

Chapter 11 Answers

Practice Examples

1a. There are three half-filled $2p$ orbitals on N, and one half-filled $5p$ orbital on I. Each half-filled $2p$ orbital from N will overlap with one half-filled $5p$ orbital of an I. Thus, there will be three N—I bonds. The I atoms will be oriented in the same direction as the three $2p$ orbitals of N: toward the x -, y -, and z -directions of a Cartesian coordinate system. Thus, the I—N—I angles will be approximately 90° (probably larger because the I atoms will repel each other). The three I atoms will lie in the same plane at the points of a triangle, with the N atom centered above them. The molecule is trigonal pyramidal.

1b. There are three half-filled orbitals on N and one half-filled orbital on each H. There will be three N—H bonds, with bond angles of approximately 90° . The molecule is trigonal pyramidal. (We obtain the same molecular shape if N is assumed to be sp^3 hybridized, but bond angles are closer to 109.5° , the tetrahedral bond angle.) VSEPR theory begins with the Lewis structure and notes that there are three bond pairs and one lone pair attached to N. This produces a tetrahedral electron pair geometry and a trigonal pyramidal molecular shape with bond angles a bit less than the tetrahedral angle of 109.5° because of the lone pair. Since VSEPR theory makes a prediction closer to the experimental bond angle of 107° , it seems more appropriate in this case.

2a. Bent molecular geometry, sp^3 hybridization.

2b. See-saw molecular geometry, sp^3d hybridization.

3a. Each central atom is surrounded by four electron pairs, requiring sp^3 hybridization. The carbon atoms have tetrahedral geometry, the oxygen atom is bent.

3b. The left-most C and the right-most O are surrounded by four electron pairs, and thus require sp^3 hybridization. The central carbon is surrounded by three electron groups and is sp^2 hybridized.

4a. There are four bond pairs around the left-hand C, requiring sp^3 hybridization. Three of the bonds that form are C—H sigma bonds resulting from the overlap of a half-filled sp^3 hybrid orbital on C with a half-filled $1s$ orbital on H. The other C has two attached electron groups, utilizing sp hybridization. The two C atoms join with a sigma bond: overlap of sp^2 on the left-hand C with sp on the right-hand C. The three bonds between C and N consist of a sigma bond (sp on C with sp on N), and two pi bonds ($2p$ on C with $2p$ on N).

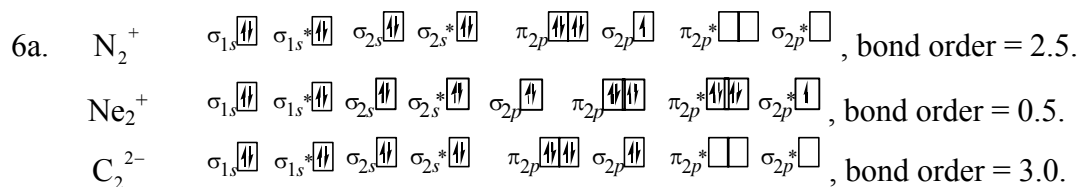
4b. structure(1) $| \text{N}_a \equiv \text{N}_b^\oplus - \bar{\text{O}} | \leftrightarrow | \underline{\text{N}}_a = \text{N}_b^\oplus = \bar{\text{O}} |$ structure(2). In both structures,

the central N is attached to two other atoms, and possesses no lone pairs. The geometry of the molecule thus is linear and the hybridization on this central N is sp . In structure (1) the $\text{N} \equiv \text{N}$ bond results from the overlap of three pairs of half-filled orbitals: (1) sp_x on N_b with $2p_x$ on N_a forming a σ bond, (2) $2p_y$ on N_b with $2p_y$ on N_a forming a π bond, and (3) $2p_z$ on N_b

