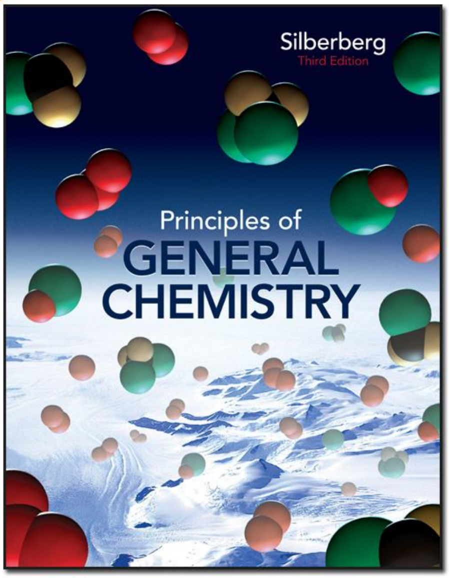


Chapter 11

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

Chapter 11

Theories of Covalent Bonding

Theories of Covalent Bonding

11.1 Valence Bond (VB) Theory and Orbital Hybridization

11.2 Modes of Orbital Overlap and the Types of Covalent Bonds

11.3 Molecular Orbital (MO) Theory and Electron Delocalization

Valence Bond (VB) Theory

The basic principle of VB theory:

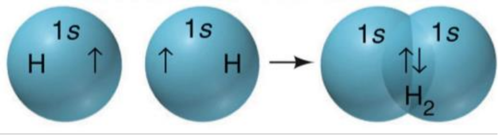
A covalent bond forms when the orbitals of two atoms ***overlap*** and a pair of electrons occupy the overlap region.

The space formed by the overlapping orbitals can accommodate a ***maximum of two electrons*** and these electrons must have ***opposite (paired) spins***.

The greater the orbital overlap, the stronger the bond.

Extent of orbital overlap depends on orbital shape and direction.

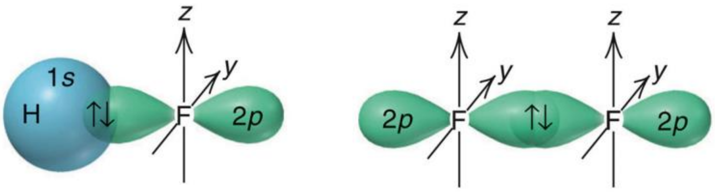
Figure 11.1 Orbital overlap and spin pairing in H_2.



A covalent bond results from the overlap of orbitals from two atoms.

The shared space is occupied by two electrons, which have opposite spins.

Figure 11.1 Orbital orientation and maximum overlap.



Hydrogen fluoride, HF.

Fluorine, F_2.

The greater the extent of orbital overlap, the stronger the bond.

VB Theory and Orbital Hybridization

The orbitals that form when bonding occurs are ***different*** from the atomic orbitals in the isolated atoms.

If no change occurred, we could not account for the molecular shapes that are observed.

Atomic orbitals “mix” or ***hybridize*** when bonding occurs to form ***hybrid orbitals***.

The spatial orientation of these hybrid orbitals correspond with observed molecular shapes.

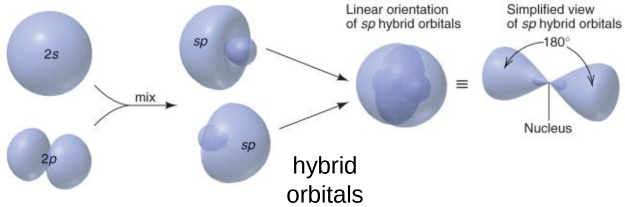
Features of Hybrid Orbitals

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.

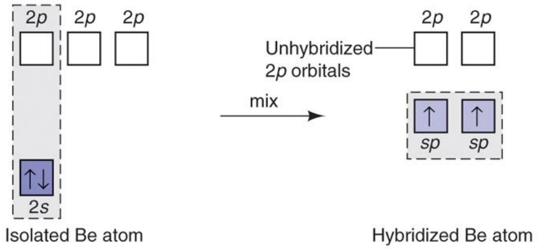
Figure 11.2 **Formation and orientation of *sp* hybrid orbitals and the bonding in $BeCl_2$.**



