Bonding: Molecular Orbitals, Hybridization & Shape

Adopted in part from materials by:

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- Professor Victor Batista, Yale University
- The Department of Chemistry, University of North Carolina

Electronic Configuration & Bonding *(Review)*

- Every element is different.
  - ❖The number of protons identifies the element.
  - ❖The number of electrons equals the number of protons in neutral atoms.
  - ❖Atoms gain or loose electrons to form ions
  - ❖Gain & loss of electrons represent ionic bonds
  - ❖Sharing electrons represent covalent bonds
- Electronic configuration is the identification of electrons in an atom. Electrons have unique probabilities of being found in certain spaces: *atomic orbitals*

Atomic Orbitals *(Review)*

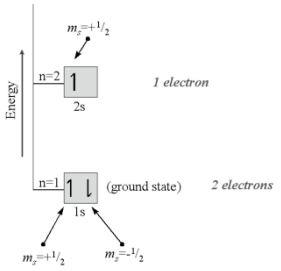
- Electrons have unique probabilities of being found in certain spaces: *atomic orbitals*
- Quantum numbers (q.n.) relate to atomic orbitals, which have discrete respective energies.
- There are four q.n. for these energies; the Periodic Table is arranged by q.n.: primary (n), angular momentum (l), magnetic (m_l) and spin (m_s)
- Orbitals are based on values of (l) and (m_l)
- Orbitals are derived from the solution of the Schrodinger Equation using wave functions that represent the behavior of the electrons.

Lithium Electronic Configuration

- The arrows indicate the value of the magnetic spin (m_s) *quantum number (up for +1/2 and down for -1/2)*
- *The occupation of the orbitals would be written in the following way:*

$1s^2 2s^1$

or, "1s two, 2s one".



http://wine1.sb.fsu.edu/chm1045/notes/Struct/EConfig/Struct08.htm

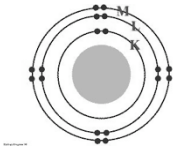
Electronic Configurations – Box Diagram

Element	Total Electrons	Orbital Diagram 1s	2s	2p	3s	Electron Configuration
H	1	↑				$1s^1$
He	2	↑↓				$1s^2$
Li	3	↑↓	↑			$1s^2\,2s^1$
Be	4	↑↓	↑↓			$1s^2\,2s^2$
B	5	↑↓	↑↓	↑		$1s^2\,2s^2\,2p^1$

- The two electrons in Helium represent the complete filling of the first electronic shell which is a very stable configuration
- **The s and p electrons in the outer shell, highest value of n (beyond the stable core), are called *valence electrons***

Valence Electrons

- **Valence electrons** are the electrons in the outer electron shell or highest energy level of an atom.
- The elements beneath He in the Periodic Table have stable configurations of 8 valence electrons



The lowest level (K), can contain 2 electrons.
The next level (L) can contain 8 electrons.
The next level (M) can contain 8 electrons.

Carbon - $1s^2 2s^2 2p^2$ - four valence electrons

Examples of Electronic Configuration

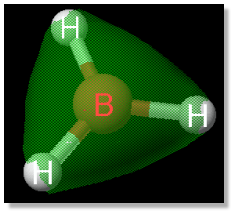
- Ne → $1s^2\ 2s^2\ 2p^6$ (10 electrons total; 8 valence electrons)
- F → $1s^2\ 2s^2\ 2p^5$ (9 electrons; 7 valence electrons)
- F^- → $1s^2\ 2s^2\ 2p^6$ (10 electrons total; 8 valence electrons)
- Mg → $1s^2\ 2s^2\ 2p^6\ 3s^2$ (12 electrons total; 2 valence electrons)
- Mg^{2+} → $1s^2\ 2s^2\ 2p^6$ (10 electrons total; 8 valence electrons)

Molecular Orbital Theory

Molecular orbital theory describes molecules in a similar way as to how atoms are described, that is, in terms of orbitals, orbital diagrams, and electron configurations.

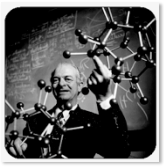
Two Theories of Bonding

- **MOLECULAR ORBITAL THEORY** — Robert Mulliken (1896-1986)
- **valence electrons are delocalized**
- valence electrons are **in orbitals** (called molecular orbitals) **spread over entire molecule.**



Two Theories of Bonding

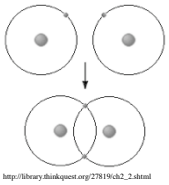
- **VALENCE BOND THEORY** — Linus Pauling
- valence electrons are localized **between atoms (or are lone pairs).**
- **half-filled atomic orbitals overlap to form bonds.**
- Two electrons of opposite spin can occupy the overlapping orbitals.
- Bonding increases the probability of finding electrons in between atoms.



