

What is the hybridization of the central atom in each molecule?



## Features of Hybrid Orbitals

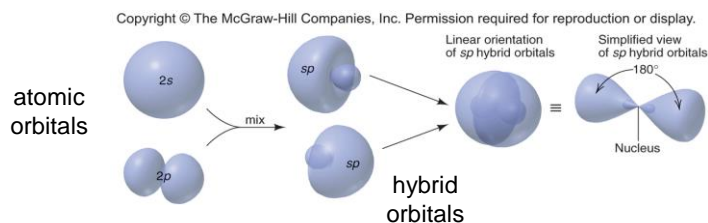
The **number** of hybrid orbitals formed **equals** the number of atomic orbitals mixed.

The **type** of hybrid orbitals formed **varies** with the types of atomic orbitals mixed.

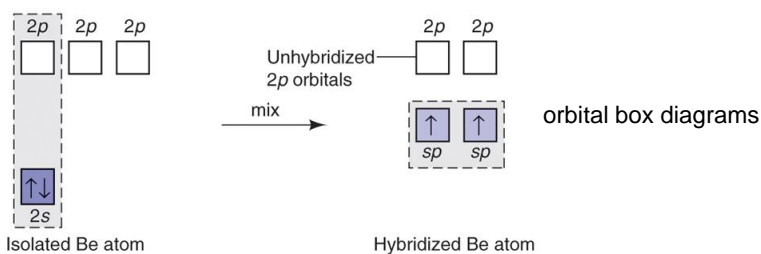
The **shape** and **orientation** of a hybrid orbital **maximizes** overlap with the other atom in the bond.



## Formation and orientation of $sp$ hybrid orbitals and the bonding in $\text{BeCl}_2$ .

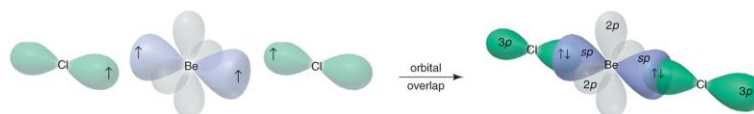
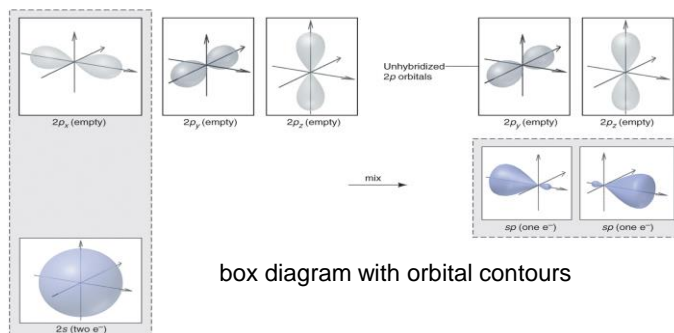


One  $2s$  and one  $2p$  atomic orbital mix to form two  $sp$  hybrid orbitals.



11-3

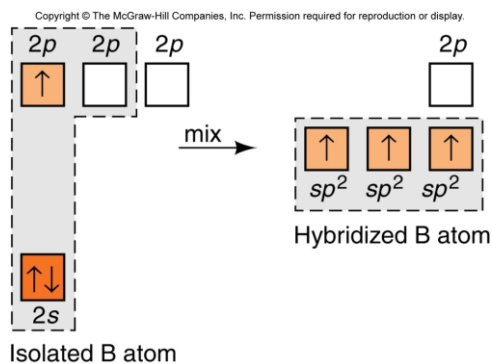
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



Overlap of Be and Cl orbitals to form  $\text{BeCl}_2$ .

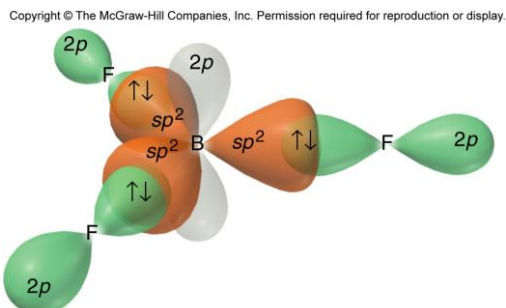
11-4

### The $sp^2$ hybrid orbitals in $\text{BF}_3$ .



Mixing one  $s$  and two  $p$  orbitals gives three  $sp^2$  hybrid orbitals.  
The third  $2p$  orbital remains unhybridized.