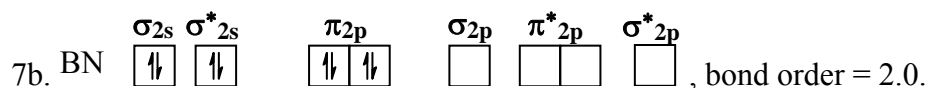
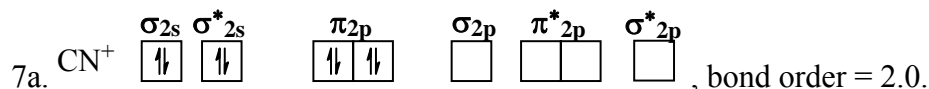
with $2p_z$ on N_a also forming a π bond. The N—O bond is a coordinate covalent bond, and forms by the overlap of the full sp_x orbital on N_b with the empty $2p$ orbital on O. In structure (2) the $N=O$ bond results from the overlap of two pairs of half-filled orbitals: (1) sp_y on N_b with $2p_y$ on O forming a σ bond and (2) $2p_z$ on N_b with $2p_z$ on O forming a π bond. The $N=N$ σ bond is a coordinate covalent bond, and is formed by two overlaps: (1) the overlap of the full sp_y orbital on N_b with the empty $2p_y$ orbital on N_a to form a σ bond, and (2) the overlap of the half-filled $2p_x$ orbital on N_b with the half-filled $2p_x$ orbital on N_a to form a π bond. Based on formal charge arguments, structure (1) is preferred, because the negative formal charge is on the more electronegative atom, O.

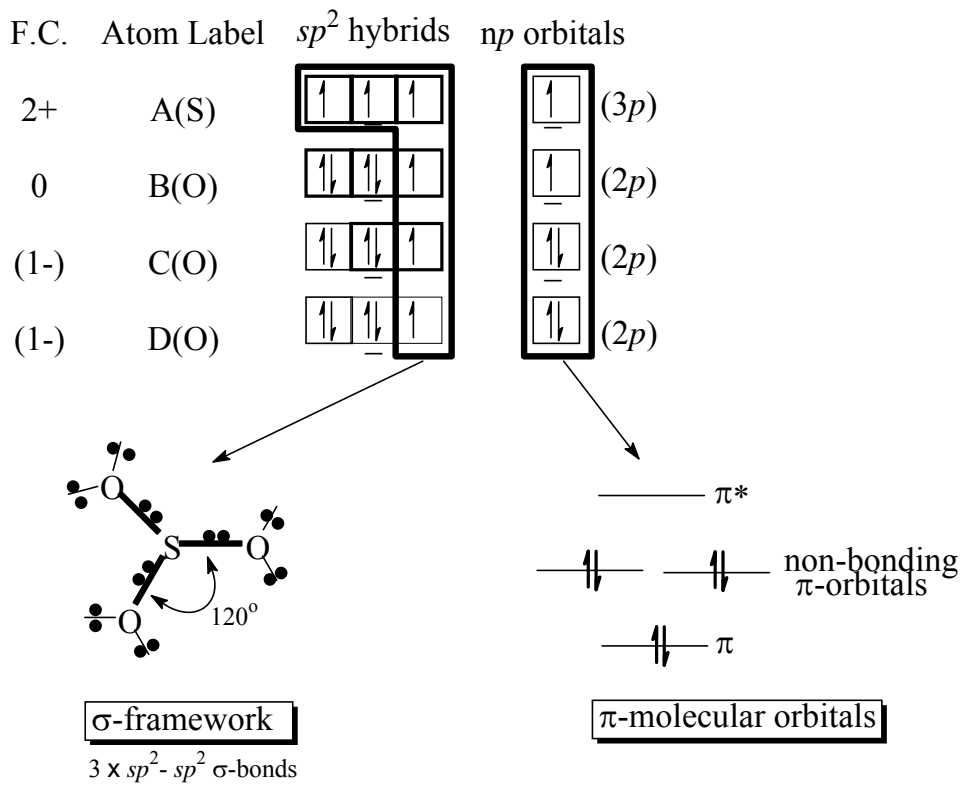
5a. 53 kJ/mol Li_2^+

5b. The bond order in H_2^- is $1/2$. We would expect the ion H_2^- to be stable, with a bond strength about half that of a hydrogen molecule.

