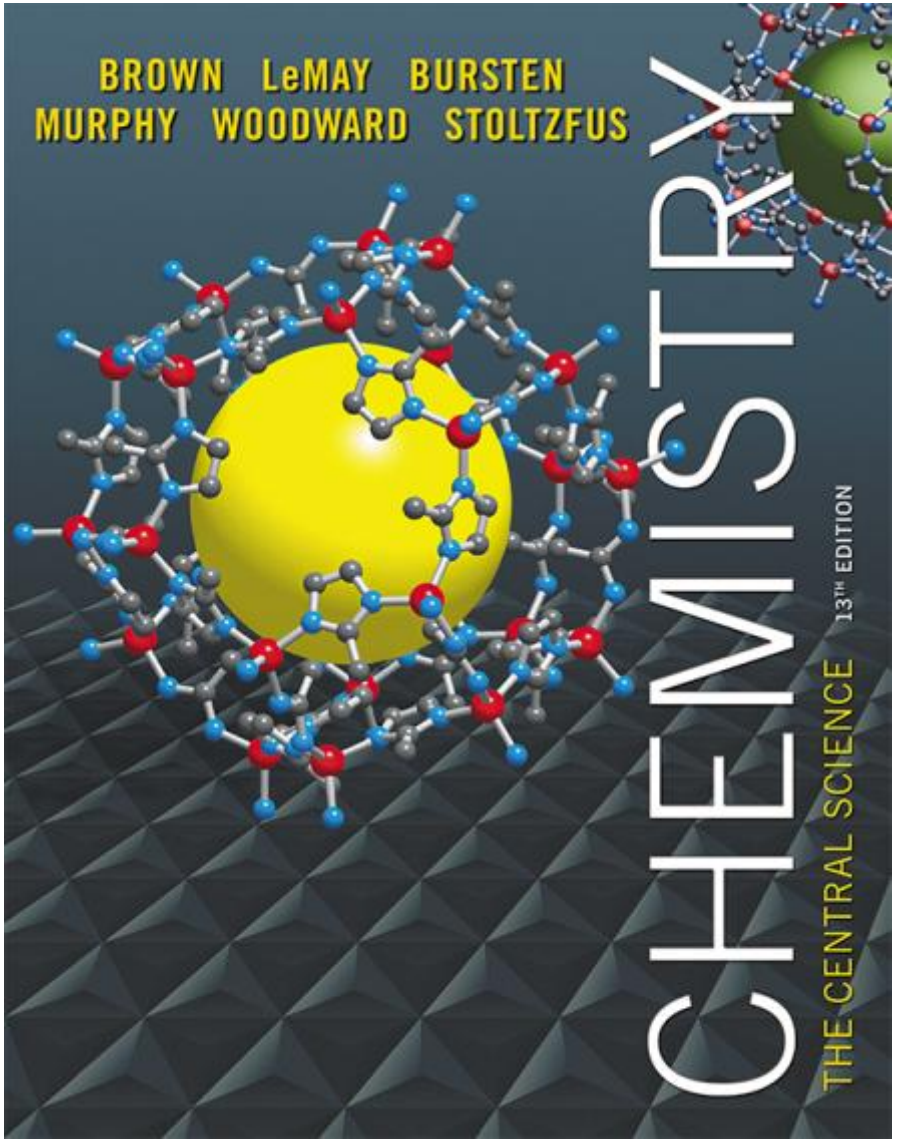


Lecture Presentation

Chapter 9

Molecular Geometry and Bonding Theories

Writing Lewis Structures (Covalent Molecules)

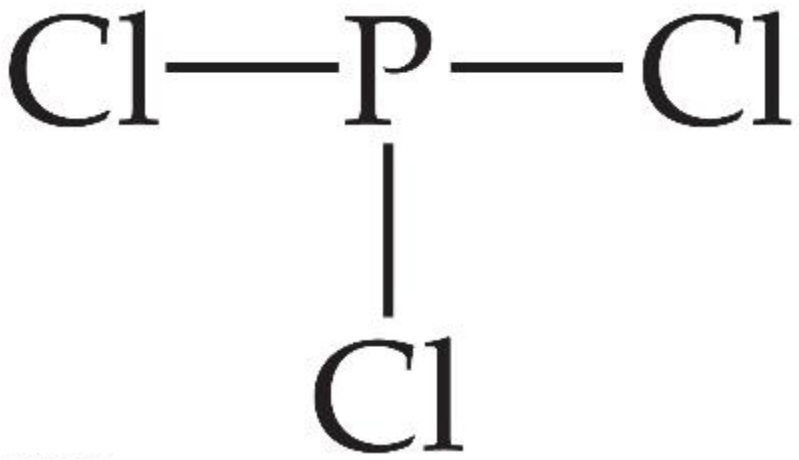
PCl_3

1. Sum the valence electrons from all atoms, taking into account overall charge.
   - If it is an anion, add one electron for each negative charge.
   - If it is a cation, subtract one electron for each positive charge.

Keep track of the electrons:

5 + 3(7) = 26

Writing Lewis Structures

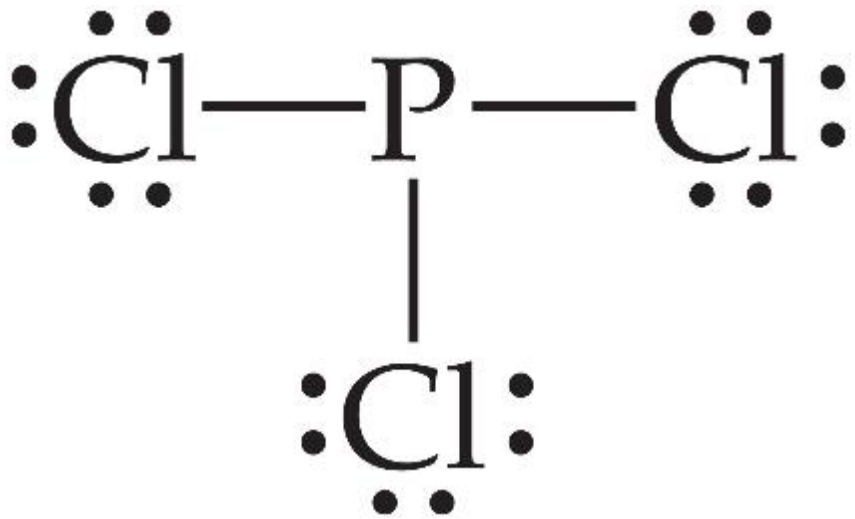


2. Write the symbols for the atoms, show which atoms are attached to which, and connect them with a single bond (a line representing two electrons).

Keep track of the electrons:

$26 - 6 = 20$

Writing Lewis Structures

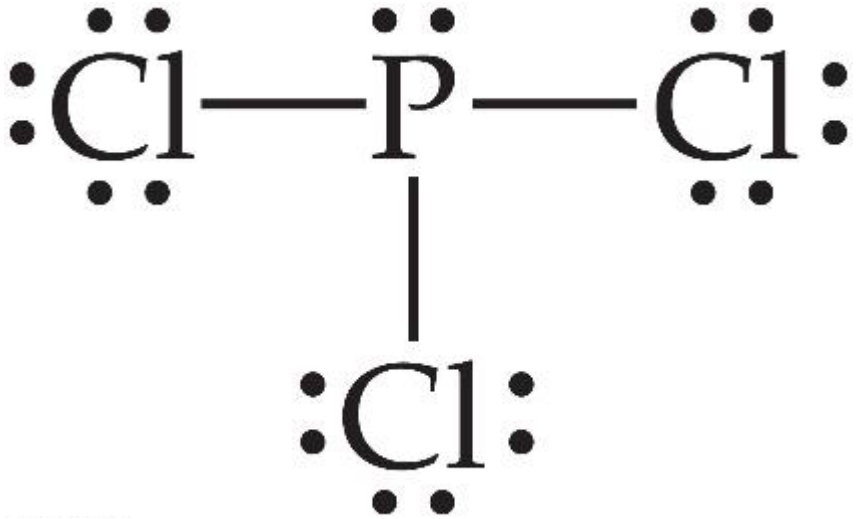


3. Complete the octets around all atoms bonded to the central atom.

Keep track of the electrons:

26 − 6 = 20; 20 − 18 = 2

Writing Lewis Structures



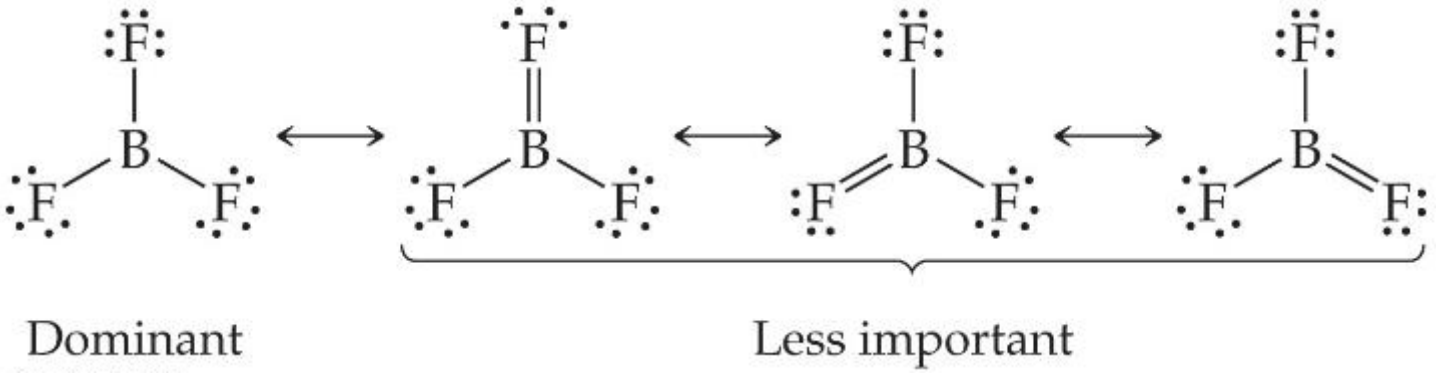
4. Place any leftover electrons on the central atom.

Keep track of the electrons:

26 − 6 = 20; 20 − 18 = 2; 2 − 2 = 0

Fewer Than Eight Electrons

- Elements in the second period *before* carbon can make stable compounds with fewer than eight electrons.
- Consider BF_3:
  - Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine.
  - This would not be an accurate picture of the distribution of electrons in BF_3.



Example

From the figure on the last slide

$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$

- In this example, one C—H bond and one Cl—Cl bond are broken; one C—Cl and one H—Cl bond are formed.

Answer

$$\Delta H = [D(\text{C—H}) + D(\text{Cl—Cl})] - [D(\text{C—Cl}) + D(\text{H—Cl})]$$

$$= [(413\ \text{kJ}) + (242\ \text{kJ})] - [(328\ \text{kJ}) + (431\ \text{kJ})]$$

$$= (655\ \text{kJ}) - (759\ \text{kJ})$$

$$= -104\ \text{kJ}$$

Bond Enthalpy and Bond Length

- We can also measure an average bond length for different bond types.
- As the number of bonds between two atoms increases, the bond length decreases.

