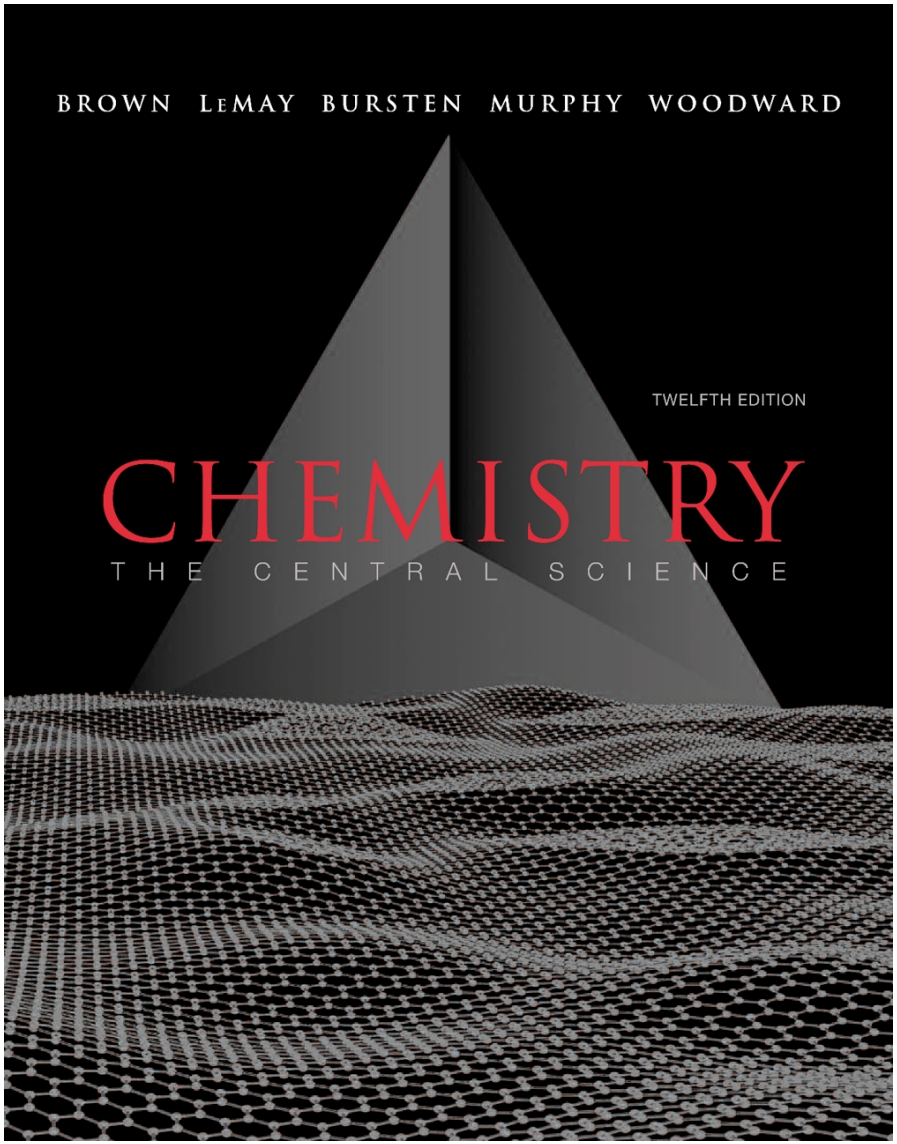

Lecture Presentation

Chapter 9

Molecular Geometries and Bonding Theories

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Chapter Goal

- Lewis structures do not show shape and size of molecules.
- Develop a relationship between two dimensional Lewis structure and three dimensional molecular shapes
- Develop a sense of shapes and how those shapes are governed in large measure by the kind of bonds exist between the atoms making up the molecule

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Molecular geometry is the general shape of a molecule, as determined by the relative positions of the atomic nuclei.

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The valence-shell electron-pair repulsion (VSEPR) model predicts the shapes of molecules and ions by assuming that the valence-shell electron pairs are arranged about each atom so that electron pairs are kept as far away from one another as possible, thereby minimizing electron pair repulsions.

The diagram on the next slide illustrates this.

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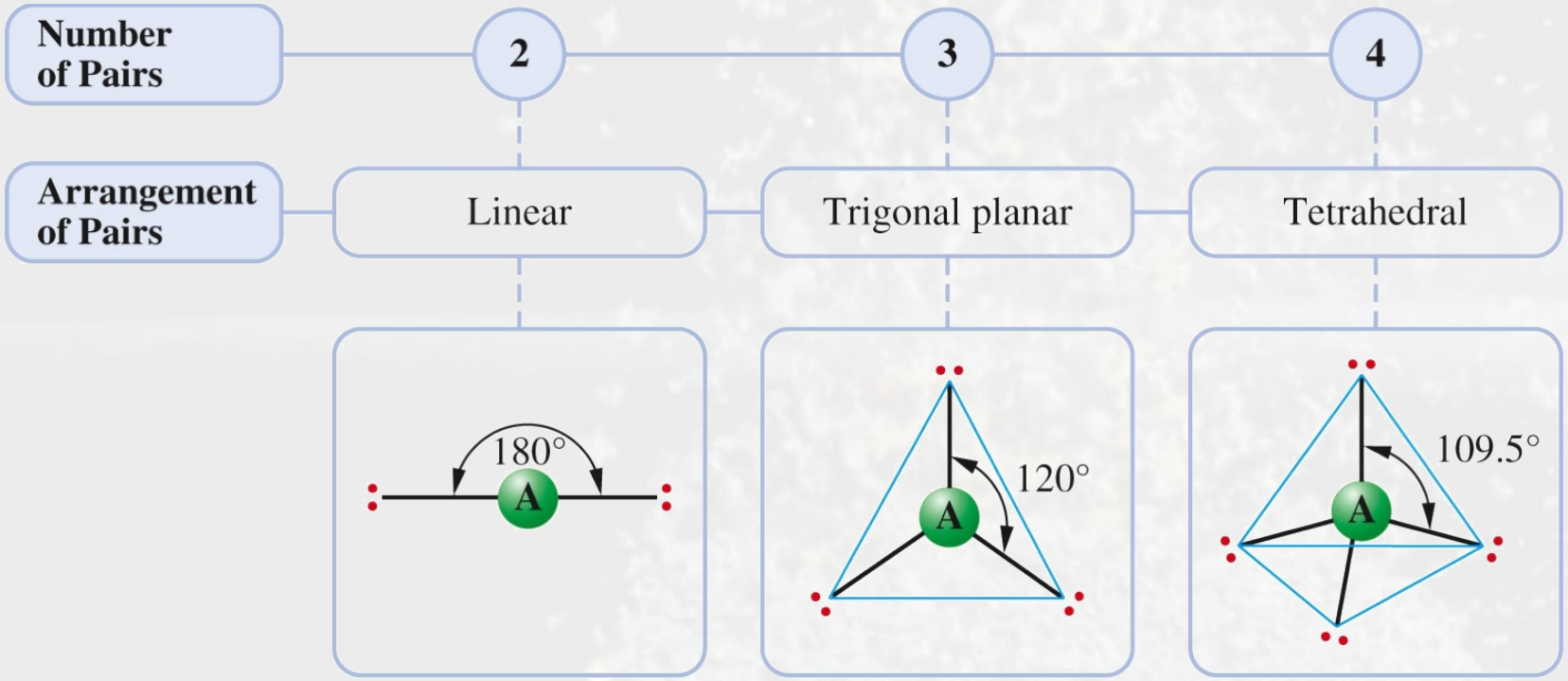

Two electron pairs are 180° apart (a linear arrangement).

Three electron pairs are 120° apart in one plane (a trigonal planar arrangement).

Four electron pairs are 109.5° apart in three dimensions (a tetrahedral arrangment).

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Five electron pairs are arranged with three pairs in a plane 120° apart and two pairs at 90°to the plane and 180° to each other (a trigonal bipyramidal arrangement).

Six electron pairs are 90° apart (an octahedral arrangement).

This is illustrated on the next slide.

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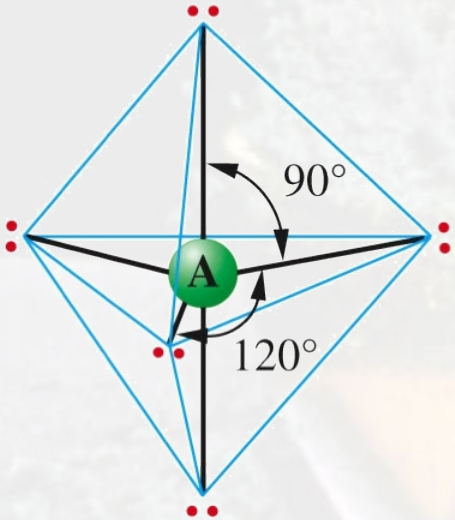
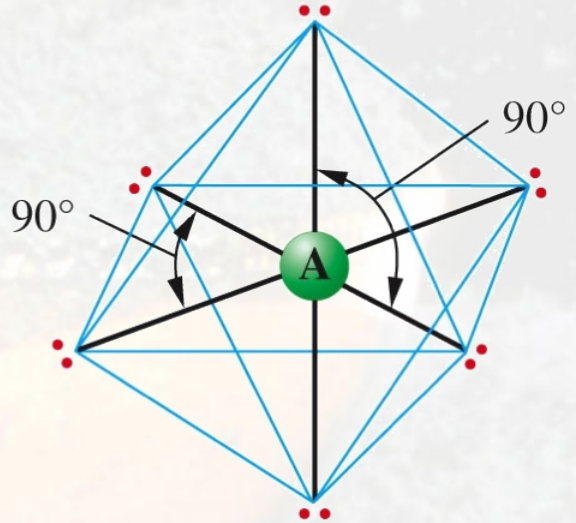
Number of Pairs	5	6
Arrangement of Pairs	Trigonal bipyramidal	Octahedral





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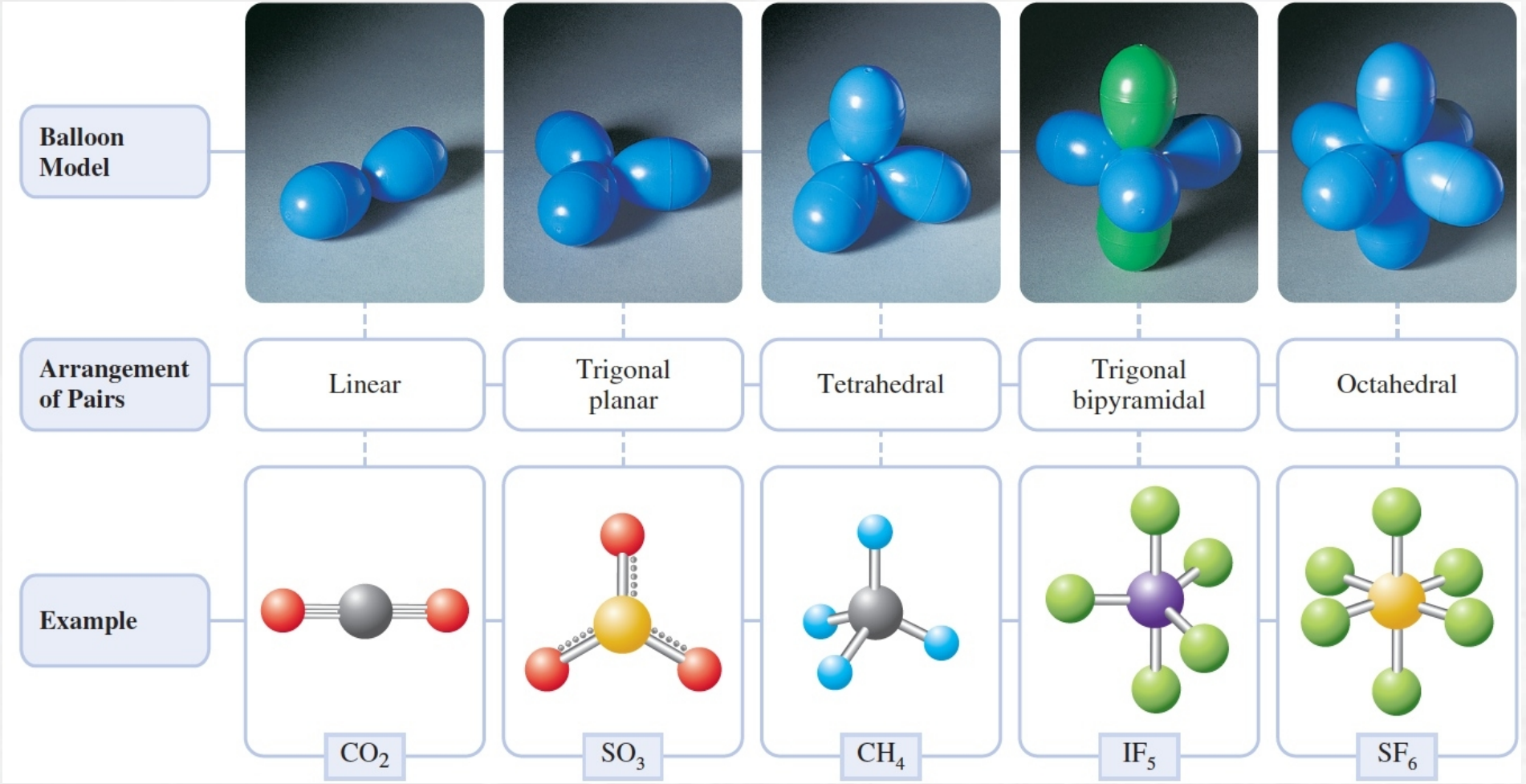
These arrangements are illustrated below with balloons and models of molecules for each.



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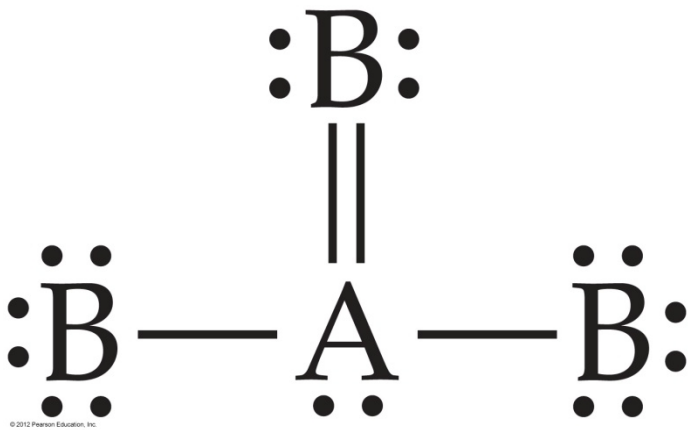
Electron Domains



- The central atom in this molecule, A, has four electron domains.

- 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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Electron-Domain Geometries

- All one must do is count the number of electron domains in the Lewis structure.
- The geometry will be that which corresponds to the number of electron domains.

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Molecular Geometries

- 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.

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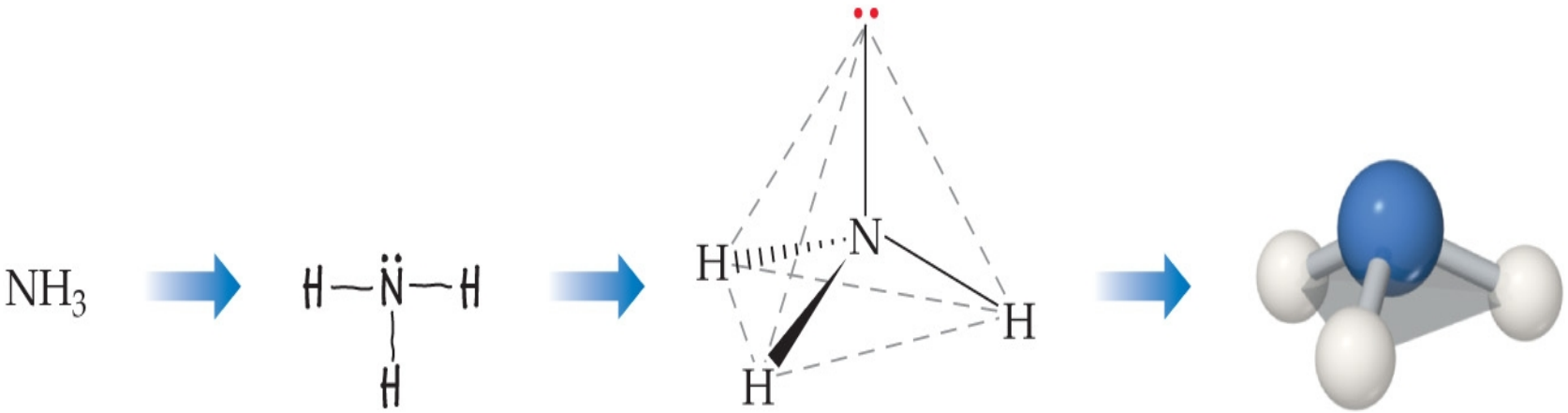

1. Draw Lewis structure

2. Determine electron-domain geometry by counting *all* electron domains, then use Table 9.1 to determine appropriate electron domain geomtry.