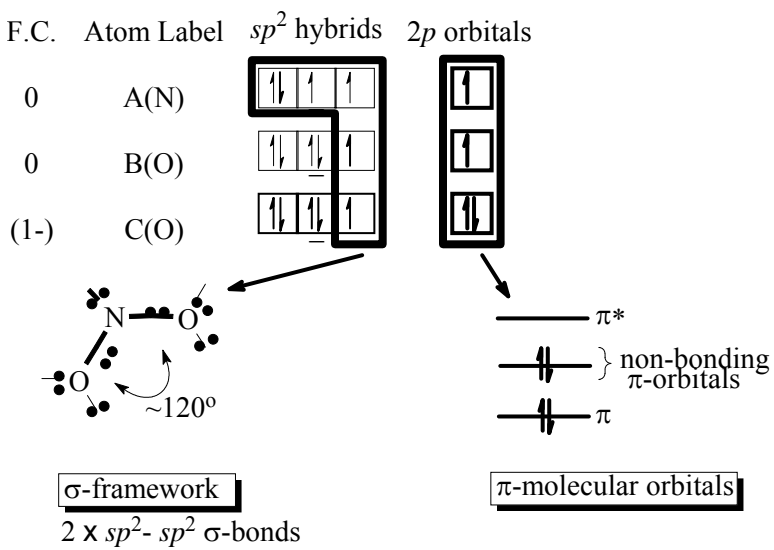


6b. The bond length increases as the bond order decreases. Longer bonds are weaker bonds.



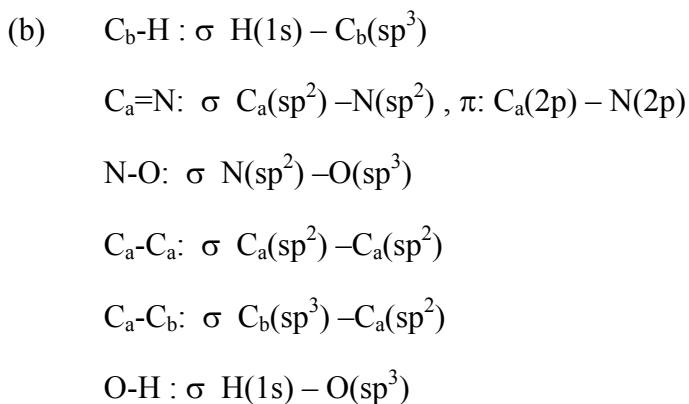
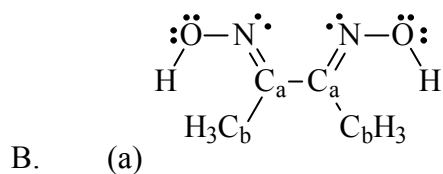
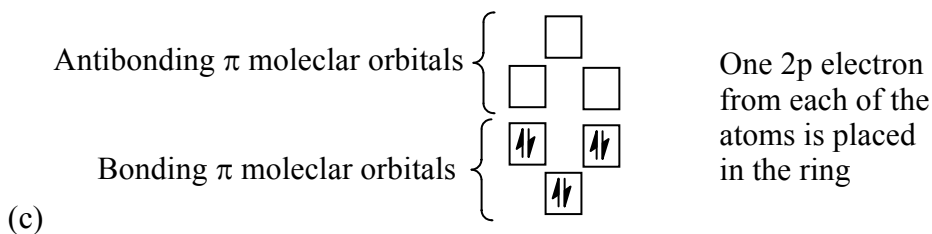
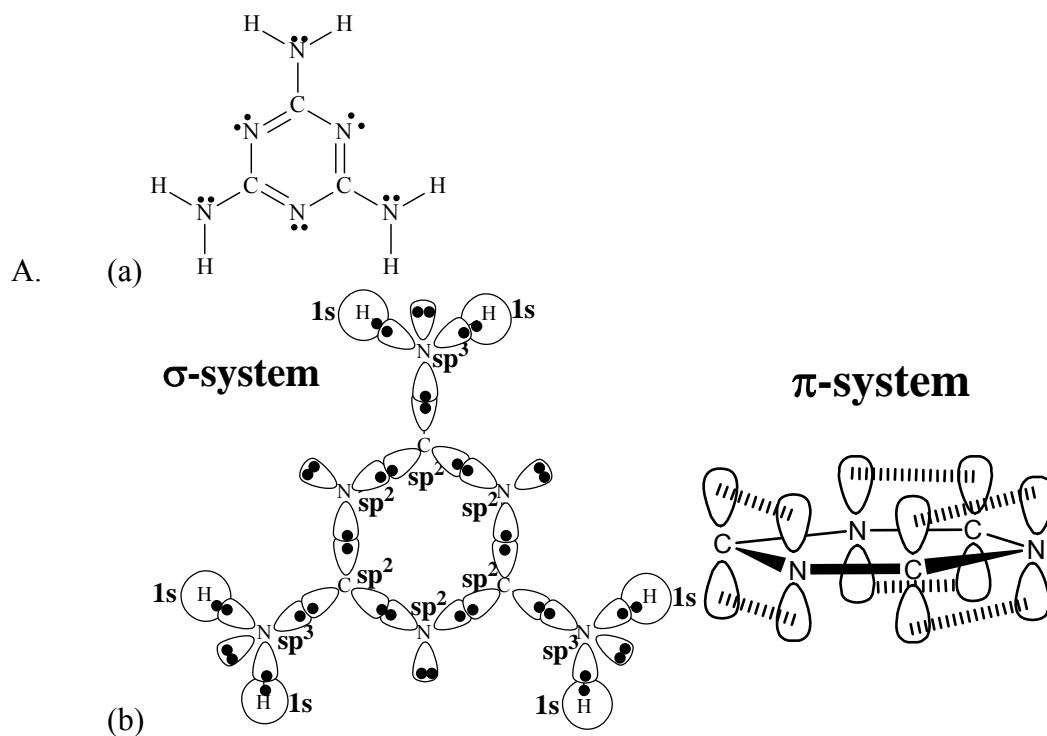


