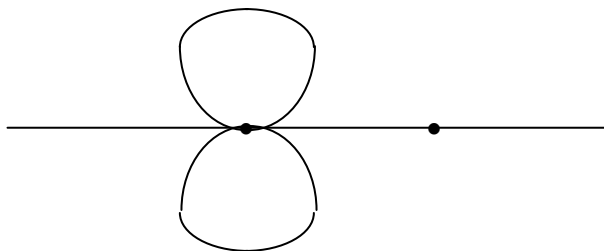


**ALE 15. Valence Bond Theory - Pi Bonding**(Reference: [Sections 11.1 and 11.2- Silberberg 5<sup>th</sup> edition](#))**What orbitals are used to form the second bond in a double bond?****The Model**

According to Valence Bond Theory, a **pi bond** is the *side to side* overlap of parallel unhybridized *p* orbitals of adjacent atoms. The overlap of two atomic orbitals results in the formation of a **molecular orbital**. The first bond between two atoms is a **sigma bond**. The second and third bonds between two atoms (if they exist) are **pi bonds**.

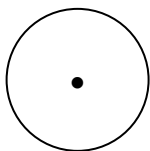
**Key Questions**

- 1a. The small black dots represent neighboring nuclei and the line segment between them represents the axis of the  $\sigma$  bond (orbitals constituting the  $\sigma$  bond not shown). The *unhybridized p* orbital on the atom on the left has been drawn for you. Draw a *p* orbital on the atom on the right such that the two *p* orbitals are parallel and are about the same size.

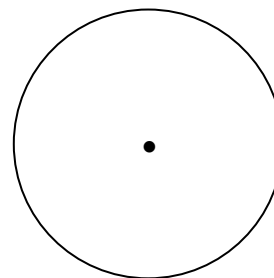


- b. Recall that the quantum mechanical model of the atom does not have a “hard” radius. It simply gets more difficult to find an electron further away from the nucleus. We draw orbitals as boundary surface diagrams of different probability limits. The more certain we want to be of the electron’s position, the larger the curve representing an orbital is drawn. For example, the curve below and on the left might represent the 50% probability contour of finding an electron around the nucleus in 1s orbital. The one on the right would then represent the 90% probability contour.

1s orbital of H  
drawn at the 50%  
probability limit



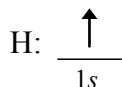
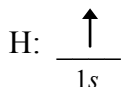
1s orbital of H  
drawn at the 90%  
probability limit



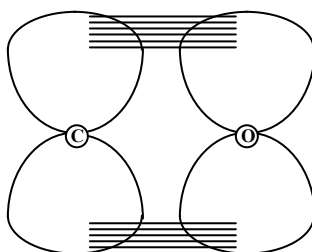
Suppose that the curves drawn in Question 1a represent the 50% probability contour. **On top of what is already drawn, sketch the 90% probability contours of the two *p* orbitals using dashed curves or by using a different pen color.**

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2. In your own words, describe a  $\pi$  bond. How does it differ from a  $\sigma$  bond?
- 3a. Look back at the figure you completed in [Question 1](#). Now, imagine the atom on the left staying put and the atom on the right rotating about the  $\sigma$  bond axis (kind of like a propeller). What happens to the  $\pi$  bond? (*i.e.*, What happens to the overlap between the two  $p$  orbitals?)
- b. Typically, there is “freedom to rotate” about a single bond, but there is no such freedom when atoms are bound multiply with double or triple bonds. Explain why. (As examples, it will be helpful to make and manipulate models of  $\text{H}_2\text{O}_2$  and *trans*- $\text{N}_2\text{H}_2$  as shown by the instructor—save the models for [question #6](#).)
- 4a. Consider the formaldehyde molecule ( $\text{H}_2\text{CO}$ ). Draw the Lewis structure of  $\text{H}_2\text{CO}$ .
- b. How many regions of electron density are there around the C and around the O? How is C hybridized? How is O hybridized?
- # regions of electron density around C: \_\_\_\_\_ hybridization of C: \_\_\_\_\_
- # regions of electron density around O: \_\_\_\_\_ hybridization of O: \_\_\_\_\_

- c. The orbital diagrams of the two H's are provided. Complete the abbreviated orbital diagrams of the *hybridized* C and of the *hybridized* O in H<sub>2</sub>CO. (How are they hybridized?)



