CHAPTER 9 suggested end-of-chapter problems

9. In the hybrid orbital model, compare and contrast $\sigma$ bonds with $\pi$ bonds. What orbitals form the $\sigma$ bonds and what orbitals form the $\pi$ bonds? Assume the $z$-axis is the internuclear axis.

12. The atoms in a single bond can rotate about the internuclear axis without breaking the bond. The atoms in a double and triple bond cannot rotate about the internuclear axis unless the bond is broken. Why?

14. What modification to the molecular orbital model was made from the experimental evidence that $B_2$ is paramagnetic?

16. The three NO bonds in $NO_3^-$ are all equivalent in length and strength. How is this explained even though any valid Lewis structure for $NO_3^-$ has one double bond and two single bonds to nitrogen?
29. For each of the following molecules, write the Lewis structure(s), predict the molecular structure (including bond angles), give the expected hybrid orbitals on the central atom, and predict the overall polarity.

   a. CF₄
   b. NF₃
   c. OF₂
   d. BF₃
   e. BeH₂
   f. TeF₄
   g. AsF₅
   h. KrF₂
   i. KrF₄
   j. SeF₆
   k. IF₅
   l. IF₃

31. Why must all six atoms in C₂H₄ lie in the same plane?

32. The allene molecule has the following Lewis structure:

   \[
   \begin{array}{c}
   \text{H} \\
   \text{C} = \text{C} = \text{C} \\
   \text{H} \\
   \end{array}
   \]

   Must all hydrogen atoms lie the same plane? If not, what is their spatial relationship? Explain.
35. Biacetyl and acetoin are added to margarine to make it taste more like butter.

\[
\begin{align*}
&\text{O} & \text{O} \\
&\text{CH}_3-\text{C} \equiv \text{C} \equiv \text{CH}_3 & \text{CH}_3-\text{CH} \equiv \text{C} \equiv \text{CH}_3 \\
&\text{OH} \\
\end{align*}
\]

**Biacetyl**  **Acetoin**

Complete the Lewis structures, predict values for all C–C–O bond angles, and give the hybridization of the carbon atoms in these two compounds. Must the four carbon atoms and two oxygen atoms in biacetyl lie the same plane? How many σ bonds and how many π bonds are there in biacetyl and acetoin?

40. The antibiotic thiarubin-\(\text{A}\) was discovered by studying the feeding habits of wild chimpanzees in Tanzania. The structure for thiarubin-\(\text{A}\) is

\[
\begin{align*}
&\text{H} & \text{H} \\
&\text{H}_3\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH} \equiv \text{CH}_2 \\
\end{align*}
\]

a. Complete the Lewis structure showing all lone pairs of electrons.

b. Indicate the hybrid orbitals used by the carbon and sulfur atoms in thiarubin-\(\text{A}\).

c. How many σ and π bonds are present in this molecule?
43. Which of the following are predicted by the molecular orbital model to be stable diatomic species?
   a. \( \text{H}_2^+, \text{H}_2, \text{H}_2^-, \text{H}_2^{2-} \)
   b. \( \text{He}_2^{2+}, \text{He}_2^+, \text{He}_2 \)

44. Which of the following are predicted by the molecular orbital model to be stable diatomic species?
   a. \( \text{N}_2^{2-}, \text{O}_2^{2-}, \text{F}_2^{2-} \)
   b. \( \text{Be}_2, \text{B}_2, \text{Ne}_2 \)

45. Using the molecular orbital model, write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic?
   a. \( \text{Li}_2 \)
   b. \( \text{C}_2 \)
   c. \( \text{S}_2 \)

46. Consider the following electron configuration:
   \[
   (\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p})^2(\pi_{3p})^4(\pi_{3p}^*)^4
   \]
   Give four species that, in theory, would have this electron configuration.

47. Using molecular orbital theory, explain why the removal of one electron in \( \text{O}_2 \) strengthens bonding, while the removal of one electron in \( \text{N}_2 \) weakens bonding.