Table 8.5 Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

22) Elements from opposite sides of the periodic table tend to form _____.
A) covalent compounds
B) ionic compounds
C) compounds that are gaseous at room temperature
D) homonuclear diatomic compounds
E) covalent compounds that are gaseous at room temperature

25) How many hydrogen atoms must bond to silicon to give it an octet of valence electrons?
A) 1
B) 2
C) 3
D) 4
E) 5

38) The ion NO^- has _____ valence electrons.
A) 15
B) 14
C) 16
D) 10
E) 12

40) The Lewis structure of AsH_3 shows _____ nonbonding electron pair(s) on As.

A) 0
B) 1
C) 2
D) 3
E) This cannot be determined from the data given.

51) How many equivalent resonance structures can be drawn for the molecule of SO_3 without having to violate the octet rule on the sulfur atom?

A) 5
B) 2
C) 1
D) 4
E) 3

52) How many different types of resonance structures can be drawn for the ion SO_3^{2-} where all atoms satisfy the octet rule?

A) 1
B) 2
C) 3
D) 4
E) 5

55) Using the table of average bond energies below, the △H for the reaction is _____ kJ.

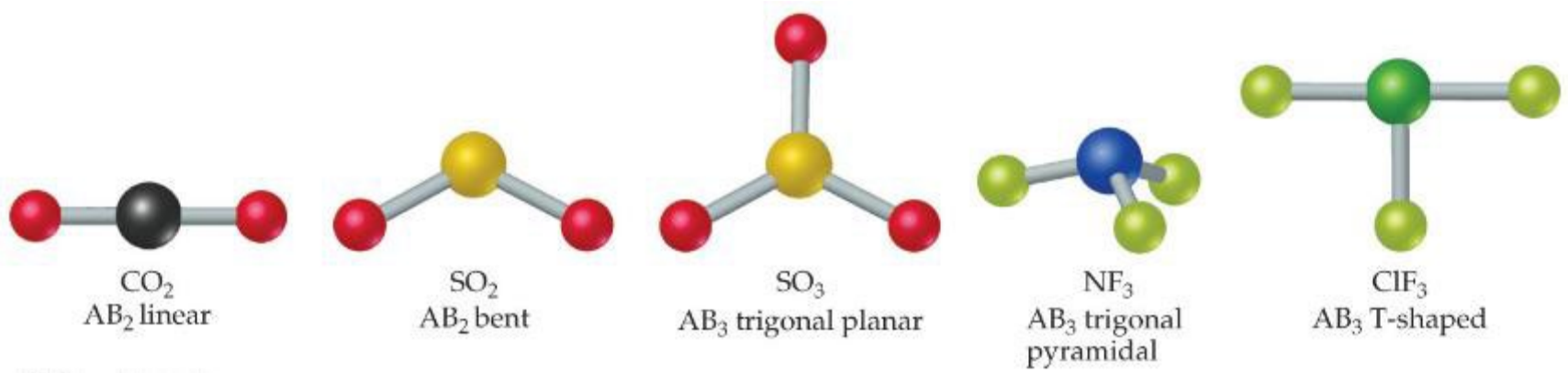
$$C{\equiv}O\ (g) + 2H_2\ (g) \rightarrow H_3C{-}O{-}H\ (g)$$

Bond:	C–O	C=O	C≡O	C–H	H–H	O–H
D (kJ/mol):	358	799	1072	413	436	463

A) +276
B) -276
C) +735
D) -735
E) -116

Molecular Shapes

- Lewis Structures show bonding and lone pairs, but do *not* denote shape.
- However, we *use* Lewis Structures to help us determine shapes.
- Here we see some common shapes for molecules with two or three atoms connected to a central atom.



Molecular Geometries and Bonding Theories

Tetracyanodibenzotetrathiafulvalene Diimides: Design, Synthesis, and Property Study

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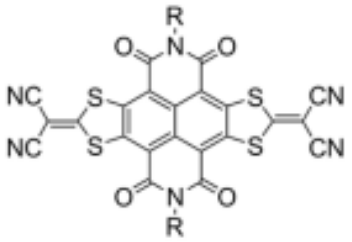
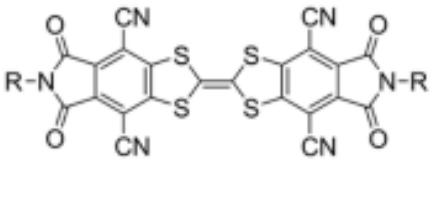
[§]Laboratory of Advanced Materials, Fudan University, Shanghai 200433, China

Supporting Information



VS

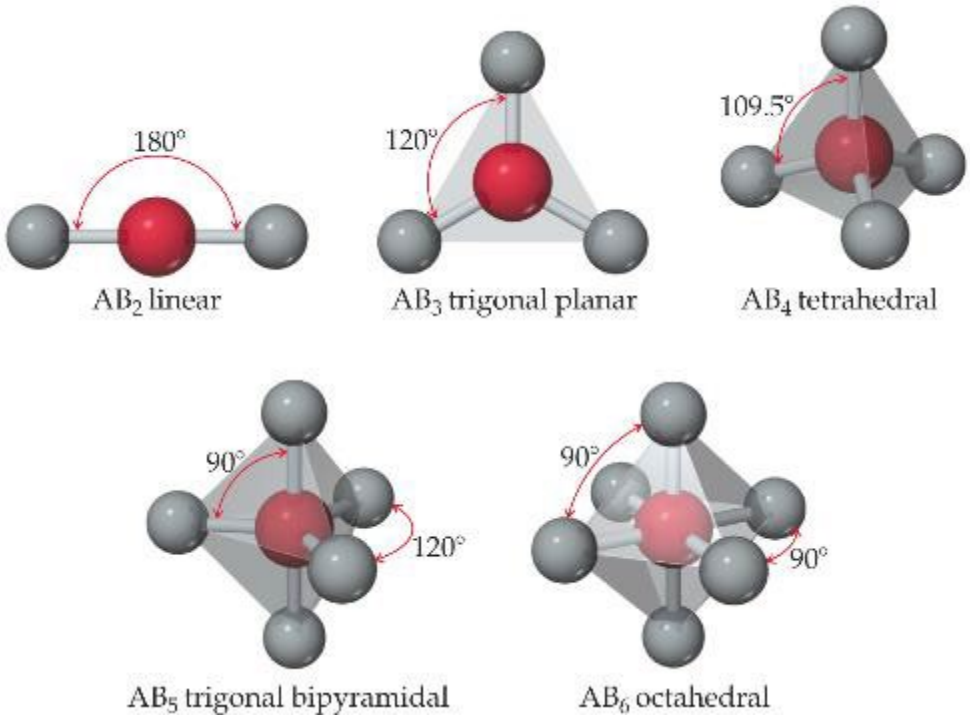


ABSTRACT: Tetracyanodibenzotetrathiafulvalene diimide (TCDBTTF-DI), an isomer of core-expanded naphthalene diimides bearing two 2-(1,3-dithiol-2-ylidene)malononitrile moieties (NDI-DTYM2), has been designed and synthesized to explore the effect of its isomeric structure on the optical and electrochemical properties of the materials. UV−vis spectra show that TCDBTTF-DI exhibits variation in its absorption peaks while maintaining a similar optical band gap to NDI-DTYM2. Electrochemical studies indicate that TCDBTTF-DI can not only accept but also lose electrons, in contrast to the solely electron-accepting behavior of NDI-DTYM2.

r
es
and Bonding
Theories

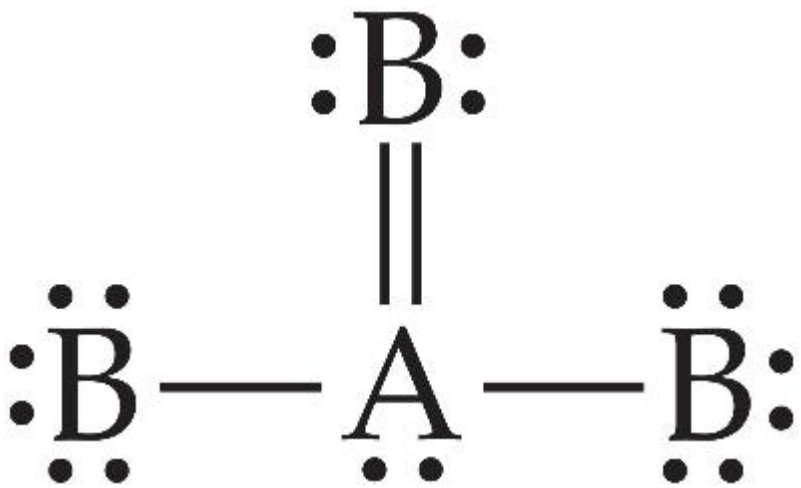
What Determines the Shape of a Molecule?

- Simply put, 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.
- This is the Valence-Shell Electron-Pair Repulsion (VSEPR) model.



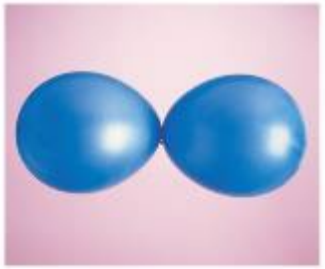
Molecular Geometries and Bonding Theories

Electron Domains



- We can refer to the directions to which electrons point as **electron domains**. This is true whether there is one or more electron pairs pointing in that direction.
- The central atom in this molecule, A, has four electron domains.

Valence-Shell Electron-Pair Repulsion (VSEPR) Model



Two balloons
linear orientation

Three balloons
trigonal-planar orientation

Four balloons
tetrahedral orientation

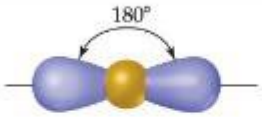
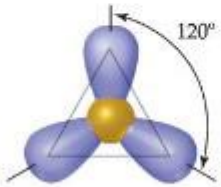
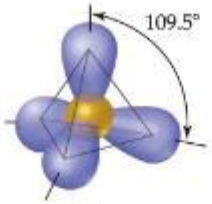
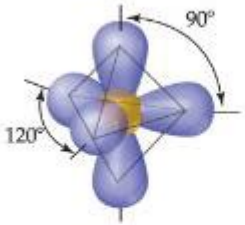
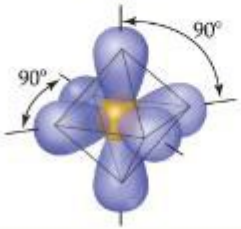
"The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them."

(The balloon analogy in the figure to the left demonstrates the maximum distances, which minimize repulsions.)