11-5

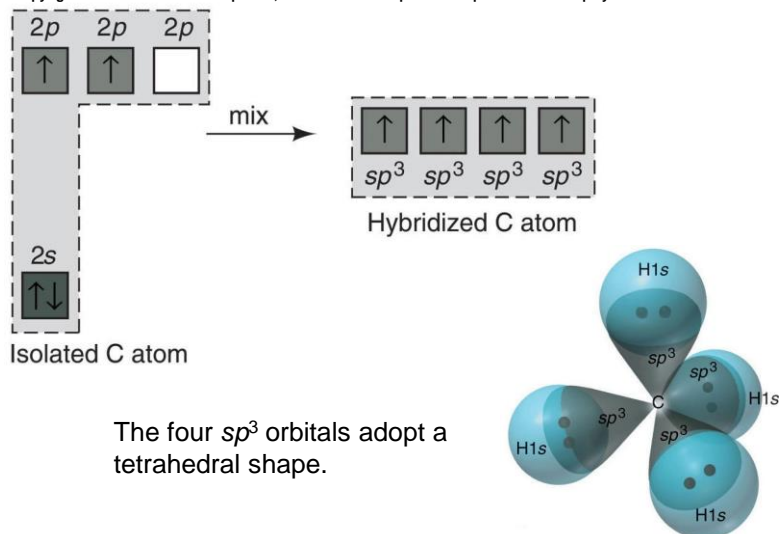


The three  $sp^2$  orbitals point to the corners of an equilateral triangle,  
their axes  $120^\circ$  apart.  
Each half-filled  $sp^2$  orbital overlaps with the half-filled  $2p$  orbital of a  
F atom.

11-6

### The $sp^3$ hybrid orbitals in $\text{CH}_4$ .

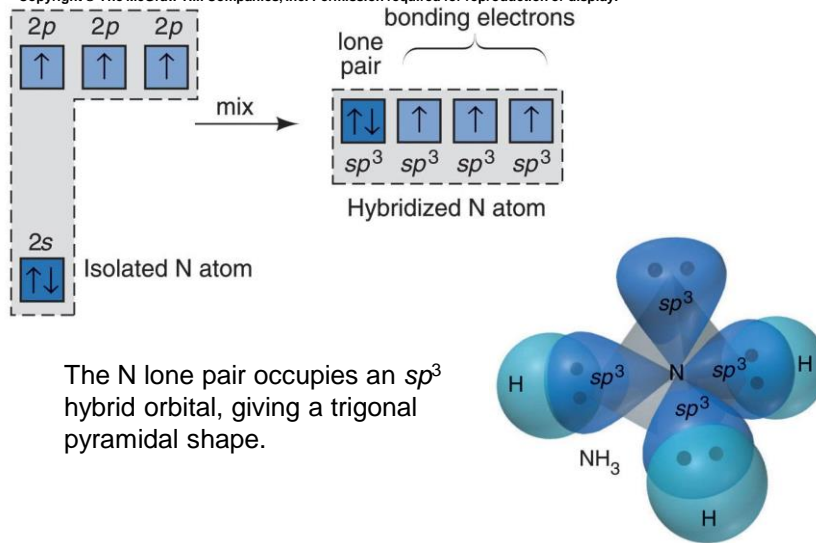
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



11-7

### The $sp^3$ hybrid orbitals in $\text{NH}_3$ .

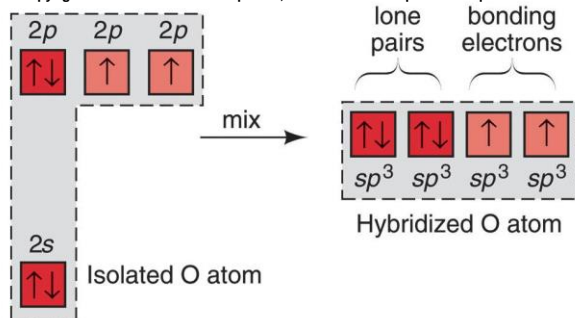
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



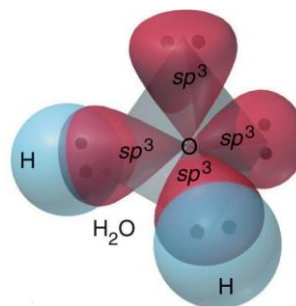
11-8

### The $sp^3$ hybrid orbitals in $H_2O$ .

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



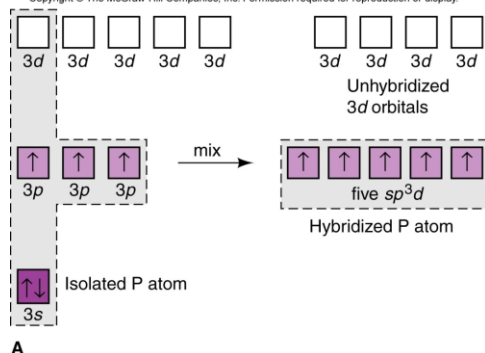
The O lone pairs occupy  $sp^3$  hybrid orbitals, giving a bent shape.