Review Lewis Structures & VSEPR Theory:
http://chemconnections.org/general/chem120/VSEPR-10/VSEPR-Shapes-10wo.htm
http://chemconnections.org/VSEPR-jmol/
http://chemconnections.org/general/movies/VSEPR.MOV

Atomic and Molecular Orbitals

- Orbital Mixing (Covalent Bonding)
  - When atoms share electrons to form a bond, their atomic orbitals mix to form bonds. In order for these orbitals to mix they must:
    - Have similar energy levels.
    - Overlap well.
    - Be close together.

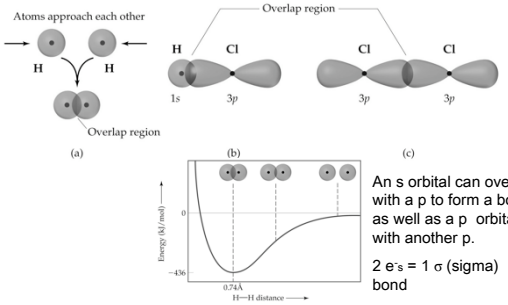


The two atoms share one valence electron each from their outer shell.

In this case both 1s orbitals overlap and share their valence electrons. 2 e⁻s = 1 σ (sigma) bond

http://library.thinkquest.org/27819/ch2_2.shtml

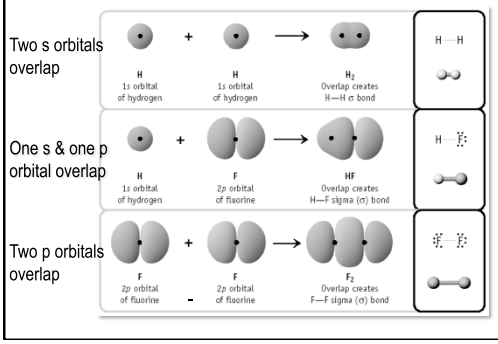
Covalent Bonding: Atomic Orbital Overlap



An s orbital can overlap with a p to form a bond as well as a p orbital with another p.

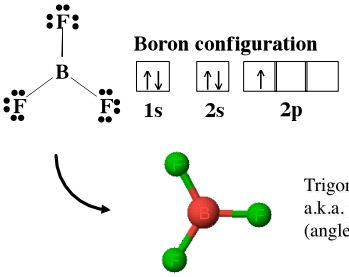
2 e⁻s = 1 σ (sigma) bond

Sigma Bond Formation



Using VB Theory

Bonding in BF_3

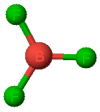


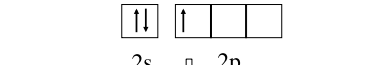
Trigonal planar
a.k.a. planar triangle
(angles = 120°)

Bonding in BF_3

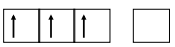
- How to account for 3 bonds 120° apart using a spherical s orbital and p orbitals that are 90° apart?
- Pauling said to modify VB approach with **ORBITAL HYBRIDIZATION**
- — mix available orbitals to form a new set of orbitals — **HYBRID ORBITALS** — that will give the maximum overlap in the correct geometry.

Bonding in BF_3





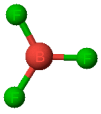
hydridize orbitals ⇩ rearrange electrons



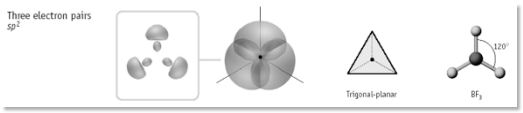
three sp^2 hybrid orbitals

unused p orbital

Bonding in BF_3

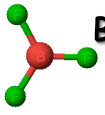


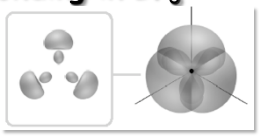
- The three hybrid orbitals are made from 1 s orbital and 2 p orbitals → 3 sp^2 hybrids.



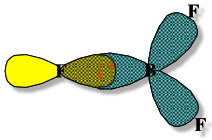
•Now there are 3, half-filled HYBRID orbitals that can be used to form B-F sigma bonds.

Bonding in BF_3

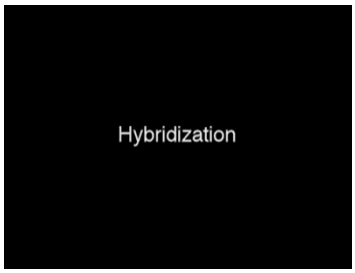




An orbital from each F overlaps one of the sp^2 hybrids to form a B-F σ bond.



Orbital Hybridization



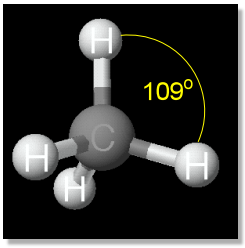
http://chemconnections.org/general/movies/Hybridization.MOV

Bonding in CH_4

How are 4 C—H sigma bonds 109° apart accounted for?

