

Chapter 9 - Covalent Bonding: Orbitals

9.1 Hybridization and the Localized Electron Model

A. Hybridization

1. The mixing of two or more atomic orbitals of similar energies on the same atom to produce new orbitals of equal energies

B. Hybrid Orbitals

1. Orbitals of equal energy produced by the combination of two or more orbitals on the same atom

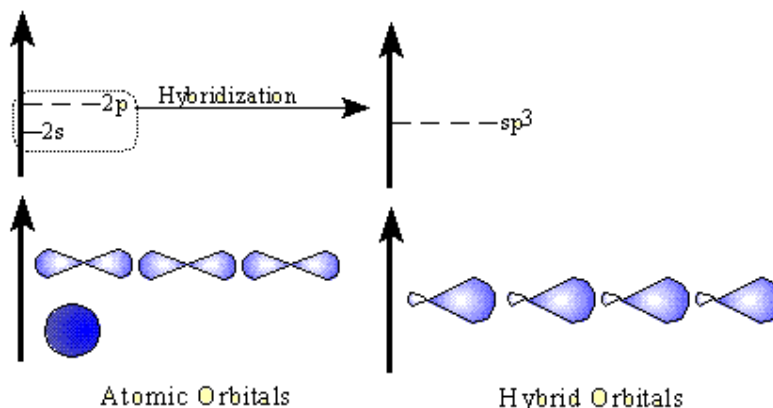
C. Evidence for hybridization of carbon - Methane and sp^3

1. Four bonds of equal length and strength



Carbon's isolated configuration

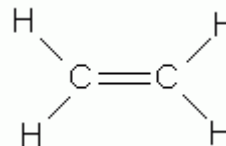
Carbon's hybridized configuration

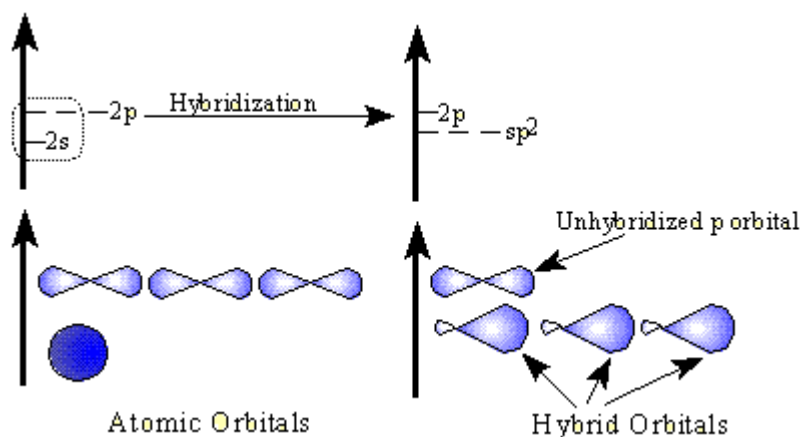


2. Four effective pairs of electrons surround the carbon
3. "Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, this model assumes that the atom adopts a set of sp^3 orbitals; the atom becomes hybridized"

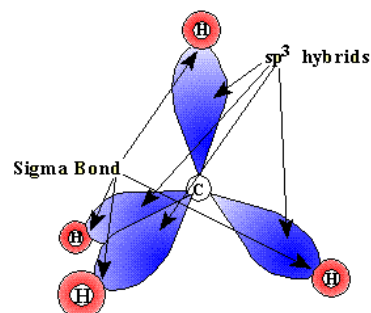
D. sp^2 hybridization

1. Trigonal planar structure, 120° angle, in ethene (ethylene) rules out sp^3 hybridization
2. sp^2 hybridization creates 3 identical orbitals of intermediate energy and length and leaves one unhybridized p orbital
3. 3 effective pairs of electrons surround the carbon (double bond treated as one effective pair)