3. Determine molecular geometry by counting *only bonding* electron domains to see arrangement of bonded atoms (trigonal pyramidal)

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Molecular Geometries and Bonding

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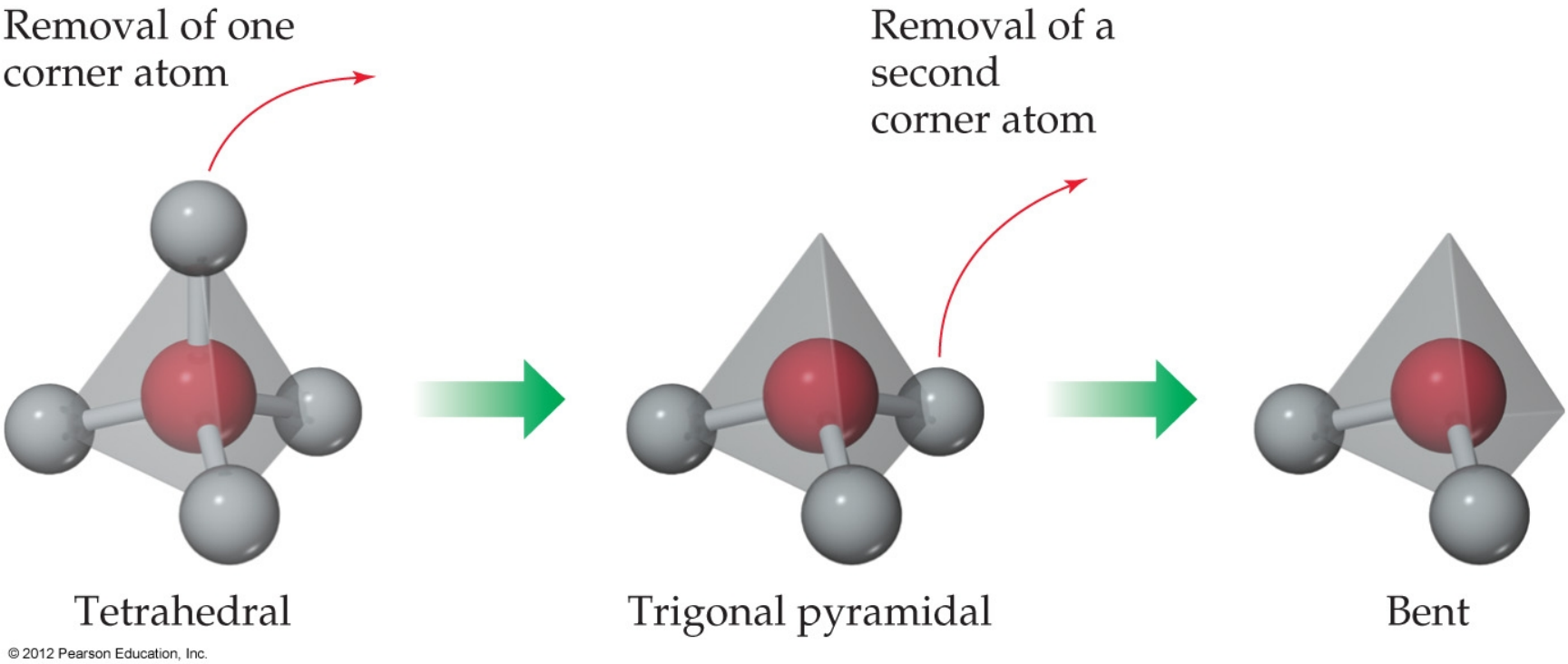
Molecular Geometries



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Within each electron domain, then, there might be more than one molecular geometry.

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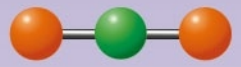
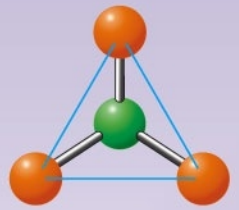
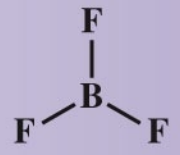
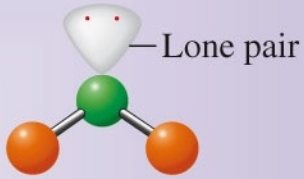
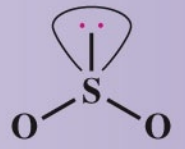
The diagrams below illustrate molecular geometry and the impact of lone pairs on it for linear and trigonal planar electron-pair arrangements.

Electron Pairs: Total	Electron Pairs: Bonding	Electron Pairs: Lone	Arrangement of Pairs	Molecular Geometry		Example	
2	2	0	Linear	Linear AX_2		BeF_2	F—Be—F
3	3	0	Trigonal planar	Trigonal planar AX_3		BF_3	
	2	1		Bent (or angular) AX_2		SO_2	

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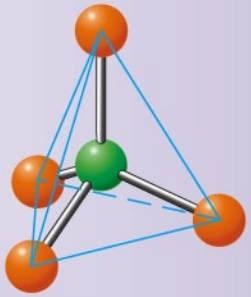
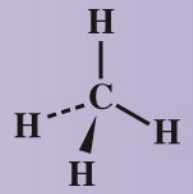
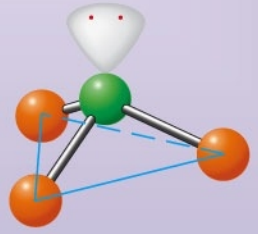
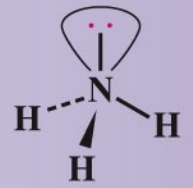
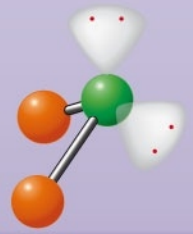
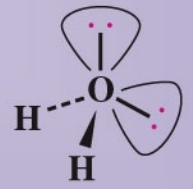
Molecular geometries with a tetrahedral electron-pair arrangement are illustrated below.

4	4	0	Tetrahedral	Tetrahedral AX_4		CH_4 
	3	1		Trigonal pyramidal AX_3		NH_3 
	2	2		Bent (or angular) AX_2		H_2O 

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Molecular geometries for the trigonal bipyramidal electron-pair arrangement are shown on the next slide.

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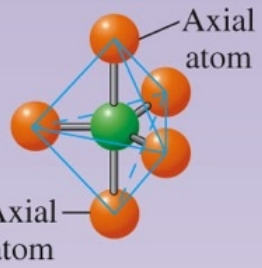
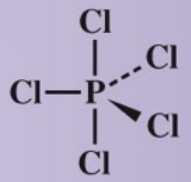
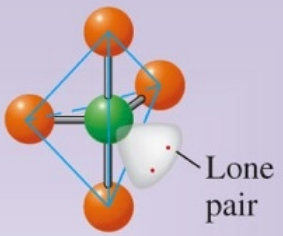
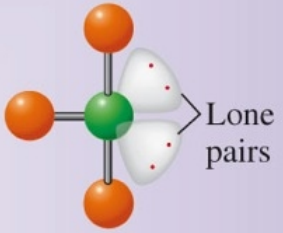
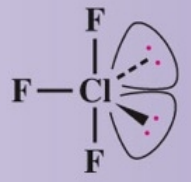
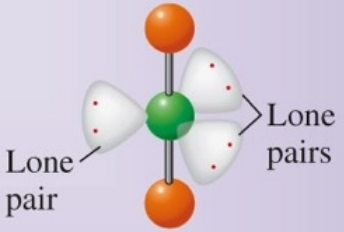
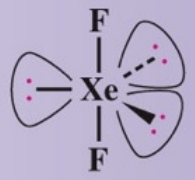
Electron Pairs: Total	Bonding	Lone	Arrangement of Pairs	Molecular Geometry	Example
5	5	0	Trigonal bipyramidal	Trigonal bipyramidal AX_5 	PCl_5 
	4	1		Seesaw (or distorted tetrahedron) AX_4 	SF_4
	3	2		T-shaped AX_3 	ClF_3 
	2	3		Linear AX_2 	XeF_2 

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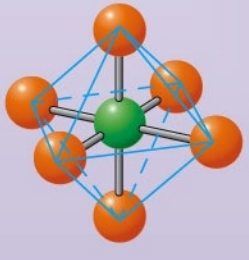
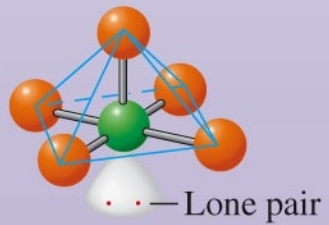
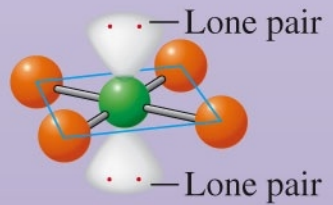
Molecular geometries for the octahedral electron-pair arrangement are shown below.

6	6	0	Octahedral	Octahedral AX_6		SF_6
	5	1		Square pyramidal AX_5		IF_5
	4	2		Square planar AX_4		XeF_4

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Predicting Bond Angles

The angles 180°, 120°, 109.5°, and so on are the bond angles when the central atom has no lone pair and all bonds are with the same other atom.

When this is not the case, the bond angles deviate from these values in sometimes predictable ways.

Because a lone pair tends to require more space than a bonding pair, it tends to reduce the bond angles.

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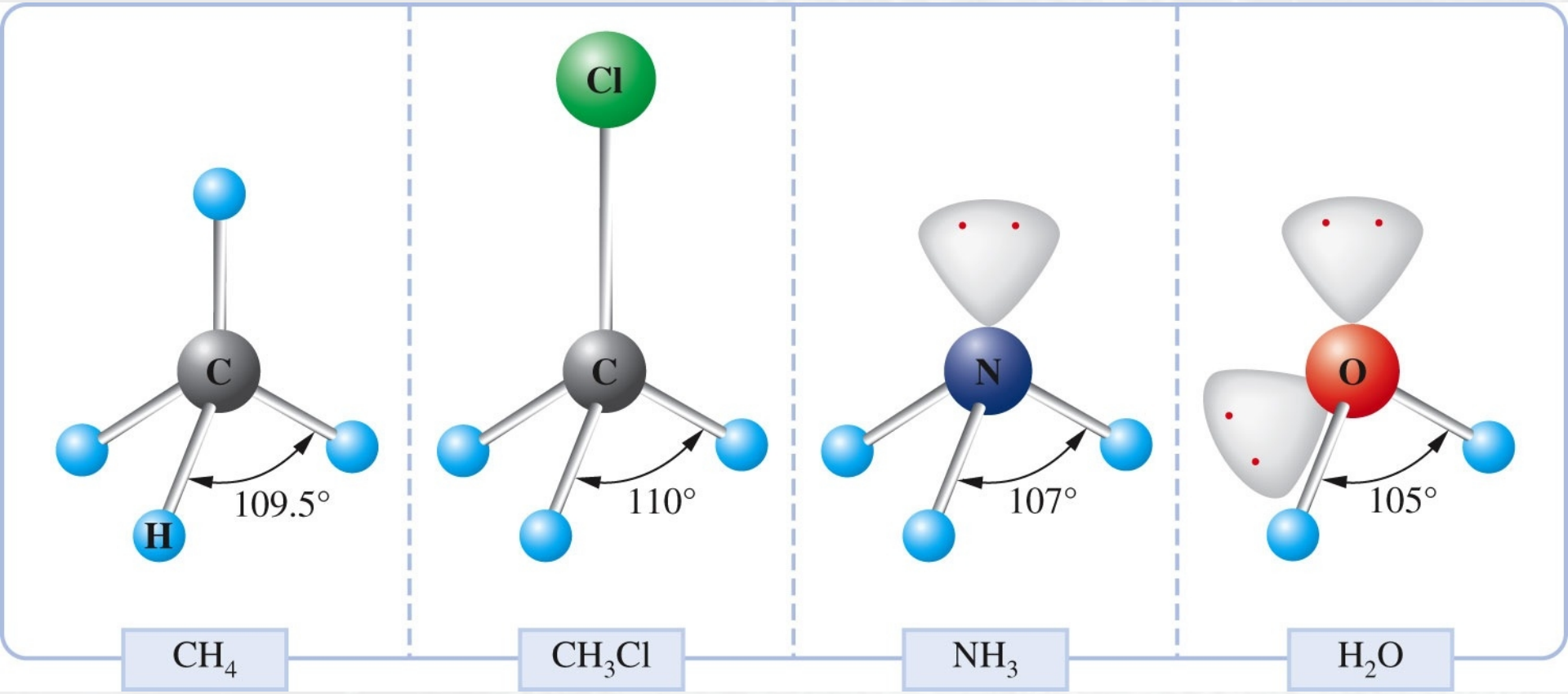
The impact of lone pair(s) on bond angle for tetrahedral electron-pair arrangements has been experimentally determined.



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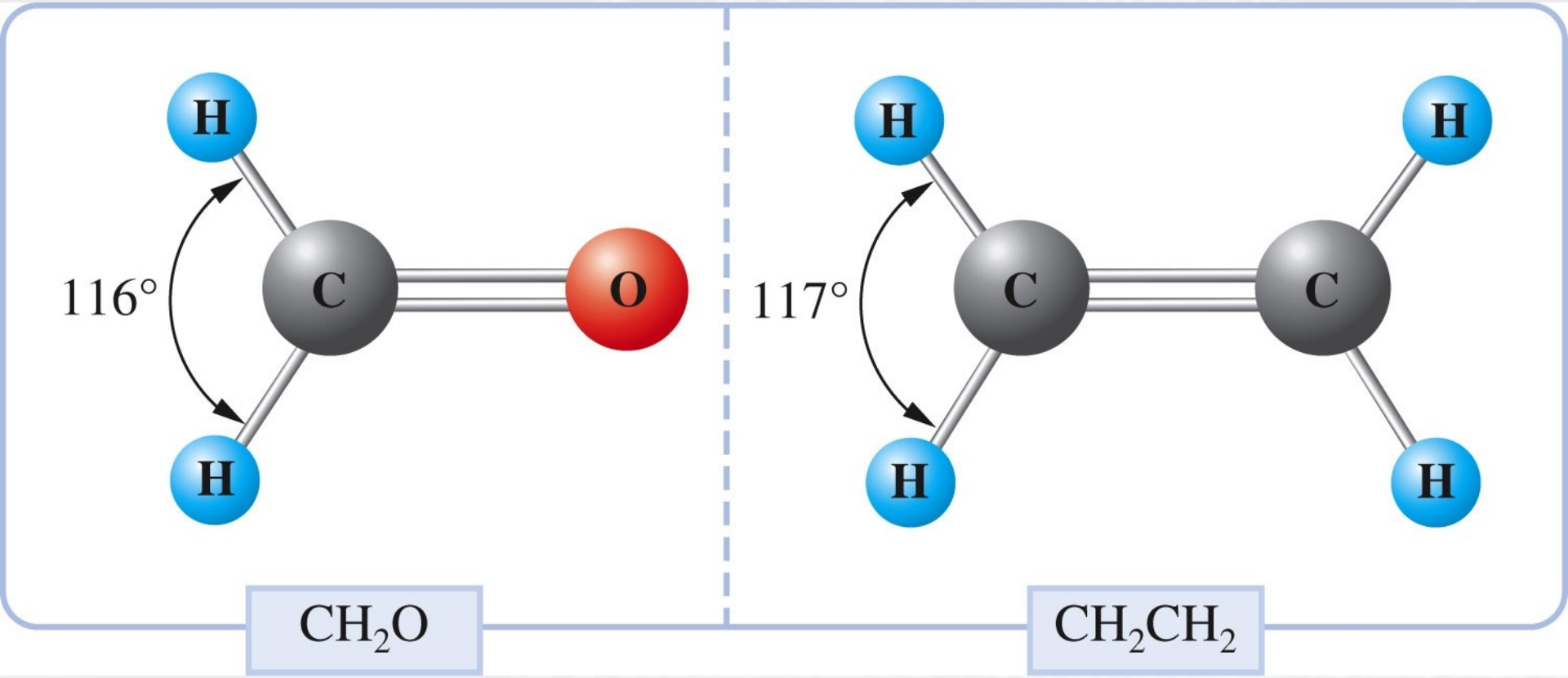
Multiple bonds require more space than single bonds and, therefore, constrict the bond angle. This situation is illustrated below, again with experimentally determined bond angles.



