

## 510 Chapter 11 Chemical Bonding II: Valence Bond and Molecular Orbital Theories

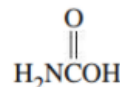
**PRACTICE EXAMPLE A:** Melamine is a carbon–hydrogen–nitrogen compound used in the manufacture of adhesives, protective coatings, and textile finishing (such as in wrinkle-free, wash-and-wear fabrics). Its mass percent composition is 28.57% C, 4.80% H, and 66.64% N. The melamine molecule features a six-member ring with alternating carbon and nitrogen atoms. Half the nitrogen atoms and all the H atoms are outside the ring. For melamine, (a) write a plausible Lewis structure, (b) describe bonding in the molecule by the valence bond method, and (c) describe bonding in the ring system through molecular orbital theory.

**PRACTICE EXAMPLE B:** Dimethylglyoxime (DMG) is a carbon–hydrogen–nitrogen–oxygen compound with a molecular mass of 116.12 u. In a combustion analysis, a 2.464 g sample of DMG yields 3.735 g CO<sub>2</sub> and 1.530 g H<sub>2</sub>O. In a separate experiment, the nitrogen in a 1.868 g sample of DMG is converted to NH<sub>3</sub>(g) and the NH<sub>3</sub> is neutralized by passing it into 50.00 mL of 0.3600 M H<sub>2</sub>SO<sub>4</sub>(aq). After neutralization of the NH<sub>3</sub> the excess H<sub>2</sub>SO<sub>4</sub>(aq) requires 18.63 mL of 0.2050 M NaOH(aq) for its neutralization. Using these data, determine for dimethylglyoxime (a) the most plausible Lewis structure, and (b) in the manner of Figure 11-19, a plausible bonding scheme.

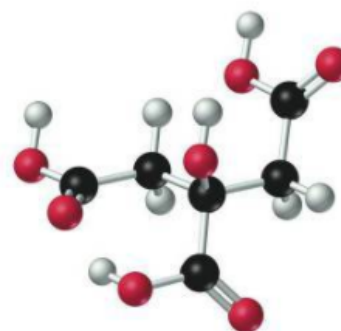
## Exercises

## Valence Bond Method

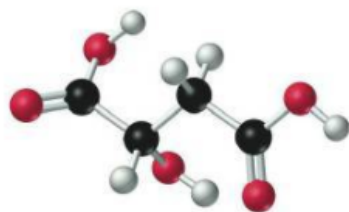
- Indicate several ways in which the valence bond method is superior to Lewis structures in describing covalent bonds.
- Explain why it is necessary to hybridize atomic orbitals when applying the valence bond method—that is, why are there so few molecules that can be described by the overlap of pure atomic orbitals only?
- Describe the molecular geometry of H<sub>2</sub>O suggested by each of the following methods: (a) Lewis theory; (b) valence bond method using simple atomic orbitals; (c) VSEPR theory; (d) valence bond method using hybridized atomic orbitals.
- Describe the molecular geometry of NH<sub>3</sub> suggested by each of the following methods: (a) Lewis theory; (b) valence bond method using simple atomic orbitals; (c) VSEPR theory; (d) valence bond method using hybridized atomic orbitals.
- In which of the following, CO<sub>3</sub><sup>2-</sup>, SO<sub>2</sub>, CCl<sub>4</sub>, CO, NO<sub>2</sub><sup>-</sup>, would you expect to find sp<sup>2</sup> hybridization of the central atom? Explain.
- In the manner of Example 11-1, describe the probable structure and bonding in (a) HI; (b) BrCl; (c) H<sub>2</sub>Se; (d) OCl<sub>2</sub>.
- For each of the following species, identify the central atom(s) and propose a hybridization scheme for those atom(s): (a) CO<sub>2</sub>; (b) HONO<sub>2</sub>; (c) ClO<sub>3</sub><sup>-</sup>; (d) BF<sub>4</sub><sup>-</sup>.
- Propose a plausible Lewis structure, geometric structure, and hybridization scheme for the ONF molecule.
- Describe a hybridization scheme for the central Cl atom in the molecule ClF<sub>3</sub> that is consistent with the geometric shape pictured in Table 10.1. Which orbitals of the Cl atom are involved in overlaps, and which are occupied by lone-pair electrons?
- Describe a hybridization scheme for the central S atom in the molecule SF<sub>4</sub> that is consistent with the geometric shape pictured in Table 10.1. Which orbitals of the S atom are involved in overlaps, and which are occupied by lone-pair electrons?
- Match each of the following species with one of these hybridization schemes: sp, sp<sup>2</sup>, sp<sup>3</sup>, sp<sup>3</sup>d, sp<sup>3</sup>d<sup>2</sup>. (a) PF<sub>6</sub><sup>-</sup>; (b) COS; (c) SiCl<sub>4</sub>; (d) NO<sub>3</sub><sup>-</sup>; (e) AsF<sub>5</sub>.
- Propose a hybridization scheme to account for bonds formed by the central carbon atom in each of the following molecules: (a) hydrogen cyanide, HCN; (b) methyl alcohol, CH<sub>3</sub>OH; (c) acetone, (CH<sub>3</sub>)<sub>2</sub>CO; (d) carbamic acid,



