Chapter 9: Molecular Geometries and Bonding Theories

Learning Outcomes:

➢Predict the three-dimensional shapes of molecules using the VSEPR model.

➢Determine whether a molecule is polar or nonpolar based on its geometry and the individual bond dipole moments.

➢Explain the role of orbital overlap in the formation of covalent bonds.

➢Determine the hybridization atoms in molecules based on observed molecular structures.

➢Sketch how orbitals overlap to form sigma (σ) and pi (π) bonds.

➢Explain the existence of delocalized π bonds in molecules such as benzene.

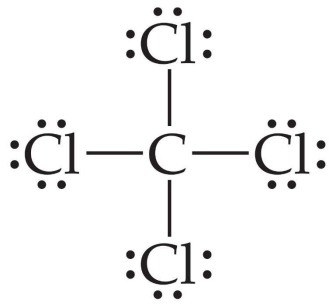
➢Count the number of electrons in a delocalized π system.

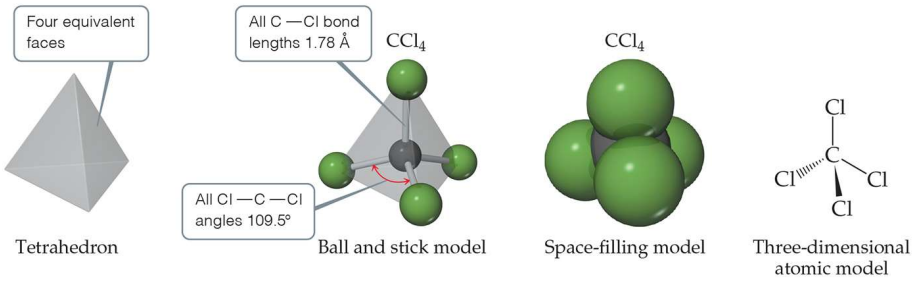
➢Explain the concept of bonding and antibonding molecular orbitals and draw examples of σ and π MOs.

➢Draw molecular orbital energy-level diagrams and place electrons into them to obtain the bond orders and electron configurations of diatomic molecules using molecular orbital theory.

➢Correlate bond order, bond strength (bond enthalpy), bond length, and magnetic properties with molecular orbital descriptions of molecules.

1





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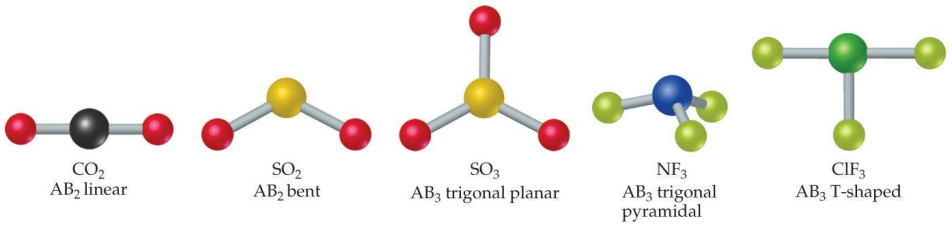
Molecular Shapes

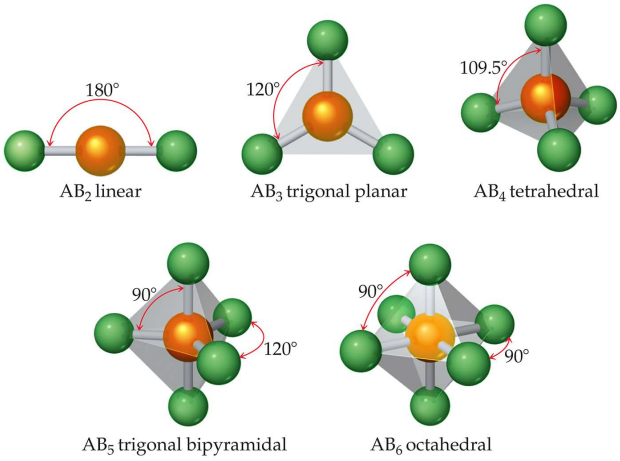
Common shapes for AB_2 and AB_3 molecules.



The shape of a molecule plays an important role in its reactivity.

3

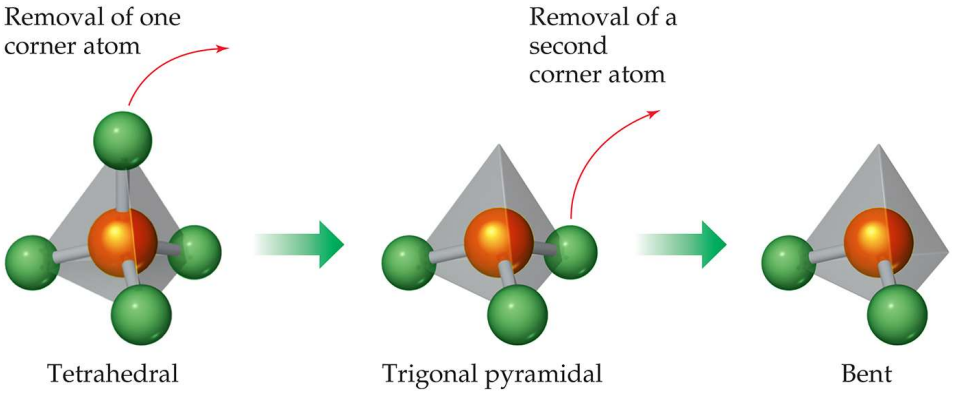
Molecular shapes tend to allow maximum distances between B atoms in AB_n molecules.



- By noting the number of bonding and nonbonding electron pairs we can easily predict the shape of the molecule.
- Additional shapes may be derived from the above shapes.

4

Two additional shapes may be derived from a tetrahedral shape by removal of corner atoms.



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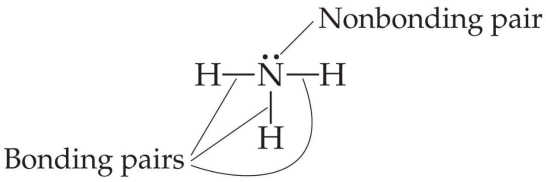
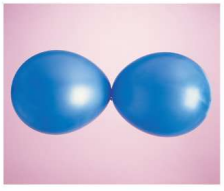
Shape of a Molecule

- Electron pairs, whether they be 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.




Two balloons
linear orientation


Three balloons
trigonal-planar orientation


Four balloons
tetrahedral orientation

6

Electron Domains

Four electron domains on the A atom

Three electron domains on the central O atom

- We can refer to the electron pairs as electron domains.
- In a *double* or *triple* bond, all electrons shared between those two atoms are on the *same side* of the central atom; therefore, they count as *one electron domain*.

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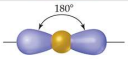
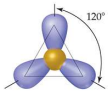
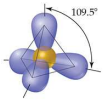
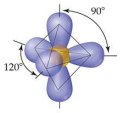
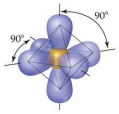
Valence Shell Electron Pair Repulsion Theory (VSEPR)

"The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them."

