

## Chapter 4 Review Questions and Text Homework Solutions

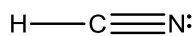
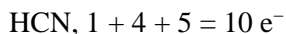
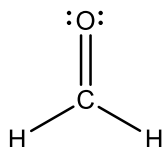
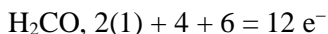
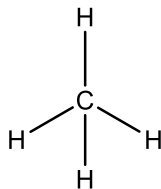
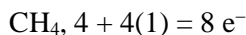
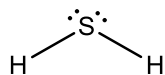
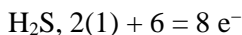
### Review Questions

4. The valence orbitals of the nonmetals are the  $s$  and  $p$  orbitals. The lobes of the  $p$  orbitals are  $90^\circ$  and  $180^\circ$  apart from each other. If the  $p$  orbitals were used to form bonds, then all bonds should be  $90^\circ$  or  $180^\circ$ . 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  $\pi$  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).



$\text{H}_2\text{S}$  and  $\text{CH}_4$  both have four effective pairs of electrons about the central atom. Both central atoms will be  $sp^3$  hybridized. For  $\text{H}_2\text{S}$ , 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  $\text{CH}_4$ , the four C–H sigma bonds are formed by overlap of the  $sp^3$  hybrid orbitals from carbon with  $1s$  orbitals on H.

H<sub>2</sub>CO has a trigonal planar geometry, so carbon is sp<sup>2</sup> hybridized. Two of the sp<sup>2</sup> hybrid orbitals overlap with hydrogen 1s orbitals to form the two C–H sigma bonds. The third sp<sup>2</sup> hybrid orbital is used to form the sigma bond in the double bond by overlapping head to head with an sp<sup>2</sup> 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.

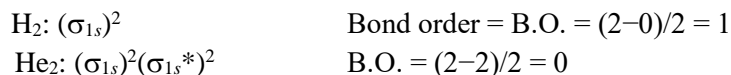
HCN has a linear geometry, so carbon is sp hybridized. HCN has one C–H sigma bond, one C–N sigma bond and two C–N π bonds. The C–H sigma bond is formed from sp–1s orbital overlap. The C–N sigma bond is formed from an sp hybrid orbital on carbon overlapping with an sp hybrid orbital from nitrogen. The 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 σ bonding and σ antibonding molecular orbitals. Reference Section 4.5 of the text for the 2p σ 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.

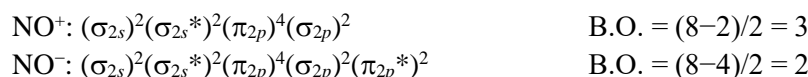
To determine the type of magnetism, measure the mass of a substance in the presence and absence of a magnetic field. A substance with unpaired electrons will be attracted by the magnetic field, giving an apparent increase in mass in the presence of the field. A greater number of unpaired electrons will 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<sub>2</sub> has two valence electrons to put in the MO diagram while He<sub>2</sub> has 4 valence electrons.



H<sub>2</sub> has a nonzero bond order so MO theory predicts it will exist. The H<sub>2</sub> molecule is stable with respect to the two free H atoms. He<sub>2</sub> has a bond order of zero so it should not form. The He<sub>2</sub> molecule is not more stable than the two free He atoms.

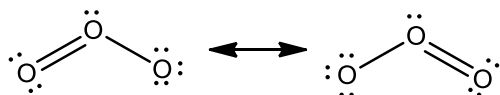
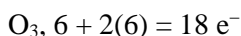
- b. See Figure 4.50 of the text for the MO energy-level diagrams of B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and F<sub>2</sub>. B<sub>2</sub> and O<sub>2</sub> have unpaired electrons in their electron configuration so they are predicted to be paramagnetic. C<sub>2</sub>, N<sub>2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



NO<sup>+</sup> has a larger bond order than NO<sup>–</sup>, so NO<sup>+</sup> should be more stable than NO<sup>–</sup>.