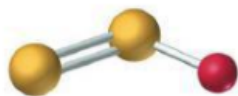
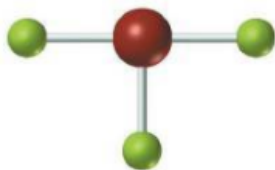
- Indicate which of the following molecules and ions are linear, which are planar, and which are neither. Then propose hybridization schemes for the central atoms. (a) Cl<sub>2</sub>C=CCl<sub>2</sub>; (b) N≡C—C≡N; (c) F<sub>3</sub>C—C≡N; (d) [S—C≡N]<sup>-</sup>.
- In the manner of Figure 11-18, indicate the structures of the following molecules in terms of the overlap of simple atomic orbitals and hybrid orbitals: (a) CH<sub>2</sub>Cl<sub>2</sub>; (b) OCN<sup>-</sup>; (c) BF<sub>3</sub>.
- Write Lewis structures for the following molecules, and then label each σ and π bond. (a) HCN; (b) C<sub>2</sub>N<sub>2</sub>; (c) CH<sub>3</sub>CHCHCl<sub>3</sub>; (d) HONO.
- Represent bonding in the carbon dioxide molecule, CO<sub>2</sub>, by (a) a Lewis structure and (b) the valence-bond method. Identify σ and π bonds, the necessary hybridization scheme, and orbital overlap.
- Use the method of Figure 11-19 to represent bonding in each of the following molecules: (a) CCl<sub>4</sub>; (b) ONCl; (c) HONO; (d) COCl<sub>2</sub>.
- Use the method of Figure 11-19 to represent bonding in each of the following ions: (a) NO<sub>2</sub><sup>-</sup>; (b) I<sub>3</sub><sup>-</sup>; (c) C<sub>2</sub>O<sub>4</sub><sup>2-</sup>; (d) HCO<sub>3</sub><sup>-</sup>.
- The molecular model below represents citric acid, an acidic component of citrus juices. Represent bonding in the citric acid molecule using the method of Figure 11-19 to indicate hybridization schemes and orbital overlaps.



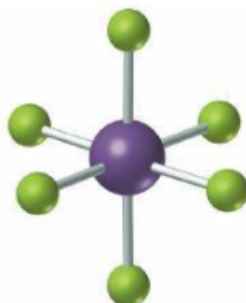
20. Malic acid is a common organic acid found in unripe apples and other fruit. With the help of the molecular model shown below, represent bonding in the malic acid molecule, using the method of Figure 11-19 to indicate hybridization schemes and orbital overlaps.



21. Shown below are ball-and-stick models. Describe hybridization and orbital-overlap schemes consistent with these structures.

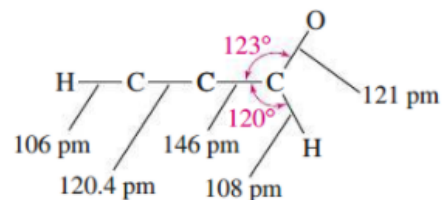
(a)  $S_2O$ (b)  $BrF_3$ 

22. Shown below are ball-and-stick models. Describe hybridization and orbital-overlap schemes consistent with these structures.

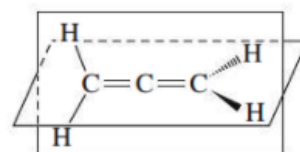
(a)  $XeF_2$ (b)  $IF_6^+$ 

23. Propose a bonding scheme that is consistent with the structure for propynal. [Hint: Consult Table 10.2

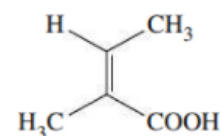
to assess the multiple-bond character in some of the bonds.]



24. The structure of the molecule allene,  $CH_2CCH_2$ , is shown here. Propose hybridization schemes for the C atoms in this molecule.

