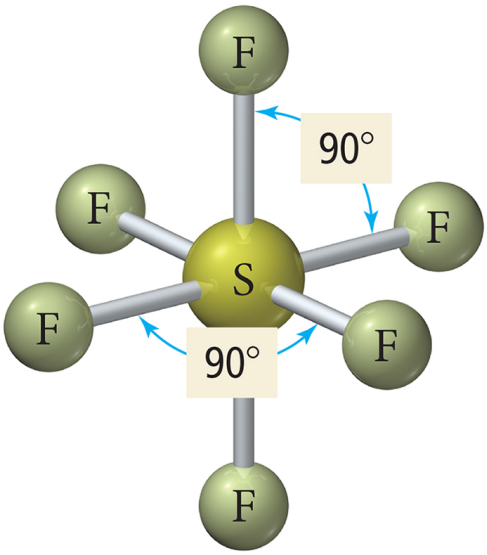
Trigonal bipyramid

Octahedral Electron Geometry

- When there are six electron groups around the central atom, they will occupy positions in the shape of two square-base pyramids that are base to base with the central atom in the center of the shared bases.
- This results in the electron groups taking an **octahedral geometry**.
  - It is called octahedral because the geometric figure has eight sides.
- All positions are equivalent.
- The bond angle is 90°.

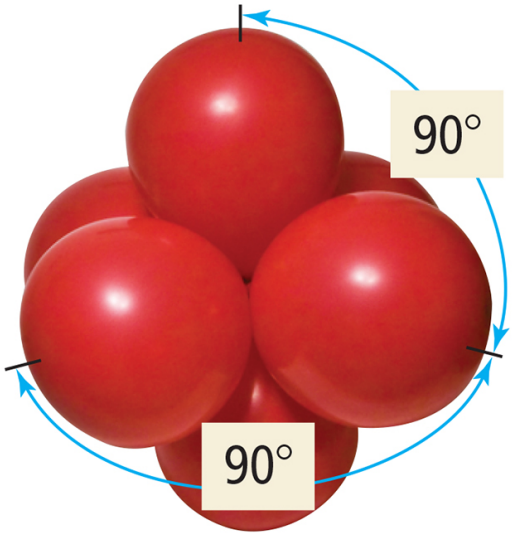
Octahedral Geometry

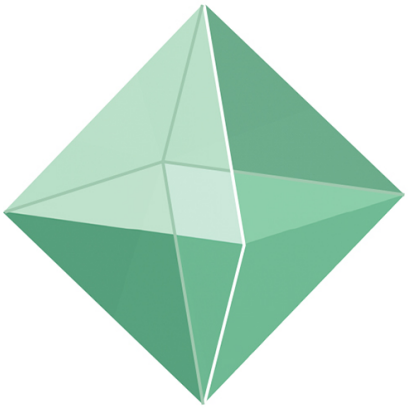




Octahedral geometry

Octahedral Geometry





Octahedral geometry

Octahedron

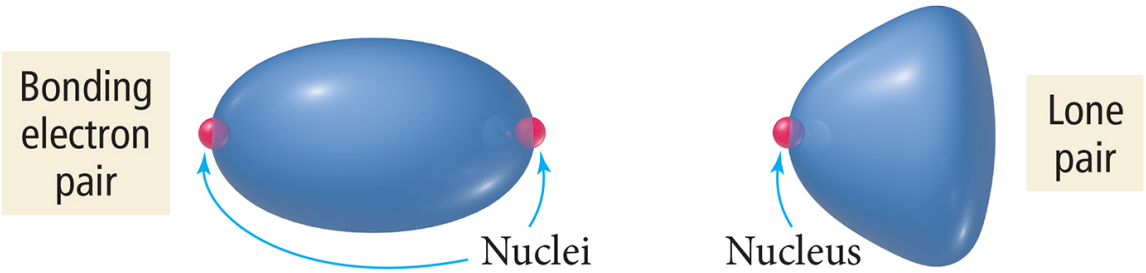
The Effect of Lone Pairs

- The actual geometry of the molecule may be different from the electron geometry.
- Lone pair electrons typically exert slightly greater repulsion than bonding electrons, affecting the bond angles.
- A lone electron pair is more spread out in space than a bonding electron pair because a lone pair is attracted to only one nucleus while a bonding pair is attracted to two nuclei.
- In general, electron group repulsions vary as follows:
  - Lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair

Pyramidal and Bent Molecular Geometries: Derivatives of Tetrahedral Electron Geometry

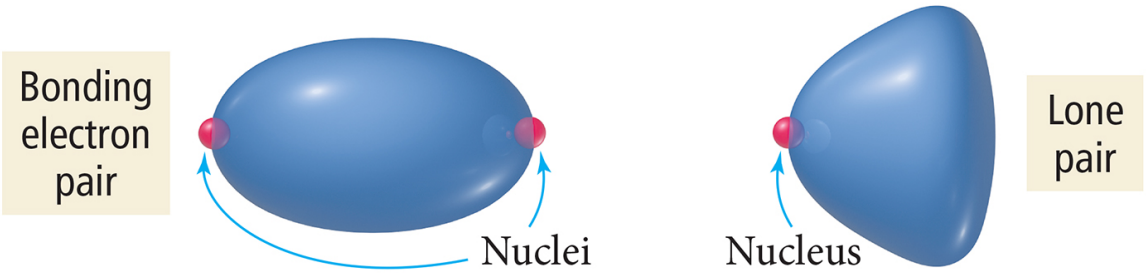
- When there are four electron groups around the central atom, and one is a lone pair, the result is called a **pyramidal shape**, because it is a triangular-base pyramid with the central atom at the apex.
- When there are four electron groups around the central atom, and two are lone pairs, the result is called a **tetrahedral-bent shape**.

Effect of Lone Pairs



The bonding electrons are shared by two atoms, so some of the negative charge is removed from the central atom.

Effect of Lone Pairs

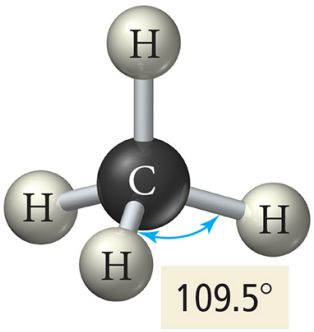


The nonbonding electrons are localized on the central atom, so the area of negative charge takes more space.

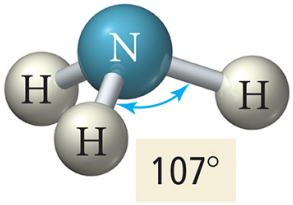
Bond Angle Distortion from Lone Pairs

Effect of Lone Pairs on Molecular Geometry

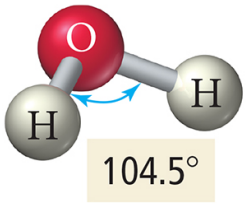
No lone pairs | One lone pair | Two lone pairs



CH_4

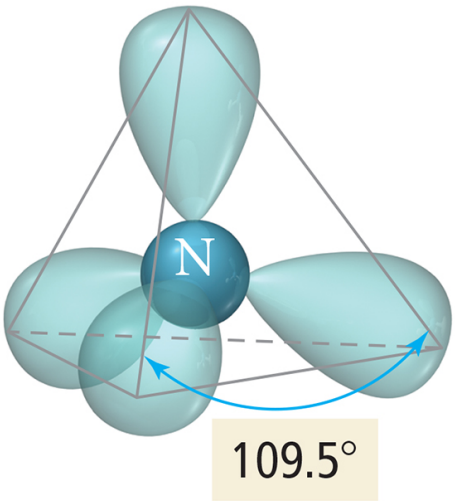


NH_3

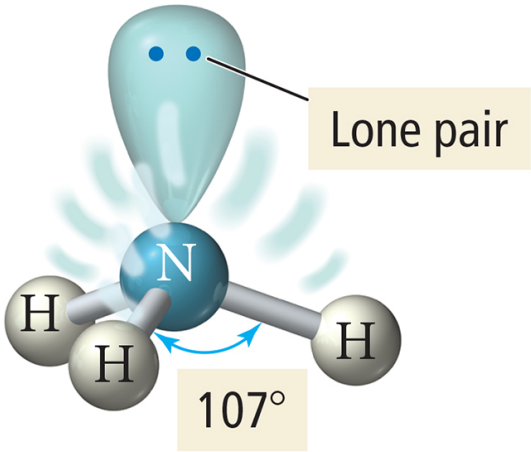


H_2O

Bond Angle Distortion from Lone Pairs

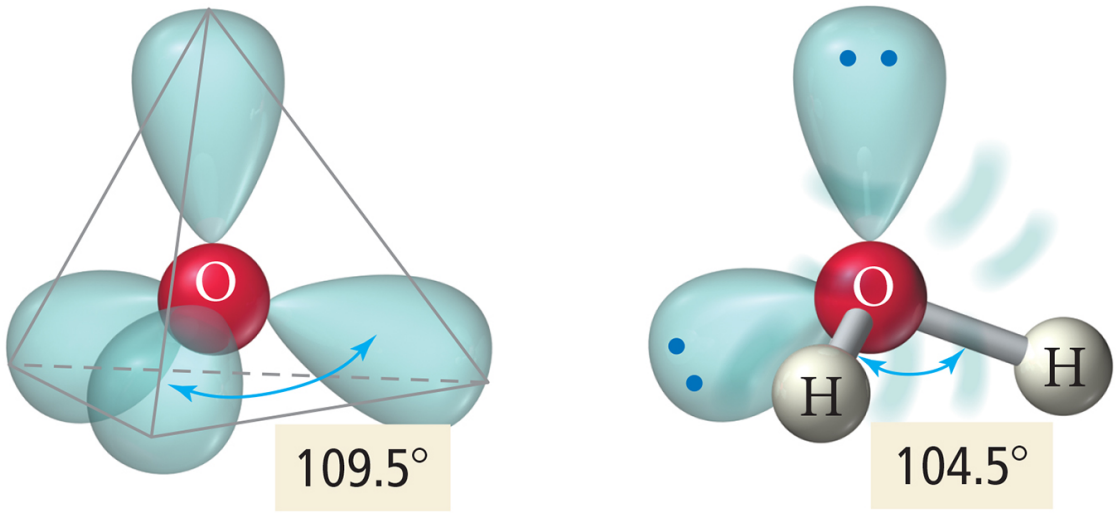


Ideal tetrahedral geometry



Actual molecular geometry

Bond Angle Distortion from Lone Pairs



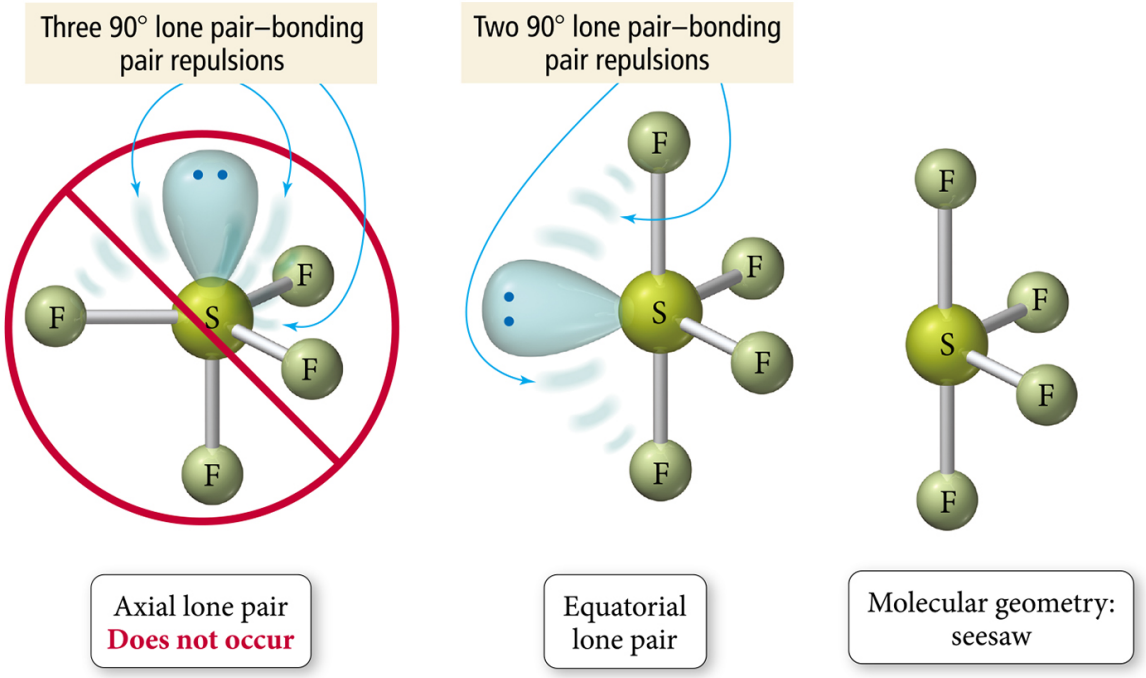
Ideal tetrahedral geometry

Actual molecular geometry

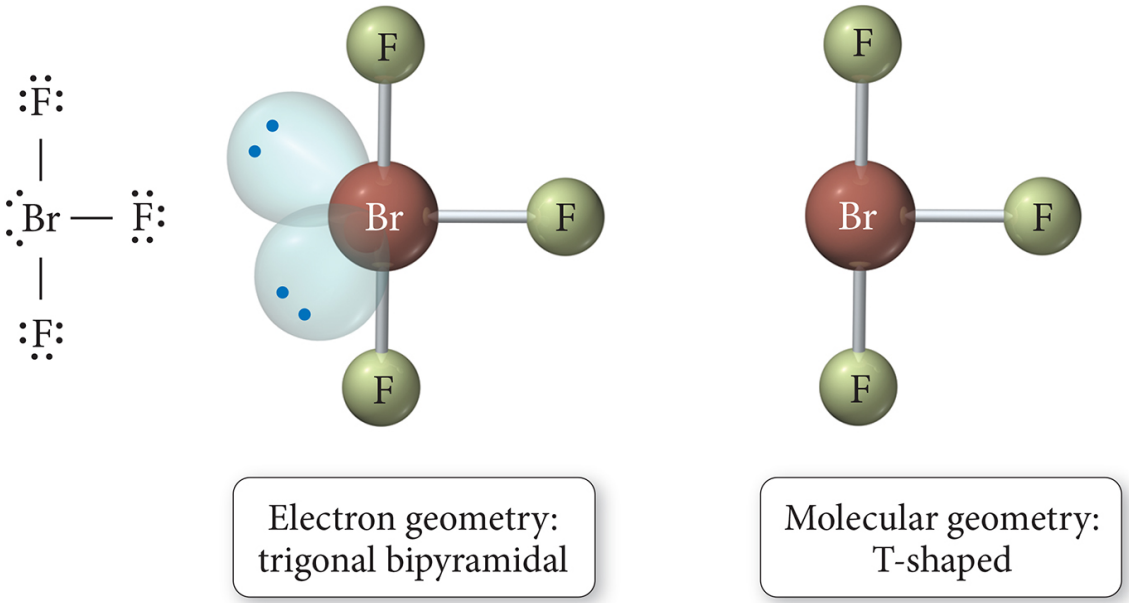
Derivatives of the Trigonal Bipyramidal Electron Geometry

