Module-15: Advanced Theory of Covalent Bonding

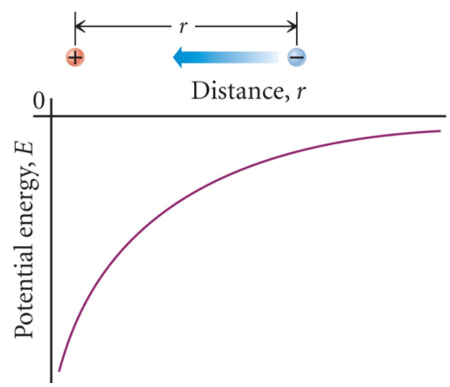
BOND FORMATION

- The potential energy (E) of two charged particles with charges q_1 and q_2 separated by distance *r* is given by the following equation,

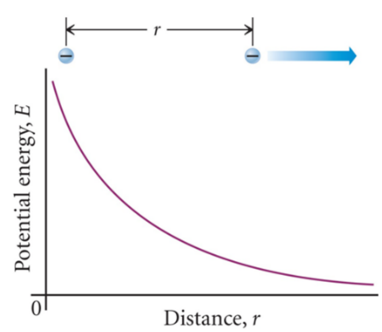
$$E_{\text{potential}} = \frac{1}{4\pi \epsilon_0}\left(\frac{q_1 \times q_2}{r}\right)$$

Where ϵ_o is a constant with a value of 8.85×10^{-12} $C^2/J.\ m$

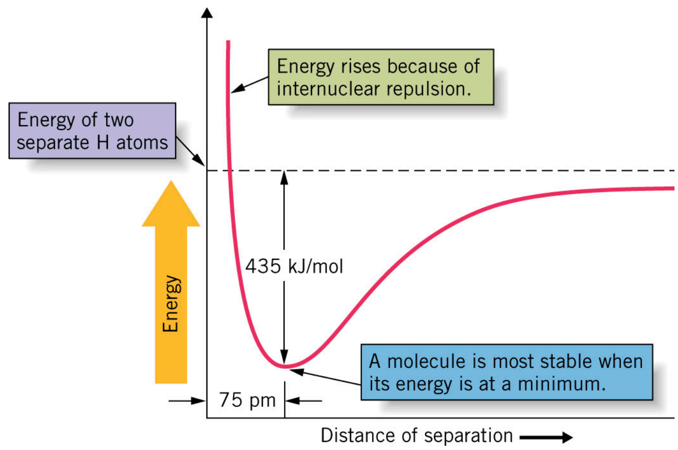
- The potential energy is positive for charges of same signs and negative for charges of opposite signs. Since the distance *r* is in the denominator, the potential is inversely proportional to the distance between the charges.
- The attraction between opposite-charged particles or ions increases as the particles get closer together. Bringing them closer lowers the potential energy of the system.



- The repulsion between like-charged particles or ions of same charge increases as the particles get closer together. To bring them closer requires the addition of more energy.



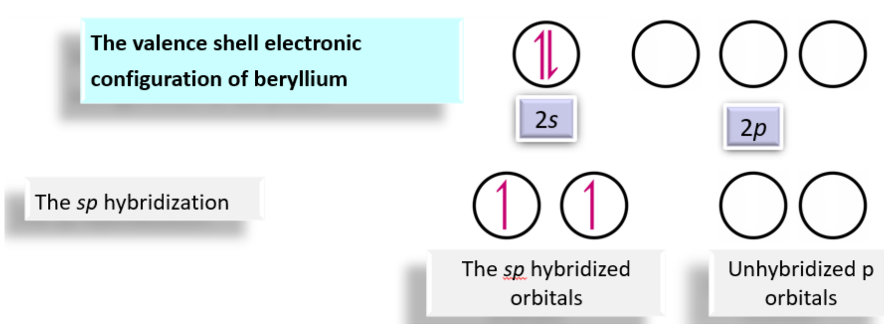
- The above discussions can be used to explain bond formation as the attraction between nucleus of one atom and the electrons in another atom.
- For example, in hydrogen molecule (H_2), the energy of the hydrogen molecule reaches a minimum when there is a balance between the attractions and repulsions.



