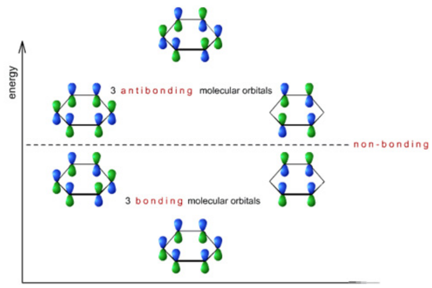
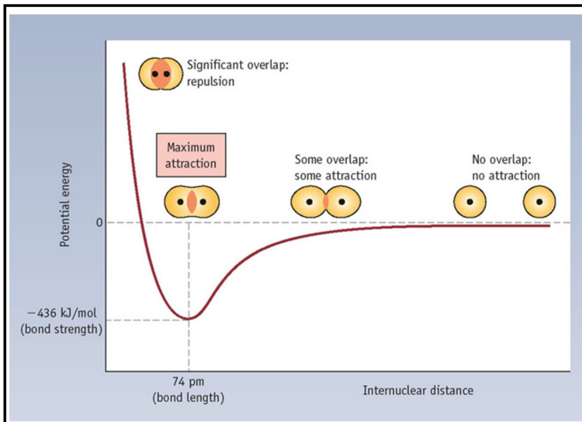
10 – Bonding and Molecular Structure: Orbital Hybridization and Molecular Orbitals





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Two ways of explaining bonding

Yes, I was from Portland, was awarded two Nobel Prizes (1950, 1954), a Nobel Peace Prize (1962) and went to OSU.

Valence Bond Theory (Linus Pauling)

Bonding electron pairs between atoms.
Lone pairs of electrons localized on a particular atom.

Bonds are formed by overlap of atomic orbitals is the basis for valence bond theory.

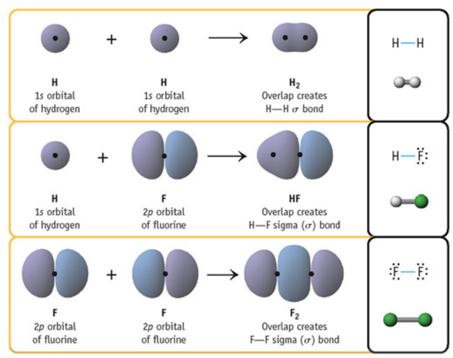
Molecular Orbital Theory (MOT) (Robert S. Mulliken)

Molecular orbitals that are "spread out", or delocalized over the molecule.

No, I am not Robert A. Millikan

I wish people would quit asking me that!

1966 Nobel Prize in Chemistry



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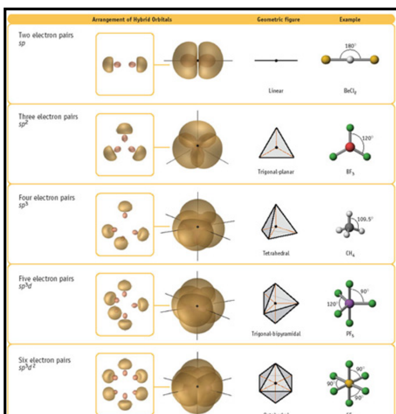
Note that not all bonds are hybridized: Example of unhybridized bonding overlap. Note that end-on overlaps are known as sigma bonds (σ).



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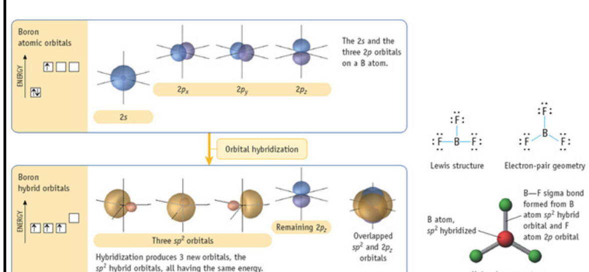
Hybridization: For predicting and explaining bond angles

Orbitals "hybridize" to form equivalent bonding orbitals.