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Use the VSEPR model to predict the geometries of the following molecules:

a. AsF_3

b. PH_4^+

c. BCl_3

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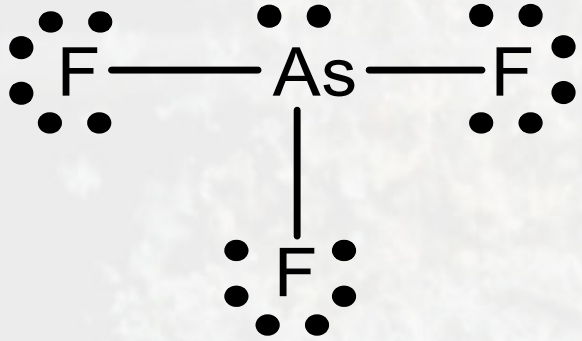
AsF_3 has 1(5) + 3(7) = 26 valence electrons; As is the central atom. The electron-dot formula is



There are four regions of electrons around As: three bonds and one lone pair.

The electron regions are arranged tetrahedrally. One of these regions is a lone pair, so the molecular geometry is trigonal pyramidal.

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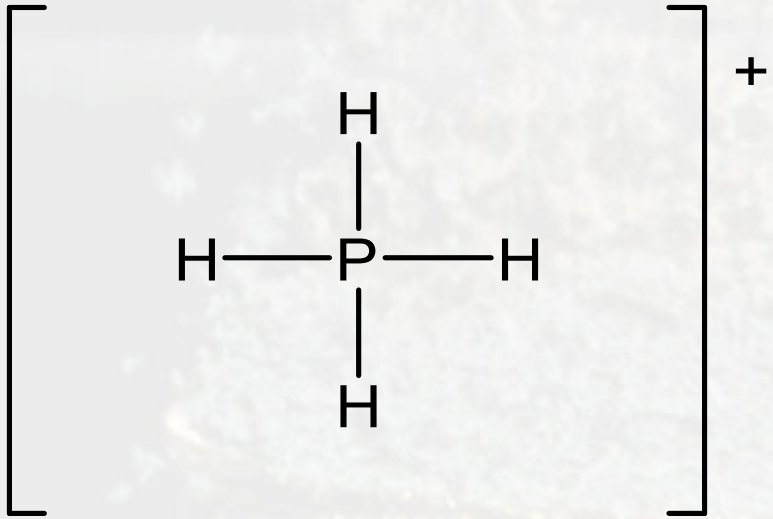
PH_4^+ has 1(5) + 4(1) – 1 = 8 valence electrons; P is the central atom. The electron-dot formula is



There are four regions of electrons around P: four bonding electron pairs.
The electron-pairs arrangement is tetrahedral.
All regions are bonding, so the molecular geometry is tetrahedral.

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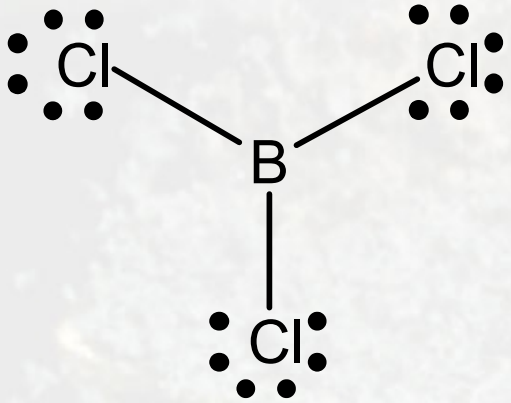
BCl_3 has 1(3) + 3(7) = 24 valence electrons;

B is the central atom.

The electron-dot formula is



There are three regions of electrons around B; all are bonding.

The electron-pair arrangement is trigonal planar.

All of these regions are bonding, so the molecular geometry is trigonal planar.

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Using the VSEPR model, predict the geometry of the following species:

a. ICl_3

b. ICl_4^-

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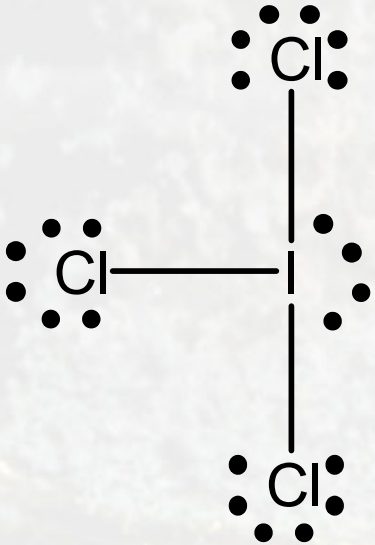
ICl_3 has 1(7) + 3(7) = 28 valence electrons. I is the central atom. The electron-dot formula is



There are five regions: three bonding and two lone pairs.
The electron-pair arrangement is trigonal bipyramidal.
The geometry is T-shaped.

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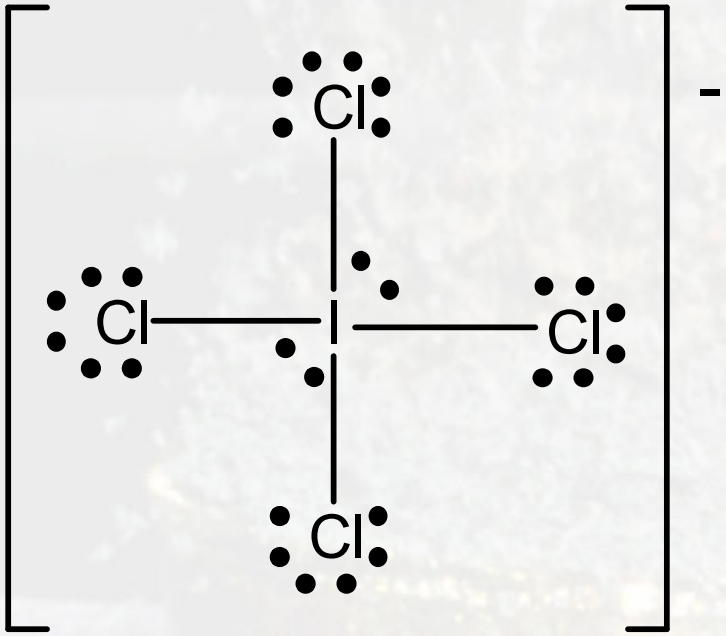
ICl_4^- has 1(7) + 4(7) + 1 = 36 valence electrons. I is the central element. The electron-dot formula is



There are six regions around I: four bonding and two lone pairs.

The electron-pair arrangement is octahedral.

The geometry is square planar.

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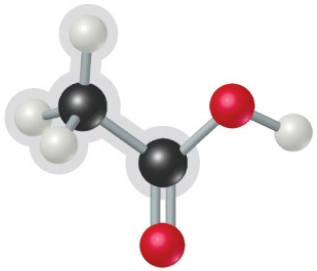
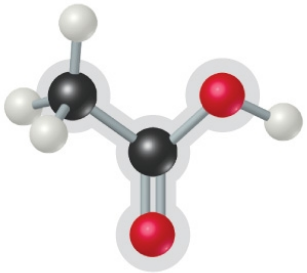
Larger Molecules

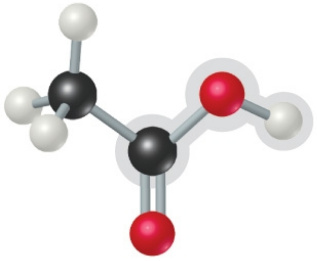
In larger molecules, it makes more sense to talk about the geometry about a particular atom rather than the geometry of the molecule as a whole.



Electron-domain geometry tetrahedral, molecular geometry tetrahedral



Electron-domain geometry trigonal planar, molecular geometry trigonal planar



Electron-domain geometry tetrahedral, molecular geometry bent

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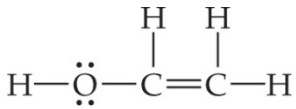
Sample Exercise 9.3 Predicting Bond Angles

Eyedrops for dry eyes usually contain a water-soluble polymer called *poly(vinyl alcohol)*, which is based on the unstable organic molecule *vinyl alcohol*:

Predict the approximate values for the H — O — C and O — C — C bond angles in vinyl alcohol.



Solution

Analyze We are given a Lewis structure and asked to determine two bond angles.
Plan To predict a bond angle,we determine the number of electron domains surrounding the middle atom in the bond. The ideal angle corresponds to the electron-domain geometry around the atom. The angle will be compressed somewhat by nonbonding electrons or multiple bonds.
Solve In H — O — C , the O atom has four electron domains (two bonding, two nonbonding). The electron-domain geometry around O is therefore tetrahedral, which gives an ideal angle of 109.5°. The H — O — C angle is compressed somewhat by the nonbonding pairs, so we expect this angle to be slightly less than 109.5° .

To predict the O — C — C bond angle, we examine the middle atom in the angle. In the molecule, there are three atoms bonded to this C atom and no nonbonding pairs, and so it has three electron domains about it. The predicted electron-domain geometry is trigonal planar, resulting in an ideal bond angle of 120°. Because of the larger size of the C = C domain, the bond angle should be slightly greater than 120°.

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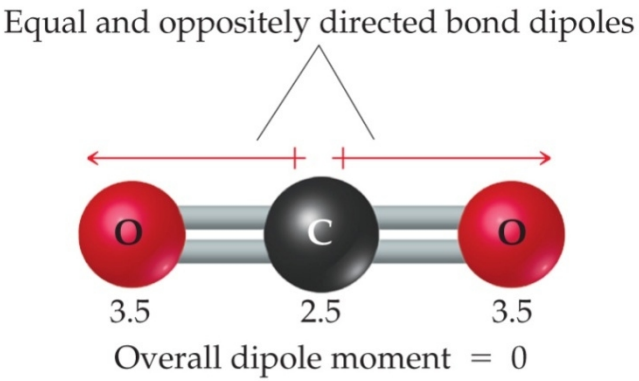
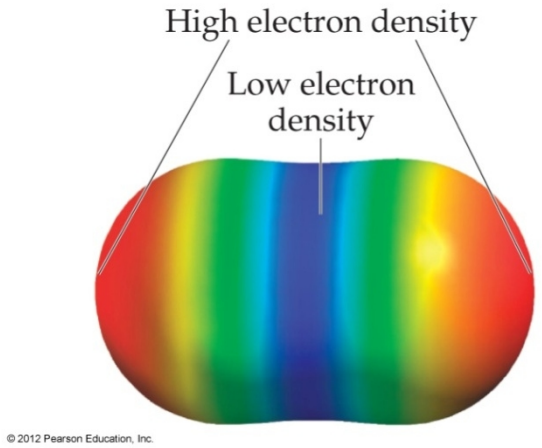
Polarity

- In Chapter 8, we discussed bond dipoles.
- But just because a molecule possesses polar bonds does not mean the molecule *as a whole* will be polar.





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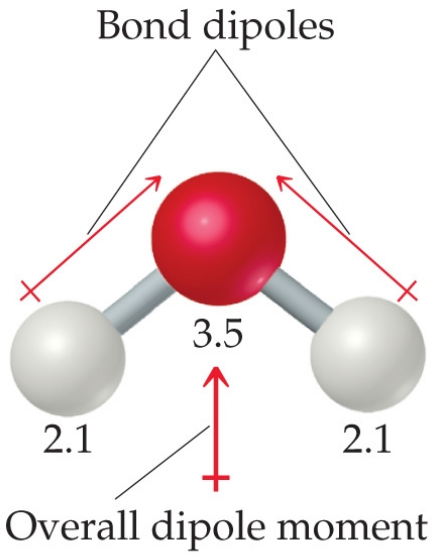
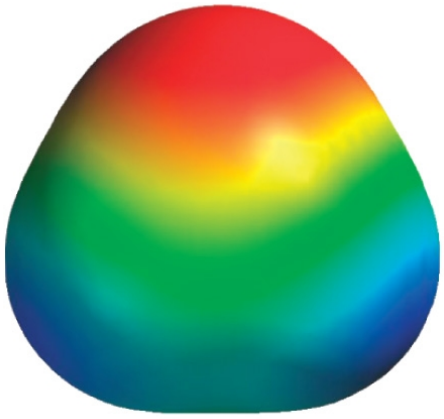
Polarity





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

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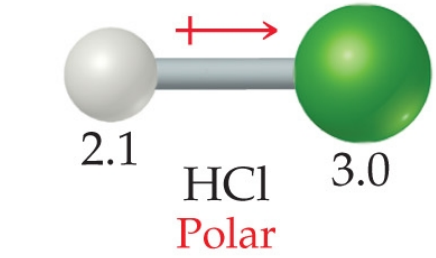
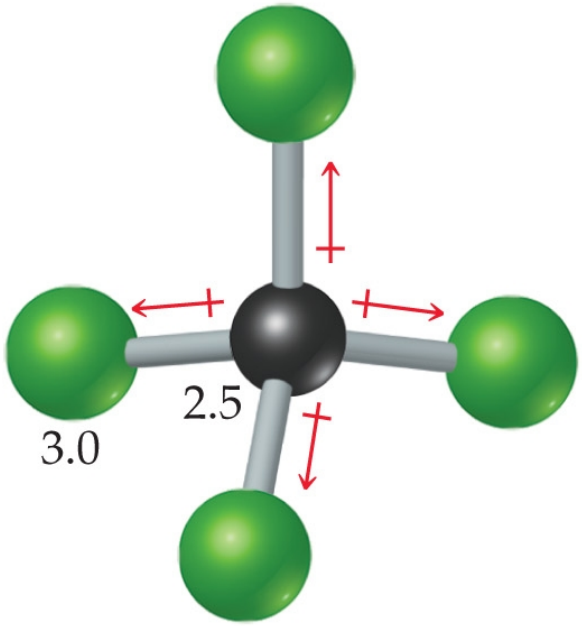
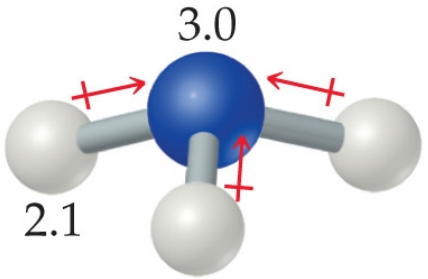
Polarity



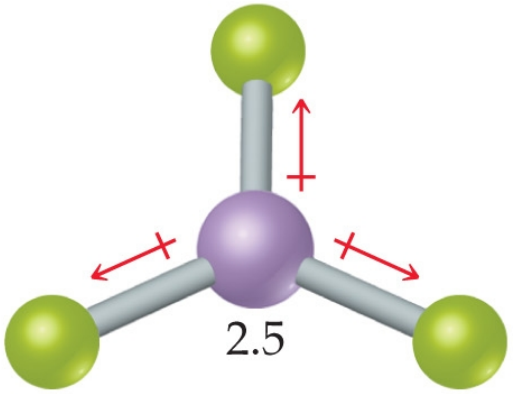
HCl
Polar



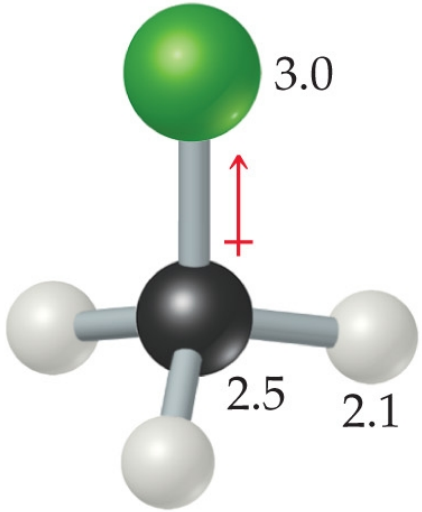
CCl_4
Nonpolar



NH_3
Polar



BF_3
Nonpolar



CH_3Cl
Polar

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Molecular Geometries and Bonding

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Sample Exercise 9.4 Polarity of Molecules

Predict whether these molecules are polar or nonpolar: (a) BrCl, (b) SO_2, (c) SF_6.

Solution

Analyze We are given three molecular formulas and asked to predict whether the molecules are polar.

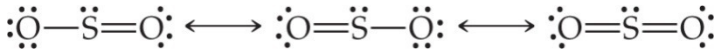
Plan A molecule containing only two atoms is polar if the atoms differ in electronegativity. The polarity of a molecule containing three or more atoms depends on both the molecular geometry and the individual bond polarities. Thus, we must draw a Lewis structure for each molecule containing three or more atoms and determine its molecular geometry.We then use electronegativity values to determine the direction of the bond dipoles. Finally, we see whether the bond dipoles cancel to give a nonpolar molecule or reinforce each other to give a polar one.