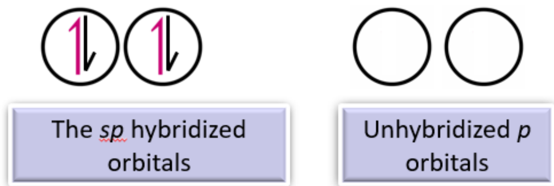
- The covalent bonds are characterized by their **bond distance**, or average distance between the nuclei of two atoms, and the **bond energy**, or amount of energy released when the bond forms.

HYBRIDIZATION

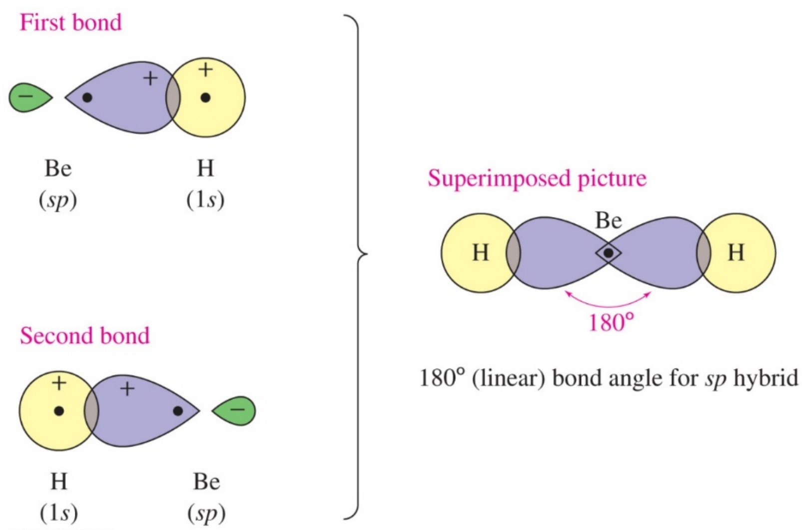
- Hybridization is a successful model in explaining bonding and shapes of molecules, this model works particularly well for organic molecules. The basic idea of hybridization is, one or more orbitals blend and produce a new set of orbitals, namely, hybrid orbitals.
- There are several kinds of hybridizations known, we will focus on *sp*, sp^2 and sp^3 hybridizations.
- The *sp* hybridization: The *sp* hybrid orbitals are formed by the hybridization (blending) of an *s* and a *p* orbital. Consider beryllium (Be) and the formation of BeH_2:



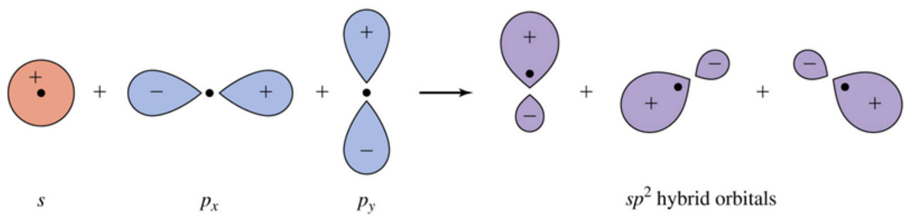
- One of the electrons from the *s* orbital is promoted to the *p* orbital with the energy available to beryllium as consequence of bonding to hydrogen atoms.
- The hybridization creates two *sp* hybrid orbitals (in Be) with each orbital containing just one electron. One electron from each hydrogen pairs with the electrons in the *sp* hybrid orbitals

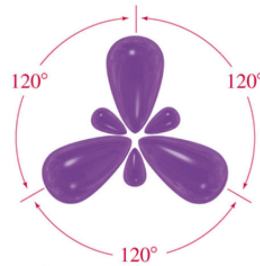


- In above figure, the red arrows represent electrons from Be, and dark arrows are electrons from H.
- The two *sp* hybrid orbitals from beryllium bond with 1s orbitals of two hydrogen atoms and form the BeH_2 molecule. The BeH_2 molecule is linear with a bond angle of 180°.

