Chapter 4 Review Questions and Text Homework Solutions

Review Questions

4. The valence orbitals of the nonmetals are the *s* and *p* orbitals. The lobes of the *p* orbitals are 90° and 180° apart from each other. If the *p* orbitals were used to form bonds, then all bonds should be 90° or 180° . This is not the case. To explain the observed geometry (bond angles) that molecules exhibit, we need to make up (hybridize) orbitals that point to where the bonded atoms and lone pairs are located. We know the geometry; we hybridize orbitals to explain the geometry.

Sigma bonds have shared electrons in the area centered on a line joining the atoms. The orbitals that overlap to form the sigma bonds must overlap head to head or end to end. The hybrid orbitals about a central atom always are directed at the bonded atoms. Hybrid orbitals will always overlap head to head to form sigma bonds.

5.	geometry	hybridization	unhybridized p atomic orbitals
	linear	sp	2
	trigonal planar	sp^2	1
	tetrahedral	sp^3	0

The unhybridized p atomic orbitals are used to form π bonds. Two unhybridized p atomic orbitals, each from a different atom, overlap side to side, resulting in a shared electron pair occupying the space above and below the line joining the atoms (the internuclear axis).



 H_2S and CH_4 both have four effective pairs of electrons about the central atom. Both central atoms will be sp^3 hybridized. For H_2S , two of the sp^3 hybrid orbitals are occupied by lone pairs. The other two sp^3 hybrid orbitals overlap with 1s orbitals from hydrogen to form the 2 S–H sigma bonds. For CH_4 , the four C–H sigma bonds are formed by overlap of the sp^3 hybrid orbitals from carbon with 1s orbitals on H.

H₂CO has a trigonal planar geometry, so carbon is sp² hybridized. Two of the *sp*² hybrid orbitals overlap with hydrogen 1*s* orbitals to form the two C–H sigma bonds. The third *sp*² hybrid orbital is used to form the sigma bond in the double bond by overlapping head to head with an *sp*² hybrid orbital from oxygen. The second bond in the double bond is a π bond. The unhybridized *p* atomic orbital on carbon will overlap with a parallel *p* atomic orbital on O to form the π bond.

HCN has a linear geometry, so carbon is *sp* hybridized. HCN has one C–H sigma bond, one C–N sigma bond and two C–N π bonds. The C–H sigma bond is formed from *sp*–1*s* orbital overlap. The C–N sigma bond is formed from an *sp* hybrid orbital on carbon overlapping with an *sp* hybrid orbital from nitrogen. The π bonds are formed from the two unhybridized *p* atomic orbitals from carbon overlapping with two unhybridized *p* atomic orbitals from N. Each π bond is formed from the *p* orbitals overlapping side to side. Because the *p* orbitals used must be perpendicular to each other, the π bonds must be in two different planes that are perpendicular to each other and perpendicular to the internuclear axis.

- 7. The electrons in sigma bonding molecular orbitals are attracted to two nuclei, which is a lower, more stable energy arrangement for the electrons than in separate atoms. In sigma antibonding molecular orbitals, the electrons are mainly outside the space between the nuclei, which is a higher, less stable energy arrangement than in the separated atoms.
- 8. See Figure 4.44 of the text for the $2s \sigma$ bonding and σ antibonding molecular orbitals. Reference Section 4.5 of the text for the $2p \sigma$ bonding, σ antibonding, π bonding, and π antibonding molecular orbitals.
- 9. Bond energy is directly proportional to bond order. Bond length is inversely proportional to bond order. Bond energy and bond length can be measured; bond order is calculated from the molecular orbital energy diagram (bond order is the difference between the number of bonding electrons and the number of antibonding electrons divided by two).

Paramagnetic: A kind of induced magnetism associated with unpaired electrons that causes a substance to be attracted into an inducing magnetic field. Diamagnetic: A type of induced magnetism associated with paired electrons that causes a substance to be repelled from the inducing magnetic field. The key is that paramagnetic substances have unpaired electrons in the molecular orbital diagram while diamagnetic substances have only paired electrons in the MO diagram.

To determine the type of magnetism, measure the mass of a substance in the presence and absence of a magnetic field. A substance with unpaired electrons will be attracted by the magnetic field, giving an apparent increase in mass in the presence of the field. A greater number of unpaired electrons will give a greater attraction and a greater observed mass increase. A diamagnetic species will not be attracted by a magnetic field and will not show a mass increase (a slight mass decrease is observed for diamagnetic species).

10. a. H_2 has two valence electrons to put in the MO diagram while He_2 has 4 valence electrons.