atomic orbitals

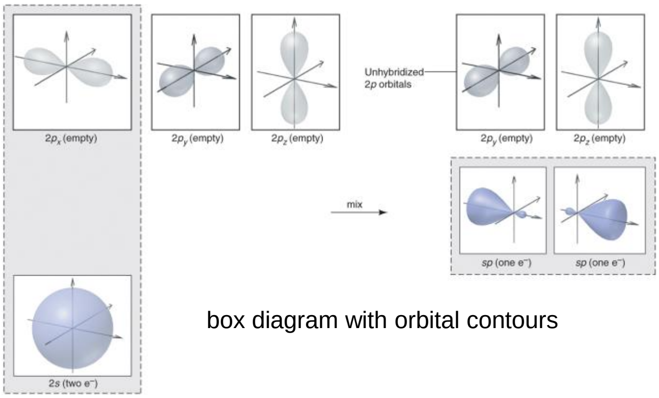
hybrid orbitals

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

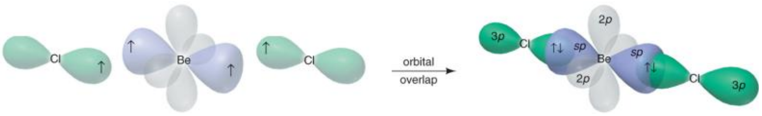


orbital box diagrams

Figure 11.2 continued

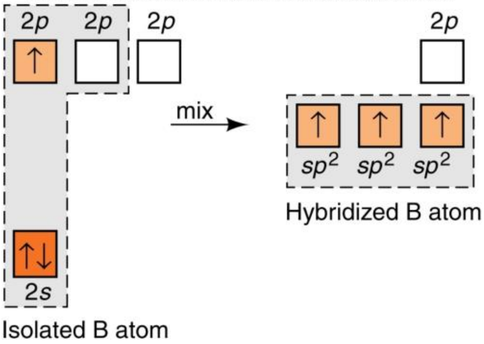


box diagram with orbital contours



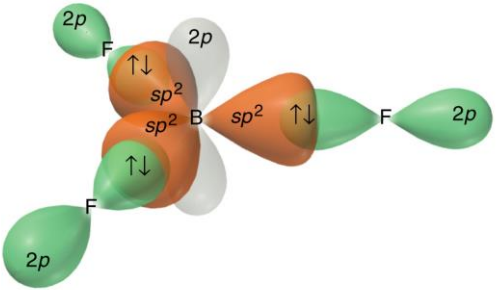
Overlap of Be and Cl orbitals to form $BeCl_2$.

Figure 11.3 The sp^2 hybrid orbitals in BF_3.



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

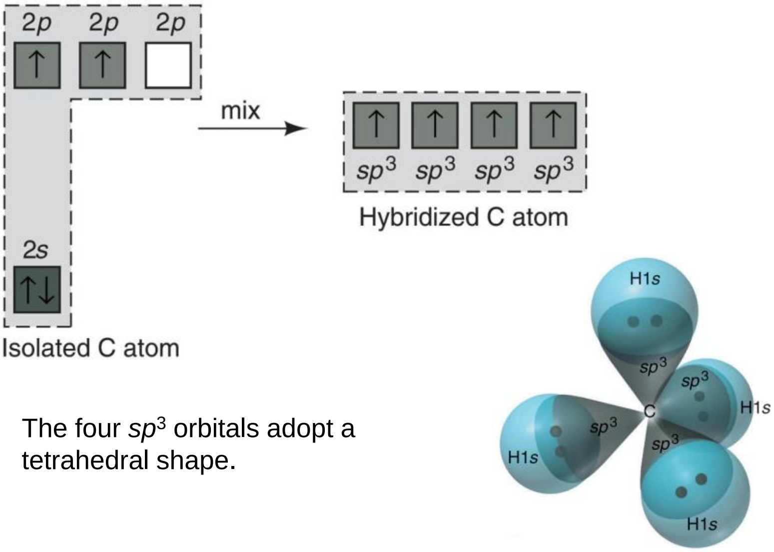
Figure 11.3 continued



The three sp^2 orbitals point to the corners of an equilateral triangle, their axes 120° apart.

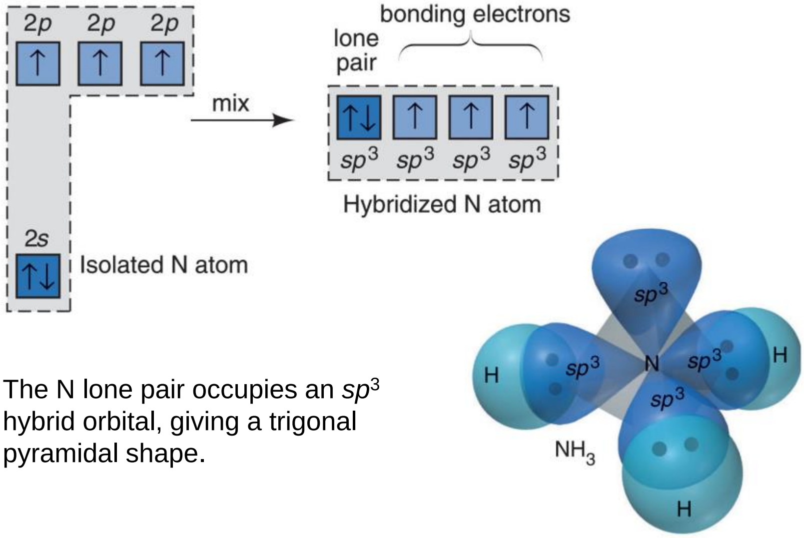
Each half-filled sp^2 orbital overlaps with the half-filled 2*p* orbital of a F atom.

Figure 11.4 The *sp*^{3} hybrid orbitals in CH_4.