8a.



8b.

Integrative Example



Exercises

1. First, valence-bond theory clearly distinguishes between sigma and pi bonds. In valence-bond theory, it is clear that a sigma bond must be stronger than a pi bond, for the orbitals overlap more effectively in a sigma bond (end-to-end) than they do in a pi bond (side-to-side). *Second*, molecular geometries are more directly obtained in valence-bond theory than in Lewis theory. *Third*, Lewis theory does not explain hindered rotation about double bonds.

3a. Lewis theory does not describe the shape of the water molecule.

3b. In valence-bond theory using simple atomic orbitals, each H—O bond results from the overlap of a $1s$ orbital on H with a $2p$ orbital on O. The angle between $2p$ orbitals is 90° so this method initially predicts a 90° bond angle.

3c. In VSEPR theory the H_2O molecule is categorized as being of the AX_2E_2 type. The lone pairs repel each other more than do the bond pairs, explaining the smaller than 109.5° tetrahedral bond angle.

3d. In valence-bond theory using hybrid orbitals, each H—O bond results from the overlap of a $1s$ orbital on H with an sp^3 orbital on O. The angle between sp^3 orbitals is 109.5° .

5. The central atom is sp^2 hybridized in SO_2 , CO_3^{2-} , and NO_2^- .

7a. C is the central atom. The molecule is linear and C is sp hybridized.

7b. N is the central atom. The molecule is trigonal planar around N which is sp^2 hybridized.

7c. Cl is the central atom. The electron-group geometry around Cl is tetrahedral, indicating that Cl is sp^3 hybridized.

7d. B is the central atom. The electron-group geometry is tetrahedral, indicating that B is sp^3 hybridized.

9. The hybridization is sp^3d . Each of the three sigma bonds are formed by the overlap of a $2p$ orbital on F with one of the half-filled dsp^3 orbitals on Cl. The two lone pairs occupy dsp^3 orbitals.

11a. sp^3d^2 .

11b. sp

11c. sp^3 .

11d. sp^2 .

11e. sp^3d .

13a. Planar molecule. The hybridization on C is sp^2 .

13b. Linear molecule. The hybridization for each C is sp .

13c. Neither linear nor planar. The shape around the left-hand C is tetrahedral and that C has sp^3 hybridization.

13d. Linear molecule. The hybridization for C is sp .

15a. $\text{H}-\text{C}\equiv\text{N}|$. The H—C bond is a σ bond, and the $\text{C}\equiv\text{N}$ bond is composed of 1 σ and 2 π bonds.

15b. $|\text{N}\equiv\text{C}-\text{C}\equiv\text{N}|$ The C—C bond is a σ bond, and each $\text{C}\equiv\text{N}$ bond is composed of 1 σ and 2 π bonds.

15c.
$$\begin{array}{ccccccc} & \text{H} & & & \text{Cl} & & \\ & | & & & | & & \\ \text{H} & -\text{C} & - & \text{C} & = & \text{C} & - & \text{C} & - & \text{Cl} \\ & | & | & | & | & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{Cl} & & & & & \end{array}$$
. All bonds are σ bonds except one of the bonds that comprise the C=C bond. The C=C bond is composed of one σ and one π bond.

