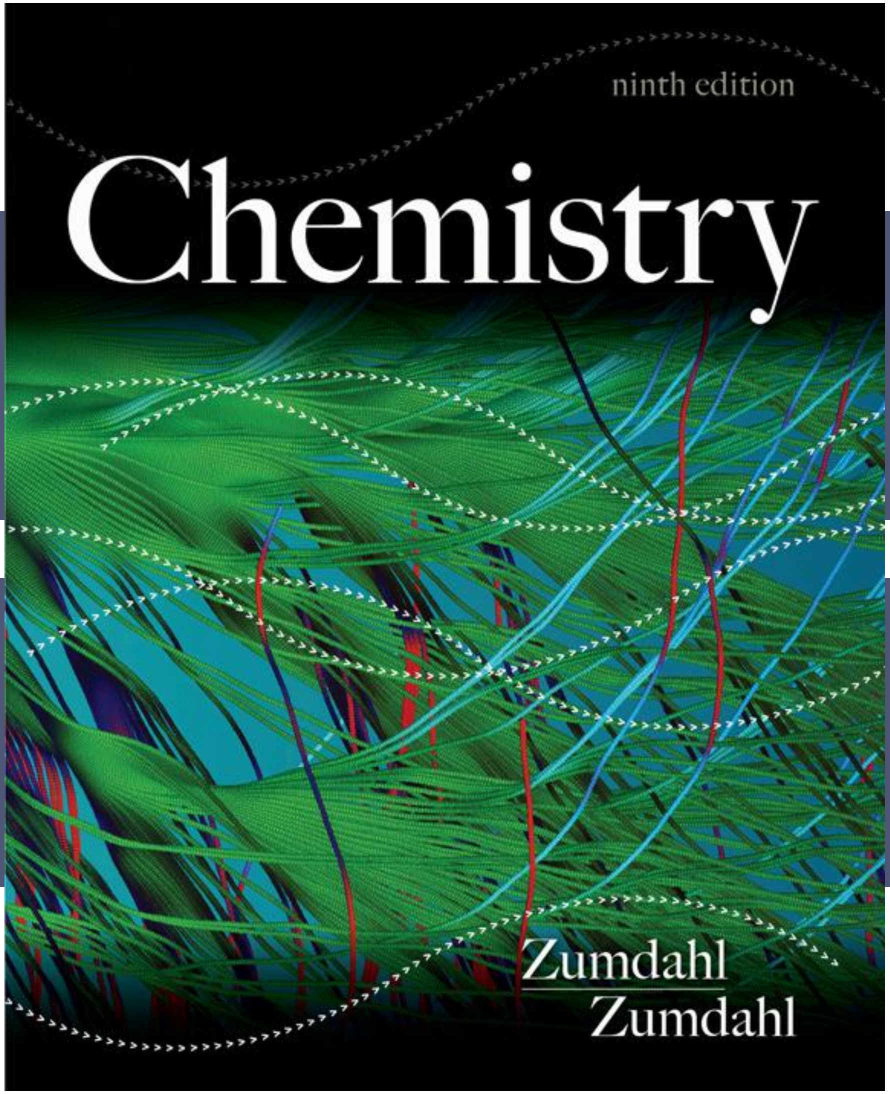


Chapter 9

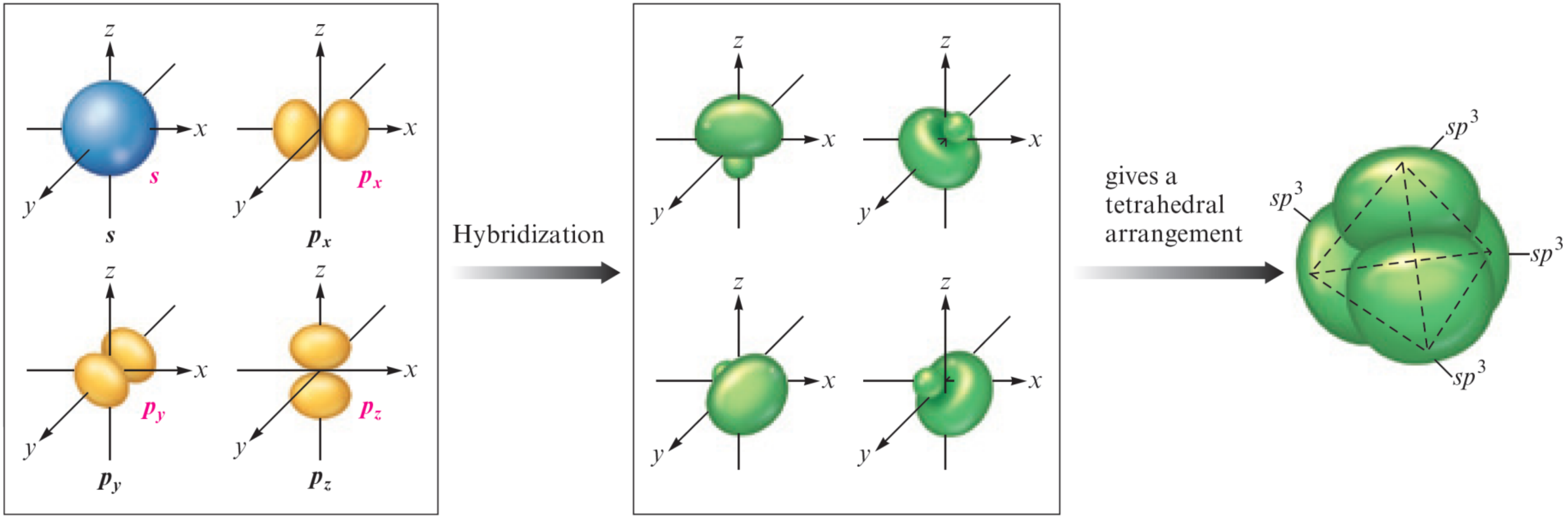
Covalent Bonding: Orbitals

Table of Contents

Hybridization

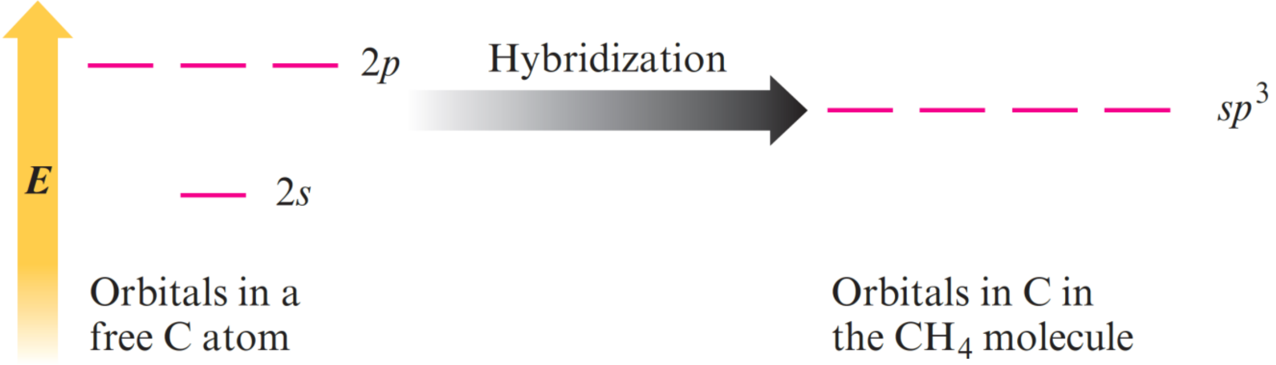
- The mixing of native orbitals to form special orbitals for bonding
- sp^3 orbitals - Formed from one 2*s* and three 2*p* orbitals
  - Atoms that undergo this process are said to be **sp^3 hybridized**

Figure 9.3 - sp^3 Hybridization of a Carbon Atom



Orbital Energy-Level Diagram

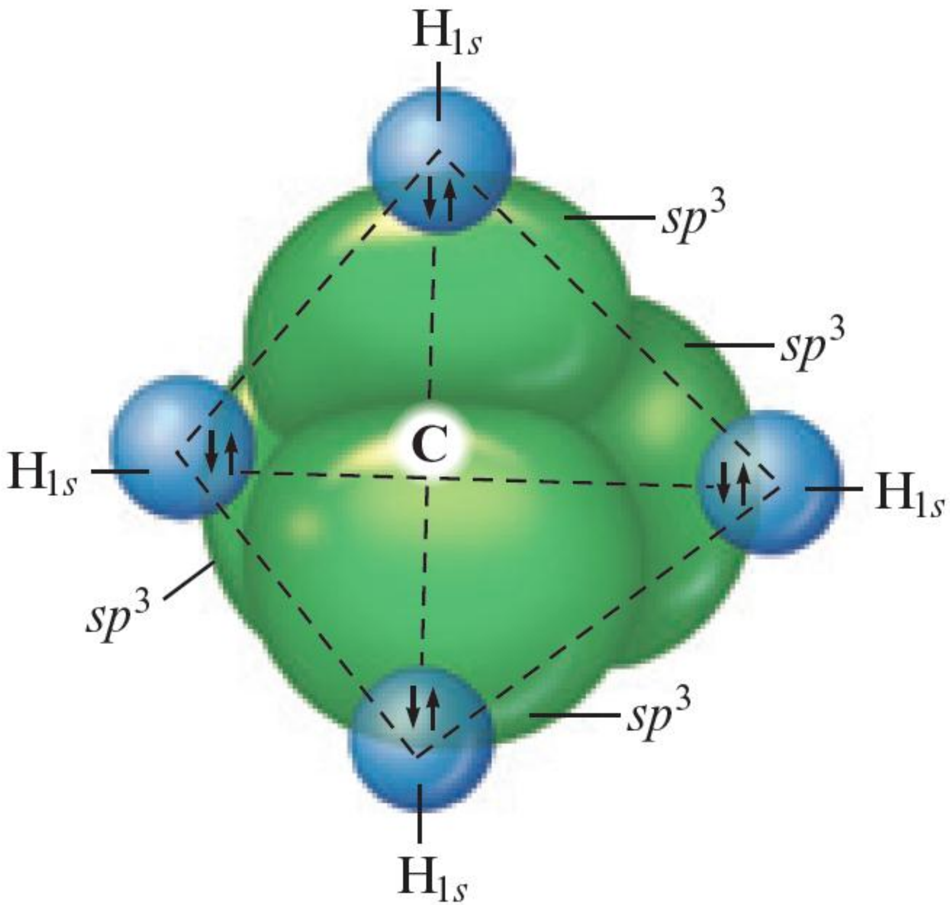
- Gives importance to the total number of electrons and the arrangement of these electrons in the molecule
  - Example - Hybridization of the carbon 2*s* and 2*p* orbitals in methane



Key Principle in sp^3 Hybridization

- Whenever an atom requires a set of equivalent tetrahedral atomic orbitals, this model assumes that the atom adopts a set of sp^3 orbitals
  - The atom undergoes sp^3 hybridization

Figure 9.6 - Tetrahedral Set of Four sp^3 Orbitals



Critical Thinking

- What if the sp^3 hybrid orbitals were higher in energy than the *p* orbitals in the free atom?
  - How would this affect our model of bonding?

Example 9.1 - The Localized Electron Model I

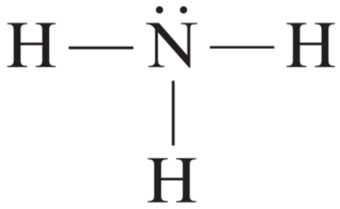
- Describe the bonding in the ammonia molecule using the localized electron model

Example 9.1 - Solution

- A complete description of the bonding involves three steps
  - Writing the Lewis structure
  - Determining the arrangement of electron pairs using the VSEPR model
  - Determining the hybrid atomic orbitals needed to describe the bonding in the molecule

Example 9.1 - Solution (Continued 1)

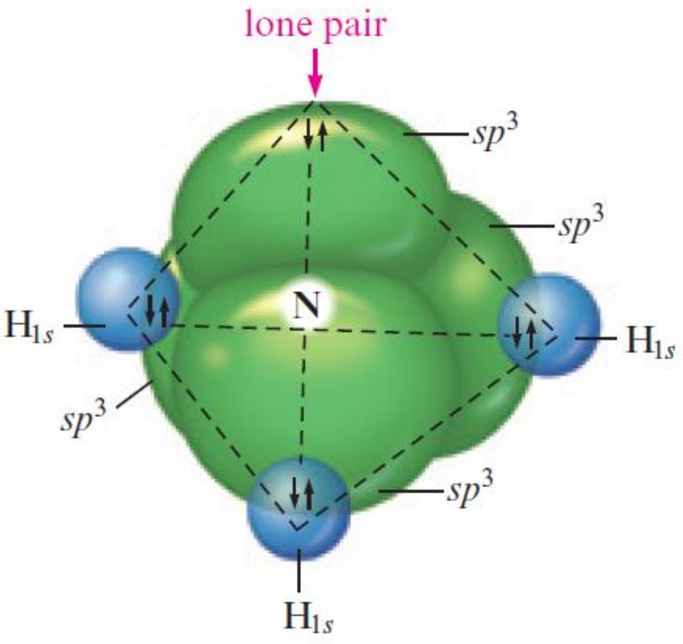
- Lewis structure for NH_3



- The four electron pairs around the nitrogen atom require a tetrahedral arrangement to minimize repulsions
  - A tetrahedral set of sp^3 hybrid orbitals is obtained by combining the 2*s* and three 2*p* orbitals

