



CHEM 1035 – Lecture 35

Bonding and Molecular Orbitals

Bonding determines the connections that exist between the atoms. As important as the connectivity between the atoms is the arrangement of the atoms in space relative to each other. The arrangement of atoms in the molecule plays a significant role in the properties of the molecules



Types of Hybrid-orbitals

- The hybrid orbitals are formed by mixing of different numbers and types of atomic orbitals.
- For example if an "s" orbital mixes with a "p" orbital then a hybrid "sp" orbital results. Likewise if an "s" orbital mixes with 2 "p" orbitals, then a hybrid "sp²" orbital is formed
- <http://alumni.imsa.edu/~ishmael/bonding/hy/>

Go through the types of hybrid orbitals that can be formed and their designation.

How many "sp" orbitals are there? Since we mix 2 individual atomic orbitals (1 s and 2 p orbital), then 2 hybrid sp orbitals are formed. The number of hybrid orbitals that are formed is equal to the number of atomic orbitals that we mixed together originally.

We have 5 basic shapes in the VSEPR theory



Types of Covalent Bonds

- Sigma bond (σ) : end-to-end overlap of the atomic/hybrid orbitals along the axis that connects the atoms
- Pi bond (π) : Side-to-side overlap that generally occurs between "p" or "d" type orbitals (e.g. unhybridized orbitals)

When atoms covalently bond, the sigma bond will form first. All bonds (single, double, or triple) begin with the end-to-end overlap of orbitals along the bond-axis.

For higher bond orders (e.g. 2 or 3) associated with double or triple bonds, the 2nd or 3rd bonds are the Pi bonds. A double bond always occurs with 1-sigma bond and 1-pi bond. A triple bond always occurs with 1-sigma bond and 2-pi bonds.

How do these different types of bonds influence molecule properties? Atoms are free to rotate about sigma bonds. Once a Pi-bond is formed, however, the presence of the pi-bond restricts rotation of the bonding atoms. Why is this? This is because rotation of the atoms would require the orbitals involved in the pi-bond to reduce (and eventually eliminate) the side-to-side interaction.




Bond Order

- 1st order bonds are always σ -bonds
- 2nd order bonds are composed of one σ -bond and 1 π -bond
- 3rd order bonds are composed of one σ -bond and 2 π -bonds

Remember, that sigma bonds form by orbital overlap along the axis that connects the bonding pair of atoms. The Pi-bonds are formed by side-to-side overlap of (generally) unhybridized “p” or “d” orbitals.

What do the presence of



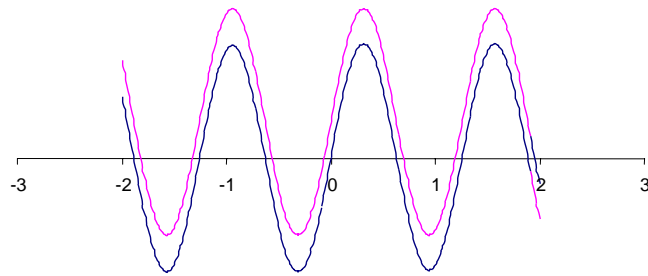
When forming a σ -bond, what is happening?

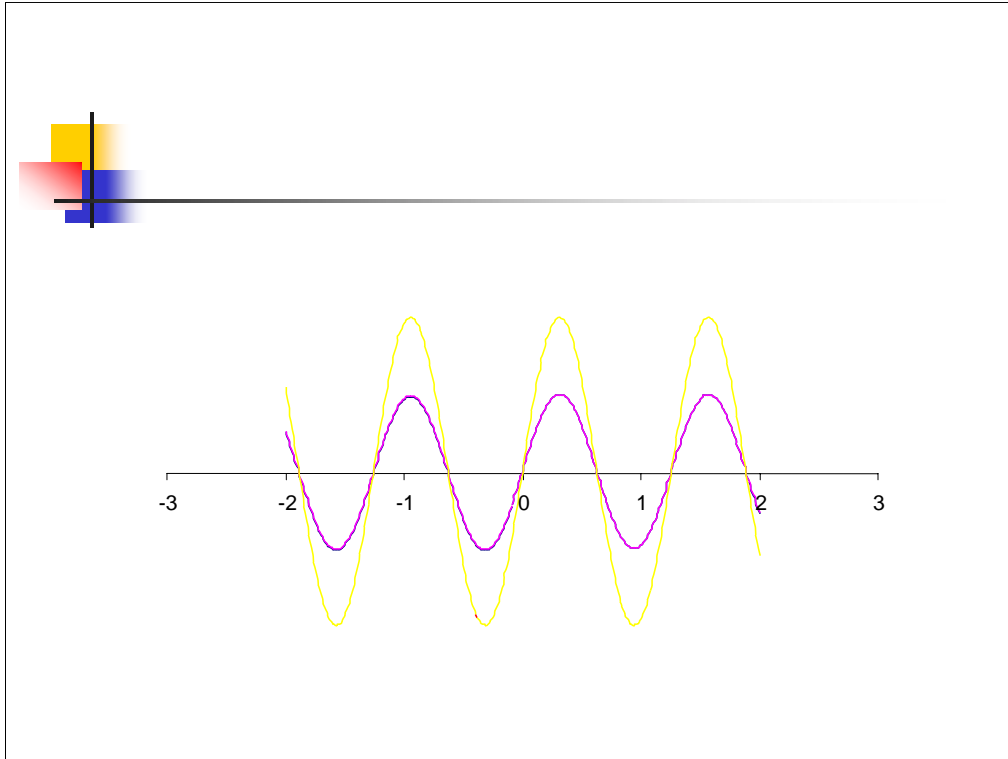
Atomic orbitals overlap to form the σ -bond. When they overlap, they share the same space.