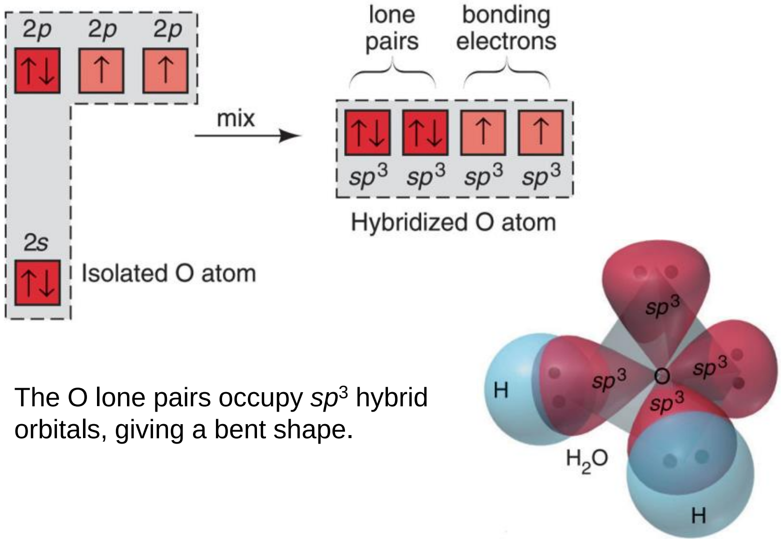
The four *sp*^{3} orbitals adopt a tetrahedral shape.

Figure 11.5 The *sp*^{3} hybrid orbitals in NH_3.



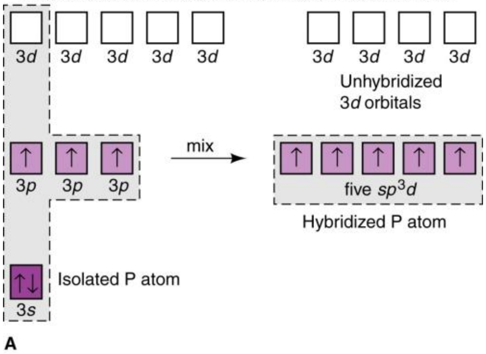
The N lone pair occupies an *sp*^{3} hybrid orbital, giving a trigonal pyramidal shape.

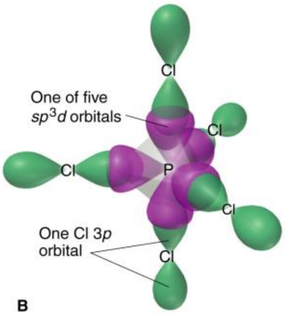
Figure 11.5 continued **The sp^3 hybrid orbitals in H_2O.**



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

Figure 11.6 **The sp^3d hybrid orbitals in PCl_5.**





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

Figure 11.7 The sp^3d^2 hybrid orbitals in SF_6.

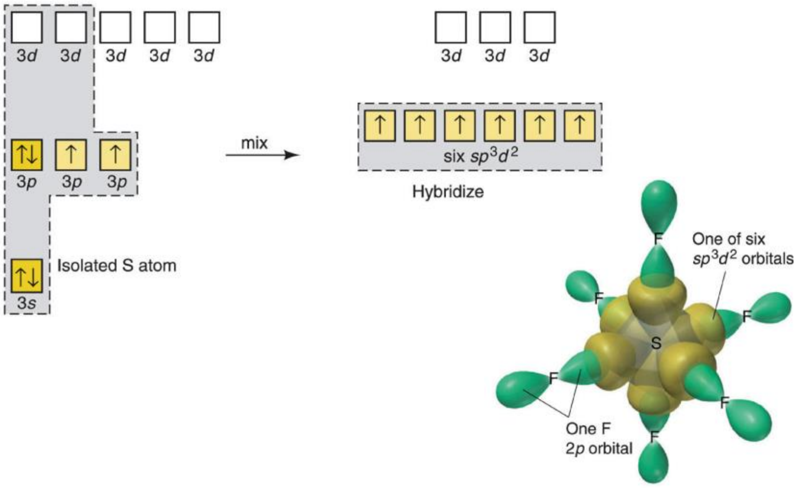
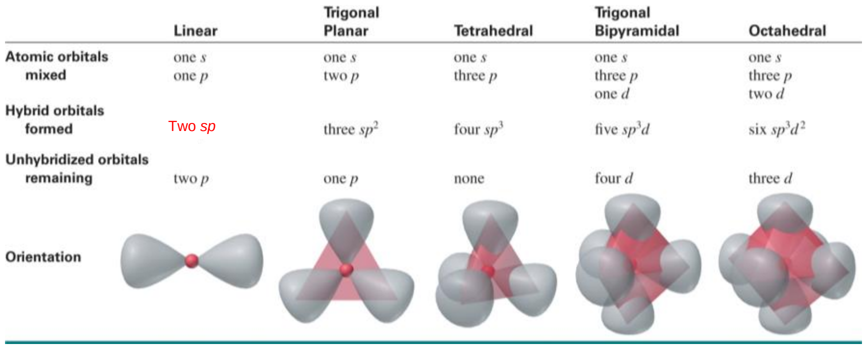
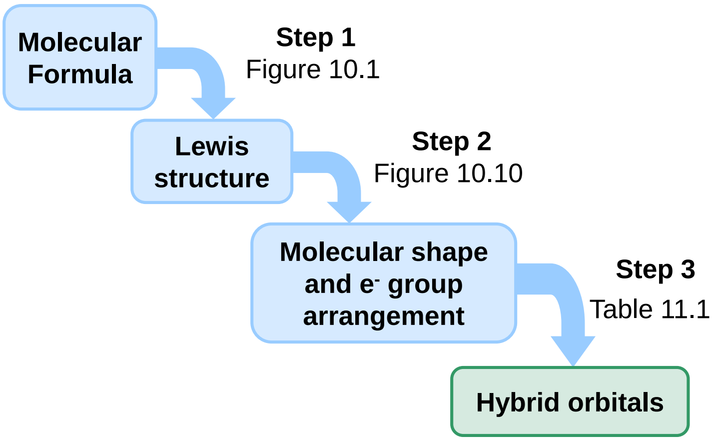


Table 11.1 Composition and Orientation of Hybrid Orbitals.