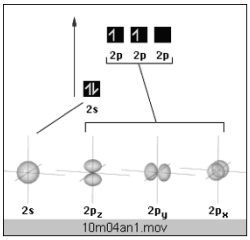
- **Carbon has 4 atomic orbitals — s, p_x, p_y, and p_z**

Form 4 new hybrid orbitals pointing in the right direction!



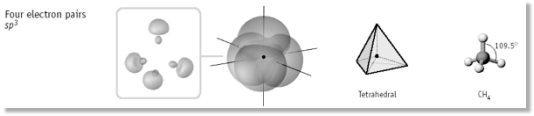
Bonding in any Tetrahedron — Formation of Hybrid Atomic Orbitals

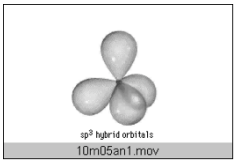
4 C atom orbitals hybridize to form four equivalent sp^3 hybrid atomic orbitals. [Four single (σ) bonds]



http://xbeams.chem.yale.edu/~batista/113/movies/10M04AN1.MOV

Bonding in a Tetrahedron — Formation of Hybrid Atomic Orbitals

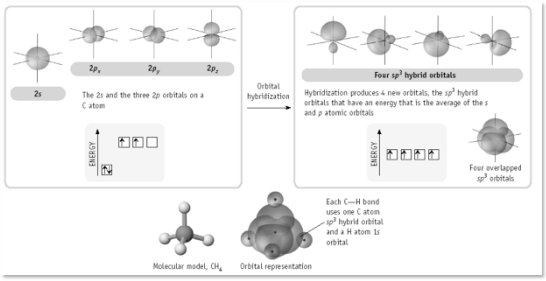




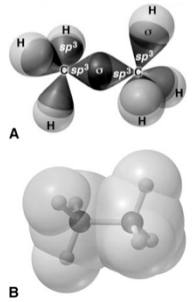
4 orbitals in Carbon (C) hybridize to form four equivalent sp^3 hybrid atomic orbitals.

http://xbeams.chem.yale.edu/~batista/113/movies/10M05AN1.MOV

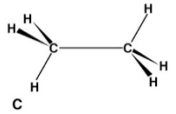
Bonding in CH_4



Single bond: C-C Bond Order =1



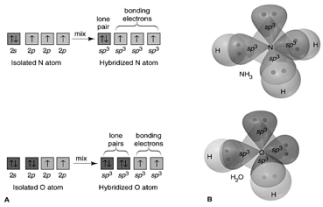
The σ Bonds in Ethane (C_2H_6)



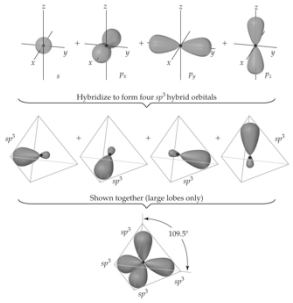
Bond Length: C-C > C=C > C≡C

Bond Energy: C-C < C=C < C≡C

The sp^3 Hybrid Orbitals in NH_3 and H_2O

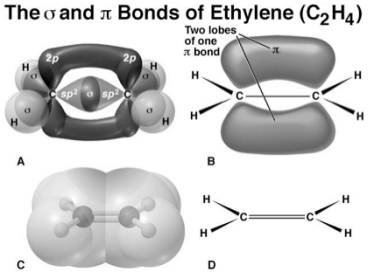


sp^2 vs. sp^3 Hybrid Orbitals



Double bond: C=C Bond Order =2

The σ and π Bonds of Ethylene (C_2H_4)

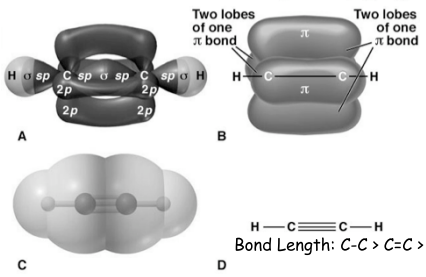


Bond Length: C-C > C=C > C≡C

Bond Energy: C-C < C=C < C≡C

Triple bond: C≡C Bond Order =3

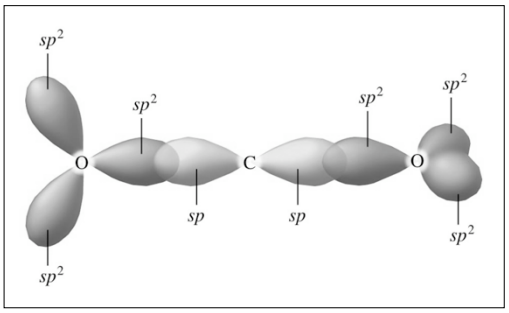
The σ and π Bonds of Acetylene (C_2H_2)