- Lone pairs on central atoms with five electron groups will occupy the equatorial positions because there is more room.
- The result is called the **seesaw shape** (aka **distorted tetrahedron**).
- When there are two lone pairs around the central atom, the result is **T-shaped**.
- When there are three lone pairs around the central atom, the result is a **linear shape**.
- The bond angles between equatorial positions are less than 120°.
- The bond angles between axial and equatorial positions are less than 90°.
  - Linear = 180° axial to axial.

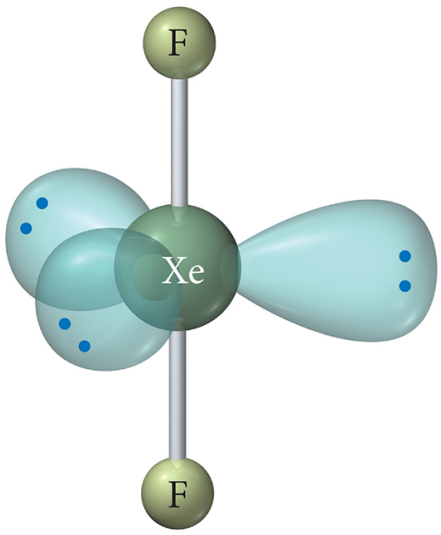
Replacing Atoms with Lone Pairs in the Trigonal Bipyramid System



T-Shape



Linear Shape



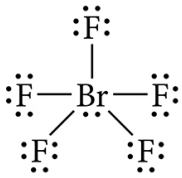
Electron geometry: trigonal bipyramidal

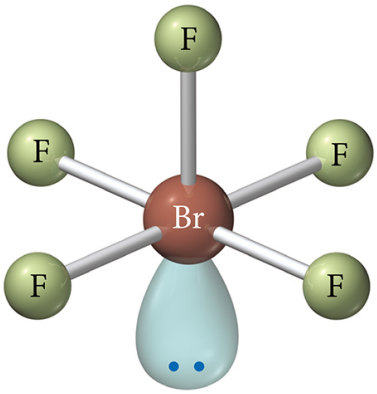
Molecular geometry: linear

Derivatives of the Octahedral Geometry

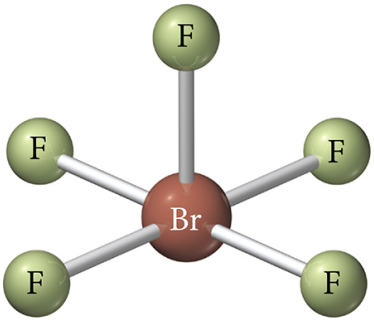
- When there are lone pairs around a central atom with six electron groups, each even number lone pair will take a position opposite the previous lone pair.
  - When one of the six electron groups is a lone pair, the result is called a **square pyramid shape**.
  - The bond angles between axial and equatorial positions are less than 90°.
  - When two of the six electron groups are lone pairs, the result is called a **square planar shape**.
  - The bond angles between equatorial positions are 90°.

Square Pyramidal Shape



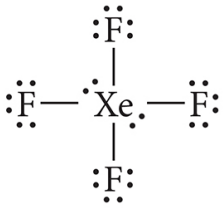


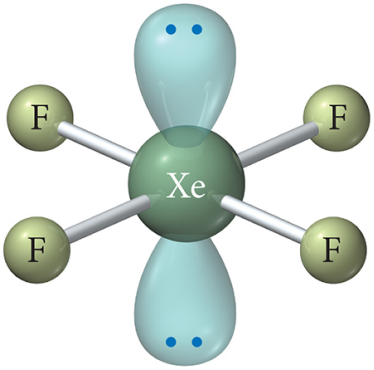
Electron geometry: octahedral



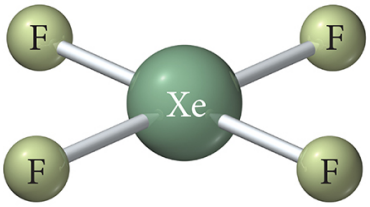
Molecular geometry: square pyramidal

Square Planar Shape



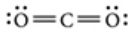
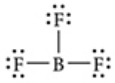
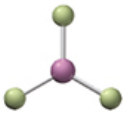
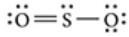
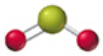
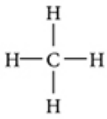
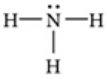
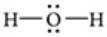


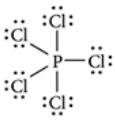
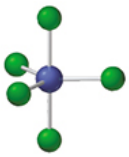
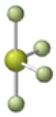
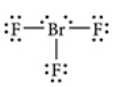
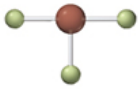
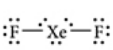
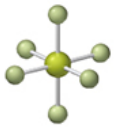
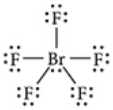
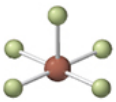
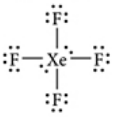
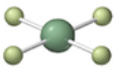
Electron geometry: octahedral



Molecular geometry: square planar

TABLE 10.1 Electron and Molecular Geometries

Electron Groups*	Bonding Groups	Lone Pairs	Electron Geometry	Molecular Geometry	Approximate Bond Angles		Example
2	2	0	Linear	Linear	180°		
3	3	0	Trigonal planar	Trigonal planar	120°		
3	2	1	Trigonal planar	Bent	<120°		
4	4	0	Tetrahedral	Tetrahedral	109.5°		
4	3	1	Tetrahedral	Trigonal pyramidal	<109.5°		
4	2	2	Tetrahedral	Bent	<109.5°		

5	5	0	Trigonal bipyramidal	Trigonal bipyramidal	120° (equatorial) 90° (axial)		
5	4	1	Trigonal bipyramidal	Seesaw	<120° (equatorial) <90° (axial)		
5	3	2	Trigonal bipyramidal	T-shaped	<90°		
5	2	3	Trigonal bipyramidal	Linear	180°		
6	6	0	Octahedral	Octahedral	90°		
6	5	1	Octahedral	Square pyramidal	<90°		
6	4	2	Octahedral	Square planar	90°		

*Count only electron groups around the central atom. Each of the following is considered one electron group: a lone pair, a single bond, a double bond, a triple bond, or a single electron.

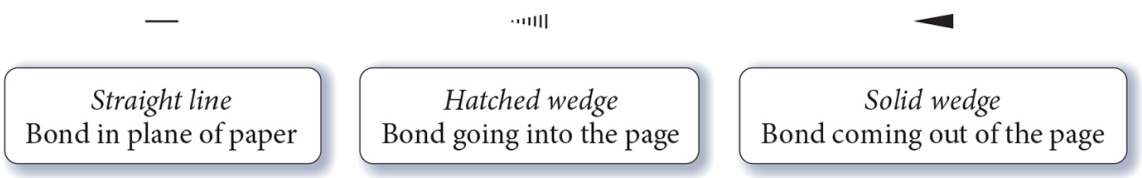
Predicting Molecular Geometry

1. Draw the Lewis structure.
2. Determine the number of electron groups around the central atom.
3. Classify each electron group as a bonding or lone pair, and then count each type.
   – Remember, multiple bonds count as one group.
4. Use Table 10.1 to determine the shape and bond angles.

Representing Three-Dimensional Shapes on Paper

- One of the problems with drawing molecules is trying to show their dimensionality.
- By convention, the central atom is put in the plane of the paper.
- Put as many other atoms as possible in the same plane and indicate with a **straight line**.
- For atoms in front of the plane, use a **solid wedge**.
- For atoms behind the plane, use a **hashed wedge**.

Representing Three-Dimensional Shapes on Paper



Multiple Central Atoms

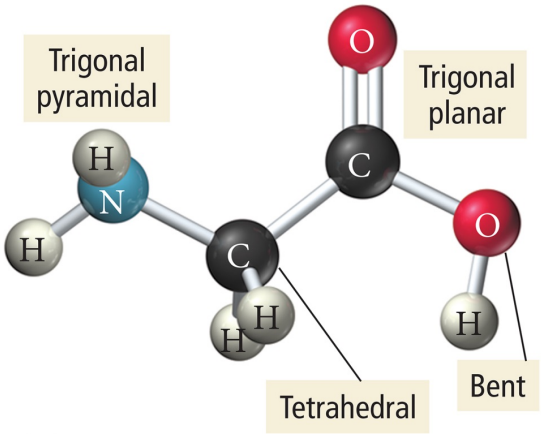
- Many molecules have larger structures with many interior atoms.
- We can think of them as having multiple central atoms.
- When this occurs, we describe the shape around each central atom in sequence.

The shape around N is trigonal pyramidal.

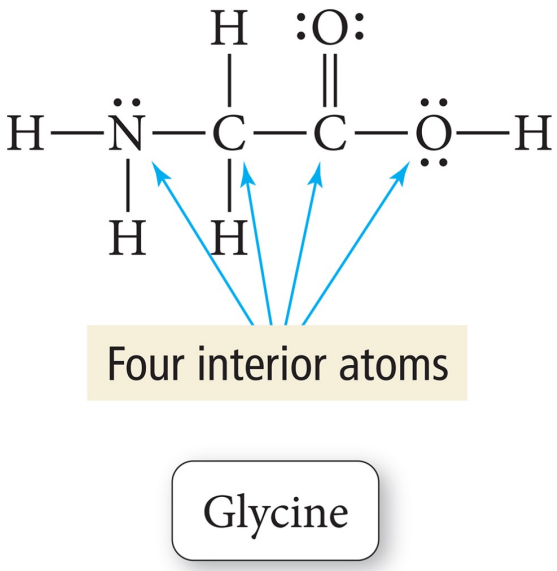
The shape around left C is tetrahedral.

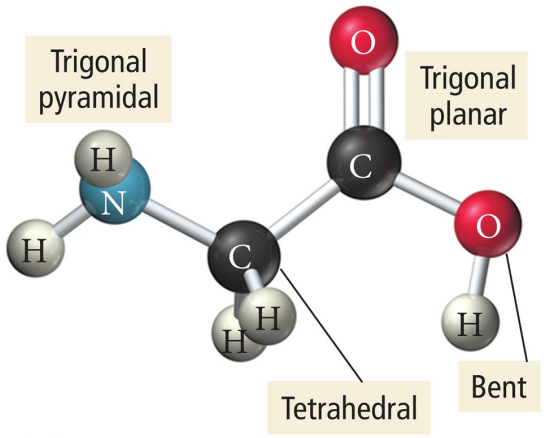
The shape around right C is trigonal planar.

The shape around right O is tetrahedral–bent.

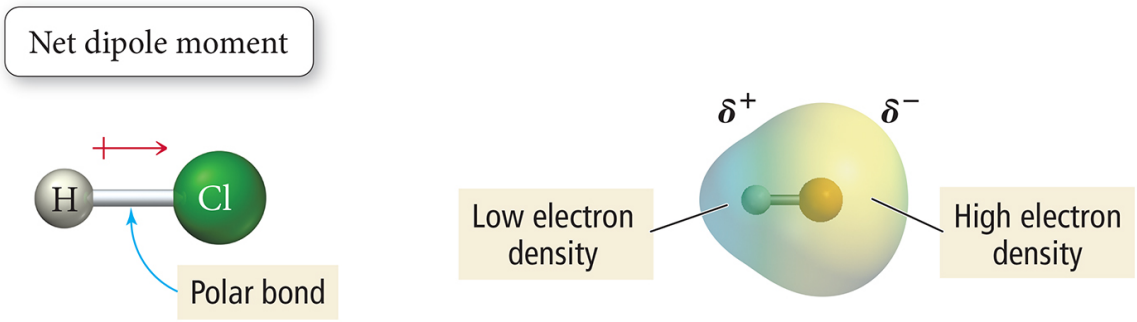


Describing the Geometry of Glycine





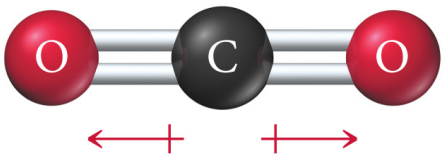
Molecular Polarity

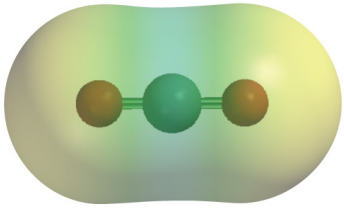


The H—Cl bond is polar. The bonding electrons are pulled toward the Cl end of the molecule. The net result is a polar molecule.