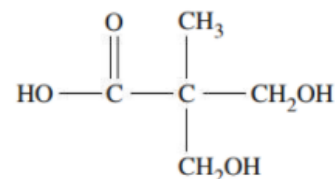


25. Angelic acid, shown below, occurs in sumbul root, a herb used as a stimulant.



Represent the bonding in the angelic acid molecule by using the method in Figure 11-19 to indicate hybridization schemes and orbital overlaps. What is the maximum number of atoms that can lie in the same plane?

26. Dimethylolpropionic acid, shown below, is used in the preparation of resins.



Represent the bonding in the dimethylolpropionic acid molecule by using the method in Figure 11-19 to indicate hybridization schemes and orbital overlaps. What is the maximum number of atoms that can lie in the same plane?

## Molecular Orbital Theory

27. Explain the essential difference in how the valence-bond method and molecular orbital theory describe a covalent bond.
28. Describe the bond order of diatomic carbon,  $C_2$ , with Lewis theory and molecular orbital theory, and explain why the results are different.
29.  $N_2(g)$  has an exceptionally high bond energy. Would you expect either  $N_2^-$  or  $N_2^{2-}$  to be a stable diatomic species in the gaseous state? Explain.
30. The paramagnetism of gaseous  $B_2$  has been established. Explain how this observation confirms that the  $\pi_{2p}$  orbitals are at a lower energy than the  $\sigma_{2p}$  orbital for  $B_2$ .
31. In our discussion of bonding, we have not encountered a bond order higher than triple. Use the energy-level diagrams of Figure 11-26 to show why this is to be expected.
32. Is it correct to say that when a diatomic molecule loses an electron, the bond energy always decreases (that is, that the bond is always weakened)? Explain.
33. For the following pairs of molecular orbitals, indicate the one you expect to have the lower energy, and state the reason for your choice. (a)  $\sigma_{1s}$  or  $\sigma_{1s}^*$ ; (b)  $\sigma_{2s}$  or  $\sigma_{2p}$ ; (c)  $\sigma_{1s}^*$  or  $\sigma_{2s}$ ; (d)  $\sigma_{2p}$  or  $\sigma_{2p}^*$ .

## 512 Chapter 11 Chemical Bonding II: Valence Bond and Molecular Orbital Theories

34. For each of the species  $C_2^+$ ,  $O_2^-$ ,  $F_2^+$ , and  $NO^+$ ,
- Write the molecular orbital occupancy diagram (as in Example 11-6).
  - Determine the bond order, and state whether you expect the species to be stable or unstable.
  - Determine if the species is diamagnetic or paramagnetic; and if paramagnetic, indicate the number of unpaired electrons.
35. Write plausible molecular orbital occupancy diagrams for the following *heteronuclear* diatomic species: (a) NO; (b)  $NO^+$ ; (c) CO; (d) CN; (e)  $CN^-$ ; (f)  $CN^+$ ; (g) BN.
36. We have used the term “isoelectronic” to refer to atoms with identical electron configurations. In molecular orbital theory, this term can be applied to molecular species as well. Which of the species in Exercise 35 are isoelectronic?
37. Consider the molecules  $NO^+$  and  $N_2^+$  and use molecular orbital theory to answer the following:
- Write the molecular orbital configuration of each ion (ignore the 1s electrons).
  - Predict the bond order of each ion.
- Which of these ions is paramagnetic? Which is diamagnetic?
  - ~~Which of these ions do you think has the greater bond length? Explain.~~
38. Consider the molecules  $CO^+$  and  $CN^-$  and use molecular orbital theory to answer the following:
- Write the molecular orbital configuration of each ion (ignore the 1s electrons).
  - Predict the bond order of each ion.
  - Which of these ions is paramagnetic? Which is diamagnetic?
  - ~~Which of these ions do you think has the greater bond length? Explain.~~
39. Construct the molecular orbital diagram for CF. Would you expect the bond length of  $CF^+$  to be longer or shorter than that of CF?
40. Construct the molecular orbital diagram for SrCl. Would you expect the bond length of  $SrCl^+$  to be longer or shorter than that of SrCl?

## Delocalized Molecular Orbitals

41. Explain why the concept of delocalized molecular orbitals is essential to an understanding of bonding in the benzene molecule,  $C_6H_6$ .
42. Explain how it is possible to avoid the concept of resonance by using molecular orbital theory.
43. In which of the following molecules would you expect to find delocalized molecular orbitals? Explain. (a)  $C_2H_4$ ; (b)  $SO_2$ ; (c)  $H_2CO$ .
44. In which of the following ions would you expect to find delocalized molecular orbitals? Explain. (a)  $HCO_2^-$ ; (b)  $CO_3^{2-}$ ; (c)  $CH_3^+$ .