Solve

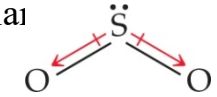
(a) Chlorine is more electronegative than bromine. All diatomic molecules with polar bonds are polar molecules. Consequently, BrCl is polar, with chlorine carrying the partial negative charge:

The measured dipole moment of BrCl is $\mu = 0.57$ D.

(b) Because oxygen is more electronegative than sulfur, SO2 has polar bonds. Three resonance forms can be written:



For each of these, the VSEPR model predicts a bent molecular geometry. Because the molecule is bent, the bond dipoles do not cancel, and the molecule is polar



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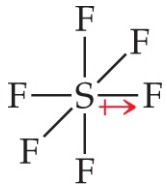
Sample Exercise 9.4 Polarity of Molecules

Continued

Experimentally, the dipole moment of SO_2 is $\mu = 1.63$ D.

(c) Fluorine is more electronegative than sulfur, so the bond dipoles point toward fluorine. For clarity, only one S — F dipole is shown. The six S — F bonds are arranged octahedrally around the central sulfur:



Because the octahedral molecular geometry is symmetrical, the bond dipoles cancel, and the molecule is nonpolar, meaning that $\mu = 0$.

Practice Exercise

Determine whether the following molecules are polar or nonpolar: (a) NF_3, (b) BCl_3.

Answers: (a) polar because polar bonds are arranged in a trigonal-pyramidal geometry, (b) nonpolar because polar bonds are arranged in a trigonal-planar geometry

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Valence bond theory is an approximate theory put forth to explain the electron pair or covalent bond by quantum mechanics.

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A bond forms when

- An orbital on one atom comes to occupy a portion of the same region of space as an orbital on the other atom. The two orbitals are said to overlap.
- The total number of electrons in both orbitals is no more than two.

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The greater the orbital overlap, the stronger the bond.

Orbitals (except *s* orbitals) bond in the direction in which they protrude or point, so as to obtain maximum overlap.

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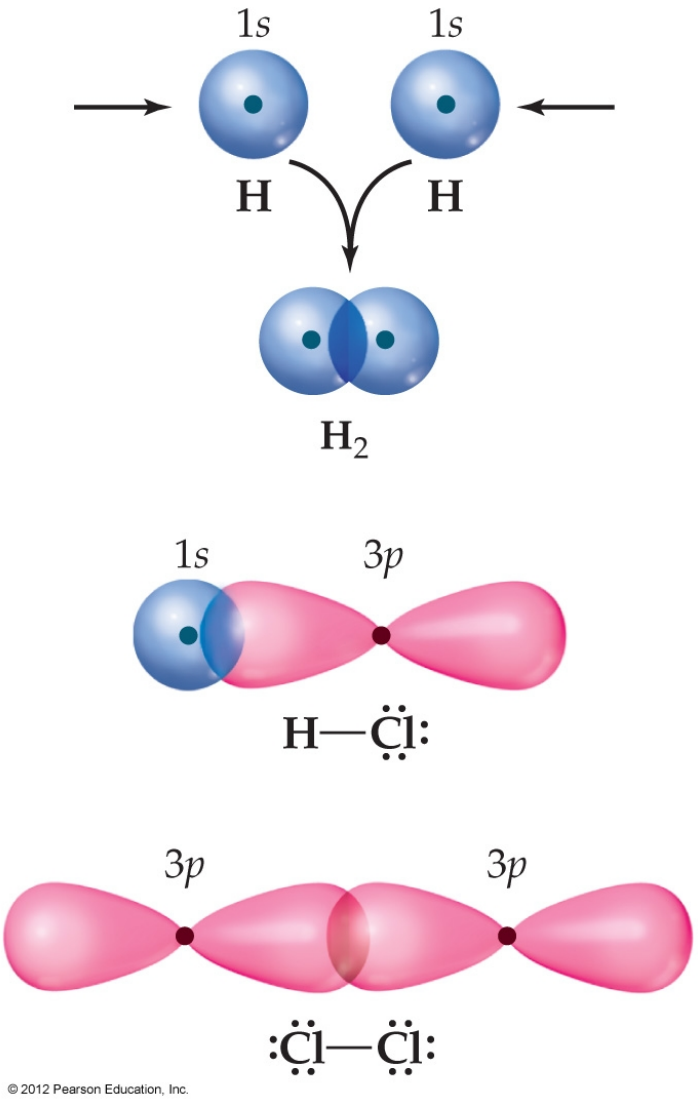
Overlap and Bonding



- We think of covalent bonds forming through the sharing of electrons by adjacent atoms.
- In such an approach this can only occur when orbitals on the two atoms overlap.

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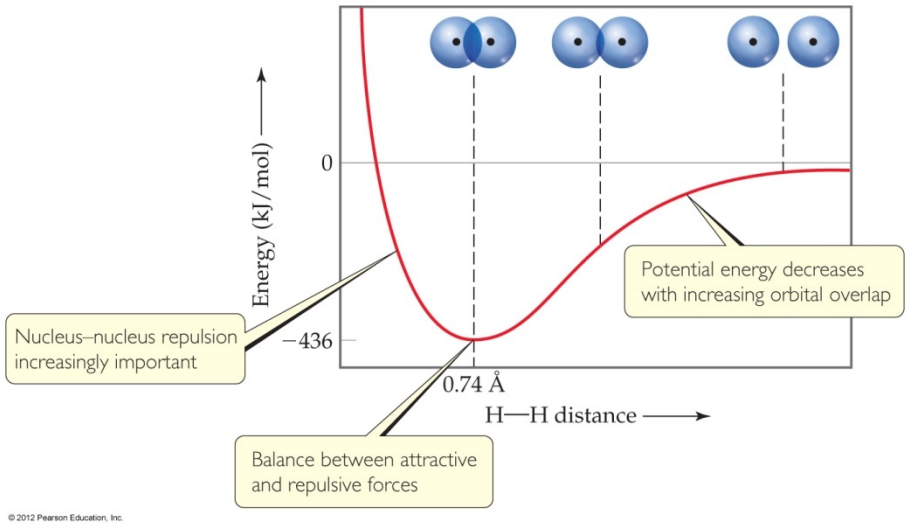
Overlap and Bonding

- Increased overlap brings the electrons and nuclei closer together while simultaneously decreasing electron–electron repulsion.
- However, if atoms get too close, the internuclear repulsion greatly raises the energy.



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Hybrid orbitals are orbitals used to describe the bonding that is obtained by taking combinations of the atomic orbitals of the isolated atoms.

The number of hybrid orbitals formed always equals the number of atomic orbitals used.

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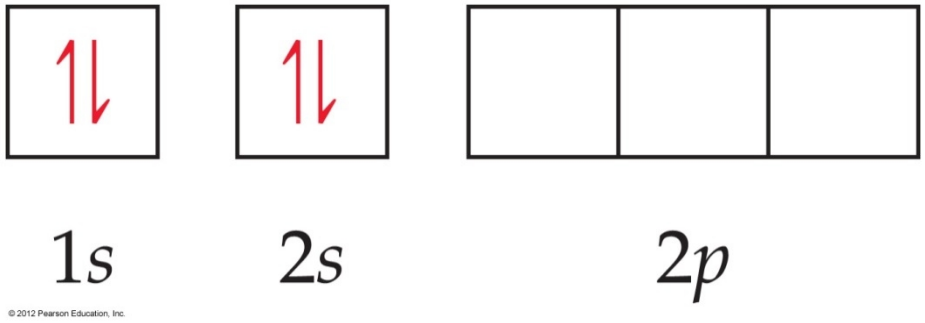
Hybrid Orbitals

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



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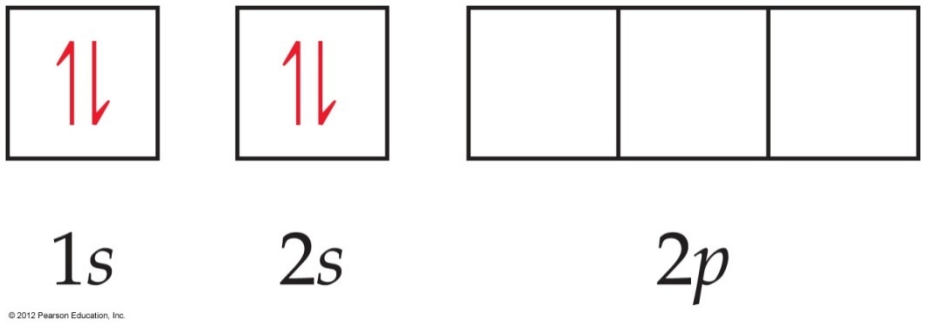
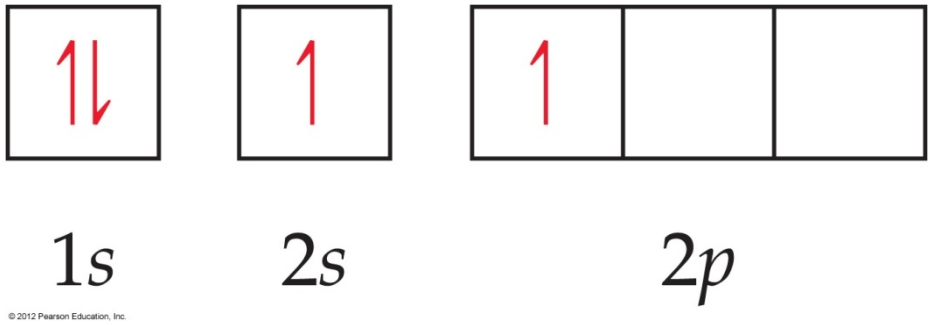
Hybrid Orbitals

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.





Molecular Geometries and Bonding

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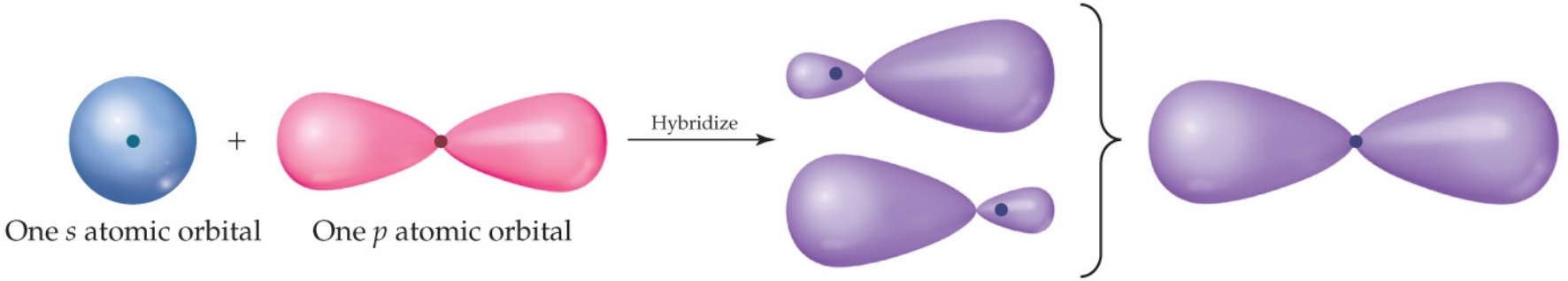
Hybrid Orbitals

- 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.



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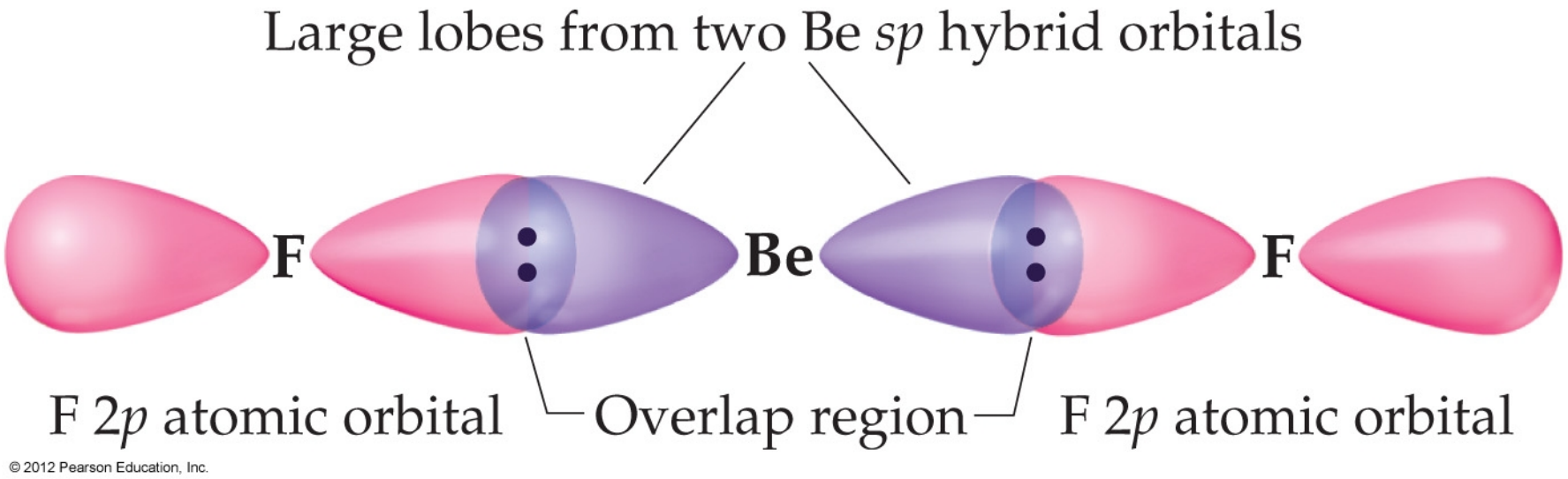
Hybrid Orbitals

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



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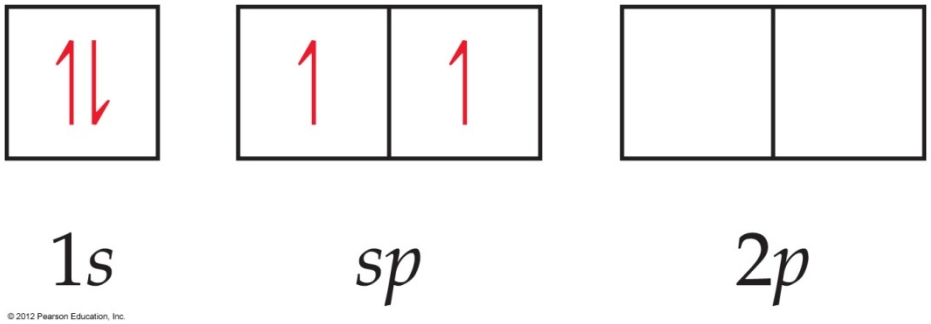
Hybrid Orbitals



- With hybrid orbitals, the orbital diagram for beryllium would look like this (Fig. 9.15).
- The *sp* orbitals are higher in energy than the 1*s* orbital, but lower than the 2*p*.