Molecular Polarity

No net dipole moment

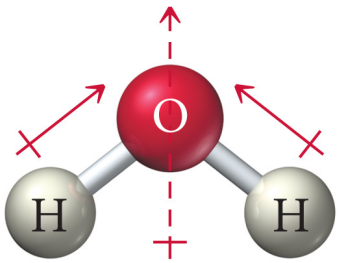


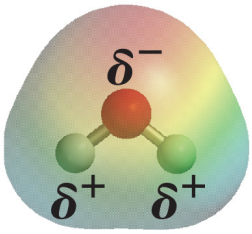


The O—C bond is polar. The bonding electrons are pulled equally toward both O ends of the molecule. The net result is a nonpolar molecule.

Molecular Polarity

Net dipole moment





The H—O bond is polar. Both sets of bonding electrons are pulled toward the O end of the molecule. Because the molecule is bent, not linear, the net result is a polar molecule.

Vector Addition

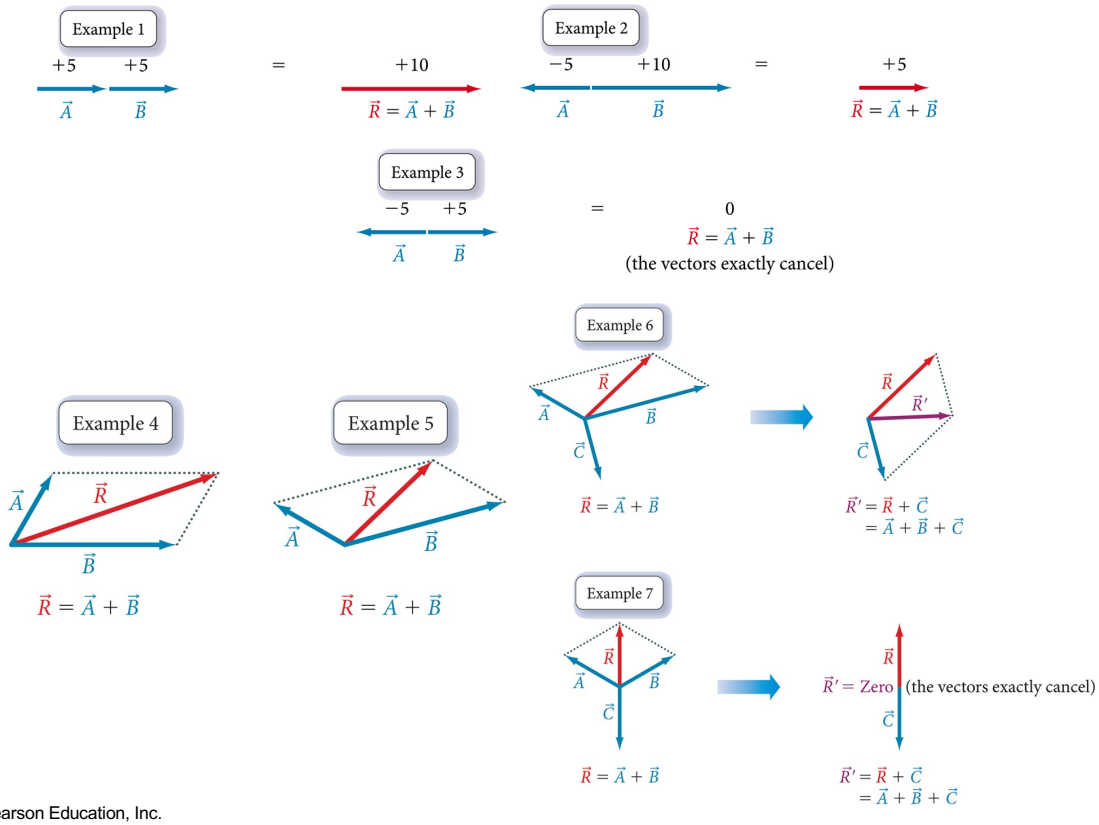
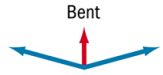


TABLE 10.2 Common Cases of Adding Dipole Moments to Determine Whether a Molecule Is Polar

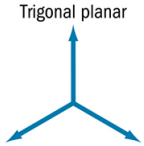
Nonpolar

The dipole moments of two identical polar bonds pointing in opposite directions cancel. The molecule is nonpolar.



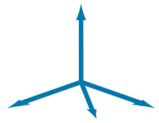
Polar

The dipole moments of two polar bonds with an angle of less than 180° between them do not cancel. The resultant dipole moment vector is shown in red. The molecule is polar.



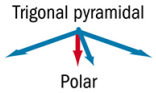
Nonpolar

The dipole moments of three identical polar bonds at 120° from each other cancel. The molecule is nonpolar.



Nonpolar

The dipole moments of four identical polar bonds in a tetrahedral arrangement (109.5° from each other) cancel. The molecule is nonpolar.



Polar

The dipole moments of three polar bonds in a trigonal pyramidal arrangement do not cancel. The resultant dipole moment vector is shown in red. The molecule is polar.

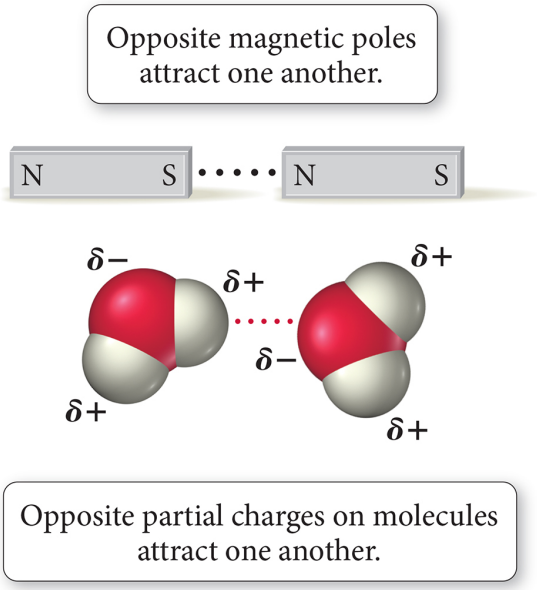
Note: In all cases in which the dipoles of two or more polar bonds cancel, the bonds are assumed to be identical. If one or more of the bonds are different from the other(s), the dipoles will not cancel and the molecule will be polar.

Predicting Polarity of Molecules

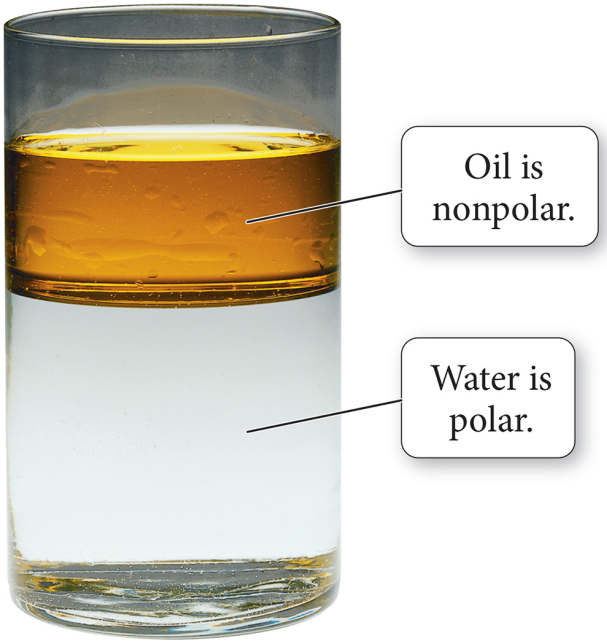
1. Draw the Lewis structure, and determine the molecular geometry.
2. Determine whether the bonds in the molecule are polar.
   a) If there are no polar bonds, the molecule is nonpolar.
3. Determine whether the polar bonds add together to give a net dipole moment.

Molecular Polarity Affects Solubility in Water

- Polar molecules are attracted to other polar molecules.
- Because water is a polar molecule, other polar molecules dissolve well in water.
  - And ionic compounds as well
- Some molecules have both polar and nonpolar parts.



Molecular Polarity Affects Solubility in Water



Problems with Lewis Theory

- Lewis theory generally predicts trends in properties but does not give good numerical predictions.
  - For example, bond strength and bond length
- Lewis theory gives good first approximations of the bond angles in molecules but usually cannot be used to get the actual angle.
- Lewis theory cannot write one correct structure for many molecules where resonance is important.
- Lewis theory often does not predict the correct magnetic behavior of molecules.
  - For example, O_2 is paramagnetic, although the Lewis structure predicts it is diamagnetic.

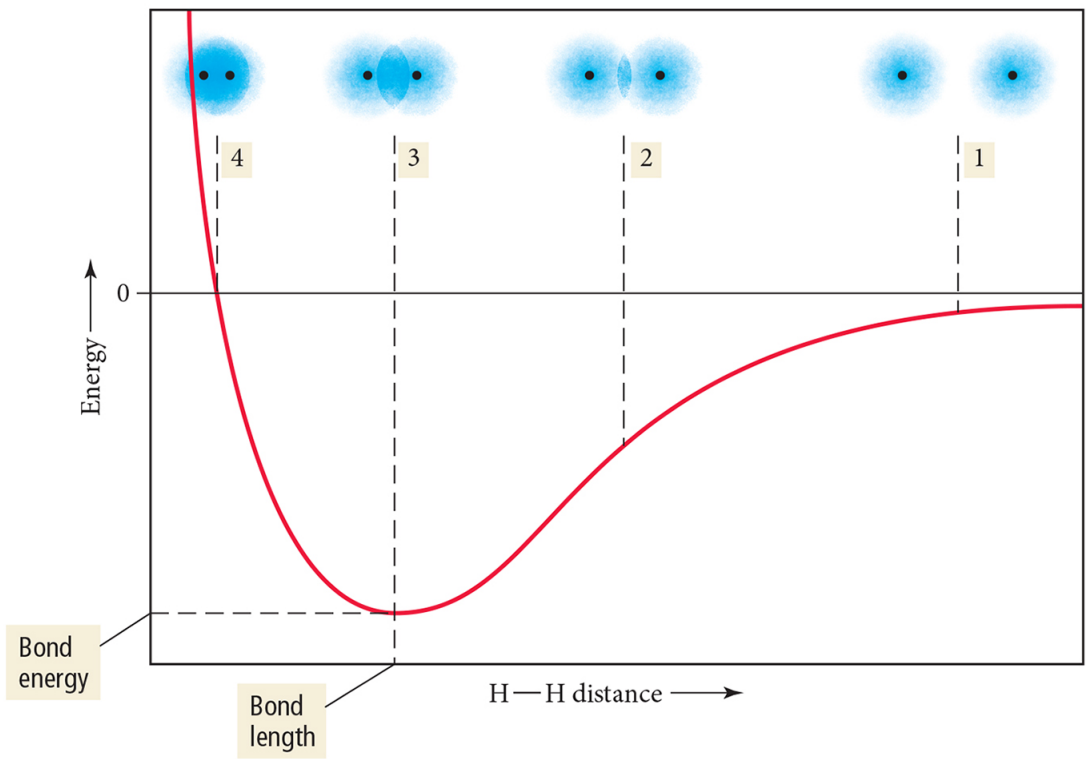
Valence Bond Theory

- **Valence Bond theory (VB)** approaches chemical bonding based on an extension of the quantum-mechanical model.
- When orbitals on atoms interact, they make a bond.
- These orbitals are **hybridized atomic orbitals**, a kind of blend or combination of two or more standard atomic orbitals.

Valence Bond Theory

- When two atoms approach each other, the electrons and nucleus of one atom interact with the electrons and nucleus of the other atom.
- If the energy of the system is lowered because of the interactions, a chemical bond forms.
- A chemical bond results from the overlap of two half-filled orbitals with spin-pairing of the two valence electrons (or less commonly the overlap of a completely filled orbital with an empty orbital).
- The geometry of the overlapping orbitals determines the shape of the molecule.