- The table shows the electron-domain geometries for two through six electron domains around a central atom.
- To determine the electron-domain geometry, count the total number of lone pairs, single, double, and triple bonds on the central atom.

TABLE 9.1 Electron-Domain Geometries as a Function of Number of Electron Domains

Number of Electron Domains*	Arrangement of Electron Domains	Electron Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

*The number of electron domains is sometimes called the *coordination number* of the atom.

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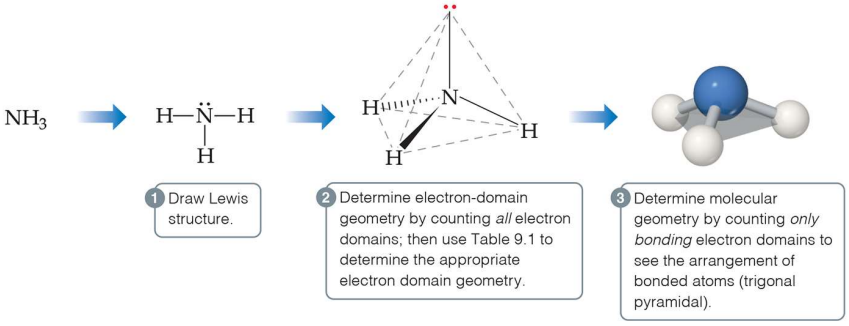
Electron-Domain Geometries



- Count the number of electron domains in the Lewis structure.
- The electron domain geometry corresponds to the base geometry with that number of electron domains.
- The electron-domain geometry is often *not* the shape of the molecule, however.
- The molecular geometry is that defined by the positions of *only* the atoms in the molecules, not the nonbonding pairs.

9

Geometries

The **molecular geometry** is the arrangement of the atoms in space.

- To determine the shape of a molecule we distinguish between *lone pairs (nonbonding domains)* and *bonding pairs (bonding domains)*.

Linear Electron Domain

TABLE 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	Linear	2	0	Linear	Ö=C=Ö

- In this domain, there is only one molecular geometry: linear.
- If there are only two atoms in the molecule, the molecule will be linear no matter what the electron domain is.

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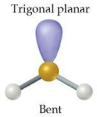
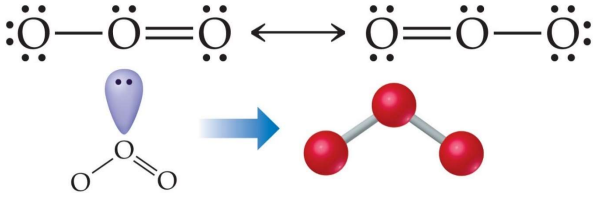
Trigonal Planar Electron Domain

TABLE 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

There are two molecular geometries:

- Trigonal planar, if all the electron domains are bonding
- Bent, if one of the domains is a nonbonding pair.



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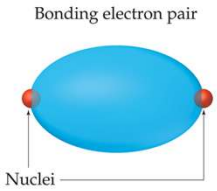
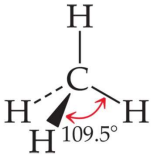
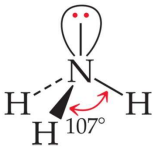
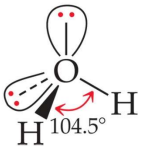
Nonbonding Pairs and Bond Angle

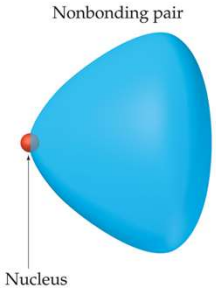
- Nonbonding pairs are physically larger than bonding pairs.
- Their repulsions are greater; this tends to decrease bond angles in a molecule.











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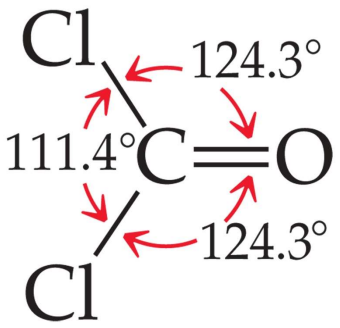
Multiple Bonds and Bond Angles



- Double and triple bonds place greater electron density on one side of the central atom than do single bonds.
- Therefore, they also affect bond angles.

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Tetrahedral Electron Domain

TABLE 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4	Tetrahedral	4	0	Tetrahedral	
		3	1	Trigonal pyramidal	
		2	2	Bent	

- Three molecular geometries:
  - Tetrahedral, if all are bonding pairs
  - Trigonal pyramidal if one is a nonbonding pair
  - Bent if there are two nonbonding pairs

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Expanded Valence Shell: Trigonal bipyramidal

There are four distinct molecular geometries in this domain:

- Trigonal bipyramidal
- Seesaw
- T-shaped
- Linear

TABLE 9.3 Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

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

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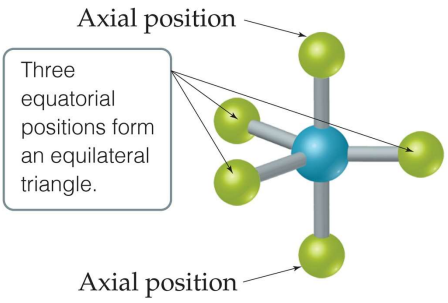
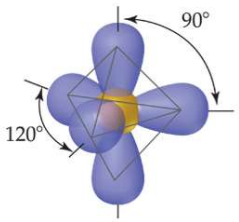
Trigonal Bipyramidal Electron Domain



- Two distinct positions in this geometry:
  - Axial
  - Equatorial



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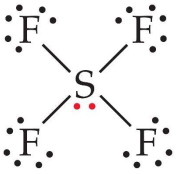
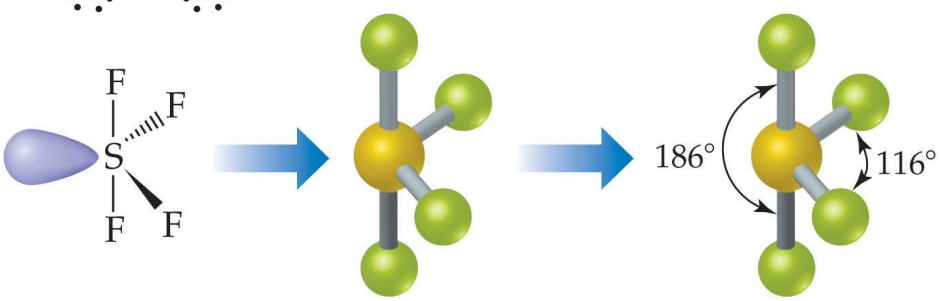
Trigonal Bipyramidal Electron Domain: Deviations from Ideal Bond Angles



sulfur tetrafluoride



Lower-energy conformations result from having nonbonding electron pairs in equatorial, rather than axial, positions in this geometry.