## Integrative and Advanced Exercises

45. The Lewis structure of  $N_2$  indicates that the nitrogen-to-nitrogen bond is a triple covalent bond. Other evidence suggests that the  $\sigma$  bond in this molecule involves the overlap of  $sp$  hybrid orbitals.
- Draw orbital diagrams for the N atoms to describe bonding in  $N_2$ .
  - Can this bonding be described by either  $sp^2$  or  $sp^3$  hybridization of the N atoms? Can bonding in  $N_2$  be described in terms of unhybridized orbitals? Explain.
46. Show that both the valence bond method and molecular orbital theory provide an explanation for the existence of the covalent molecule  $Na_2$  in the gaseous state. Would you predict  $Na_2$  by the Lewis theory?
47. A group of spectroscopists believe that they have detected one of the following species:  $NeF$ ,  $NeF^+$ , or  $NeF^-$ . Assume that the energy-level diagrams of Figure 11-25 apply, and describe bonding in these species. Which of these species would you expect the spectroscopists to have observed?
48. Lewis theory is satisfactory to explain bonding in the ionic compound  $K_2O$ , but it does not readily explain formation of the ionic compounds potassium superoxide,  $KO_2$ , and potassium peroxide,  $K_2O_2$ .
- Show that molecular orbital theory can provide this explanation.
  - Write Lewis structures consistent with the molecular orbital explanation.
49. The compound potassium sesquioxide has the empirical formula  $K_2O_3$ . Show that this compound can be described by an appropriate combination of potassium, peroxide, and superoxide ions. Write a Lewis structure for a formula unit of the compound.
50. Draw a Lewis structure for the urea molecule,  $CO(NH_2)_2$ , and predict its geometric shape with the VSEPR theory. Then revise your assessment of this molecule, given the fact that all the atoms lie in the same plane, and all the bond angles are  $120^\circ$ . Propose a hybridization and bonding scheme consistent with these experimental observations.
51. Methyl nitrate,  $CH_3NO_3$ , is used as a rocket propellant. The skeletal structure of the molecule is  $CH_3ONO_2$ . The N and three O atoms all lie in the same plane, but the  $CH_3$  group is not in the same plane as the  $NO_3$  group. The bond angle  $C-O-N$  is  $105^\circ$ , and the bond angle  $O-N-O$  is  $125^\circ$ . One nitrogen-to-oxygen bond length is 136 pm, and the other two are 126 pm.
- Draw a sketch of the molecule showing its geometric shape.
  - Label all the bonds in the molecule as  $\sigma$  or  $\pi$ , and indicate the probable orbital overlaps involved.
  - Explain why all three nitrogen-to-oxygen bond lengths are not the same.

52. Fluorine nitrate,  $\text{FONO}_2$ , is an oxidizing agent used as a rocket propellant. A reference source lists the following data for  $\text{FO}_a\text{NO}_2$ . (The subscript "a" shows that this O atom is different from the other two.)

Bond lengths:  $\text{N}-\text{O} = 129 \text{ pm}$ ;

$\text{N}-\text{O}_a = 139 \text{ pm}$ ;  $\text{O}_a-\text{F} = 142 \text{ pm}$

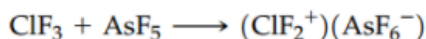
Bond angles:  $\text{O}-\text{N}-\text{O} = 125^\circ$ ;

$\text{F}-\text{O}_a-\text{N} = 105^\circ$

$\text{NO}_a\text{F}$  plane is perpendicular to the  $\text{O}_2\text{NO}_a$  plane

Use these data to construct a Lewis structure(s), a three-dimensional sketch of the molecule, and a plausible bonding scheme showing hybridization and orbital overlaps.

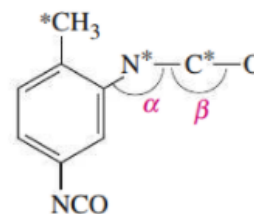
53. Draw a Lewis structure(s) for the nitrite ion,  $\text{NO}_2^-$ . Then propose a bonding scheme to describe the  $\sigma$  and  $\pi$  bonding in this ion. What conclusion can you reach about the number and types of  $\pi$  molecular orbitals in this ion? Explain.
54. Think of the reaction shown here as involving the transfer of a fluoride ion from  $\text{ClF}_3$  to  $\text{AsF}_5$  to form the ions  $\text{ClF}_2^+$  and  $\text{AsF}_6^-$ . As a result, the hybridization scheme of each central atom must change. For each reactant molecule and product ion, indicate (a) its geometric structure and (b) the hybridization scheme for its central atom.