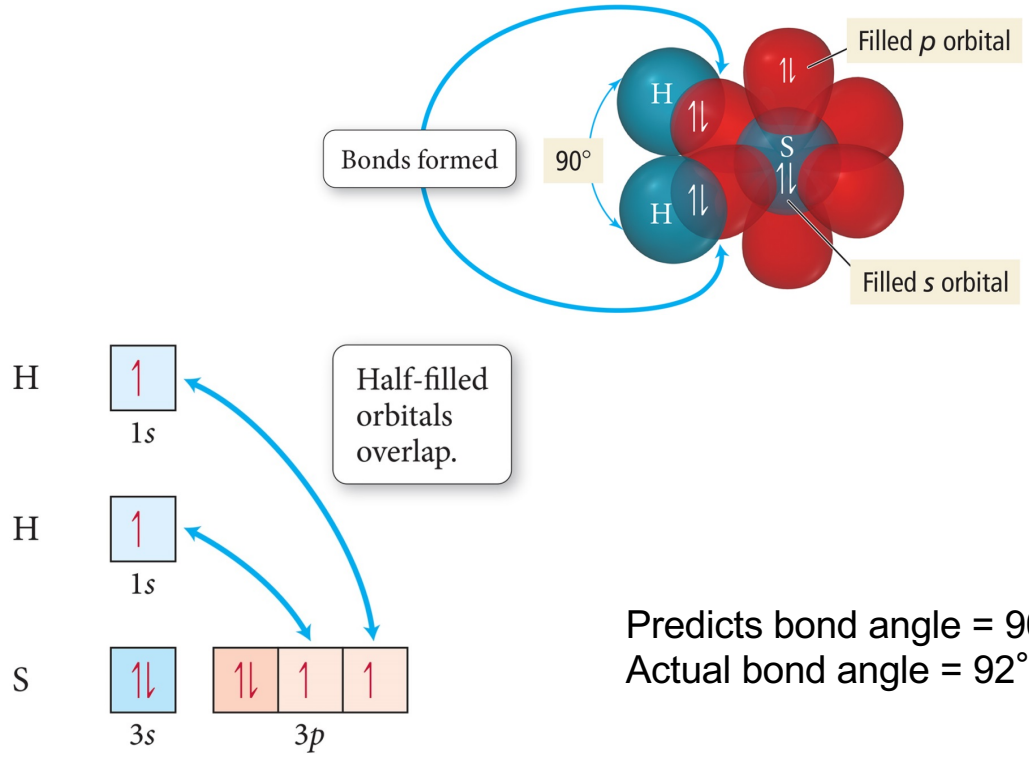
Interaction Energy of Two Hydrogen Atoms



Orbital Interaction

- As two atoms approach each other, the half-filled valence atomic orbitals on each atom would interact to form **molecular orbitals**.
  - Molecular orbitals are regions of high probability of finding the shared electrons in the molecule.
- The molecular orbitals would be more stable than the separate atomic orbitals because they would contain paired electrons shared by both atoms.
  - The potential energy is lowered when the molecular orbitals contain a total of two paired electrons compared to separate, one-electron atomic orbitals.

Orbital Diagram for the Formation of H_2S

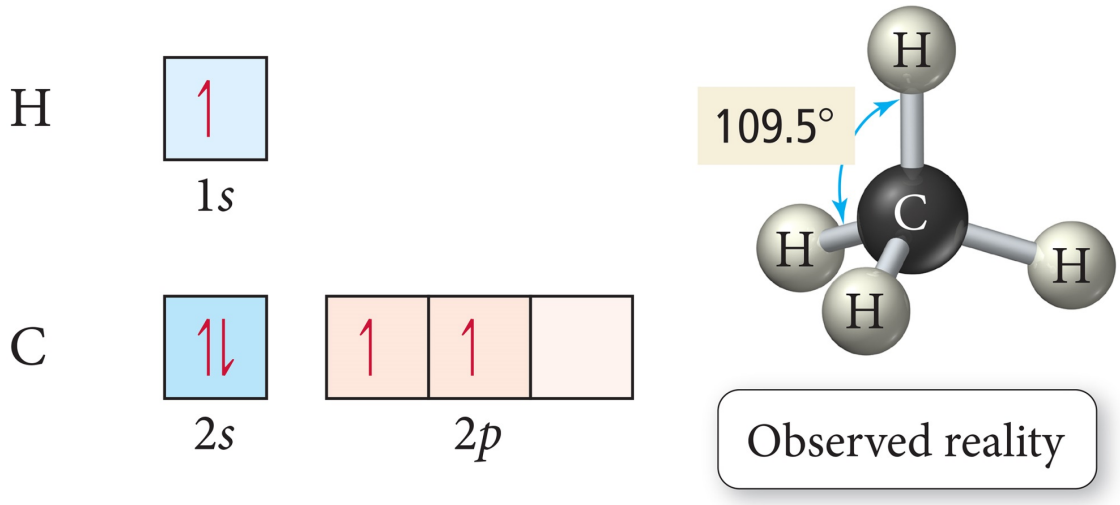


Predicts bond angle = 90°
Actual bond angle = 92°

Valence Bond Theory: Hybridization

- One of the issues that arises is that the number of partially filled or empty atomic orbitals did not predict the number of bonds or orientation of bonds.
  - C = $2s^2 2p_x^1 2p_y^1 2p_z^0$ would predict two or three bonds that are 90° apart, rather than four bonds that are 109.5° apart.
- To adjust for these inconsistencies, it was postulated that the valence atomic orbitals could **hybridize** before bonding took place.
  - One hybridization of C is to mix all the 2*s* and 2*p* orbitals to get four orbitals that point at the corners of a tetrahedron.

Unhybridized C Orbitals Predict the Wrong Bonding and Geometry



Valence Bond Theory: Main Concepts

1. The valence electrons of the atoms in a molecule reside in quantum-mechanical atomic orbitals. The orbitals can be the standard *s, p, d,* and *f* orbitals, *or* they may be hybrid combinations of these.
2. A chemical bond results when these atomic orbitals interact and there is a total of two electrons in the new molecular orbital.
   – The electrons must be spin paired.
3. The shape of the molecule is determined by the geometry of the interacting orbitals.

Hybridization

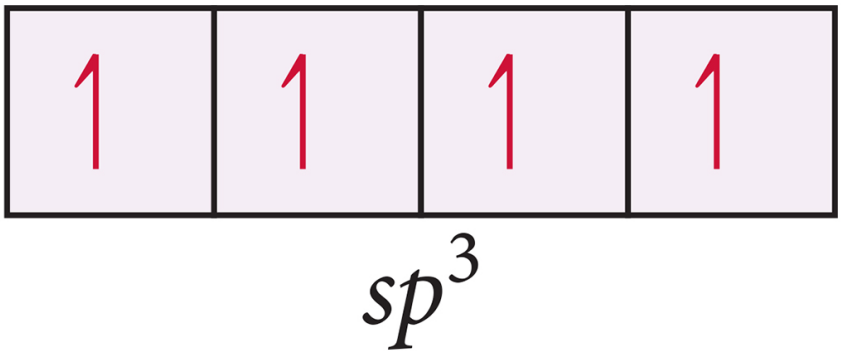
- Some atoms **hybridize** their orbitals to maximize bonding.
  - More bonds = more full orbitals = more stability
- Hybridizing is mixing different types of orbitals in the valence shell to make a new set of degenerate orbitals.
  - sp, sp^2, sp^3, sp^3d, sp^3d^2
- The same type of atom can have different types of hybridization.
  - C = sp, sp^2, sp^3

Hybrid Orbitals

- The number of standard atomic orbitals combined = the number of hybrid orbitals formed.
  - Combining a 2*s* with a 2*p* gives two 2*sp* hybrid orbitals.
  - H cannot hybridize!
    - Its valence shell has only one orbital.
- The number and type of standard atomic orbitals combined determines the shape of the hybrid orbitals.
- The particular kind of hybridization that occurs is the one that yields the lowest overall energy for the molecule.

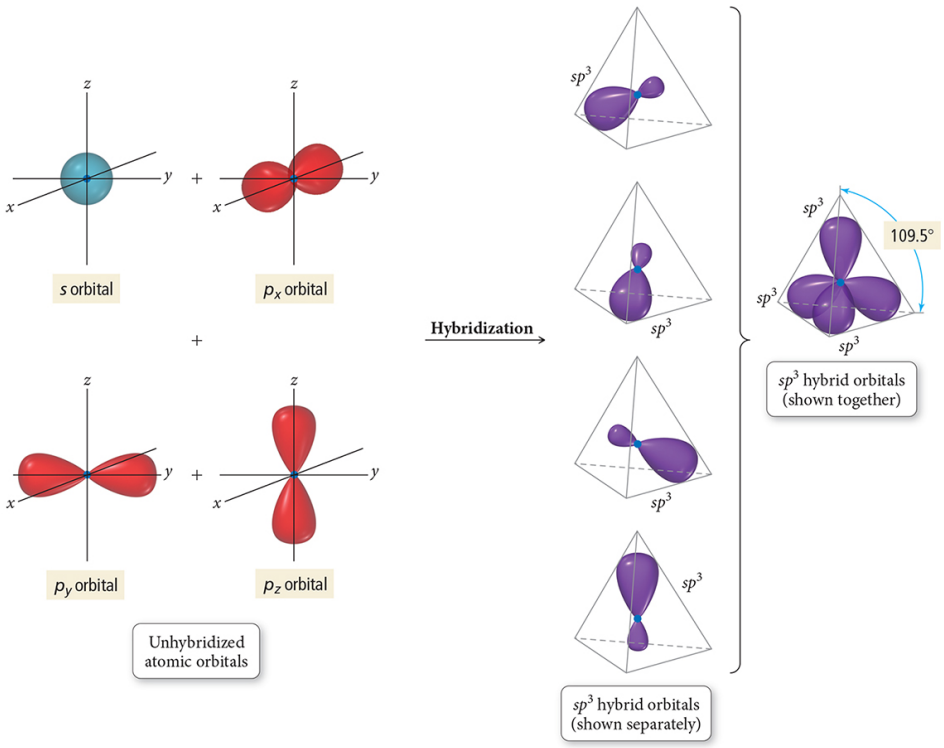
Orbital Diagram of the sp^3 Hybridization of C

C



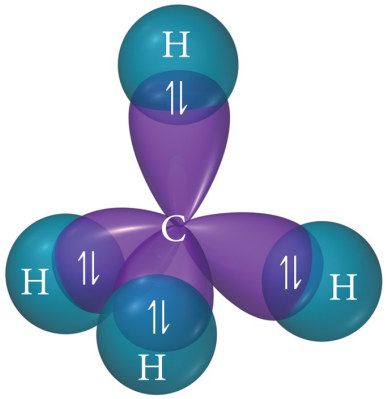
Formation of sp^3 Hybrid Orbitals

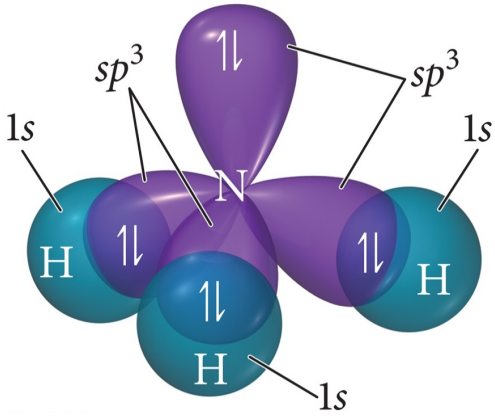
One *s* orbital and three *p* orbitals combine to form four sp^3 orbitals.



sp^3 Hybridization

- Atom with four electron groups around it
  - Tetrahedral geometry
  - 109.5° angles between hybrid orbitals
- Atom uses hybrid orbitals for all bonds and lone pairs.