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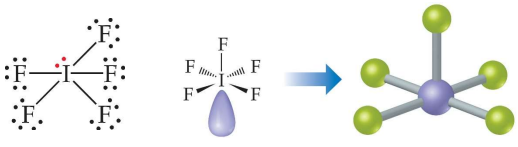
Octahedral Electron Domain

TABLE 9.3 Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	Octahedral	6	0	Octahedral	SF_6
		5	1	Square pyramidal	BrF_5
		4	2	Square planar	XeF_4



All positions are equivalent in the octahedral domain.

Three molecular geometries can be derived from the octahedral electron domain geometry:

- Octahedral
- Square pyramidal
- Square planar

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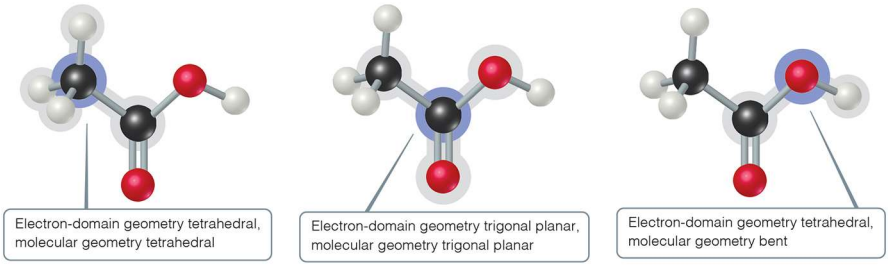
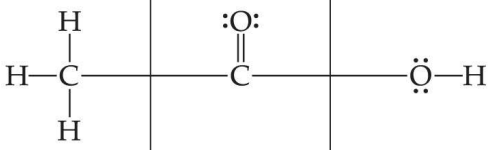
Larger Molecules



In larger molecules, it makes more sense to talk about the geometry about a particular atom rather than the geometry of the molecule as a whole.

			
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

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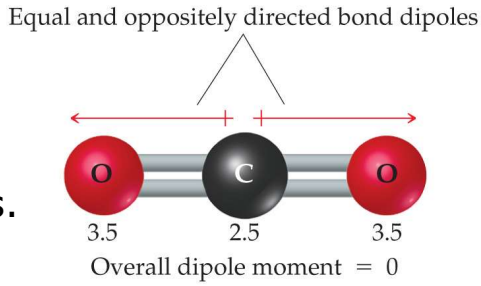
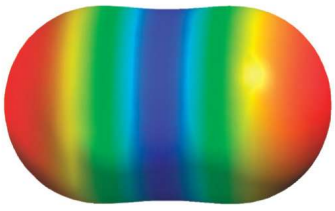
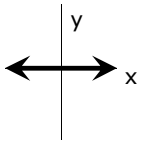
Polarity of Molecules

- Previously we discussed bond dipoles.
- But just because a molecule possesses polar bonds does not mean the molecule *as a whole* will be polar.

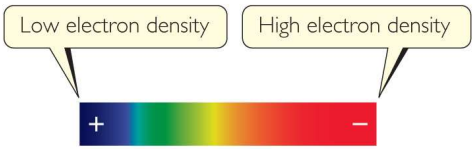






$$\sum x = 0 \quad \sum y = 0$$

$$\text{overall} \sum = 0$$



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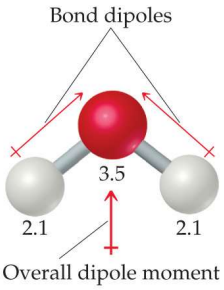
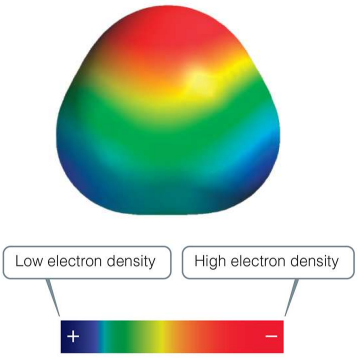
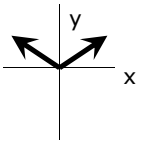


Polarity of Molecules

By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.





$$\sum x = 0 \quad \sum y \neq 0$$

$$\text{overall} \sum \neq 0$$

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Polarity of Molecules

For nonionic molecules, determine if the BONDS polar? (Do they have a **bond dipole**?)

a. NO: The molecule is NONPOLAR!

b. YES: Continue—Do the AVERAGE position of $\delta+$ and $\delta-$ coincide? (Is the **overall dipole moment** equal to ZERO?)

1) YES: The molecule is NONPOLAR.

2) NO: The molecule is POLAR.

NOTE: Different atoms attached to the central atom have different polarity of bonds.

Convention:

Pauling electronegativity difference	Type of bond
< 0.4	nonpolar covalent
0.4-1.7	polar covalent
> 1.7	ionic

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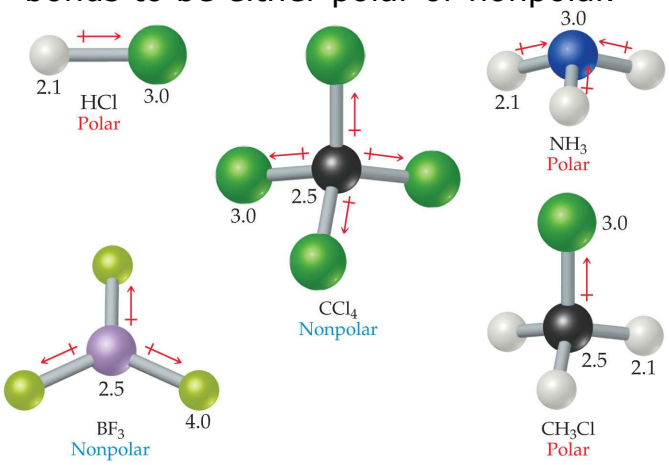
Polarity

It is possible for a molecule with polar bonds to be either polar or nonpolar.



Examine each structure independently to determine if a molecule or ion is polar or nonpolar.

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Example: Polarity of Molecules

Draw the Lewis structure and determine the molecular geometry to determine if a molecular is polar.

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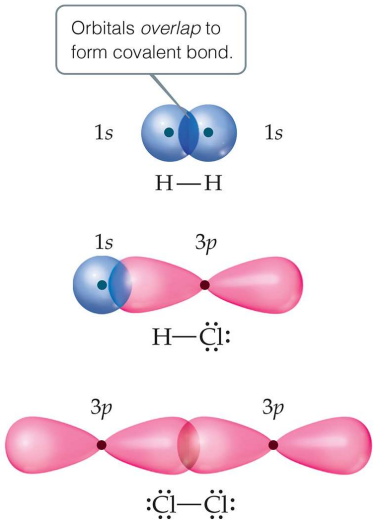
Valence Bond Theory: Overlap and Bonding

- Covalent bonds form when orbitals on two adjacent atoms overlap.
- The shared region of space between the orbitals is called the *orbital overlap*.
- There are two electrons (usually one from each atom) of opposite spin in the orbital overlap.