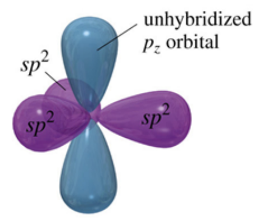


- <u>The *sp*^{2} hybridization:</u> When an ***s* orbital** combines with **two *p* orbitals in an atom**, three ***sp*^{2}** hybrid orbitals are formed
- The bond angles associated with this trigonal structure are about 120°. The remaining *p*-orbital that is not part of hybridization, is perpendicular to the plane of the three hybrid orbitals.



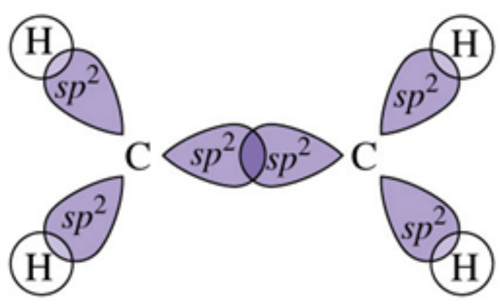


three sp^2 hybrid orbitals superimposed

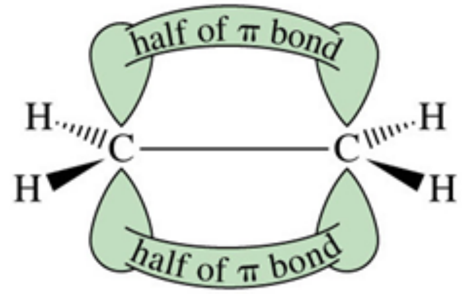


sp^2 hybrid carbon atom
(viewed from the side)

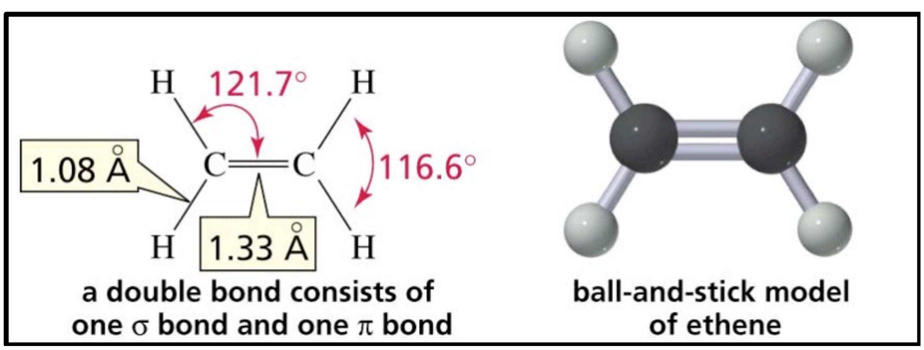
- In ethylene (C_2H_4), the two carbon atoms are sp^2 hybridized and they are linked to each other by a σ-bond and a π-bond. The π-bond is formed by lateral overlap of unhybridized *p*-orbitals and the σ-bond is formed by head-on overlap of sp^2 hybrid orbitals. Overall, the two carbon atoms are linked by two bonds or a double bond.



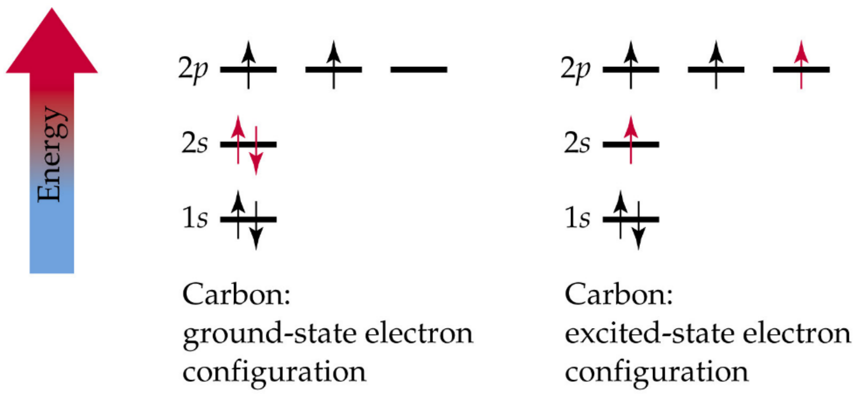
σ bond framework
(viewed from above the plane)