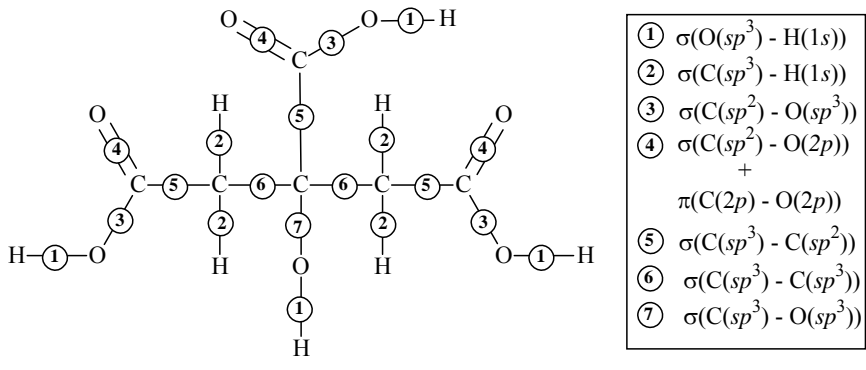
15d. $\text{H}-\text{O}=\text{N}=\text{O}$. All single bonds in this structure are σ bonds. The double bond is composed of one σ and one π bond.

17a. The geometry at C is tetrahedral; C is sp^3 hybridized. Cl—C—Cl bond angles are 109.5° . Each C—Cl bond is represented by $\sigma: \text{C}(sp^3)^1 - \text{Cl}(3p)^1$

17b. The e^- group geometry around N is trigonal planar, and N is sp^2 hybridized. The O—N—C bond angle is about 120° . The bonds are: $\sigma: \text{O}(2p_y)^1 - \text{N}(sp^2)^1$ $\sigma: \text{N}(sp^2)^1 - \text{Cl}(3p_z)^1$
 $\pi: \text{O}(2p_z)^1 - \text{N}(2p_z)^1$.

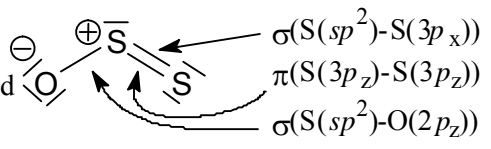
17c. $\text{H}-\text{O}_a-\text{N}=\text{O}_b$. The geometry of O_a is tetrahedral, O_a is sp^3 hybridized and the H— O_a —N bond angle is (at least close to) 109.5° . The e^- group geometry at N is trigonal, N is sp^2 hybridized, and the O_a —N— O_b bond angle is 120° . The four bonds are represented as follows. $\sigma: \text{H}(1s)^1 - \text{O}_a(sp^3)^1$
 $\sigma: \text{O}_a(sp^3)^1 - \text{N}(sp^2)^1$ $\sigma: \text{N}(sp^2)^1 - \text{O}_b(2p_y)^1$ $\pi: \text{N}(2p_z)^1 - \text{O}_b(2p_z)^1$.

17d. The e^- group geometry around C is trigonal planar; all bond angles around C are 120° , and the hybridization of C is sp^2 . The four bonds in the molecules are:
 $2 \times \sigma: \text{Cl}(3p_x)^1 - \text{C}(sp^2)^1$ $\sigma: \text{O}(2p_y)^1 - \text{C}(sp^2)^1$ $\pi: \text{O}(2p_z)^1 - \text{C}(2p_z)^1$.



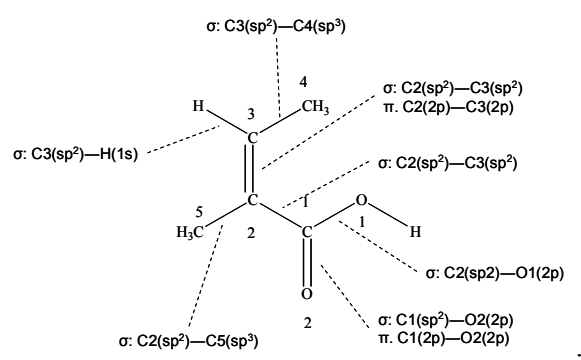
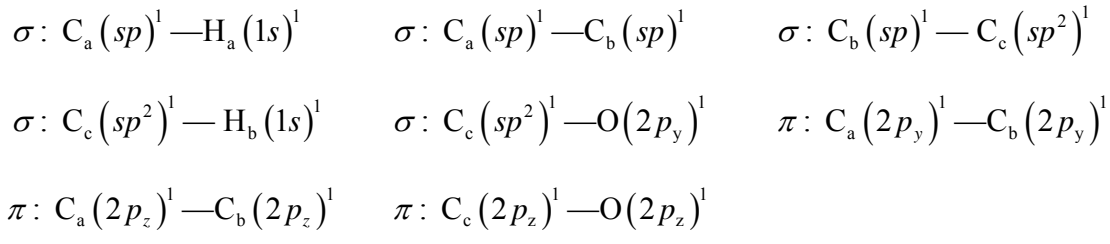
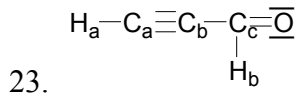
19.