 $H_2: (\sigma_{1s})^2$ Bond order = B.O. = (2-0)/2 = 1 $He_2: (\sigma_{1s})^2 (\sigma_{1s}^*)^2$ B.O. = (2-2)/2 = 0

 H_2 has a nonzero bond order so MO theory predicts it will exist. The H_2 molecule is stable with respect to the two free H atoms. He_2 has a bond order of zero so it should not form. The He_2 molecule is not more stable than the two free H atoms.

- b. See Figure 4.50 of the text for the MO energy-level diagrams of B₂, C₂, N₂, O₂, and F₂. B₂ and O₂ have unpaired electrons in their electron configuration so they are predicted to be paramagnetic. C₂, N₂ and F₂ have no unpaired electrons in the MO diagrams; they are all diamagnetic.
- c. From the MO energy diagram in Figure 4.50, N₂ maximizes the number of electrons in the lower energy bonding orbitals and has no electrons in the antibonding 2*p* molecular orbitals. N₂ has the highest possible bond order of three so it should be a very strong (stable) bond.
- d. NO⁺ has 5 + 6 1 = 10 valence electrons to place in the MO diagram and NO⁻ has 5 + 6 + 1 = 12 valence electrons. The MO diagram for these two ions is assumed to be the same as that used for N₂. The MO electron configurations are:

NO ⁺ : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$	B.O. = $(8-2)/2 = 3$
NO ⁻ : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2 (\pi_{2p}^*)^2$	B.O. = $(8-4)/2 = 2$

 NO^+ has a larger bond order than NO^- , so NO^+ should be more stable than NO^- .

12. Molecules that exhibit resonance have delocalized π bonding. This means that the π electrons are not permanently stationed between two specific atoms, but instead can roam about over the surface of a molecule. We use the concept of delocalized π electrons to explain why molecules that exhibit resonance have equal bonds in terms of strength. Because the π electrons can roam about over the entire surface of the molecule, the π electrons are shared by all of the atoms in the molecule giving rise to equal bond strengths.

The classic example of delocalized π electrons is benzene, C₆H₆. Figure 4.59 of the text shows the π molecular orbital system for benzene. Each carbon in benzene is sp^2 hybridized, leaving one unhybridized *p* atomic orbital. All six of the carbon atoms in benzene have an unhybridized *p* orbital pointing above and below the planar surface of the molecule. Instead of just two unhybridized *p* orbitals overlapping, we say all six of the unhybridized *p* orbitals overlap resulting in delocalized π electrons roaming about above and below the entire surface of the benzene molecule.

$$O_3, 6 + 2(6) = 18 e^{-1}$$



Ozone has a delocalized π system. Here the central atom is sp^2 hybridized. The unhybridized p atomic orbital on the central oxygen will overlap with parallel p orbitals on each adjacent O atom. All three of these p orbitals overlap together resulting in the π electrons moving about above and below the surface of the O₃ molecule. With the delocalized π electrons, the O–O bond lengths in O₃ are equal (and are not different as each individual Lewis structure indicates).

Text Homework

- 11. In hybrid orbital theory, some or all the valence atomic orbitals of the central atom in a molecule are mixed together to form hybrid orbitals; these hybrid orbitals point to where the bonded atoms and lone pairs are oriented. The sigma bonds are formed from the hybrid orbitals overlapping head-to-head with an appropriate orbital from the bonded atom. The π bonds, in hybrid orbital theory, are formed from unhybridized p atomic orbitals. The p orbitals overlap side to side to form the π bond, where the π electrons occupy the space above and below a line joining the atoms (the internuclear axis). Assuming the z-axis is the internuclear axis, then the p_z atomic orbital will always be hybridized whether the hybridization is sp, sp², sp³, dsp³ or d²sp³. For sp hybridization, the p_x and p_y atomic orbitals are unhybridized; they are used to form two π bonds to the bonded atom(s). For sp² hybridization, either the p_x or the p_y atomic orbital is hybridized (along with the s and p_z orbitals); the other p orbital is used to form a π bond to a bonded atom. For sp³ hybridization, the s and all the p orbitals are hybridized; no unhybridized p atomic orbitals are present, so no π bonds form with sp³ hybridization. For dsp³ and d²sp³ hybridization, we just mix in one or two d orbitals into the hybridization process. Which specific d orbitals are used is not important to our discussion.
- 16. Rotation occurs in a bond as long as the orbitals that go to form that bond still overlap when the atoms are rotating. Sigma bonds, with the head-to-head overlap, remain unaffected by rotating the atoms in the bonds. Atoms that are bonded together by only a sigma bond (single bond) exhibit this rotation phenomenon. The π bonds, however, cannot be rotated. The p orbitals must be parallel to each other to form the π bond. If we try to rotate the atoms in a π bond, the p orbitals would no longer have the correct alignment necessary to overlap. Because π bonds are present in double and triple bonds (a double bond is composed of 1 σ and 1 π bond, and a triple bond is always 1 σ and 2 π bonds), the atoms in a double or triple bond cannot rotate (unless the bond is broken).
- 18. From experiment, B_2 is paramagnetic. If the σ_{2p} MO is lower in energy than the two degen-erate π_{2p} MOs, the electron configuration for B_2 would have all electrons paired. Experiment tells us we must have unpaired electrons. Therefore, the MO diagram is modified to have the π_{2p} orbitals lower in energy than the σ_{2p} orbitals. This gives two unpaired electrons in the electron configuration for B_2 , which explains the paramagnetic properties of B_2 . The model allowed for s and p orbitals to mix, which shifted the energy of the σ_{2p} orbital to above that of the π_{2p} orbitals.
- 39. H_2O has 2(1) + 6 = 8 valence electrons.



