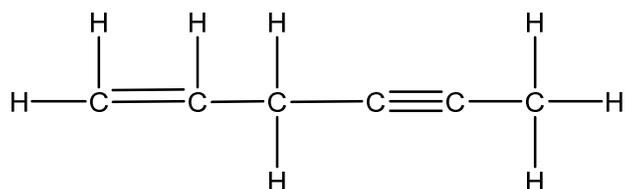


Read Chapter 9 and complete the following problems:

1. Figure 9.15 is listed on page 361 of the textbook and shows the potential energy of two hydrogen atoms as a function of the distance between them. (a) To what does a zero energy correspond in the diagram? (b) According to valence bond theory, why does the energy decrease as the H atoms move from a large separation to a small one? (c) What is the significance of the H - H bond distance at the minimum point in the plot? (d) Why does the energy rise at the H - H distances less than the minimum point in the plot?

2. The molecule difluoromethane ( $\text{CH}_2\text{F}_2$ ) is used as a refrigerant. Sketch the Lewis structure and determine if the molecule has a non-zero dipole moment. If the molecule is polar, in what direction does the overall dipole moment vector point in the molecule?

3. Consider the hydrocarbon shown below.



(a) What is the hybridization at each carbon atom in the molecule? (b) How many  $\sigma$  and how many  $\pi$  bonds are there in the molecule?

4. Consider the bonding in an  $\text{MgH}_2$  molecule. (a) Draw the Lewis structure and predict its molecular geometry. (b) Before forming the hybrid orbitals on the central atom Mg, the Mg atom must exist in an excited state. Why does this excited state have to occur to allow the Mg to hybridize? (c) What is the hybridization on the Mg central atom? (d) Sketch the two bonds between the Mg hybrids and the two H 1s orbitals. Are these  $\sigma$  or  $\pi$  bonds?

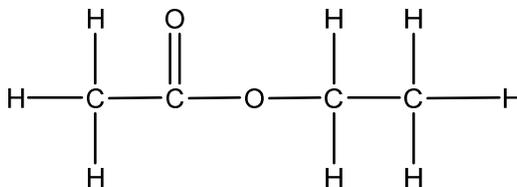
5. (a) Draw a Lewis structure for  $\text{SiH}_4$  and predict its molecular geometry. (b) What is the hybridization of the central atom Si in  $\text{SiH}_4$ ? (c) What must happen to a ground state Si atom in order for hybridization to occur? (d) Sketch the four bonds that occur between the hybrid orbitals on the Si central atom and the four H 1s orbitals. (e) What is the bond angle that forms between each bond?

6. (a) If the valence atomic orbitals on an atom are  $sp$  hybridized, how many unhybridized p orbitals remain in the valence shell? How many  $\pi$  bonds can the atom form? (b) If the valence atomic orbitals on an atom are  $sp^2$  hybridized, how many unhybridized p orbitals remain in the valence shell? How many  $\pi$  bonds can the atom form? (c) If the valence atomic orbitals on an atom are  $sp^3$  hybridized, how many unhybridized p orbitals remain in the valence shell? How many  $\pi$  bonds can the atom form?

7. (a) Draw Lewis structures for methane ( $CH_4$ ) and formaldehyde ( $H_2CO$ ). (b) What is the hybridization at the carbon atom in  $CH_4$  and  $H_2CO$ ? (c) The carbon atom in  $H_2CO$  can form multiple bonds, whereas  $CH_4$  can only form single bonds. Explain this observation using the hybridization at the central carbon atom.

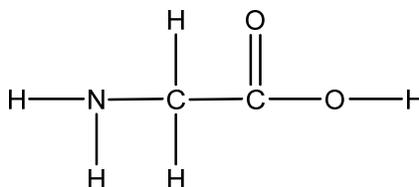
8. The nitrogen atoms in  $N_2$  form multiple bonds, while the nitrogen atoms in  $N_2H_4$  do not. How can you explain this observation?

9. Ethyl acetate,  $C_4H_8O_2$ , is shown below.



(a) What is the hybridization at each of the carbon atoms in this molecule?  
(b) How many  $\sigma$  and how many  $\pi$  bonds are there in the molecule?  
(c) What are the bond angles about each carbon atom?

10. Consider the Lewis structure for glycine shown below.



(a) What are the approximate bond angles and hybridizations about each of the carbon and nitrogen atoms in the molecule? (b) How many  $\sigma$  and how many  $\pi$  bonds are there in the molecule?

11. (a) What is the difference between a localized and delocalized  $\pi$  bond in a molecule? (b) How can you determine whether a molecule or ion will exhibit delocalized  $\pi$  bonding? (c) Is the  $\pi$  bond in  $\text{NO}_2^-$  localized or delocalized?