Example 9.1 - Solution (Continued 2)

- In the NH_3 molecule, three of the *sp*^{3} orbitals are used to form bonds to the three hydrogen atoms, and the fourth *sp*^{3} orbital holds the lone pair



sp^2 Hybridization

- Combination of one 2*s* and two 2*p* orbitals
- Gives a trigonal planar arrangement of atomic orbitals
  - Bond angles - 120 degrees
- One 2*p* orbital is not used
  - Oriented perpendicular to the plane of the *sp*^{2} orbitals

Figure 9.8 - Formation of *sp*^{2} Orbitals

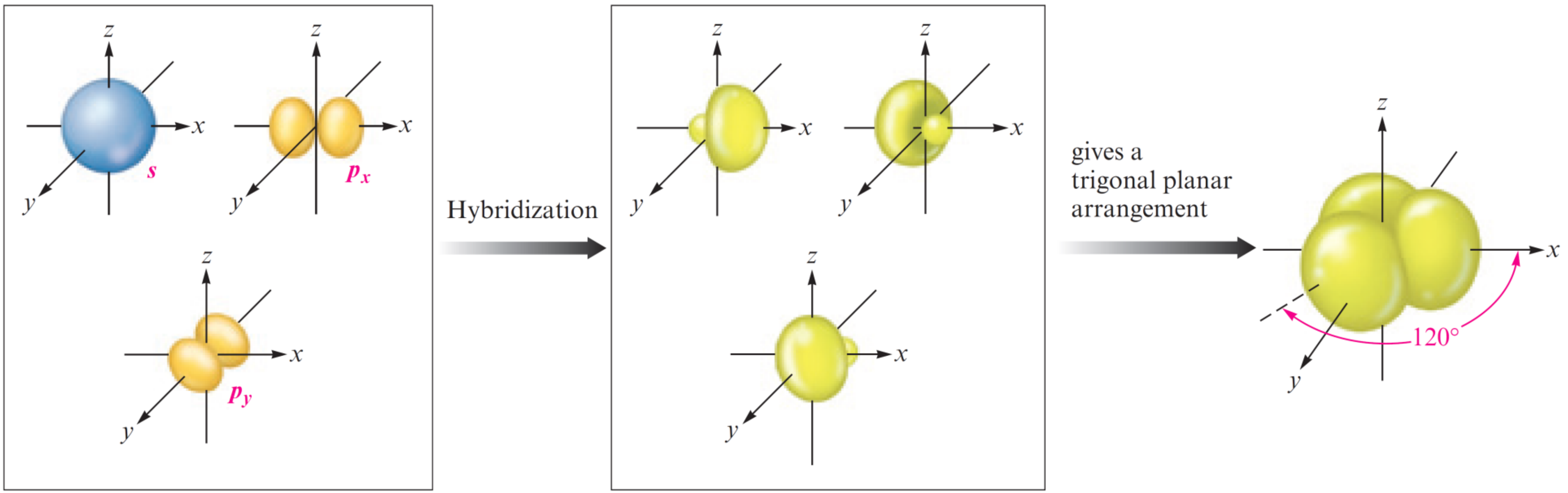


Figure 9.9 - Orbital Energy-Level Diagram for the Formation of sp^2 Orbitals in Ethylene

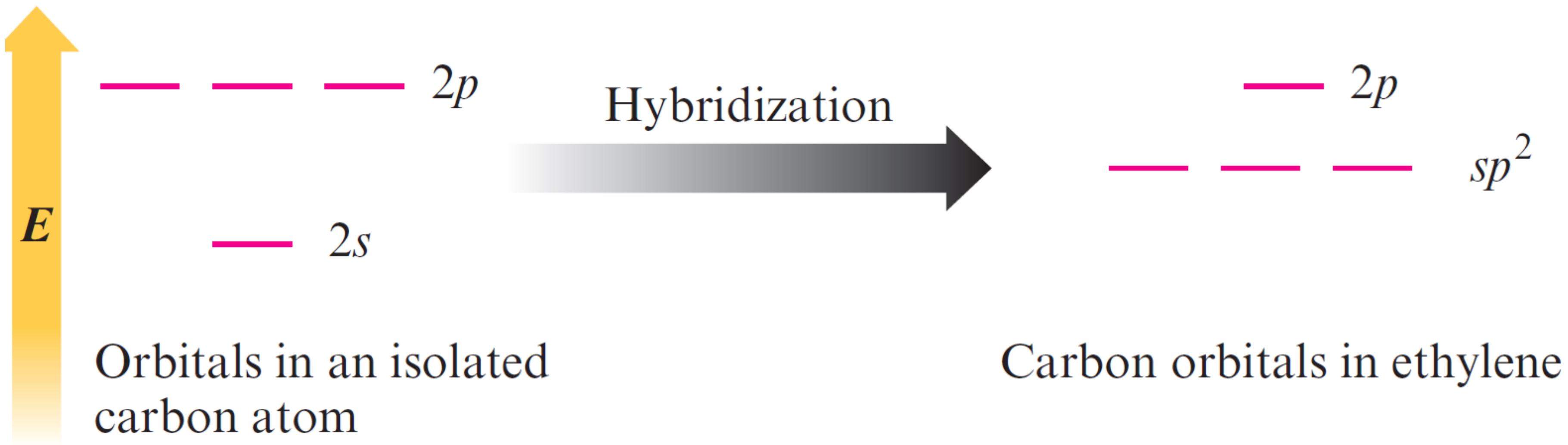
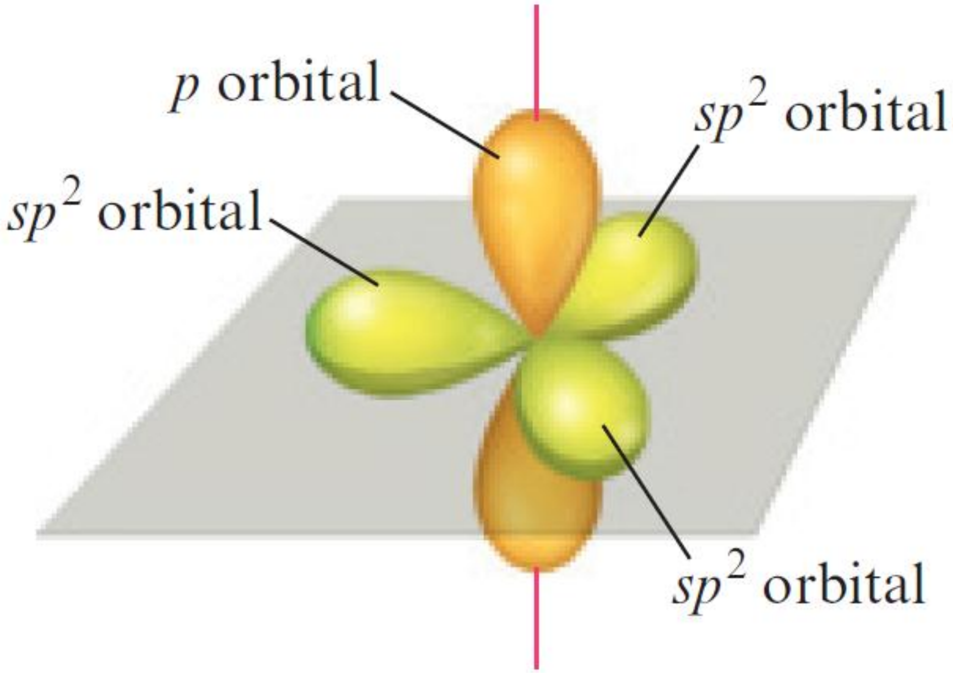


Figure 9.10 - *sp*^{2} Hybridization

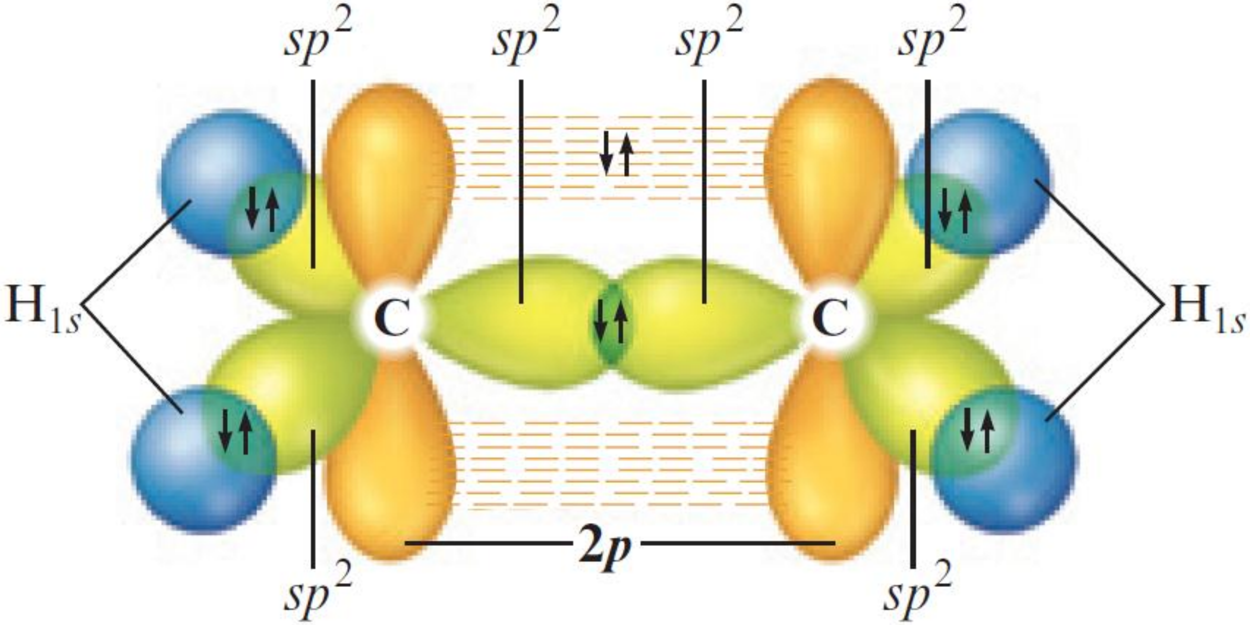


Types of sp^2 Hybridized Bonds

- **Sigma (σ) bond**: Formed by electron sharing in an area centered on a line running between the atoms
- **Pi (π) bond**: Parallel *p* orbitals share an electron pair occupying the space above and below the σ bond
- A double bond always consists of one σ bond and one π bond

Key Principle in *sp*^{2} Hybridization

- If an atom is surrounded by three effective pairs, a set of *sp*^{2} hybrid orbitals is required



sp Hybridization

- Involves one *s* and one *p* orbital
- Two effective pairs around an atom will always requires *sp* hybridization
- Example - Carbon atoms in carbon dioxide
  - Two 2*p* orbitals are unaffected
    - Used in formation of π bonds with oxygen atoms