sp^2 hybrids



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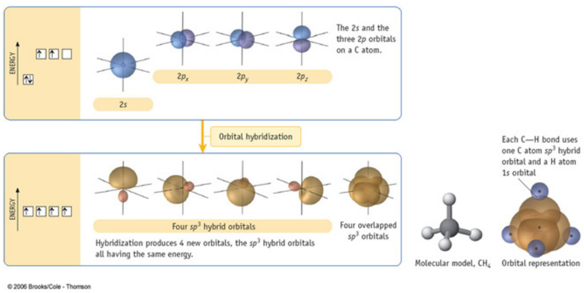
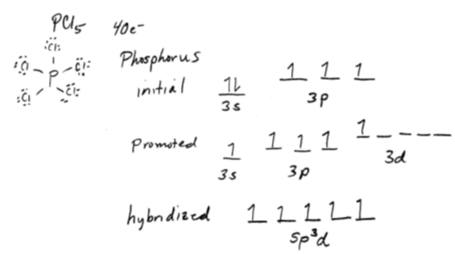
Orbital Energy in Hybridized Orbitals

sp^3 hybrids

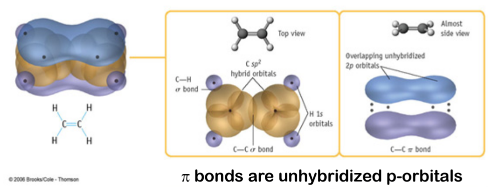


Example:

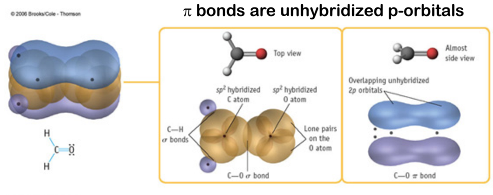
Use orbital box diagrams to show the hybridization of phosphorus in PCl_5



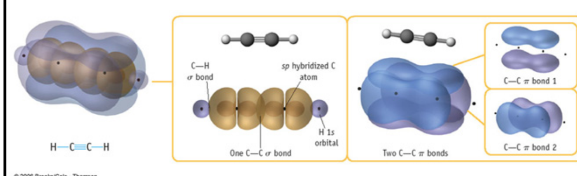
Multiple Bonds in Valence Bond Theory



π bonds are unhybridized p-orbitals

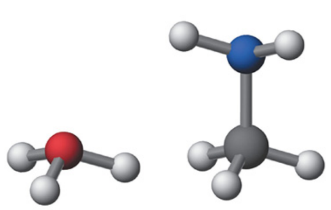


Triple Bonds



Example:

Use valence bond theory to describe the bonding in the hydronium ion, H_3O^+, and methylamine, CH_3NH_2.



Hydronium ion, H_3O^+ Methylamine, CH_3NH_2

hydronium	**sp^3 hybridized** **tetrahedral electronic geometry** **trigonal pyramidal molecular geometry**
methylamine	**sp^3 hybridized** **tetrahedral electronic geometry**
carbon:	**tetrahedral molecular**
nitrogen:	**trigonal pyramidal**

Examples

Identify the hybridization of the central atom in the following compounds and ions:

a) BH_4^-
b) SF_5^-
c) OSF_4
d) ClF_3
e) BCl_3
f) XeO_6^{4-}

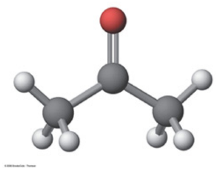
Answers:

a) sp^3
b) sp^3d^2
c) sp^3d
d) sp^3d
e) sp^2
f) sp^3d^2

Examples:

Use valence bond theory to describe the bonding in acetone, CH_3COCH_3.

Answer:
Central carbon is sp^2 hybridized. The end carbons are sp^3 hybridized. The oxygen is sp^2 hybridized.



Describe the bonding in a nitrogen molecule, N_2.

Answer: Each nitrogen is sp hybridized with a triple bond (one hybridized sigma bond and two overlapping unhybridized p-orbitals) between the nitrogens.