12. (a) What are the similarities and differences between atomic orbitals and molecular orbitals? (b) Why are the electrons in a bonding molecular orbital of  $\text{H}_2$  at lower energy than the electron in a ground state hydrogen atom? (c) How many electrons can be placed in each molecular orbital of a molecule?

13. (a) Why is the anti-bonding molecular orbital in an  $\text{H}_2$  molecule at a higher energy than the  $1s$  orbital in a ground state hydrogen atom? (b) If two  $p$  orbitals on one atom combine with two  $p$  orbitals on another atom, how many molecular orbitals result?

14. (a) Sketch the  $\sigma$  and  $\sigma^*$  molecular orbitals resulting from the combination of two  $p_z$  atomic orbitals. (b) Sketch the  $\pi$  and  $\pi^*$  MOs resulting from the combination of two  $p_y$  orbitals. (c) Assuming no mixing of the  $s$  and  $p$  orbitals, arrange the MOs from part (a) and (b) in order of increasing energy.

15. (a) What is the relationship between bond order, bond length, and bond energy? (b) According to molecular orbital theory, would  $\text{Be}_2$  or  $\text{Be}_2^+$  be more stable? Why? Would you expect either molecule to exist?

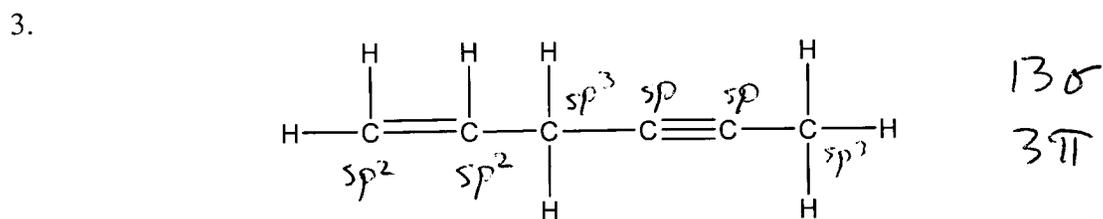
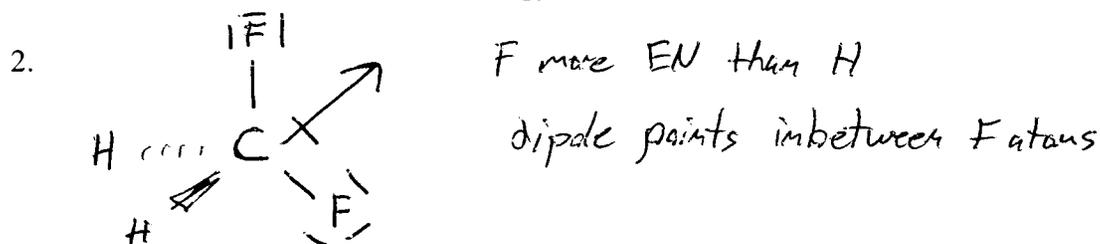
16. (a) What is meant by the term diamagnetism? (b) How does a diamagnetic substance respond to a magnetic field? (c) Which of the following would you expect to be diamagnetic:  $\text{N}_2^-$ ,  $\text{O}_2^{2-}$ ,  $\text{Be}_2^+$ ,  $\text{C}_2^-$ ?

17. (a) What is meant by the term paramagnetism? (b) How can you determine experimentally whether a substance is paramagnetic? (c) Which of the following would you expect to be paramagnetic:  $\text{O}_2^+$ ,  $\text{N}_2^{2-}$ ,  $\text{Li}_2^+$ ,  $\text{O}_2^{2-}$ ?

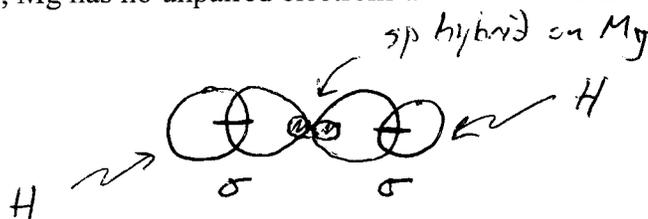
18. Draw out the molecular orbital diagram for  $\text{B}_2^+$ ,  $\text{Li}_2^+$ ,  $\text{N}_2^+$ , and  $\text{Ne}_2^+$ . Would the addition of an electron stabilize or destabilize the resulting molecule?