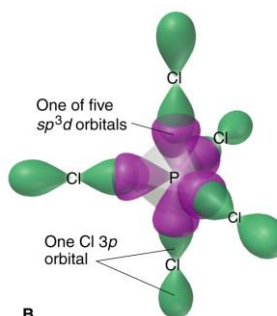
11-9

### The $sp^3d$ hybrid orbitals in $PCl_5$ .

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



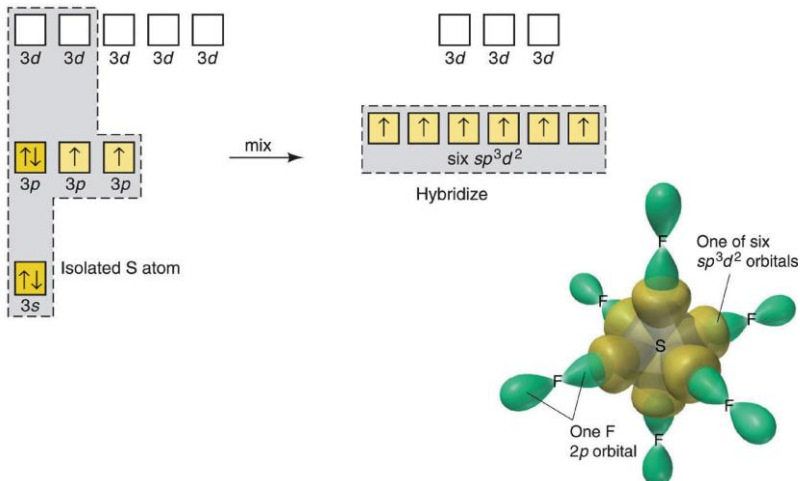
The formation of more than four bonding orbitals requires  $d$  orbital involvement in hybridization.



11-10

## The $sp^3d^2$ hybrid orbitals in $SF_6$ .

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



11-11

## Composition and Orientation of Hybrid Orbitals

	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
<b>Atomic orbitals mixed</b>	one $s$ one $p$	one $s$ two $p$	one $s$ three $p$	one $s$ three $p$ one $d$	one $s$ three $p$ two $d$
<b>Hybrid orbitals formed</b>	two $sp$	three $sp^2$	four $sp^3$	five $sp^3d$	six $sp^3d^2$
<b>Unhybridized orbitals remaining</b>	two $p$	one $p$	none	four $d$	three $d$
<b>Orientation</b>					

11-12

What is the orbital hybridization of the central atoms in the following molecules?

(a) Methanol,  $\text{CH}_3\text{OH}$

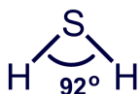
(b) Sulfur tetrafluoride,  $\text{SF}_4$

11-13

## Limitations of the Hybridization Model

Hybridization is not always consistent with observed molecular shapes.

This is particularly true for the bonding of larger atoms.



The bond angle in  $\text{H}_2\text{S}$  is closer to the angle between unhybridized  $p$  orbitals.

$d$ -Orbitals do not hybridize effectively with  $s$  and  $p$  orbitals, which are much lower in energy and more stable.

11-14

## Types of Covalent Bonds

A **sigma ( $\sigma$ )** bond is formed by **end-to-end** overlap of orbitals.

**All single bonds are  $\sigma$  bonds.**

A **pi ( $\pi$ )** bond is formed by **sideways** overlap of orbitals.

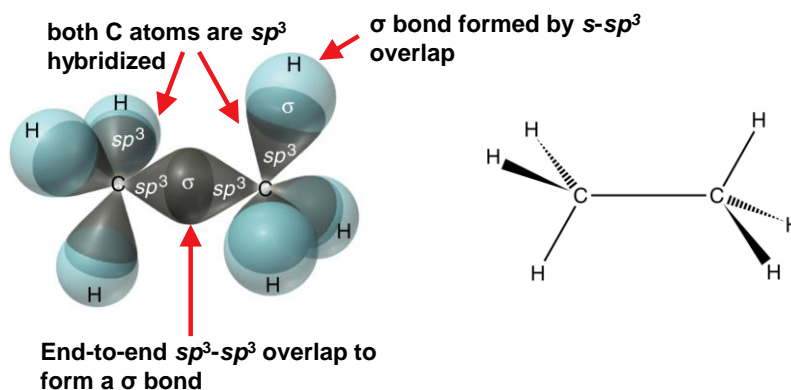
A  $\pi$  bond is weaker than a  $\sigma$  bond because sideways overlap is less effective than end-to-end overlap.

