CHAPTER 11 IN REVIEW

TERMS

Section 11.2

valence shell electron pair repulsion (VSEPR) theory (438)
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linear geometry (439)
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tetrahedral geometry (440)
trigonal bipyramidal geometry (441)
octahedral geometry (441)

Section 11.3

electron geometry (442)
molecular geometry (442)
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bent geometry (443)
seesaw geometry (444)
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Section 11.6

valence bond theory (455)

Section 11.7

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hybrid orbitals (457)
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Section 11.8

molecular orbital (MO) theory (471)
bonding orbital (472)
antibonding orbital (472)
bond order (473)
nonbonding orbitals (481)

CONCEPTS

Molecular Shape and VSEPR Theory (11.1–11.4)

- The properties of molecules are directly related to their shapes. In VSEPR theory, molecular geometries are determined by the repulsions between electron groups on the central atom. An electron group can be a single bond, double bond, triple bond, lone pair, or even a single electron.
- The five basic molecular shapes are linear (two electron groups), trigonal planar (three electron groups), tetrahedral (four electron groups), trigonal bipyramidal (five electron groups), and octahedral (six electron groups).
- When lone pairs are present on the central atom, the *electron* geometry is still one of the five basic shapes, but one or more positions are occupied by lone pairs. The *molecular* geometry is therefore different from the electron geometry. Lone pairs are positioned so as to minimize repulsions with other lone pairs and with bonding pairs.

Polarity (11.5)

- The polarity of a polyatomic molecule containing polar bonds depends on its geometry. If the dipole moments of the polar bonds are aligned in such a way that they cancel one another, the molecule is not polar. If they are aligned in such a way as to sum together, the molecule is polar.
- Highly symmetric molecules tend to be nonpolar, whereas asymmetric molecules containing polar bonds tend to be polar. The polarity of a molecule dramatically affects its properties.

Valence Bond Theory (11.6–11.7)

- In contrast to the Lewis model, in which a covalent chemical bond is the sharing of electrons represented by dots, in valence bond theory a chemical bond is the overlap of half-filled atomic orbitals (or in some cases the overlap between a completely filled orbital and an empty one).
- The overlapping orbitals may be the standard atomic orbitals, such as $1s$ or $2p$, or they may be hybridized atomic orbitals, which are mathematical combinations of the standard orbitals on a single atom. The basic hybridized orbitals are sp, sp^2, sp^3, sp^3d, and sp^3d^2.
- The geometry of the molecule is determined by the geometry of the overlapping orbitals.
- In our treatment of valence bond theory, we use the electron geometry determined by VSEPR theory to determine the correct hybridization scheme.
- In valence bond theory, we distinguish between two types of bonds, σ (sigma) and π (pi). In a σ bond, the orbital overlap occurs in the region that lies directly between the two bonding atoms. In a π bond, formed from the side-by-side overlap of p orbitals, the overlap occurs above and below the region that lies directly between the two bonding atoms.
- Rotation about a σ bond is relatively free, whereas rotation about a π bond is restricted.

Molecular Orbital Theory (11.8)

- The simplest molecular orbitals are linear combinations of atomic orbitals (LCAOs), weighted averages of the atomic orbitals of the different atoms in the molecule.
- When two atomic orbitals combine to form molecular orbitals, they form one molecular orbital of lower energy (the bonding orbital) and one of higher energy (the antibonding orbital).
- A set of molecular orbitals fills in much the same way as atomic orbitals.
- The stability of the molecule and the strength of the bond depend on the number of electrons in bonding orbitals compared to the number in antibonding orbitals.

EQUATIONS AND RELATIONSHIPS

Bond Order of a Diatomic Molecule (11.8)

$$\text{Bond order} = \frac{(\text{number of electrons in bonding MOs}) - (\text{number of electrons in antibonding MOs})}{2}$$

LEARNING OUTCOMES

Chapter Objectives	Assessment
Predict the basic shapes of molecules according to VSEPR theory (11.2)	Example 11.1 **For Practice** 11.1 **Exercises** 31–34
Predict how lone pairs and electron groups affect molecular geometry (11.3, 11.4)	Examples 11.2, 11.3 **For Practice** 11.2, 11.3 **Exercises** 35–45
Predict the shape of larger molecules (11.4)	Example 11.4 **For Practice** 11.4 **Exercises** 46
Predict the polarity of a molecular compound (11.5)	Example 11.5 **For Practice** 11.5 **Exercises** 47–52
Determine the hybridization and bonding scheme of a molecule using valence bond theory (11.6, 11.7)	Examples 11.6, 11.7, 11.8 **For Practice** 11.6, 11.7, 11.8 **For More Practice** 11.8 **Exercises** 53–68
Predict properties of diatomic molecules using molecular orbital theory (11.8)	Examples 11.9, 11.10, 11.11 **For Practice** 11.9, 11.10, 11.11 **For More Practice** 11.10 **Exercises** 69–82

EXERCISES

Mastering Chemistry provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

REVIEW QUESTIONS

1. Why is molecular geometry important? Cite some examples.

2. According to VSEPR theory, what determines the geometry of a molecule?

3. Name and sketch the five basic electron geometries, and state the number of electron groups corresponding to each. What constitutes an *electron group*?

4. Explain the difference between electron geometry and molecular geometry. Under what circumstances are they not the same?