Central S is sp^2 hybridized and the terminal O and S atoms are unhybridized



21a.

21b.



25. . There are 8 atoms that are on the same plane (O1, O2, C1-5, H att. To C3). Furthermore, depending on the angle of rotation of the $-\text{CH}_3$ groups (C4 and C5), two H atoms can also be added to this total.

27. The valence-bond method describes a covalent bond as the result of the overlap of atomic orbitals. Molecular orbital theory describes a bond as a region of space in a molecule where there is a good chance of finding the bonding electrons. The molecular orbital bond does not have to be created from atomic orbitals (although it often is) and the orientations of atomic orbitals do not have to be manipulated to obtain the correct geometric shape. There is little concept of the relative energies of bonding in valence-bond theory. In molecular orbital theory, bonds are ordered energetically.

29. N_2^- bond order = 2.5 (stable), N_2^{2-} bond order = 2 (stable).

31. In order to have a bond order higher than three, there would have to be a region in a molecular orbital diagram where four bonding orbitals occur together in order of increasing energy, with no intervening antibonding orbitals. No such region exists in any of the molecular orbital diagrams in Figure 11-25.

33a. σ_{1s}

33b. σ_{2s}

33c. σ_{1s}^*

33d. σ_{2p}

35a. NO : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*1}$

35b. NO^+ : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4$

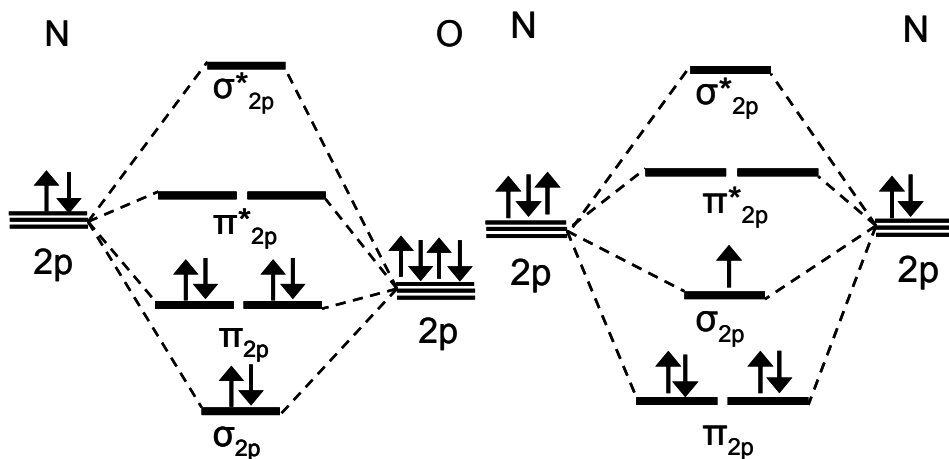
35c. CO : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4$

35d. CN : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^1$

35e. CN^- : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^2$

35f. CN^+ : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4$

35g. BN : $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4$

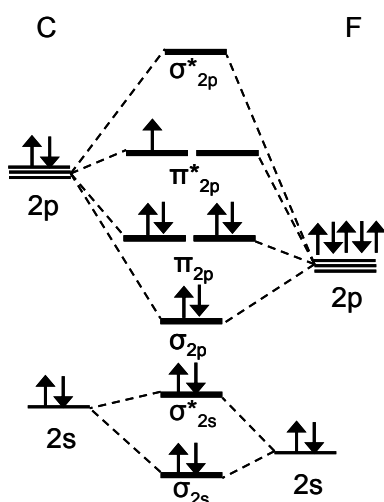


37a.

37b. Bond order is 3 for NO⁺, 2.5 for N₂⁺.

37c. NO⁺ is diamagnetic (all paired electrons), N₂⁺ is paramagnetic.

37d. N₂⁺ has the greater bond length, because there is less electron density between the two nuclei.