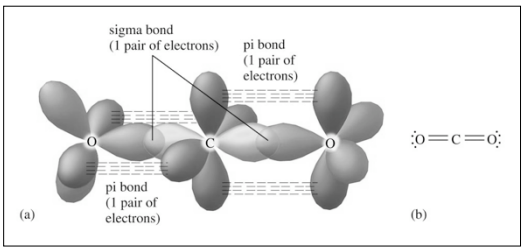
Bond Length: C-C > C=C > C≡C

Bond Energy: C-C < C=C < C≡C

sp Hybrid Orbitals



sp Hybrid Orbitals



Orbital Hybridization

BONDS	SHAPE	HYBRID	REMAIN
2	linear	sp	2 p's
3	trigonal planar	sp^2	1 p
4	tetrahedral	sp^3	none

QUESTION

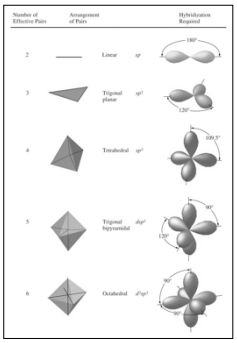
Consider the skeletal structure shown below:

N—C—C—N

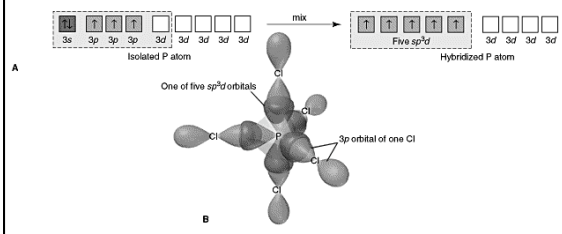
Draw the Lewis structure and answer the following: How many of the atoms are sp hybridized?

A) 0
B) 1
C) 2
D) 3
E) 4

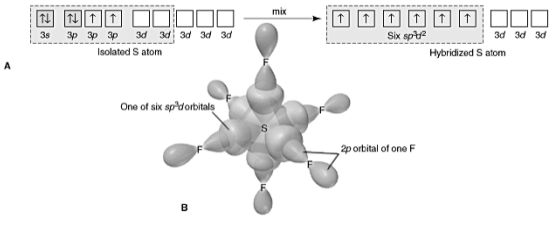
Summary: Hybrid Orbitals



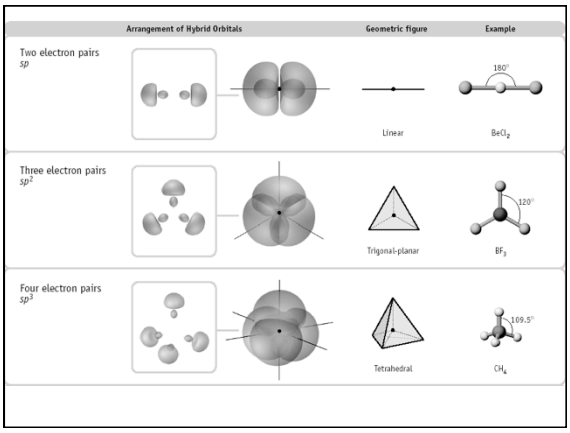
The sp^3d Hybrid Orbitals in PCl_5



The sp^3d^2 Hybrid Orbitals in SF_6



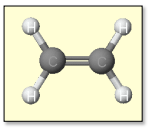
Sulfur Hexafluoride -- SF_6



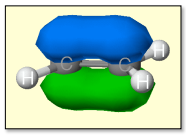
QUESTION

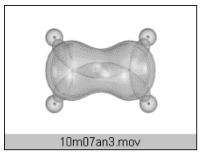
The bond angle formed between three carbon atoms in a compound is approximately 120°C. Which of the following is the most likely type of hybridization for the middle carbon atom?