48. Using the molecular orbital model to describe the bonding in \( \text{F}_2^+, \text{F}_2, \text{and} \ \text{F}_2^- \), predict the bond orders and the relative bond lengths for these three species. How many unpaired electrons are present in each species?
51. Using the molecular orbital model, write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic? Place the species in order of increasing bond length and bond energy.

   a. CO
   b. CO⁺
   c. CO²⁺

53. In which of the following diatomic molecules would the bond strength be expected to weaken as an electron is removed?

   a. H₂
   b. B₂
   c. C₂²⁻
   d. OF
66. Give the expected hybridization for the molecular structures illustrated below.

a.

b.

c.

d.

e.
73. The $\text{N}_2\text{O}$ molecule is linear and polar.

a. On the basis of this experimental evidence, which arrangement, $\text{NNO}$ or $\text{NON}$, is correct? Explain your answer.

b. On the basis of your answer to part a, write the Lewis structure of $\text{N}_2\text{O}$ (including resonance forms). Give the formal charge on each atom and the hybridization of the central atom.

c. How would the multiple bonding in $:\text{N}=\text{N}=:\text{O}:$ be described in terms of orbitals?
9. In hybrid orbital theory, some or all of 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 \( \pi \) bonds, in hybrid orbital theory, are formed from unhybridized \( p \) atomic orbitals. The \( p \) orbitals overlap side to side to form the \( \pi \) bond, where the \( \pi \) 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 \( sp \), \( sp^2 \), \( sp^3 \), \( dsp^3 \) or \( d^3sp^3 \). For \( sp \) hybridization, the \( p_x \) and \( p_y \) atomic orbitals are unhybridized; they are used to form two \( \pi \) bonds to the bonded atom(s). For \( sp^3 \) 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 \( \pi \) bond to a bonded atom. For \( sp^3 \) hybridization, the \( s \) and all the \( p \) orbitals are hybridized; no unhybridized \( p \) atomic orbitals are present, so no \( \pi \) bonds form with \( sp^3 \) hybridization. For \( dsp^3 \) and \( d^3sp^3 \) 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.

12. 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).

14. 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.

16. \[ \text{NO}_3^- \] 
\[ \begin{align*}
\text{NO}_3^-: & \quad 5 + 3(6) + 1 = 24 \text{ e}^- \\
\begin{array}{c}
\begin{array}{c}
\text{:\scriptsize{O}} \quad \text{\scriptsize{O}} \quad \text{\scriptsize{O}} \\
\text{:\scriptsize{O}} \quad \text{\scriptsize{O}} \quad \text{\scriptsize{O}}
\end{array}
\end{array}
\end{align*} \]
When resonance structures can be drawn, it is usually due to a multiple bond that can be in different positions. This is the case for NO$_3^-$.

Experiment tells us that the three N–O bonds are equivalent in length and strength. To explain this, we say the $\pi$ electrons are delocalized in the molecule. For NO$_3^-$, the $\pi$ bonding system is composed of an unhybridized p atomic orbital from all the atoms in NO$_3^-$.

These p orbitals are oriented perpendicular to the plane of the atoms in NO$_3^-$. The $\pi$ bonding system consists of all of the perpendicular p orbitals overlapping forming a diffuse electron cloud above and below the entire surface of the NO$_3^-$ ion. Instead of having the $\pi$ electrons situated above and below two specific nuclei, we think of the $\pi$ electrons in NO$_3^-$ as extending over the entire surface of the molecule (hence the term delocalized). See Figure 9.48 for an illustration of the $\pi$ bonding system in NO$_3^-$. 

![Chemical structures](image)

29. a. 

- tetrahedral
- 109.5°
- nonpolar

b. 

- trigonal pyramid
- <109.5°
- polar

The angles in NF$_3$ should be slightly less than 109.5° because the lone pair requires more space than the bonding pairs.

c. 

- V-shaped
- <109°.5
- polar

d. 