19. Predict the bond order and magnetism of  $\text{CO}^+$ ,  $\text{NO}^-$ ,  $\text{OF}^+$ , and  $\text{NeF}^+$ .
20. Calculate the bond order and determine the magnetism for  $\text{CN}^+$ ,  $\text{CN}$ , and  $\text{CN}^-$ . Which molecule/ion would molecular orbital theory predict to be the most stable?
21. The nitric oxide molecule readily loses one electron to form the  $\text{NO}^+$  ion. (a) Using molecular orbital theory, explain why this observation makes sense chemically. (b) Arrange the following in order of increasing bond strength:  $\text{NO}$ ,  $\text{NO}^+$ ,  $\text{NO}^-$  and indicate if each molecule/ion is paramagnetic or diamagnetic. (c) Isoelectronic species have the same number of electrons. With what neutral homonuclear diatomic molecule are the  $\text{NO}^+$  and  $\text{NO}^-$  ions isoelectronic?
22. (a) Draw the molecular orbital diagram for  $\text{IBr}$  and determine its bond order. (b) Are the atomic orbitals for I or Br lower in energy? Why?
23. The molecules  $\text{SiF}_4$ ,  $\text{SF}_4$ , and  $\text{XeF}_4$  all have the same molecular formula  $\text{AX}_4$  yet they have different geometries. Predict the shapes of each molecule and explain why the shapes are different.
24. The  $\text{PF}_3$  molecule has a dipole moment of 1.03 D, but the  $\text{BF}_3$  molecule has a dipole moment of zero. How can you explain this difference?
25. It is often observed that  $\sigma$  bonds involving an  $sp$  hybrid are shorter than those involving  $sp^2$  or  $sp^3$  hybrid orbitals. Can you propose a reason for this?
26. The magnetic properties of a compound can be measured using an instrument called a Guoy balance. When the magnetic measurements are made, the sample is generally covered by an atmosphere of pure nitrogen gas rather than in air? Why do you suppose chemists go through the hassle of using a nitrogen atmosphere in these measurements?

1. (a) The zero energy corresponds to the energies of the hydrogen atomic orbitals. (b) The overlap of the 1s orbitals increases. (c) It is the equilibrium bond distance. (d) The nucleus is positively charged and if the H - H distance gets too close the nuclei will repel each other and increase the overall energy.



4. (a) H - Mg - H is linear in its electron domain and molecular geometry. (b) The Mg atom has 2 electrons in its 2s orbital; these electrons are paired. Without promotion to an sp excited state, Mg has no unpaired electrons available to form bonds with hydrogen. (c) sp (d)

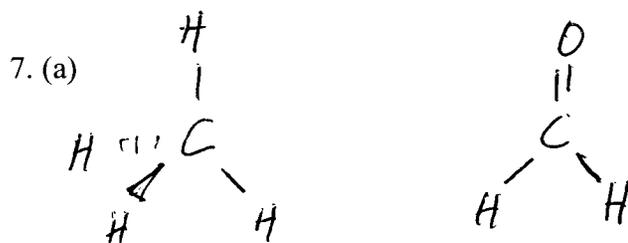


5. (a) SiH<sub>4</sub> has a tetrahedral electron domain and molecular geometries. (b) sp<sup>3</sup> (c) See page 364. The same hybridization occurs in CH<sub>4</sub>. (d)



(e) 109.5 degrees

6. (a) There are two unhybridized p orbitals in an sp hybrid set. These two orbitals can form 2 π bonds. (b) There is one unhybridized p orbital in an sp<sup>2</sup> hybrid. This hybrid can form one π bond. (c) There are zero unhybridized p orbitals in an sp<sup>3</sup> hybrid. This hybrid cannot form any π bonds.



(b)  $sp^3$  and  $sp^2$  (c) The C atom in  $CH_4$  is  $sp^3$  hybridized; there are no unhybridized p orbitals available for the  $\pi$  overlap required for a multiple bond. In  $CH_2O$  the C atom is  $sp^2$  hybridized, which allows one of the  $\pi$  orbitals to form a multiple bond. In this case a carbon - oxygen double bond.

8. In  $N_2$  the hybridization is  $sp$ , while in  $N_2H_4$  the hybridization is  $sp^3$ . In an  $sp^3$  hybrid there are no p orbitals available for multiple bonding. In  $sp$  hybridization the two unhybridized p orbitals are available for multiple bonding.

9. (a)  $sp^3$ ,  $sp^2$ ,  $sp^3$ , and  $sp^3$  (b) 12 sigma and 1 pi (c) all the  $sp^3$  angles are 109.5 degrees and the  $sp^2$  angles are 120 degrees.