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

Figure 11.8 **From molecular formula to hybrid orbitals.**



Molecular Formula

Step 1
Figure 10.1

Lewis structure

Step 2
Figure 10.10

Molecular shape and e^- group arrangement

Step 3
Table 11.1

Hybrid orbitals

Sample Problem 11.1 Postulating Hybrid Orbitals in a Molecule

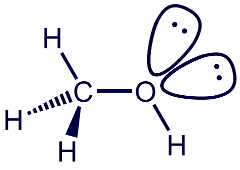
PROBLEM: Use partial orbital diagrams to describe how mixing of the atomic orbitals of the central atom(s) leads to hybrid orbitals in each of the following:

(a) Methanol, CH_3OH **(b)** Sulfur tetrafluoride, SF_4

PLAN: We use the molecular formula to draw the Lewis structure and determine the electron-group arrangement around each central atom. We then postulate the type of hybrid orbitals required and write a partial orbital diagram.

SOLUTION:

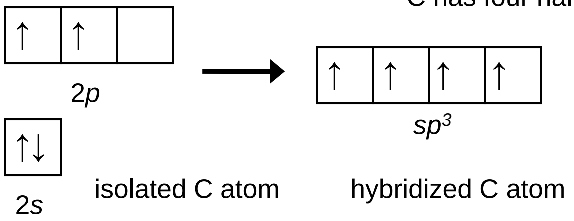
(a) CH_3OH



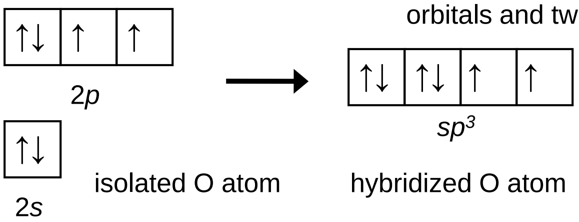
The electron-group arrangement is tetrahedral around both the C and the O atom.

Sample Problem 11.1

C has four half-filled sp^3 orbitals.

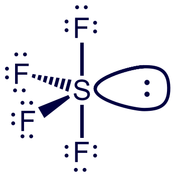


The O atom has two half-filled sp^3 orbitals and two filled with lone pairs.

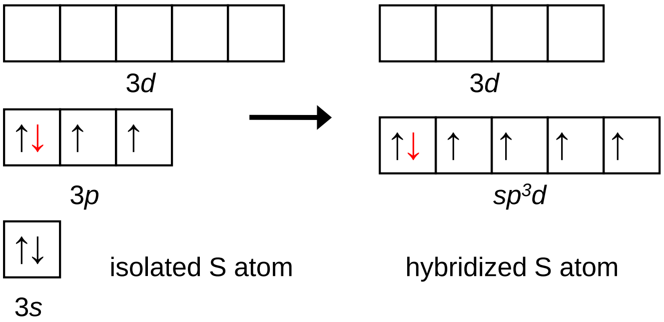


Sample Problem 11.1

(a) SF_4



The electron-group arrangement is trigonal bipyramidal, so the central S atom is sp^3d hybridized.



Types of Covalent Bonds

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

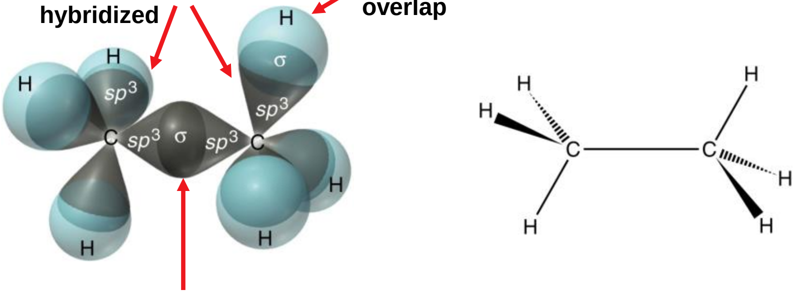
All single bonds are σ bonds.

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

A π bond is weaker than a σ bond because sideways overlap is less effective than end-to-end overlap.

A double bond consists of one σ bond and one π bond

Figure 11.9 The σ bonds in ethane (C_2H_6).



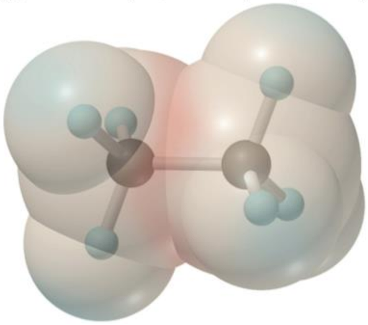
both C are *sp*^{3} hybridized

σ bond formed by *s-sp*^{3} overlap

End-to-end *sp*^{3}-*sp*^{3} overlap to form a σ bond

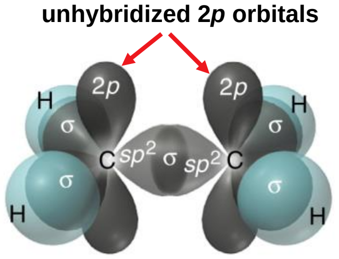
A σ bond is cylindrically symmetrical, with its highest electron density along the bond axis.