5. Give the correct electron and molecular geometries that correspond to each set of electron groups around the central atom of a molecule.

  a. four electron groups overall; three bonding groups and one lone pair
  b. four electron groups overall; two bonding groups and two lone pairs
  c. five electron groups overall; four bonding groups and one lone pair
  d. five electron groups overall; three bonding groups and two lone pairs
  e. five electron groups overall; two bonding groups and three lone pairs
  f. six electron groups overall; five bonding groups and one lone pair
  g. six electron groups overall; four bonding groups and two lone pairs

6. How do you apply VSEPR theory to predict the shape of a molecule with more than one interior atom?

7. How do you determine whether a molecule is polar? Why is polarity important?

8. What is a chemical bond according to valence bond theory?

9. In valence bond theory, what determines the geometry of a molecule?

10. In valence bond theory, the interaction energy between the electrons and nucleus of one atom with the electrons and nucleus of another atom is usually negative (stabilizing) when ____________ .

11. What is hybridization? Why is hybridization necessary in valence bond theory?

12. How does hybridization of the atomic orbitals in the central atom of a molecule help lower the overall energy of the molecule?

13. How is the *number* of hybrid orbitals related to the number of standard atomic orbitals that are hybridized?

14. Sketch each set of hybrid orbitals.

  a. sp **b.** sp^2 **c.** sp^3
  d. sp^3d **e.** sp^3d^2

15. In the Lewis model, the two bonds in a double bond look identical. However, valence bond theory shows that they are not. Describe a double bond according to valence bond theory. Explain why rotation is restricted about a double bond but not about a single bond.

16. Name the hybridization scheme that corresponds to each electron geometry.

  a. linear
  b. trigonal planar
  c. tetrahedral
  d. trigonal bipyramidal
  e. octahedral

17. What is a chemical bond according to MO theory?

18. Explain the difference between hybrid atomic orbitals in valence bond theory and LCAO molecular orbitals in MO theory.

19. What is a bonding molecular orbital?

20. What is an antibonding molecular orbital?

21. What is the role of wave interference in determining whether a molecular orbital is bonding or antibonding?

22. In MO theory, what is bond order? Why is it important?

23. How is the number of molecular orbitals approximated by a linear combination of atomic orbitals related to the number of atomic orbitals used in the approximation?

24. Sketch each molecular orbital.

a. σ_{2s} **b.** σ^*_{2s} **c.** σ_{2p}
d. σ^*_{2p} **e.** π_{2p} **f.** π^*_{2p}

25. Draw an energy diagram for the molecular orbitals of period 2 diatomic molecules. Show the difference in ordering for B_2, C_2, and N_2 compared to O_2, F_2, and Ne_2.

26. Why does the energy ordering of the molecular orbitals of the period 2 diatomic molecules change in going from N_2 to O_2?

27. Explain the difference between a paramagnetic species and a diamagnetic one.

28. When applying MO theory to heteronuclear diatomic molecules, the atomic orbitals used may be of different energies. If two atomic orbitals of different energies make two molecular orbitals, how are the energies of the molecular orbitals related to the energies of the atomic orbitals? How is the shape of the resultant molecular orbitals related to the shape of the atomic orbitals?

29. In MO theory, what is a nonbonding orbital?

30. Write a short paragraph describing chemical bonding according to the Lewis model, valence bond theory, and MO theory. Indicate how the theories differ in their description of a chemical bond and describe the strengths and weaknesses of each theory. Which theory is correct?

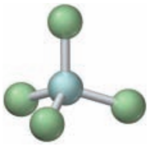
PROBLEMS BY TOPIC

VSEPR Theory and Molecular Geometry

31. A molecule with the formula AB_3 has a trigonal pyramidal geometry. How many electron groups are on the central atom (A)?
MISSED THIS? *Read Section 11.2; Watch KCV 11.2, IWE 11.1*

32. A molecule with the formula AB_3 has a trigonal planar geometry. How many electron groups are on the central atom?

33. For each molecular geometry, list the number of total electron groups, the number of bonding groups, and the number of lone pairs on the central atom. **MISSED THIS?** *Read Sections 11.2, 11.3; Watch KCV 11.2, 11.3, IWE 11.1, 11.2*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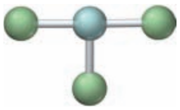
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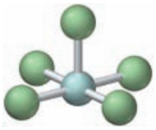
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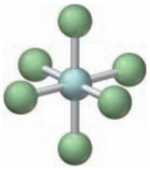
34. For each molecular geometry, list the number of total electron groups, the number of bonding groups, and the number of lone pairs on the central atom.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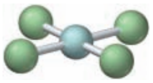
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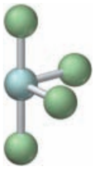
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35. Determine the electron geometry, molecular geometry, and idealized bond angles for each molecule. In which cases do you expect deviations from the idealized bond angle?
MISSED THIS? *Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2*

a. PF_3 **b.** SBr_2 **c.** $CHCl_3$ **d.** CS_2

36. Determine the electron geometry, molecular geometry, and idealized bond angles for each molecule. In which cases do you expect deviations from the idealized bond angle?

a. CF_4 **b.** NF_3 **c.** OF_2 **d.** H_2S

37. Which species has the smaller bond angle, H_3O^+ or H_2O? Explain.
MISSED THIS? *Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2*

38. Which species has the smaller bond angle, ClO_4^- or ClO_3^-? Explain.

39. Determine the molecular geometry and sketch each molecule or ion using the bond conventions shown in “Representing Molecular Geometries on Paper” in Section 11.4.
MISSED THIS? *Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2*

a. SF_4 **b.** ClF_3 **c.** IF_2^- **d.** IBr_4^-

40. Determine the molecular geometry and sketch each molecule or ion, using the bond conventions shown in “Representing Molecular Geometries on Paper” in Section 11.4.