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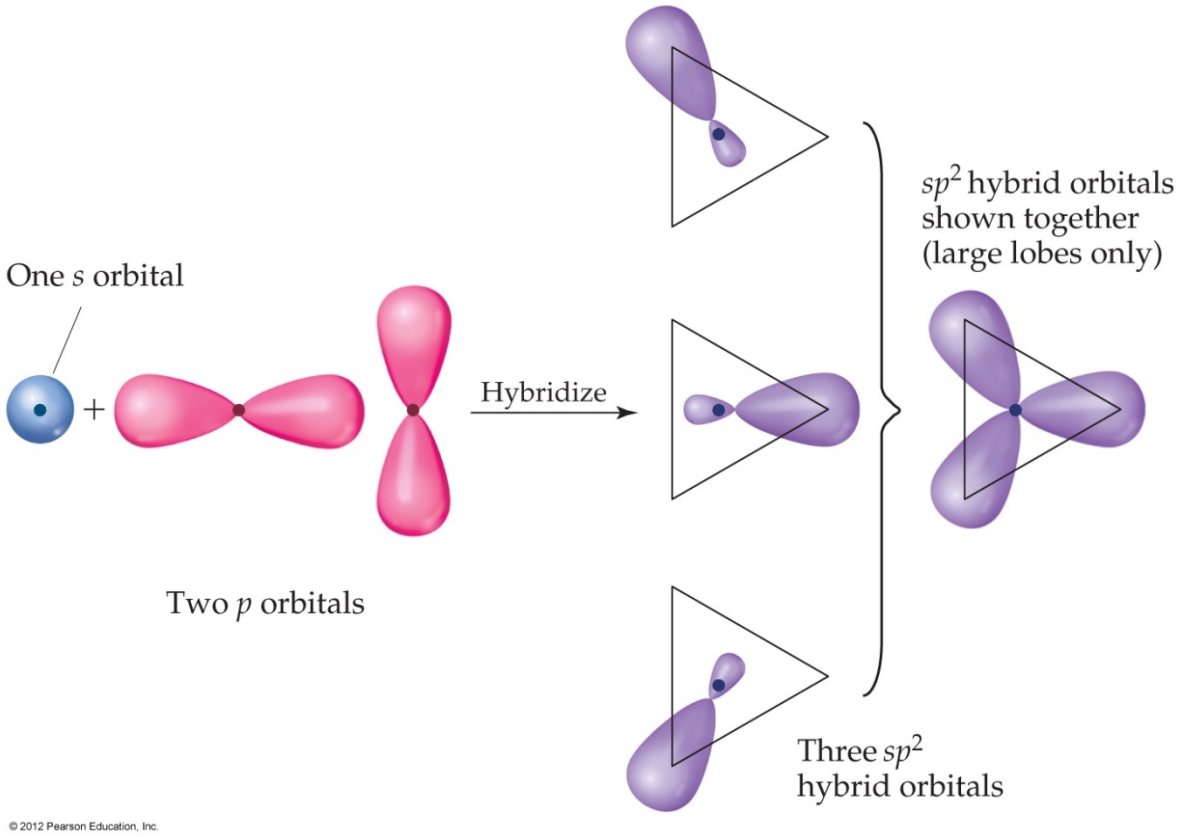
Hybrid Orbitals

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



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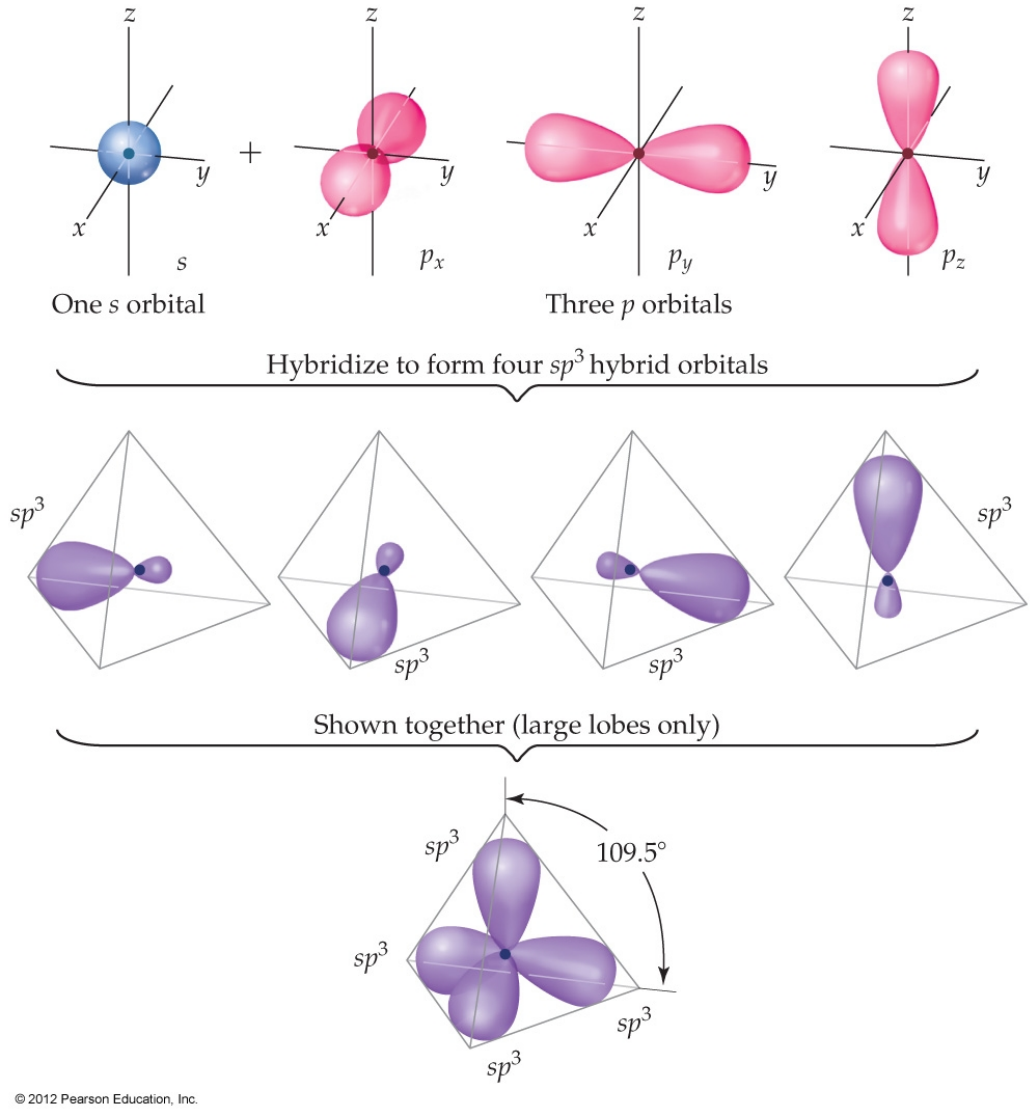
Hybrid Orbitals

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



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sp^3d and sp^3d^2 Hybridization

- Examples:
- PCl_5
- SF_6

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Hybridization

- Some atoms ***hybridize*** their orbitals to maximize bonding.
  - Hybridizing is mixing different types of orbitals to make a new set of degenerate orbitals.
  - sp, sp^2, sp^3, sp^3d, sp^3d^2
  - more bonds = more full orbitals = more stability
- Same type of atom can have different hybridizations depending on the compound.
  - C = sp, sp^2, sp^3

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Hybrid Orbitals

- The number of standard atomic orbitals combined equals the number of hybrid orbitals formed.
  - H cannot hybridize!
    - Its valence shell only has one orbital.
- The number and type of standard atomic orbitals combined determine 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.

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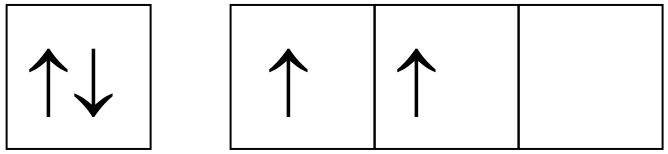
Carbon Hybridizations

Unhybridized

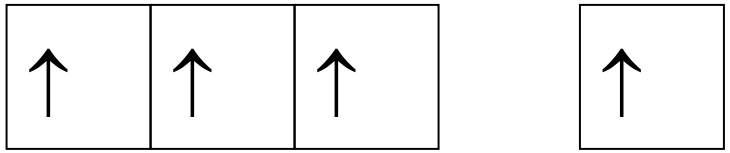


2*s* 2*p*

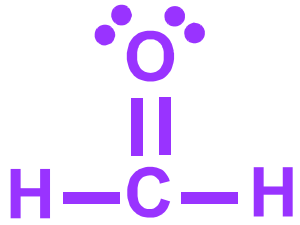
sp hybridized

2*sp* 2*p*

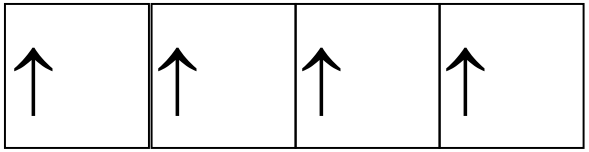
sp^2 hybridized



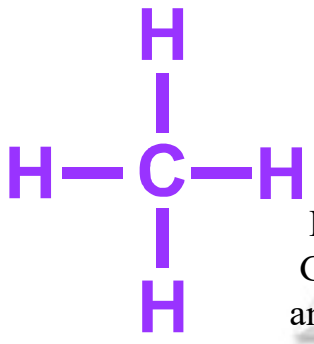
$2sp^2$ 2*p*



sp^3 hybridized



$2sp^3$



Molecular Geometries and Bonding

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Valence Bond Theory

- Hybridization is a major player in this approach to bonding.
- There are two ways orbitals can overlap to form bonds between atoms.

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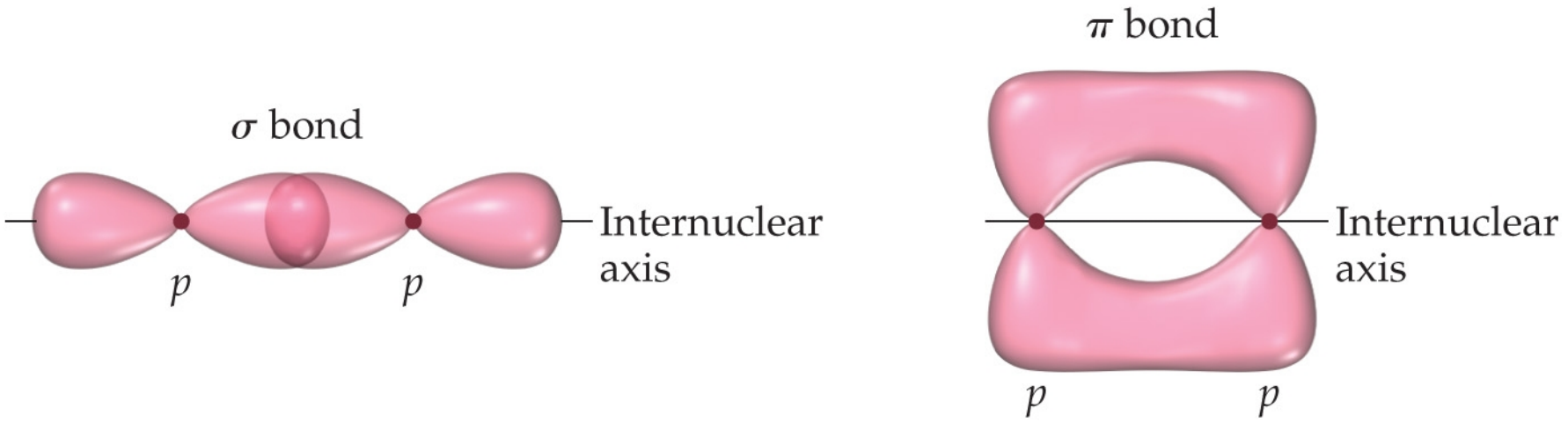
Sigma (σ) Bonds



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- Sigma bonds are characterized by
  - Head-to-head overlap.
  - Cylindrical symmetry of electron density about the internuclear axis.

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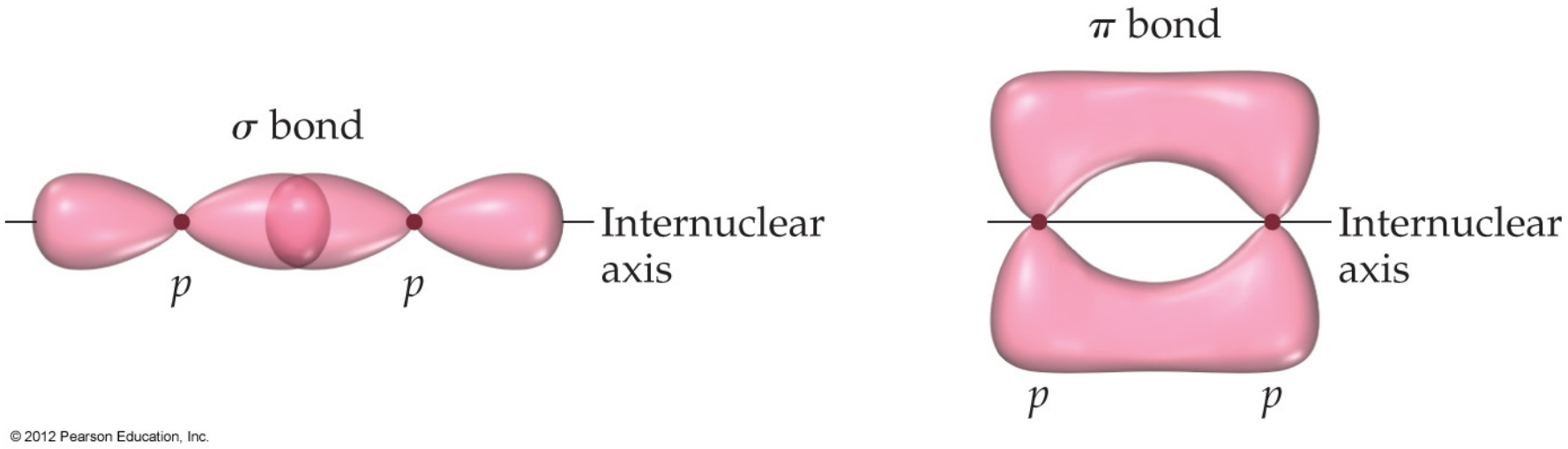
Pi (π) Bonds



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- Pi bonds are characterized by
  - Side-to-side overlap.
  - Electron density above and below the internuclear axis.

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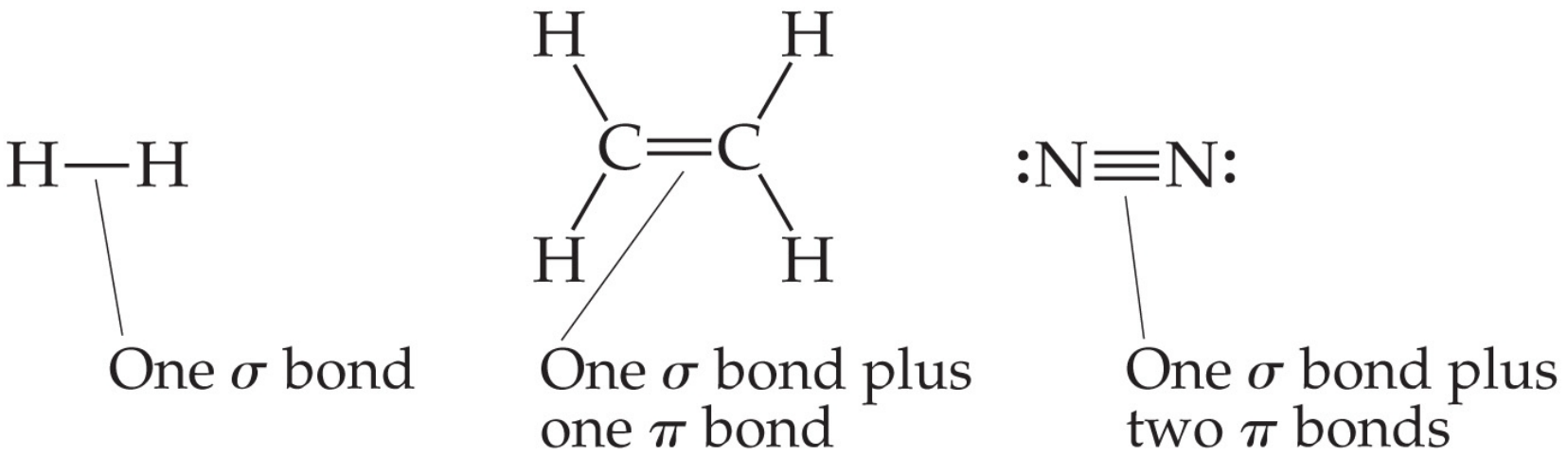
Single Bonds

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



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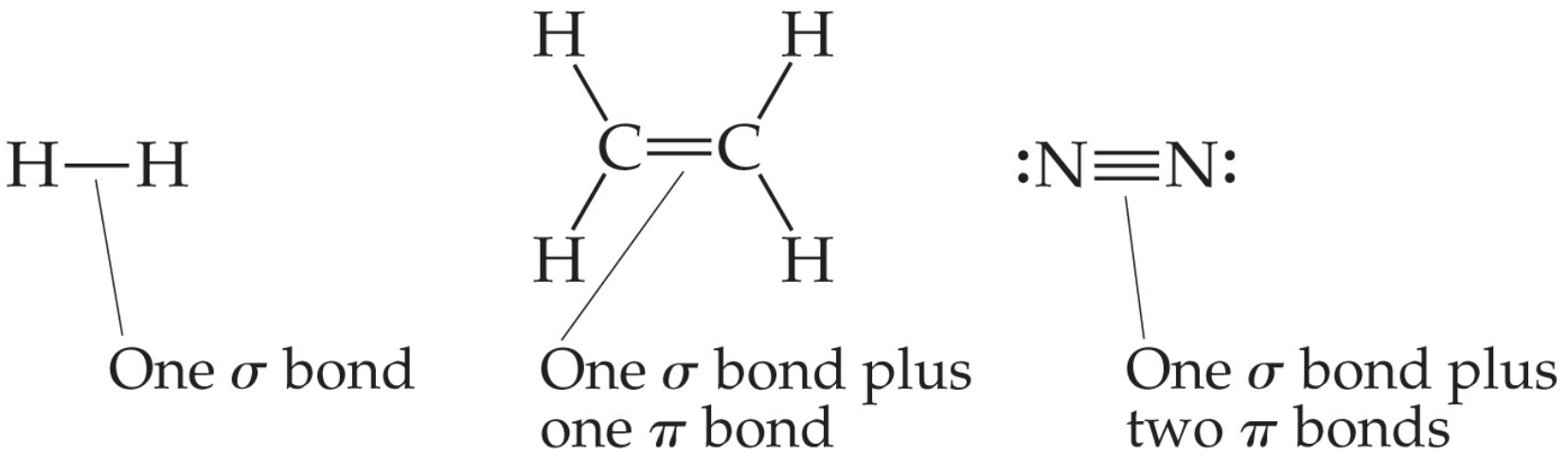
Multiple Bonds