Figure 11.9 continued

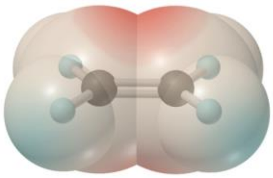


There is relatively even distribution of electron density over all σ bonds.

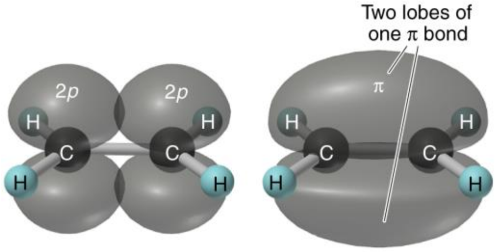
Figure 11.10 The σ and π bonds in ethylene (C_2H_4).



unhybridized 2*p* orbitals



A π bond has two regions of electron density.



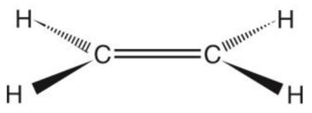
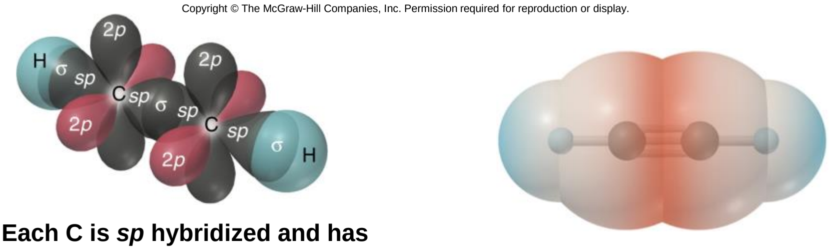


Figure 11.11 The σ and π bonds in acetylene (C_2H_2).



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

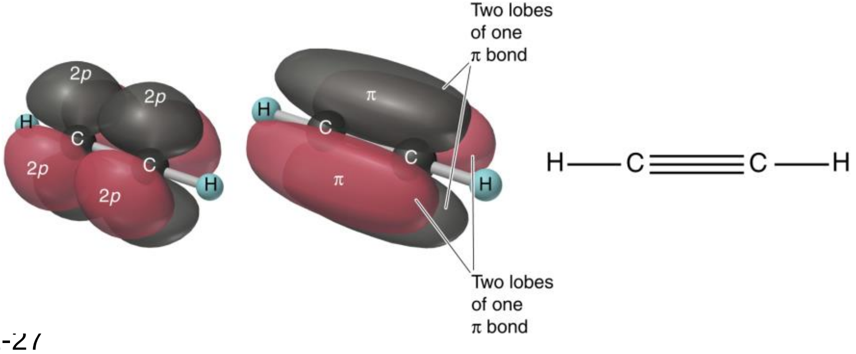
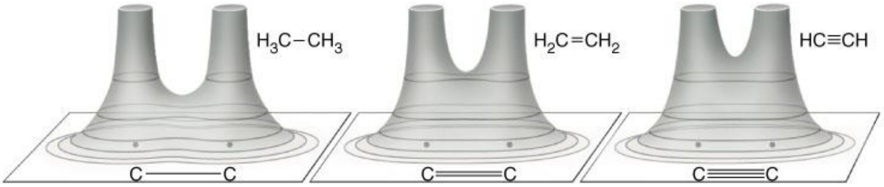


Figure 11.12 Electron density and bond order in ethane, ethylene, and acetylene.



A double bond is less than twice as strong as a single bond, because a π bond is weaker than a σ bond.

However, in terms of bond order, a single bond has BO = 1, a double bond has BO = 2, and a triple bond has BO = 3.

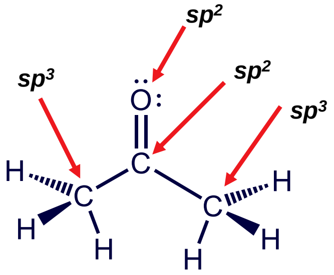
Sample Problem 11.2

Describing the Types of Bonds in Molecules

PROBLEM: Describe the types of bonds and orbitals in acetone, $(CH_3)_2CO$.

PLAN: We use the Lewis structures to determine the arrangement of groups and shape at each central atom. We postulate the hybrid orbitals, taking note of the multiple bonds present.

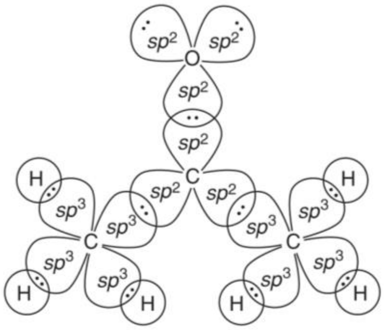
SOLUTION:



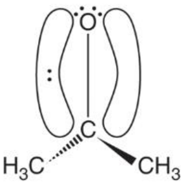
Sample Problem 11.2

The *sp*^{3} hybridized C atoms form σ bonds using *sp*^{3} hybrid orbitals.