What happens when 2 waves overlap/share the same space?

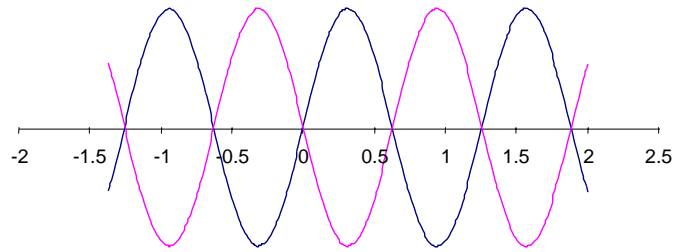
Atomic orbital hybridization occurs when the atomic orbitals are allowed to mix. Forming a covalent bond inherently involves mixing of orbital space. So, when a bond forms, a type of “hybridization” occurs, but it is occurring between orbitals that exist on 2 different atoms. This is the formation of a “Molecular Orbital”

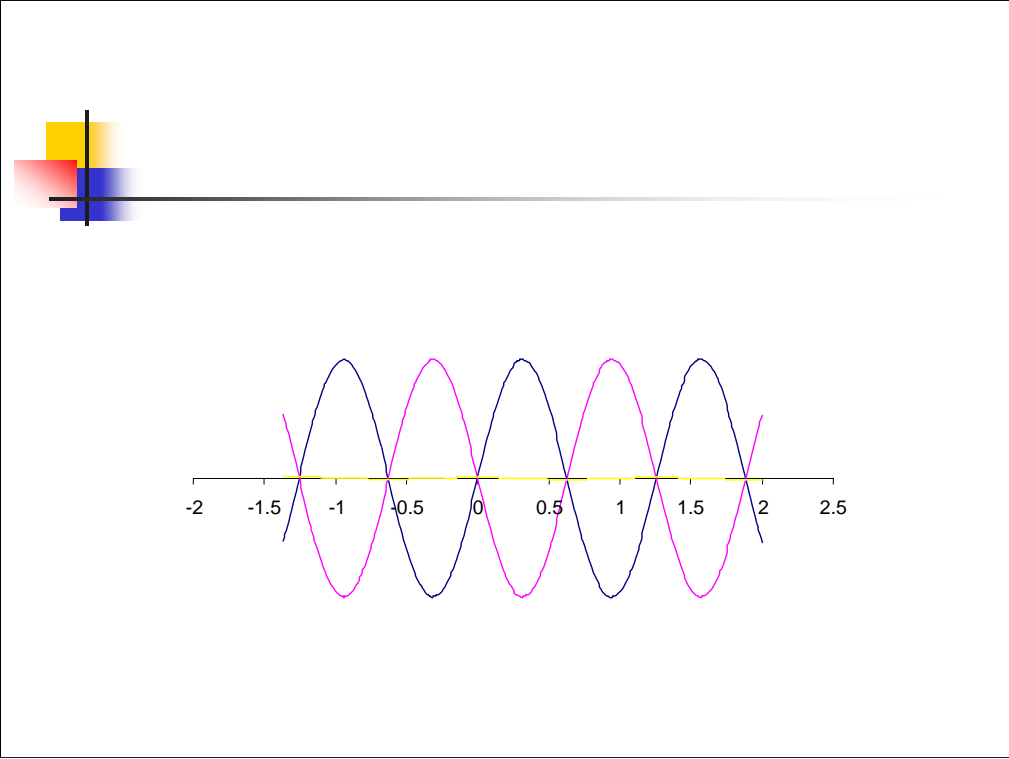
Waves that are in-phase and add





Waves that are out-of-phase
and subtract







Molecular Orbitals

- [Molecular Hydrogen animation](#)
- Molecular orbital diagram for dihydrogen.

Relative energy of the Molecular orbitals:

Bonding – lower in energy because the electrons have more space to be dispersed in the MO – less repulsion between the 2 electrons in the orbital, and with the electrons between the nuclei, the repulsion between the nuclei is reduced.

Antibonding – higher in energy because the electron density exists outside of the area between the nuclei, this does not provide shielding between the nuclear charge and increases the energy.

How do the electrons fill the orbitals? Follows the auf bau principle