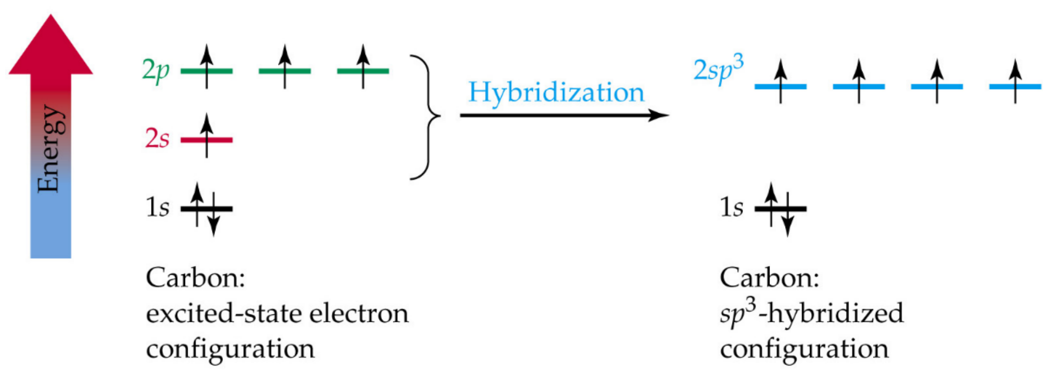
π bond
(viewed from alongside the plane)



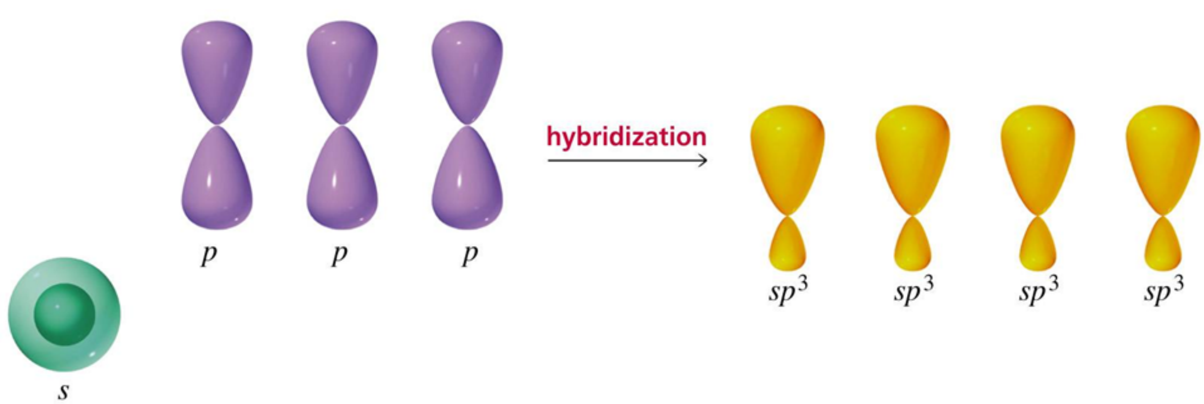
- <u>The *sp*³ hybridization:</u> To understand sp^3 hybridization we will use methane (CH_4) molecule for our discussions.
- In methane (CH_4), in order for carbon atom to form four bonds, an electron from the filled *2s orbital* would have to be excited to the empty 2*p* orbital, giving the excited-state electronic state configuration shown below.



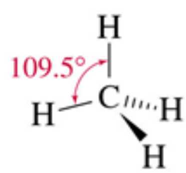
- Due to the hybridization we find that in methane all four bonds are identical in all aspects, such as bond angles, bond lengths and bond energies.