Figure 9.14 - Formation of *sp* Orbitals

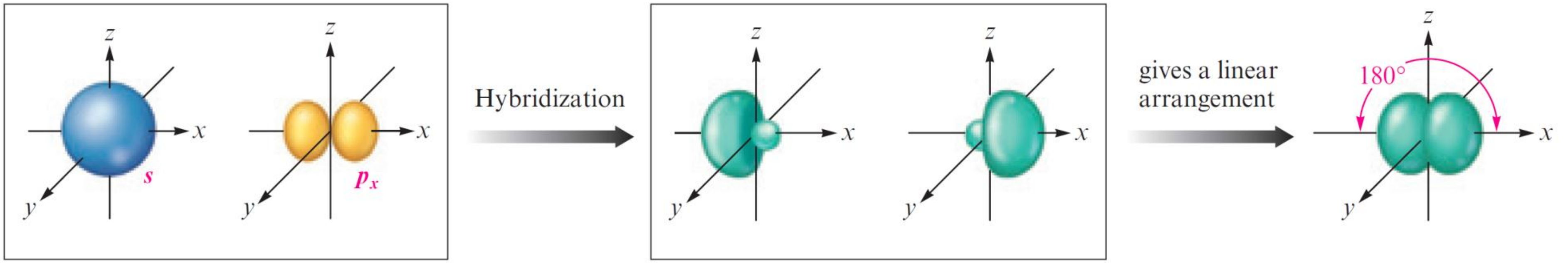


Figure 9.15 - Hybrid Orbitals in the CO_2 Molecule

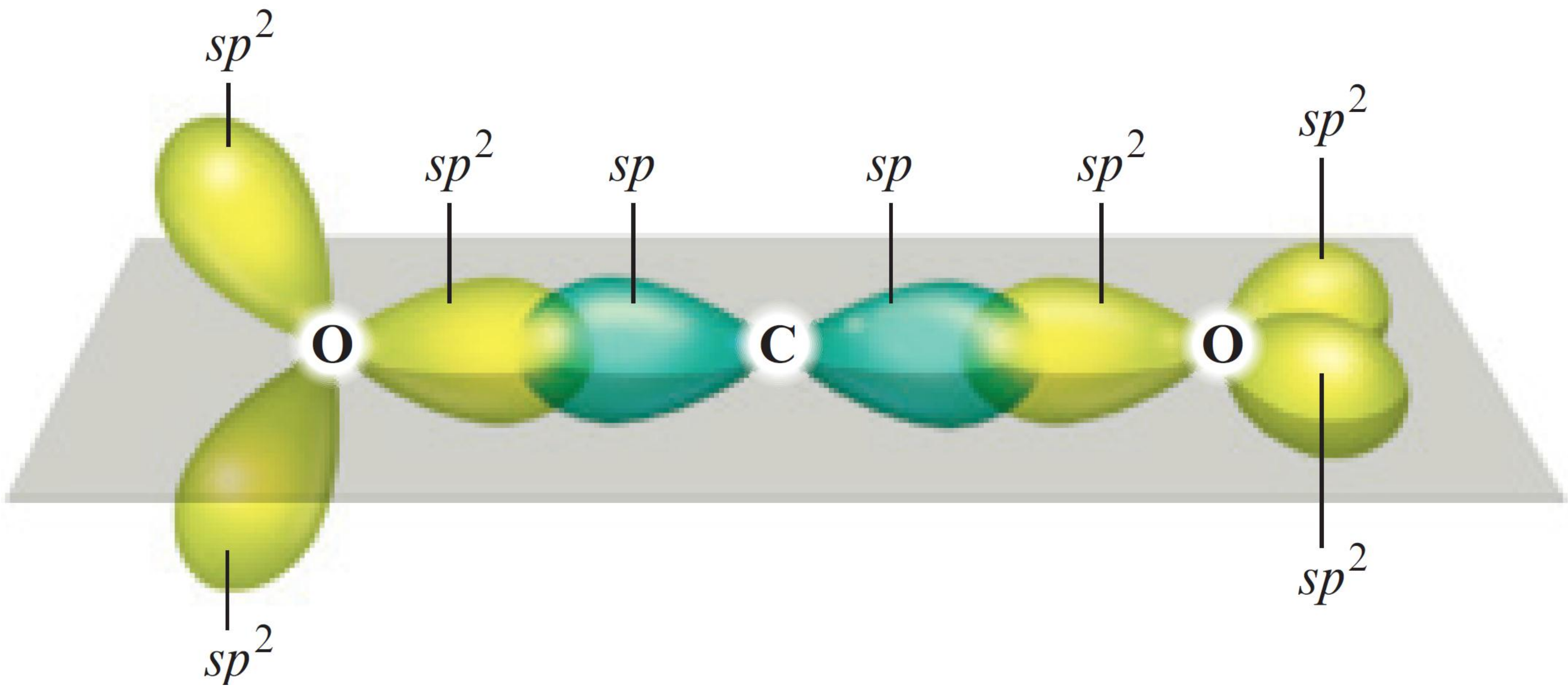


Figure 9.16 - Orbital Energy-Level Diagram for the Formation of *sp* Hybrid Orbitals on Carbon

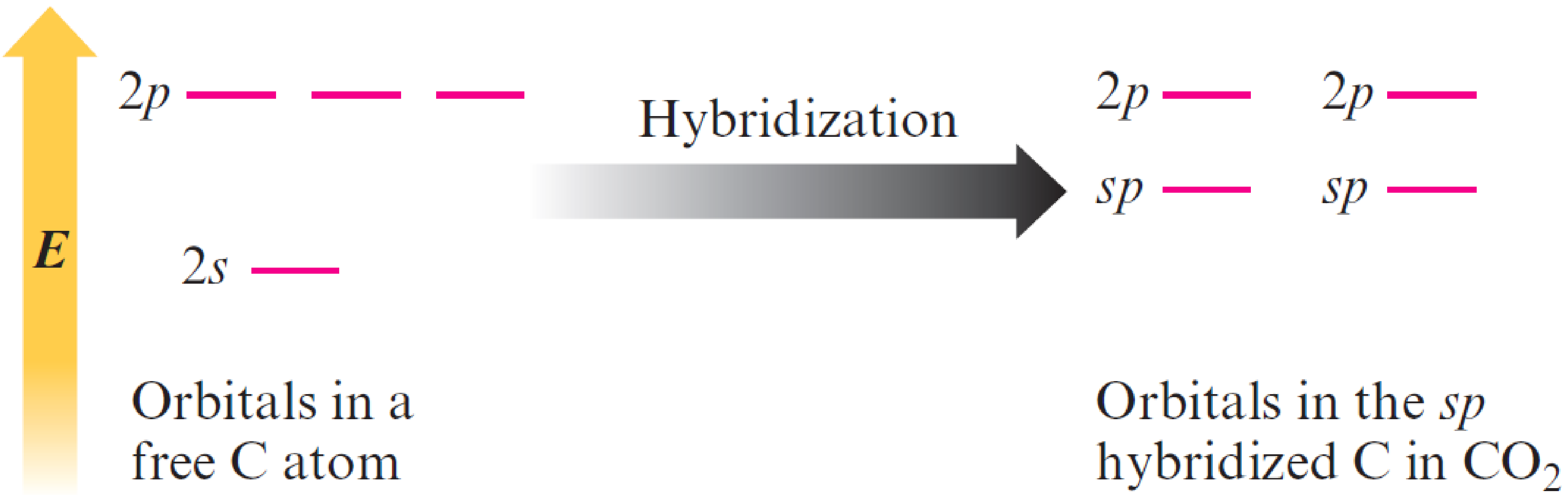


Figure 9.17 - An *sp* Hybridized Carbon Atom

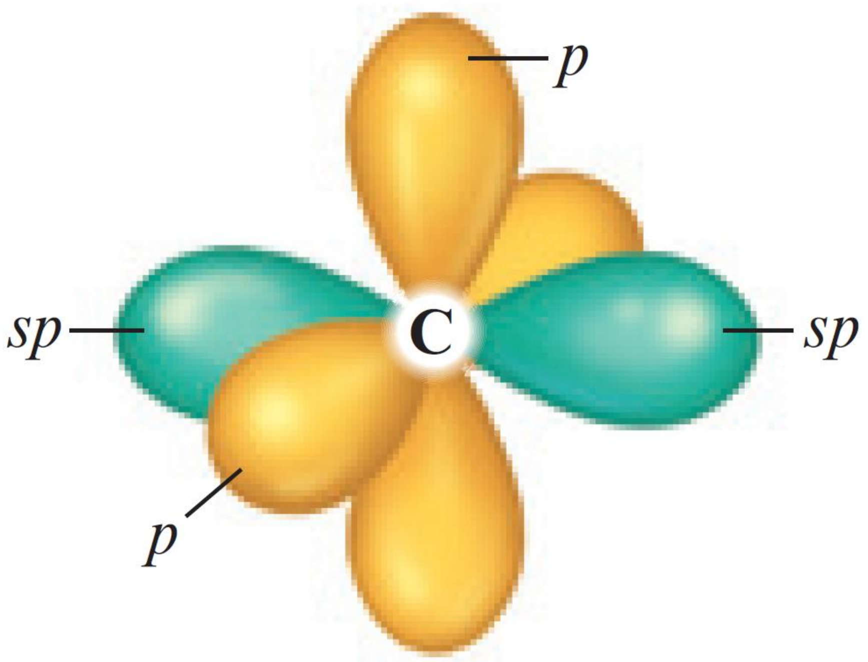
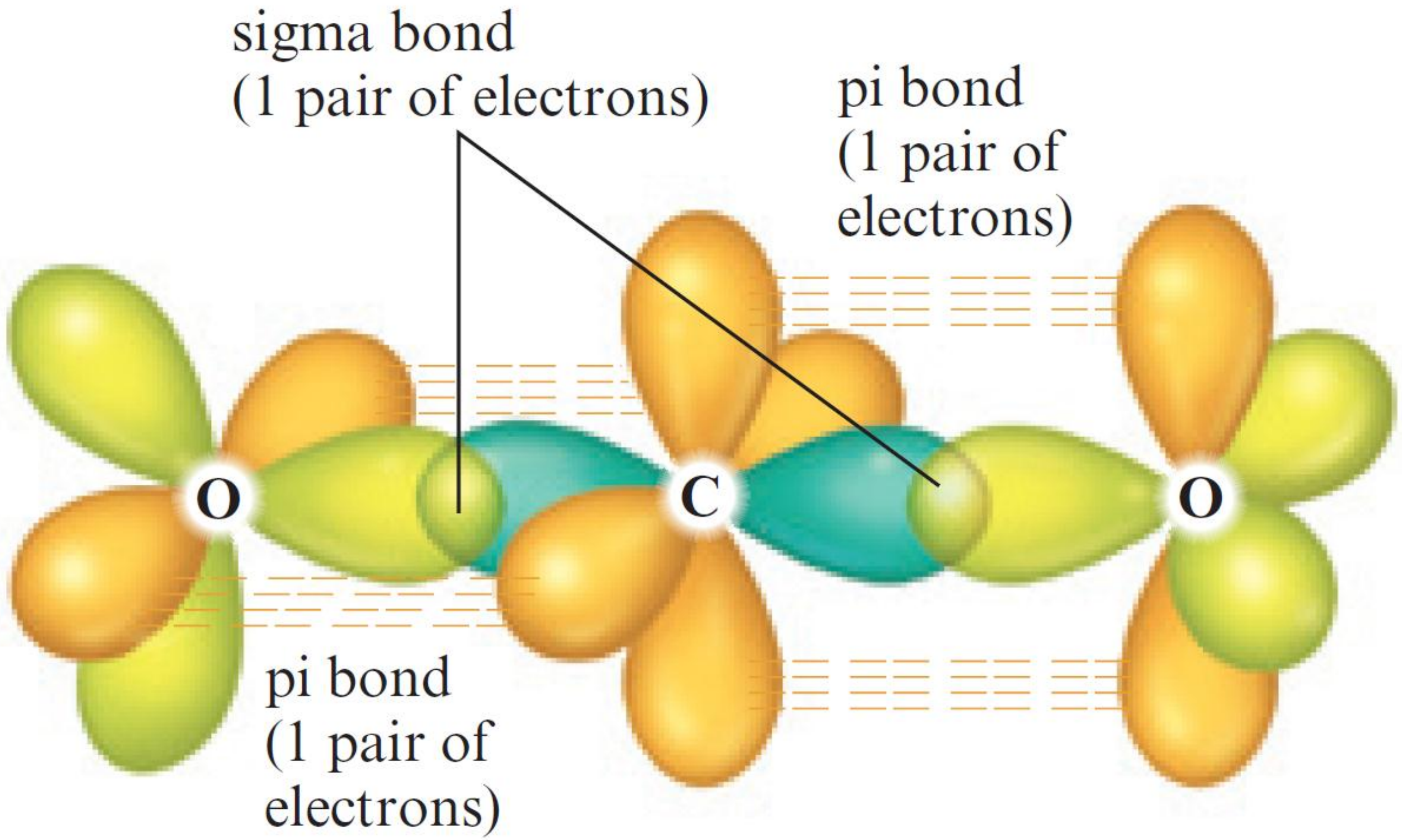


Figure 9.19 (a) - Orbitals Forming Bonds in Carbon Dioxide



Example 9.2 - The Localized Electron Model II

- Describe the bonding in the N_2 molecule

Example 9.2 - Solution

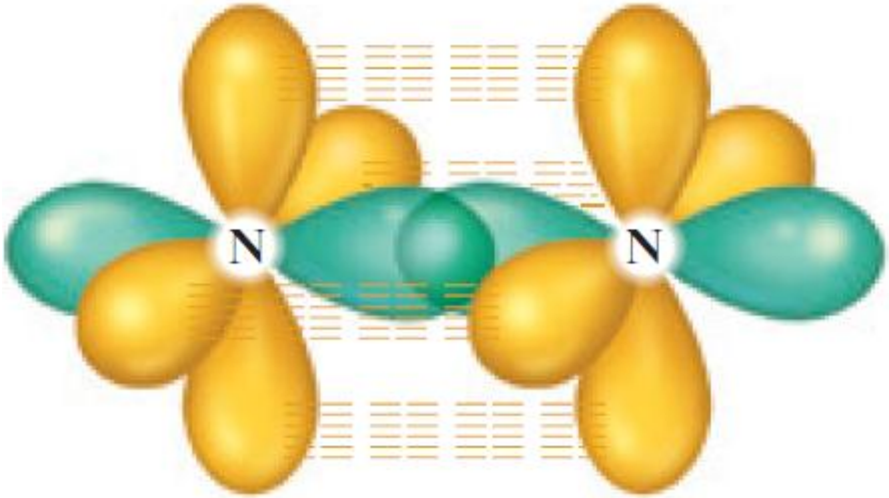
- The Lewis structure for N_2 is $:N\equiv N:$
- Each nitrogen atom is surrounded by two effective pairs
  - Gives a linear arrangement requiring a pair of oppositely directed orbitals
    - Requires *sp* hybridization

Example 9.2 - Solution (Continued 1)