A double bond consists of one  $\sigma$  bond and one  $\pi$  bond.

11-15

### The $\sigma$ bonds in ethane ( $\text{C}_2\text{H}_6$ ).

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

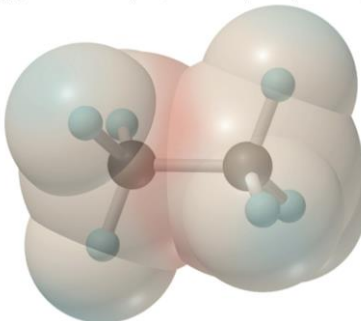


A  $\sigma$  bond is cylindrically symmetrical, with its highest electron density along the bond axis.

11-16



Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



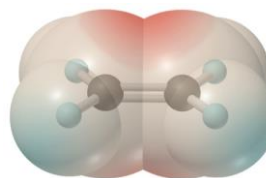
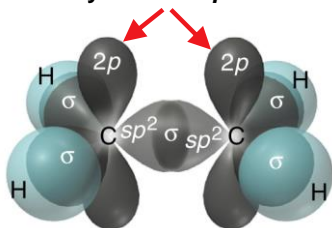
There is relatively even distribution of electron density over all  $\sigma$  bonds.

11-17

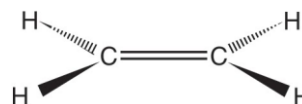
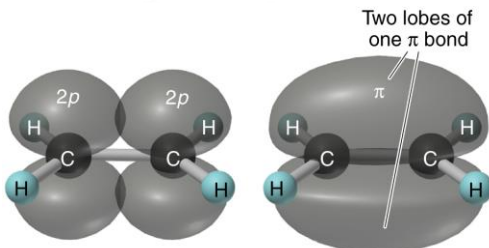
### The $\sigma$ and $\pi$ bonds in ethylene ( $\text{C}_2\text{H}_4$ ).

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

unhybridized  $2p$  orbitals



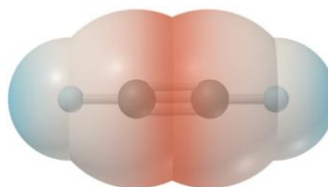
A  $\pi$  bond has two regions of electron density.



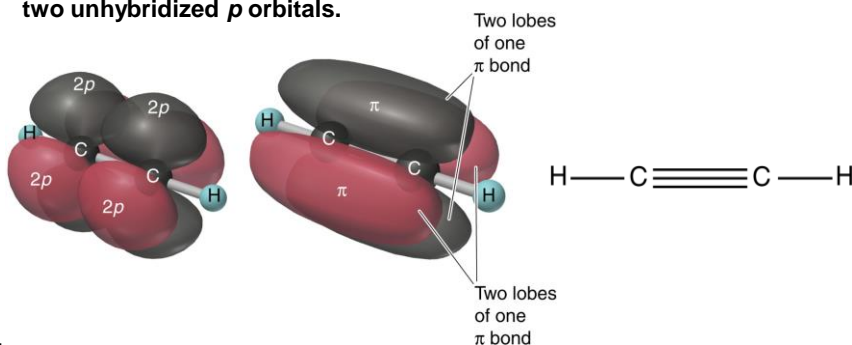
11-18

### The $\sigma$ and $\pi$ bonds in acetylene ( $\text{C}_2\text{H}_2$ ).

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



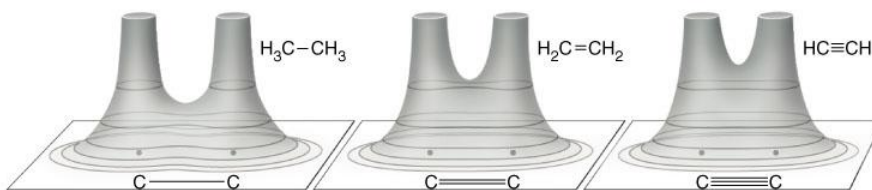
Each C is  $sp$  hybridized and has two unhybridized  $p$  orbitals.