A. sp
B. sp^2
C. sp^3
D. sp^3d



Multiple Bonding in C_2H_4

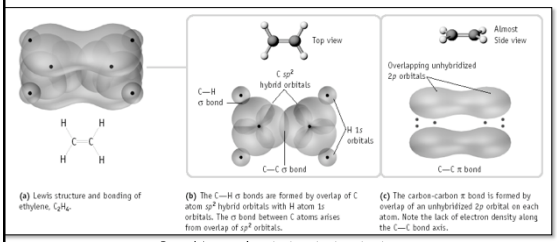




http://xbeams.chem.yale.edu/~batista/113/movies/10M07AN3.MOV

σ and π Bonding in C_2H_4

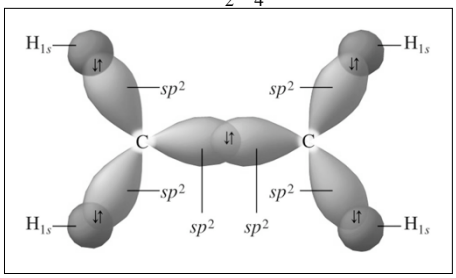
Double bond: C=C Bond Order =2



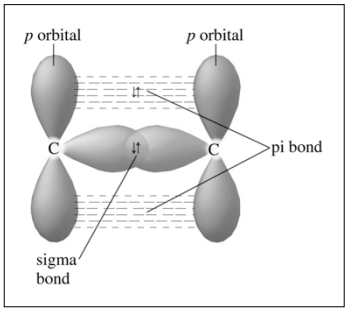
Bond Length: C-C > C=C > C≡C

Bond Energy: C-C < C=C < C≡C

The Sigma Bonds in Ethylene C_2H_4



Carbon-Carbon Double Bond Consists of a sigma and a pi Bond



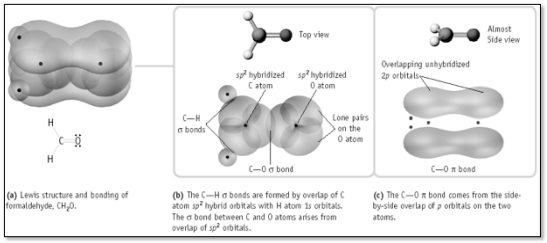
QUESTION

Atoms which are sp^2 hybridized form ____ pi bond(s).

A) 0
B) 1
C) 2
D) 3
E) 4

σ and π Bonding in CH_2O

C=O Bond Order =2



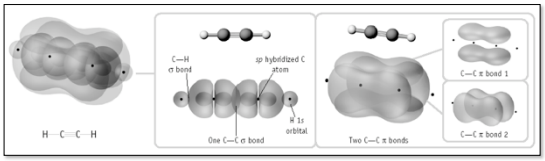
QUESTION

Formaldehyde and methanol both have a carbon to oxygen bond. Yet the oxygen atom in methanol, CH_3OH, can freely spin around without causing the C to move with it . In formaldehyde, CH_2O, any spin on the oxygen causes the C to spin with it. What type of hybridization and what consequence is found for the carbon in each of these useful compounds? (Hint examine the Lewis structures)

A. Methanol—sp^3; formaldehyde—sp; the unhybridized p orbitals get in the way of free rotation for the C to O bond.
B. Methanol—sp^2; formaldehyde—sp^2; the unhybridized p orbital in methanol forms a new bond with the other three H atoms that allows the bond to be stronger and rotate on its own.
C. Methanol—sp^3; formaldehyde—sp^2; the unhybridized p orbital of C in formaldehyde forms a bond with an oxygen p orbital to further lock their positions together.
D. I don't see the connection here.

σ and π Bonding in C_2H_2

Triple bond: C≡C Bond Order =3



Bond Length: C-C > C=C > C≡C

Bond Energy: C-C < C=C < C≡C

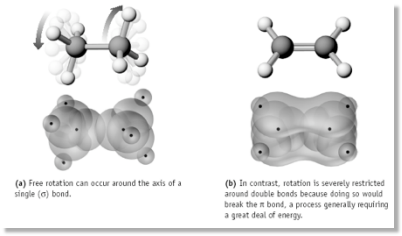
QUESTION

As the bond order of a bond increases, the bond energy _____ and the bond length _____.

A) increases; increases
B) decreases; decreases
C) increases; decreases
D) decreases; increases
E) More information is needed to answer this question.

Consequences of Multiple Bonding

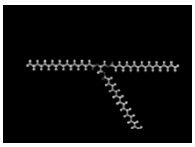
There is restricted rotation around C=C bond.

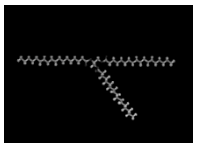


Consequences of Multiple Bonding

Unrestricted rotation around C-C bonds, "saturated" molecules.

Restricted rotation around C=C bonds, "unsaturated" molecules.

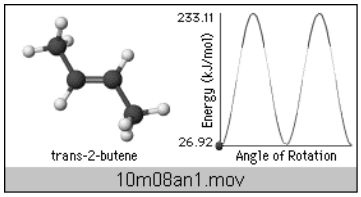




Saturated vs. Unsaturated Fats
Arterial Effects?

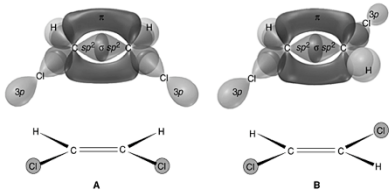
Consequences of Multiple Bonding

Restricted rotation around C=C bond.



http://xbeams.chem.yale.edu/~batista/113/movies/10M08AN1.MOV

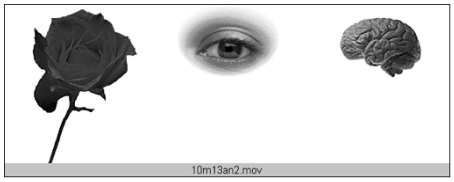
Restricted Rotation of π-Bonded Molecules: Isomers