 H_2O has a tetrahedral arrangement of the electron pairs about the O atom that requires sp³ hybridization. Two of the four sp³ hybrid orbitals are used to form bonds to the two hydrogen atoms, and the other two sp³ hybrid orbitals hold the two lone pairs on oxygen. The two O–H bonds are formed from overlap of the sp³ hybrid orbitals from oxygen with the 1s atomic orbitals from the hydrogen atoms. Each O–H covalent bond is called a sigma (σ) bond since the shared electron pair in each bond is centered in an area on a line running between the two atoms.

40. CCl₄ has 4 + 4(7) = 32 valence electrons.



 CCl_4 has a tetrahedral arrangement of the electron pairs about the carbon atom that requires sp³ hybridization. The four sp³ hybrid orbitals from carbon are used to form the four bonds to chlorine. The chlorine atoms also have a tetrahedral arrangement of electron pairs, and we will assume that they are also sp³ hybridized. The C–Cl sigma bonds are all formed from overlap of sp³ hybrid orbitals from each chlorine atom.

41. H_2CO has 2(1) + 4 + 6 = 12 valence electrons.



The central carbon atom has a trigonal planar arrangement of the electron pairs that requires sp² hybridization. The two C–H sigma bonds are formed from overlap of the sp² hybrid orbitals from carbon with the hydrogen 1s atomic orbitals. The double bond between carbon and oxygen consists of one σ and one π bond. The oxygen atom, like the carbon atom, also has a trigonal planar arrangement of the electrons that requires sp² hybridization. The σ bond in the double bond is formed from overlap of a carbon sp² hybrid orbital with an oxygen sp² hybrid orbital. The π bond in the double bond is formed from overlap of the unhybridized p atomic orbitals. Carbon and oxygen each has one unhybridized p atomic orbital that is parallel with the other. When two parallel p atomic orbitals overlap, a π bond results where the shared electron pair occupies the space above and below a line joining the atoms in the bond.

42. C_2H_2 has 2(4) + 2(1) = 10 valence electrons.

Н—С≡С—Н

Each carbon atom in C_2H_2 is sp hybridized since each carbon atom is surrounded by two effective pairs of electrons; i.e., each carbon atom has a linear arrangement of the electrons. Since each carbon atom is sp hybridized, then each carbon atom has two unhybridized p atomic orbitals. The two C-H sigma bonds are formed from overlap of carbon sp hybrid orbitals with hydrogen 1s atomic orbitals. The triple bond is composed of one σ bond and two π bonds. The sigma bond between to the carbon atoms is formed from overlap of sp hybrid orbitals from each carbon atom. The two π bonds of the triple bond are formed from parallel overlap of the two unhybridized p atomic orbitals from each carbon. 43. Ethane, C_2H_6 , has 2(4) + 6(1) = 14 valence electrons.



The carbon atoms are sp^3 hybridized. The six C–H sigma bonds are formed from overlap of the sp^3 hybrid orbitals from C with the 1s atomic orbitals from the hydrogen atoms. The carbon-carbon sigma bond is formed from overlap of an sp^3 hybrid orbital from each C atom.

Ethanol, C_2H_6O has $2(4) + 6(1) + 6 = 20 e^{-1}$



The two C atoms and the O atom are sp³ hybridized. All bonds are formed from overlap with these sp³ hybrid orbitals. The C–H and O–H sigma bonds are formed from overlap of sp³ hybrid orbitals with hydrogen 1s atomic orbitals. The C–C and C–O sigma bonds are formed from overlap of the sp³ hybrid orbitals from each atom.

