

Chapter 9 – Covalent Bonding: Orbitals

9.1 Hybridization and Localized Electron Model

sp³ Hybridization

- atomic orbitals are different than their “native form”

ex. CH₄ – if this weren't the case, then there would be two different types of C-H bonds.

Bond angles would be perpendicular to one another.

- The mixing of “native” atomic orbitals to form special orbitals for bonding is called hybridization.

- The sp³ orbitals are formed by the fusion of one s-orbital and 3 p-orbitals (sp³ hybridization or sp³ hybridized)

- These orbitals are arranged in a tetrahedral arrangement (requires sp³ hybridization, 109.5° bond angles, and 4 effective bonds)

Sample 9.1

Describe the bonding in the ammonia molecule using the localized electron model.

Solution

The Lewis structure for NH₃ is

The four electron pairs around the nitrogen atom require a tetrahedral arrangement to minimize repulsions. We have seen that a tetrahedral set of sp³ hybrid orbitals is obtained by combining the 2s and three 2p orbitals. In the NH₃ molecule three of the sp³ orbitals are used to form bonds to the three hydrogen atoms, and the fourth sp³ orbital holds the lone pair.

sp² Hybridization

- required for atoms that have trigonal planar arrangements (has 120° bond angles, 3 effective bonds)

1 s and 2 p-orbitals fuse to become sp² hybridized leaving 1 p unhybridized

ex. C₂H₄ (ethylene)

- electrons centered between the bonded atoms are called a σ (sigma) covalent bond
- a π (pi) covalent bond is made up of electrons which are shared between two parallel p-orbitals
- a double bond is made up of a σ and a π bond

sp Hybridization

sp hybridization involves 1 s-orbital and 1 p-orbital (2 effective pairs of electrons, 180° bond angle [linear])

ex. CO₂

dsp³ Hybridization

involves the hybridization of 1 d-orbital, one 1 s-orbital, and 3 p-orbitals (5 effective pairs of electrons, trigonal bipyramidal: 90° and 120° bond angles)

ex. PCl₅

d²sp³ Hybridization

- involves the hybridization of 2 d-orbitals, 1 s-orbital, and 3 p-orbitals (6 effective pairs of electrons, octahedral: 90° bond angles)

ex. SF₆

atoms adjust their orbitals by hybridization to allow the molecule to adopt a structure that gives minimum energy

Sample 9.5

For each of the following molecules or ions, predict the hybridization of each atom, and describe the molecular structure

- CO
- BF_4^-
- XeF_2

Solution

a. The CO molecule has 10 valence electrons, and its Lewis structure is

Each atom has two effective pairs, which means that both are sp hybridized. The triple bond consists of a σ bond produced by overlap of an sp orbital from each atom and two π bonds produced by overlap of $2p$ orbitals from each atom. The lone pairs are in sp orbitals. Since the CO molecule has only two atoms, it must be linear.

b. The BF_4^- ion has 32 valence electrons. The Lewis structure shows four pairs of electrons around the boron atom, which means a tetrahedral arrangement:

This requires sp^3 hybridization of the boron atom. Each fluorine atom also has four electron pairs and can be assumed to be sp^3 hybridized (only one sp^3 orbital is shown for each fluorine atom). The BF_4^- ion's molecular structure is tetrahedral

c. the XeF_4 molecule has 22 valence electrons. The Lewis structure shows five electron pairs on the xenon atom, which requires a trigonal bipyramidal arrangement:

Note that the lone pairs are placed in the plane where they are 120 degrees apart. To accommodate five pairs at the vertices of a trigonal bipyramid