39.

. The bond length in CF⁺ would be shorter.

41. The π bonding requires that all six C—C π bonds must be equivalent. This can be achieved by creating six π molecular orbitals—three bonding and three antibonding—into which the 6 π electrons are placed. This creates a single delocalized structure for the C₆H₆ molecule.

43a. Delocalized molecular orbitals required.

43b. Delocalized molecular orbitals required.

43c. Delocalized molecular orbitals not required.

45a. Atomic number, which provides the location of the element in the periodic table, has some minimal predictive value in determining metallic character.

45b. The answer for this part is much the same as the answer to part (a), since atomic mass generally parallels atomic number for the elements.

45c. The number of valence electrons has no bearing on the metallic character of an element.

45d. Because metals occur in every period of the periodic table, there is no particular relationship between the number of electron shells and the metallic behavior of an element.

47. 7.02×10^{20} energy levels, 7.02×10^{20} electrons.

49a. Electrical conductor

49b. Insulator

49c. Insulator

49d. Semiconductor

49e. Electrical conductor

49f. Insulator

51a. No

51b. No

51c. No

51d. Yes

51e. No

51f. Yes

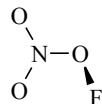
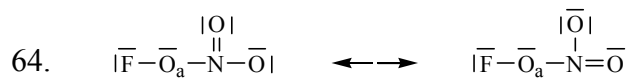
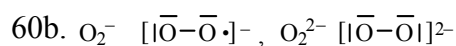
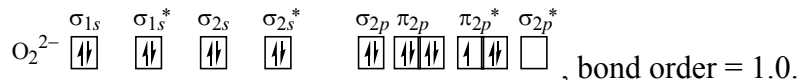
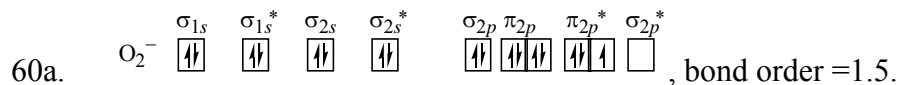
53. In ultra pure crystalline silicon, there are no extra electrons in the lattice that can conduct an electric current. If, however, the silicon becomes contaminated with arsenic atoms, then there will be one additional electron added to the silicon crystal lattice for each arsenic atom that is introduced. The arsenic atoms increase the conductivity of the solid by providing additional electrons that can carry a current after they are promoted into the conduction band by thermal excitation.

55. 1090 nm. This is IR-radiation.

Integrative and Advanced Exercises

58. $[\text{Ne}]_{3s} \uparrow$ The half-filled 3s orbital on each Na overlaps with another to form a σ covalent bond. There are 22 electrons in Na_2 . These electrons are distributed in the molecular orbitals as

follows. $\begin{array}{cccc} \sigma_{1s} & \sigma_{1s}^* & \sigma_{2s} & \sigma_{2s}^* \\ \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \end{array} \quad \begin{array}{cccc} \sigma_{2p} & \pi_{2p} & \pi_{2p}^* & \sigma_{2p}^* \\ \uparrow\downarrow & \uparrow\downarrow\uparrow\downarrow & \uparrow\downarrow\uparrow\downarrow & \uparrow\downarrow \end{array} \quad \begin{array}{c} \sigma_{3s} \\ \uparrow\downarrow \end{array}$ Again, we predict a single bond for Na_2 . A Lewis-theory picture of the bonding would have the two Lewis symbols for two Na atoms uniting to form a bond: $\text{Na} \cdot \cdot \text{Na} \longrightarrow \text{Na} - \text{Na}$ Thus, the bonding in Na_2 is very much like that in H_2 .



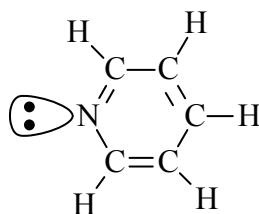
66a. For ClF_3 the electron group geometry is trigonal bipyramidal and the molecule is T-shaped. For AsF_5 the electron group geometry and molecular shape are trigonal bipyramidal. For ClF_2^+ the electron group geometry is tetrahedral and the ion is bent in shape. For AsF_6^- the electron group geometry and the shape of this ion are octahedral.