11-19

### Electron density and bond order in ethane, ethylene, and acetylene.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

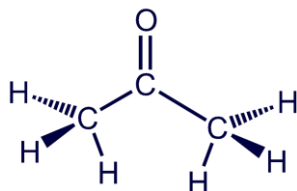


A double bond is less than twice as strong as a single bond, because a  $\pi$  bond is weaker than a  $\sigma$  bond.

However, in terms of bond order, a single bond has  $\text{BO} = 1$ , a double bond has  $\text{BO} = 2$ , and a triple bond has  $\text{BO} = 3$ .

11-20

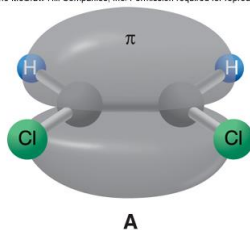
Describe the types of bonds and orbitals in acetone,  $(\text{CH}_3)_2\text{CO}$ .



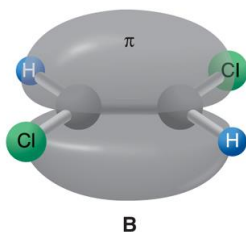
11-21

### Restricted rotation around a $\pi$ bond.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



*cis*-1,2-Dichloroethylene



*trans*-1,2-Dichloroethylene

11-22

## Molecular Orbital (MO) Theory

The combination of orbitals to form bonds is viewed as the combination of **wave functions**.

**Atomic** wave functions (AOs) combine to form **molecular** wave functions (MOs).

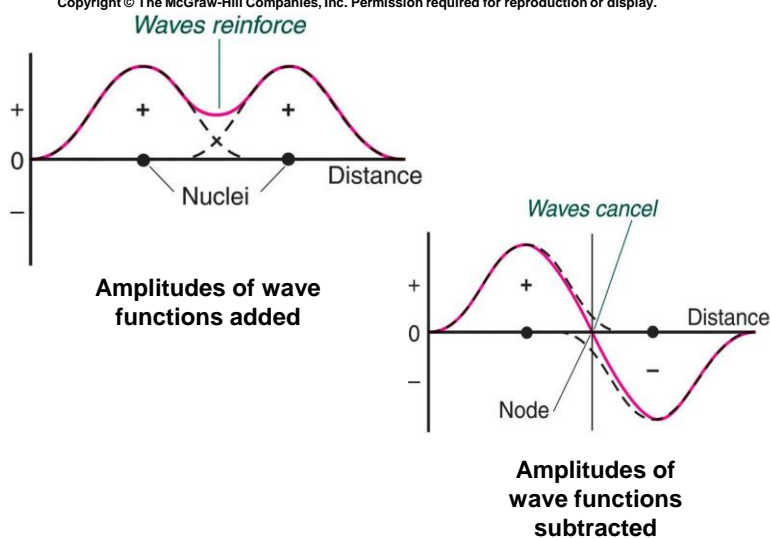
**Addition** of AOs forms a **bonding MO**, which has a region of **high** electron density between the nuclei.

**Subtraction** of AOs forms an **antibonding MO**, which has a **node**, or region of **zero** electron density, between the nuclei.

11-23

### An analogy between light waves and atomic wave functions.

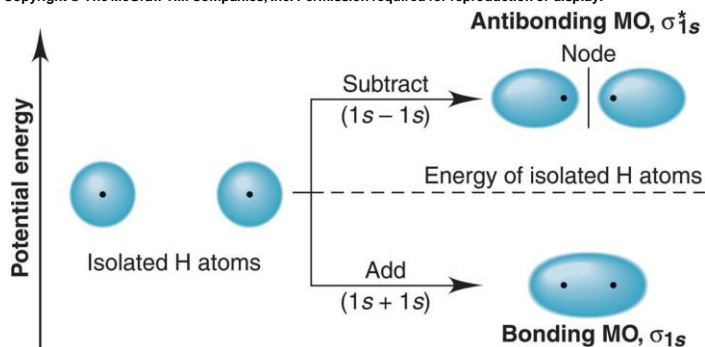
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



11-24

## Contours and energies of $H_2$ bonding and antibonding MOs.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



The bonding MO is lower in energy and the antibonding MO is higher in energy than the AOs that combined to form them.

11-25

## Molecular Orbital Diagrams

An **MO diagram**, just like an atomic orbital diagram, shows the relative energy and number of electrons in each MO.