- Each nitrogen atom has two *sp* hybrid orbitals and two unchanged *p* orbitals
  - *sp* orbitals form the σ bond between the nitrogen atoms and hold lone pairs
  - *p* orbitals form the two π bonds
- Each pair of overlapping parallel *p* orbitals holds one electron pair
  - Accounts for electron arrangement given in the Lewis structure

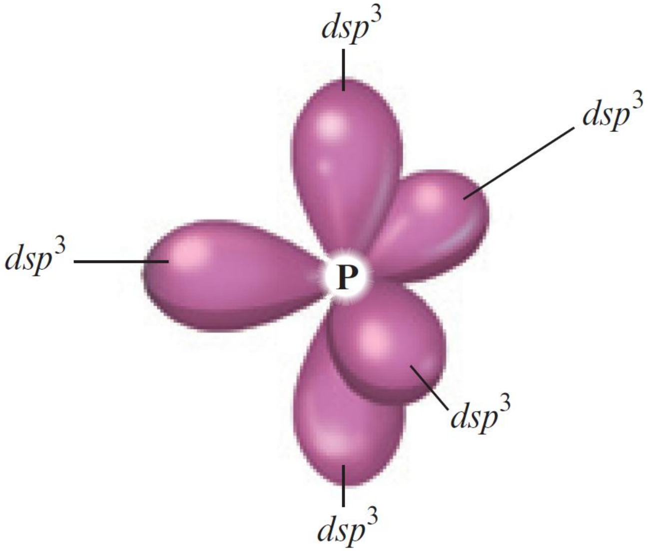
Example 9.2 - Solution (Continued 2)

- The triple bond consists of a σ bond and two π bonds
- A lone pair occupies an *sp* orbital on each nitrogen atom



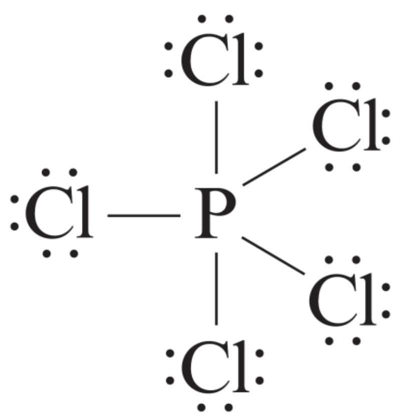
*dsp*³ Hybridization

- Combination of one *d*, one *s*, and three *p* orbitals
- A set of five effective pairs around a given atom always requires a trigonal bipyramidal arrangement
  - Requires dsp^3 hybridization of that atom



dsp^3 Hybridization (Continued)

- Each chlorine atom in PCl_5 is surrounded by four electron pairs
  - Requires a tetrahedral arrangement
  - Each chlorine atom requires four *sp*^{3} orbitals



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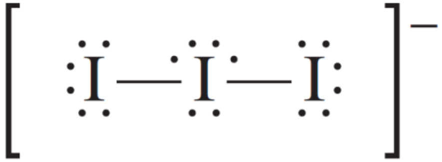
Example 9.3 - The Localized Electron Model III

- Describe the bonding in the triiodide ion (I_3^-)

Example 9.3 - Solution

- The Lewis structure for I_3^-



- The central iodine atom has five pairs of electrons
    - Requires a trigonal bipyramidal arrangement, which in turn requires a set of dsp^3 orbitals
- Outer iodine atoms have four pairs of electrons
    - Requires tetrahedral arrangement and sp^3 hybridization

Example 9.3 - Solution (Continued)

- The central iodine atom is dsp^3 hybridized
  - Three hybrid orbitals hold lone pairs
  - Two hybrid orbitals overlap with sp^3 orbitals of the other two iodine atoms to form σ bonds

d^2sp^3 Hybridization

- Combination of two *d*, one *s*, and three *p* orbitals
- Requires an octahedral arrangement of six equivalent hybrid orbitals
- Six electron pairs around an atom are always arranged octahedrally
  - Require d^2sp^3 hybridization of the atom

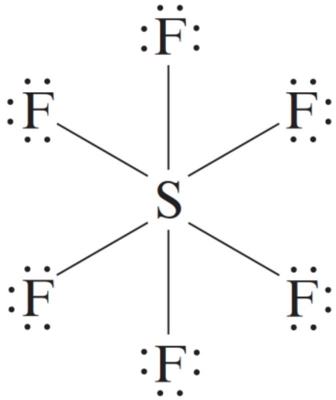
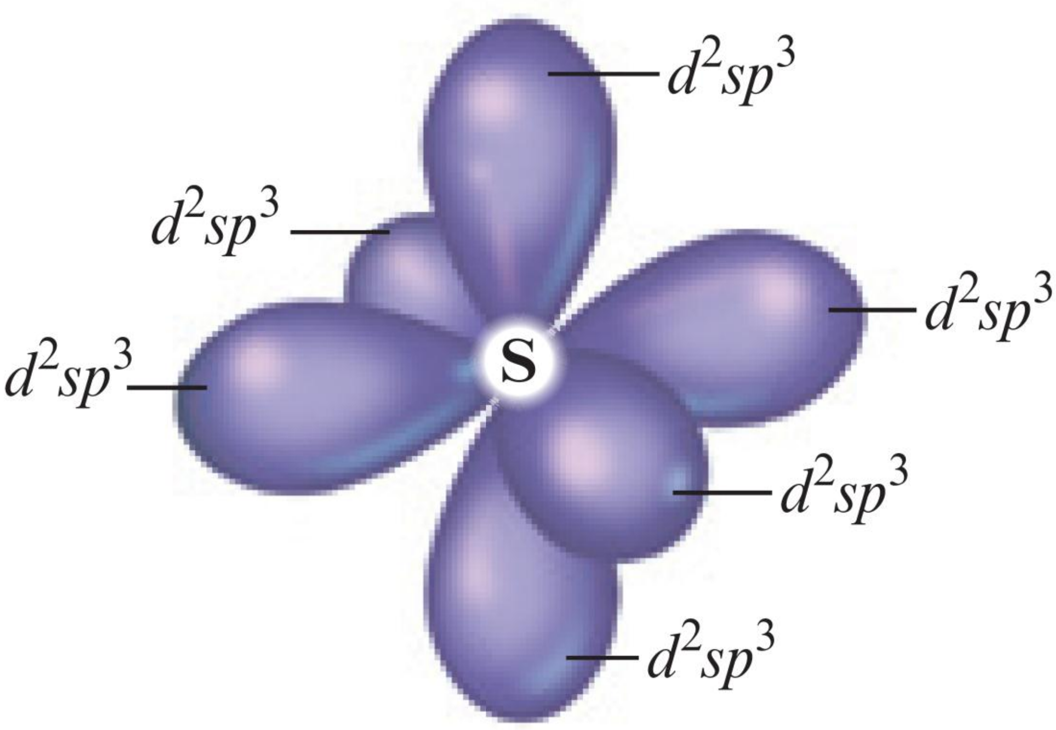


Figure 9.23 - An Octahedral Set of d^2sp^3 Orbitals on a Sulfur Atom



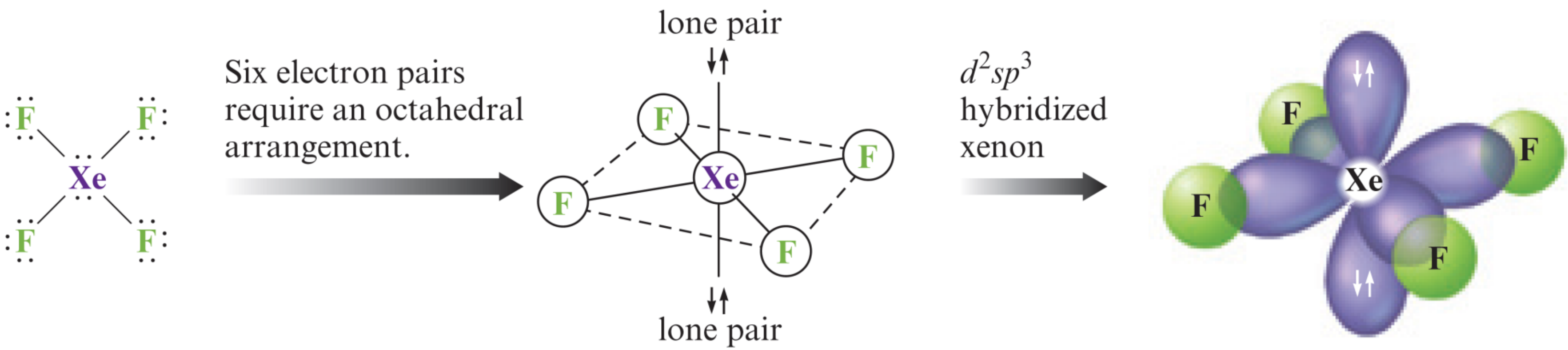
Interactive Example 9.4 - The Localized Electron Model IV

- How is the xenon atom in XeF_4 hybridized?

Interactive Example 9.4 - Solution

- XeF_4 has six pairs of electrons around xenon that are arranged octahedrally to minimize repulsions
  - An octahedral set of six atomic orbitals is required to hold these electrons, and the xenon atom is d^2sp^3 hybridized

Interactive Example 9.4 - Solution (Continued)



Lewis structure

Octahedral arrangement of six electron pairs

Xenon uses six d^2sp^3 hybrid atomic orbitals to bond to the four fluorine atoms and to hold the two lone pairs.

Problem Solving Strategy - Using the Localized Electron Model

- Draw the Lewis structure(s)
- Determine the arrangement of electron pairs using the VSEPR model
- Specify the hybrid orbitals required to accommodate the electron pairs

Figure 9.24 - Relationship between the Number of Effective Pairs, Spatial Arrangement, and Hybrid Orbitals

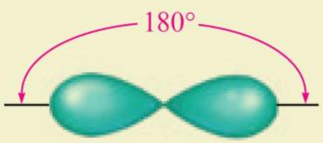
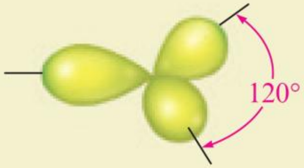
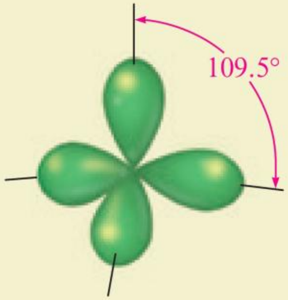
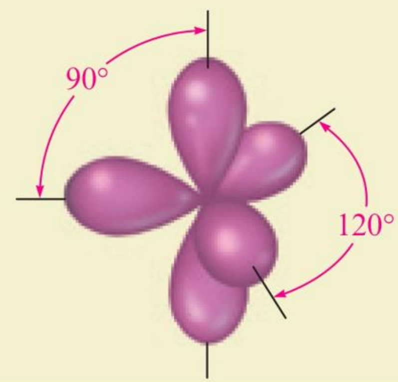
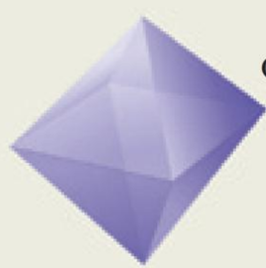
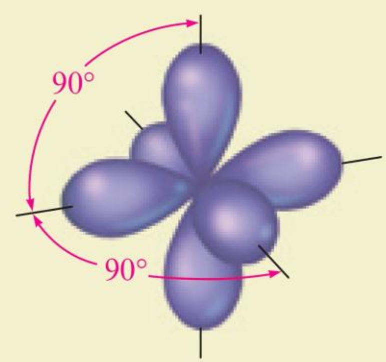
Number of Effective Pairs	Arrangement of Pairs	Hybridization Required
2	Linear	*sp* 
3	 Trigonal planar	sp^2 
4	 Tetrahedral	sp^3 

Figure 9.24 - Relationship between the Number of Effective Pairs, Spatial Arrangement, and Hybrid Orbitals (Continued)

Number of Effective Pairs	Arrangement of Pairs	Hybridization Required
5	 Trigonal bipyramidal	dsp^3 
6	 Octahedral	d^2sp^3 

Interactive Example 9.5 - The Localized Electron Model V

- For each of the following molecules or ions, predict the hybridization of each atom, and describe the molecular structure
  a. CO
  b. BF_4^-
  c. XeF_2

Interactive Example 9.5 - Solution (a)

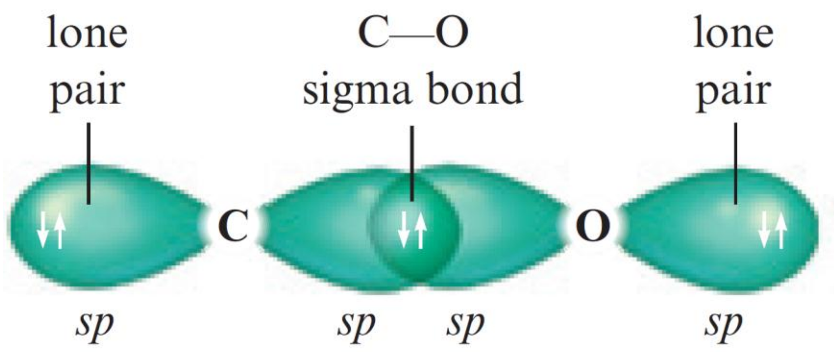
- The CO molecule has 10 valence electrons