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



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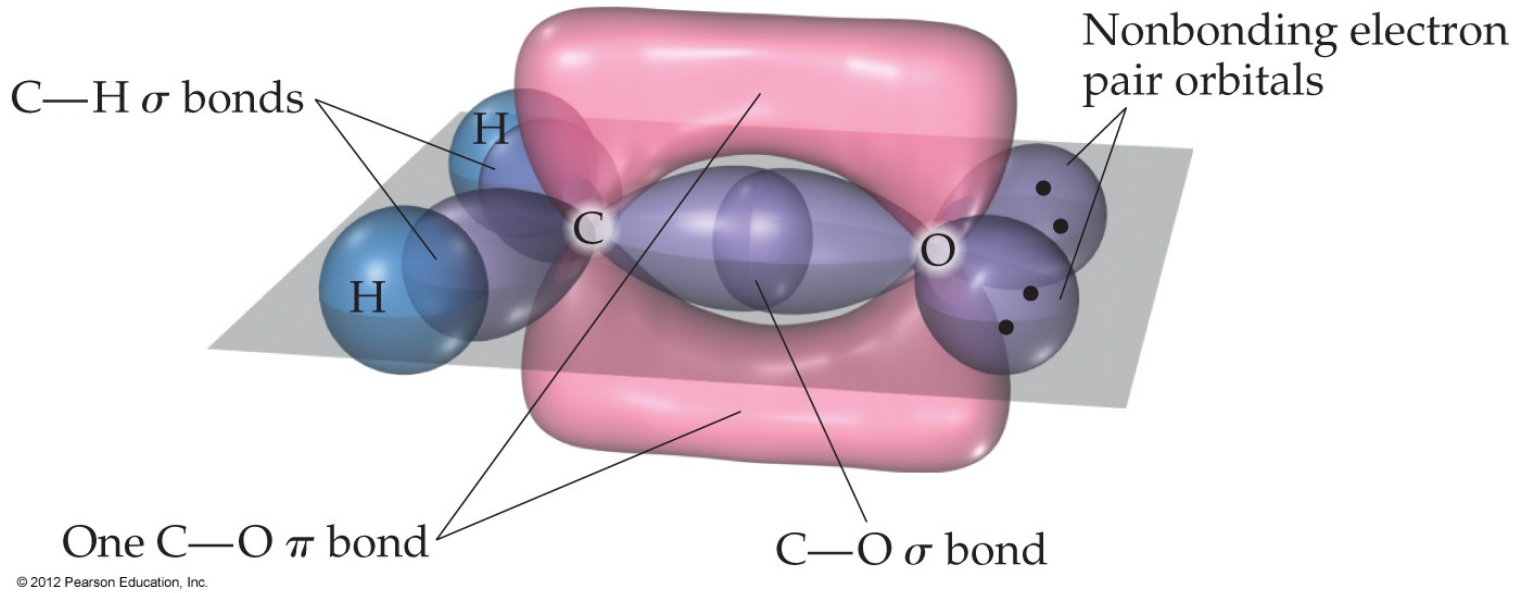
Multiple Bonds



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- In a molecule like formaldehyde (shown at left), an sp^2 orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.
- The unhybridized *p* orbitals overlap in π fashion.

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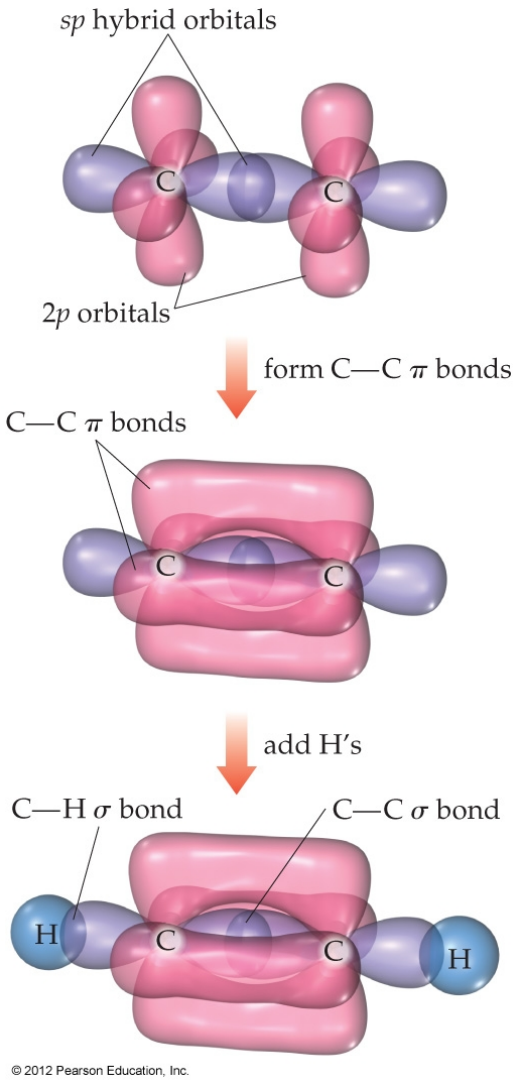
Multiple Bonds

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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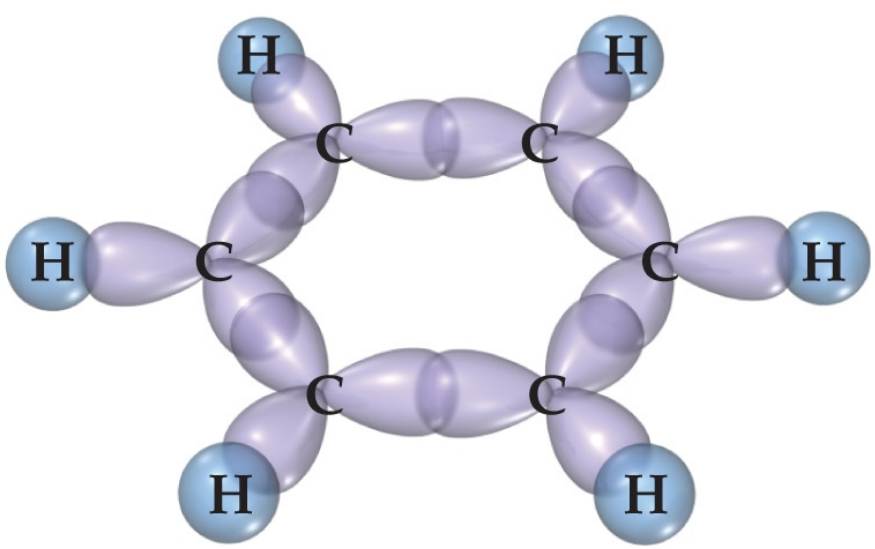
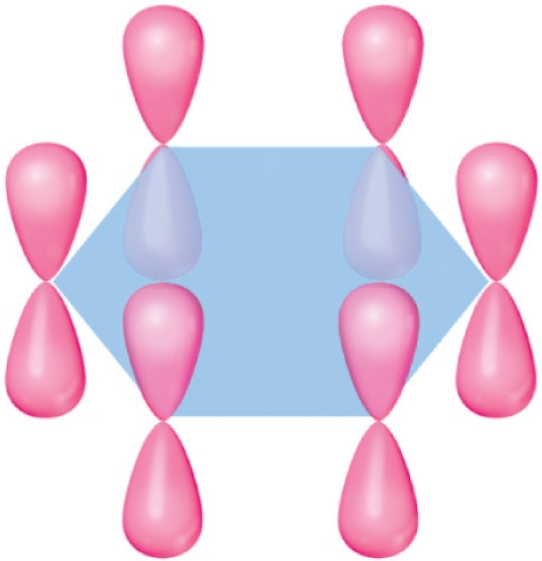
Resonance

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



(a) σ bonds



(b) $2p$ atomic orbitals

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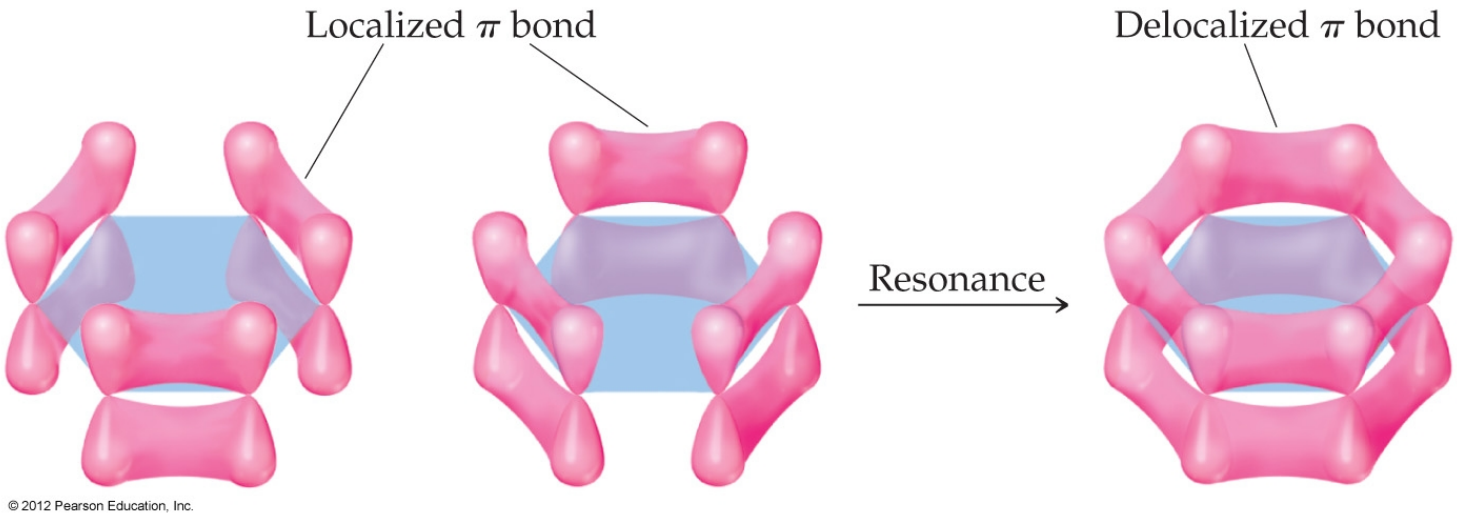
Resonance

- In reality 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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Molecular Orbital Theory

- In MO theory, we apply Schrödinger's wave equation to the molecule to calculate a set of **molecular orbitals**.

- In this treatment, the electrons belong to the whole molecule—so the orbitals belong to the whole molecule.
  - delocalization

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LCAO

- The simplest assumption starts with the atomic orbitals of the atoms adding together to make molecular orbitals. This is called the **linear combination of atomic orbitals** method.

- Because the orbitals are wave functions, the waves can combine either **constructively** or **destructively**.

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Molecular Orbitals

- When the wave functions combine constructively, the resulting molecular orbital has less energy than the original atomic orbitals and 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 and is called an **antibonding molecular orbital**.
  - σ^*, π^*
  - most of the electron density outside the nuclei
  - nodes between nuclei

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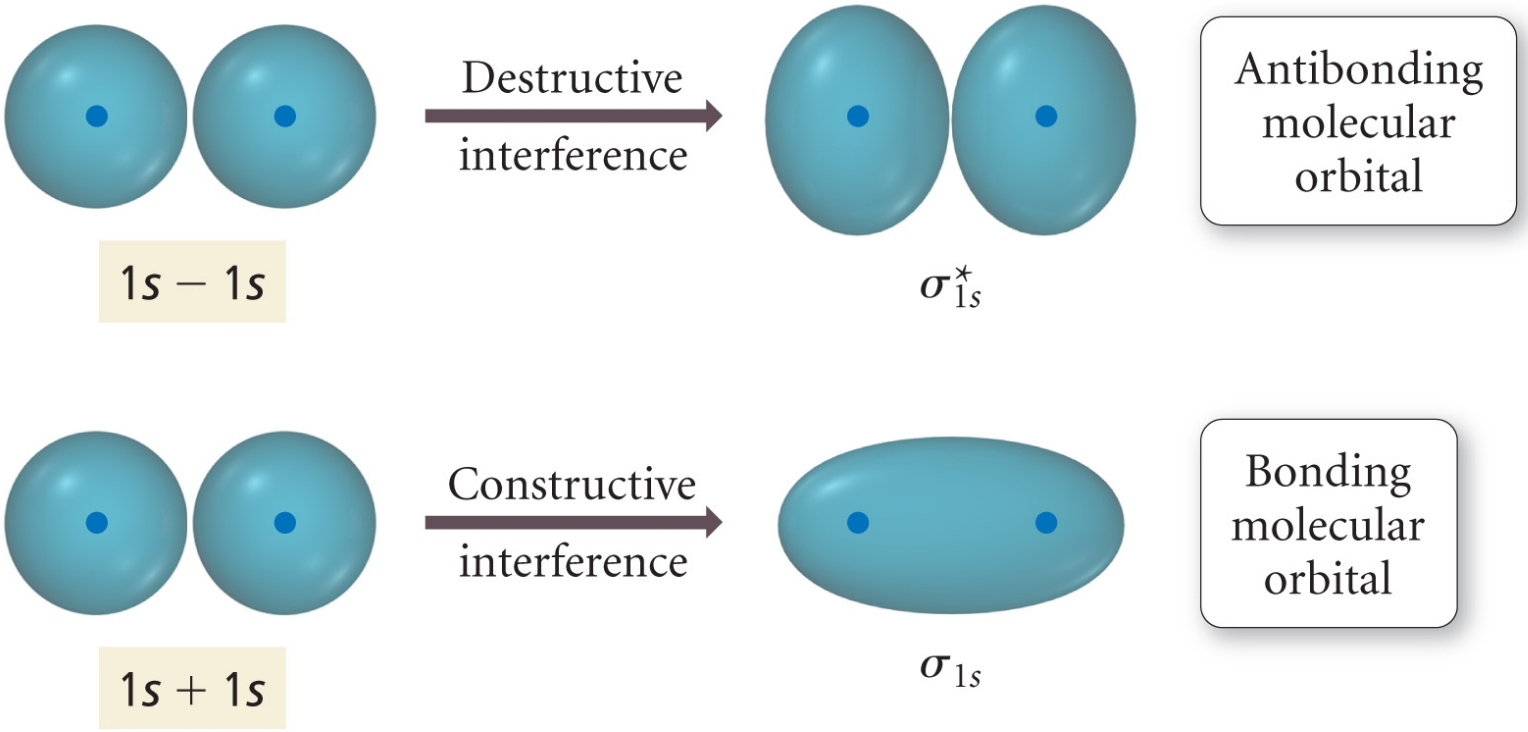
Interaction of 1*s* Orbitals



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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

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MO and Properties

- Bond order is the 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 are paired, it is diamagnetic.

$$\text{Bond Order} = \frac{\#\,\text{Bond Elec.} - \#\,\text{Antibond Elec.}}{2}$$

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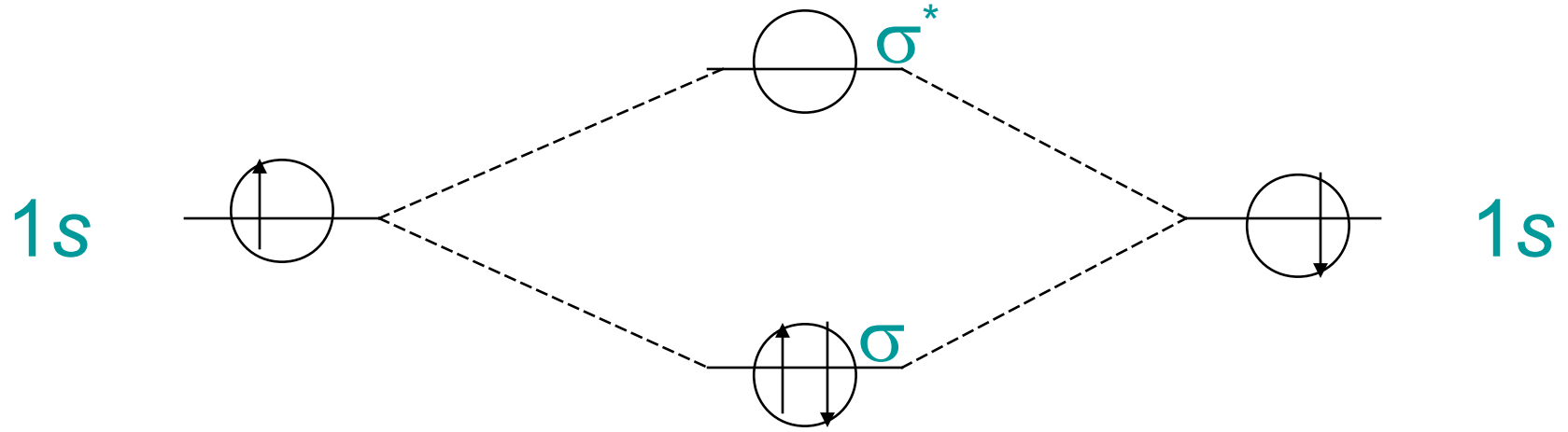
Dihydrogen, H_2

hydrogen atomic orbital

molecular orbitals

hydrogen atomic orbital



Since more electrons are in bonding orbitals than in antibonding orbitals, there is a net bonding interaction.