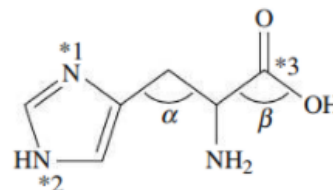
55. In the gaseous state,  $\text{HNO}_3$  molecules have two nitrogen-to-oxygen bond distances of 121 pm and one of 140 pm. Draw a plausible Lewis structure(s) to represent this fact, and propose a bonding scheme in the manner of Figure 11-19.
56.  $\text{He}_2$  does not exist as a stable molecule, but there is evidence that such a molecule can be formed between electronically excited He atoms. Write an electron configuration for  $\text{He}_2$  to account for this.
57. The molecule formamide,  $\text{HCONH}_2$ , has the approximate bond angles  $\text{H}-\text{C}-\text{O}$ ,  $123^\circ$ ;  $\text{H}-\text{C}-\text{N}$ ,  $113^\circ$ ;  $\text{N}-\text{C}-\text{O}$ ,  $124^\circ$ ;  $\text{C}-\text{N}-\text{H}$ ,  $119^\circ$ ;  $\text{H}-\text{N}-\text{H}$ ,  $119^\circ$ . The  $\text{C}-\text{N}$  bond length is 138 pm. Two Lewis structures can be written for this molecule, with the true structure being a resonance hybrid of the two. Propose a hybridization and bonding scheme for each structure.
58. Pyridine,  $\text{C}_5\text{H}_5\text{N}$ , is used in the synthesis of vitamins and drugs. The molecule can be thought of in terms of replacing one CH unit in benzene with a N atom. Draw orbital diagrams to show the orbitals of the C and N atoms involved in the  $\sigma$  and  $\pi$  bonding in pyridine. How many bonding and antibonding  $\pi$ -type molecular orbitals are present? How many delocalized electrons are present?
59. One of the characteristics of antibonding molecular orbitals is the presence of a nodal plane. Which of the bonding molecular orbitals considered in this chapter have nodal planes? Explain how a molecular orbital can have a nodal plane and still be a bonding molecular orbital.
60. The ion  $\text{F}_2\text{Cl}^-$  is linear, but the ion  $\text{F}_2\text{Cl}^+$  is bent. Describe hybridization schemes for the central Cl atom consistent with this difference in structure.
61. Ethyl cyanoacetate, a chemical used in the synthesis of dyes and pharmaceuticals, has the mass percent

composition: 53.09% C, 6.24% H, 12.39% N, and 28.29% O. In the manner of Figure 11-19, show a bonding scheme for this substance. The scheme should designate orbital overlaps,  $\sigma$  and  $\pi$  bonds, and expected bond angles.

62. A certain monomer used in the production of polymers has one nitrogen atom and the mass composition 67.90% C, 5.70% H, and 26.40% N. Sketch the probable geometric structure of this molecule, labeling all the expected bond lengths and bond angles.
63. A solar cell that is 15% efficient in converting solar to electric energy produces an energy flow of  $1.00 \text{ kW/m}^2$  when exposed to full sunlight.
- (a) If the cell has an area of  $40.0 \text{ cm}^2$ , what is the power output of the cell, in watts?
- (b) If the power calculated in part (a) is produced at 0.45 V, how much current does the cell deliver?
64. Toluene-2,4-diisocyanate is used in the manufacture of polyurethane foam. An incomplete structure is shown below. Describe the hybridization scheme for the atoms marked with an asterisk, and indicate the values of the bond angles marked  $\alpha$  and  $\beta$ .



65. Histidine, an essential amino acid, serves as a part of the active center in many enzymes. It is the precursor to histamine, a neurotransmitter and a component of the body's immune response. The structure of histidine is shown below.



Identify the hybridization scheme for the atoms marked with an asterisk, and indicate the values of the bond angles marked  $\alpha$  and  $\beta$ .