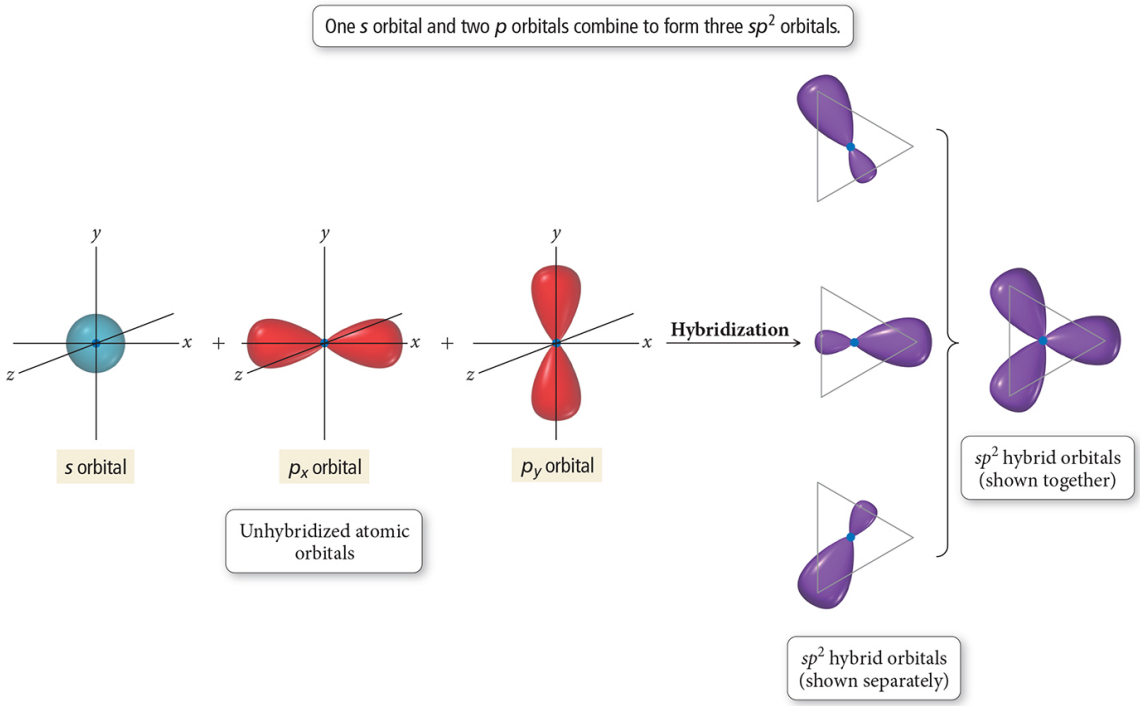




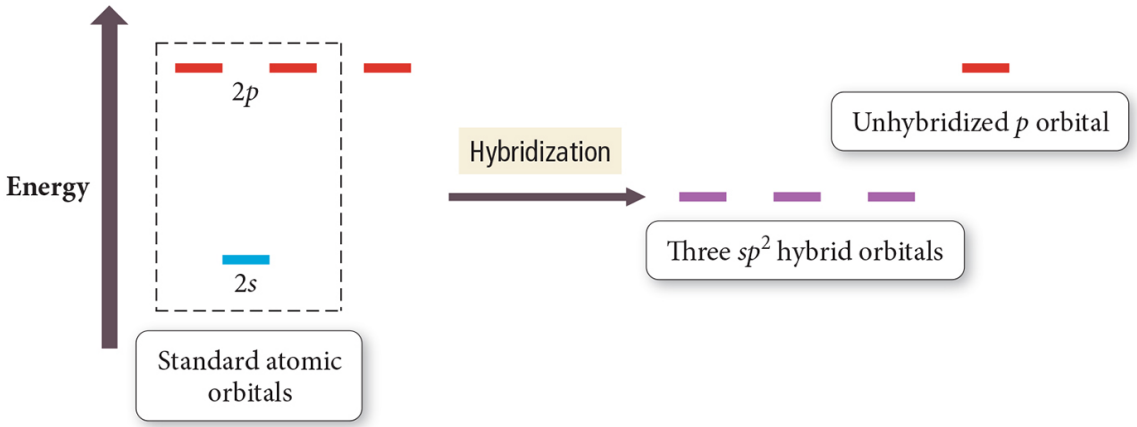
Bonding with Valence Bond Theory

- According to valence bond theory, bonding takes place between atoms when their atomic or hybrid orbitals interact.
  - "Overlap"
- To interact, the orbitals must either
  - be aligned along the axis between the atoms, *or*
  - be parallel to each other and perpendicular to the interatomic axis.

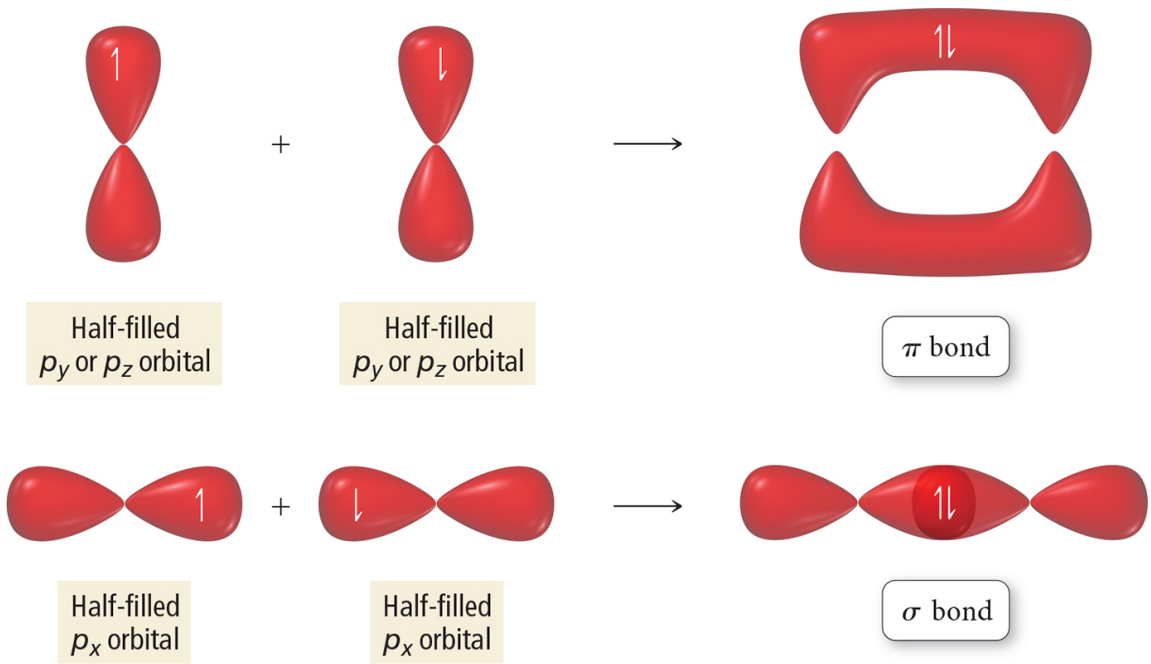
Formation of sp^2 Hybrid Orbitals

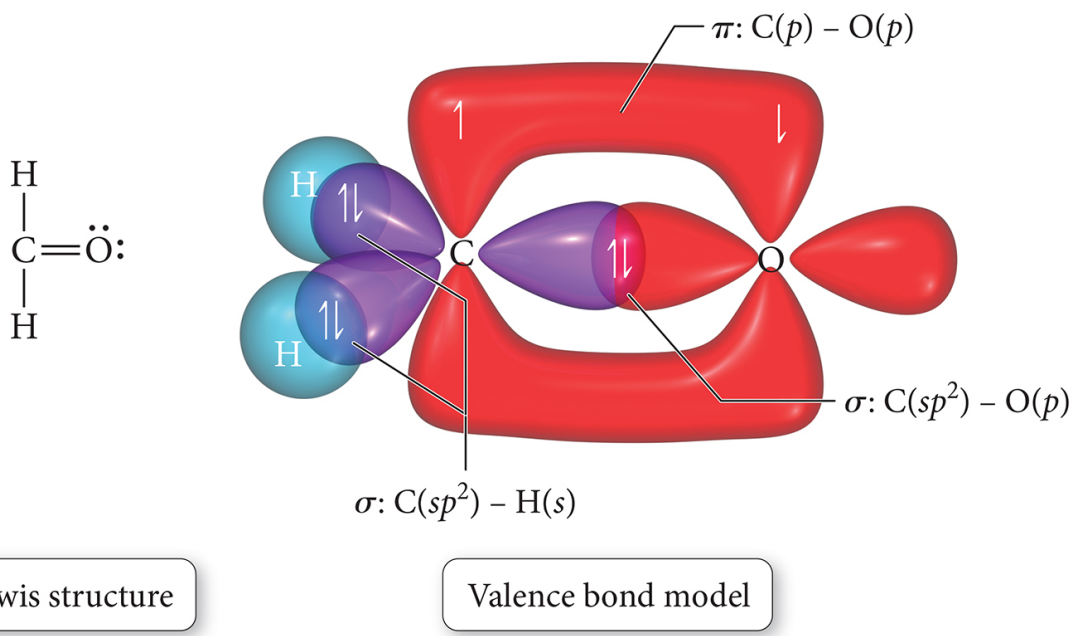


sp^2 Hybridization



- Hybrid orbitals will overlap on axis with orbitals from other atoms.
- Unhybridized *p* orbital will overlap sideways, or side by side, with an unhybridized *p* orbital of another atom.



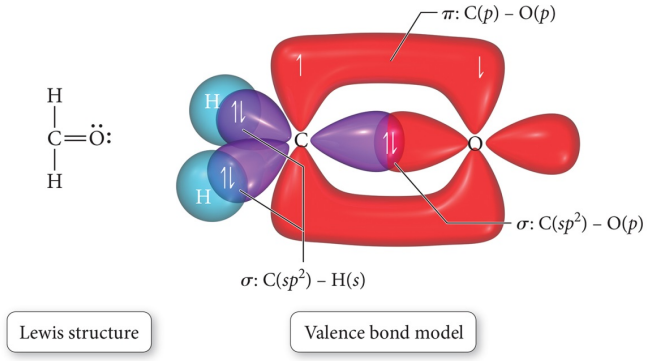


Types of Bonds

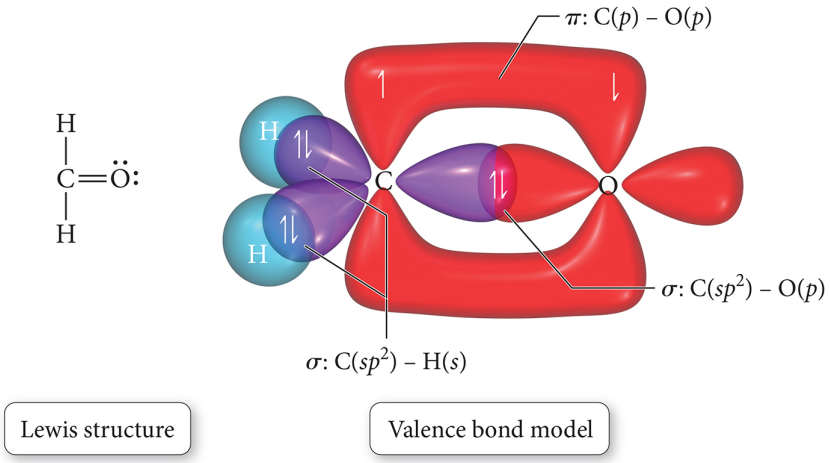
- A **sigma (σ) bond** results when the interacting atomic orbitals point along the axis connecting the two bonding nuclei.
  - Either standard atomic orbitals or hybrids
    - *s* to *s*, *p* to *p*, hybrid to hybrid, *s* to hybrid, etc.
- A **pi (π) bond** results when the bonding atomic orbitals are parallel to each other and perpendicular to the axis connecting the two bonding nuclei.
  - Between unhybridized parallel *p* orbitals
- The interaction between parallel orbitals is not as strong as between orbitals that point at each other; therefore, *σ bonds are stronger than π bonds*.

Orbital Diagrams of Bonding

- "Overlap" between a hybrid orbital on one atom with a hybrid or nonhybridized orbital on another atom results in a σ bond.
- "Overlap" between unhybridized *p* orbitals on bonded atoms results in a π bond.



Orbital Diagrams of Bonding (cont.)

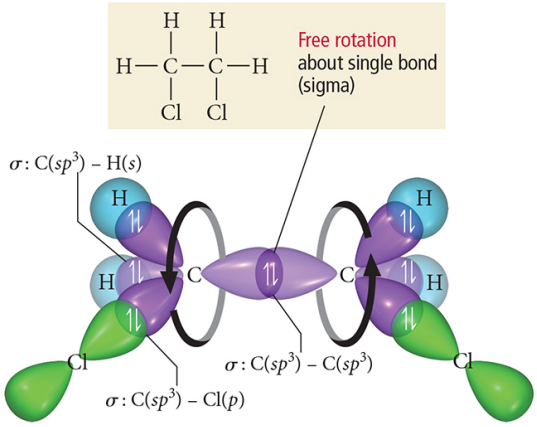


Hybrid orbitals overlap to form a σ bond.
Unhybridized *p* orbitals overlap to form a π bond.

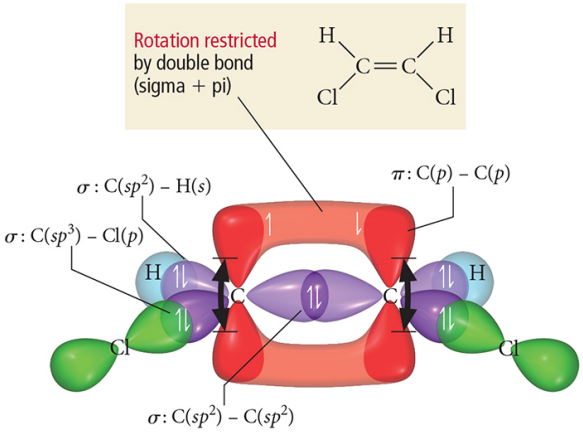
Bond Rotation

- Because the orbitals that form the σ bond point along the internuclear axis, rotation around that bond does not require breaking the interaction between the orbitals.
- But, the orbitals that form the π bond interact above and below the internuclear axis, so rotation around the axis requires the breaking of the interaction between the orbitals.