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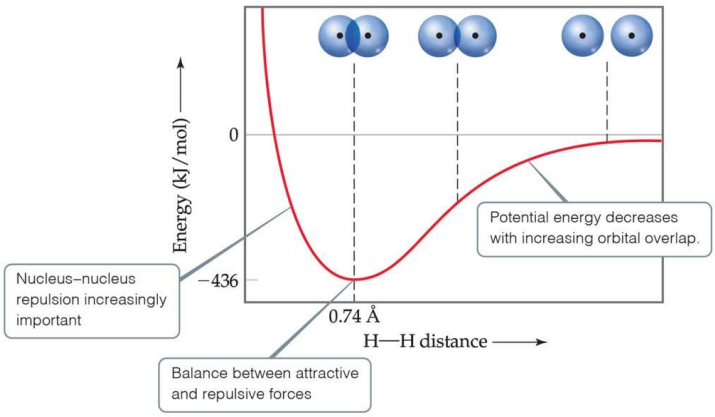
Overlap and Bonding



- Increased overlap brings the atoms together until a balance is reached between the like charge repulsions and the electron-nucleus attraction.
- Atoms can't get too close because the internuclear repulsions get too great.

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VSEPR and Hybrid Orbitals

VSEPR predicts shapes of molecules very well.

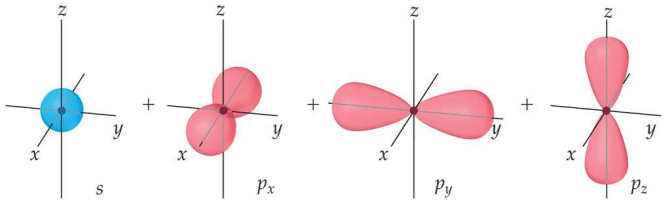
How does that fit with orbitals?

- Let's use H_2O as an example:
- If we draw the best Lewis structure to assign VSEPR, it becomes bent.
- If we look at oxygen, its electron configuration is $1s^2 2s^2 2p^4$. If it shares two electrons to fill its valence shell, they should be in $2p$.
- Wouldn't that make the angle 90°? Why is it 104.5°?

27

Hybrid Orbitals

But it's hard to imagine tetrahedral, trigonal bipyramidal, and other geometries arising from the atomic orbitals we recognize.



- **Hybrid orbitals** form by "mixing" of atomic orbitals to create new orbitals of equal energy, called degenerate orbitals.
- This process is called **hybridization**.
- When two orbitals "mix" they create two hybrid orbitals; when three orbitals mix, they create three hybrid orbitals.

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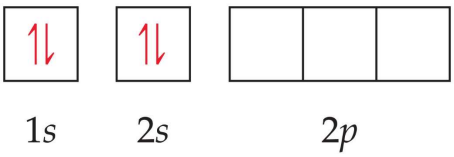
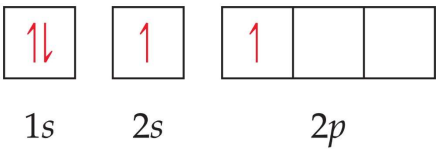
Hybrid Orbitals – *sp* hybrid

Beryllium & BeF_2:

- In its ground electronic state, it would not be able to form bonds because it has no singly-occupied orbitals.
- But if it absorbs the small amount of energy needed to promote an electron from the 2*s* to the 2*p* orbital, it can form two bonds.





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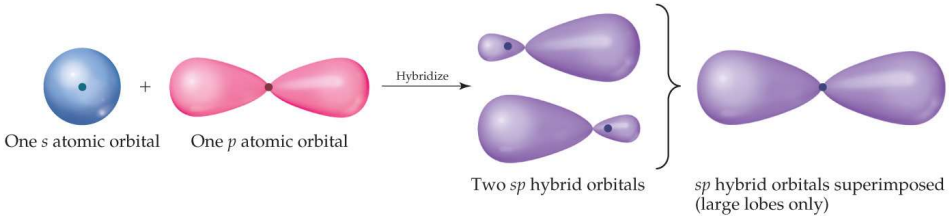
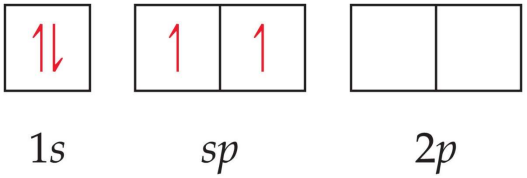
Hybrid Orbitals - *sp*

Mixing the *s* and *p* orbitals yields two degenerate orbitals that are hybrids of the two orbitals.

- These *sp* hybrid orbitals have two lobes like a *p* orbital.
- One of the lobes is larger and more rounded as is the *s* orbital.

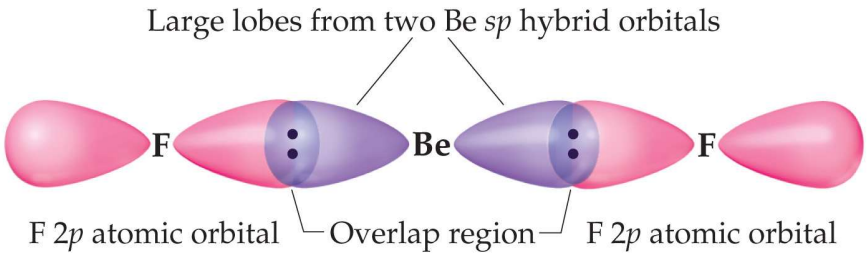




30

Hybrid Orbitals

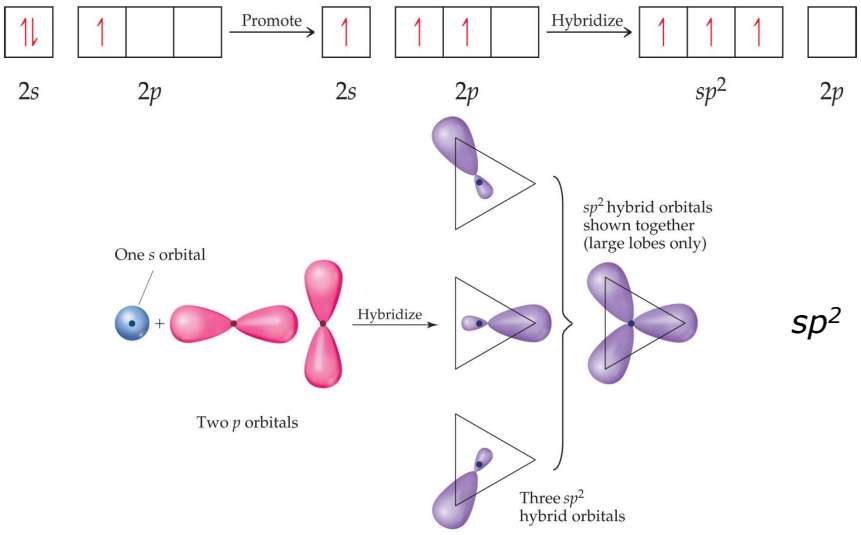
- Two degenerate orbitals align themselves 180° from each other.
- This is consistent with the observed geometry of beryllium compounds: linear.