A) cis –(Z) 1,2 dichloroethylene **B)** trans –(E) 1,2 dichloroethylene

http://chemconnections.org/organic/chem227/227assign-10.html#vision

Double Bonds and Vision

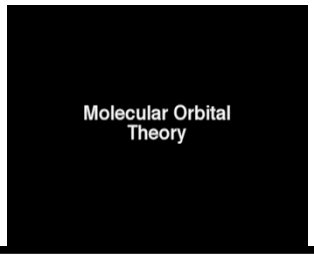


http://chemconnections.org/general/movies/TransRhodop2.gt

See a **recent publication** on the underlying molecular rearrangements

http://xbeams.chem.yale.edu/~batista/113/movies/10M05AN1.MOV

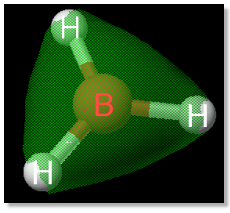
Molecular Orbital Theory



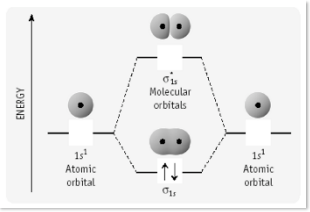
http://chemconnections.org/general/movies/html_swf/MolecularOrbitalTheory/MolecularOrbitalTheory.html

Molecular Orbital Theory

- Valence electrons are delocalized in molecular orbitals spread over entire molecule.
- ***First Principle:*** The total # of molecular orbitals equals the number of atomic orbitals contributed by the atoms that have combined.
- ***Second Principle:*** The bonding molecular orbitals are lower in energy than the parents orbitals and the antibonding orbitals are higher in energy.
- ***Third Principle:*** The electrons of the molecule are assigned to orbitals of successively higher energy according to the Pauli exclusion principle and Hund's rule.



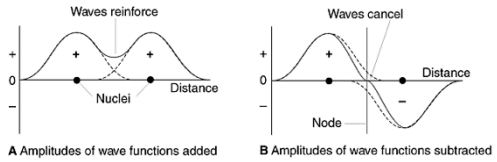
Molecular Orbital Theory



1. # MO's = # atomic orbitals used.
2. Bonding MO is lower in energy than atomic orbitals. Antibonding MO is higher.
3. Electrons assigned to MO's of higher and higher energy.

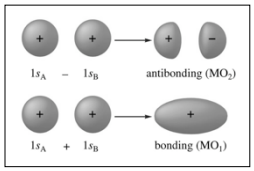
Bond order = 1/2 [# e- in bonding MOs
- # e- in antibonding MOs]

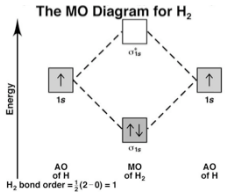
Analogy between Light Waves and Atomic Wave Functions