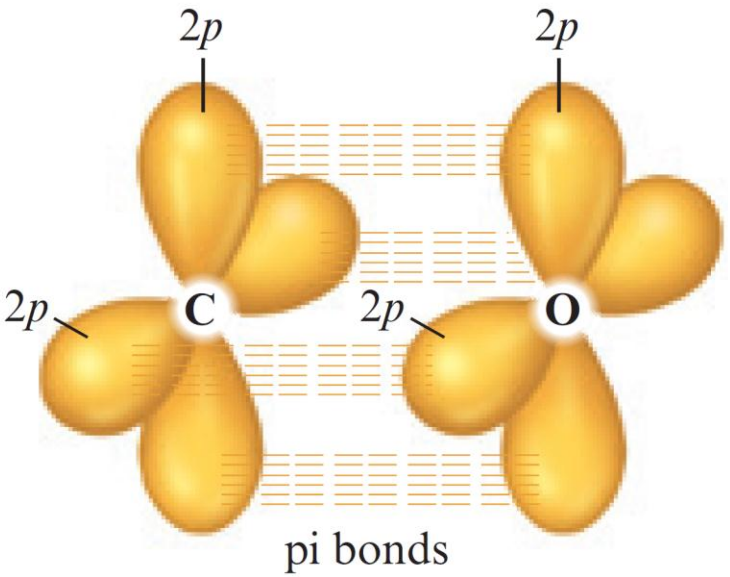
$$:C\equiv O:$$

  - Each atom has two effective pairs, which means that both are *sp* hybridized
  - The triple bond consists of:
    - One σ bond produced by overlap of an *sp* orbital from each atom
    - Two π bonds produced by overlap of 2*p* orbitals from each atom

Interactive Example 9.5 - Solution (a) (Continued)

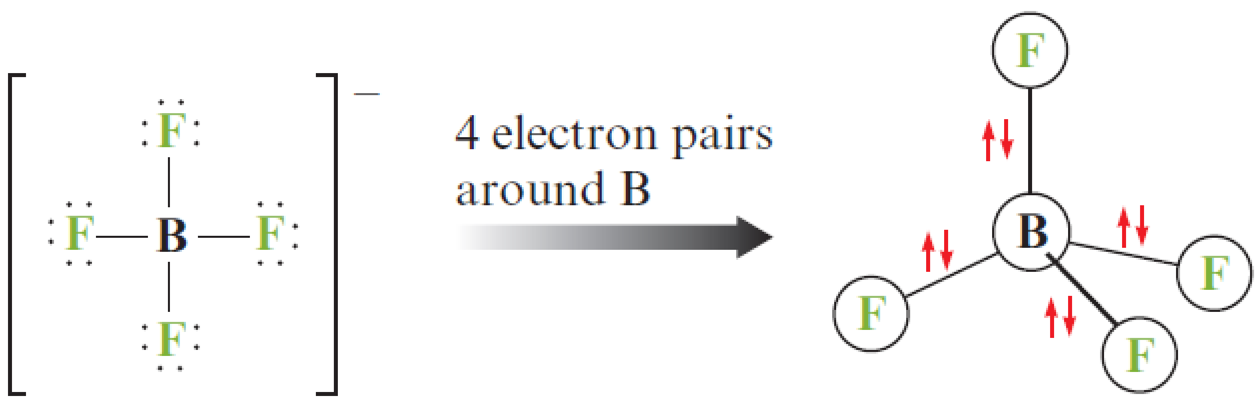
- The lone pairs are in *sp* orbitals
- The molecule exhibits a linear arrangement of atoms





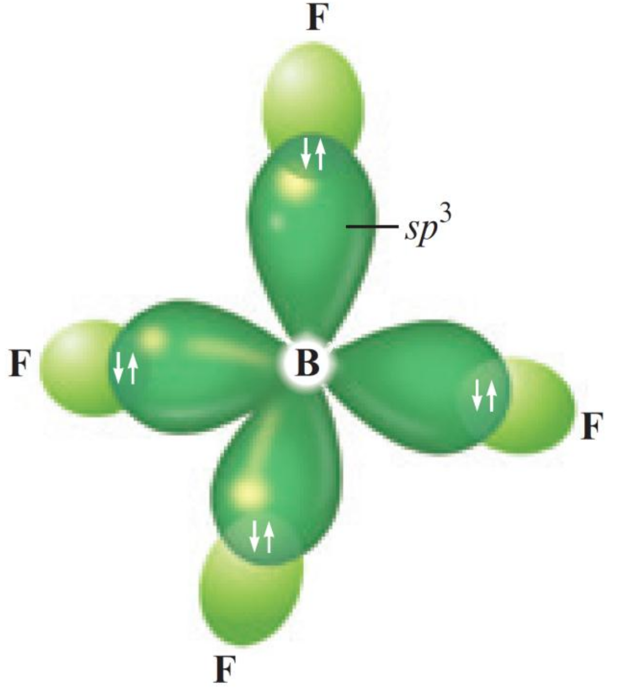
Interactive Example 9.5 - Solution (b)

- BF_4^- ion has 32 valence electrons
  - The boron atom is surrounded by four pairs of electrons
    - Requires tetrahedral arrangement and *sp*^{3} hybridization of the boron atom



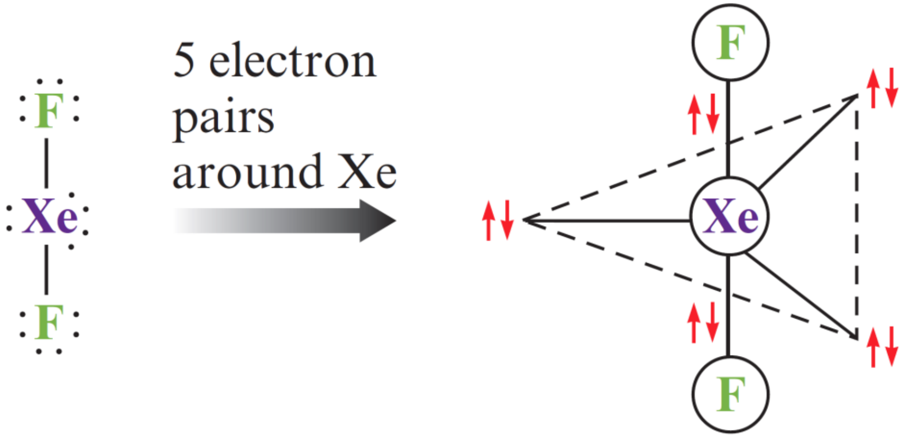
Interactive Example 9.5 - Solution (b) (Continued)

- Each fluorine atom has four electron pairs
  - Assumed to be sp^3 hybridized
- Molecular structure - Tetrahedral



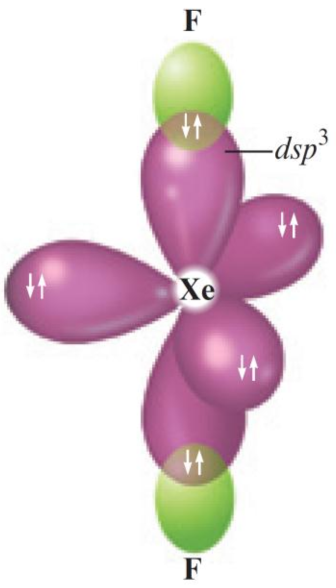
Interactive Example 9.5 - Solution (c)

- XeF_2 has 22 valence electrons
  - The xenon atom is surrounded by five electron pairs
    - Requires a trigonal bipyramidal arrangement



Interactive Example 9.5 - Solution (c) (Continued)

- The lone pairs are placed in the plane where they are 120 degrees apart
- To accommodate five pairs at the vertices of a trigonal bipyramid requires that the xenon atom adopt a set of five *dsp*^{3} orbitals
- Each fluorine atom has four electron is assumed to be *sp*^{3} hybridized
- The molecule has a linear arrangement of atoms



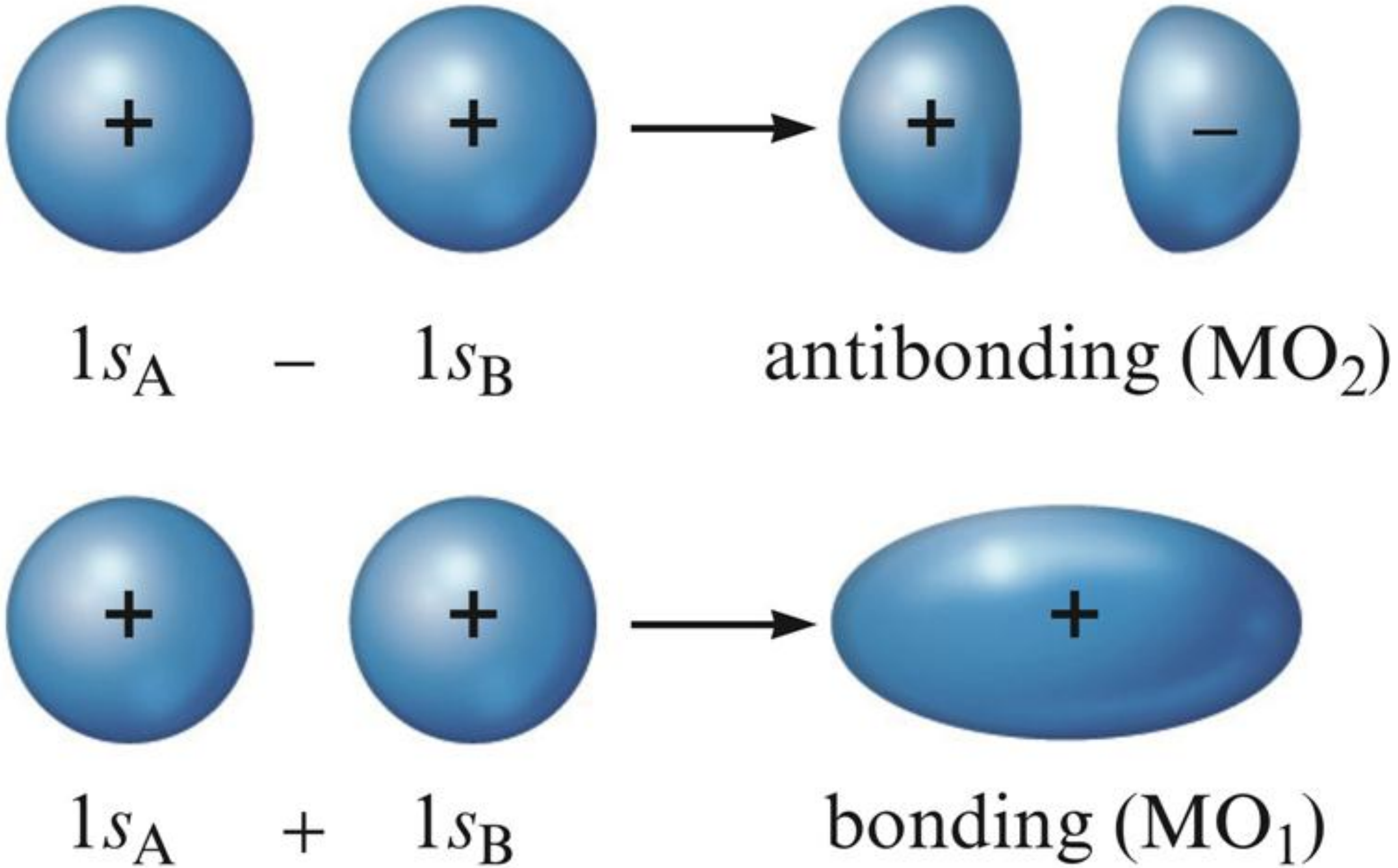
Limitations of the Localized Electron Model

- Incorrectly assumes that electrons are localized
  - Concept of resonance must be added
- Does not deal effectively with molecules containing unpaired electrons
- Does not provide direct information about bond energies

Molecular Orbitals (MOs)

- Have the same characteristics as atomic orbitals
  - Can hold two electrons with opposite spins
  - The square of the molecular orbital wave function indicates electron probability