Molecular Orbital Theory

Assumes that pure s and p atomic orbitals of the atoms in the molecule combine to produce orbitals that are *spread out, or delocalized*, over several atoms or even over an entire molecule.

Correctly explains certain characteristics of molecules not explained by valence bond theory (e.g. paramagetism of O_2).

Most of the focus on MOT will be on homonuclear diatomic molecules (such as N_2)

Begin with a given arrangement of atoms in the molecule at the known bond distances, then determine sets of molecular orbitals

There are three types of molecular orbitals that can form:

Bonding orbital: Contributes to the bond between atoms

Antibonding orbital: Detracts from the bond between atoms (increases repulsion between nuclei)

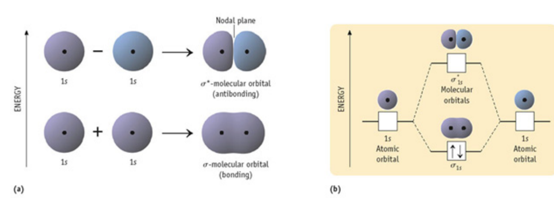
Nonbonding orbital: Neither adds nor subtracts to the bonds in a molecule

Principles of Molecular Orbital Theory:

1st: The total number of molecular orbitals is always equal to the total number of atomic orbitals contributed by the atoms that have combined.

2nd: The bonding molecular orbital is lower in energy than the parent orbitals, and the antibonding orbital is higher in energy.

3rd: Electrons of the molecule are assigned to orbitals of successively higher energy according to the Pauli exclusion principle, Aufbau principle <u>and</u> Hund's rule.



Formation of homonuclear diatomic H_2 molecule

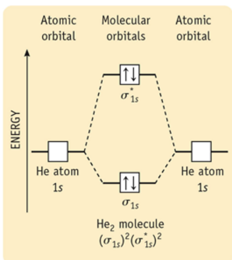
Note two orbitals in = two molecular orbitals out

The bonding molecular orbital is designated by σ_{1s} (pronounced sigma one-ess. (1s + 1s)

The antibonding molecular orbital is designated by σ^*_{1s} (pronounced sigma one-ess star)(1s – 1s)

Bond order and why He_2 does not form

Bond Order = ½ (number of electrons in bonding MOs – number of electrons in antibonding MOs)



Note that the bond order of diatomic helium = 0 is not conducive to the formation of this molecule

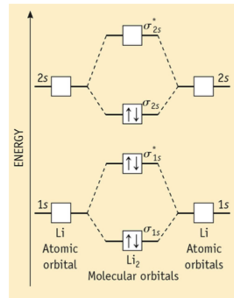
Is He_2^+ and H_2^+ likely to exist?

Answer:
He_2^+ = ½ (2 – 1) = ½ (some stability)
$(\sigma 1s)^2(\sigma^* 1s)^1$

H_2^+ = ½ (1 – 0) = ½
$(\sigma 1s)^1$

Molecular Orbitals of Higher Energy Molecules

4th principle: Atomic orbitals combine to form molecular orbitals most effectively when the atomic orbitals are of similar energy.



The bond order for Li_2 is 1

The configuration can be written as

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

[core electrons]$(\sigma_{2s})^2$

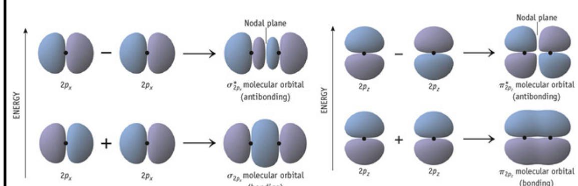
The core electrons make no contribution to the bond.

Would diatomic beryllium be expected to exist? What is its bond order and electron configuration?

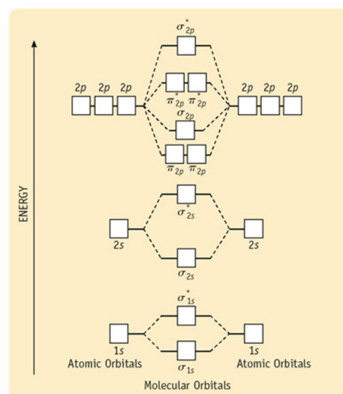
$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2\ (\sigma^* 2s)^2$
Bond order: ½ (2 – 2) = 0 No.