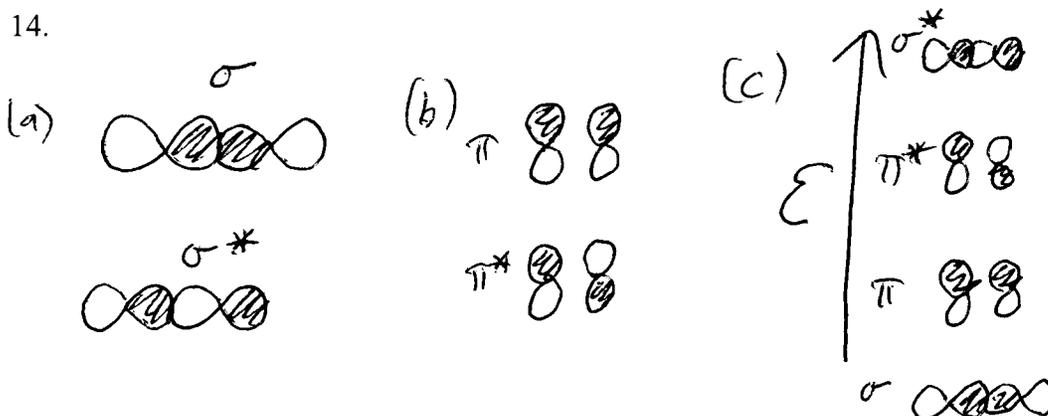
10. (a) all the  $sp^3$  angles are 109.5 degrees and the  $sp^2$  angles are 120 degrees. (b) 9 sigma and 1 pi bond

11. (a) In a localized  $\pi$  bond, the electron density is concentrated between the two atoms forming the bond. In a delocalized  $\pi$  bond, the electron density is spread over all the atoms that contribute p orbitals in the bonding network.

12. (a) Both atomic and molecular orbitals have a characteristic energy and shape; each can hold a maximum of two electrons; Atomic orbitals are localized with their energies resulting from the interactions between subatomic particles in a single atom. Molecular orbitals can delocalize and their energies are influenced by interactions between electrons on several atoms. (b) There is a net lowering in energy that accompanies bond formation because the electrons in  $H_2$  are attracted to both H nuclei. (c) 2

13. (a) This stems from the law of conservation of energy. Each bonding interaction must be accompanied by an antibonding interaction. (b) 4

14.

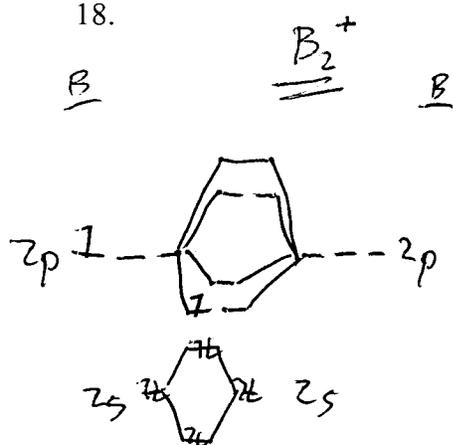


15. (a) When comparing the same two bonded atoms, bond order and bond energy are directly related, while bond order and bond length are inversely related. (b)  $\text{Be}_2$  has a bond order of zero and it is not expected to exist.  $\text{Be}_2^+$  has a bond order of 0.5 and is slightly favored over isolated Be atoms and would most likely exist under extreme conditions.

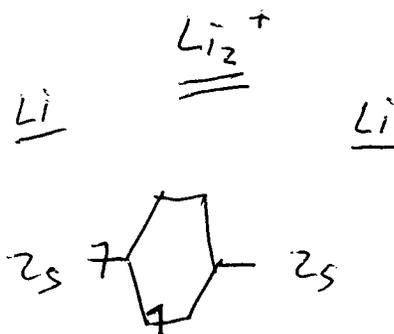
16. (a, b) A diamagnetic substance does not have any unpaired electrons. These substances are not attracted to a magnetic field. (c)  $\text{O}_2^{2-}$  and  $\text{Be}_2^{2+}$

17. (a, b) A paramagnetic substance has unpaired electrons. These substances are attracted to a magnetic field. (c)  $\text{O}_2^+$ ,  $\text{N}_2^{2-}$ , and  $\text{Li}^+$

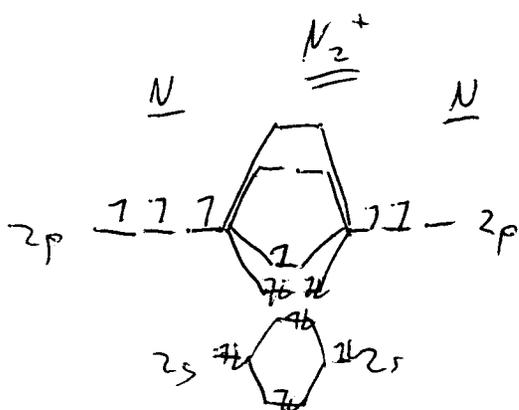
18.