Molecular Geometries and Bonding

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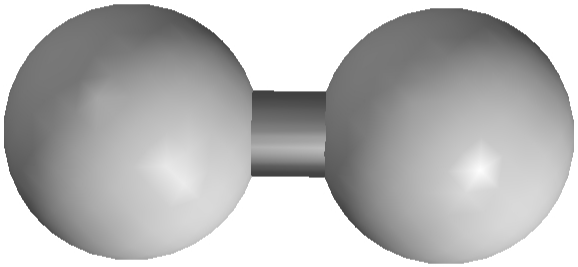
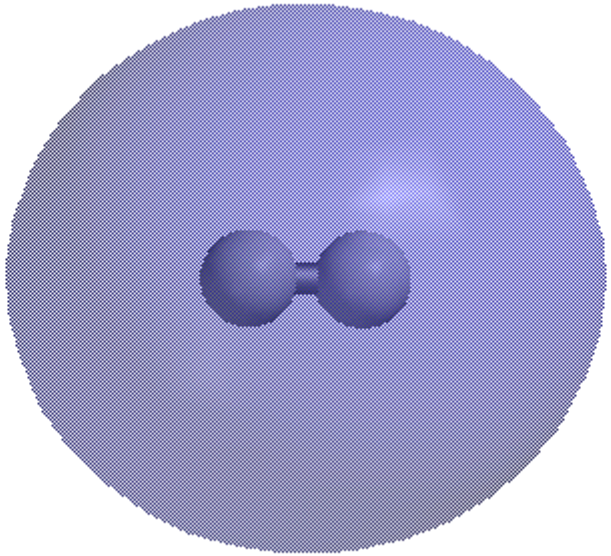
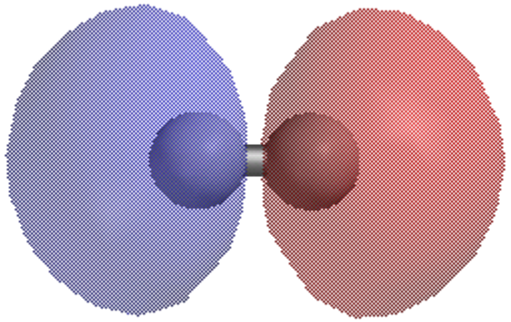


H_2



σ bonding MO
HOMO



σ* Antibonding MO
LUMO

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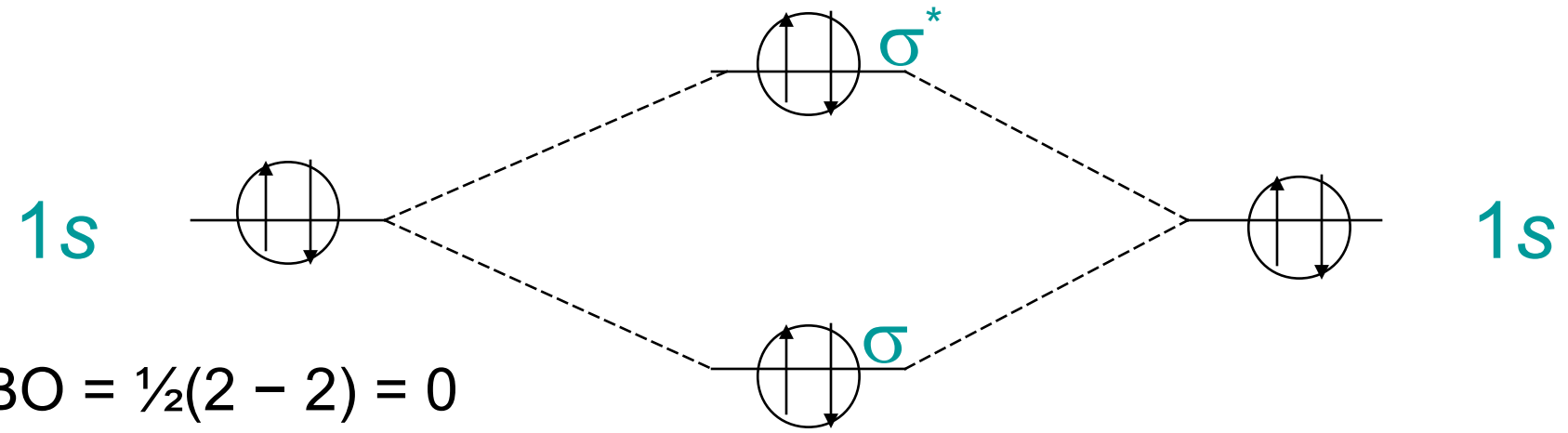
Dihelium, He_2 molecular orbitals

helium atomic orbital

helium atomic orbital



BO = ½(2 − 2) = 0

Since there are as many electrons in antibonding orbitals as in bonding orbitals, there is no net bonding interaction.

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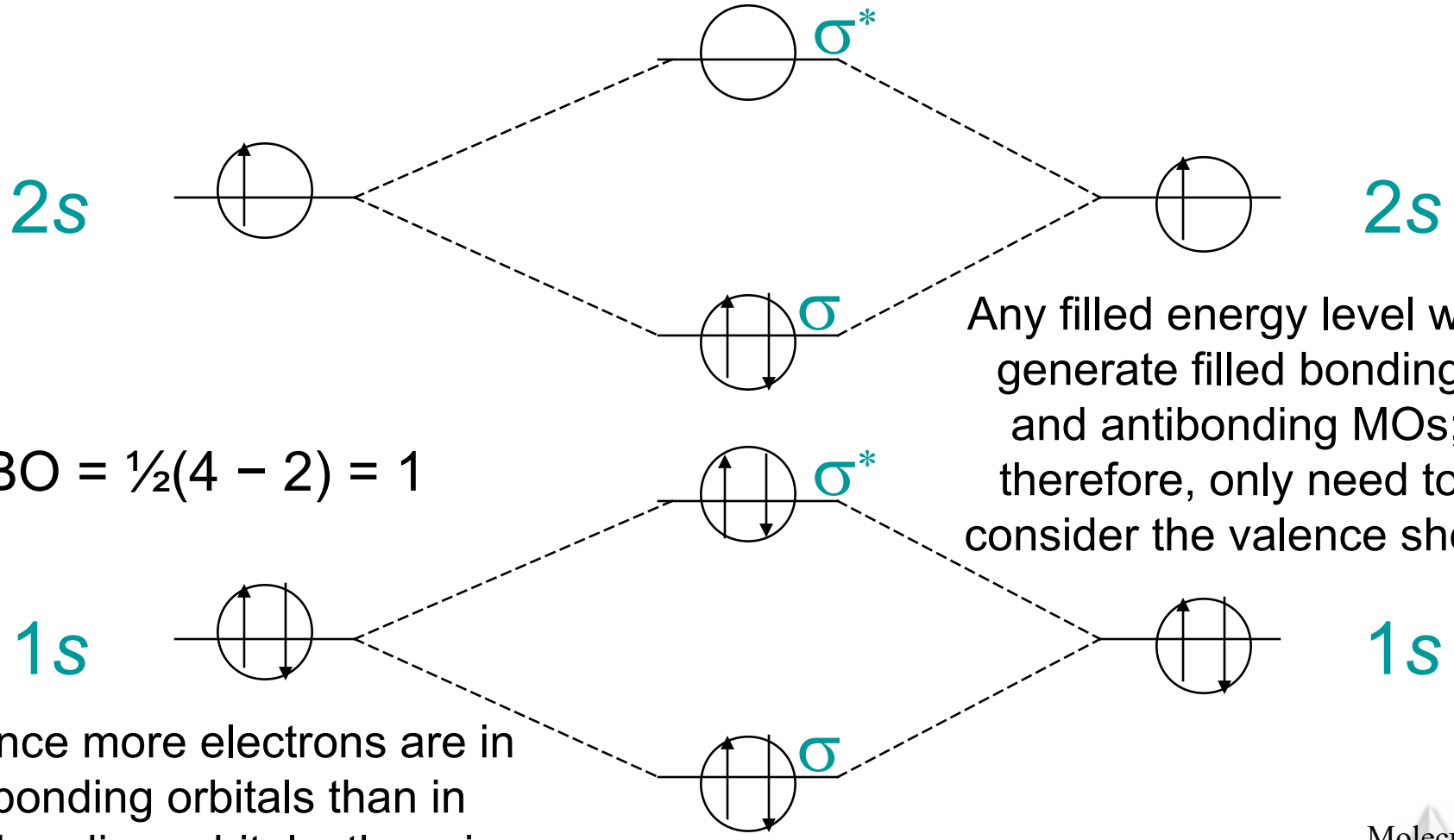
lithium atomic orbitals

Dilithium, Li_2 molecular orbitals

lithium atomic orbitals



Any filled energy level will generate filled bonding and antibonding MOs; therefore, only need to consider the valence shell.

BO = ½(4 − 2) = 1

Since more electrons are in bonding orbitals than in antibonding orbitals, there is a net bonding interaction.

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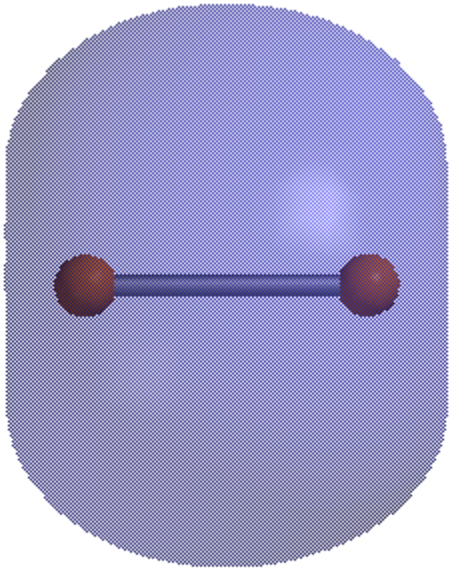
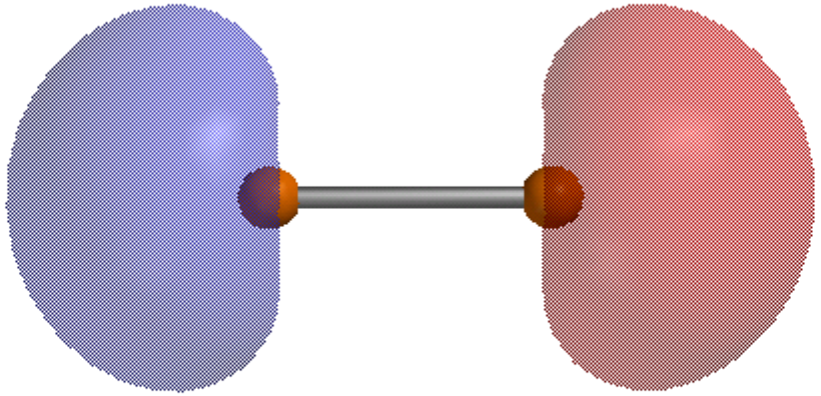
Li_2



σ bonding MO
HOMO



σ* Antibonding MO
LUMO

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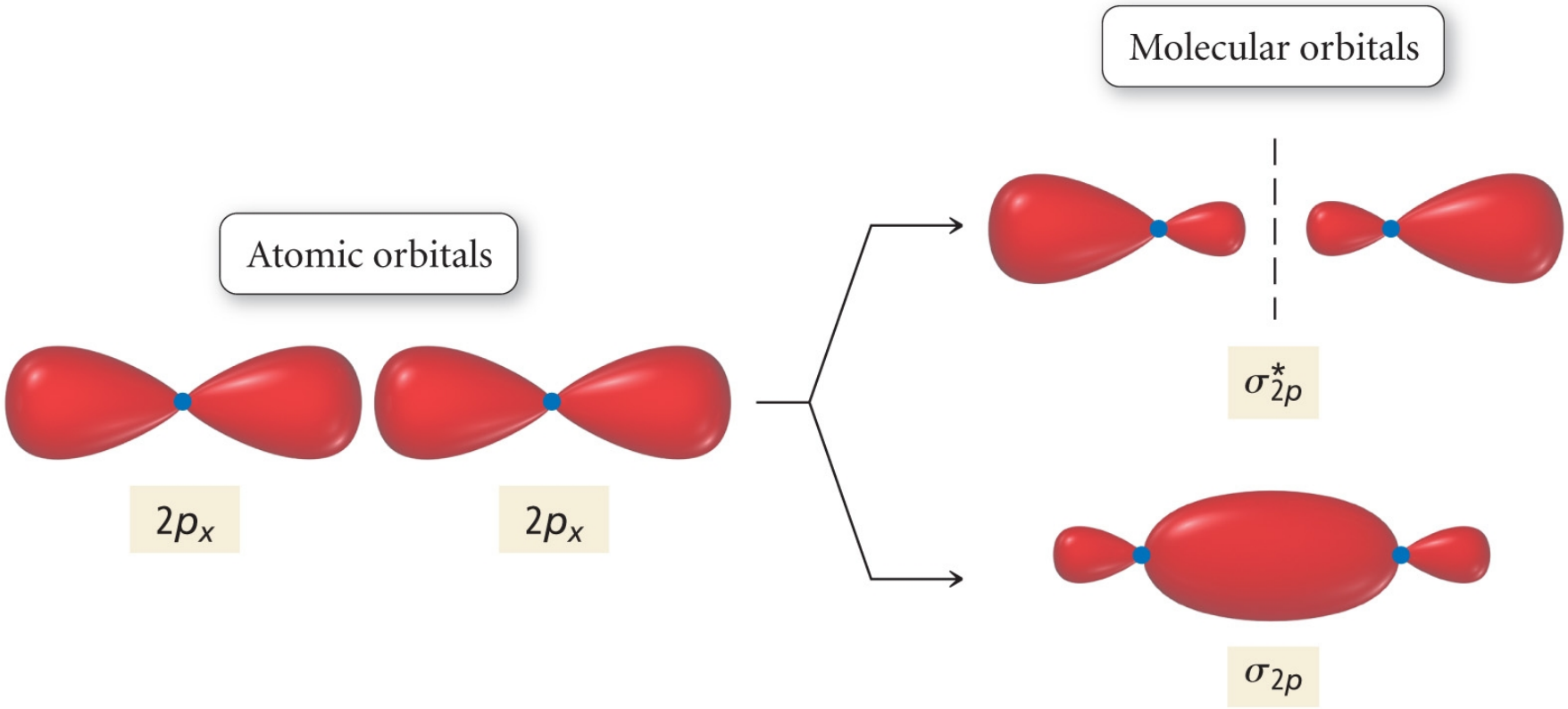
Interaction of *p* Orbitals