The *sp*^{2} hybridized C and O atoms form σ bonds using *sp*^{2} hybrid orbitals, and the π bond of the C=O double bond is formed using *p* orbitals.



σ bonds



π bond (shown with molecule rotated 90°).

Molecular Orbital (MO) Theory

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

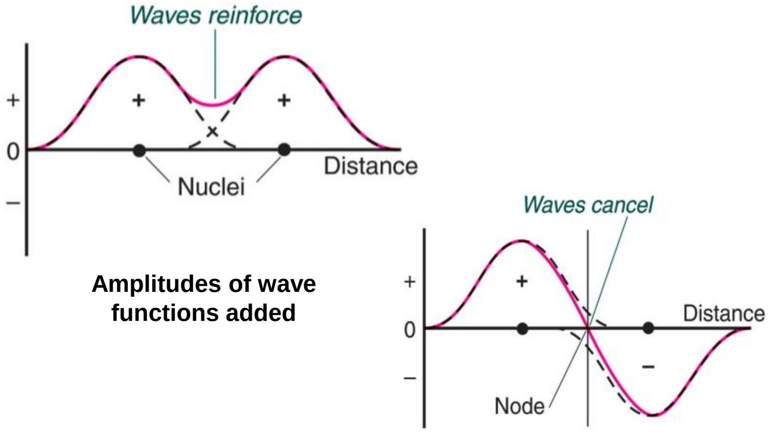
Atomic wave functions (AOs) combine to form ***molecular*** wave functions (MOs).

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.

Figure 11.13

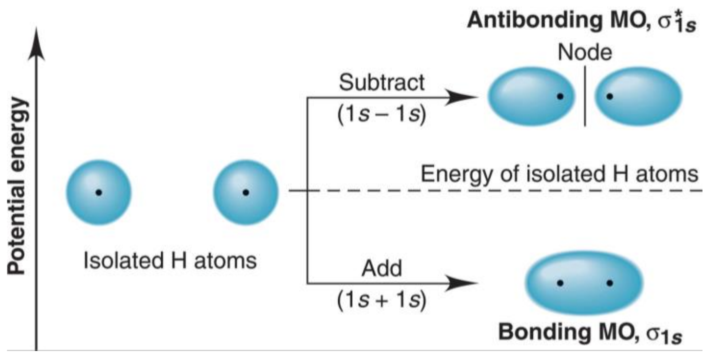
An analogy between light waves and atomic wave functions.



Amplitudes of wave functions added

Amplitudes of wave functions subtracted

Figure 11.14 Contours and energies of H_2 bonding and antibonding MOs.



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

Molecular Orbital Diagrams

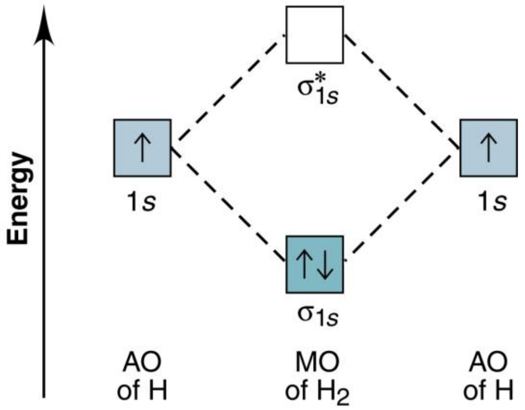
An ***MO diagram***, just like an atomic orbital diagram, shows the relative energy and number of electrons in each MO.

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

Bond order is calculated as follows:

½[(# of e^- in bonding MO) – (# of e^- in antibonding MO)]

Figure 11.15 **MO diagram for H_2.**



H_2 bond order = ½ (2 − 0) = 1

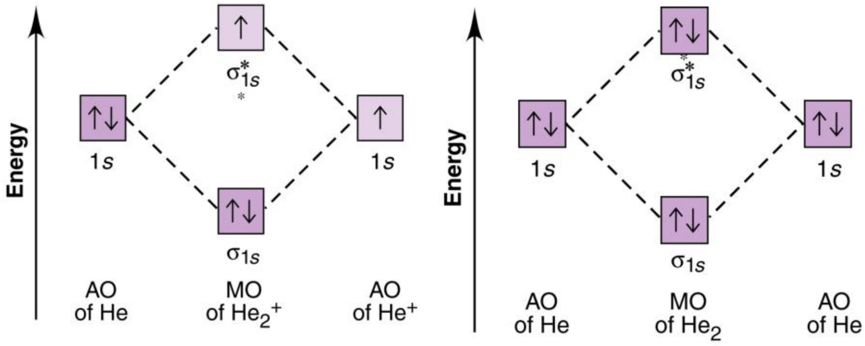
Electrons in Molecular Orbitals

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^- with 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^- each contains. For H_2 the configuration is $(\sigma_{1s})^2$.