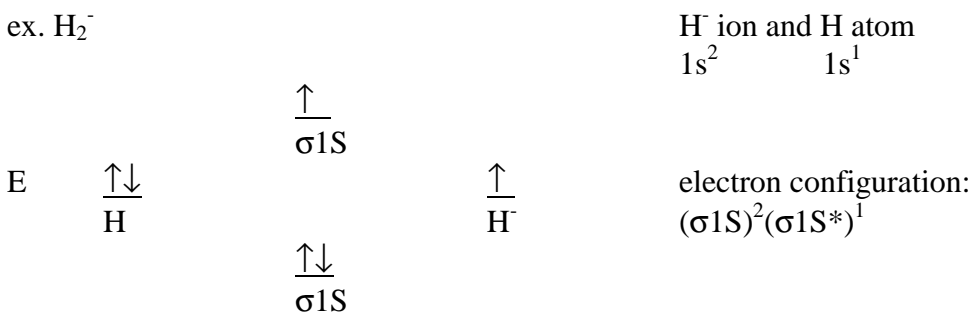
requires that the xenon atoms adopt a set of five dsp^3 orbitals. Each fluorine atom has four electron pairs and can be assumed to be sp^3 hybridized. The XeF_2 molecule has a linear arrangement of atoms.

9.2 The Molecular Orbital Model

- it deals with electrons that are delocalized, unpaired electrons and gives information towards bond energies
- molecular orbitals (MO's) are the solutions to molecules as quantum mechanics are to atoms

Molecular Orbitals

1. sigma molecular orbitals- the electron probability centered along the line passing through two nuclei
- 2.A nature tends to seek the lowest energy state, sp molecular formation is favored when bonding electrons occupy MO's with the lowest energy (bonding)- bonding molecular orbital
- 2.B if electrons occupy the higher energy MO then they would be considered antibonding (antibonding molecular orbital)
3. molecular orbitals indicate symmetry (σ, π), parent atomic orbitals (s,p,d), and whether they are bonding or antibonding (*)
4. molecular electron configurations can be written similar to that of atomic electron configuration
5. each molecular orbital can hold 2 electrons with opposite spins
6. orbitals are conserved molecular orbitals equal the number of atomic orbitals used to construct them



H_2^- ion is stable because more electrons are bonding than antibonding
 Bond Strength- Which is a higher bond strength out of H_2 and H_2^- ?

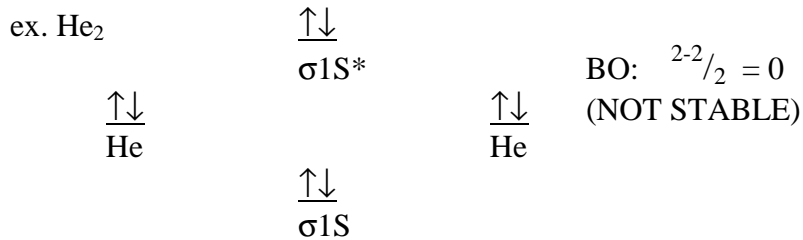
$H_2 > H_2^-$ because H_2 has both electrons lower in energy where H_2^- has a net of one electron lower in energy

Bond Order - indicates bond strength by taking the difference between the number of bonding electrons and the number of antibonding electrons divided by two

$$\text{Bond Order (BO)} = \frac{\# \text{ of bonding electrons} - \# \text{ of antibonding electrons}}{2}$$

ex. $H_2: 2-0/2 = 1$ $H_2^-: 2-1/2 = 1/2$

- larger bond orders mean greater bond strength, bond orders of 0 (zero) indicate that the molecule does not exist



9.3 Bonding in Homonuclear Diatomic Molecules

- only electrons in atomic orbitals that overlap in space participate in bonding

ex. Li_2

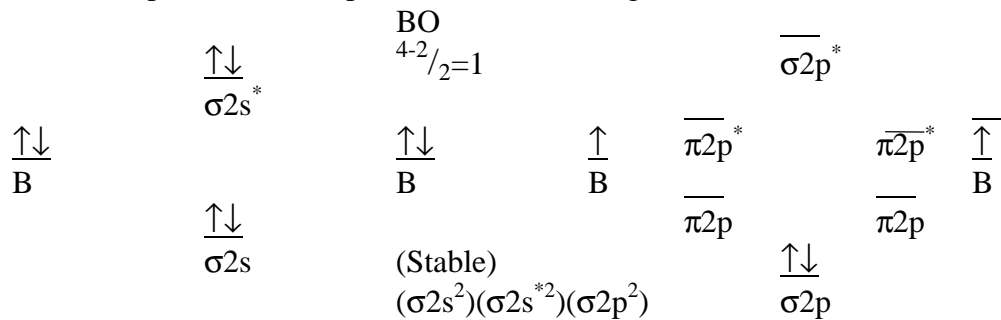
electron configuration is $\sigma 2s^2$, Bond Order $2-0/2 = 1$

pi (π) molecular orbitals – formed by parallel p-orbitals

sigma interactions are stronger than pi interaction

ex. $B_2 (1s^2, 2s^2, 2p^1)$

(Expected Electron Configuration)