Figure 9.25 - Formation of Molecular Orbitals



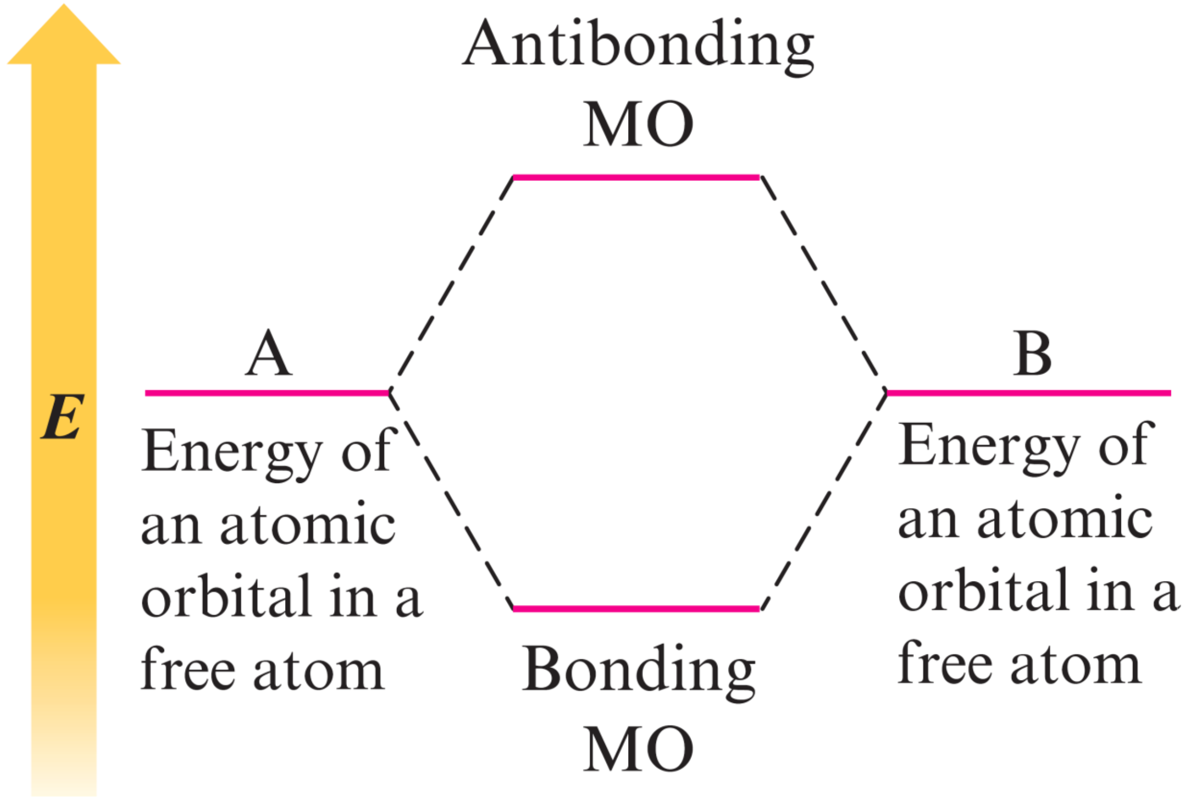
Properties of Molecular Orbitals

- The electron probability of both molecular orbitals is centered along the line passing through the two nuclei
  - MO_1 and MO_2 are referred to as **sigma (σ) molecular orbitals**
- In the molecule, only the molecular orbitals are available for occupation by electrons

Properties of Molecular Orbitals (Continued 1)

- Bonding and antibonding
  - **Bonding molecular orbital**: Lower in energy than the atomic orbitals from which it is composed
    - Electrons in this orbital will favor bonding
  - **Antibonding molecular orbital**: Higher in energy than the atomic orbitals from which it is composed
    - Electrons in this orbital will favor the separated atoms

Figure 9.27 - Bonding and Antibonding Molecular Orbitals



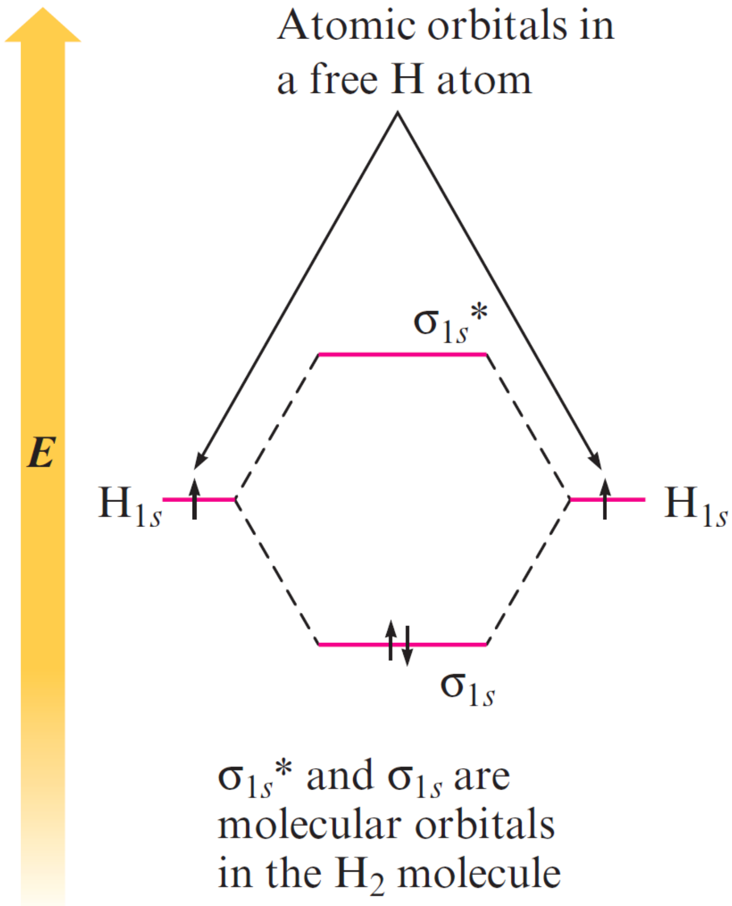
Properties of Molecular Orbitals (Continued 2)

- The MO model is physically reasonable
  - There is high probability of finding electrons between nuclei in bonding MOs
  - Electrons are outside the space between the nuclei in antibonding MOs
- Labels on molecular orbitals indicate their shape, the parent atomic orbitals, and whether they are bonding or antibonding
  - Antibonding character is indicated by an asterisk

Properties of Molecular Orbitals (Continued 3)

- Molecular electronic configuration can be written in the same way as atomic configurations
- Each molecular orbital can hold two electrons
  - The spins should be opposite
- Molecular orbitals are conserved
  - The number of MOs will be equal to the number of atomic orbitals used to construct them

Figure 9.28 - Molecular Energy-Level Diagram for the H_2 Molecule



Bond Order

- Used to indicate bond strength

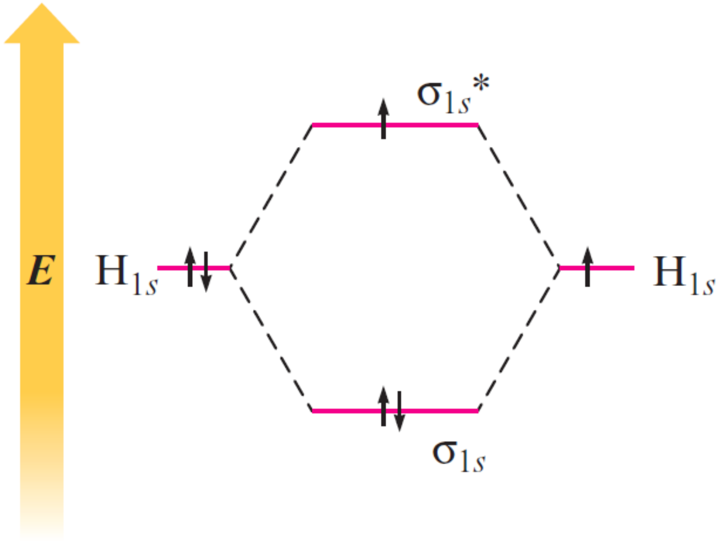
$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

  - Bonds are perceived in terms of pairs of electrons
- Larger the bond, greater the bond strength

Bond Order (Continued)

- Consider the H_2^- ion
  - Contains two bonding electrons and one antibonding electron

$$\text{Bond order} = \frac{2-1}{2} = \frac{1}{2}$$

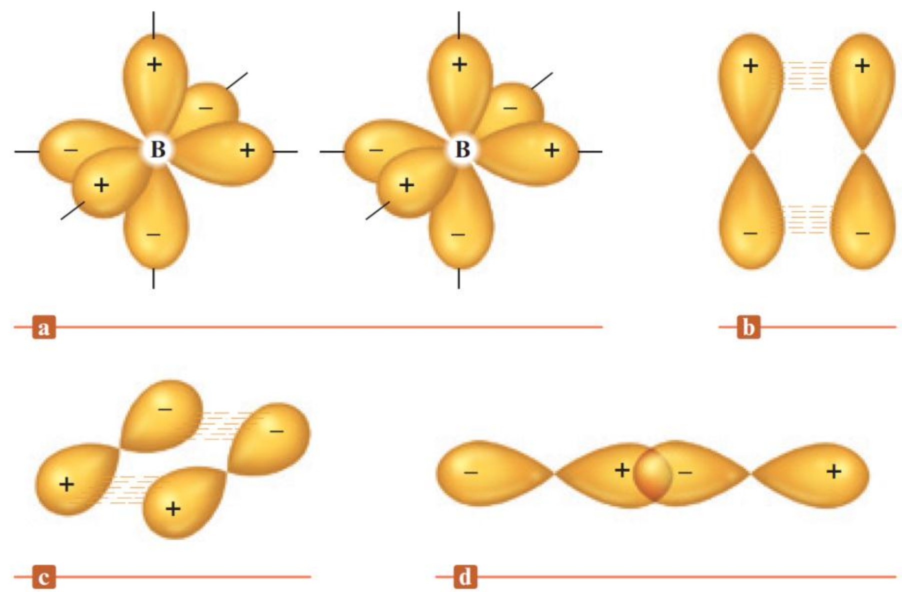


Homonuclear Diatomic Molecules

- Composed of two identical atoms
- Only the valence orbitals of the atoms contribute significantly to the molecular orbitals of a particular molecule

Homonuclear Diatomic Molecules - Boron

- Electron configuration - $1s^2 2s^2 2p^1$
  - B_2 molecule is described based on how *p* atomic orbitals combine to form molecular orbitals
    - *p* orbitals occur in sets of three mutually perpendicular orbitals
    - Two pairs of *p* orbitals can overlap in a parallel fashion and one pair can overlap head-on



Homonuclear Diatomic Molecules - Boron (Continued 1)

- Consider the molecular orbitals from the head-on overlap
  - Bonding orbital is formed by reversing the sign of the right orbital
    - Produces constructive interference
    - There is enhanced electron probability between the nuclei
  - Antibonding orbital is formed by the direct combination of the orbitals
    - Produces destructive inference
    - There is decreased electron probability between the nuclei

Homonuclear Diatomic Molecules - Boron (Continued 2)

- MOs are σ molecular orbitals
- Combination of parallel *p* orbitals with matched positive and negative phases results in constructive interference
  - Gives a bonding π orbital
- If the signs of one orbital are reversed, an antibonding π orbital is formed

Homonuclear Diatomic Molecules - Boron (Continued 3)

- Both *p* orbitals are pi (π) molecular orbitals
  - **Pi (π) molecular orbitals**: Electron probability lies above and below the line between the nuclei
  - π_{2p} - Bonding MO
  - π_{2p}* - Antibonding MO

Figure 9.34 - The Expected MO Energy-Level Diagram Resulting from the Combination of the 2*p* Orbitals on Two Boron Atoms

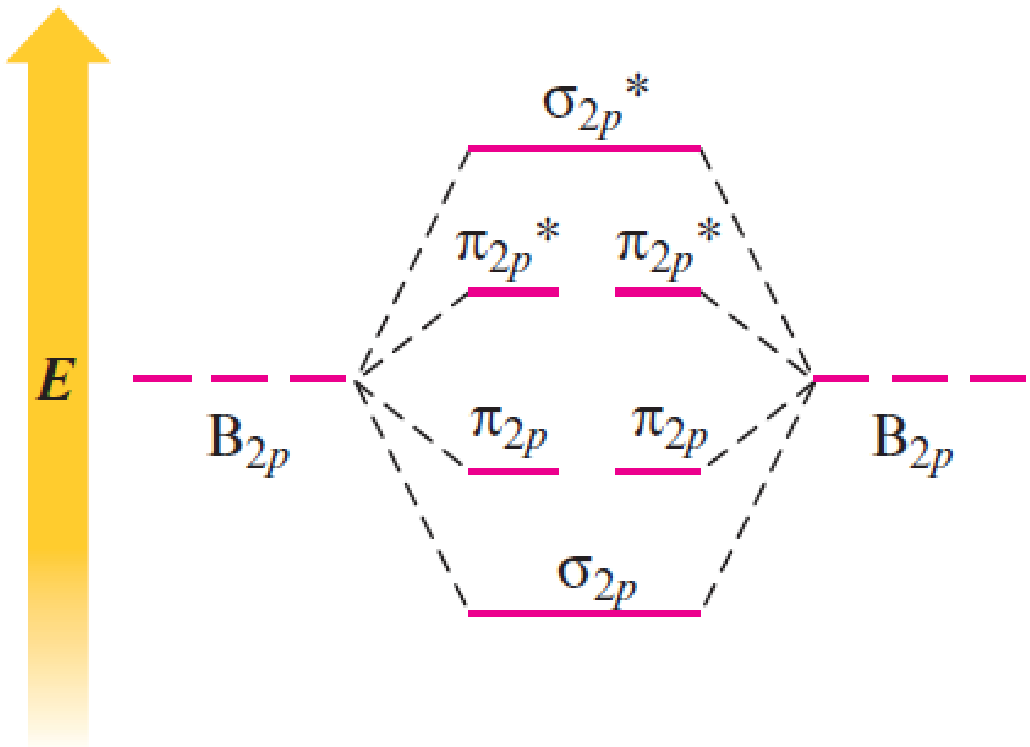
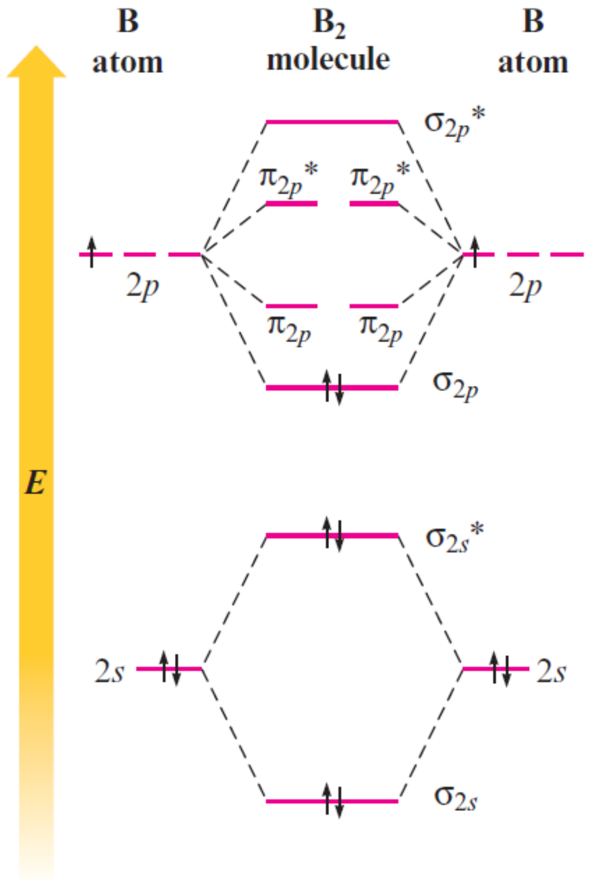