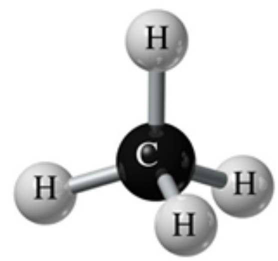


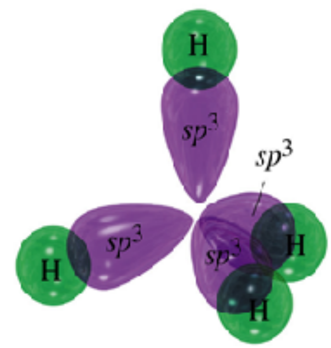
- The shapes of sp^3 hybrid orbitals are different from *s* or *p* orbitals.



- Methane has tetrahedral geometry, using four ***sp^3* hybrid orbitals** to form sigma bonds to the four hydrogen atoms.
- When we say, for example, carbon has *sp^3* hybrid orbitals, the **superscript indicates the number of *p* orbitals** involved in the hybridization.
- In any molecule with a carbon atom forming four single bonds, it will be ***sp^3* hybridized and have a tetrahedral geometry**.





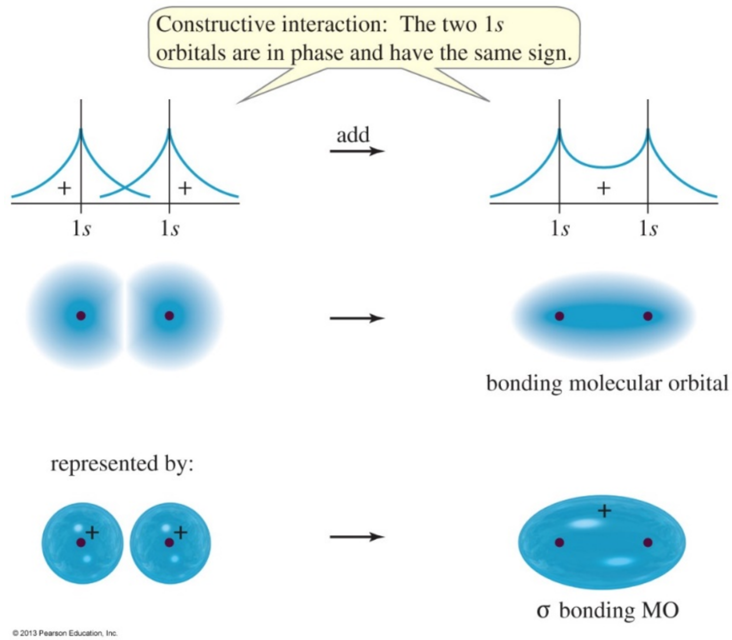


- <u>Bonding in acetylene (C_2H_2):</u> Each carbon atom in acetylene is *sp* hybridized, this leaves out two of the three *p*-orbitals unhybridized.
- The *sp* hybrid orbitals in each carbon atom are used for bonding to hydrogen atoms and to form σ-bonds between the two carbon atoms. The two unhybridized *p*-orbitals on each carbon atom form the two π-bonds.
- Overall, the two carbon atoms are linked to each other by two π-bonds and one σ-bond, which results in a triple bond.

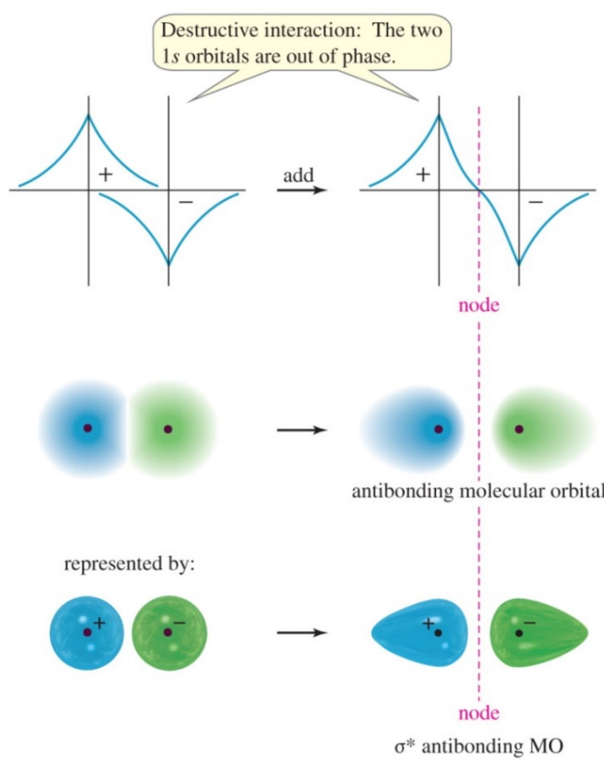
Ethyne or acetylene	C_2H_2	$H{-}C{\equiv}C{-}H$
	Formula	Structural formula