- trigonal planar
- 120°
- nonpolar
For the p orbitals to properly line up to form the \( \pi \) bond, all six atoms are forced into the same plane. If the atoms are not in the same plane, then the \( \pi \) bond could not form since the p orbitals would no longer be parallel to each other.
32. No, the CH₂ planes are mutually perpendicular to each other. The center C atom is sp hybridized and is involved in two π bonds. The p orbitals used to form each π bond must be perpendicular to each other. This forces the two CH₂ planes to be perpendicular.

![Diagram of CH₂ planes]

35. To complete the Lewis structures, just add lone pairs of electrons to satisfy the octet rule for the atoms with fewer than eight electrons.

Biacetyl (C₄H₆O₂) has 4(4) + 6(1) + 2(6) = 34 valence electrons.

![Diagram of Biacetyl]

All CCO angles are 120°. The six atoms are not forced to lie in the same plane because of free rotation about the carbon-carbon single (sigma) bonds. There are 11 σ and 2 π bonds in biacetyl.

Acetoin (C₄H₆O₂) has 4(4) + 8(1) + 2(6) = 36 valence electrons.

![Diagram of Acetoin]

The carbon with the doubly bonded O is sp² hybridized. The other three C atoms are sp³ hybridized. Angle a = 120° and angle b = 109.5°. There are 13 σ and 1 π bonds in acetoin.

Note: All single bonds are σ bonds, all double bonds are one σ and one π bond, and all triple bonds are one σ and two π bonds.
40. a. To complete the Lewis structure, add two lone pairs to each sulfur atom.

\[
\begin{array}{c}
\text{sp}^3 \quad \text{sp} \quad \text{sp} \quad \text{sp} \\
\text{H}_3\text{C} - \text{C} = \text{C} - \text{C} = \text{C} - \text{C} = \text{C} - \text{C} = \text{CH} = \text{CH}_2
\end{array}
\]

b. See the Lewis structure. The four carbon atoms in the ring are all sp\(^2\) hybridized, and the two sulfur atoms are sp\(^3\) hybridized.

c. 23 \(\sigma\) and 9 \(\pi\) bonds. Note: CH\(_3\)(H\(_2\)C), CH\(_2\), and CH are shorthand for carbon atoms singly bonded to hydrogen atoms.

43. If we calculate a nonzero bond order for a molecule, then we predict that it can exist (is stable).

a. \(\text{H}_2^+\): \(\sigma_{1s}\)^2 \hspace{1cm} \text{B.O. = bond order} = (1-0)/2 = 1/2, \text{ stable}
   \(
   \text{H}_2: \quad (\sigma_{1s})^2 \
   \text{B.O.} = (2 - 0)/2 - 1, \text{ stable}
   \)
   \(\text{H}_2^-: \quad (\sigma_{1s})^2(\sigma_{1s}^*)^1 \
   \text{B.O.} = (2-1)/2 = 1/2, \text{ stable}
   \)
   \(\text{H}_2^-: \quad (\sigma_{1s})^2(\sigma_{1s}^*)^2 \
   \text{B.O.} = (2-2)/2 = 0, \text{ not stable}
   \)

b. \(\text{He}_2^+\): \(\sigma_{1s}\)^2 \hspace{1cm} \text{B.O.} = (2-0)/2 = 1, \text{ stable}
   \(\text{He}_2^+: \quad (\sigma_{1s})^2(\sigma_{1s}^*)^1 \
   \text{B.O.} = (2-1)/2 = 1/2, \text{ stable}
   \)
   \(\text{He}_2^-: \quad (\sigma_{1s})^2(\sigma_{1s}^*)^2 \
   \text{B.O.} = (2-2)/2 = 0, \text{ not stable}
   \)