Molecular Geometries and Bonding Theories

Electron-Domain Geometries

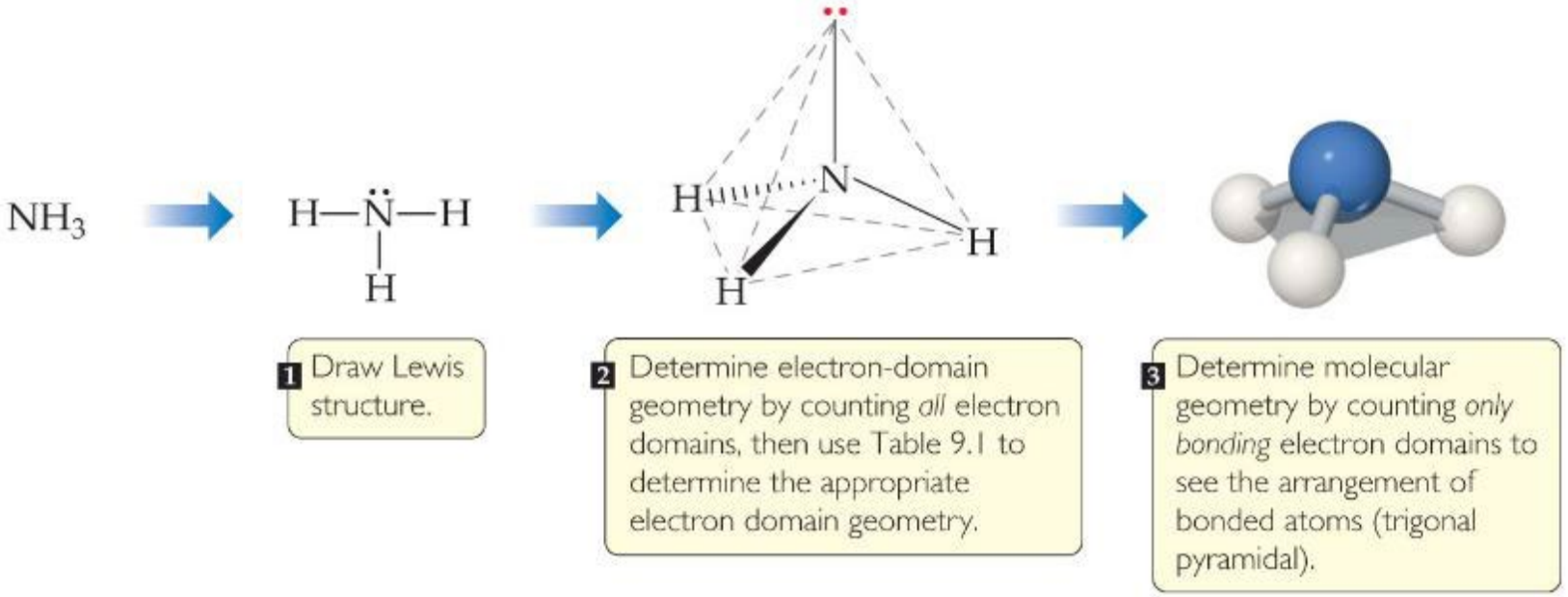
Table 9.1 Electron-Domain Geometries as a Function of Number of Electron Domains

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 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.

Molecular Geometries and Bonding Theories

Molecular Geometries



- Once you have determined the electron-domain geometry, use the arrangement of the bonded atoms to determine the **molecular geometry**.
- Tables 9.2 and 9.3 show the potential molecular geometries. We will look at each electron domain to see what molecular geometries are possible.

Molecular Geometries and Bonding Theories

Linear Electron Domain

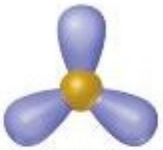
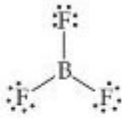
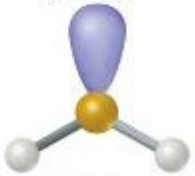
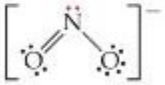
Table 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

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

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

Trigonal Planar Electron Domain

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

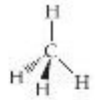
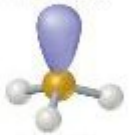
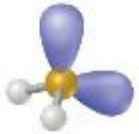
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

- There are two molecular geometries:
  - trigonal planar, if all electron domains are bonding, and
  - bent, if one of the domains is a nonbonding pair.

Molecular Geometries and Bonding Theories

Tetrahedral Electron Domain

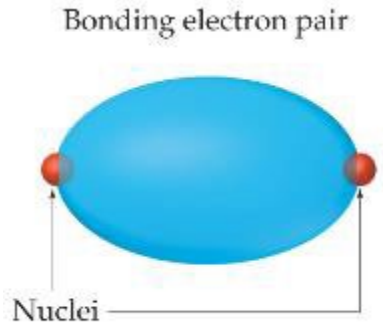
Table 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

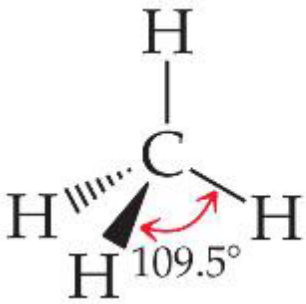
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

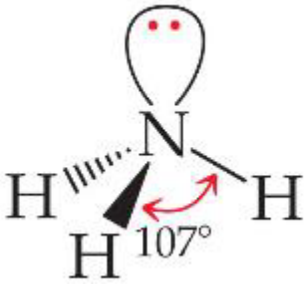
- There are three molecular geometries:
  - tetrahedral, if all are bonding pairs,
  - trigonal pyramidal, if one is a nonbonding pair, and
  - bent, if there are two nonbonding pairs.

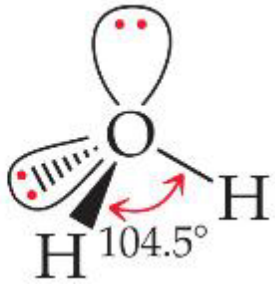
Nonbonding Pairs and Bond Angle

- Nonbonding pairs are physically larger than bonding pairs.
- Therefore, their repulsions are greater; this tends to compress bond angles.



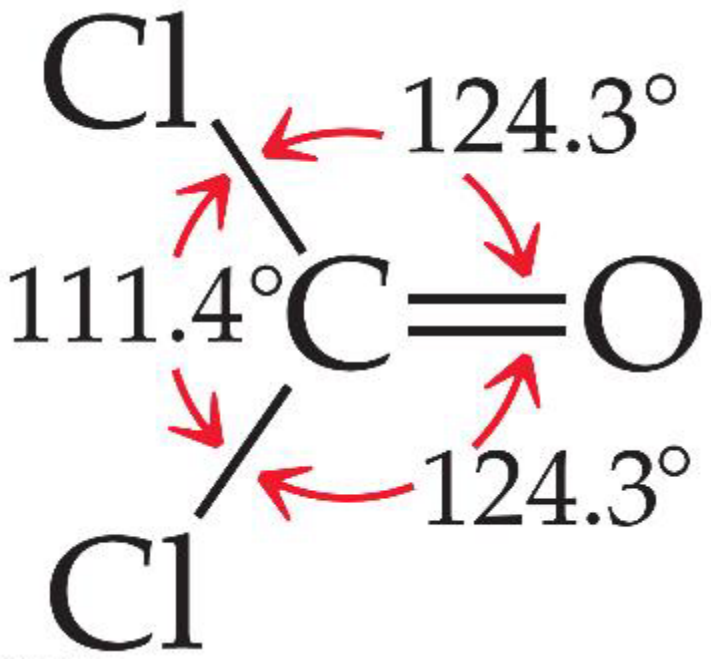






Molecular Geometries and Bonding Theories

Multiple Bonds and Bond Angles

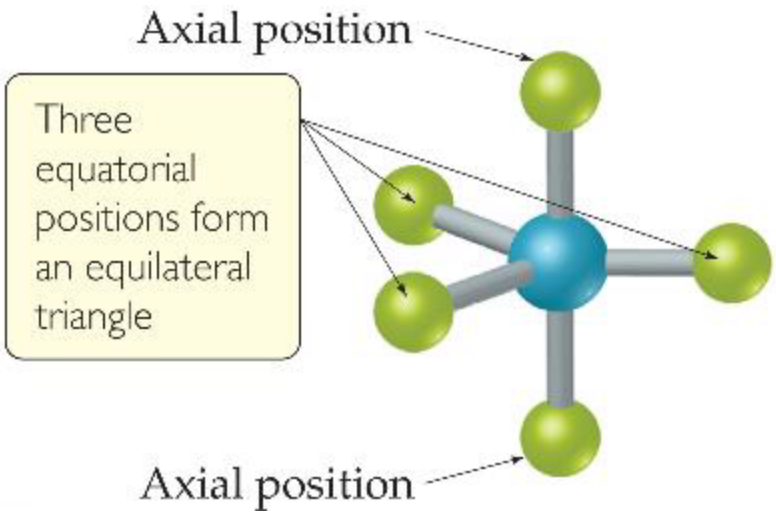


- Double and triple bonds have larger electron domains than single bonds.
- They exert a greater repulsive force than single bonds, making their bond angles greater.

Expanding beyond the Octet Rule

- Remember that some elements can break the octet rule and make *more* than four bonds (or have more than four electron domains).
- The result is two more possible electron domains: five = trigonal bipyramidal; six = octahedral (as was seen in the slide on electron-domain geometries).

Trigonal Bipyramidal Electron Domain

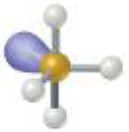
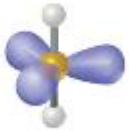


- There are two distinct positions in this geometry:
  - Axial
  - Equatorial
- Lone pairs occupy equatorial positions.

Trigonal Bipyramidal Electron Domain

- 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

Molecular Geometries and Bonding Theories

Octahedral Electron Domain

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

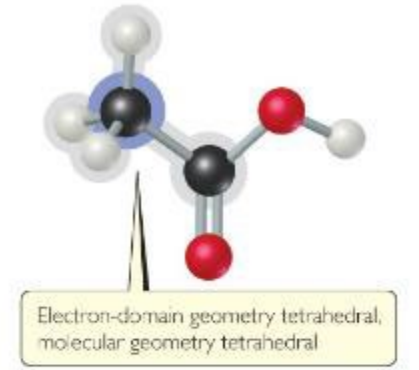
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

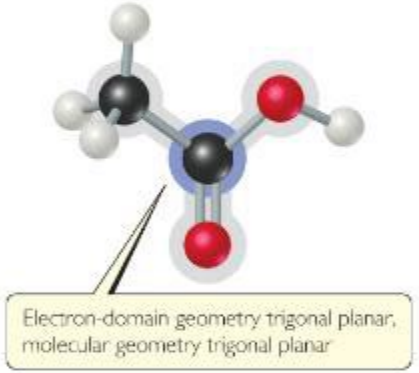
- All positions are equivalent in the octahedral domain.
- There are three molecular geometries:
  - Octahedral
  - Square pyramidal
  - Square planar

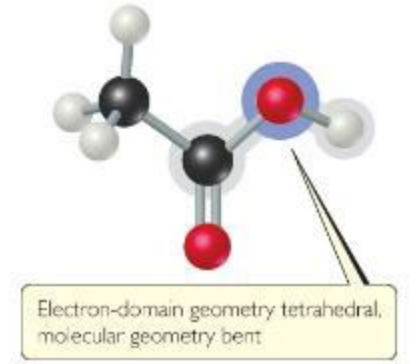
Molecular Geometries and Bonding Theories

Shapes of Larger Molecules

For larger molecules, look at the geometry about each atom rather than the molecule as a whole.







Polarity of Molecules

Ask yourself:

COVALENT or IONIC? If COVALENT:

Are the BONDS polar?

a. NO: The molecule is NONPOLAR!

b. YES: Continue—Do the AVERAGE position of δ+ and δ– coincide?