66b. Trigonal bipyramidal electron group geometry is associated with sp^3d hybridization. The Cl in ClF_3 and As in AsF_5 both have sp^3d hybridization. Tetrahedral electron group geometry is associated with sp^3 hybridization. Thus Cl in ClF_2^+ has sp^3 hybridization. Octahedral electron group geometry is associated with sp^3d^2 hybridization, which is the hybridization adopted by As in AsF_6^- .

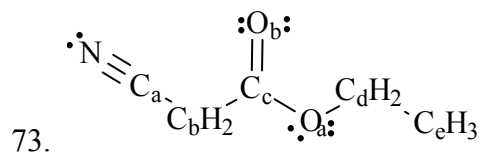
68. Suppose two He atoms in the excited state $1s^1 2s^1$ unite to form an He_2 molecule. One possible configuration is $\sigma_{1s}^2 \sigma_{1s}^{*0} \sigma_{2s}^2 \sigma_{2s}^{*0}$. The bond order would be $(4-0)/2 = 2$.

70. The orbital diagrams for C and N are as follows. C $[\text{He}]^{sp^2} \uparrow\uparrow\uparrow 2p \uparrow$, N $[\text{He}]^{sp^2} \uparrow\uparrow\uparrow 2p \uparrow$

antibonding π molecular orbitals $\left\{ \begin{array}{c} \square \\ \square \end{array} \right.$
bonding π molecular orbitals $\left\{ \begin{array}{c} \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{array} \right.$



Number of π -bonds = 3
This π -bonding scheme produces three π -bonds, which is identical to the number predicted by Lewis theory.



C_b-H , C_d-H , C_e-H : σ $H(1s) - C(sp^3)$ (all tetrahedral carbon uses sp^3 hybrid orbitals)

$C_c=O_b$: σ $C_c(sp^2) - O_b(2p \text{ or } sp^2)$, π : $C_c(2p) - O_b(2p)$

C_c-O_a : σ $C_c(sp^2) - O_a(2p \text{ or } sp^3)$

C_d-O_a : σ $C_d(sp^3) - O_a(2p \text{ or } sp^3)$

$C_a \equiv N$: σ $C_a(sp) - N(sp)$

Two mutually perpendicular π -bonds: $C(2p) - N(2p)$

C_a-C_b : σ $C_b(sp^3) - C_a(sp)$

C_d-C_e : σ $C_d(sp^3) - C_e(sp^3)$

C_c-C_b : σ $C_b(sp^3) - C_c(sp^2)$

75a. 4.00 watts

75b. 8.9 amps

79. The wavelength for both will be the same, because they both have a conjugated π system.

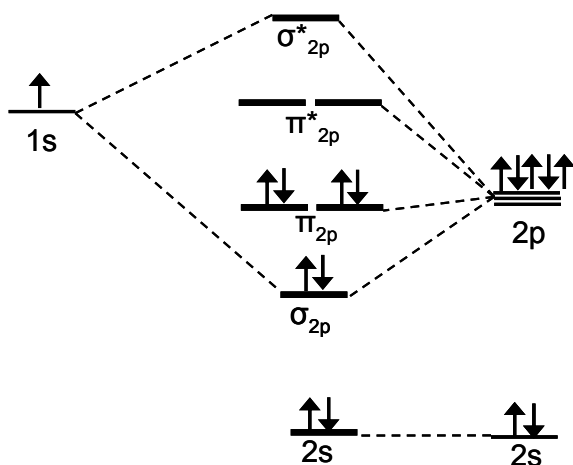
Feature Problems

80a. -205.4 kJ

80b. -117.9 kJ

80c. -148.3 kJ

80d. $\Delta H^\circ_{\text{atomization}} = 5358$ kJ (per mole of C_6H_6), Resonance energy = -168 kJ.



87.

Self-Assessment Exercises

91. The answer is (c).

92. The answer is (c).

93. The answer is (a).

94. The answer is (b).

95. The answer is (c).

96. The answer is (d).

97. The answer is (a).

98. The answer is (c).

99. The valence-bond method using pure s and p orbitals incorrectly predicts a trigonal pyramidal shape with 90° F—B—F bond angles.

100. BrF_5 has six constituents around it; five are fluorine atoms, and the sixth is a lone pair. Therefore, the hybridization is sp^3d^2 , but the geometry is square pyramidal.

101. There are (a) 6 σ and (b) 2 π bonds.

102. All three are paramagnetic. B_2^- has 3 bonding electrons, so the B—B bond is the strongest.

103. The answer is (c).

104. C_2^+

105. C_2 has the greater bond energy.