66. The anion  $\text{I}_4^{2-}$  is linear, and the anion  $\text{I}_5^-$  is V-shaped, with a  $95^\circ$  angle between the two arms of the V. For the central atoms in these ions, propose hybridization schemes that are consistent with these observations.
67. Pentadiene,  $\text{C}_5\text{H}_8$ , has three isomers, depending on the position of the two double bonds. Determine the shape of these isomers by using VSEPR theory. Describe the bonding in these molecules by using the valence bond method. Do the shapes agree in the two theories? Use molecular orbital theory to decide which of these molecules has a delocalized  $\pi$  system. Sketch the molecular orbital and an energy-level diagram.
68. A conjugated hydrocarbon has an alternation of double and single bonds. Draw the molecular orbitals of the  $\pi$  system of 1,3,5-hexatriene. If the energy required to excite an electron from the HOMO to the LUMO corresponds to a wavelength of 256 nm, do

## 514 Chapter 11 Chemical Bonding II: Valence Bond and Molecular Orbital Theories

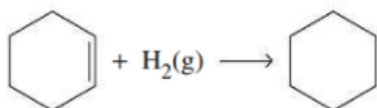
you expect the wavelength for the corresponding excitation in 1,3,5,7-octatetraene to be a longer or shorter wavelength? [Hint: Refer to Figure 11-34.]

69. An elusive intermediate of atmospheric reactions of HONO may be nitrosyl O-hydroxide, HOON. Electronic structure calculations seem to indicate that HOON is best represented by a combination of three

resonance structures, with major contribution from a radical-pair structure (involving HO and NO radicals), significant contribution from a molecular structure, and a small contribution from an ion-pair structure (involving HO<sup>-</sup> and NO<sup>+</sup> ions). Use the information to represent the structure of HOON in terms of these three resonance structures.

## Feature Problems

70. Resonance energy is the difference in energy between a real molecule—a resonance hybrid—and its most important contributing structure. To determine the resonance energy for benzene, we can determine an energy change for benzene and the corresponding change for one of the Kekulé structures. The resonance energy is the difference between these two quantities.
- (a) Use data from Appendix D to determine the enthalpy of hydrogenation of liquid benzene to liquid cyclohexane.
- (b) Use data from Appendix D to determine the enthalpy of hydrogenation of liquid cyclohexene to liquid cyclohexane.



For the enthalpy of formation of liquid cyclohexene, use  $\Delta_f H^\circ = -38.5 \text{ kJ/mol}$ .

- (c) Assume that the enthalpy of hydrogenation of 1,3,5-cyclohexatriene is three times as great as that of cyclohexene, and calculate the resonance energy of benzene.
- (d) Another way to assess resonance energy is through bond energies. Use bond energies from Table 10.3 (page 451) to determine the total enthalpy change required to break all the bonds in a Kekulé structure of benzene. Next, determine the enthalpy change for the dissociation of C<sub>6</sub>H<sub>6</sub>(g) into its gaseous atoms by using data from Table 10.3 and Appendix D. Then calculate the resonance energy of benzene.
71. Furan, C<sub>4</sub>H<sub>4</sub>O, is a substance derivable from oat hulls, corn cobs, and other cellulosic waste. It is a starting material for the synthesis of other chemicals used as pharmaceuticals and herbicides. The furan molecule is planar and the C and O atoms are bonded into a five-membered pentagonal ring. The H atoms are attached to the C atoms. The chemical behavior of the molecule suggests that it is a resonance hybrid of several contributing structures. These structures show that the double bond character is associated with the entire ring in the form of a  $\pi$  electron cloud.
- (a) Draw Lewis structures for the several contributing structures to the resonance hybrid mentioned above.
- (b) Draw orbital diagrams to show the orbitals that are involved in the  $\sigma$  and  $\pi$  bonding in furan.

[Hint: You need use only one of the contributing structures, such as the one with no formal charges.]

(c) How many  $\pi$  electrons are there in the furan molecule? Show that this number of  $\pi$  electrons is the same, regardless of the contributing structure you use for this assessment.

72. As discussed in Are You Wondering 11-1, the  $sp$  hybrid orbitals are algebraic combinations of the  $s$  and  $p$  orbitals. The required combinations of  $2s$  and  $2p$  orbitals are

$$\psi_1(sp) = \frac{1}{\sqrt{2}}[\psi(2s) + \psi(2p_z)]$$

$$\psi_2(sp) = \frac{1}{\sqrt{2}}[\psi(2s) - \psi(2p_z)]$$

(a) By combining the appropriate functions given in Table 8.2, construct a polar plot in the manner of Figure 8-24 for each of the above functions in the  $xz$  plane. In a polar plot, the value of  $r/a_0$  is set at a fixed value (for example, 1). Describe the shapes and phases of the different portions of the hybrid orbitals, and compare them with those shown in Figure 11-12.

(b) Convince yourself that the combinations employing the  $2p_x$  or  $2p_y$  orbital also give similar hybrid orbitals but pointing in different directions.