a. BrF_5
b. SCl_6
c. PF_5
d. IF_4^+

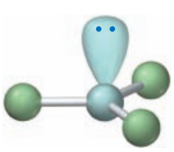
41. Determine the molecular geometry about each interior atom and sketch each molecule.
MISSED THIS? *Read Section 11.4; Watch IWE 11.4*

a. C_2H_2 (skeletal structure HCCH)
b. C_2H_4 (skeletal structure H_2CCH_2)
c. C_2H_6 (skeletal structure H_3CCH_3)

42. Determine the molecular geometry about each interior atom and sketch each molecule.

a. N_2
b. N_2H_2 (skeletal structure HNNH)
c. N_2H_4 (skeletal structure H_2NNH_2)

43. Each ball-and-stick model shows the electron and molecular geometry of a generic molecule. Explain what is wrong with each molecular geometry and provide the correct molecular geometry, given the number of lone pairs and bonding groups on the central atom.
MISSED THIS? *Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2*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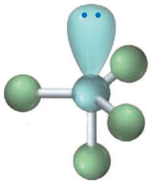
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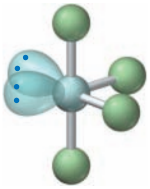
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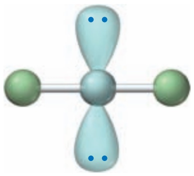
44. Each ball-and-stick model shows the electron and molecular geometry of a generic molecule. Explain what is wrong with each molecular geometry and provide the correct molecular geometry, given the number of lone pairs and bonding groups on the central atom.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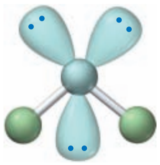
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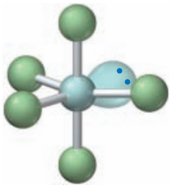

(c)

45. Determine the geometry about each interior atom in each molecule and sketch the molecule. (Skeletal structure is indicated in parentheses.)
MISSED THIS? *Read Section 11.4; Watch IWE 11.4*

a. $CH_3OH(H_3COH)$ **b.** $CH_3OCH_3(H_3COCH_3)$
c. $H_2O_2(HOOH)$

46. Determine the geometry about each interior atom in each molecule and sketch the molecule. (Skeletal structure is indicated in parentheses.)

a. $CH_3NH_2(H_3CNH_2)$
b. $CH_3CO_2CH_3$ ($H_3CCOOCH_3$ one O atom attached to 2nd C atom; the other O atom is bonded to the 2nd and 3rd C atom)
c. NH_2CO_2H (H_2NCOOH both O atoms attached to C)

Molecular Shape and Polarity

47. Explain why CO_2 and CCl_4 are both nonpolar, even though they contain polar bonds.
MISSED THIS? *Read Section 11.5; Watch KCV 11.5, IWE 11.5*

48. CH_3F is a polar molecule, even though the tetrahedral geometry often leads to nonpolar molecules. Explain.

49. Determine whether each molecule in Exercise 35 is polar or nonpolar.
MISSED THIS? *Read Section 11.5; Watch KCV 11.5, IWE 11.5*

50. Determine whether each molecule in Exercise 36 is polar or nonpolar.

51. Determine whether each molecule is polar or nonpolar.
MISSED THIS? *Read Section 11.5; Watch KCV 11.5, IWE 11.5*

a. SCl_2 **b.** SCl_4 **c.** $BrCl_5$

52. Determine whether each molecule is polar or nonpolar.

a. $SiCl_4$ **b.** CF_2Cl_2
c. SeF_6 **d.** IF_5

Valence Bond Theory

53. The valence electron configurations of several atoms are shown here. How many bonds can each atom make without hybridization? **MISSED THIS?** *Read Section 11.6; Watch KCV 11.6*

a. Be $2s^2$ **b.** P $3s^23p^3$ **c.** F $2s^22p^5$

54. The valence electron configurations of several atoms are shown here. How many bonds can each atom make without hybridization?

a. B $2s^22p^1$ **b.** N $2s^22p^3$ **c.** O $2s^22p^4$

55. Write orbital diagrams (boxes with arrows in them) to represent the electron configurations—without hybridization—for all the atoms in PH_3. Circle the electrons involved in bonding. Draw a three-dimensional sketch of the molecule and show orbital overlap. What bond angle do you expect from the unhybridized orbitals? How well does valence bond theory agree with the experimentally measured bond angle of 93.3°?
MISSED THIS? *Read Section 11.6; Watch KCV 11.6*

56. Write orbital diagrams (boxes with arrows in them) to represent the electron configurations—without hybridization—for all the atoms in SF_2. Circle the electrons involved in bonding. Draw a three-dimensional sketch of the molecule and show orbital overlap. What bond angle do you expect from the unhybridized orbitals? How well does valence bond theory agree with the experimentally measured bond angle of 98.2°?

57. Write orbital diagrams (boxes with arrows in them) to represent the electron configuration of carbon before and after sp^3 hybridization.
MISSED THIS? *Read Section 11.7; Watch KCV 11.7*

58. Write orbital diagrams (boxes with arrows in them) to represent the electron configurations of carbon before and after sp hybridization.