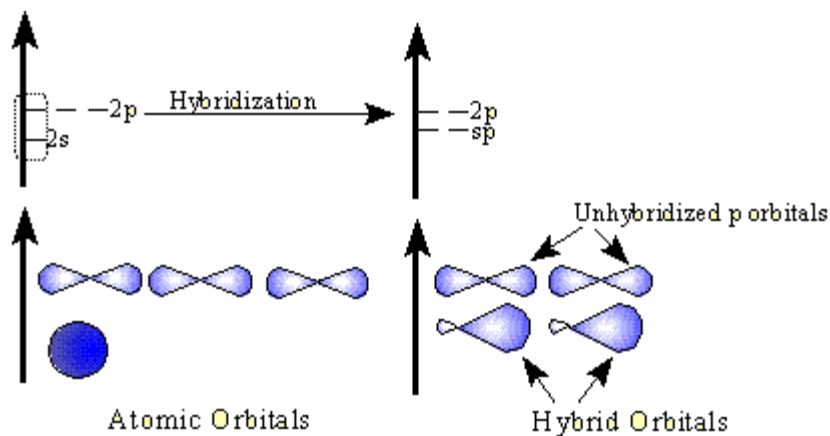
4. Sigma bonds (σ bond)
 - a. Bond in which the electron pair is shared in an area centered on a line running between the atoms
 - b. Lobes of bonding orbital point toward each other
 - c. All bonds in methane are sigma bonds



5. Pi bonds (π bonds)
 - a. Electron pair above and below the σ bond
 - b. Created by overlapping of nonhybridized 2p orbitals on each carbon
6. Double bonds
 - a. Double bonds always consist of one σ bond and one π bond



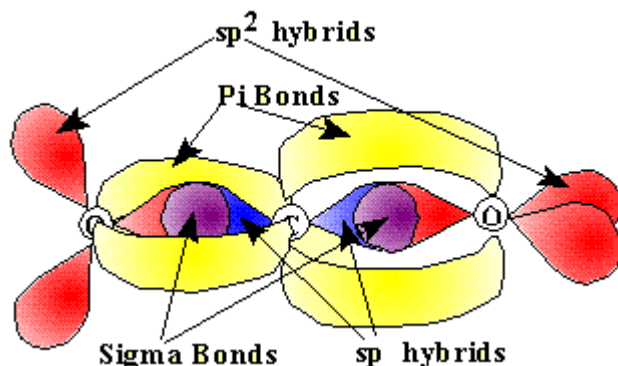
C. sp Hybridization



1. Each carbon has two hybrid orbitals and two unhybridized 2p orbitals

2. Carbon dioxide

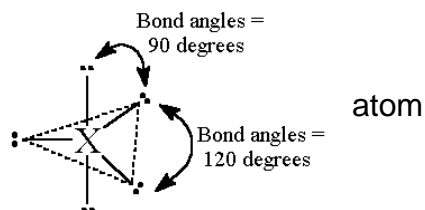
- Oxygens have 3 effective pairs of electrons (sp^2 hybrids)
 - 1 double bond, two lone pairs
- Carbons have 2 effective pairs (2 double bonds)



Notice that the sp^2 orbitals on the two oxygens are at 90° angles, as are the π bond between carbon and oxygen

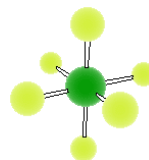
D. dsp^3 Hybridization

- Five effective pairs around a central
- Trigonal bipyramidal shape
- PCl_5 is an example



E. d^2sp^3 Hybridization

- Six effective pairs around a central atom
- Octahedral structure
- SF_6 is an example



Question: Why doesn't carbon undergo dsp^3 or d^2sp^3 hybridization, while phosphorous and sulfur do undergo this type of hybridization?

Atomic Orbitals	Type of hybridization	# of hybrid orbitals	Geometry	# of Effective pairs
s, p	sp	2	Linear	2
s, p, p	sp^2	3	Trigonal-planar	3
s, p, p, p	sp^3	4	Tetrahedral	4
s, p, p, p, d	dsp^3	5	Trigonal bipyramidal	5
s, p, p, p, d, d	d^2sp^3	6	Octagonal	6

9.2 The Molecular Orbital Model

A. Shortcomings of the Localized Electron Model

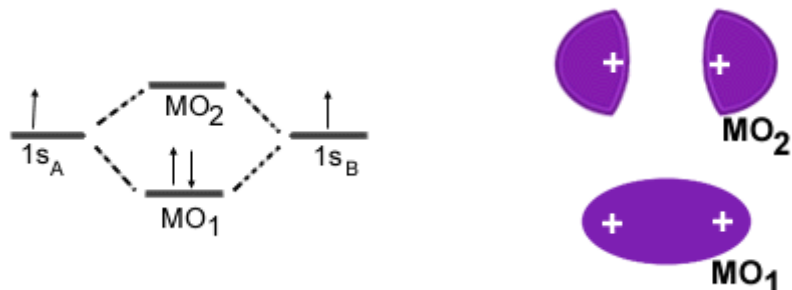
1. Electrons are not actually localized
2. Does not deal effectively with molecules containing unpaired electrons
3. Gives no direct information about bond energies