31

Hybrid Orbitals – sp^2

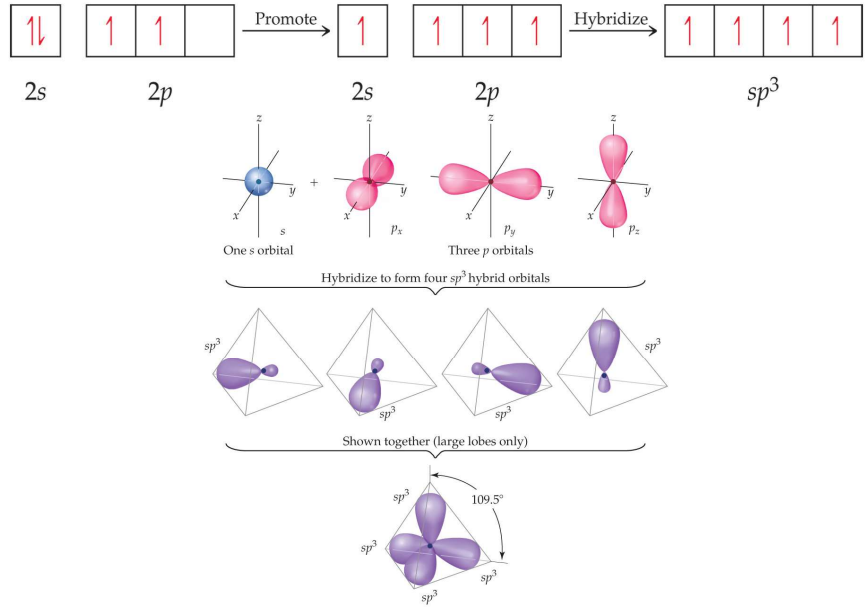
Using a similar model for boron leads to…



32

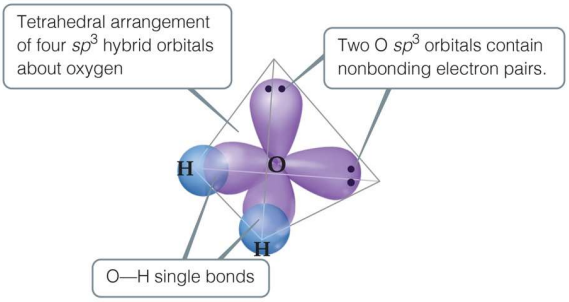
Hybrid Orbitals – sp^3

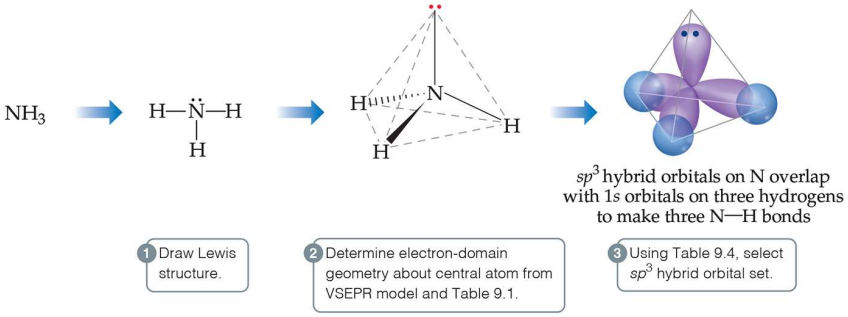
With carbon we get…



33

H_2O





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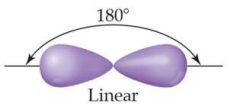
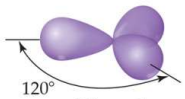
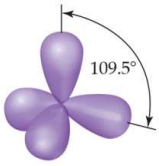
Hybrid Orbitals

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

TABLE 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,*p*	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,*p*,*p*	Three sp^2	 Trigonal planar	BF_3, SO_3
s,*p*,*p*,*p*	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

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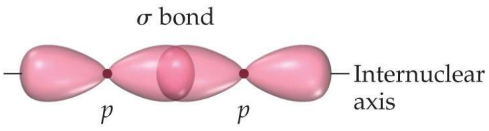
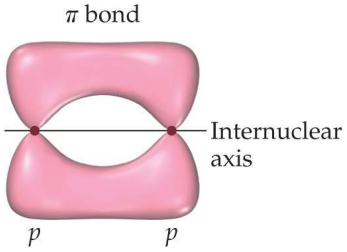
Multiple Bonds





Sigma (σ) bonds are characterized by

- Head-to-head overlap.
- Cylindrical symmetry of electron density about the internuclear axis.

Pi (π) bonds are characterized by

- Side-to-side overlap.
- Electron density above and below the internuclear axis.

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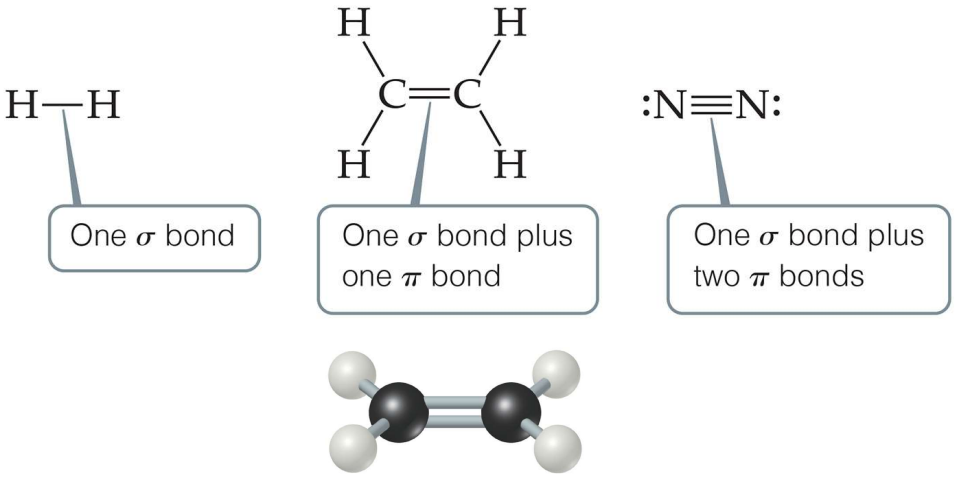
Multiple Bonds

In a multiple bond one of the bonds is a σ bond and the rest are π bonds.



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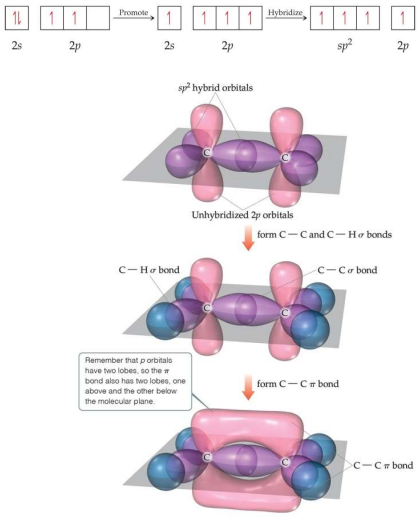
Multiple Bonds

- In C_2H_4 an sp^2 orbital on each carbon overlaps in σ fashion with the corresponding orbital on the other carbon and two hydrogens.
- The unhybridized *p* orbitals overlap in π fashion.