59. Which hybridization scheme allows the formation of at least one π bond? **MISSED THIS?** *Read Section 11.7; Watch KCV 11.7*

$$sp^3,\ sp^2,\ sp^3d^2$$

60. Which hybridization scheme allows the central atom to form more than four bonds?

$$sp^3,\ sp^3d,\ sp^2$$

61. Write a hybridization and bonding scheme for each molecule. Sketch the molecule, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.
MISSED THIS? *Read Section 11.7; Watch KCV 11.7, IWE 11.8*

a. CCl_4 **b.** NH_3 **c.** OF_2 **d.** CO_2

62. Write a hybridization and bonding scheme for each molecule. Sketch the molecule, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.

a. CH_2Br_2 **b.** SO_2 **c.** NF_3 **d.** BF_3

63. Write a hybridization and bonding scheme for each molecule or ion. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.
MISSED THIS? *Read Section 11.7; Watch KCV 11.7, IWE 11.8*

a. $COCl_2$ (carbon is the central atom)
b. BrF_5 **c.** XeF_2 **d.** I_3^-

64. Write a hybridization and bonding scheme for each molecule or ion. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.

a. SO_3^{2-} **b.** PF_6^-
c. BrF_3 **d.** HCN

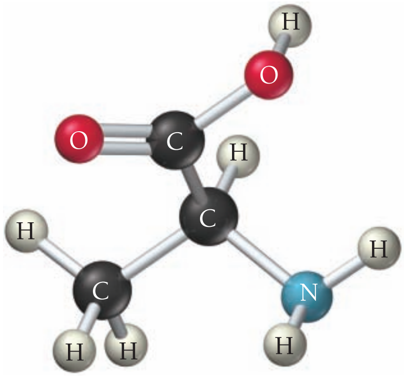
65. Write a hybridization and bonding scheme for each molecule that contains more than one interior atom. Indicate the hybridization about each interior atom. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.
MISSED THIS? *Read Section 11.7; Watch KCV 11.7, IWE 11.8*

a. N_2H_2 (skeletal structure HNNH)
b. N_2H_4 (skeletal structure H_2NNH_2)
c. CH_3NH_2 (skeletal structure H_3CNH_2)

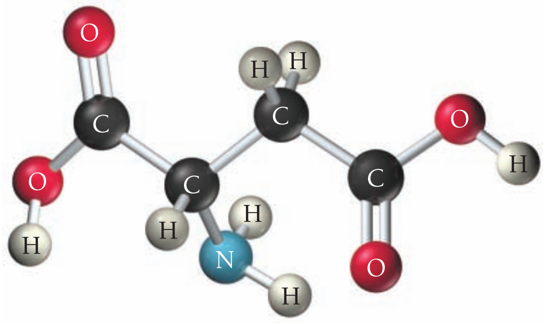
66. Write a hybridization and bonding scheme for each molecule that contains more than one interior atom. Indicate the hybridization about each interior atom. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.

a. C_2H_2 (skeletal structure HCCH)
b. C_2H_4 (skeletal structure H_2CCH_2)
c. C_2H_6 (skeletal structure H_3CCH_3)

67. Consider the structure of the amino acid alanine. Indicate the hybridization about each interior atom.
MISSED THIS? *Read Section 11.7; Watch KCV 11.7, IWE 11.8*



68. Consider the structure of the amino acid aspartic acid. Indicate the hybridization about each interior atom.



Molecular Orbital Theory

69. Sketch the bonding molecular orbital that results from the linear combination of two 1*s* orbitals. Indicate the region where interference occurs and state the kind of interference (constructive or destructive).
MISSED THIS? *Read Section 11.8*

70. Sketch the antibonding molecular orbital that results from the linear combination of two 1*s* orbitals. Indicate the region where interference occurs and state the kind of interference (constructive or destructive).

71. Draw an MO energy diagram and predict the bond order of Be_2^+ and Be_2^-. Do you expect these molecules to exist in the gas phase?
MISSED THIS? *Read Section 11.8; Watch IWE 11.10*

72. Draw an MO energy diagram and predict the bond order of Li_2^+ and Li_2^-. Do you expect these molecules to exist in the gas phase?

73. Sketch the bonding and antibonding molecular orbitals that result from linear combinations of the $2p_x$ atomic orbitals in a homonuclear diatomic molecule. (The $2p_x$ orbitals are those whose lobes are oriented along the bonding axis.)
MISSED THIS? *Read Section 11.8*

74. Sketch the bonding and antibonding molecular orbitals that result from linear combinations of the $2p_z$ atomic orbitals in a homonuclear diatomic molecule. (The $2p_z$ orbitals are those whose lobes are oriented perpendicular to the bonding axis.) How do these molecular orbitals differ from those obtained from linear combinations of the $2p_y$ atomic orbitals? (The $2p_y$ orbitals are also oriented perpendicular to the bonding axis but are also perpendicular to the $2p_z$ orbitals.)