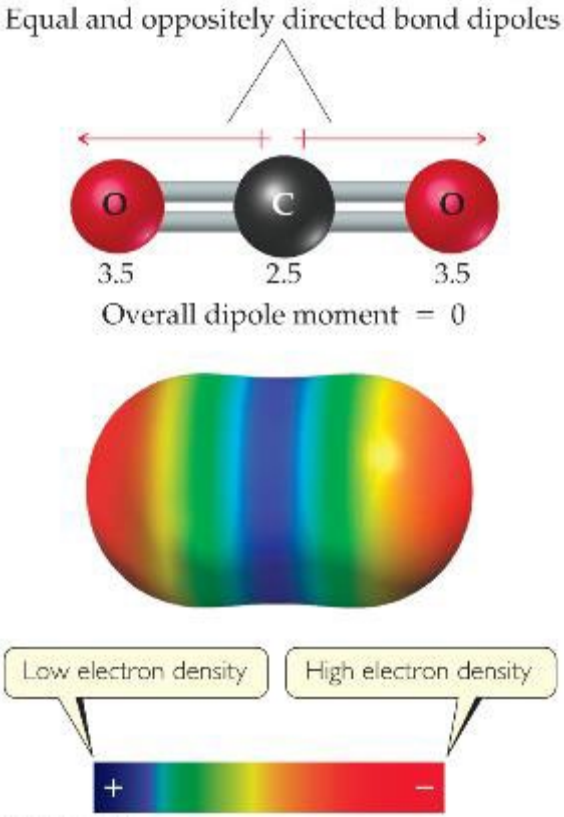
1) YES: The molecule is NONPOLAR.

2) NO: The molecule is POLAR.

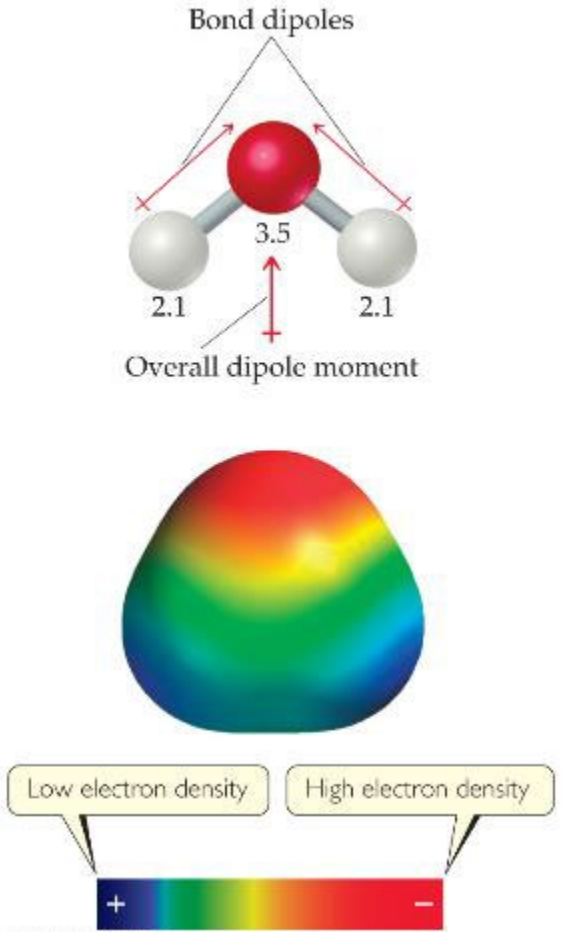
NOTE: Different atoms attached to the central atom have different polarity of bonds.

Comparison of the Polarity of Two Molecules

A NONPOLAR molecule

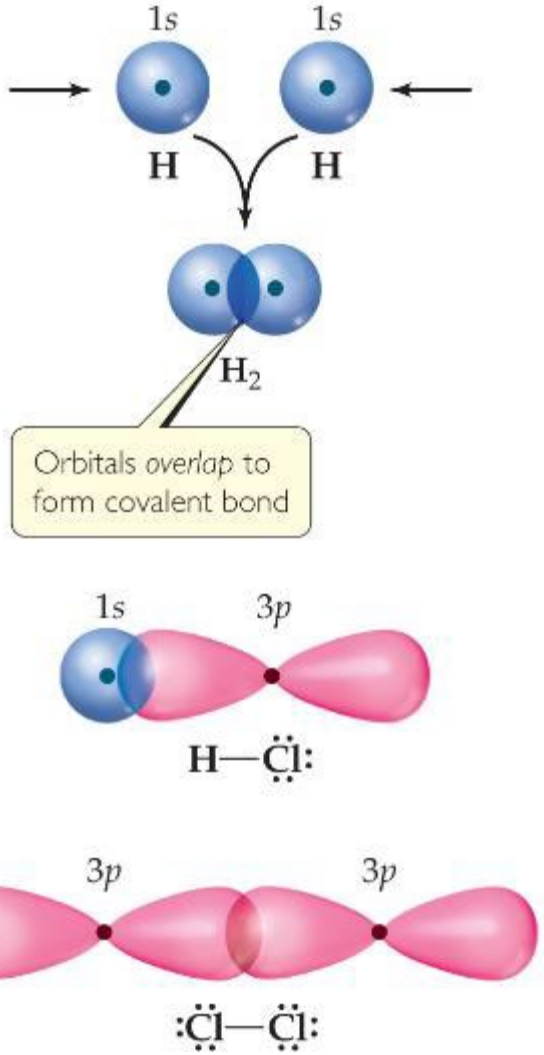


A POLAR molecule



Molecular Geometries and Bonding Theories

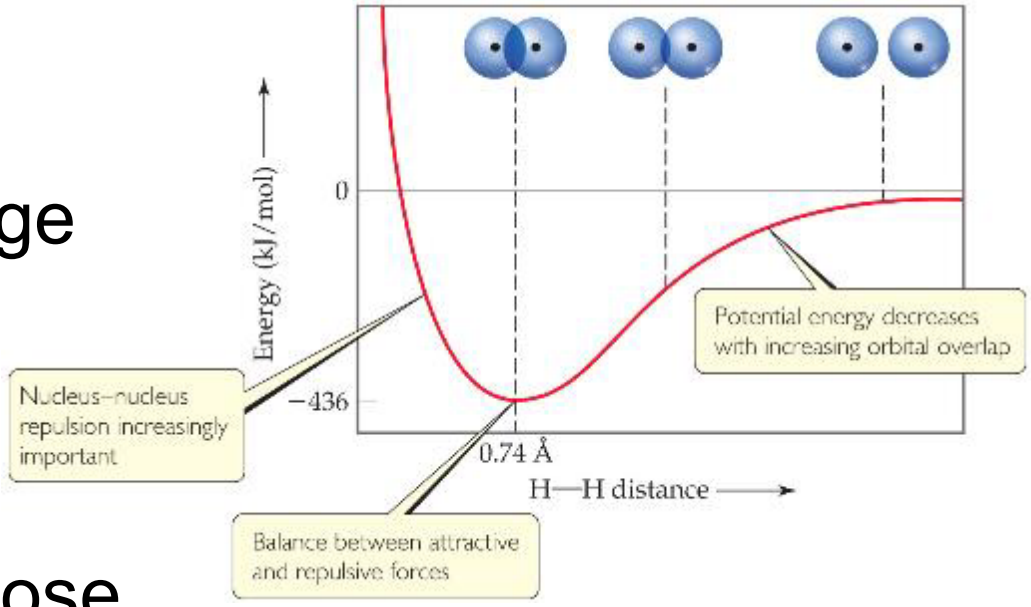
Valence-Bond Theory



- In Valence-Bond Theory, electrons of two atoms begin to occupy the same space.
- This is called “overlap” of orbitals.
- The sharing of space between two electrons of opposite spin results in a covalent bond.

Overlap and Bonding

- Increased overlap brings the electrons and nuclei closer 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.



VSEPR and Hybrid Orbitals

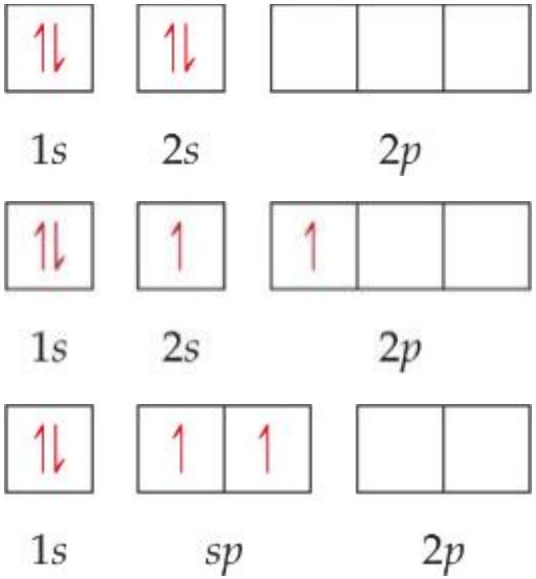
- VSEPR predicts shapes of molecules very well.
- How does that fit with orbitals?
- Let's use H_2O as an example:
- If we draw the best Lewis structure to assign VSEPR, it becomes bent.
- If we look at oxygen, its electron configuration is $1s^2 2s^2 2p^4$. If it shares two electrons to fill its valence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

Hybrid Orbitals

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

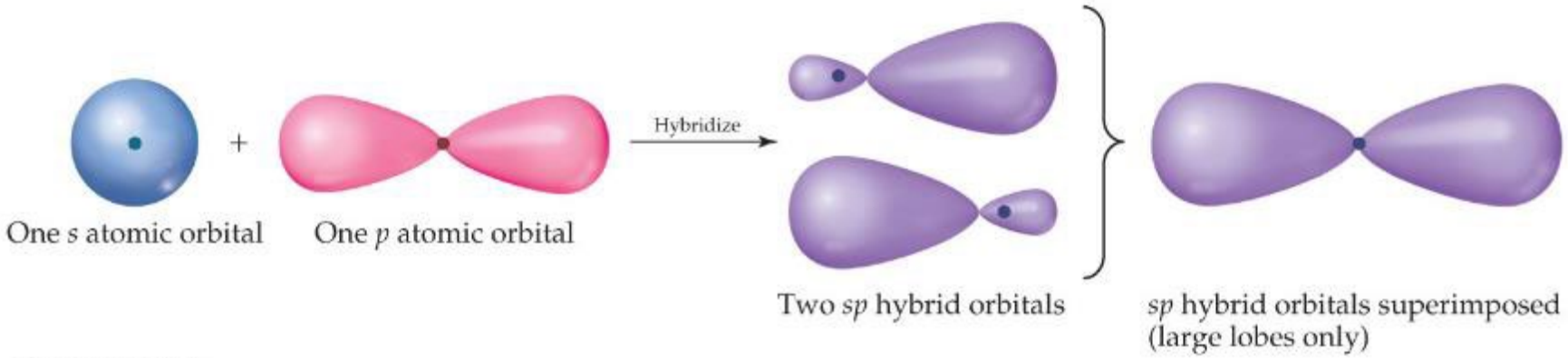
Be—*sp* hybridization

- When we look at the orbital diagram for beryllium (Be), we see that there are only paired electrons in full sub-levels.
- Be makes electron deficient compounds with two bonds for Be. Why? *sp* hybridization (mixing of one *s* orbital and one *p* orbital)