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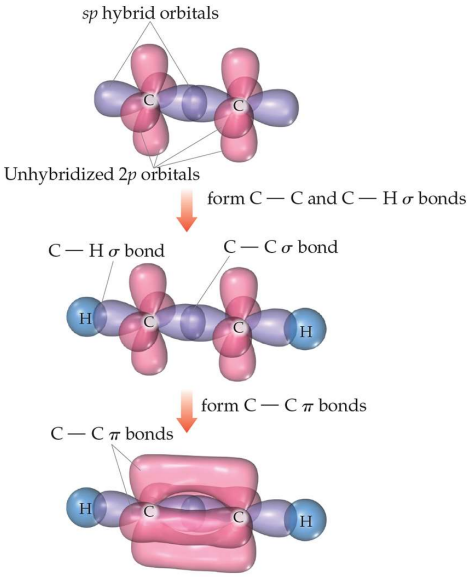
Multiple Bonds: acetylene

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.



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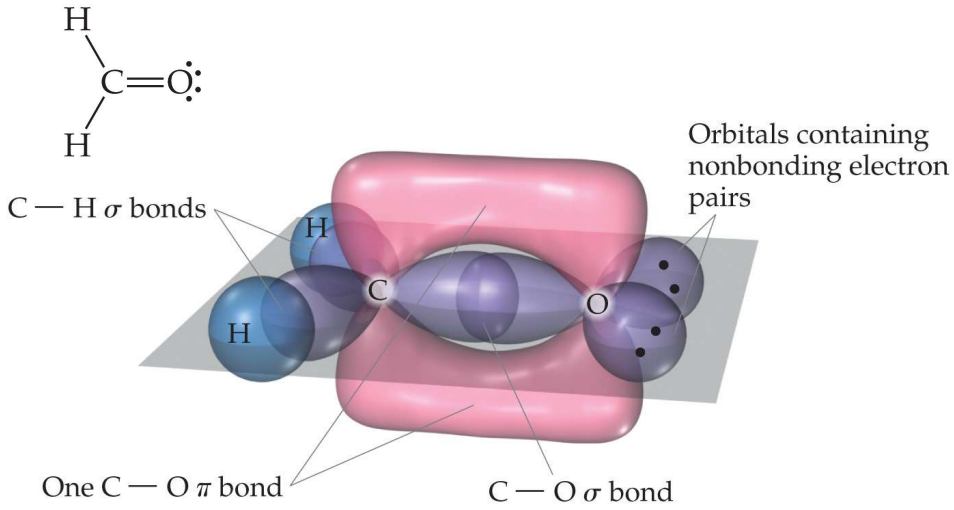
Multiple Bonds: formaldehyde



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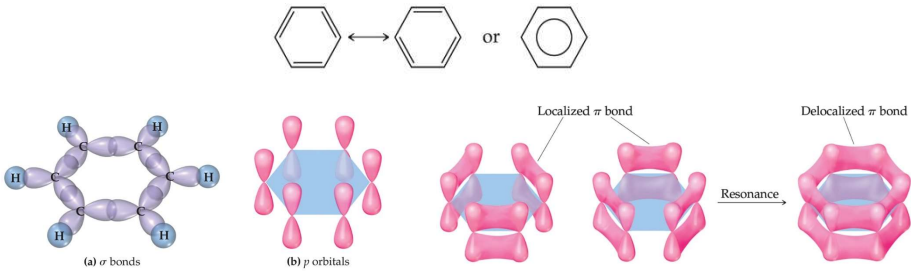
Resonance in Benzene

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



- The π electrons in benzene are not localized, but delocalized.
- The even distribution of the π electrons in benzene makes the molecule unusually stable.

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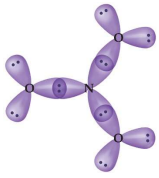
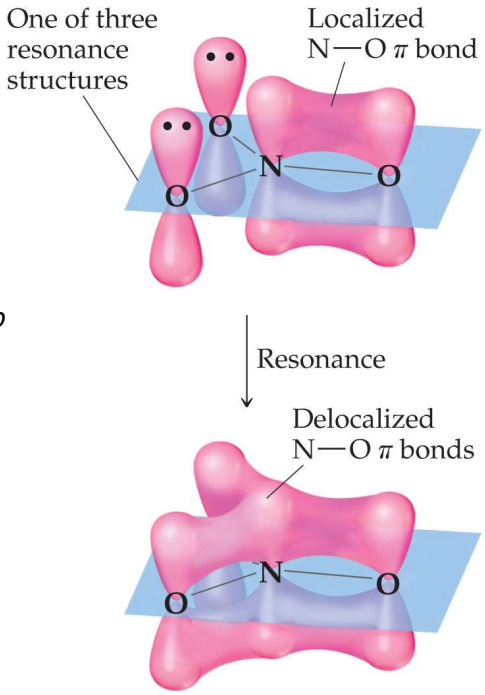
Delocalized Electrons: Resonance



- In reality, each of the four atoms in the nitrate ion has a *p* orbital.
- The *p* orbitals on all three oxygens overlap with the *p* orbital on the central nitrogen.
- This means the π electrons are not localized between the nitrogen and one of the oxygens, but rather are delocalized throughout the ion.



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Example

Which of the following molecules or ions will exhibit <u>delocalized</u> bonding: SO_3, SO_3^{2-}, H_2CO, O_3, NH_4^+?

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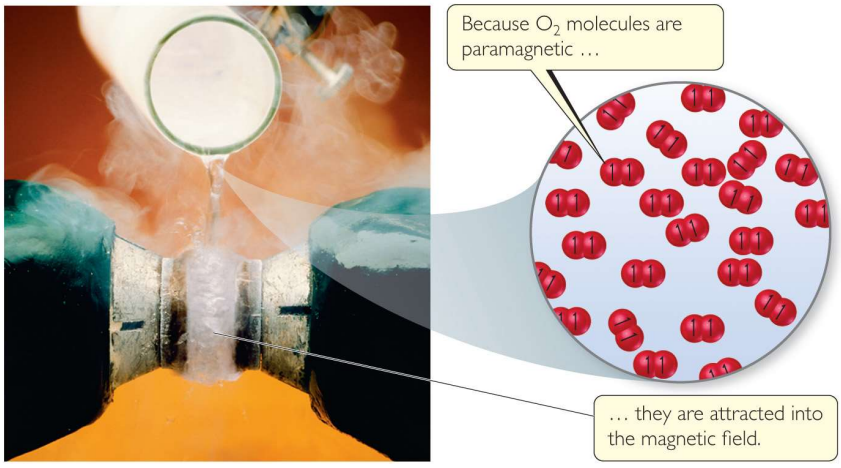
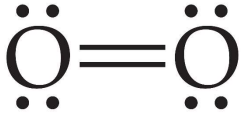
Limitation of Valence Bond Theory



Though valence bond theory effectively conveys most observed properties of ions and molecules, there are some concepts better represented by molecular orbitals.