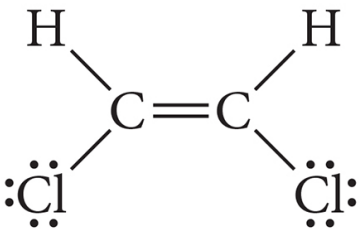
Bond Rotation

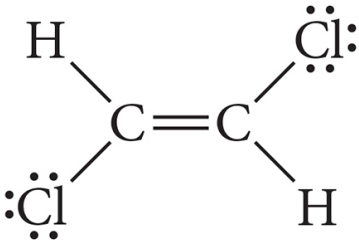


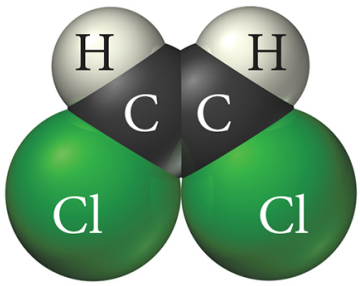
1,2-Dichloroethane

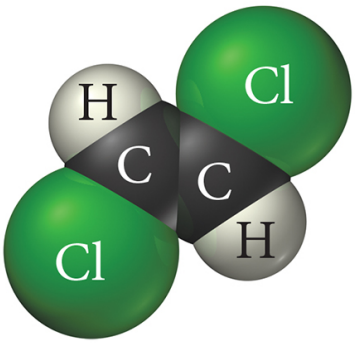


1,2-Dichloroethene





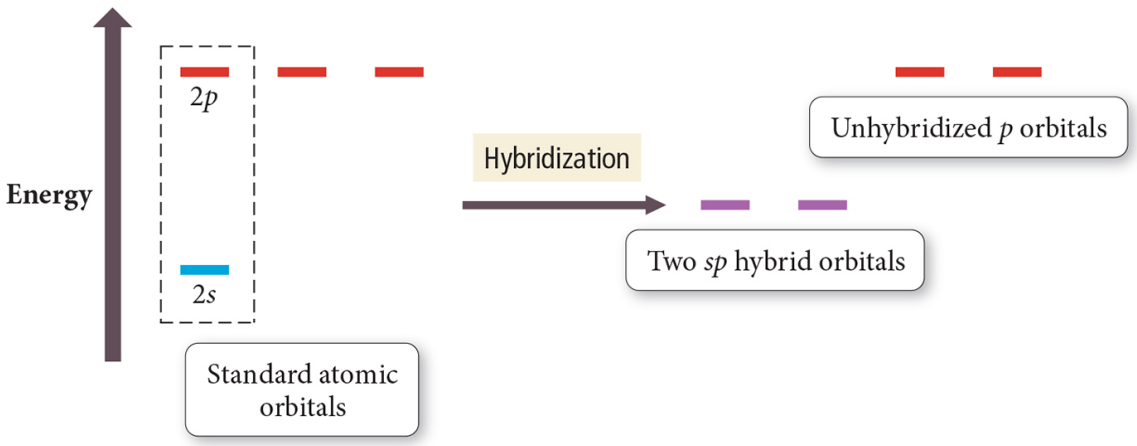




cis-1,2-Dichloroethene

trans-1,2-Dichloroethene

sp Hybridization

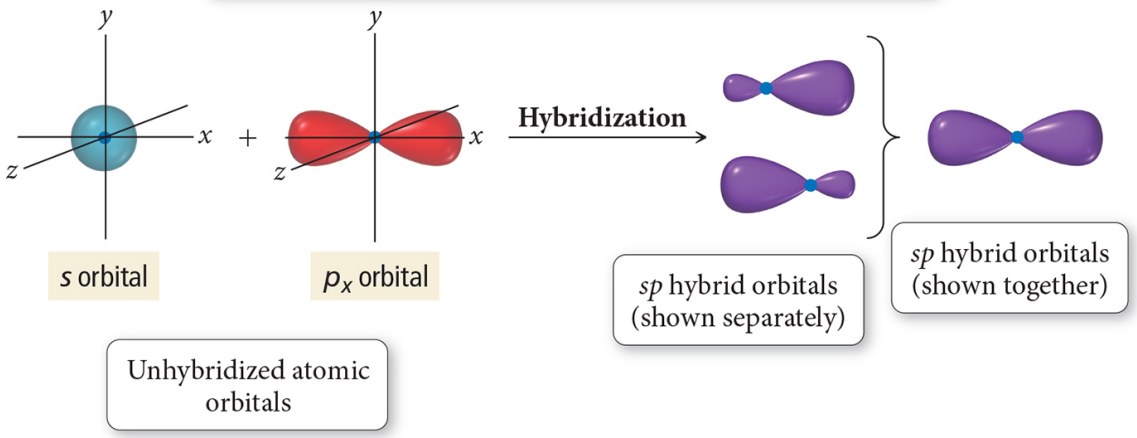


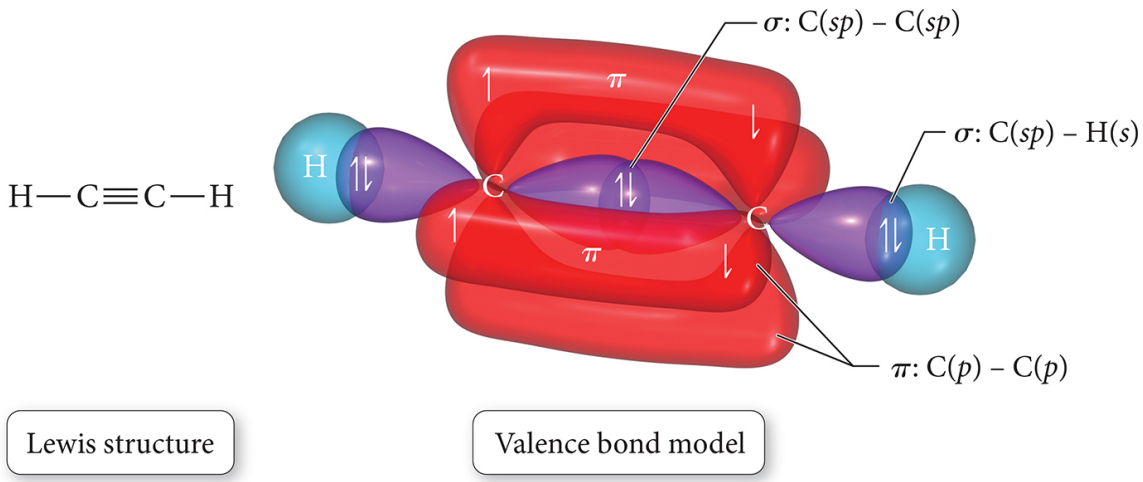
sp Hybridization

- Atom with two electron groups; for C_2H_2
  - Linear shape
  - 180° bond angle
- Atom uses hybrid orbitals for σ bonds or lone pairs and uses nonhybridized *p* orbitals for π bonds
- Usually will for two σ bonds and two π bonds

Formation of *sp* Hybrid Orbitals

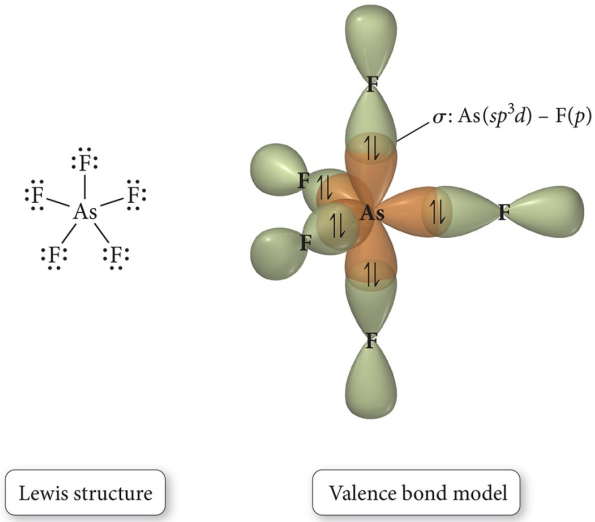
One *s* orbital and one *p* orbital combine to form two *sp* orbitals.

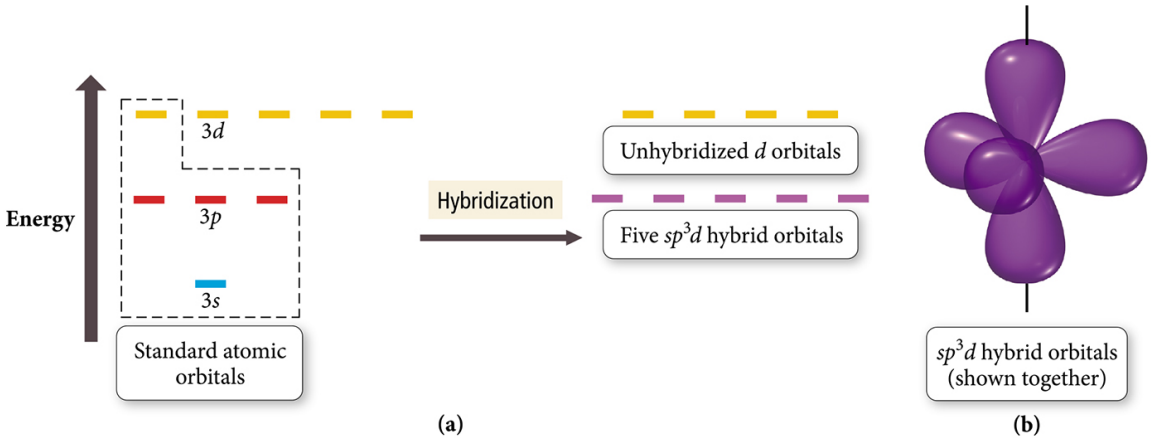




sp^3d Hybridization

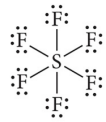
- Atom with five electron groups around it
  - Trigonal bipyramid electron geometry
  - Seesaw, T-shape, linear
  - 120° and 90° bond angles
- Use empty *d* orbitals from valence shell



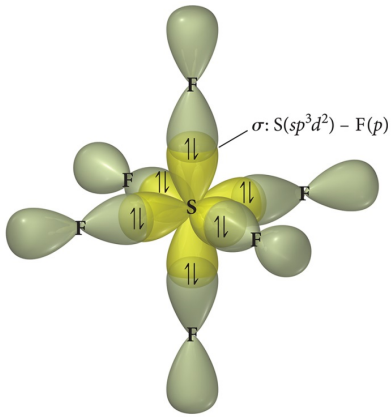


sp^3d^2

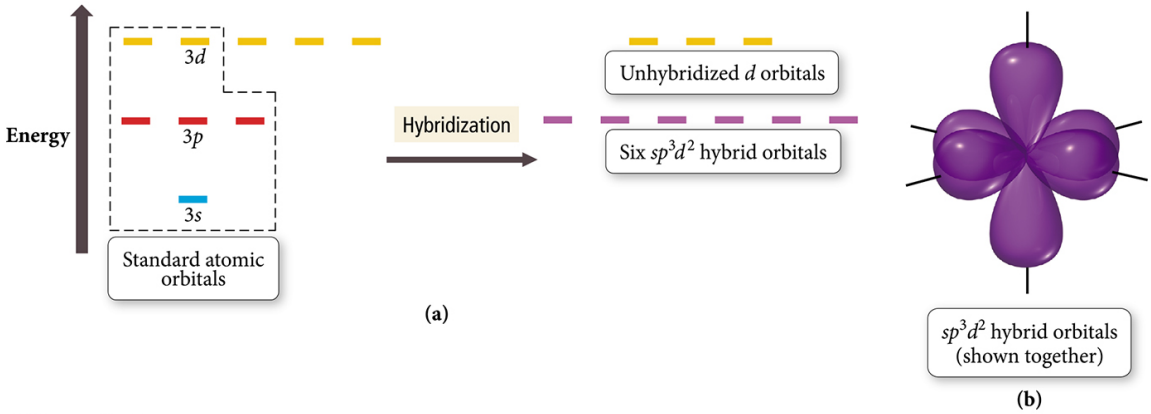
- Atom with six electron groups around it
  - Octahedral electron geometry
  - Square pyramid, Square planar
  - 90° bond angles
- Use empty *d* orbitals from valence shell to form hybrid



Lewis structure

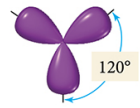
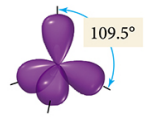
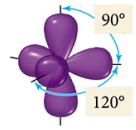
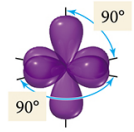


Valence bond model



(a) (b)

TABLE 10.3 Hybridization Scheme from Electron Geometry

Number of Electron Groups	Electron Geometry (from VSEPR Theory)	Hybridization Scheme	
2	Linear	sp	
3	Trigonal planar	sp^2	
4	Tetrahedral	sp^3	
5	Trigonal bipyramidal	sp^3d	
6	Octahedral	sp^3d^2	

Predicting Hybridization and Bonding Scheme

1. Start by drawing the Lewis structure.
2. Use VSEPR theory to predict the electron group geometry around each central atom.
3. Use Table 10.3 to select the hybridization scheme that matches the electron group geometry.
4. Sketch the atomic and hybrid orbitals on the atoms in the molecule, showing overlap of the appropriate orbitals.
5. Label the bonds as σ or π.

Limitations of Valence Bond (VB) Theory

- VB theory predicts many properties better than Lewis theory.
  - Bonding schemes, bond strengths, bond lengths, bond rigidity
- VB theory presumes the electrons are localized in orbitals on the atoms in the molecule; it doesn't account for delocalization.
- There are still many properties of molecules it doesn't predict perfectly.
  - Magnetic behavior of O_2

Molecular Orbital (MO) Theory

- In MO theory, we apply Schrödinger's wave equation to the molecule to calculate a set of **molecular orbitals**.
  - In practice, the equation solution is estimated.
  - We start with good guesses from our experience as to what the orbital should look like.
  - Then we test and tweak the estimate until the energy of the orbital is minimized.
- In this treatment, the electrons belong to the whole molecule, so the orbitals belong to the whole molecule.
  - Delocalization

Linear Combination of Atomic Orbitals (LCAO)

- The simplest guess starts with the atomic orbitals of the atoms adding together to make molecular orbitals; this is called the **linear combination of atomic orbitals (LCAO)** method.
  - Weighted sum
- Because the orbitals are wave functions, the waves can combine either **constructively** or **destructively**.