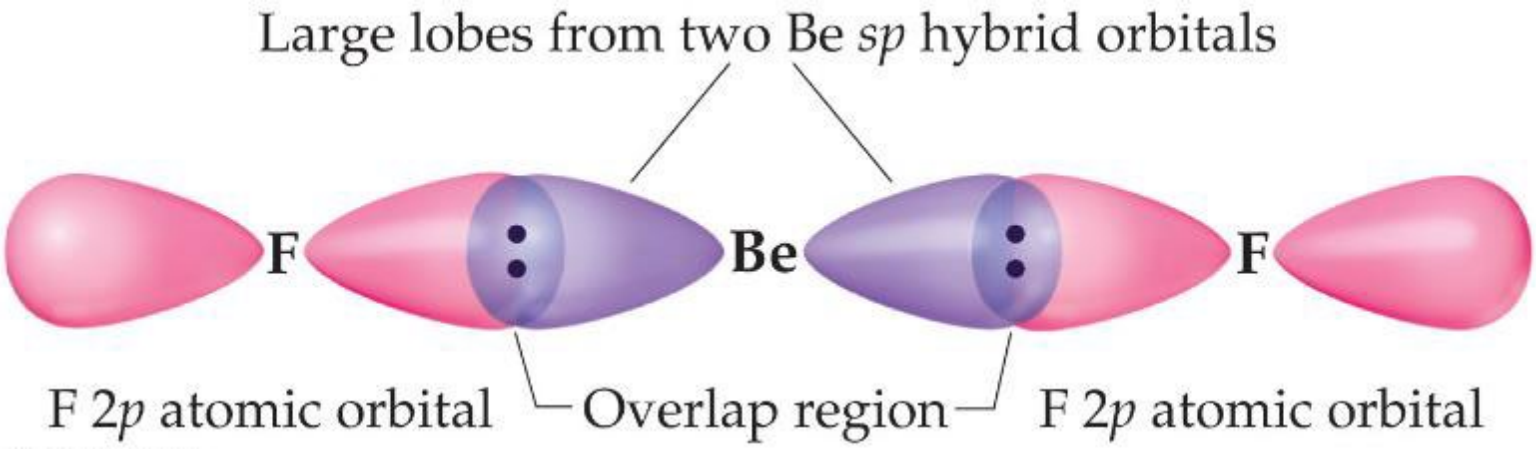
sp Orbitals

- 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.



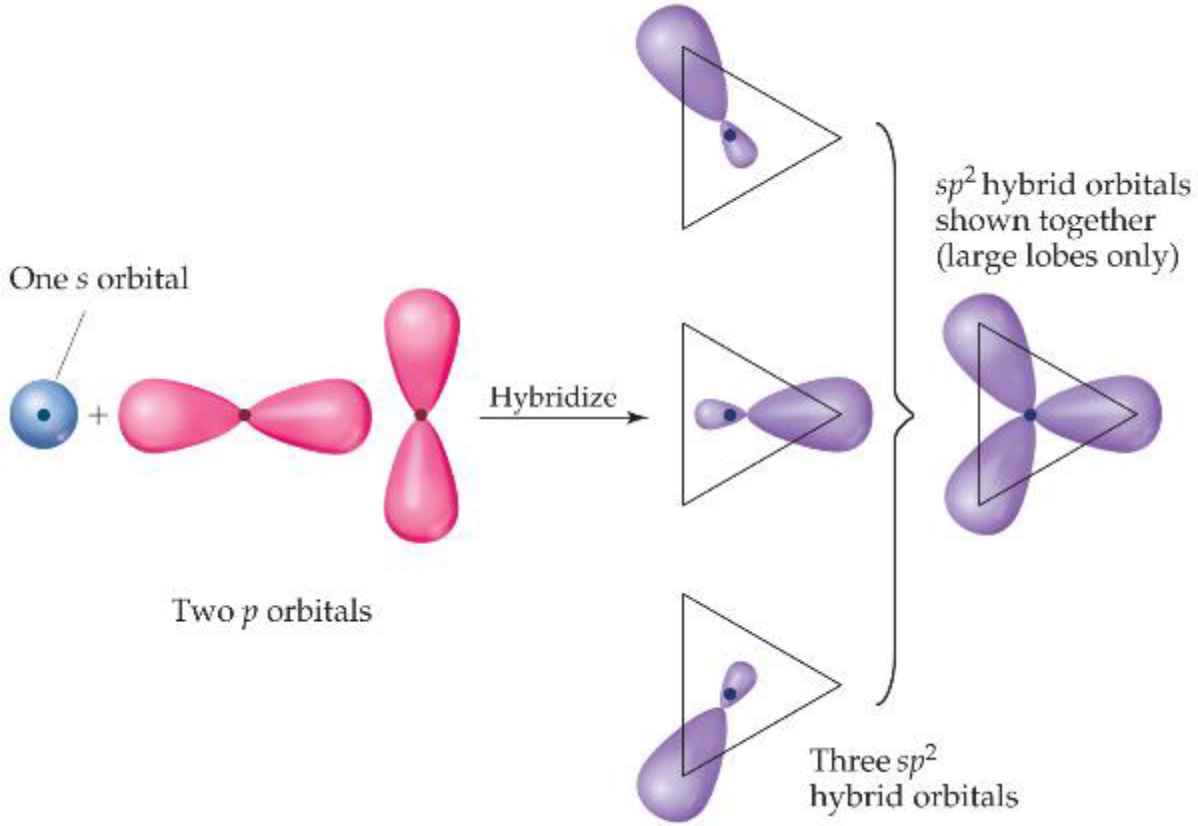
Position of *sp* Orbitals

- These two degenerate orbitals would align themselves 180° from each other.
- This is consistent with the observed geometry of Be compounds (like BeF_2) and VSEPR: linear.



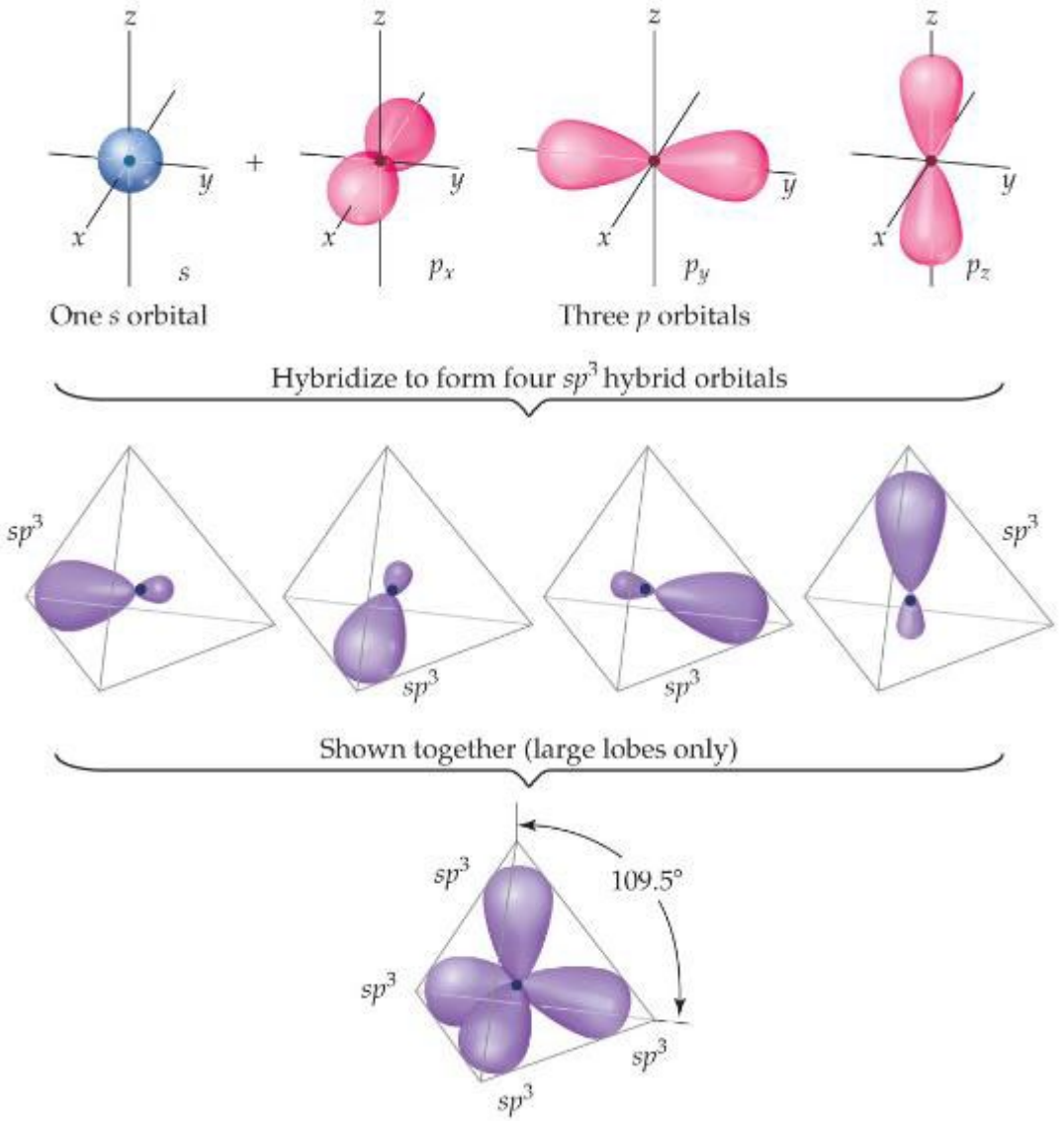
Boron—Three Electron Domains Gives sp^2 Hybridization

Using a similar model for boron leads to three degenerate sp^2 orbitals.



Carbon: sp^3 Hybridization

With carbon, we get four degenerate sp^3 orbitals.



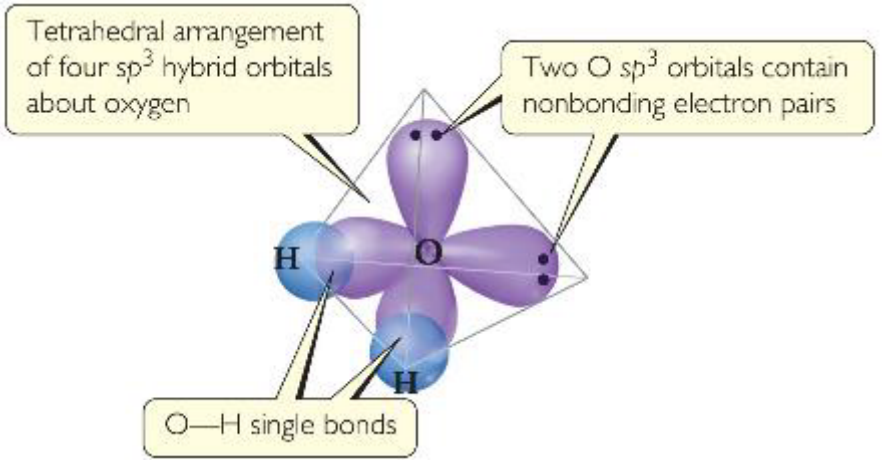
Molecular Geometries and Bonding Theories

Hypervalent Molecules

- The elements which have *more* than an octet
- Valence-Bond model would use *d* orbitals to make more than four bonds.
- This view works for period 3 and below.
- Theoretical studies suggest that the energy needed would be too great for this.
- A more detailed bonding view is needed than we will use in this course.