44. HCN, 1 + 4 + 5 = 10 valence electrons

H____C

Assuming N is hybridized, both C and N atoms are sp hybridized. The C–H σ bond is formed from overlap of a carbon sp³ hybrid orbital with a hydrogen 1s atomic orbital. The triple bond is composed of one σ bond and two π bonds. The sigma bond is formed from head-to-head overlap of the sp hybrid orbitals from the C and N atoms. The two π bonds in the triple bond are formed from overlap of the two unhybridized p atomic orbitals from each C and N atom.

 $COCl_2$, 4 + 6 + 2(7) = 24 valence electrons



Assuming all atoms are hybridized, the carbon and oxygen atoms are sp^2 hybridized, and the two chlorine atoms are sp^3 hybridized. The two C–Cl σ bonds are formed from overlap of sp^2 hybrids from C with sp^3 hybrid orbitals from Cl. The double bond between the carbon and oxygen atoms consists of one σ and one π bond. The σ bond in the double bond is formed from head-to-head overlap of an sp^2 orbital from carbon with an sp^2 hybrid orbital from oxy-gen. The π bond is formed from parallel overlap of the unhybridized p atomic orbitals from each atom of C and O.

57. a. Add lone pairs to complete octets for each O and N.



Azodicarbonamide

methyl cyanoacrylate

Note: NH₂, CH₂ and CH₃ are shorthand for nitrogen or carbon atoms singly bonded to hydrogen atoms.

- b. In azodicarbonamide, the two carbon atoms are sp² hybridized, the two nitrogen atoms with hydrogens attached are sp³ hybridized, and the other two nitrogen atoms are sp² hybridized. In methyl cyanoacrylate, the CH₃ carbon is sp³ hybridized, the carbon with the triple bond is sp hybridized, and the other three carbons are sp² hybridized.
- c. Azodicarbonamide contains three π bonds and methyl cyanoacrylate contains four π bonds.
- d. a) $\approx 109.5^{\circ}$ b) 120° c) $\approx 120^{\circ}$ d) 120° e) 180° f) 120° g) $\approx 109.5^{\circ}$ h) 120°
- 59. To complete the Lewis structure, just add lone pairs of electrons to satisfy the octet rule for the atoms that have fewer than eight electrons.



a. 6 b. 4 c. The center N in -N=N=N group

d. 33σ e. 5π bonds f.

g. $\approx 109.5^{\circ}$ h. sp³

61. a. The bonding molecular orbital is on the right and the antibonding molecular orbital is on the left. The bonding MO has the greatest electron probability between the nuclei, while the antibonding MO has greatest electron probability on either side of the nuclei.

180°

b. The bonding MO is lower in energy. Because the electrons in the bonding MO have the greatest probability of lying between the two nuclei, these electrons are attracted to two different nuclei, resulting in a lower energy.



When p orbitals are combined head-to-head and the phases are the same sign, a sigma bonding molecular orbital is formed.

b. _____ π_p

When parallel p orbitals are combined in-phase (the signs match up), a pi bonding molecular orbital is formed.



When p orbitals are combined head-to-head and the phases are opposite, a sigma antibonding molecular orbital is formed.

d.



When parallel p orbitals are combined out-of-phase (the orbital lobes have opposite signs), a pi antibonding molecular orbital is formed.

65. The electron configurations are:

- a. Li₂: $(\sigma_{2s})^2$ B.O. = (2-0)/2 = 1, diamagnetic (0 unpaired e⁻)
- b. C₂: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$ B.O. = (6-2)/2 = 2, diamagnetic (0 unpaired e⁻)
- c. S₂: $(\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p})^2(\pi_{3p}^*)^2$ B.O. = (8-4)/2 = 2, paramagnetic (2 unpaired e⁻)

66. There are 14 valence electrons in the MO electron configuration. Also, the valence shell is n = 3. Some possibilities from row 3 having 14 valence electrons are Cl₂, SCl⁻, S₂²⁻, and Ar₂²⁺.

67.
$$O_2$$
: $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^2$
 N_2 : $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2$
B.O. = $(8 - 4)/2 = 2$
B.O. = $(8 - 2)/2 = 3$

In O₂, an antibonding electron is removed, which will increase the bond order to 2.5 [= (8-3)/2]. The bond order increases as an electron is removed, so the bond strengthens. In N₂, a bonding electron is removed, which decreases the bond order to 2.5 = [(7-2)/2]. So the bond strength weakens as an electron is removed from N₂.