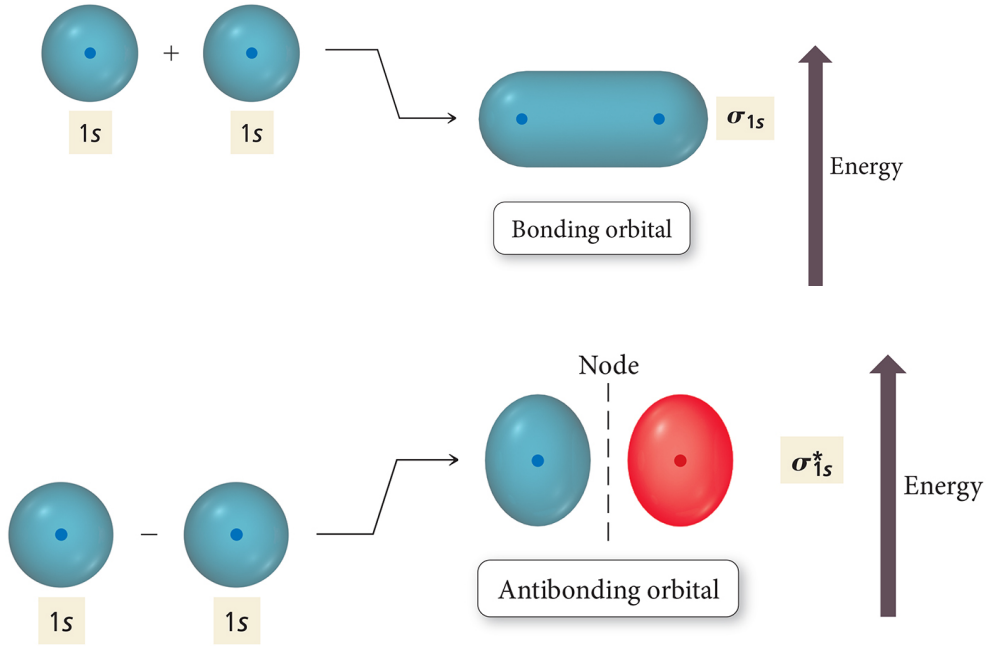
Molecular Orbitals

- When the wave functions combine constructively, the resulting molecular orbital has less energy than the original atomic orbitals; it is called a **bonding molecular orbital**.

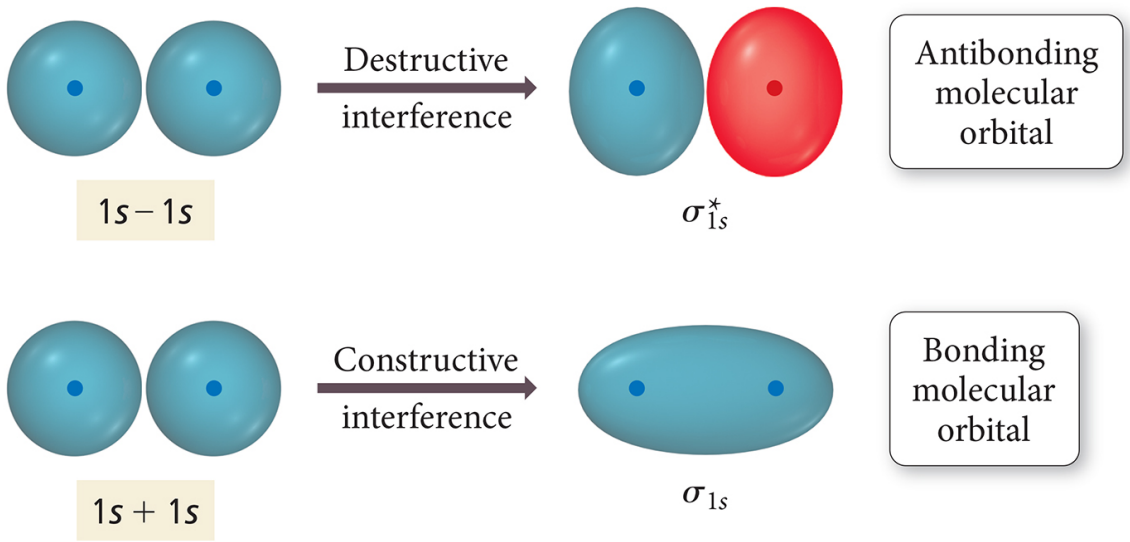
  σ, π
  - Most of the electron density between the nuclei
- When the wave functions combine destructively, the resulting molecular orbital has more energy than the original atomic orbitals; it is called an **antibonding molecular orbital**.

  σ^*, π^*
  - Most of the electron density outside the nuclei
  - Nodes between nuclei

Energy Comparisons of Atomic Orbitals to Molecular Orbitals



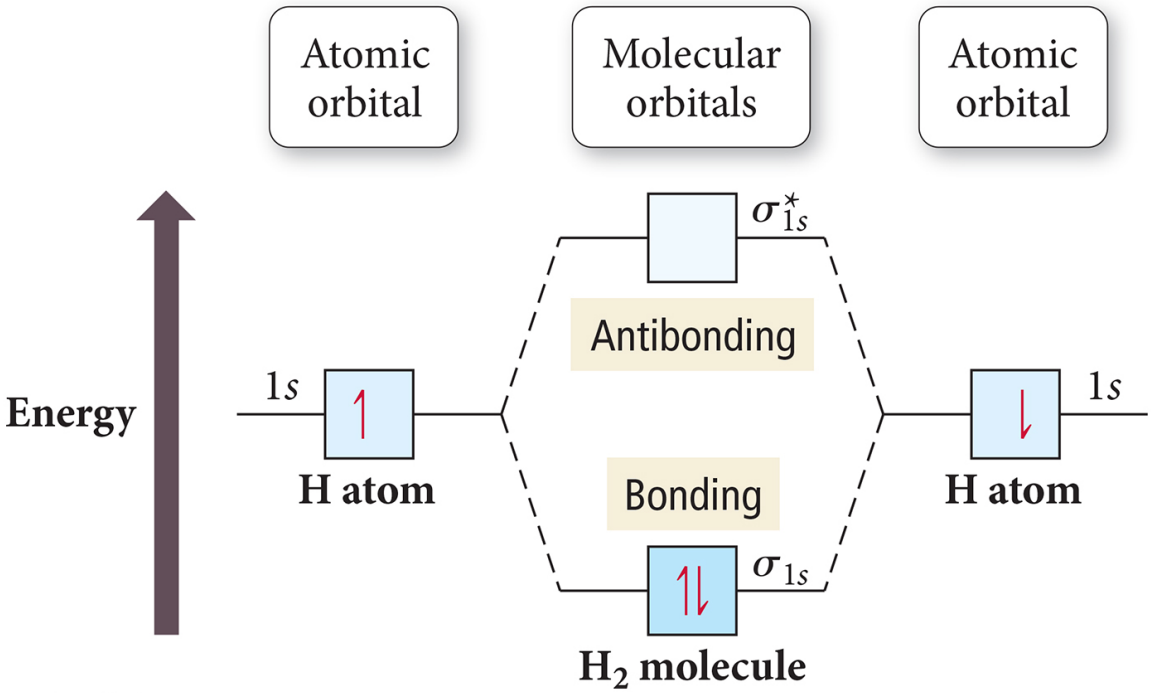
Interaction of 1s Orbitals



Molecular Orbital Theory

- Electrons in bonding MOs are stabilizing.
  - Lower energy than the atomic orbitals
- Electrons in antibonding MOs are destabilizing.
  - Higher in energy than atomic orbitals
  - Electron density located outside the internuclear axis
  - Electrons in antibonding orbitals cancel stability gained by electrons in bonding orbitals.

H_2 Molecule

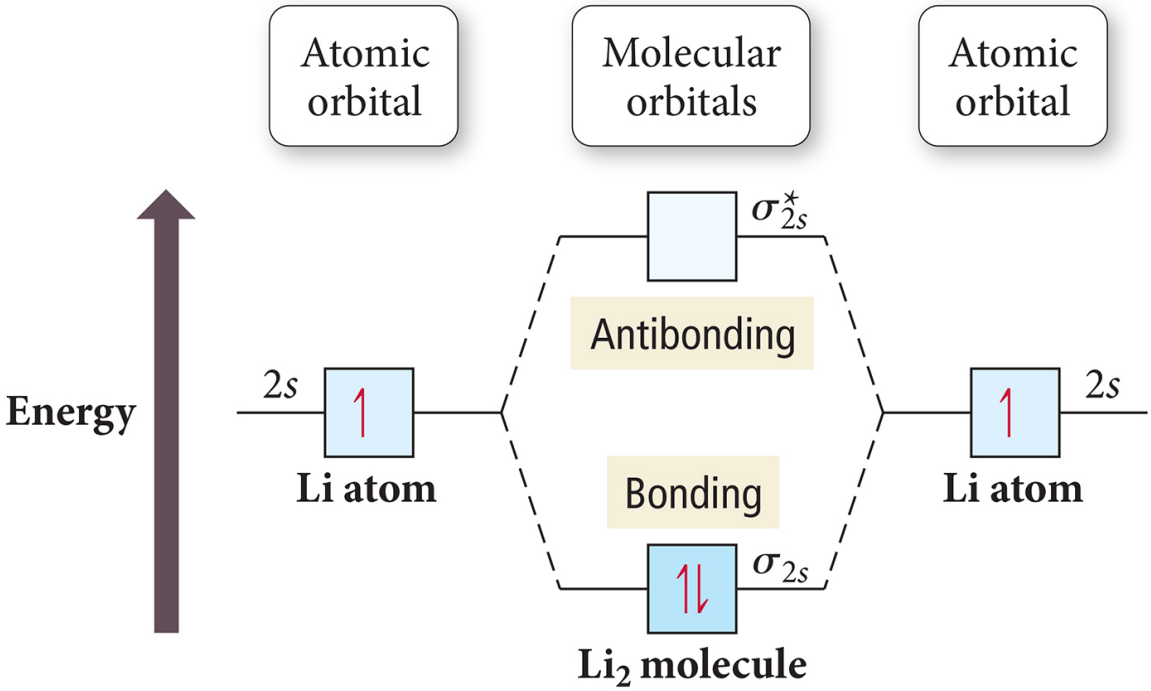


MO and Properties

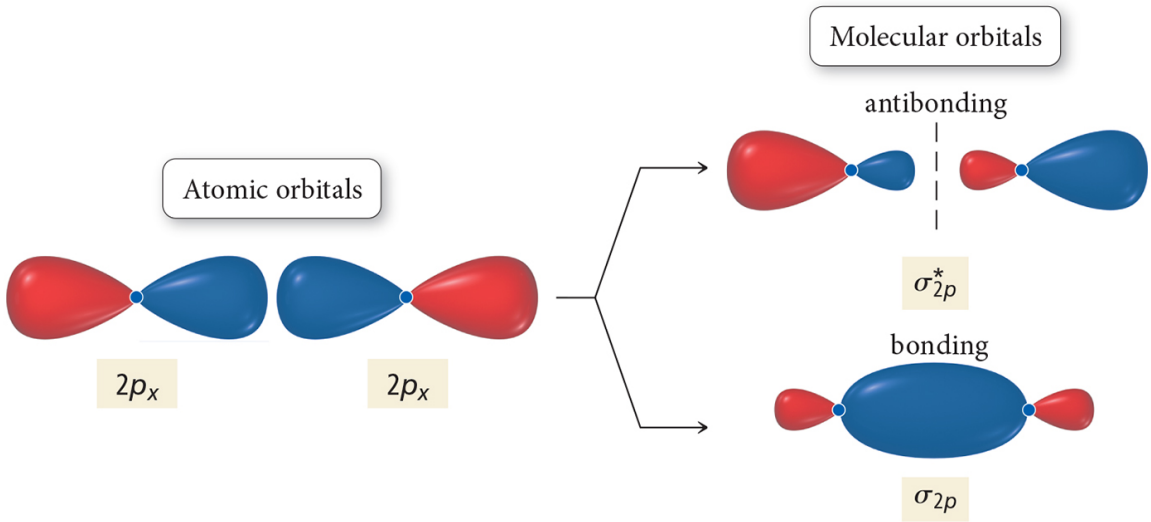
- Bond order = difference between number of electrons in bonding and antibonding orbitals
  - Only need to consider valence electrons
  - May be a fraction
  - Higher bond order = stronger and shorter bonds
  - If bond order = 0, then bond is unstable compared to individual atoms, and no bond will form.
- A substance will be paramagnetic if its MO diagram has unpaired electrons.
  - If all electrons paired, it is diamagnetic

$$\text{Bond Order} = \frac{\#\ \text{Bonding Electrons} - \#\ \text{Antibonding Electrons}}{2}$$