75. Using the molecular orbital energy ordering for second-row homonuclear diatomic molecules in which the π_{2p} orbitals lie at *lower* energy than the σ_{2p}, draw MO energy diagrams and predict the bond order in a molecule or ion with each number of total valence electrons. Will the molecule or ion be diamagnetic or paramagnetic?
MISSED THIS? *Read Section 11.8; Watch IWE 11.10*

a. 4 **b.** 6 **c.** 8 **d.** 9

76. Using the molecular orbital energy ordering for second-row homonuclear diatomic molecules in which the π_{2p} orbitals lie at *higher* energy than the σ_{2p}, draw MO energy diagrams and predict the bond order in a molecule or ion with each number of total valence electrons. Will the molecule or ion be diamagnetic or paramagnetic?

a. 10 **b.** 12 **c.** 13 **d.** 14

77. Use MO theory to predict if each molecule or ion exists in a relatively stable form.
MISSED THIS? *Read Section 11.8; Watch IWE 11.10*

a. H_2^{2-} **b.** Ne_2 **c.** He_2^{2+} **d.** F_2^{2-}

78. Use MO theory to predict if each molecule or ion exists in a relatively stable form.

a. C_2^{2+} **b.** Li_2 **c.** Be_2^{2+} **d.** Li_2^{2-}

79. According to MO theory, which molecule or ion has the highest bond order? Highest bond energy? Shortest bond length?
MISSED THIS? *Read Section 11.8; Watch IWE 11.10*

C_2, C_2^+, C_2^-

80. According to MO theory, which molecule or ion has the highest bond order? Highest bond energy? Shortest bond length?

O_2, O_2^-, O_2^{2-}

81. Draw an MO energy diagram for CO. (Use the energy ordering of O_2.) Predict the bond order and make a sketch of the lowest energy bonding molecular orbital.
MISSED THIS? *Read Section 11.8*

82. Draw an energy diagram for HCl. Predict the bond order and make a sketch of the lowest energy bonding molecular orbital.

CUMULATIVE PROBLEMS

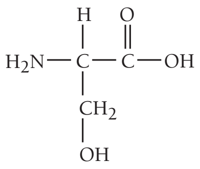
83. For each compound, draw the Lewis structure, determine the geometry using VSEPR theory, determine whether the molecule is polar, identify the hybridization of all interior atoms, and make a sketch of the molecule, according to valence bond theory, showing orbital overlap.

a. COF_2 (carbon is the central atom)
b. S_2Cl_2 (ClSSCl)
c. SF_4

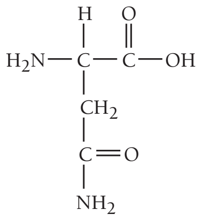
84. For each compound, draw the Lewis structure, determine the geometry using VSEPR theory, determine whether the molecule is polar, identify the hybridization of all interior atoms, and make a sketch of the molecule, according to valence bond theory, showing orbital overlap.

a. IF_5
b. CH_2CHCH_3
c. CH_3SH

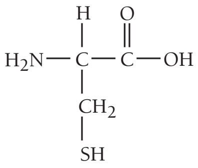
85. Amino acids are biological compounds that link together to form proteins, the workhorse molecules in living organisms. The skeletal structures of several simple amino acids are shown here. For each skeletal structure, complete the Lewis structure, determine the geometry and hybridization about each interior atom, and make a sketch of the molecule, using the bond conventions of Section 11.4.



(a) serine



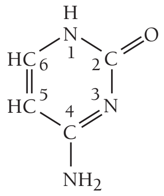
(b) asparagine

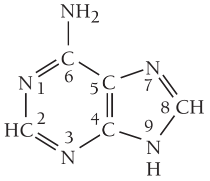


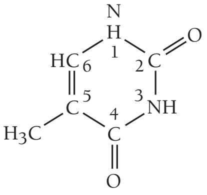
(c) cysteine

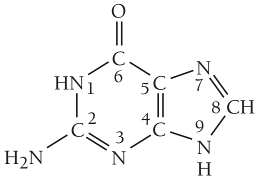
86. The genetic code is based on four different bases with the structures shown here. Assign a geometry and hybridization to each interior atom in these four bases.

a. cytosine **b.** adenine **c.** thymine **d.** guanine

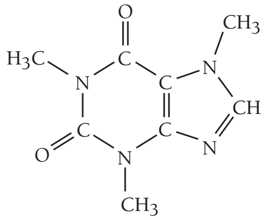

(a)


(b)

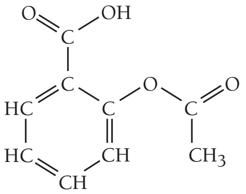

(c)


(d)

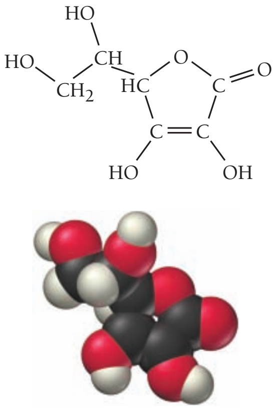
87. The structure of caffeine, present in coffee and many soft drinks, is shown here. How many pi bonds are present in caffeine? How many sigma bonds? Insert the lone pairs in the molecule. What kinds of orbitals do the lone pairs occupy?

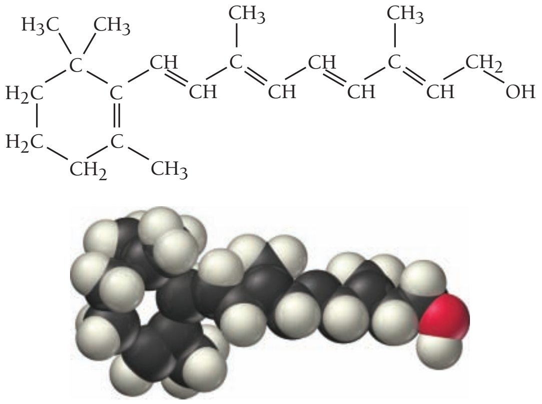


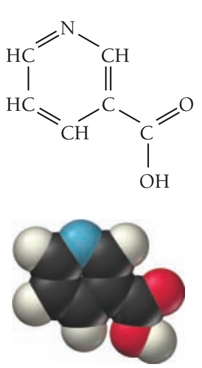
88. The structure of acetylsalicylic acid (aspirin) is shown here. How many pi bonds are present in acetylsalicylic acid? How many sigma bonds? What parts of the molecule are free to rotate? What parts are rigid?