12. Molecules that exhibit resonance have delocalized  $\pi$  bonding. This means that the  $\pi$  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  $\pi$  electrons to explain why molecules that exhibit resonance have equal bonds in terms of strength. Because the  $\pi$  electrons can roam about over the entire surface of the molecule, the  $\pi$  electrons are shared by all of the atoms in the molecule giving rise to equal bond strengths.

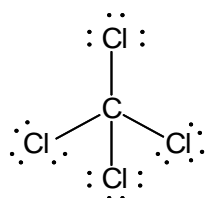
The classic example of delocalized  $\pi$  electrons is benzene, C<sub>6</sub>H<sub>6</sub>. Figure 4.59 of the text shows the  $\pi$  molecular orbital system for benzene. Each carbon in benzene is *sp*<sup>2</sup> hybridized, leaving one unhybridized *p* atomic orbital. All six of the carbon atoms 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  $\pi$  electrons roaming about above and below the entire surface of the benzene molecule.



Ozone has a delocalized  $\pi$  system. Here the central atom is *sp*<sup>2</sup> 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  $\pi$  electrons moving about above and below the surface of the O<sub>3</sub> molecule. With the delocalized  $\pi$  electrons, the O–O bond lengths in O<sub>3</sub> are equal (and are not different as each individual Lewis structure indicates).

## Text Homework

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  $\pi$  bonds, however, cannot be rotated. The p orbitals must be parallel to each other to form the  $\pi$  bond. If we try to rotate the atoms in a  $\pi$  bond, the p orbitals would no longer have the correct alignment necessary to overlap. Because  $\pi$  bonds are present in double and triple bonds (a double bond is composed of 1  $\sigma$  and 1  $\pi$  bond, and a triple bond is always 1  $\sigma$  and 2  $\pi$  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  $\sigma_{2p}$  MO is lower in energy than the two degenerate  $\pi_{2p}$  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  $\pi_{2p}$  orbitals lower in energy than the  $\sigma_{2p}$  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  $\sigma_{2p}$  orbital to above that of the  $\pi_{2p}$  orbitals.
40.  $CCl_4$  has  $4 + 4(7) = 32$  valence electrons.



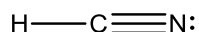
$CCl_4$  has a tetrahedral arrangement of the electron pairs about the carbon atom that requires  $sp^3$  hybridization. The four  $sp^3$  hybrid orbitals from carbon are used to form the four bonds to chlorine. The chlorine atoms also have a tetrahedral arrangement of electron pairs, and we will assume that they are also  $sp^3$  hybridized. The C–Cl sigma bonds are all formed from overlap of  $sp^3$  hybrid orbitals from carbon with  $sp^3$  hybrid orbitals from each chlorine atom.

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



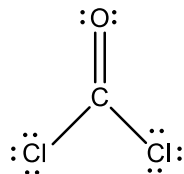
Each carbon atom in  $C_2H_2$  is  $sp$  hybridized since each carbon atom is surrounded by two effective pairs of electrons; i.e., each carbon atom has a linear arrangement of the electrons. Since each carbon atom is  $sp$  hybridized, then each carbon atom has two unhybridized p atomic orbitals. The 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  $\sigma$  bond and two  $\pi$  bonds. The sigma bond between the carbon atoms is formed from overlap of  $sp$  hybrid orbitals from each carbon atom. The two  $\pi$  bonds of the triple bond are formed from parallel overlap of the two unhybridized p atomic orbitals from each carbon.

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



Assuming N is hybridized, both C and N atoms are  $sp$  hybridized. The C–H  $\sigma$  bond is formed from overlap of a carbon  $sp^3$  hybrid orbital with a hydrogen  $1s$  atomic orbital. The triple bond is composed of one  $\sigma$  bond and two  $\pi$  bonds. The sigma bond is formed from head-to-head overlap of the  $sp$  hybrid orbitals from the C and N atoms. The two  $\pi$  bonds in the triple bond are formed from overlap of the two unhybridized  $p$  atomic orbitals from each C and N atom.