Figure 9.35 - The Expected Molecular Orbital Energy-Level Diagram for the B_2 Molecule

$$\text{Bond order} = \frac{4 - 2}{2} = 1$$

- B_2 should be a stable molecule



Types of Magnetism in the Presence of a Magnetic Field

- **Paramagnetism**: Substance is attracted into the inducing magnetic field
  - Associated with unpaired electrons
- **Diamagnetism**: Substance is repelled from the inducing magnetic field
  - Associated with paired electrons
- Substance that has both paired and unpaired electrons will exhibit a net paramagnetism

Figure 9.36 - Measuring Paramagnetism

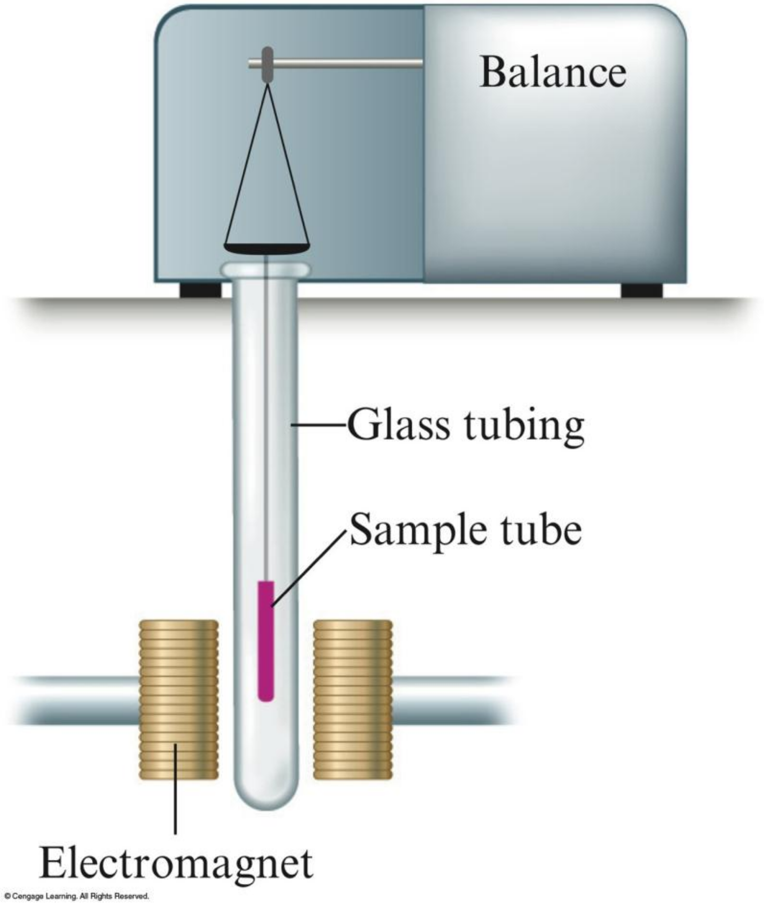
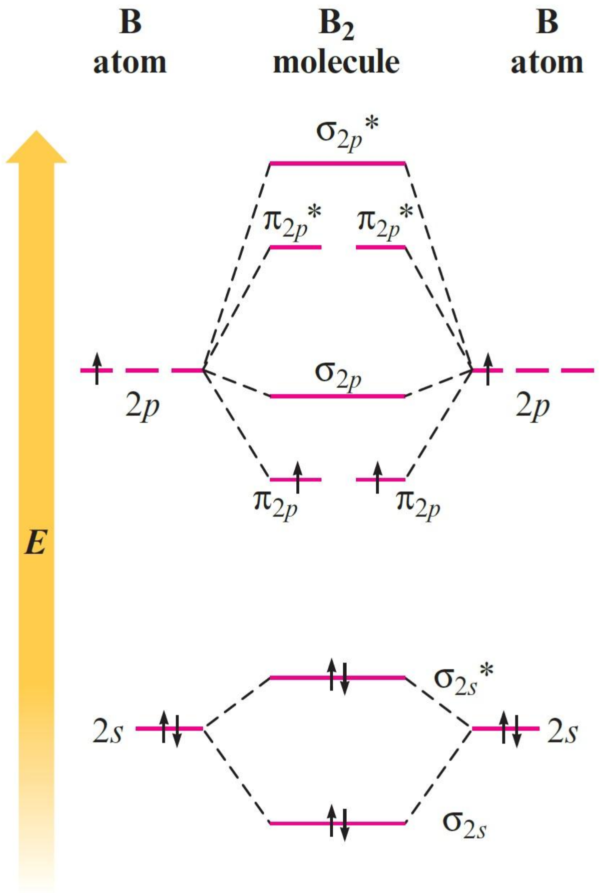


Figure 9.37 - The Correct Molecular Orbital Energy-Level Diagram for B_2

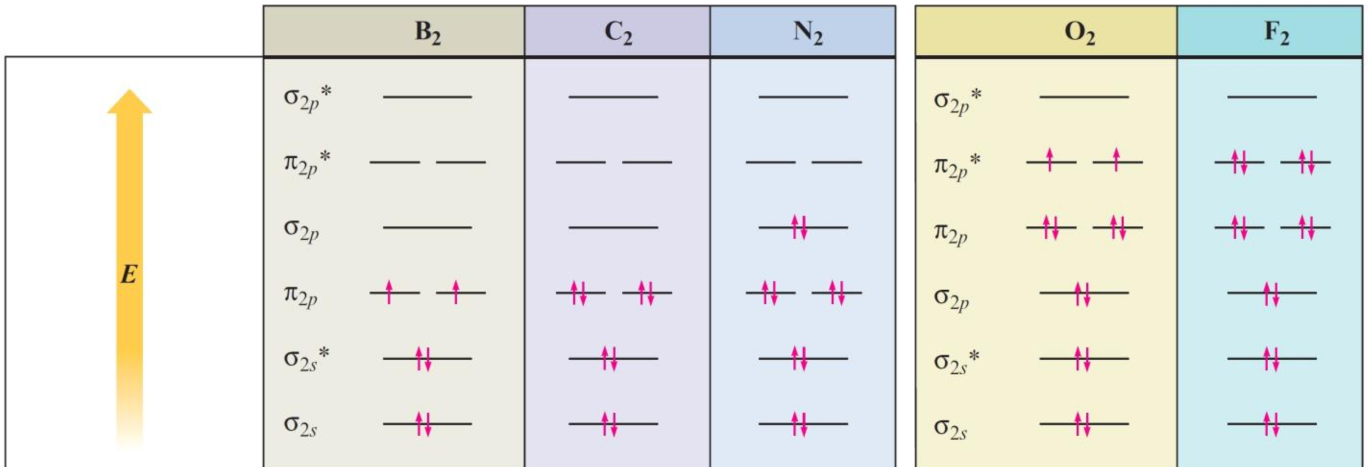
- Diagram explains the observed paramagnetism of B_2
  - When *p*–*s* mixing is allowed, the energies of the σ_{2p} and π_{2p} orbitals are reversed
    - Two electrons from the B 2*p* orbitals now occupy separate, degenerate π_{2p} molecular orbitals and have parallel spins



Critical Thinking

- What if π_{2p} orbitals were lower in energy than σ_{2p} orbitals?
    - What would you expect the B_2 molecular orbital energy-level diagram to look like (without considering *p–s* mixing)?
        - Compare the expected diagram to figures 9.34 and 9.35, and state the differences from each

Figure 9.38 - Molecular Orbital Summary of Second Row Diatomic Molecules



	B_2	C_2	N_2	O_2	F_2
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

Key Points regarding Period 2 Diatomics

- There are definite correlations between bond order, bond energy, and bond length
- Bond order cannot be associated with a particular bond energy
- The large bond energy associated with the N_2 molecule will have a triple bond
- The O_2 molecule is paramagnetic

Interactive Example 9.7 - The Molecular Orbital Model II

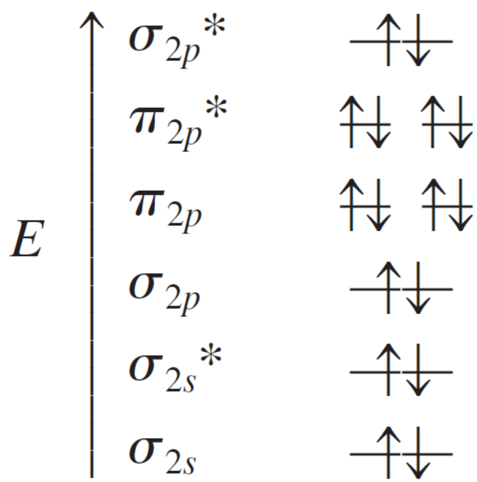
- Use the molecular orbital model to predict the bond order and magnetism of each of the following molecules
  a. Ne_2
  b. P_2

Interactive Example 9.7 - Solution (a)

- The valence orbitals for Ne are 2*s* and 2*p*
  - The Ne_2 molecule has 16 valence electrons (8 from each atom)

Interactive Example 9.7 - Solution (a) (Continued)

- Placing these electrons in the appropriate molecular orbitals produces the following diagram



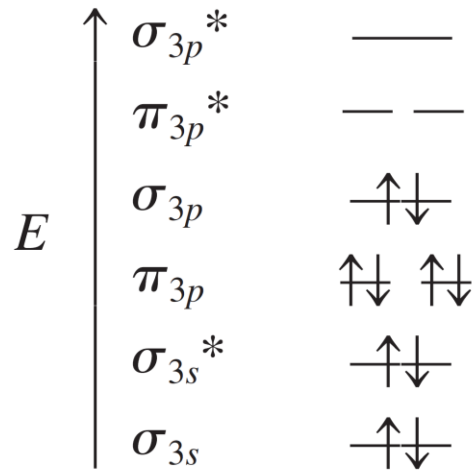
- The bond order is (8 – 8)/2 = 0
  - Ne_2 does not exist

Interactive Example 9.7 - Solution (b)

- P_2 contains phosphorus atoms from the third row of the periodic table
  - Assume that the diatomic molecules of the Period 3 elements can be treated in a way similar to that which has been used so far
  - Draw the MO diagram for P_2 analogous to that for N_2
    - The only change will be that the molecular orbitals will be formed from 3*s* and 3*p* atomic orbitals

Interactive Example 9.7 - Solution (b) (Continued)

- The P_2 molecule has 10 valence electrons (5 from each phosphorus atom)



- Bond order = 3
- The molecule is expected to be diamagnetic

Heteronuclear Diatomic Molecules

- **Heteronuclear**: Different atoms
- A special case involves molecules containing atoms adjacent to each other in the periodic table
  - MO diagram can be used for homonuclear molecules as atoms involved in such molecules are similar

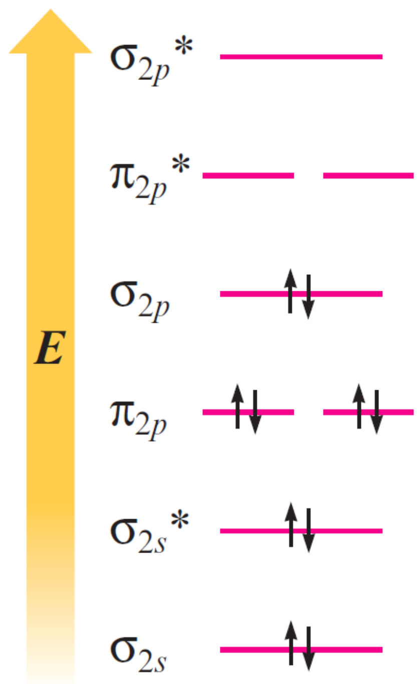
Interactive Example 9.8 - The Molecular Orbital Model III