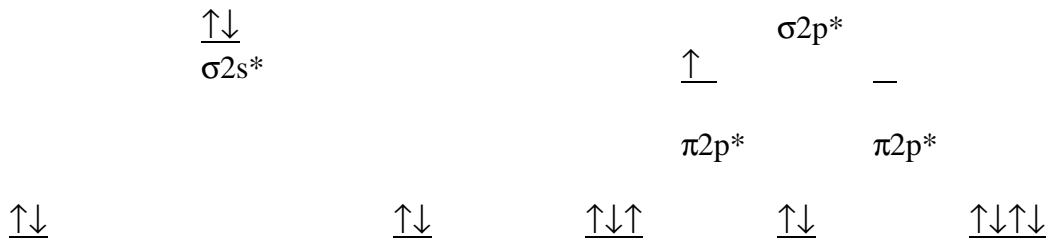
Paramagnetism – substance is attracted into the inducing magnetic field (associated with unpaired electrons)

Diamagnetism – substance is repelled from the inducing magnetic field (associated with paired electrons)

s and p-orbitals mix from B_2 to N_2 in period 2 and have a different than expected molecular orbital energy levels

O_2 and F_2 have expected molecular orbital energy levels

ex. NO

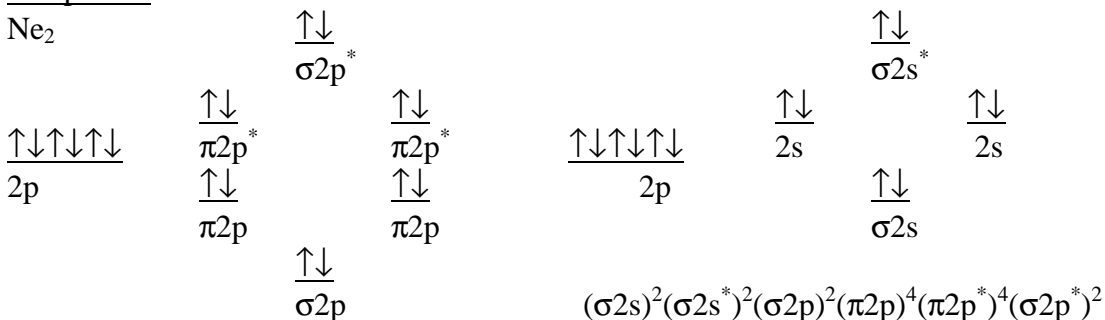




Trends in Orbital Diagrams

- as bond order increased the bond energy increases and the bond length decreases
- bond order can't automatically be associated with a particular bond energy (B₂ and N₂, although both molecules have a bond order of 1, B₂ appears to be twice as strong as F₂ [due to electron repulsions])
- the MO model helps to predict whether a molecule is paramagnetic or diamagnetic

Sample 9.7



The bond order for Ne₂ is 0 (zero), which tells us that Ne₂ does not exist, this can also be seen in any of the noble gases.

9.4 Bonding in Heteronuclear Diatomic Molecules (molecules containing atoms adjacent to each other)

- we use the molecular orbital diagram for homonuclear molecules
ex. NO, NO⁺, CN⁻ (use "N" MO)
- if two atoms of a diatomic molecule are very different, the energy level diagram for homonuclear molecules can no longer be used

9.5 Combining the Localized Electron and Molecular Orbital Models

- these models can be combined to describe resonance
- the π bond is delocalized in molecules that have resonance (LE model to describe σ bonding and MO's describe π bonding)
ex C₆H₆, O₃, and NO₃⁻
(p-orbitals form π molecular orbitals)