(c) The combinations for the  $sp^2$  hybrids in the  $xy$  plane are

$$\psi_1(sp^2) = \frac{1}{\sqrt{3}}\psi(2s) + \frac{\sqrt{2}}{\sqrt{3}}\psi(2p_x)$$

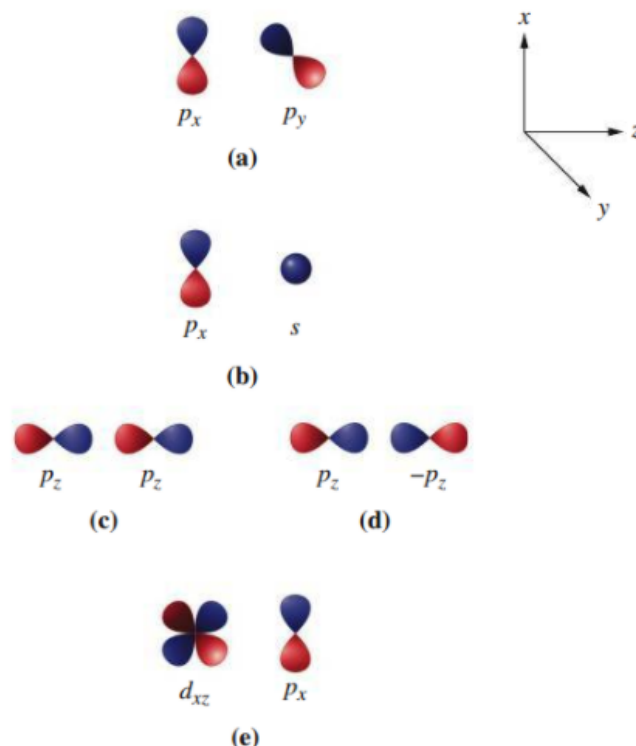
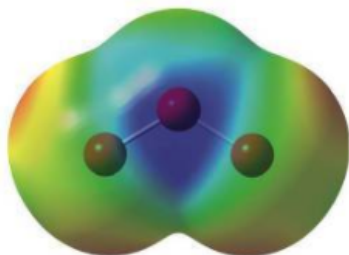
$$\psi_2(sp^2) = \frac{1}{\sqrt{3}}\psi(2s) - \frac{1}{\sqrt{6}}\psi(2p_x) + \frac{1}{\sqrt{2}}\psi(2p_y)$$

$$\psi_3(sp^2) = \frac{1}{\sqrt{3}}\psi(2s) - \frac{1}{\sqrt{6}}\psi(2p_x) - \frac{1}{\sqrt{2}}\psi(2p_y)$$

By constructing polar plots (in the  $xy$  plane), show that these functions correspond to the  $sp^2$  hybrids depicted in Figure 11-10.

73. In Chapter 10, we saw that electronegativity differences determine whether bond dipoles exist in a molecule and that molecular shape determines whether bond dipoles cancel (nonpolar molecules) or combine to produce a resultant dipole moment (polar molecules). Thus,

the ozone molecule,  $O_3$ , has no bond dipoles because all the atoms are alike. Yet,  $O_3$  *does* have a resultant dipole moment:  $\mu = 0.534$  D. The electrostatic potential map for ozone is shown below. Use the electrostatic potential map to decide the direction of the dipole. Using the ideas of delocalized bonding in molecules, can you rationalize this electrostatic potential map?



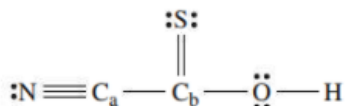
74. Borazine,  $B_3N_3H_6$  is often referred to as inorganic benzene because of its similar structure. Like benzene, borazine has a delocalized  $\pi$  system. Describe the molecular orbitals of the  $\pi$  system. Identify the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). How many nodes does the LUMO possess?
75. Which of the following combinations of orbitals give rise to bonding molecular orbitals? For those combinations that do, label the resulting bonding molecular orbital as  $\sigma$  or  $\pi$ .
76. Construct a molecular orbital diagram for HF, and label the molecular orbitals as bonding, antibonding, or nonbonding.