THE MOLECULAR ORBITALS

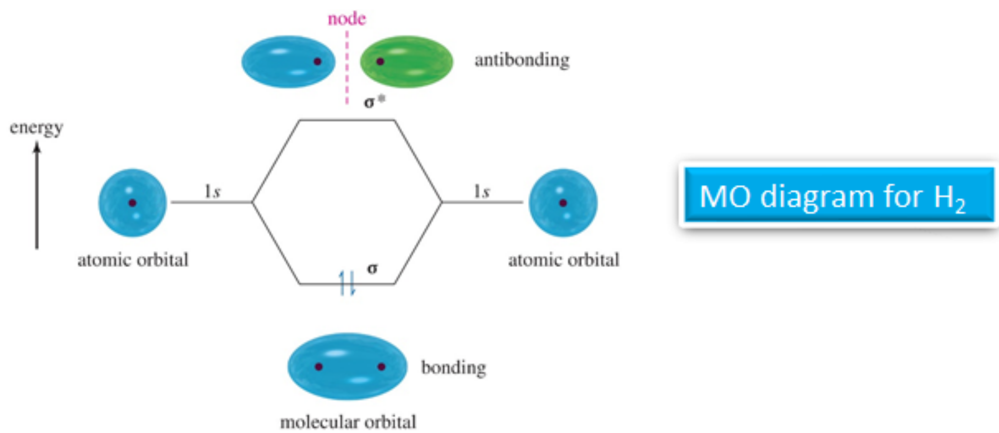
- Hydrogen molecule (H_2): When the 1*s* orbitals of two hydrogen atoms overlap in phase with each other, they interact constructively to form a bonding MO (σ).



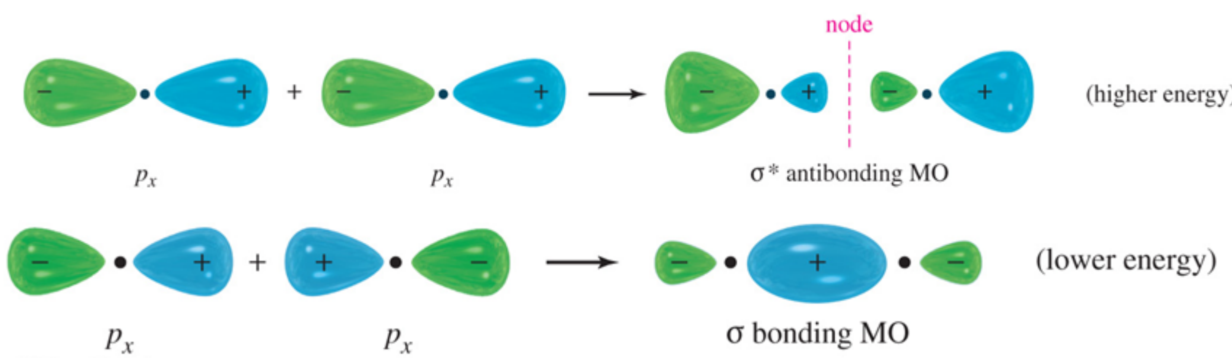
- When two 1*s* orbitals overlap out of phase, they interact destructively to form an antibonding MO (σ*).