$\text{COCl}_2$ ,  $4 + 6 + 2(7) = 24$  valence electrons

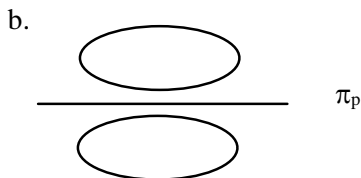


Assuming all atoms are hybridized, the carbon and oxygen atoms are  $sp^2$  hybridized, and the two chlorine atoms are  $sp^3$  hybridized. The two C–Cl  $\sigma$  bonds are formed from overlap of  $sp^2$  hybrids from C with  $sp^3$  hybrid orbitals from Cl. The double bond between the carbon and oxygen atoms consists of one  $\sigma$  and one  $\pi$  bond. The  $\sigma$  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 oxygen. The  $\pi$  bond is formed from parallel overlap of the unhybridized  $p$  atomic orbitals from each atom of C and O.

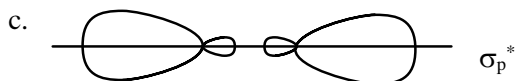
62.



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

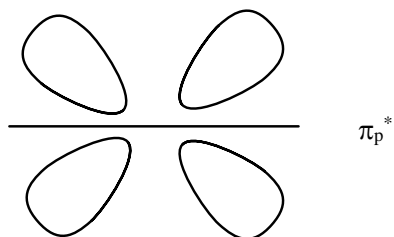


When parallel  $p$  orbitals are combined in-phase (the signs match up), a pi bonding molecular orbital is formed.



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

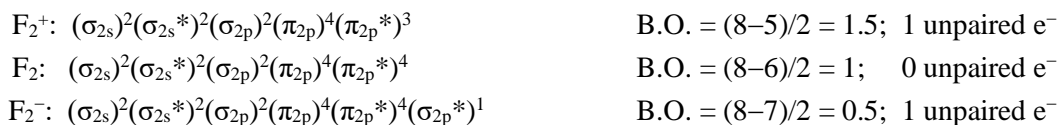
d.



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

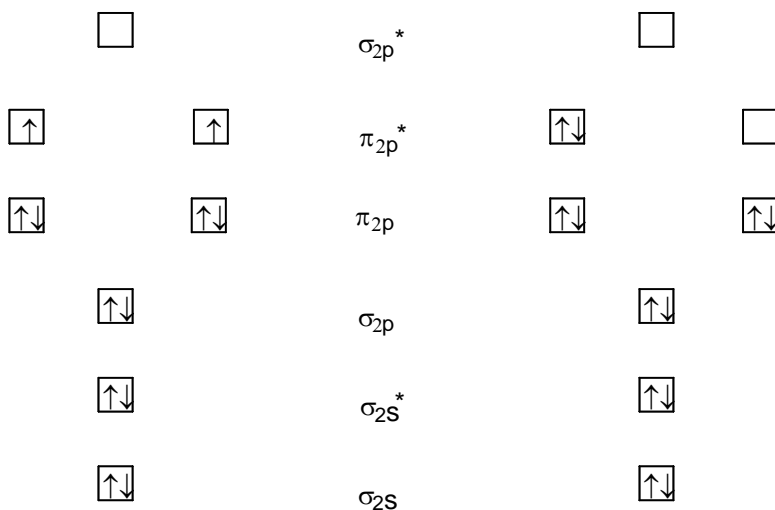
66. There are 14 valence electrons in the MO electron configuration. Also, the valence shell is  $n = 3$ . Some possibilities from row 3 having 14 valence electrons are  $\text{Cl}_2$ ,  $\text{SCl}^-$ ,  $\text{S}_2^{2-}$ , and  $\text{Ar}_2^{2+}$ .

68. The electron configurations are:



From the calculated bond orders, the order of bond lengths should be  $\text{F}_2^+ < \text{F}_2 < \text{F}_2^-$ .

70. Considering only the 12 valence electrons in  $\text{O}_2$ , the MO models would be:



$\text{O}_2$  ground state

Arrangement of electrons consistent 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.

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.  $F_2$ :  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$ ;  $F_2$  should have a lower ionization energy than F. The electron removed from  $F_2$  is in a  $\pi_{2p}^*$  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.