Figure 11.16 **MO diagram for He_2^+ and He_2.**



He_2^+ bond order = ½

$(\sigma_{1s})^2(\sigma^*_{1s})^1$

He_2 bond order = 0

$(\sigma_{1s})^2(\sigma^*_{1s})^2$

Sample Problem 11.3 Predicting Stability of Species Using MO Diagrams

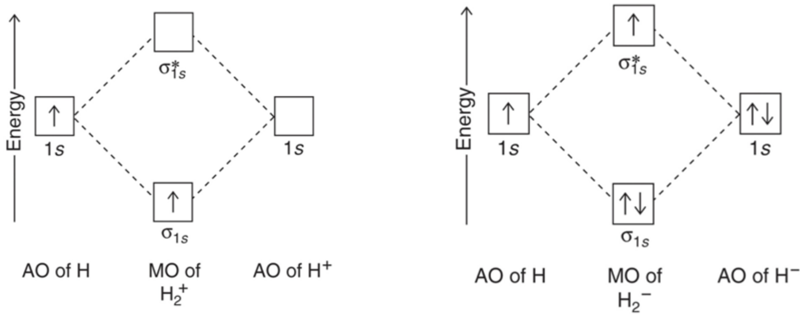
PROBLEM: Use MO diagrams to find bond orders and predict whether H_2^+ and H_2^- exist. If either exists, write its electron configuration.

PLAN: Since the 1*s* AOs form the MOs, the MO diagrams are similar to the one for H_2. We find the number of electrons in each species and distribute them one at a time to the MOs following the rules for orbital filling. We calculate the bond order and predict stability.

SOLUTION:

H_2^+ has one electron to place in its MOs while H_2^- has three electrons to place.

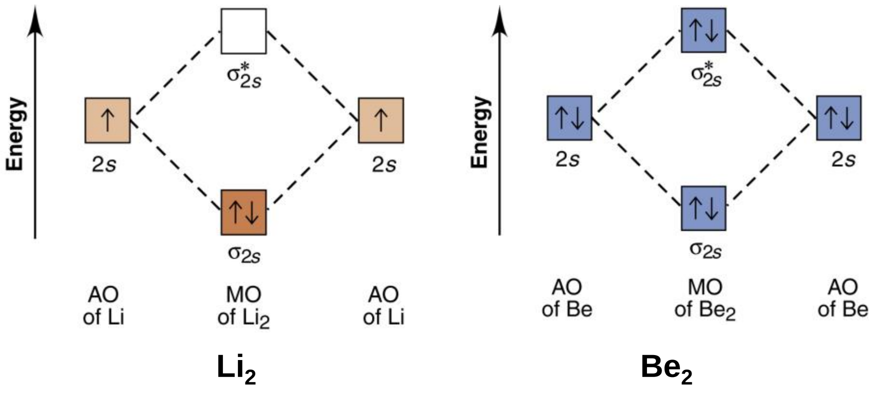
Sample Problem 11.3



For H_2^+, the bond order is
½(1 – 0) = ½;
so we predict that H_2^+ exists.
The configuration is $(\sigma_{1s})^1$.

For H_2^-, the bond order is
½(2 – 1) = ½;
so we predict that H_2^- exists.
The configuration is $(\sigma_{1s})^2(\sigma^*_{1s})^1$

Figure 11.17 Bonding in *s*-block homonuclear diatomic molecules.



Li_2 bond order = 1

Be_2 bond order = 0

Figure 11.18 Shapes and energies of σ and π MOs from combinations of 2*p* atomic orbitals.

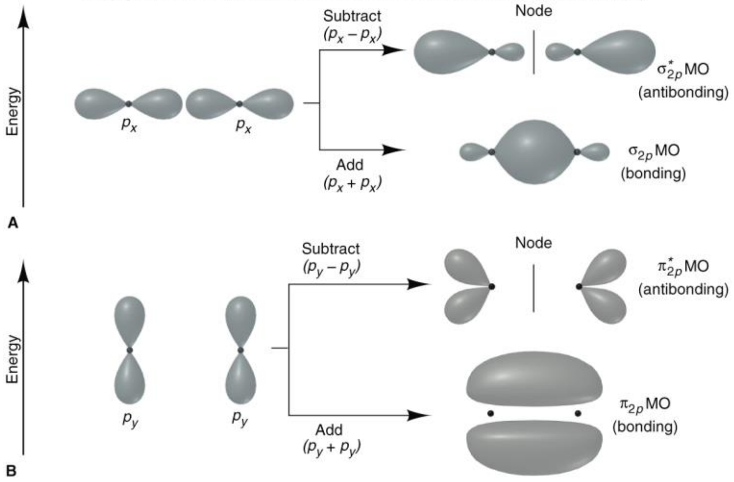


Figure 11.19 Relative MO energy levels for Period 2 homonuclear diatomic molecules.