What Happens with Water?

- We started this discussion with H_2O and the angle question: Why is it 104.5° instead of 90° ?
- Oxygen has two bonds and two lone pairs—four electron domains.
- The result is sp^3 hybridization!

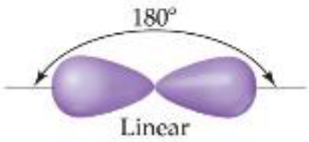
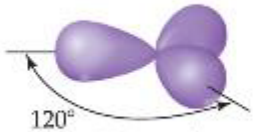
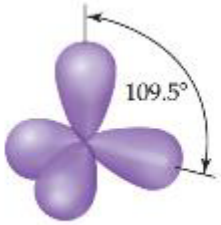


Molecular Geometries and Bonding Theories

Hybrid Orbital Summary

1) Draw the Lewis structure.
2) Use VSEPR to determine the electron-domain geometry.
3) Specify the hybrid orbitals needed to accommodate these electron pairs.

Table 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets

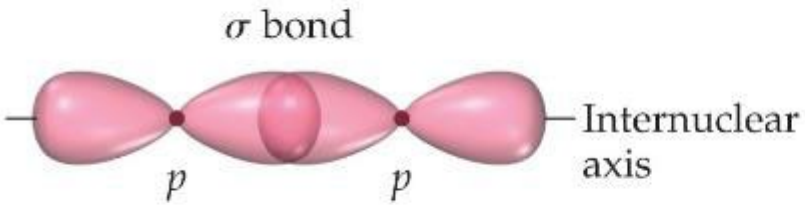
Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

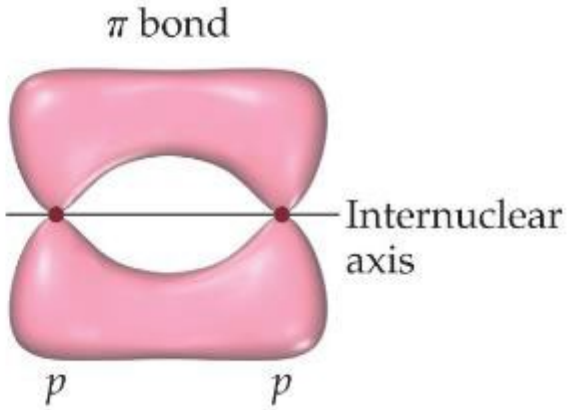
Molecular Geometries and Bonding Theories

Types of Bonds

- How does a double or triple bond form?
- It *can't*, if we only use hybridized orbitals.
- *However*, if we use the orbitals which are *not* hybridized, we can have a "side-ways" overlap.
- Two types of bonds:
- Sigma (σ) bond
- Pi (π) bond

Sigma (σ) and Pi (π) Bonds

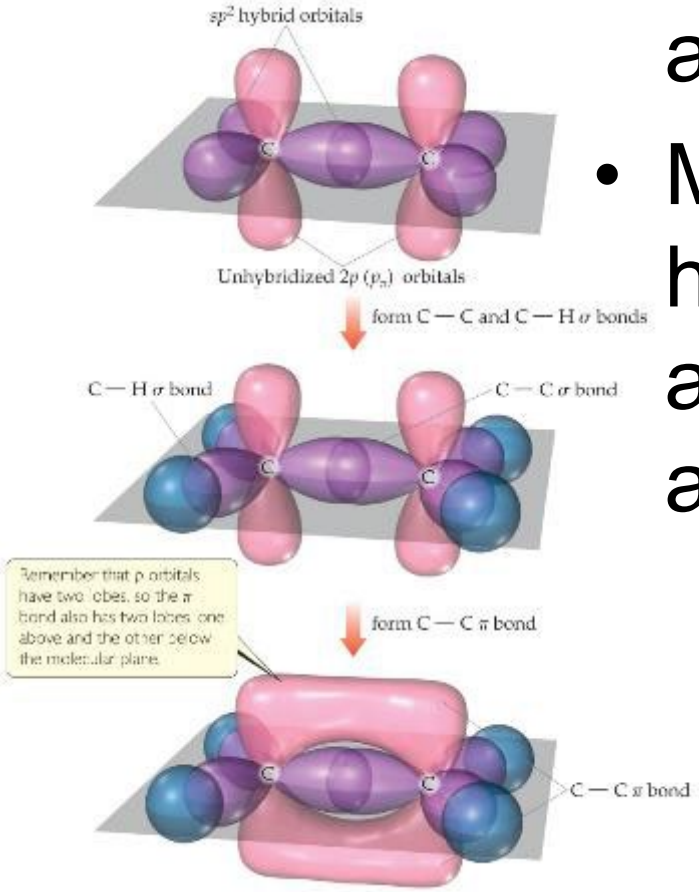


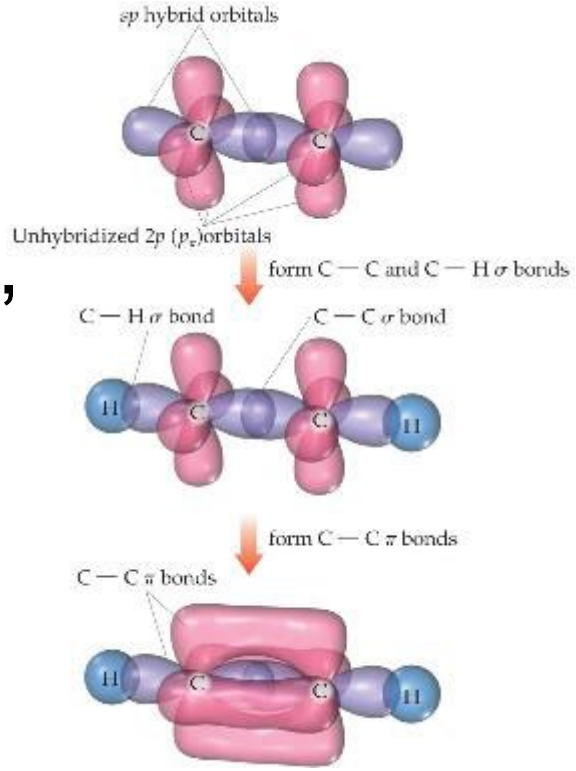


- Sigma bonds are characterized by
  - head-to-head overlap.
  - cylindrical symmetry of electron density about the internuclear axis.
- Pi bonds are characterized by
  - side-to-side overlap.
  - electron density above and below the internuclear axis.

Bonding in Molecules

- Single bonds are always σ-bonds.
- Multiple bonds have one σ-bond, all other bonds are π-bonds.





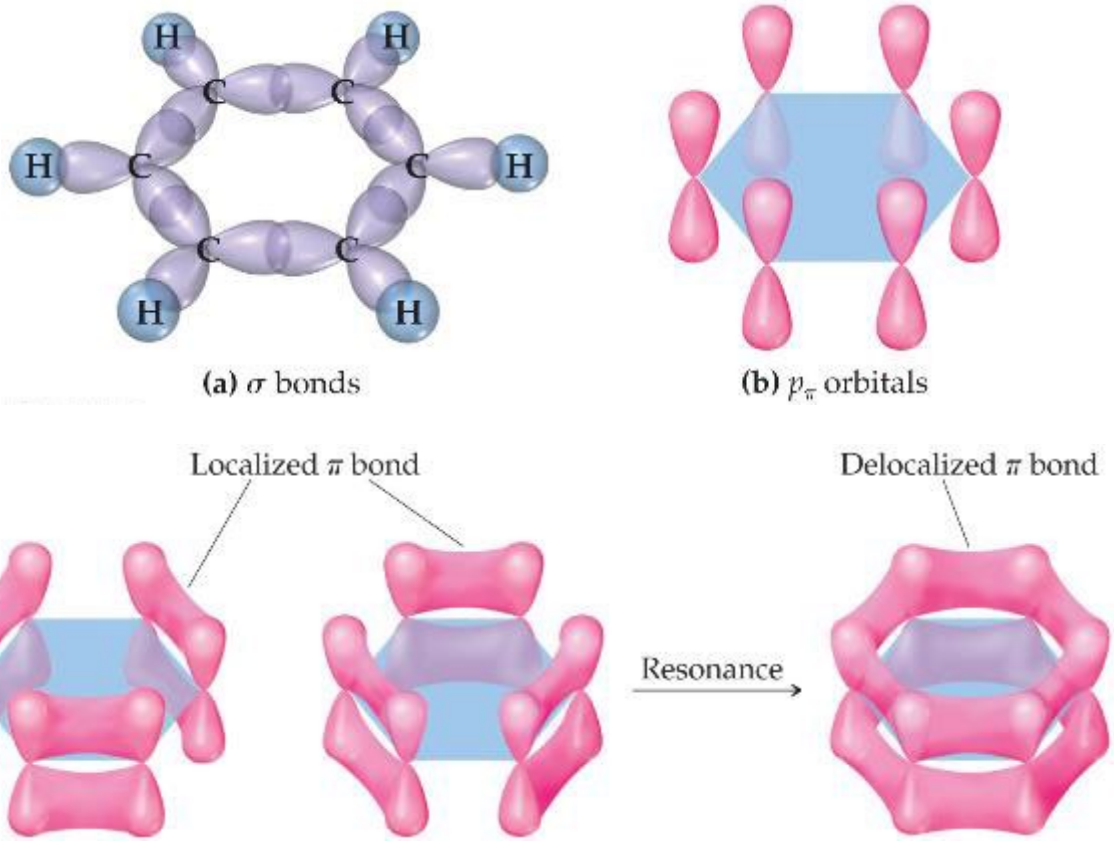
Molecular Geometries and Bonding Theories

Localized or Delocalized Electrons

- Bonding electrons (σ or π) that are specifically shared between two atoms are called **localized** electrons.
- In many molecules, we can't describe all electrons that way (resonance); the other electrons (shared by multiple atoms) are called **delocalized** electrons.

Benzene

The organic molecule benzene (C_6H_6) has six σ-bonds and a *p* orbital on each C atom, which form delocalized bonds using one electron from each *p* orbital.