- Use the molecular orbital model to predict the magnetism and bond order of the NO^+ and CN^- ions

Interactive Example 9.8 - Solution

- The NO^+ ion has 10 valance electrons (5 + 6 – 1)
- The CN^- ion also has 10 valance electrons (4 + 5 + 1)
- Both ions are diamagnetic

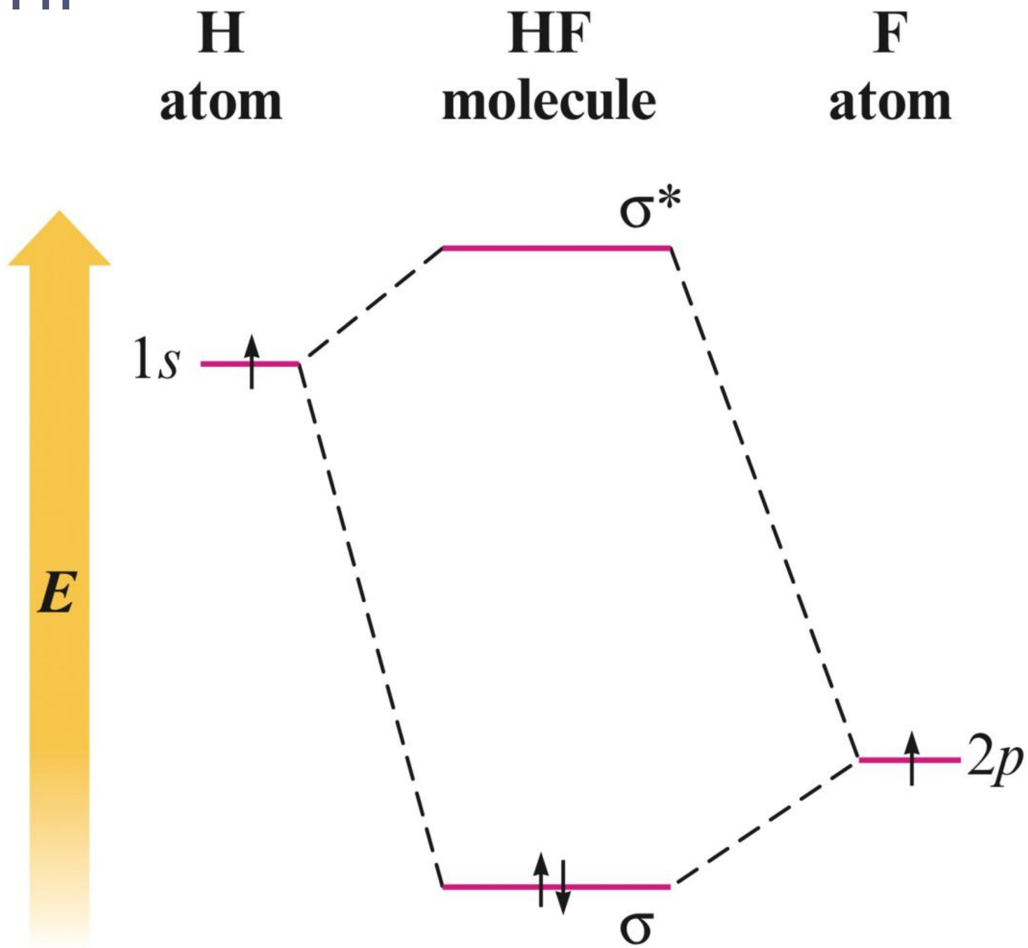
$$\text{Bond order} = \frac{8-2}{2} = 3$$



Energy-Level Diagrams for Diatomic Molecules

- When the two atoms of a diatomic molecule are very different, the energy-level diagram for homonuclear molecules cannot be used
- Consider the hydrogen fluoride (HF) molecule
  - Electron configuration of hydrogen - $1s^1$
  - Electron configuration of fluorine - $1s^2 2s^2 2p^5$
  - Assume that fluorine uses only one of its 2*p* orbitals to bond to hydrogen

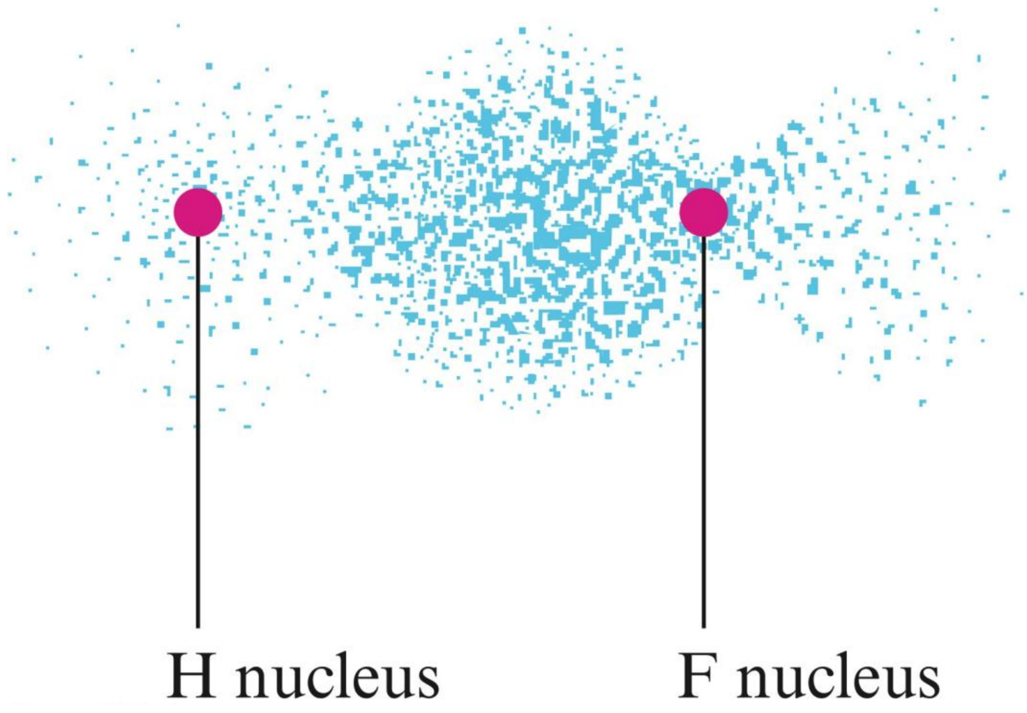
Figure 9.42 - Partial Molecular Orbital Energy-Level Diagram for HF



Energy-Level Diagrams for Diatomic Molecules (Continued)

- The HF molecule should be stable as both electrons are lowered in energy relative to their energy in the free hydrogen and fluorine atoms
- Electrons prefer to be closer to the fluorine atom
    - The electron pair is not shared equally
- Fluorine has a slight excess of negative charge, and hydrogen is partially positive

Figure 9.43 - Electron Probability Distribution in the Bonding Molecular Orbital of the HF Molecule

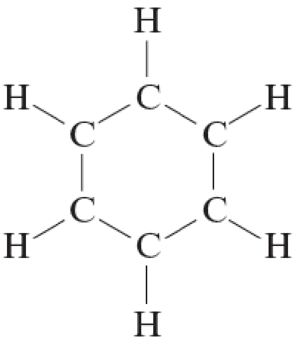


Combining the Localized Electron and MO Models

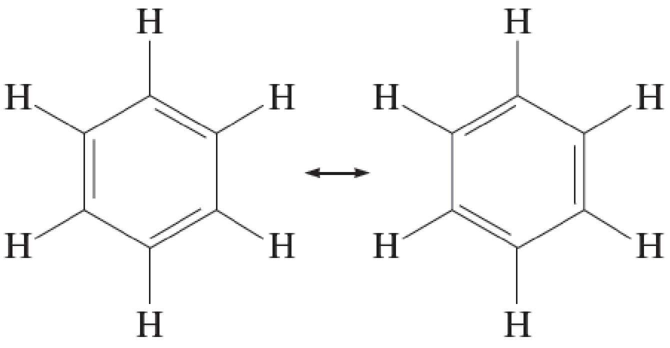
- The σ bonds in a molecule can be described as being localized
- The π bonds must be treated as being delocalized
- For molecules that require resonance:
  - The localized electron model can be used to describe the σ bonding
  - The MO model can be used to describe the π bonding

General Model - Benzene Molecule and its Resonance Structures

- All atoms in benzene are in the same plane
  - All the C—C bonds are known to be equivalent
- To account for the six equivalent C—C bonds, the localized electron model must invoke resonance



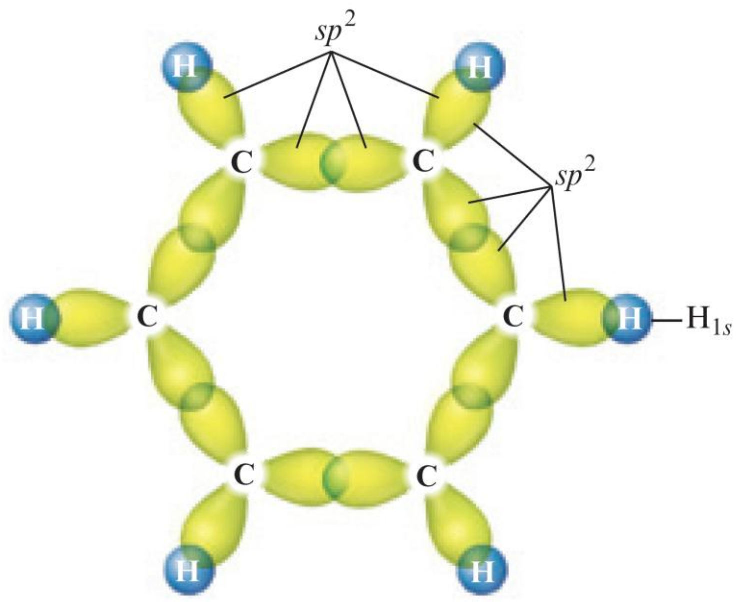
a



b

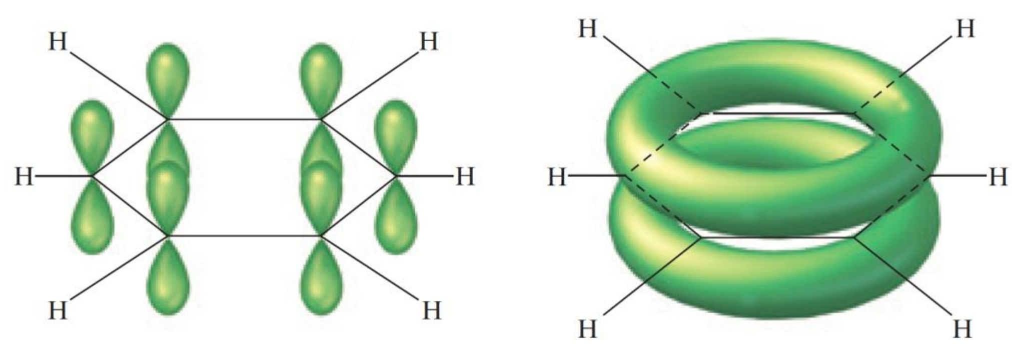
Combination of Models - Identifying σ bonds

- Assumption - The σ bonds of carbon involve sp^2 orbitals
  - The bonds are centered in the plane of the molecule

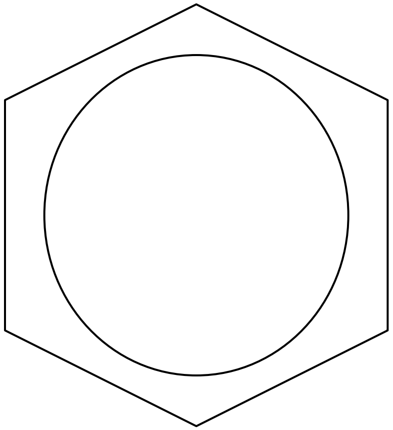


Combination of Models - Identifying π bonds

- Each carbon atom is sp^2 hybridized
  - A *p* orbital perpendicular to the plane of the ring remains on each carbon atom
    - Used to form π molecular orbitals
- The electrons in the resulting π molecular orbitals are delocalized above and below the plane of the ring



Benzene Structure



- Indicates the delocalized π bonding in the molecule

Electron Spectroscopy

- Uses
  - Determines the relative energies of electrons in individual atoms and molecules
  - Characterizes and tests molecular bonding theories
  - Helps in the study of the electron energy levels of atoms
- Involves bombarding the sample with high-energy photons
  - Kinetic energies of the ejected electrons are measured

Electron Spectroscopy (Continued)

- Formula used to determine energy of the electron

$$E_{electron} = h\nu - \mathrm{KE}$$

  - *E* - Energy of electron
  - $h\nu$ - Energy of photons used
  - KE - Kinetic energy of the electron

Figure 9.50 - The Idealized PES Spectrum of Phosphorus