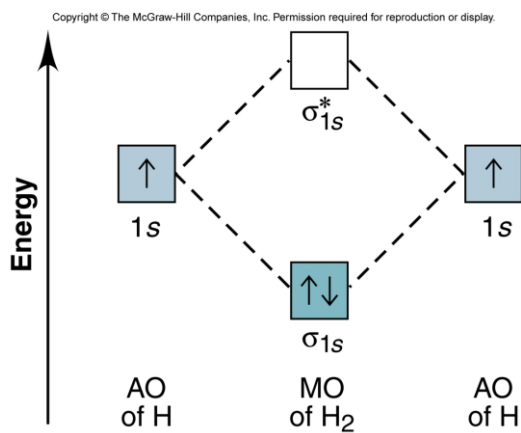
The MO diagram also shows the AOs from which each MO is formed.

Bond order is calculated as follows:

$$\frac{1}{2}[(\text{\# of } e^- \text{ in bonding MO}) - (\text{\# of } e^- \text{ in antibonding MO})]$$

11-26

### MO diagram for H<sub>2</sub>.



$$\text{H}_2 \text{ bond order} = \frac{1}{2} (2 - 0) = 1$$

11-27

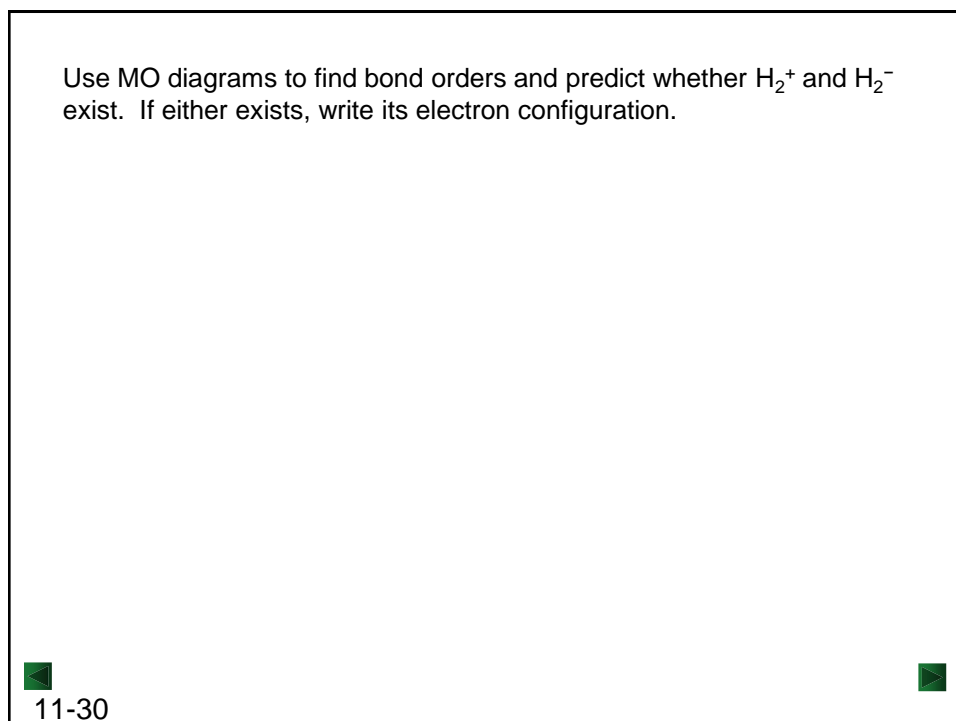
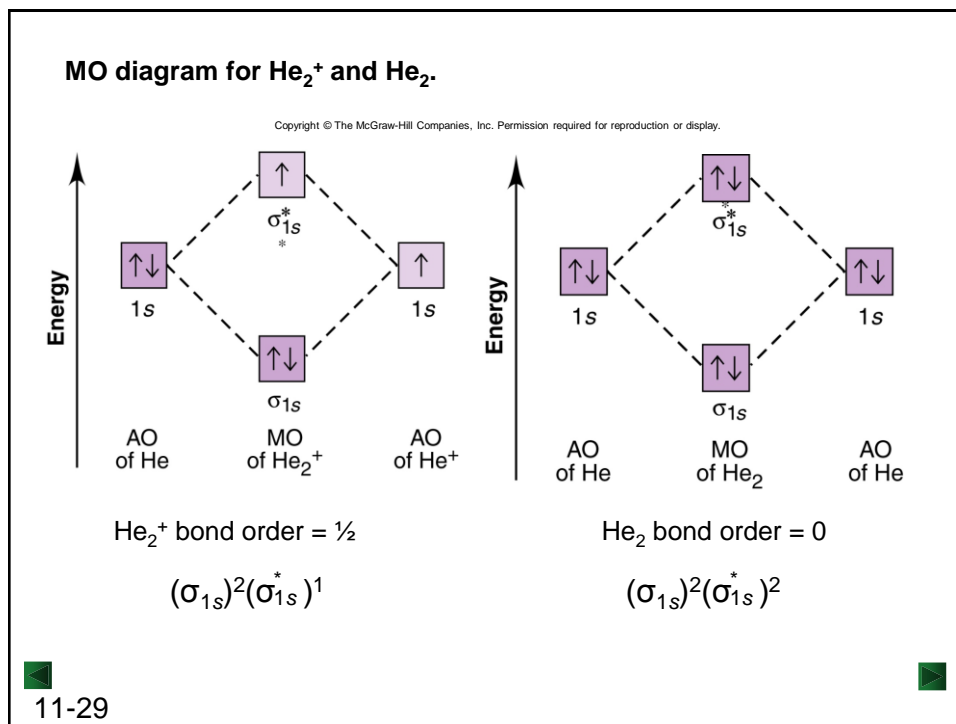
### Electrons in Molecular Orbitals