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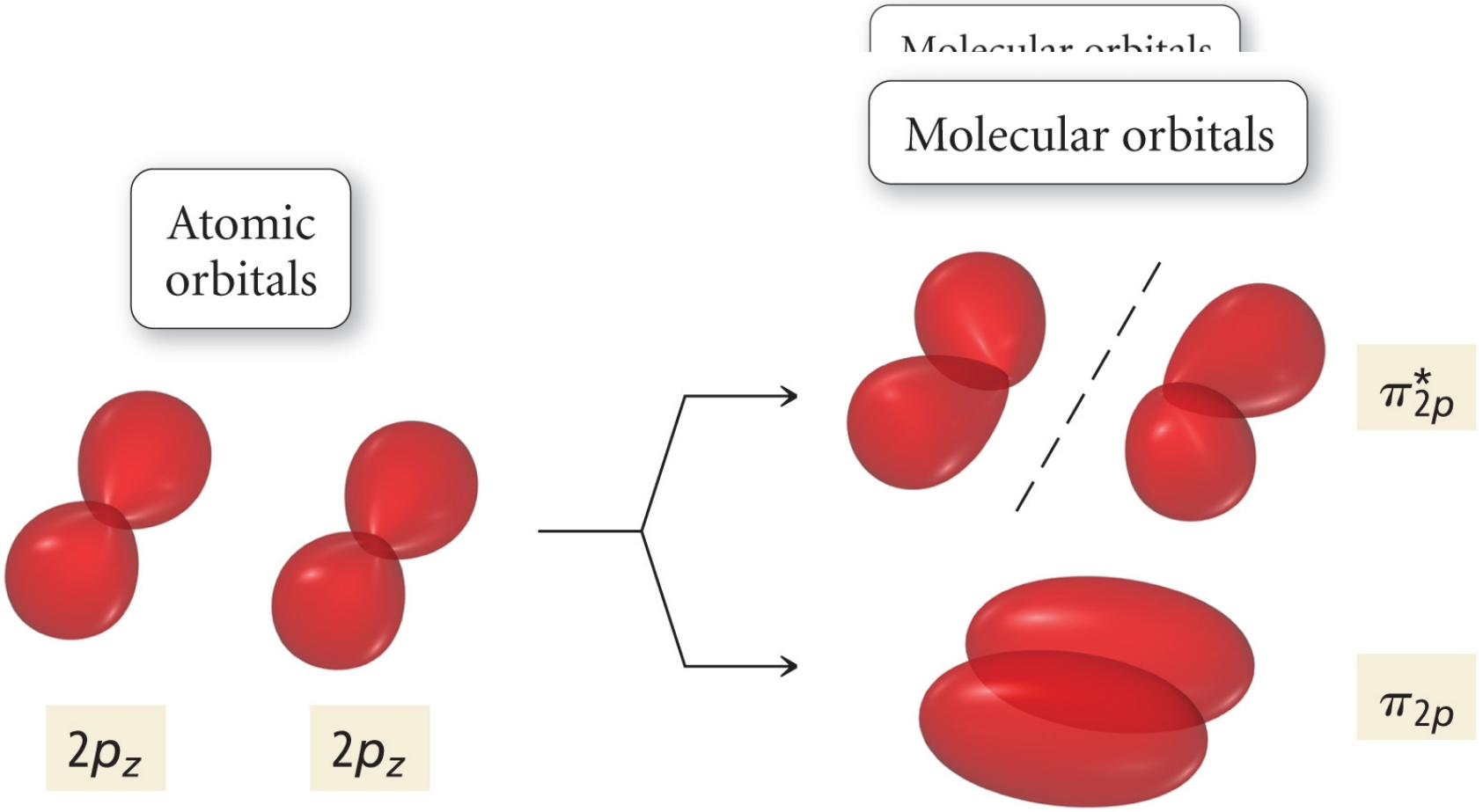
Interaction of *p* Orbitals



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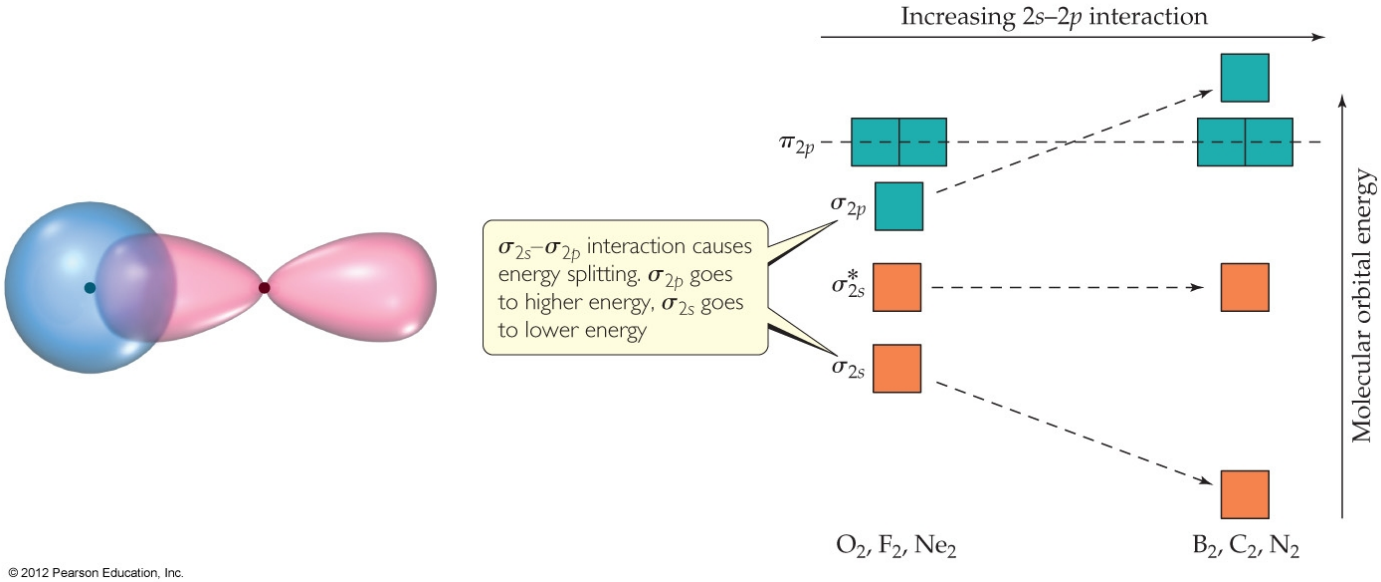
MO Theory



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- The smaller *p*-block elements in the second period have a sizable interaction between the *s* and *p* orbitals.
- This flips the order of the σ and π molecular orbitals in these elements.

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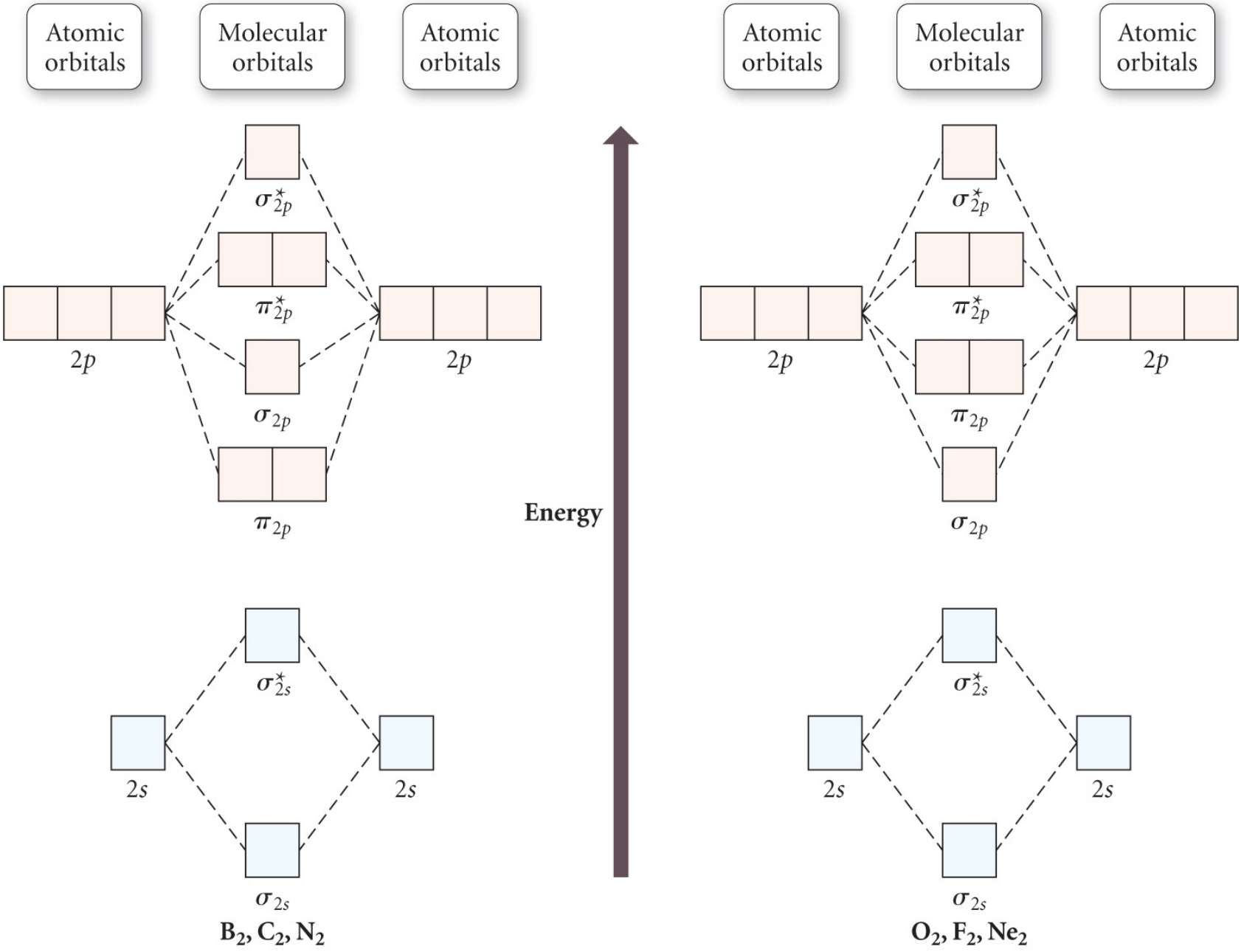

B_2, C_2, N_2

O_2, F_2, Ne_2

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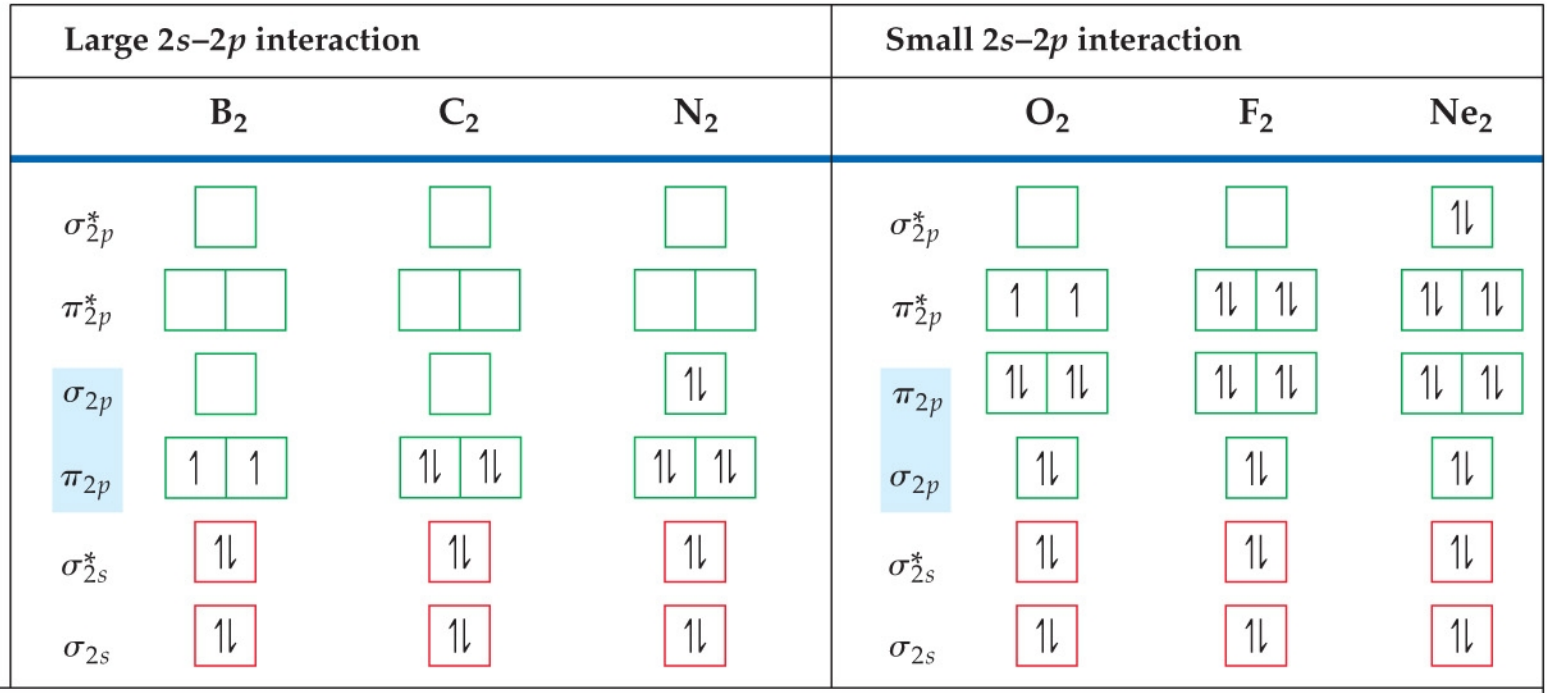
Second-Row MO Diagrams



	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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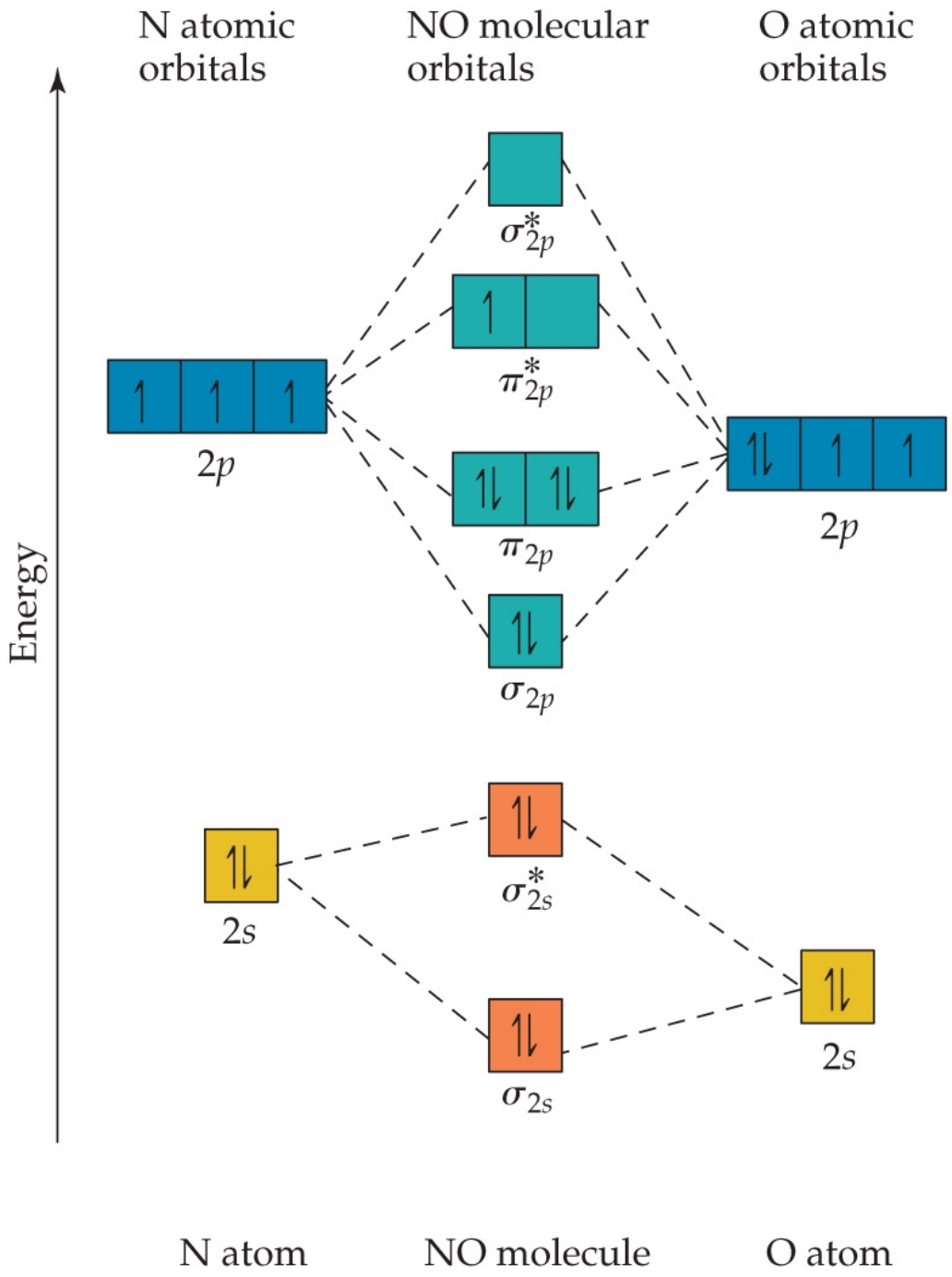

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