A Amplitudes of wave functions added

B Amplitudes of wave functions subtracted

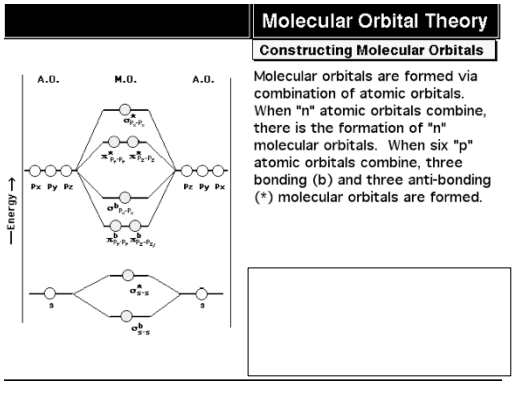


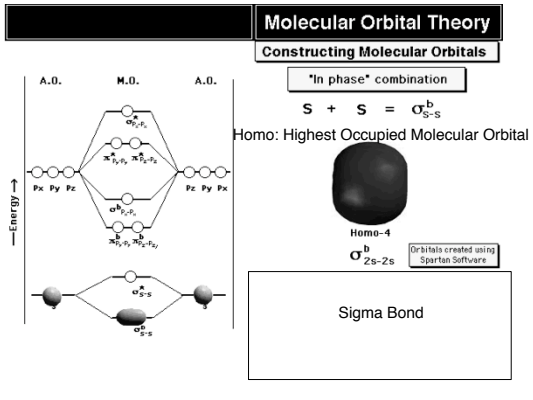


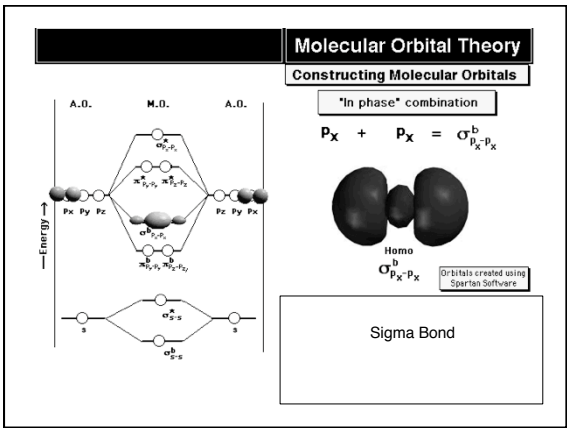
QUESTION

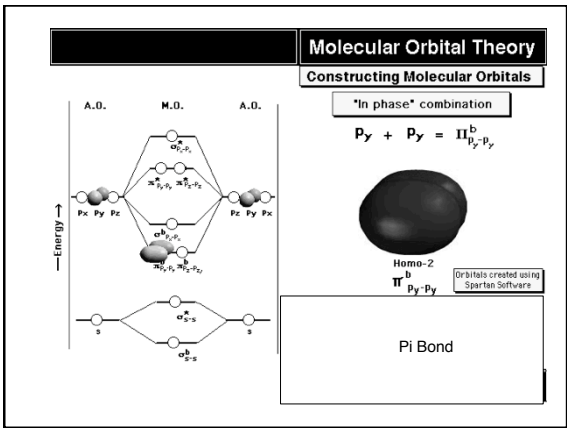
When comparing the M.O. theory of bonding to the Localized Electron model which of the following would be an incorrect claim?

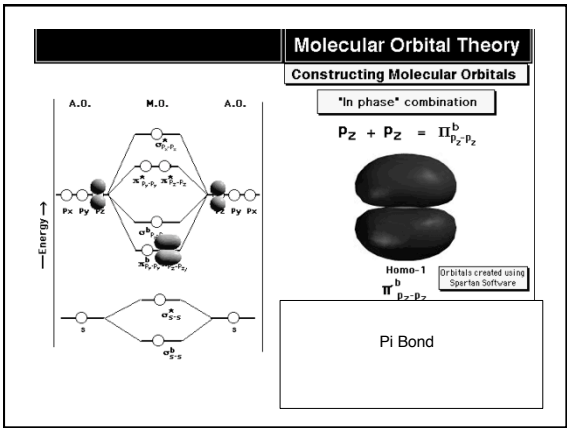
A. For a molecule of H_2; $MO_1 = 1s\ A + 1s\ B$; $MO_2 = 1s\ A - 1s\ B$
B. The molecular orbitals (both bonding and antibonding) still have a maximum electron occupancy of two just as the localized orbitals.
C. In H_2, the bonding orbital (MO_1) is lower in energy than the 1*s* orbital of hydrogen.
D. Although not used in the molecular bonding, the 1*s* orbital of hydrogen is present.

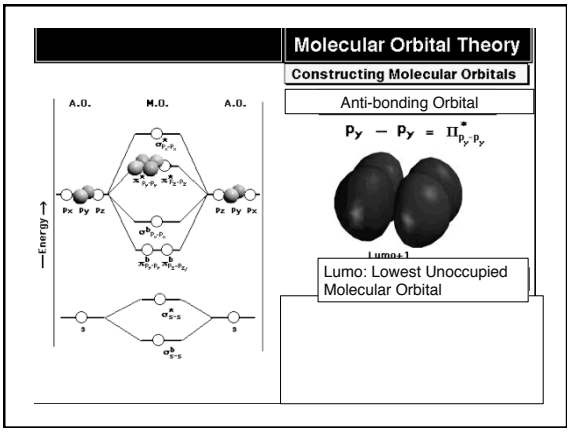


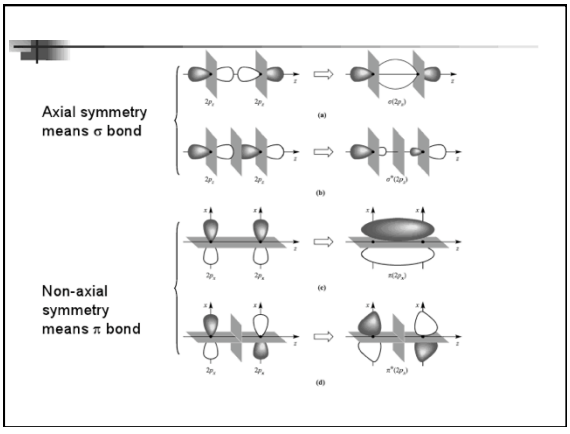




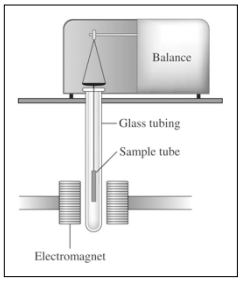




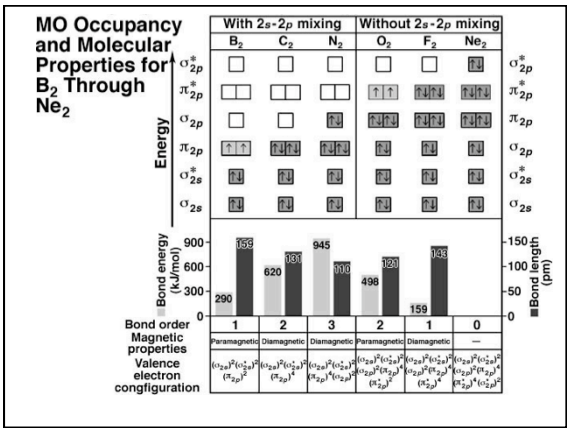




Apparatus Used to Measure Paramagnetism
NOTE: O_2 is paramagnetic; Why?