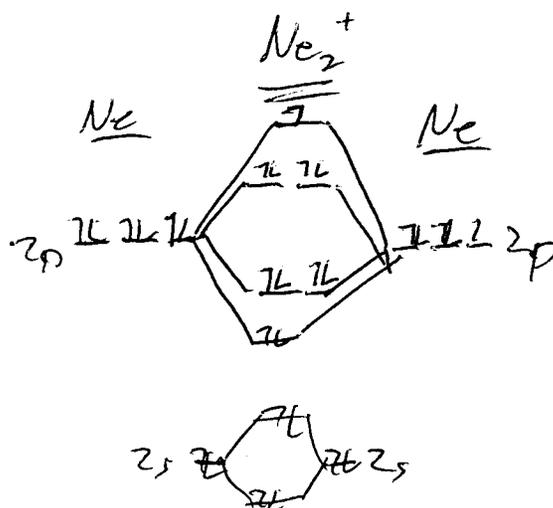
Adding an  $e^-$  to  $\text{B}_2^+$  puts an  $e^-$  into a bonding MO  
 $\rightarrow$  stabilization ( $\uparrow$  B.O.)



Adding an  $e^-$  to  $\text{Li}_2^+$   
 put an  $e^-$  into a bonding MO  $\Rightarrow$  stabilization ( $\uparrow$  B.O.)



Adding an  $e^-$  to  $\text{N}_2^+$   
 puts an  $e^-$  into a bonding orbital  $\rightarrow$  stabilization ( $\uparrow$  B.O.)



Adding an  $e^-$  to  $\text{Ne}_2^+$  puts an  $e^-$  into an anti-bonding orbital  
 $\rightarrow$  destabilized ( $\downarrow$  B.O.)

19.  $\text{CO}^+$  has a bond order of 2.5 and it is paramagnetic.  $\text{NO}^-$  has a bond order of 2 and it is paramagnetic.  $\text{OF}^+$  has a bond order of 2 and is paramagnetic.  $\text{NeF}^+$  has a bond order of 1 and it is diamagnetic.

20.  $\text{CN}^+$  has a bond order of 2 and is paramagnetic.  $\text{CN}^-$  has a bond order of 3 and is diamagnetic.  $\text{CN}$  has a bond order of 2.5 and is paramagnetic. Molecular orbital theory predicts the following trend [most stable]  $\text{CN}^- > \text{CN} > \text{CN}^+$  [least stable]

21. (a) The electron is taken away from an anti-bonding molecular orbital and upon removal the bond order increases, making  $\text{NO}^+$  more stable. (b) [weakest bond]  $\text{NO}^- < \text{NO} < \text{NO}^+$  [strongest bond].  $\text{NO}$  and  $\text{NO}^-$  are paramagnetic and  $\text{NO}^+$  is diamagnetic. (c)  $\text{NO}^+$  is isoelectronic with  $\text{N}_2$  and  $\text{NO}^-$  is isoelectronic with  $\text{O}_2$ .

22. (a) Bond Order = 1 (b) The atomic orbitals for I are lower in energy because the I is more electronegative than the Br.

23.  $\text{SiF}_4$  is tetrahedral,  $\text{SF}_4$  is see-saw, and  $\text{XeF}_4$  is square planar. The shapes are different because the number of pairs of electrons about the central atom is different leading to a difference in electron domain geometries.

24. The  $\text{PF}_3$  molecule has a trigonal pyramid molecular geometry due to the lone pair on the central atom. This lone pair makes the  $\text{PF}_3$  molecule polar, whereas in  $\text{BF}_3$  the electron domain geometry is trigonal planar with no lone pairs of electrons around the B central atom and this molecule is non-polar.

25. In an  $sp$  hybrid the central atom can form a triple bond or two double bonds. An  $sp^2$  hybrid can form one double bond, but never a triple bond, while an  $sp^3$  hybrid can only form single bonds.

26. Air contains  $\text{O}_2$ , which is paramagnetic. Any measurements made in an oxygen atmosphere could potentially give false positive results for paramagnetism due to the presence of  $\text{O}_2$ .  $\text{N}_2$  is diamagnetic and would have a magnetic moment of zero and would have no influence on the Guoy balance measurements.