- d. What overlap of orbitals describes the  $\sigma$  bond between the C and the O? (*i.e.*, What orbital of C overlaps with what orbital of O to form the  $\sigma$  bond between the two atoms?)
- e. What overlap of orbitals describes the  $\pi$  bond between the C and the O? (*i.e.*, What orbital of C overlaps with what orbital of O to form the  $\pi$  bond between the two atoms?)
- f. Below is shown the unhybridized  $2p$  orbitals of the C and of the O and their “through space” overlap. They are in the plane of the paper. Complete the Valence Bond drawing of the remaining orbitals of C overlapping with the orbitals of O and with the orbitals of the two H's. Also show the orbitals containing the O's lone pairs. Use arrows ( $\uparrow$  and  $\downarrow$ ) to represent electrons. Use “bold curves” and “dashed curves” to represent orbitals coming out or going in to the plane of the paper, respectively. Label the orbitals and label the  $\sigma$  bonds and the  $\pi$  bond.



- 5a. Consider the carbon monoxide (CO) molecule. Draw the Lewis structure of CO that is *not* favored by formal charge—*i.e.* draw the Lewis structure with a +1 F.C. on the oxygen and a -1 F.C. on the carbon.

- b. If the C and the O are use hybrid orbitals, what is their hybridization?

hybridization of C: \_\_\_\_\_ hybridization of O: \_\_\_\_\_

- c. Write abbreviated orbital diagrams of *hybridized* C and *hybridized* O in CO *taking their formal charges into account*.

- d. Sketch the Valence Bond drawing of CO, using arrows ( $\uparrow$  and  $\downarrow$ ) to represent electrons. Recall the relative orientation of  $2p$  orbitals in the same subshell. You will, therefore, need to use “bold curves” and “dashed curves” to represent orbitals coming out or going in to the plane of the paper, respectively. Label the orbitals and label the  $\sigma$  bonds and the  $\pi$  bonds.

6. The following Lewis structures of  $\text{H}_2\text{O}_2$  and *trans*- $\text{H}_2\text{N}_2$  suggest that both compounds are nonpolar.



However hydrogen peroxide is quite polar ( $\mu = 2.13$  D) while *trans*-diazene is nonpolar ( $\mu = 0$  D). Explain why. (*Hint*: Look back at [Question 3](#).)

**Exercises**

7. Are the following statements true or false? Correct those that are false.
- Two  $\sigma$  bonds comprise a double bond.
  - A triple bond consists of one  $\pi$  bond and two  $\sigma$  bonds.
  - Bonds formed by atomic s orbitals are always  $\sigma$  bonds.
  - A  $\pi$  bond restricts rotation around about the  $\sigma$ -bond axis.
  - A  $\pi$  bond consists of two pairs of electrons.
  - End-to-end overlap results in a bond with electron density above and below the bond axis.
8. Draw the Lewis structure and then label the hybrid orbitals used by the central atom(s) and the type(s) of bonds formed ( $\sigma$  or  $\pi$ ) in each of the following compounds

	<b>Lewis Structure</b>	<b>Hybridization</b>	<b>Type of Bond(s)</b>
Boron trifluoride: <b>BF<sub>3</sub></b>		B:	B–F:
Propyne: <b>CH<sub>3</sub>C≡CH</b> ↑ ↑ ↑ a b c		C <sub>a</sub> : C <sub>b</sub> : C <sub>c</sub> :	C <sub>a</sub> –H: C <sub>a</sub> –C <sub>b</sub> : C <sub>b</sub> –C <sub>c</sub> : C <sub>c</sub> –H:
Sulfur dioxide, <b>SO<sub>2</sub></b>		S:	S–O: (the 1 <sup>st</sup> one)  S–O: (the 2 <sup>nd</sup> one)