B. Molecular Orbitals

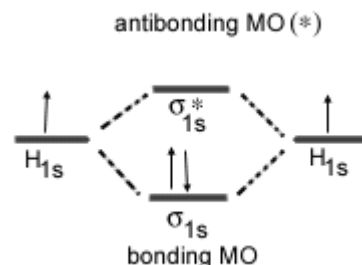
1. Can hold two electrons with opposite spins
2. Square of the orbital's wave function indicates electron probability

C. The Hydrogen Molecule (H_2)

1. Two possible bonding orbitals, shapes determine by Ψ^2



2. Bonding takes place in MO_1 in which electrons achieve lower energy (greater stability), with electrons between the two nuclei
3. Both orbitals are in line with the nuclei, so they are σ molecular orbitals
4. Higher energy orbital is designated as antibonding (*).
5. Electron configuration of H_2 can be written as σ_{1s}^2



D. Bond Order

1. Bond order is the difference between the number of bonding electrons and the number of antibonding electrons, divided by two
2. Larger bond order =
 - a. greater bond strength
 - b. greater bond energy
 - c. shorter bond length

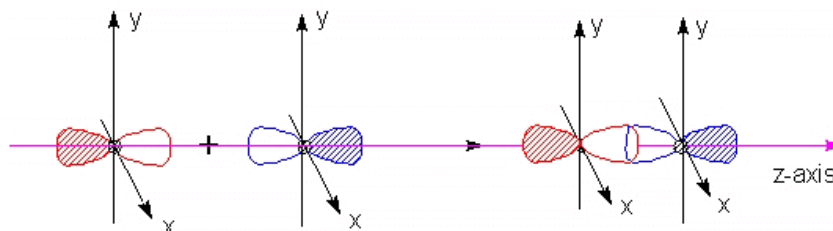
9.3 Bonding in Homonuclear Diatomic Molecules

A. In order to participate in molecular orbitals, atomic orbitals must overlap in space

B. Larger bond order is favored

C. When molecular orbitals are formed from p orbitals, σ orbitals are favored over π orbitals (σ interactions are stronger than π interactions)