When s orbitals combine to make molecular orbitals, they are of the σ type.

When p orbitals combine to make molecular orbitals, the first set is a σ set (σ, σ*) and the others are π type (π, π*)(see below)



A similar set of these would be formed for the p_y orientation.



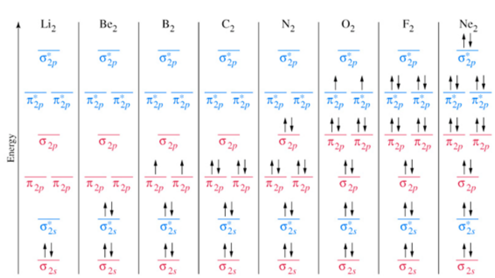
Arrangement of molecular orbitals when p-orbitals are involved

(Note again: Six p-orbitals involved, six molecular orbitals out.

Period 2 Homonuclear Diatomic Elements

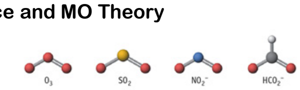
Accounts for the paramagnetism of O_2.
Note change in MO energy after N_2
Accounts for bond order and relative bond energy

What are the bond orders of B_2 and N_2? Answer: 1 and 3 respectively



Resonance and MO Theory

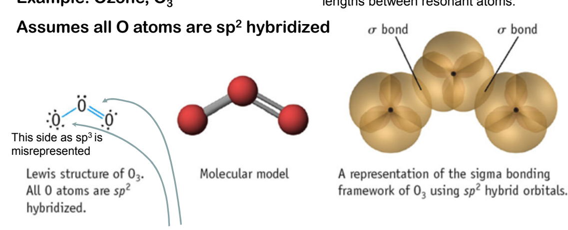
Note: The “polarity” of ozone can be determined from formal charges.



Examples of molecules (/ions) with equal bond lengths between resonant atoms.

Example: Ozone, O_3

Assumes all O atoms are sp^2 hybridized



Lewis structure of O_3. All O atoms are sp^2 hybridized.

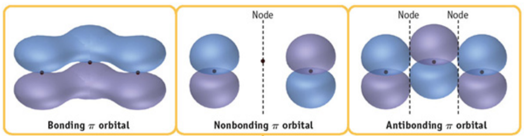
Molecular model

A representation of the sigma bonding framework of O_3 using sp^2 hybrid orbitals.

The π bond is represented by the remaining two *pairs* of electrons.

The three unhybridized p-orbitals of the three oxgens combine to form three molecular orbitals.

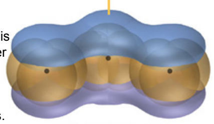
One of the π_p molecular orbitals is <u>bonding</u>, one is <u>nonbonding</u> and one is <u>antibonding</u>.



In phase

Out of Phase

One of the two remaining pairs is in the bonding MO and the other is in the nonbonding (NOT antibonding) MO; Bond order is .5 b/c bonding electrons are spread over the two O-O bonds.



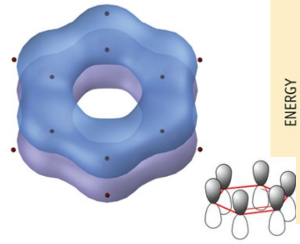
σ and π bonding in ozone

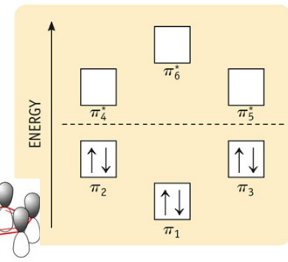
The overall bond order is 1.5 (.5 for π and 1 for σ)

The Benzene Ring Revisited

Molecular orbitals (π) created from the 6 unhybridized orbitals of the carbon atoms in benzene.

Accounts for the stability of benzene.





Projection