Electrons are placed in MOs just as they are in AOs.

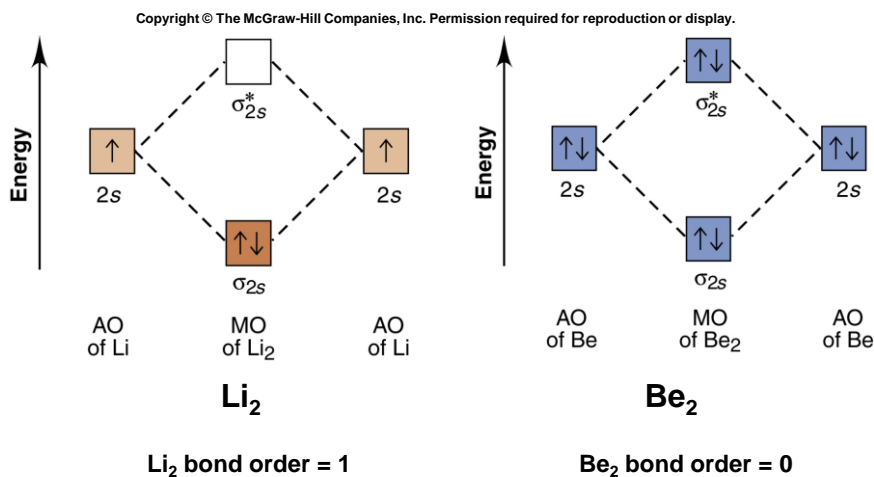
- MOs are filled in order of increasing energy.
- An MO can hold a maximum of 2 e<sup>-</sup>, as long as they have opposite spins.
- Orbitals of equal energy are half-filled, with spins parallel, before pairing spins.

A molecular electron configuration shows the type of MO and the number of e<sup>-</sup> each contains. For H<sub>2</sub> the configuration is  $(\sigma_{1s})^2$ .