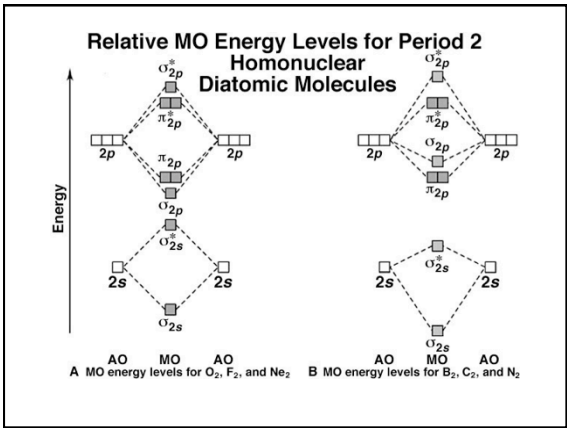
http://chemconnections.org/general/movies/O2-paramagnetism.MOV



QUESTION

The carbon monoxide molecule can bond to hemoglobin, causing severe oxygen shortages in humans, at a rate up to 200 times faster than oxygen. What is the bond order and magnetic characteristic of CO?

A. Three; diamagnetic
B. Two; diamagnetic
C. Three; paramagnetic
D. Two paramagnetic



Quantum Mechanics: Molecular Orbital Theory

Quantum mechanics describes the energy in terms of interactions among nuclei and electrons. This is given by the Schrödinger equation.

The Schrödinger equation may be solved exactly for the hydrogen atom.

$H\Psi = E\Psi$

H = Hamiltonian

H *is an operator corresponding to the total energy of the system. Kinetic + potential energy*

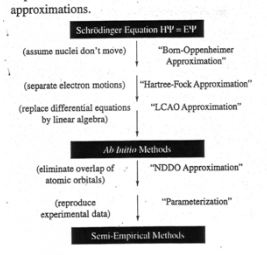
$$\left(\frac{-\hbar^2}{8\pi^2 m}\nabla^2 + V(x,y,z)\right)\psi(x,y,z) = E\,\psi(x,y,z)$$

potential energy; total energy; kinetic energy; wavefunction describing the system

Its solutions are very familiar to chemists as atomic orbitals.

Quantum Mechanics: Molecular Orbital Theory

While the Schrödinger equation may easily be written down for real atoms and molecules, it is impossible to solve. It can be simplified by several approximations.



Bridging to the Nano realm

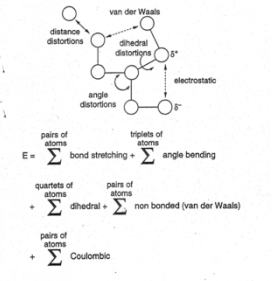
Molecular Modeling: Visualizations & Predictions

- **Numerical Methods**
- **Integral Method**
- ***Ab Initio* Methods**
- **Semi-Empirical MO-SCF Methods**
- **Approximate MO Methods**

The cost of calculations (cpu time required) increases rapidly as the basis set size is increased and as the amount of electron correlation increases.

Molecular Mechanics

Molecular mechanics describes the energy in terms of distortions of bond distances and angles away from idealized values, together with corrections for nonbonded interactions.



$$E = \sum_{\text{pairs of atoms}} \text{bond stretching} + \sum_{\text{triplets of atoms}} \text{angle bending} + \sum_{\text{quartets of atoms}} \text{dihedral} + \sum_{\text{pairs of atoms}} \text{non bonded (van der Waals)} + \sum_{\text{pairs of atoms}} \text{Coulombic}$$

Web MO

http://butane.cabrillo.edu/

Username: your last name, all lower case

password: username

- *Web MO*: undergraduate molecular modeling college consortium
- Web-based, on-line accessible molecular modeling software, Graphic User Interface (GUI), free to DVC students, no cpu charges
- Uses MOPAC 7, GAMESS 2000, and GAUSSIAN

Web MO

http://butane.cabrillo.edu/

Username: your last name, all lower case

password: username

Output:

- ❖Dipole moment
- ❖Bond Orders
- ❖Partial Charges
- ❖Vibrational Modes
- ❖Molecular Orbitals
- ❖Ultraviolet-Visible-Infrared Graphics
- ❖NMR Chemical Shifts