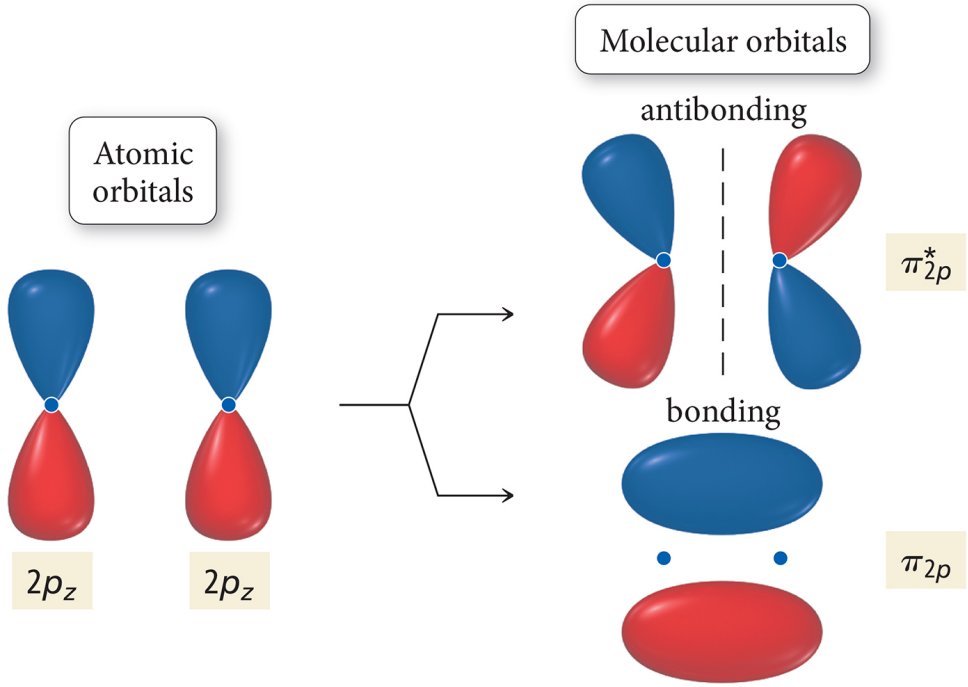
Period Two Homonuclear Diatomic Molecules



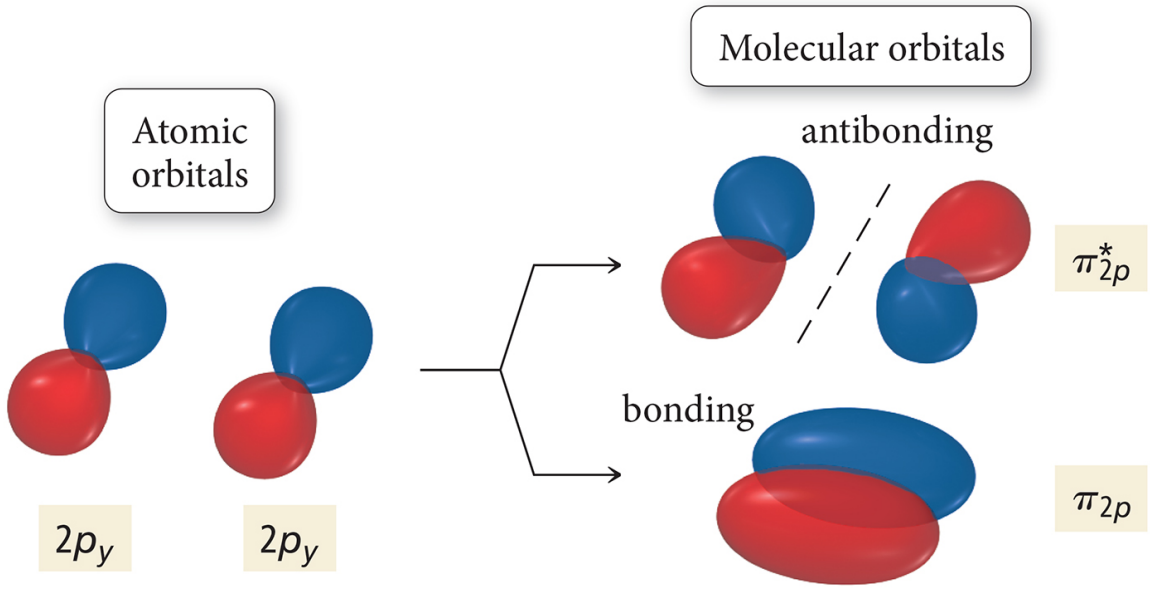
Interaction of *p* Orbitals

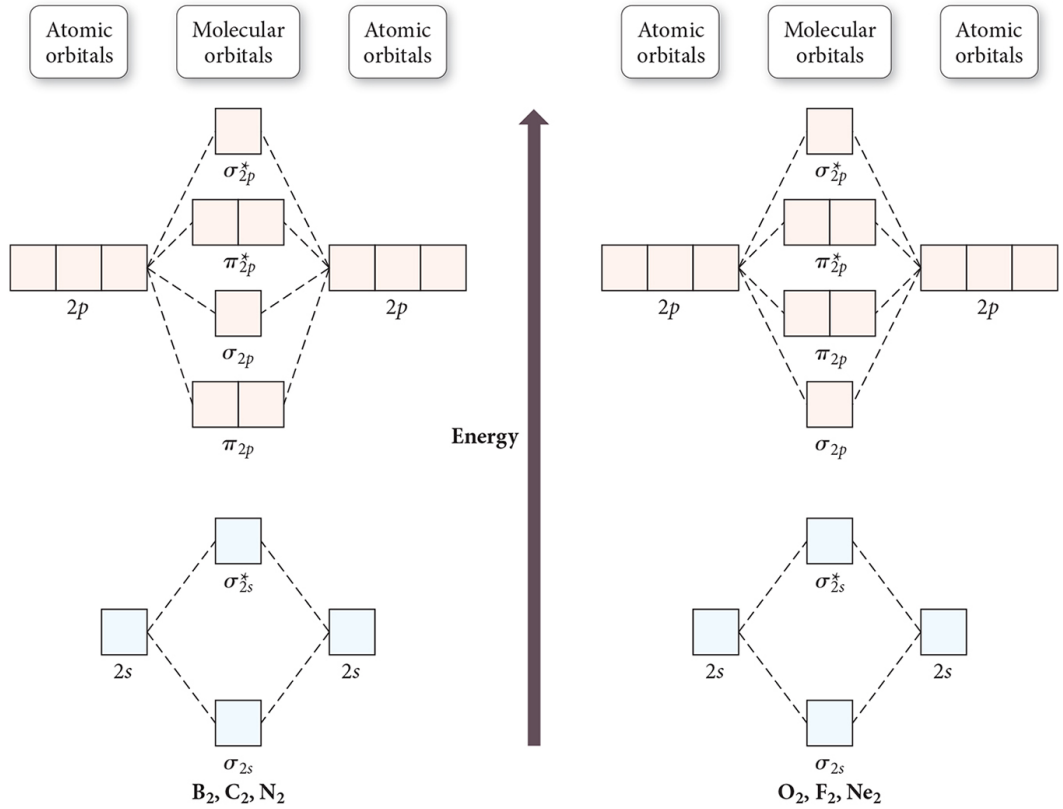


Interaction of *p* Orbitals



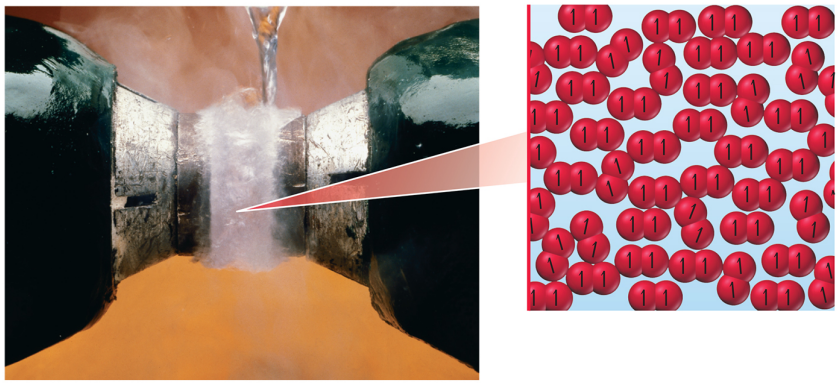
Interaction of *p* Orbitals



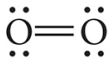


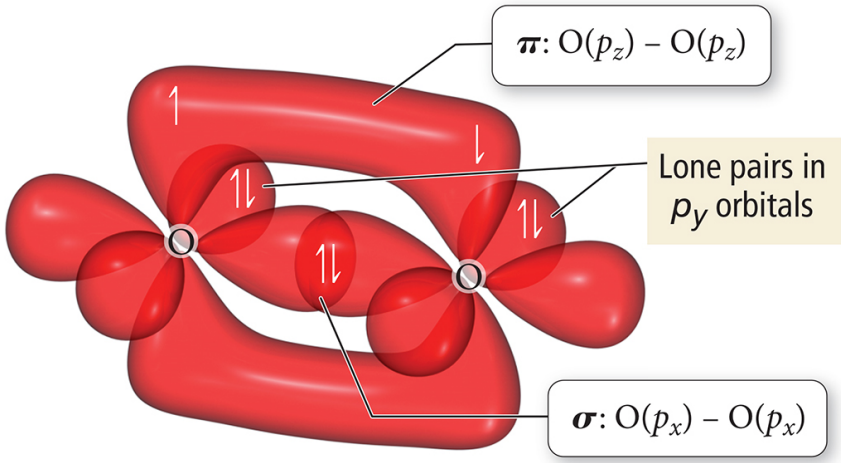
O_2

- Dioxygen is paramagnetic.
- Paramagnetic material has unpaired electrons.
- Neither Lewis theory nor valence bond theory predict this result.



O_2 as Described by Lewis and VB Theory





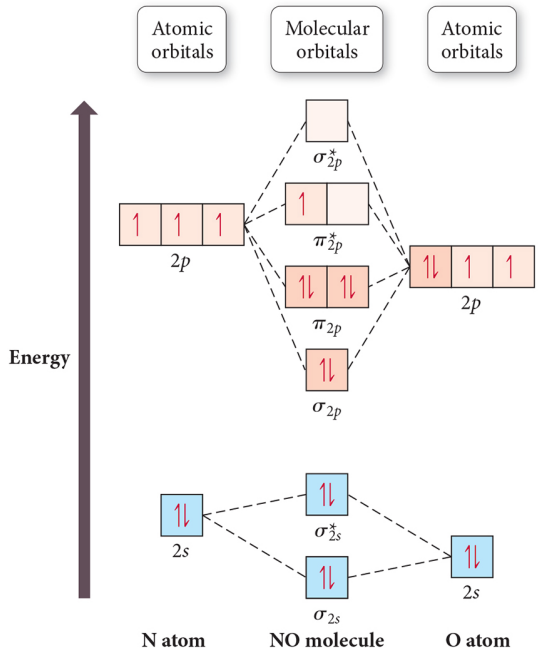
Heteronuclear Diatomic Molecules and Ions

- When the combining atomic orbitals are identical and of equal energy, the contribution of each atomic orbital to the molecular orbital is equal.
- When the combining atomic orbitals are different types and energies, the atomic orbital closest in energy to the molecular orbital contributes more to the molecular orbital.

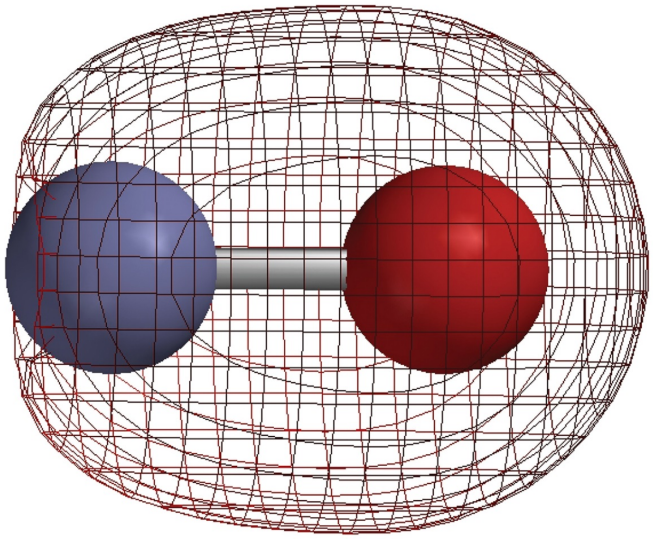
Heteronuclear Diatomic Molecules and Ions

- The more electronegative an atom is, the lower in energy its orbitals are.
- Lower-energy atomic orbitals contribute more to the bonding MOs.
- Higher-energy atomic orbitals contribute more to the antibonding MOs.
- Nonbonding MOs remain localized on the atom donating its atomic orbitals.

Second-Period Heteronuclear Diatomic Molecules



NO



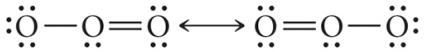
σ_{2s} bonding MO

shows more electron density near O because it is mostly O's 2*s* atomic orbital.

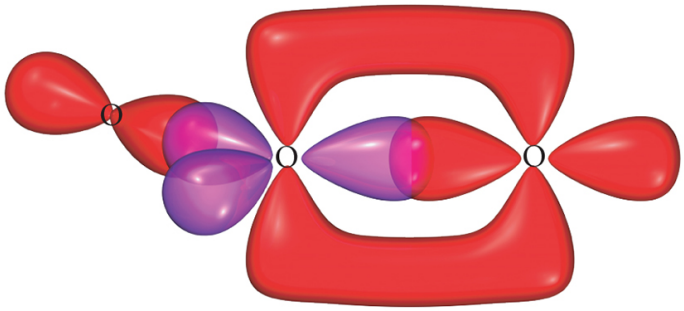
Polyatomic Molecules

- When many atoms are combined together, the atomic orbitals of all the atoms are combined to make a set of molecular orbitals, which are delocalized over the entire molecule.
- This gives results that better match real molecule properties than either Lewis or valence bond theories.

Ozone, O_3



Lewis structure



Valence bond model

Ozone, O_3