11-28

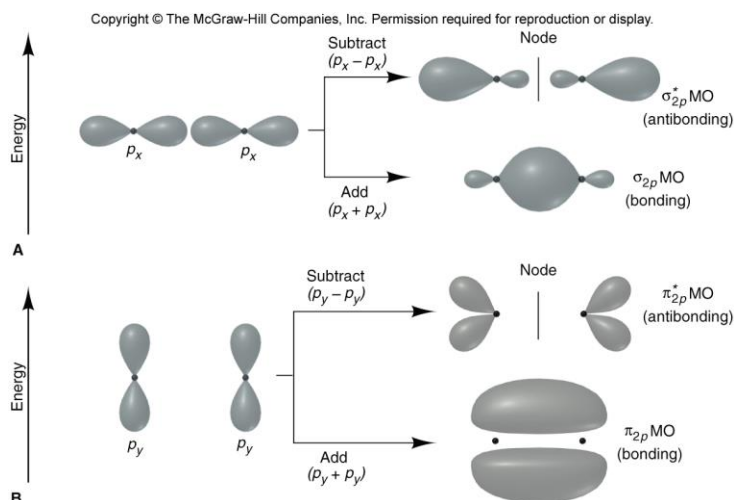


## Bonding in s-block homonuclear diatomic molecules.



11-31

## Shapes and energies of $\sigma$ and $\pi$ MOs from combinations of $2p$ atomic orbitals.

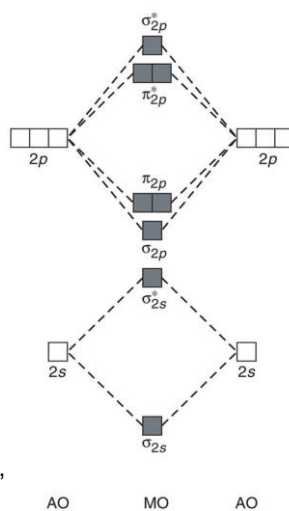


11-32



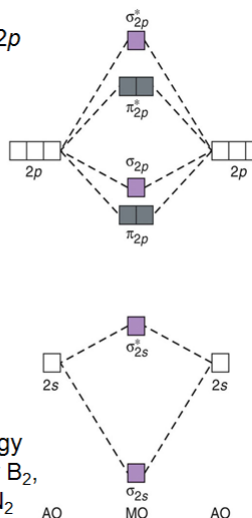
# Relative MO energy levels for Period 2 homonuclear diatomic molecules.

without 2s-2p mixing



MO energy levels for  $O_2$ ,  $F_2$ , and  $Ne_2$

with 2s-2p mixing

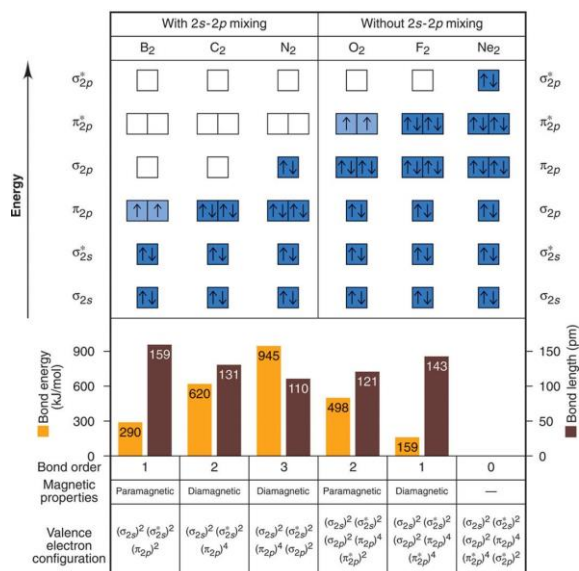


MO energy levels for  $B_2$ ,  $C_2$  and  $N_2$

11-33

## MO occupancy and molecular properties for $B_2$ through $Ne_2$ .

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



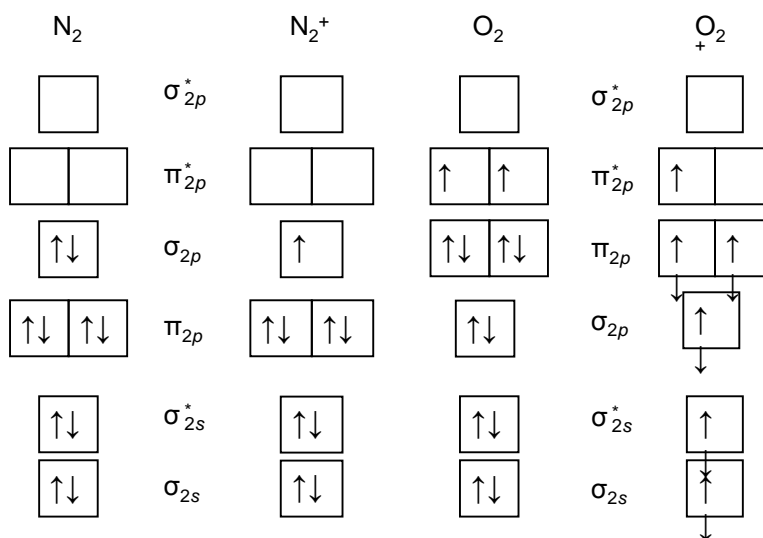
11-34

Explain the following data with diagrams showing the occupancy of MOs:

	$\text{N}_2$	$\text{N}_2^+$	$\text{O}_2$	$\text{O}_2^+$
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

11-35

**SOLUTION:** showing MOs only



11-36

Calculating bond orders:

For  $\text{N}_2$   $\frac{1}{2}(8 - 2) = 3$

For  $\text{N}_2^+$   $\frac{1}{2}(7 - 2) = 2.5$

$\text{N}_2^+$  has a longer, weaker bond than  $\text{N}_2$  because to form  $\text{N}_2^+$ , a *bonding* electron is removed and the bond order decreases.

For  $\text{O}_2$   $\frac{1}{2}(8 - 4) = 2$

For  $\text{O}_2^+$   $\frac{1}{2}(8 - 3) = 2.5$

$\text{O}_2^+$  has a shorter, stronger bond than  $\text{O}_2$  because to form  $\text{O}_2^+$ , an *antibonding* electron is removed and the bond order increases.



11-37