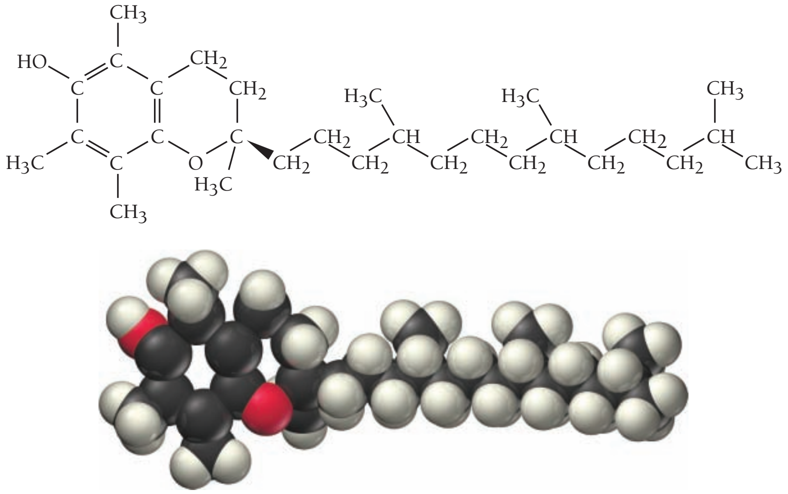


89. Most vitamins can be classified as either fat soluble, which results in their tendency to accumulate in the body (so that taking too much can be harmful), or water soluble, which results in their tendency to be quickly eliminated from the body in urine. Examine the structural formulas and space-filling models of these vitamins and determine whether each one is fat soluble (mostly nonpolar) or water soluble (mostly polar).

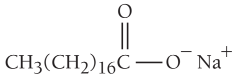

(a) vitamin C


(b) vitamin A

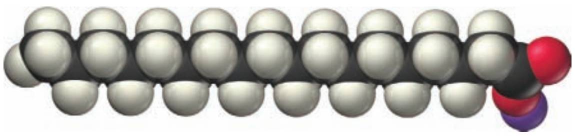

(c) niacin (vitamin B_3)


(d) vitamin E

90. Water does not easily remove grease from dishes or hands because grease is nonpolar and water is polar. The addition of soap to water, however, allows the grease to dissolve. Study the structure of sodium stearate (a soap) and describe how it works.



$CH_3(CH_2)_{16}C(=O)—O^- Na^+$



91. Draw a molecular orbital energy diagram for ClF. (Assume that the σ_p orbitals are lower in energy than the π orbitals.) What is the bond order in ClF?

92. Draw Lewis structures and MO diagrams for CN^+, CN, and CN^-. According to the Lewis model, which species is most stable? According to MO theory, which species is most stable? Do the two theories agree?

93. Bromine can form compounds or ions with any number of fluorine atoms from one to five. Write the formulas of all five of these species, assign a hybridization, and describe their electron and molecular geometry.

94. The compound C_3H_4 has two double bonds. Describe its bonding and geometry, using a valence bond approach.

95. Draw the structure of a molecule with the formula $C_4H_6Cl_2$ that has a dipole moment of 0.

96. Draw the structures of two compounds that have the composition CH_3NO_2 and have all three H atoms bonded to the C. Predict which compound has the larger ONO bond angle.

97. How many types of hybrid orbitals do we use to describe each molecule?

a. N_2O_5

b. C_2H_5NO (four C—H bonds and one O—H bond)

c. BrCN (no formal charges)

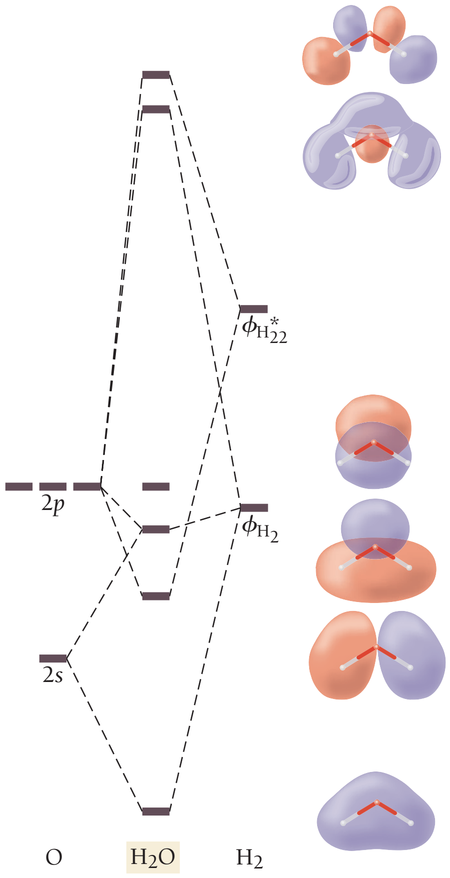
98. Indicate which orbitals overlap to form the σ bonds in each molecule.