Molecular Geometries and Bonding Theories

Molecular Orbital (MO) Theory

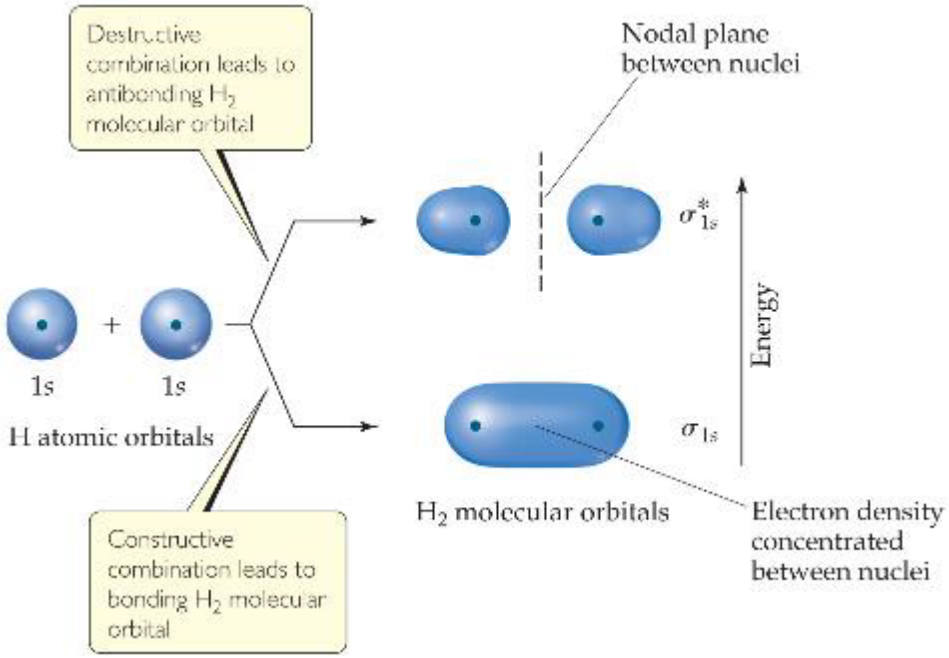
- Wave properties are used to describe the energy of the electrons in a molecule.
- **Molecular orbitals** have many characteristics like atomic orbitals:
  - maximum of two electrons per orbital
  - Electrons in the same orbital have opposite spin.
  - Definite energy of orbital
  - Can visualize electron density by a contour diagram

More on MO Theory

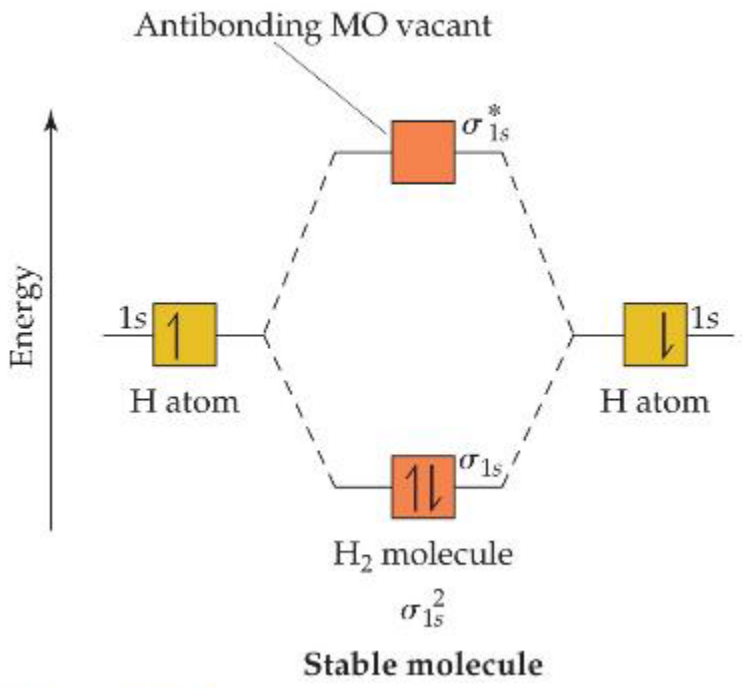
- They differ from atomic orbitals because they represent the entire molecule, not a single atom.
- Whenever two atomic orbitals overlap, two molecular orbitals are formed: one bonding, one antibonding.
- **Bonding orbitals** are constructive combinations of atomic orbitals.
- **Antibonding orbitals** are destructive combinations of atomic orbitals. They have a new feature unseen before: A **nodal plane** occurs where electron density equals zero.

Molecular Orbital (MO) Theory

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.



MO Diagram

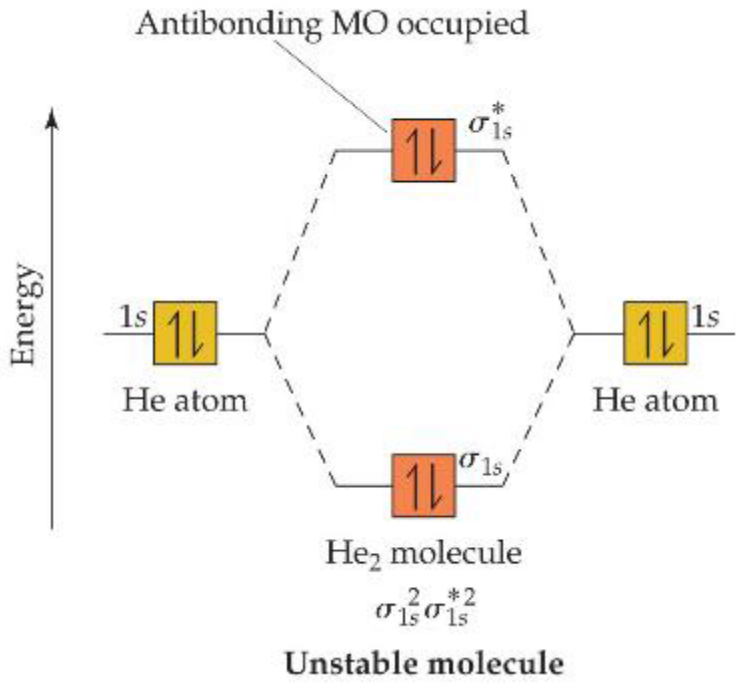


- An **energy-level diagram**, or **MO diagram** shows how orbitals from atoms combine to give the molecule.
- In H_2 the two electrons go into the bonding molecular orbital (lower in energy).
- **Bond order** = ½(# of bonding electrons – # of antibonding electrons) = ½(2 – 0) = 1 bond

Molecular Geometries and Bonding Theories

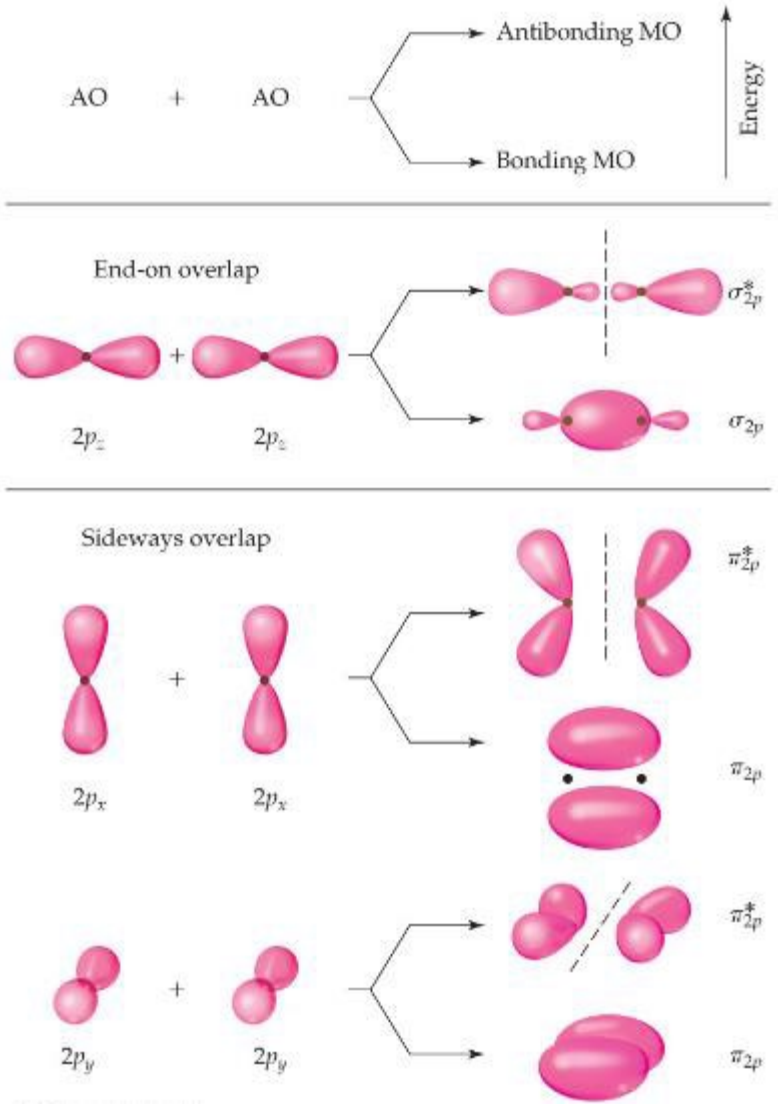
Can He_2 Form? Use MO Diagram and Bond Order to Decide!

- Bond Order = ½(2 – 2) = 0 bonds
- Therefore, He_2 does *not* exist.



Molecular Geometries and Bonding Theories

s and *p* Orbitals Can Interact

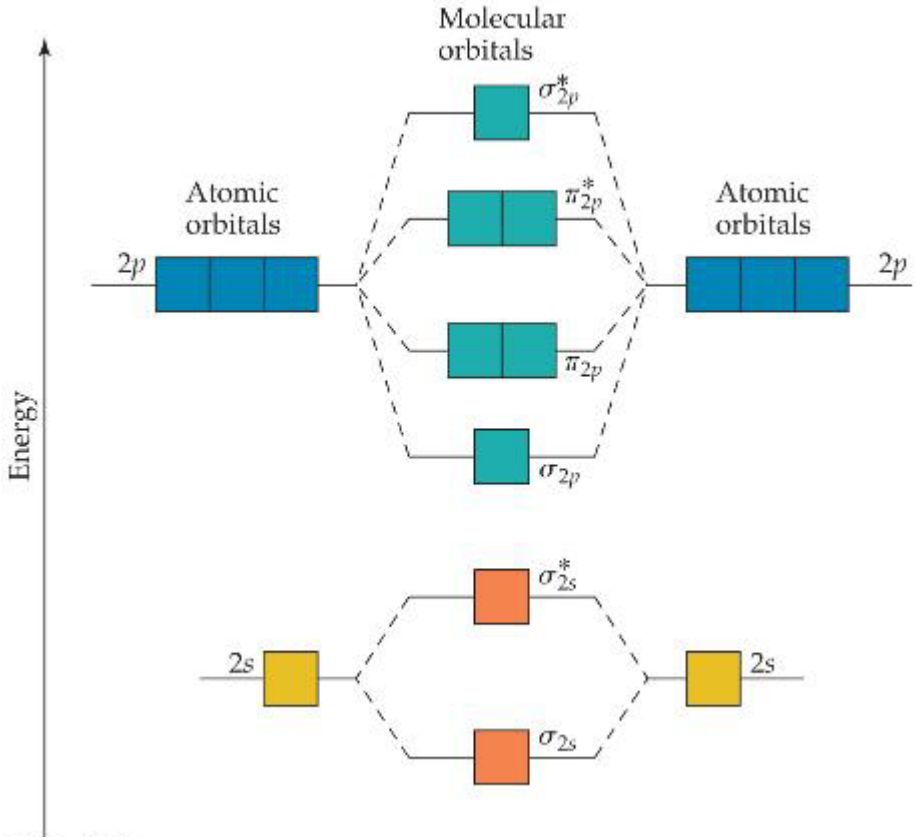


- For atoms with both *s* and *p* orbitals, there are two types of interactions:
- The *s* and the *p* orbitals that face each other overlap in σ fashion.
- The other two sets of *p* orbitals overlap in π fashion.
- These are, again, direct and "side-ways" overlap of orbitals.