68. The electron configurations are:

F_2^+ : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$	B.O. = $(8-5)/2 = 1.5$; 1 unpaired e ⁻
F ₂ : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$	B.O. = $(8-6)/2 = 1;$ 0 unpaired e ⁻
$F_2^{-:} (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^4 (\sigma_{2p}^*)^1$	B.O. = $(8-7)/2 = 0.5$; 1 unpaired e ⁻

From the calculated bond orders, the order of bond lengths should be $F_2^+ < F_2 < F_2^-$.

70. Considering only the 12 valence electrons in O₂, the MO models would be:



with the Lewis structure (double bond and no unpaired electrons).

It takes energy to pair electrons in the same orbital. Thus the structure with no unpaired electrons is at a higher energy; it is an excited state.

71. The electron configurations are (assuming the same orbital order as that for N₂):

a.	CO: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$	B.O. = $(8-2)/2 = 3$, diamagnetic
b.	CO ⁺ : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$	B.O. = $(7-2)/2 = 2.5$, paramagnetic
c.	CO ²⁺ : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$	B.O. = $(6-2)/2 = 2$, diamagnetic

Because bond order is directly proportional to bond energy and inversely proportional to bond length:

Shortest \rightarrow longest bond length: CO < CO⁺ < CO²⁺

Smallest \rightarrow largest bond energy: $CO^{2+} < CO^{+} < CO$

74. CN: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$ NO: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^1$ $O_2^{2^+}$: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4$ $N_2^{2^+}$: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$

If the added electron goes into a bonding orbital, the bond order would increase, making the species more stable and more likely to form. Between CN and NO, CN would most likely form CN^- since the bond order increases (unlike NO^- , where the added electron goes into an antibonding orbital). Between O_2^{2+} and N_2^{2+} , N_2^{2+} going to N_2^+ would most likely occur since the bond order increases (unlike O_2^{2+} going to O_2^+).

- 76. F_2 : $(\sigma_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p})^4$; F_2 should have a lower ionization energy than F. The electron removed from F_2 is in a π_{2p}^* antibonding molecular orbital that is higher in energy than the 2p atomic orbitals from which the electron in atomic fluorine is removed. Because the electron removed from F_2 is higher in energy than the electron removed from F, it should be easier to remove an electron from F_2 than from F.
- 97. For carbon, nitrogen, and oxygen atoms to have formal charge values of zero, each C atom will form four bonds to other atoms and have no lone pairs of electrons, each N atom will form three bonds to other atoms and have one lone pair of electrons, and each O atom will form two bonds to other atoms and have two lone pairs of electrons. Following these bonding requirements gives the following two resonance structures for vitamin B₆:



a.

21 σ bonds; 4 π bonds (The electrons in the three π bonds in the ring are delocalized.)

- b. Angles a), c), and g): $\approx 109.5^{\circ}$; angles b), d), e), and f): $\approx 120^{\circ}$
- c. 6 sp² carbons; the five carbon atoms in the ring are sp² hybridized, as is the carbon with the double bond to oxygen.
- d. 4 sp³ atoms; the two carbons that are not sp² hybridized are sp³ hybridized, and the oxygens marked with angles a and c are sp³ hybridized.
- e. Yes, the π electrons in the ring are delocalized. The atoms in the ring are all sp² hybridized. This leaves a p orbital perpendicular to the plane of the ring from each atom. Overlap of all six of these p orbitals results in a π molecular orbital system where the electrons are delocalized above and below the plane of the ring (similar to benzene in Figure 4-59 of the text).
- 101. For carbon, nitrogen, and oxygen atoms to have formal charge values of zero, each C atom will form four bonds to other atoms and have no lone pairs of electrons, each N atom will form three bonds to other atoms and have one lone pair of electrons, and each O atom will form two bonds to other atoms and have two lone pairs of electrons. Following these bonding requirements, a Lewis structure for aspartame is:



Another resonance structure could be drawn having the double bonds in the benzene ring moved over one position.

Atoms that have trigonal planar geometry of electron pairs are assumed to have sp^2 hybridization, and atoms with tetrahedral geometry of electron pairs are assumed to have sp^3 hybridization. All the N atoms have tetrahedral geometry, so they are all sp^3 hybridized (no sp^2 hybridization). The oxygens double bonded to carbon atoms are sp^2 hybridized; the other two oxygens with two single bonds are sp^3 hybridized. For the carbon atoms, the six carbon atoms in the benzene ring are sp^2 hybridized, and the three carbons double bonded to oxygen are also sp^2 hybridized (tetrahedral geometry).

Answering the questions:

- 9 sp² hybridized C and N atoms (9 from C's and 0 from N's)
- 7 sp³ hybridized C and O atoms (5 from C's and 2 from O's)
- 39 σ bonds and 6 π bonds (this includes the 3 π bonds in the benzene ring that are delocalized