a. $BeBr_2$ **b.** $HgCl_2$ **c.** ICN

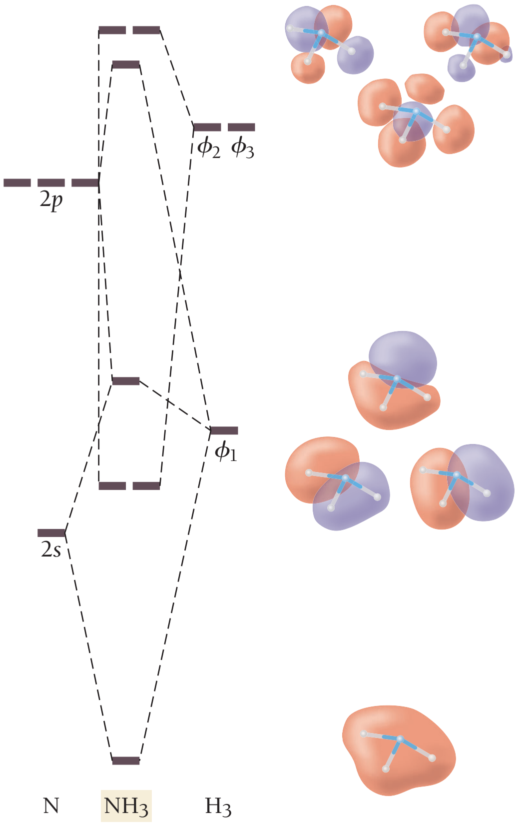
CHALLENGE PROBLEMS

99. In VSEPR theory, which uses the Lewis model to determine molecular geometry, the trend of decreasing bond angles in CH_4, NH_3, and H_2O is accounted for by the greater repulsion of lone pair electrons compared to bonding pair electrons. How would this trend be accounted for in valence bond theory?

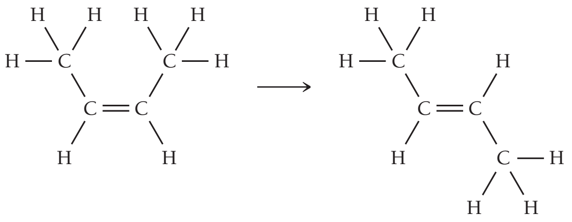
100. The results of a molecular orbital calculation for H_2O are shown here. Examine each of the orbitals and classify them as bonding, antibonding, or nonbonding. Assign the correct number of electrons to the energy diagram. According to this energy diagram, is H_2O stable? Explain.



101. The results of a molecular orbital calculation for NH_3 are shown here. Examine each of the orbitals and classify them as bonding, antibonding, or nonbonding. Assign the correct number of electrons to the energy diagram. According to this energy diagram, is NH_3 stable? Explain.



102. *cis*-2-Butene isomerizes to *trans*-2-butene via the reaction shown here.



a. If isomerization requires breaking the π bond, what minimum energy is required for isomerization in J/mol? In J/molecule?

b. If the energy for isomerization came from light, what minimum frequency of light would be required? In what portion of the electromagnetic spectrum does this frequency lie?

103. The species NO_2, NO_2^+, and NO_2^- in which N is the central atom have very different bond angles. Predict what these bond angles might be with respect to the ideal angles and justify your prediction.

104. The bond angles increase steadily in the series PF_3, PCl_3, PBr_3, and PI_3. After consulting the data on atomic radii in Chapter 9, provide an explanation for this observation.

105. The ion CH_5^+ can form under very special high-energy conditions in the vapor phase in a mass spectrometer. Propose a hybridization for the carbon atom and predict the geometry.

106. Neither the VSEPR model nor the hybridization model is able to account for the experimental observation that the F—Ba—F bond angle in gaseous BaF_2 is 108° rather than the predicted 180°. Suggest some possible explanations for this observation.

107. Draw the Lewis structure for acetamide (CH_3CONH_2), an organic compound, and determine the geometry about each interior atom. Experiments show that the geometry about the nitrogen atom in acetamide is nearly planar. What resonance structure can account for the planar geometry about the nitrogen atom?

108. Use VSEPR theory to predict the geometry (including bond angles) about each interior atom of methyl azide (CH_3N_3), and make a sketch of the molecule. Would you expect the bond angle between the two interior nitrogen atoms to be the same or different? Would you expect the two nitrogen–nitrogen bond lengths to be the same or different?

CONCEPTUAL PROBLEMS

109. Which statement best captures the fundamental idea behind VSEPR theory? Explain what is wrong with each of the other statements.

a. The angle between two or more bonds is determined primarily by the repulsions between the electrons within those bonds and other (lone pair) electrons on the central atom of a molecule. Each of these electron groups (bonding electrons or lone pair electrons) will lower its potential energy by maximizing its separation from other electron groups, thus determining the geometry of the molecule.

b. The angle between two or more bonds is determined primarily by the repulsions between the electrons within those bonds. Each of these bonding electrons will lower its potential energy by maximizing its separation from other electron groups, thus determining the geometry of the molecule.

c. The geometry of a molecule is determined by the shapes of the overlapping orbitals that form the chemical bonds. Therefore, to determine the geometry of a molecule, you must determine the shapes of the orbitals involved in bonding.

110. Suppose that a molecule has four bonding groups and one lone pair on the central atom. Suppose further that the molecule is confined to two dimensions (this is a purely hypothetical assumption for the sake of understanding the principles behind VSEPR theory). Make a sketch of the molecule and estimate the bond angles.

111. How does each of the three major bonding theories (the Lewis model, valence bond theory, and MO theory) define a single chemical bond? A double bond? A triple bond? How are these definitions similar? How are they different?