## Self-Assessment Exercises

77. In your own words, define the following terms or symbols: (a)  $sp^2$ ; (b)  $\sigma_{2p}^*$ ; (c) bond order; (d)  $\pi$  bond.
78. Briefly describe each of the following ideas: (a) hybridization of atomic orbitals; (b)  $\sigma$ -bond framework; (c) Kekulé structures of benzene,  $C_6H_6$ .
79. Explain the important distinctions between the terms in each of the following pairs: (a)  $\sigma$  and  $\pi$  bonds; (b) localized and delocalized electrons; (c) bonding and antibonding molecular orbitals.
80. A molecule in which  $sp^2$  hybrid orbitals are used by the central atom in forming covalent bonds is (a)  $PCl_5$ ; (b)  $N_2$ ; (c)  $SO_2$ ; (d)  $He_2$ .
81. The bond angle in  $H_2Se$  is best described as (a) between  $109^\circ$  and  $120^\circ$ ; (b) less than in  $H_2S$ ; (c) less than in  $H_2S$ , but not less than  $90^\circ$ ; (d) less than  $90^\circ$ .
82. The hybridization scheme for the central atom includes a  $d$  orbital contribution in (a)  $I_3^-$ ; (b)  $PCl_3$ ; (c)  $NO_3^-$ ; (d)  $H_2Se$ .
83. Of the following, the species with a bond order of 1 is (a)  $H_2^+$ ; (b)  $Li_2$ ; (c)  $He_2$ ; (d)  $H_2^-$ .
84. The hybridization scheme for Xe in  $XeF_2$  is (a)  $sp$ ; (b)  $sp^3$ ; (c)  $sp^3d$ ; (d)  $sp^3d^2$ .
85. Delocalized molecular orbitals are found in (a)  $H_2$ ; (b)  $HS^-$ ; (c)  $CH_4$ ; (d)  $CO_3^{2-}$ .
86. Explain why the molecular structure of  $BF_3$  cannot be adequately described through overlaps involving pure  $s$  and  $p$  orbitals.
87. Why does the hybridization  $sp^3d$  not account for bonding in the molecule  $BrF_5$ ? What hybridization scheme does work? Explain.
88. What is the total number of (a)  $\sigma$  bonds and (b)  $\pi$  bonds in the molecule  $CH_3NCO$ ?
89. Which of the following species are paramagnetic? (a)  $B_2$ ; (b)  $B_2^-$ ; (c)  $B_2^+$ . Which species has the strongest bond?
90. Use the valence molecular orbital configuration to determine which of the following species is expected to have the lowest ionization energy: (a)  $C_2^+$ ; (b)  $C_2$ ; (c)  $C_2^-$ .
91. Use the valence molecular orbital configuration to determine which of the following species is expected to have the greatest electron affinity: (a)  $C_2^+$ ; (b)  $Be_2$ ; (c)  $F_2$ ; (d)  $B_2^+$ .
92. Which of these diatomic molecules do you think has the greater bond energy,  $Li_2$  or  $C_2$ ? Explain.
93. For each of the following ions or molecules, decide whether the structure is best described by a single Lewis structure or by resonance structures. (a)  $C_2O_4^{2-}$ ; (b)  $H_2CO$ ; (c)  $NO_3^-$ .
94. Draw Lewis structures for the  $NO_2^-$  and  $NO_2^+$  ions, and determine the likely geometry for each by using VSEPR theory. How does the hybridization of N differ in these two species?

## 516 Chapter 11 Chemical Bonding II: Valence Bond and Molecular Orbital Theories

95. In which of the following is the central atom  $sp$  hybridized? (a)  $\text{BeCl}_2$ ; (b)  $\text{BCl}_3$ ; (c)  $\text{CCl}_4$ ; (d)  $\text{NCl}_3$ ; (e) none of these.
96. Which of the following can be used to explain why all bond distances and angles in methane,  $\text{CH}_4$ , are the same? (a) resonance; (b) delocalization of electrons; (c) bond polarities; (d) electronegativity; (e) orbital hybridization.
97. According to molecular orbital theory, the  $\text{O}_2^{2-}$  ion has which of the following? (a) two unpaired electrons; (b) a bond order of two; (c) its highest energy electron in a  $\sigma^*$  orbital; (d) no  $2s$  electrons; (e) all of these.
98. What is the angle between the hybrid orbitals obtained by combining the  $2s$  and two  $2p$  orbitals of an atom? (a)  $90^\circ$ ; (b)  $120^\circ$ ; (c)  $180^\circ$ ; (d)  $109.5^\circ$ ; (e) none of these.
99. Consider the molecule with the Lewis structure given below.



- (a) How many  $\sigma$  and  $\pi$  bonds are there?  
 (b) What is the appropriate hybridization scheme for each of  $\text{C}_a$ ,  $\text{C}_b$ , and  $\text{O}$ ?  
 (c) In which orbitals are the lone pairs located?  
 (d) What are the (ideal) values of the following bond angles?



100. Construct a concept map that embodies the ideas of valence bond theory.
101. Construct a concept map that connects the ideas of molecular orbital theory.
102. Construct a concept map that describes the interconnection between valence bond theory and molecular orbital theory in the description of resonance structures.