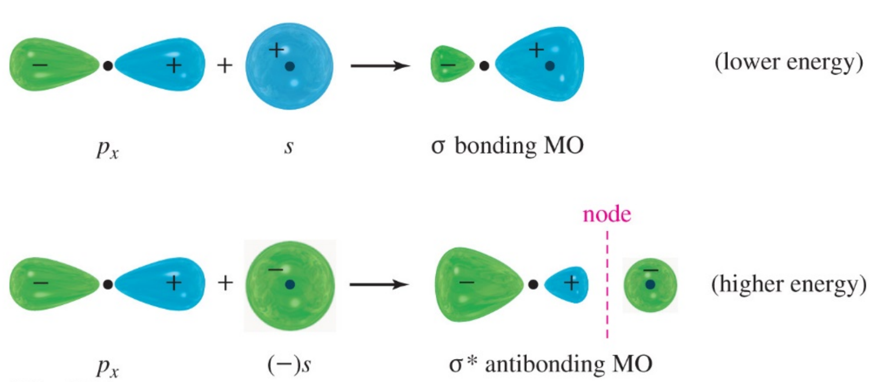
- The **bonding MO** (σ) and one **antibonding MO** (σ^*) are sigma orbitals because the electron density is concentrated along the imaginary line that passes through both nuclei.



- Other interactions that lead to σ-bonding: In diatomic chlorine molecule (Cl_2), when two *p* orbitals overlap along the line between the nuclei, a bonding orbital and an antibonding orbital result. This linear overlap is another type of sigma bonding MO.

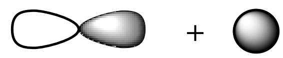


- Overlap of an ***s*-orbital** with a ***p*-orbital** gives a σ-bonding MO and a σ^*-antibonding MO.



Practice Problems

1. What kind of molecular orbital (σ, σ^*, π, or π^*) results when the two atomic orbitals shown below interact in the manner indicated?



(A) σ (B) σ^* (C) π (D) π^*

2. Which of the following is the best explanation for a covalent bond?

(A) an interaction between core electrons

(B) the overlapping of unoccupied orbitals of two or more atoms

(C) electrons simultaneously attracted by more than one nucleus

(D) a positive ion attracting negative ions

3. During the formation of a chemical bond between two hydrogen atoms, which of the following statements is always true?

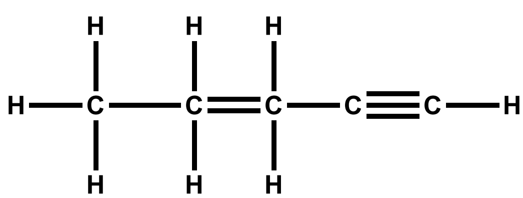
(A) a polar covalent bond is formed.

(B) energy is released during the formation of the bond.

(C) one of the hydrogen atoms is ionized.

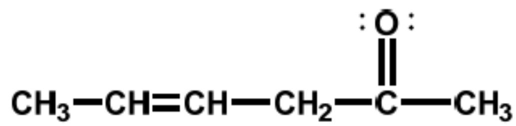
(D) both hydrogen atoms are *sp* hybridized

4. How many σ and π bonds are present in the following compound?



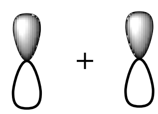
	σ-bonds	π-bonds
(A)	11	4
(B)	10	3
(C)	10	2
(D)	12	3

5. How many **atoms** in the compound drawn below are *sp*^{2} hybridized?



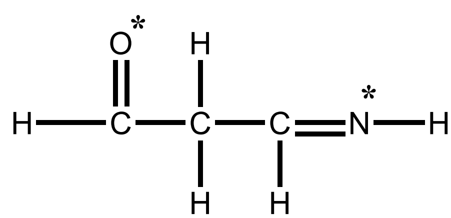
(A) 1 (B) 2 (C) 3 (D) 4

6. What kind on molecular orbital results when the two atomic orbitals shown below interact in the manner indicated?



(A) σ (B) σ* (C) π (D) π*

7. In the following compound what are the hybridizations of the elements that are marked by asterisks?



	O	N
(A)	*sp*^{3}	*sp*^{3}
(B)	*sp*^{2}	*sp*^{3}
(C)	*sp*^{2}	*sp*^{2}
(D)	*sp*	*sp*^{2}

8. If four orbitals on one atom overlap four orbitals on a second atom, how many molecular orbitals will form?

(A) 4 (B) 8 (C) 2 (D) 16