Molecular Geometries and Bonding Theories

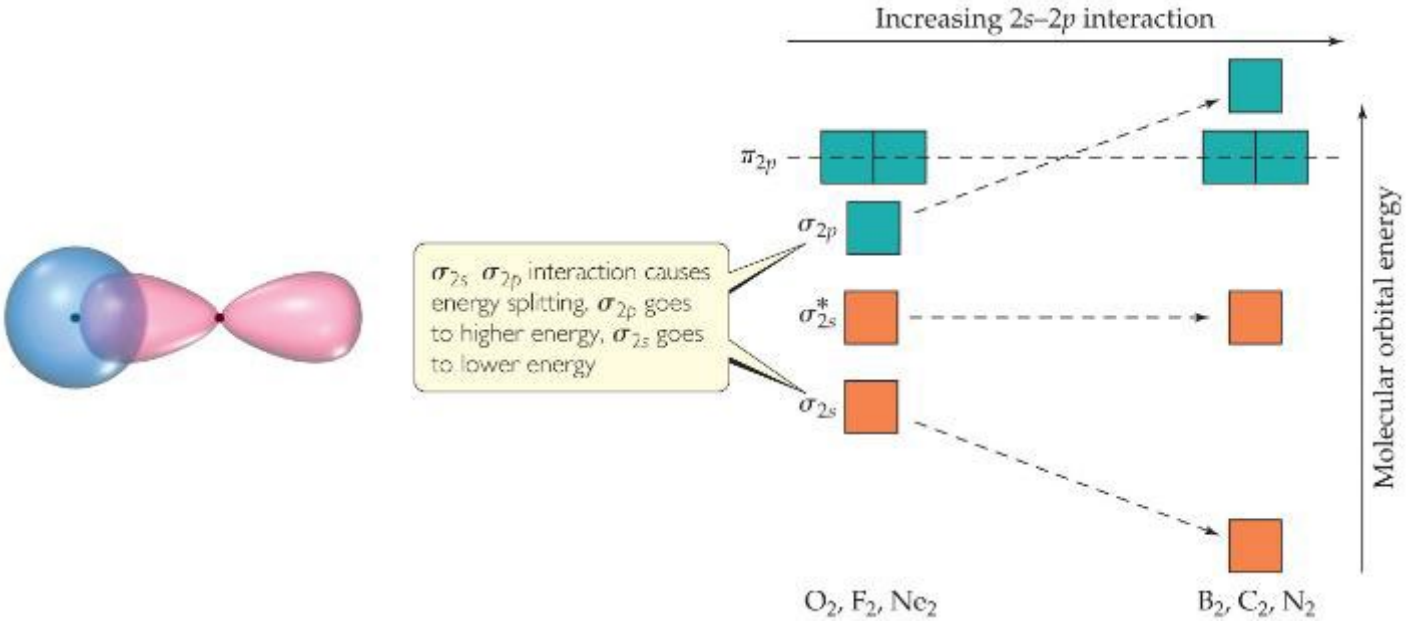
MO Theory

- The resulting MO diagram:
  - There are σ and σ^* orbitals from *s* and *p* atomic orbitals.
  - There are π and π^* orbitals from *p* atomic orbitals.
  - Since direct overlap is stronger, the effect of raising and lowering energy is greater for σ and σ^*.



Molecular Geometries and Bonding Theories

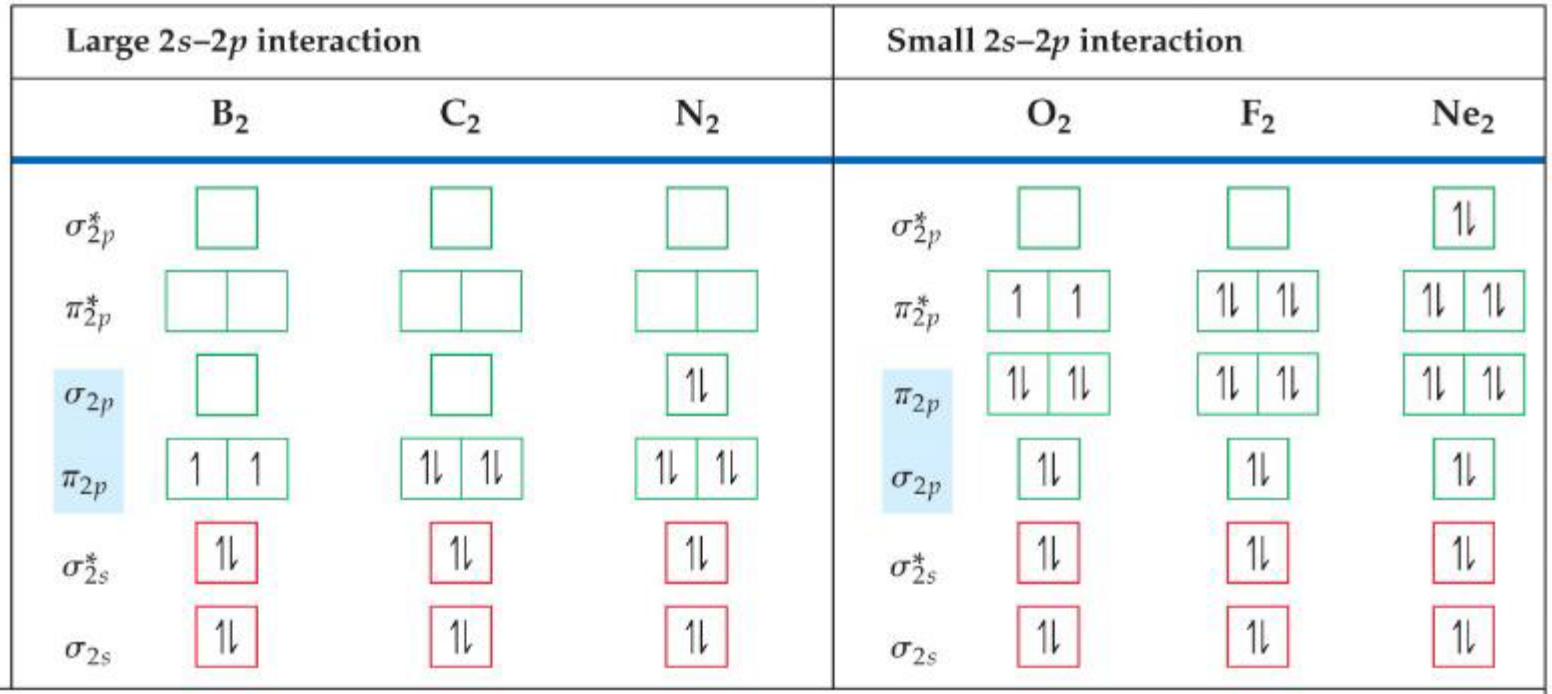
s and *p* Orbital Interactions



- In some cases, *s* orbitals can interact wit the p_z orbitals more than the p_x and p_y orbitals.
- It raises the energy of the p_z orbital and lowers the energy of the *s* orbital.
- The p_x and p_y orbitals are degenerate orbitals.

Molecular Geometries and Bonding Theories

MO Diagrams for Diatomic Molecules of 2nd Period Elements



	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	—

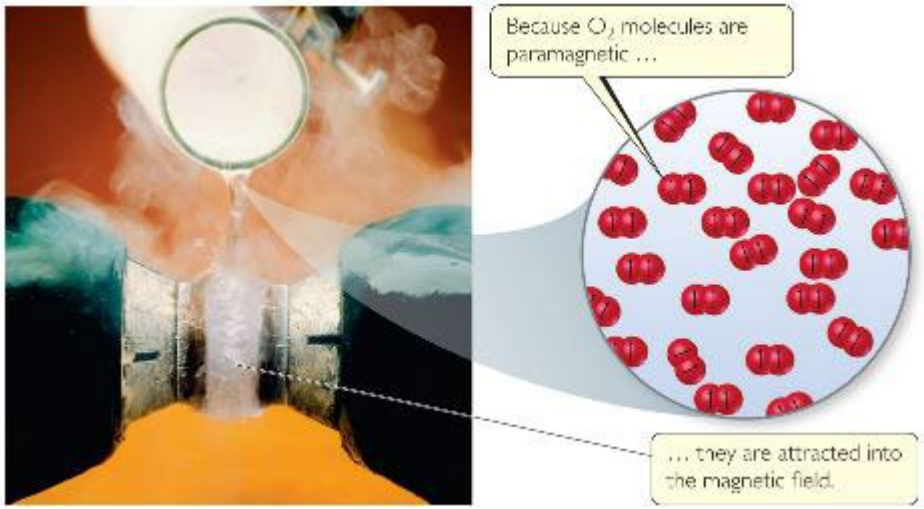
Molecular Geometries and Bonding Theories

MO Diagrams and Magnetism

- **Diamagnetism** is the result of all electrons in every orbital being spin paired. These substances are weakly repelled by a magnetic field.
- **Paramagnetism** is the result of the presence of one or more unpaired electrons in an orbital.
- Is oxygen (O_2) paramagnetic or diamagnetic? Look back at the MO diagram! It is paramagnetic.

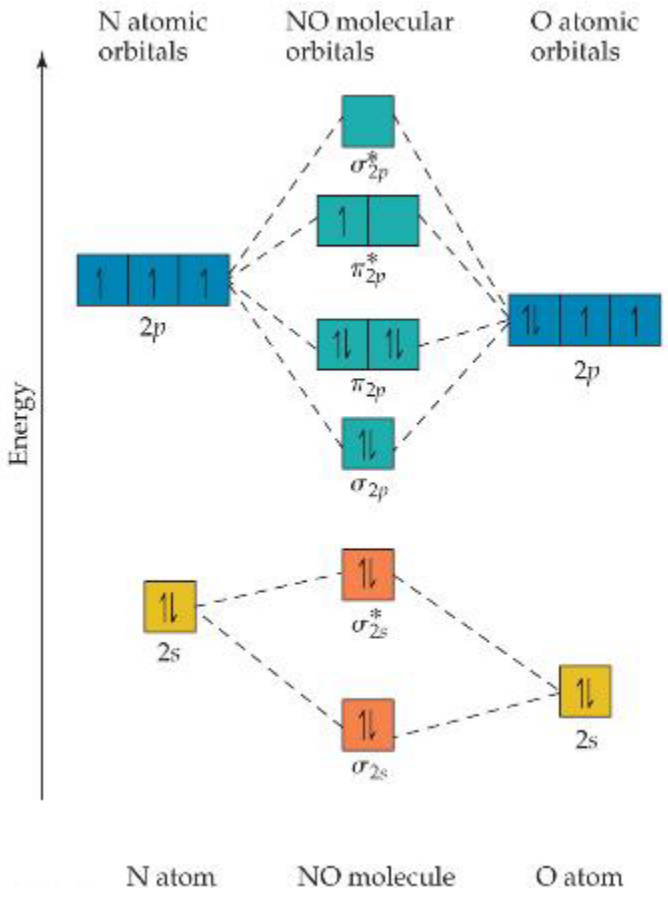
Paramagnetism of Oxygen

- Lewis structures would *not* predict that O_2 is paramagnetic.
- The MO diagram clearly shows that O_2 is paramagnetic.
- Both show a double bond (bond order = 2).



Heteronuclear Diatomic Molecules

- Diatomic molecules can consist of atoms from different elements.
- How does a MO diagram reflect differences?
- 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.



Molecular Geometries and Bonding Theories