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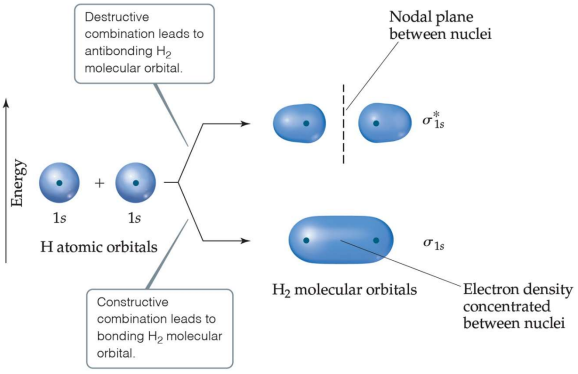
Molecular Orbital (MO) Theory

- In MO theory, we invoke the wave nature of electrons.
- If waves interact constructively, the resulting orbital is lower in energy: a bonding molecular orbital.
- If waves interact destructively, the resulting orbital is higher in energy: an antibonding molecular orbital.



A **nodal plane** occurs where electron density equals zero.

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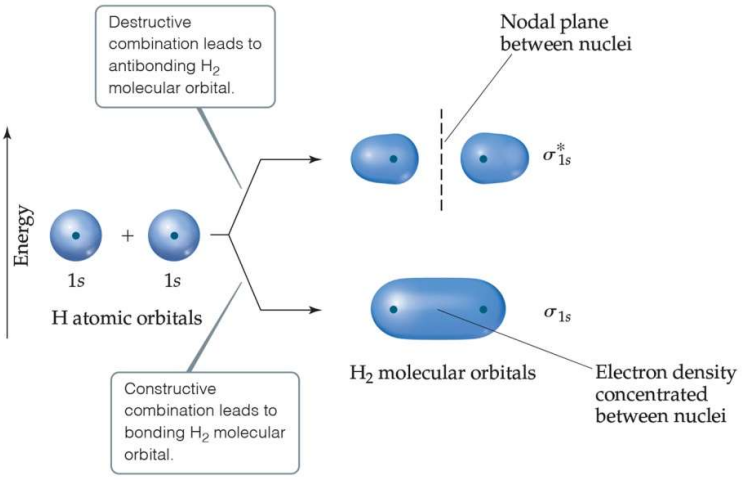
Whenever there is direct overlap of orbitals, forming a bonding and an antibonding orbital, they are called **sigma (*σ*) molecular orbitals**. The antibonding orbital is distinguished with an asterisk as ***σ****. Here is an example for the formation of a hydrogen molecule from two atoms.



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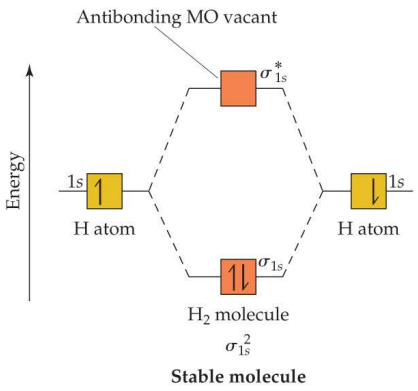
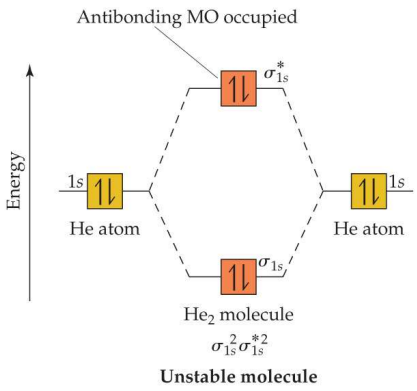
MO Theory

bond order = ½ (#bonding electrons – #antibonding electrons)





½(2 – 0) = 1 bond

½(2 – 2) = 0 bond

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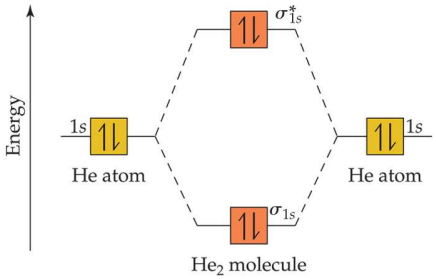
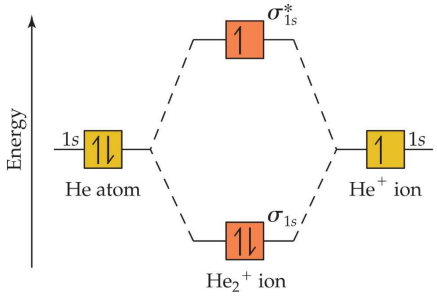
MO Theory

In the case of He_2, the bond order would be:

$$\frac{1}{2}(2 - 2) = 0$$

Therefore, He_2 does not exist.





$$\frac{1}{2}(2 - 1) = 1/2$$

He_2^+ forms

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Guiding Principles for the Formation of Molecular Orbitals

1) The number of MOs formed equals the number of AOs combined.
2) AOs combine with AOs of similar energy.
3) The effectiveness with which two AOs combine is proportional to their overlap.
4) Each MO can accommodate at most two electrons with opposite spin. (They follow the Pauli exclusion principle.)
5) When MOs of the same energy are populated, one electron enters each orbital (same spin) before pairing. (They follow Hund's rules.)

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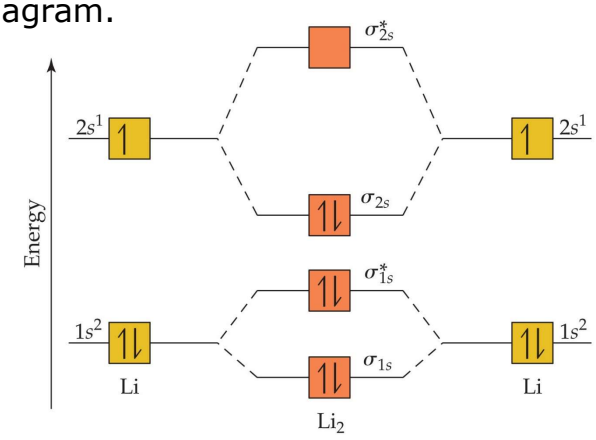
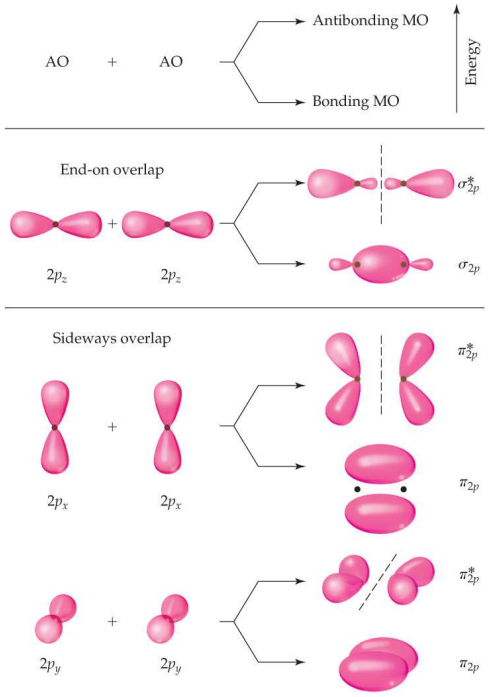
- Li_2 (g) occurs at high temperatures.
- Lewis structure: Li — Li.
- The MO diagram is on the right.
- Notice that core electrons don't play a major part in bonding, so we usually don't include them in the MO diagram.