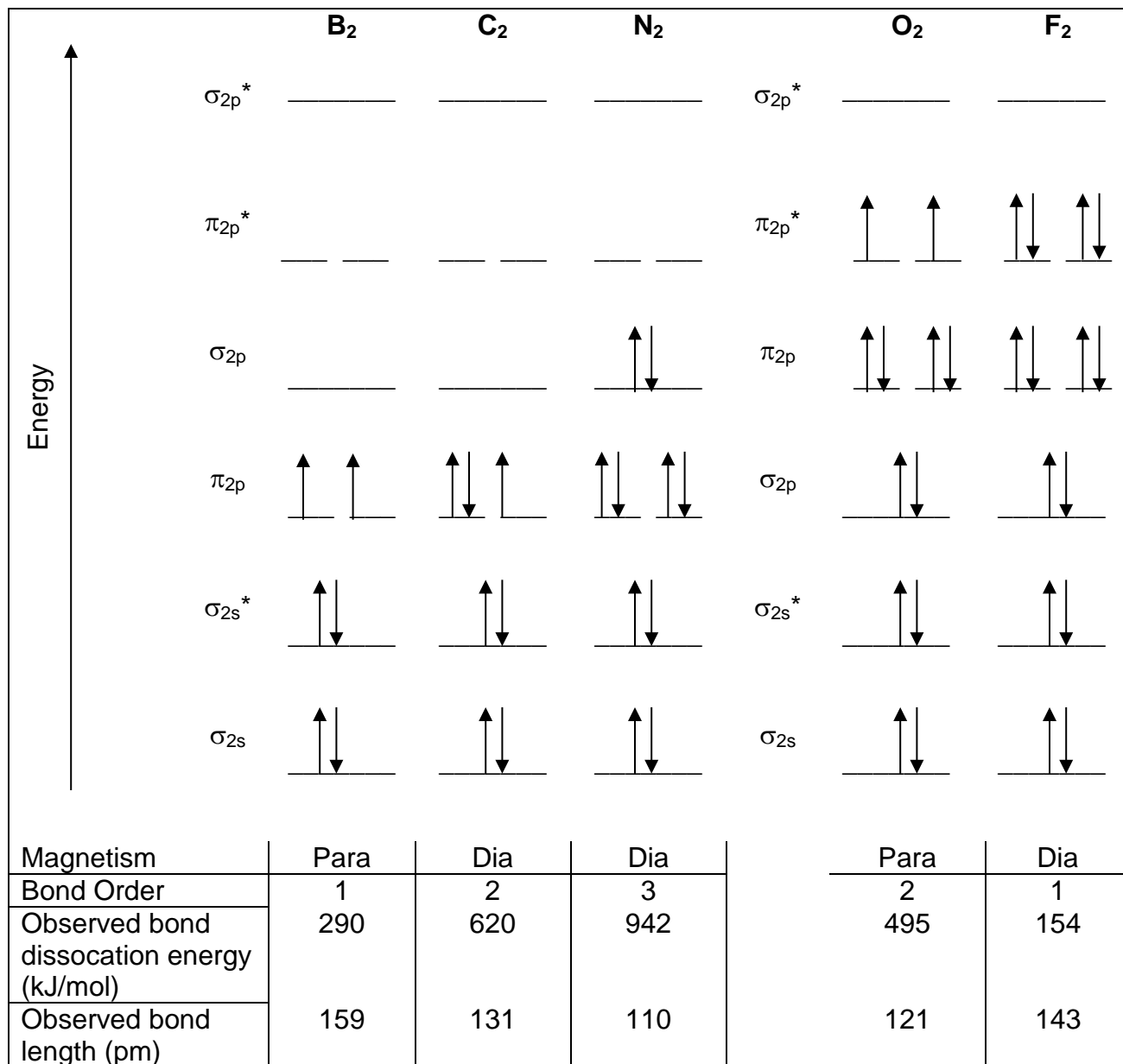
1. Electrons are closer to the nucleus = lower energy



D. Paramagnetism

1. Magnetism can be induced in some nonmagnetic materials when in the presence of a magnetic field
 - a. Paramagnetism causes the substance to be attracted into the inducing magnetic field
 - (1) associated with unpaired electrons
 - b. Diamagnetism causes the substance to be repelled from the inducing magnetic field
 - (1) associated with paired electrons

Figure 9.39



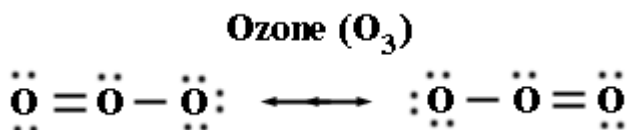
One can measure magnetic properties FIRST, and use the results (dia- or para-) to determine the energy order of the molecular orbitals

9.4 Bonding in Heteronuclear Diatomic Molecules

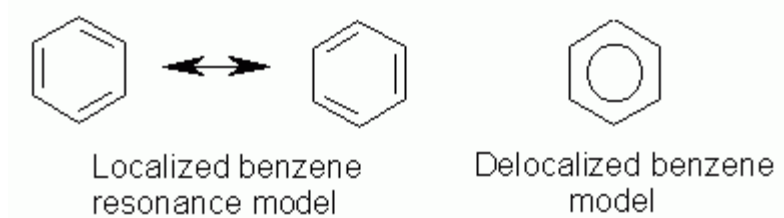
- A. Similar, but not identical atoms
 - 1. Use molecular orbital diagrams for homonuclear molecules
- B. Significantly different atoms
 - 1. Each molecule must be examined individually
 - 2. There is no universally accepted molecular orbital energy order

9.5 Combining the Localized Electron and Molecular Orbital Models

- A. Resonance
 - 1. Attempt to draw localized electrons in a structure in which electrons are not localized



- 2. σ bonds can be described using localized electron model
 - 3. π bonds (delocalized) must be described using the molecular orbital model
- B. Benzene
 - 1. σ bonds (C - H and C - C) are sp² hybridized
 - a. Localized model
 - 2. π bonds are a result of remaining p orbitals above and below the plane of the benzene ring



9.6 Photoelectron Spectroscopy (PES)