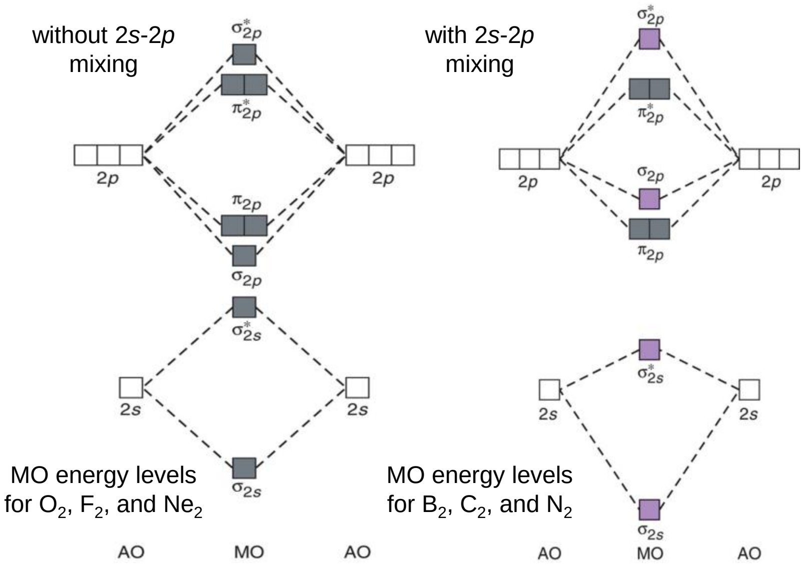


Figure 11.20

MO occupancy and molecular properties for B_2 through Ne_2.

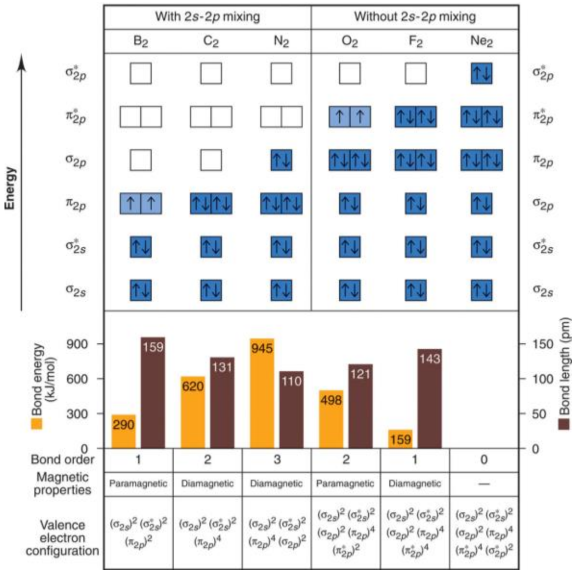


Figure 11.21 **The paramagnetic properties of O_2.**

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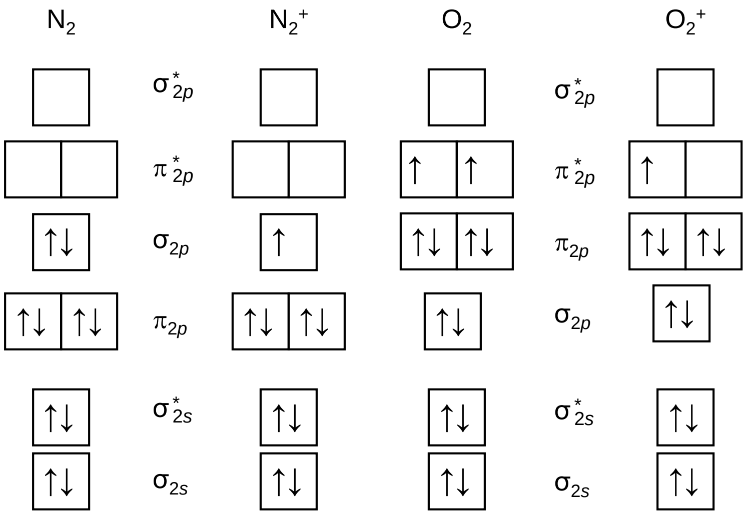
Sample Problem 11.4 **Using MO Theory to Explain Bond Properties**

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

	N_2	N_2^+	O_2	O_2^+
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

PLAN: The data show that removing an electron from each parent molecule has opposite effects: N_2^+ has a weaker longer bond than N_2, but O_2^+ has a stronger, shorter bond than O_2. We determine the valence electrons in each species, draw the sequence of MO energy levels (showing orbital mixing in N_2 but not in O_2), and fill them with electrons. We then calculate bond orders, which relate directly to bond energy and inversely to bond length.

Sample Problem 11.4 **SOLUTION:**



N_2		N_2^+	O_2		O_2^+
☐	σ^*_{2p}	☐	☐	σ^*_{2p}	☐
☐ ☐	π^*_{2p}	☐ ☐	↑ ↑	π^*_{2p}	↑ ☐
↑↓	σ_{2p}	↑	↑↓ ↑↓	π_{2p}	↑↓ ↑↓
↑↓ ↑↓	π_{2p}	↑↓ ↑↓	↑↓	σ_{2p}	↑↓
↑↓	σ^*_{2s}	↑↓	↑↓	σ^*_{2s}	↑↓
↑↓	σ_{2s}	↑↓	↑↓	σ_{2s}	↑↓

Sample Problem 11.4

Calculating bond orders:

For N_2 ½(8 – 2) = 3 For N_2^+ ½(7 – 2) = 2.5

N_2^+ has a longer, weaker bond than N_2 because to form N_2^+, a *bonding* electron is removed and the bond order decreases.

For O_2 ½(8 – 4) = 2 For O_2^+ ½(8 – 3) = 2.5

O_2^+ has a shorter, stronger bond than O_2 because to form O_2^+, an *antibonding* electron is removed and the bond order increases.