50



MO Theory

For atoms with both *s* and *p* orbitals, there are two types of interactions:

- The *s* and the *p* orbitals that face each other overlap in σ fashion.
- The other two sets of *p* orbitals overlap in π fashion.

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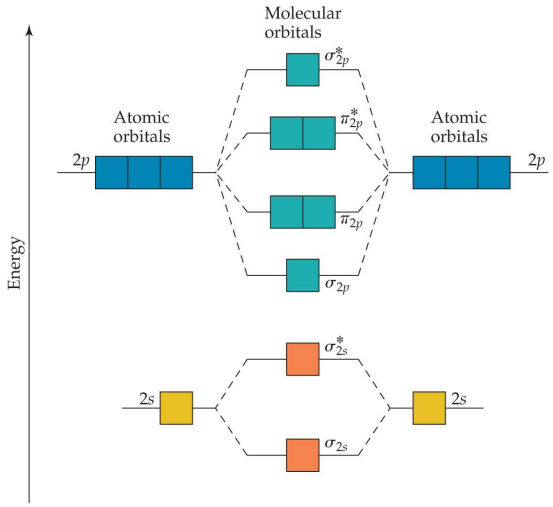
MO Diagram – Second Period

- The resulting MO diagram looks like this for O_2, N_2, F_2.
- There are both σ and π bonding molecular orbitals and σ* and π* antibonding molecular orbitals.



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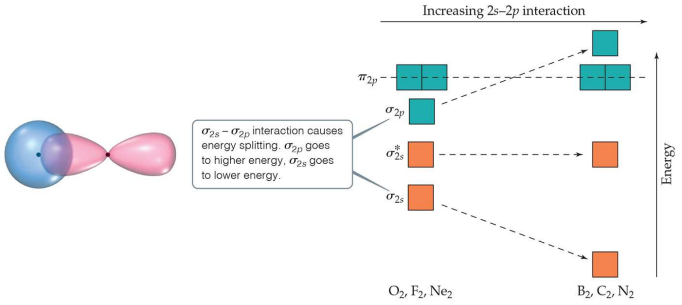
s and *p* Orbital Interactions



- Early *p*-block elements in the second period have a sizeable interaction (overlap) between *s* and *p* orbitals.
- This changes the order of the σ and π molecular orbitals in B_2, C_2, and N_2 compared to O_2, N_2, and Ne_2.
  - Energy of σ_{2p} is higher than π_{2p} for B_2, C_2, and N_2.
  - Energy of π_{2p} is higher than σ_{2p} for O_2, F_2, and Ne_2.

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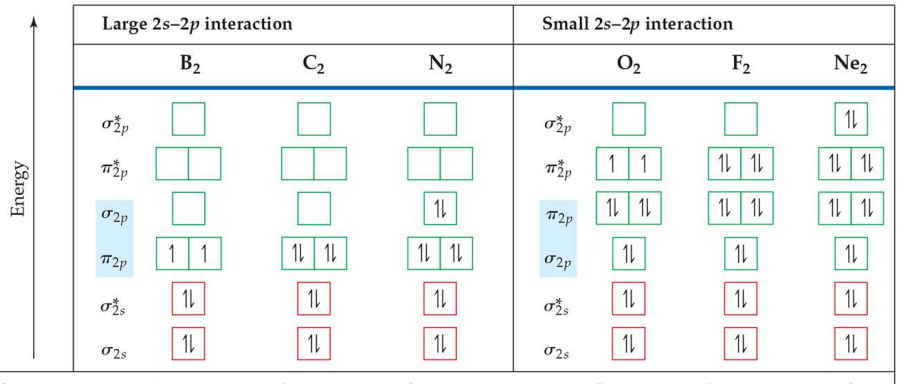
Second Period MO Diagrams



	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

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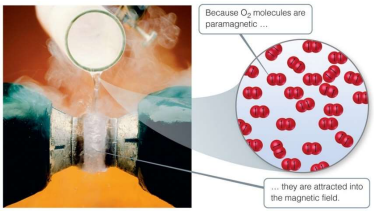
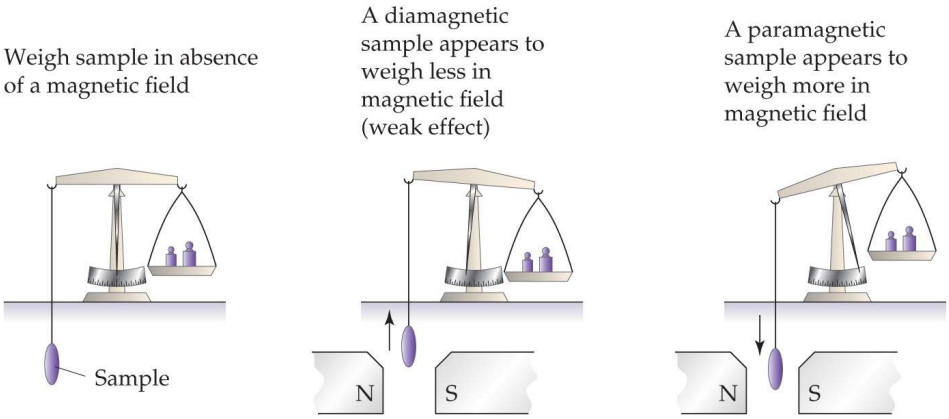
Paramagnetic – has unpaired electrons, attracted to magnetic field.

Diamagnetic – has **no** unpaired electrons, weakly repelled by magnetic field.





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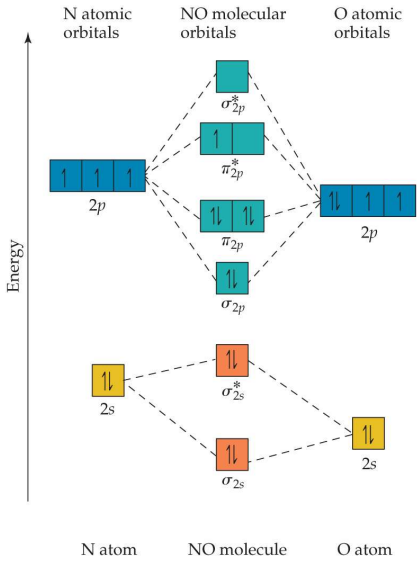
Heteronuclear Diatomic Molecules



Bond Order
1/2(8-3) = 2.5

- The atomic orbitals have different energy, so the interactions change slightly.
- The more electronegative atom has orbitals lower in energy, so the bonding orbitals will more resemble them in energy.

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