112. The most stable forms of the nonmetals in groups 4A, 5A, and 6A of the second period are molecules with multiple bonds. Beginning with the third period, the most stable forms of the nonmetals of these groups are molecules without multiple bonds. Propose an explanation for this observation based on valence bond theory.

QUESTIONS FOR GROUP WORK

Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

113. In complete sentences, describe why someone might expect the bond angles in methane (CH_4) to be 90° even though the bond angles are actually 109.5°.

114. At least two different numbers of electron groups can result in a linear molecule. What are they? What are the numbers of bonding groups and lone pairs in each case? Provide an example of a linear molecule in each case.

115. Have each member of your group select one of the molecules shown below and complete steps a–d. Each member should then present his or her results to the rest of the group, explaining the reasoning used to determine the answers.

CS_2 NCl_3 CF_4 CH_2F_2

a. Draw the Lewis dot structure.

b. Determine the molecular geometry and draw it accurately.

c. Indicate the polarity of any polar bonds within the structure.

d. Classify the molecule as polar or nonpolar.

116. How many atomic orbitals form a set of sp^3 hybrid orbitals? A set of sp^2 hybrid orbitals? A set of sp hybrid orbitals? What is the relationship between these numbers and the number of electron groups around the central atom?

117. Use MO theory to explain in detail why N_2^+ and N_2^- have similar bond strengths and both are very different from neutral N_2.

DATA INTERPRETATION AND ANALYSIS

Using Distances between Atoms to Predict Bond Angles

118. The VSEPR model is useful in predicting bond angles for many compounds. However, as we have seen, other factors (such as type of bond and atomic radii) may also influence bond angles. Consider that data for bond angles in related species in the tables and answer the questions.

Bond Angles in NO_2 and Associated Ions

Species	Bond Angle
NO_2	134°
NO_2^+	180°
NO_2^-	115°

Bond Angles in PX_3 Compounds

Compounds	Bond Angle
PH_3	94°
PF_3	97°
PCl_3	100°
PI_3	102°

a. Draw Lewis structures for all of the species in the Bond Angles in NO_2 and Associated Ions Table.
b. Use the Lewis structures from part a to explain the observed bond angles in NO_2 and its associated ions.
c. Draw Lewis structures for all of the species in the Bond Angles in PX_3 Compounds Table.
d. Make your own table showing the atomic radii of H, F, Cl, and I.
e. Use your answers to parts c and d to explain the observed bond angles in PH_3, PF_3, PCl_3, and PI_3.

Cc ANSWERS TO CONCEPTUAL CONNECTIONS

Electron Groups and Molecular Geometry

11.1 **(b)** Two electron groups with no lone pairs on a central atom in a molecule result in a linear geometry.

Molecular Geometry

11.2 **(a)** Linear. HCN has two electron groups (the single bond and the triple bond) resulting in a linear geometry.

Lone Pairs and Molecular Geometry I

11.3 **(d)** Three bonding groups and one lone pair lead to a trigonal pyramidal geometry.

Lone Pair Repulsions

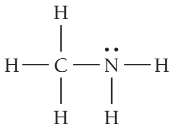
11.4 **(c)** Positions 1 and 4 would put the greatest distance between the lone pairs and minimize lone pair–lone pair repulsions.

Molecular Geometry and Electron Group Repulsions

11.5 **(d)** All electron groups on the central atom (or interior atoms, if there is more than one) determine the shape of a molecule according to VSEPR theory.

The Shape of Larger Molecules

11.6 **(c)** The nitrogen atom has four electron groups and one lone pair, as the Lewis structure illustrates; therefore, the molecular geometry about the nitrogen atom is trigonal pyramidal.



Polarity of Molecules

11.7 **(b)** Even through the molecule has polar bonds, the dipole moments of the three bonds cancel out because of the trigonal planar geometry, and the molecule is not polar.

What Is a Chemical Bond? Part I

11.8 **(b)** In valence bond theory, a covalent chemical bond is the overlap of half-filled atomic orbitals.

Number of Hybrid Orbitals

11.9 **(d)** The number of hybrid orbitals that form must always equal the number of orbitals that are combined. Since one *s* and three *p* orbitals are combined, four hybrid orbitals form. You can also determine the number of hybrid orbitals by summing the superscripts in the hybridization notation. For sp^3, you add the implied 1 superscript on the *s* to the 3 superscript on the *p* and you get $1 + 3 = 4$.

Single and Double Bonds

11.10 **(a)** Applying valence bond theory, we see that a double bond is actually composed of two different kinds of bonds, one σ and one π. The orbital overlap in the π bond is side to side between two *p* orbitals and consequently different from the end-to-end overlap in a σ bond. Since the bonds are different types, the bond energy of the double bond is not just twice the bond energy of the single bond.

Hybridization

11.11 **(a)** Because carbon has two electron groups in carbon dioxide (the two double bonds), the geometry is linear and the hybridization is *sp*.

Bond Order

11.12 **(b)** The bond order is 1.5. Remember that bond order is equal to the number of bonding electrons minus the number of antibonding electrons, all divided by two, so you get that the bond order $= (6 - 3)/2 = 1.5$.

What Is a Chemical Bond? Part II

11.13 **(c)** According to MO theory, atoms join together (or bond) when the electrons in the atoms can lower their energy by occupying the molecular orbitals of the resultant molecule. Unlike the Lewis model or valence bond theory, the chemical “bonds” in MO theory are not localized between atoms but are spread throughout the entire molecule.