44. a. \(\text{N}_2^+: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^4(\pi_{2p})^4(\pi_{2p}^*)^2 \
   \text{B.O. = bond order} = (8-4)/2 = 2, \text{ stable}
   \)
   \(\text{O}_2^+: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\pi_{2p}^*)^4 \
   \text{B.O.} = (8-6)/2 = 1, \text{ stable}
   \)
   \(\text{F}_2^+: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\pi_{2p}^*)^4(\pi_{2p}^*)^2 \
   \text{B.O.} = (8-8)/2 = 0, \text{ not stable}
   \)

b. \(\text{Be}_2\): \(\sigma_{2s}\)^2 \hspace{1cm} \text{B.O.} = (2-2)/2 = 0, \text{ not stable}
   \(\text{B}_2: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^4(\pi_{2p})^2 \
   \text{B.O.} = (4-2)/2 - 1, \text{ stable}
   \)
   \(\text{Ne}_2: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^4(\pi_{2p})^4(\pi_{2p}^*)^4(\pi_{2p}^*)^2 \
   \text{B.O.} = (8-8)/2 = 0, \text{ not stable}
   \)

45. The electron configurations are:

a. \(\text{Li}_2\): \(\sigma_{2s}\)^2 \hspace{1cm} \text{B.O.} = (2-0)/2 = 1, \text{ diamagnetic (0 unpaired }e^-)\)

b. \(\text{C}_2\): \(\sigma_{2s}\)^2(\sigma_{2s}^*)^4 \hspace{1cm} \text{B.O.} = (6-7)/2 = 2, \text{ diamagnetic (0 unpaired }e^-)\)

c. \(\text{S}_2\): \(\sigma_{3s}\)^2(\sigma_{3s}^*)^2(\pi_{3p})^2(\pi_{3p}^*)^2 \hspace{1cm} \text{B.O.} = (8-4)/2 = 2, \text{ paramagnetic (2 unpaired }e^-)\)
46. 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 \( \text{Ar}_2^{2+} \).

47. \( \text{O}_2: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{3p}^*)^2 \quad \text{B.O. = bond order} = (8 - 4)/2 = 2 \)

\( \text{N}_2: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{3p})^4(\pi_{3p}^*)^2 \quad \text{B.O.} = (8 - 2)/2 = 3 \)

In \( \text{O}_2 \), an antibonding electron is removed, which will increase the bond order to 2.5 [\( = (8 - 5)/2 \)]. The bond order increases as an electron is removed, so the bond strengthens. In \( \text{N}_2 \), 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 \( \text{N}_2 \).

48. The electron configurations are:

\( F_2^+: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^3(\pi_{2p})^2(\pi_{3p}^*)^3 \quad \text{B.O.} = (8 - 5)/2 = 1.5; \quad 1 \text{ unpaired } e^- \)

\( F_2: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\pi_{3p}^*)^4 \quad \text{B.O.} = (8 - 6)/2 = 1; \quad 0 \text{ unpaired } e^- \)

\( F_2^-: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{3p})^4(\pi_{3p}^*)^4(\pi_{3p}^*)^4 \quad \text{B.O.} = (8 - 7)/2 = 0.5; \quad 1 \text{ unpaired } e^- \)

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

51. The electron configurations are (assuming the same orbital order as that for \( \text{N}_2 \)):

a. \( \text{CO}: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\pi_{3p})^2 \quad \text{B.O.} = (8 - 2)/2 = 3, \text{ diamagnetic} \)

b. \( \text{CO}^+: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\pi_{3p})^1 \quad \text{B.O.} = (7 - 2)/2 = 2.5, \text{ paramagnetic} \)

c. \( \text{CO}^{2+}: \quad (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4 \quad \text{B.O.} = (6 - 2)/2 = 2, \text{ diamagnetic} \)

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

Shortest \( \rightarrow \) longest bond length: \( \text{CO} < \text{CO}^+ < \text{CO}^{2+} \)

Smallest \( \rightarrow \) largest bond energy: \( \text{CO}^{2+} < \text{CO}^+ < \text{CO} \)
53. a. \( \text{H}_2: \ (\sigma_{1s})^2 \)

\[ \text{D}_2: \ (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2 \]

b. \( \text{C}_2^ {2-}: \ (\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{3p})^2 \)

\[ \text{OF:} \ (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{3p})^2(\pi_{2p})^4(\pi_{2p}^*)^3 \]

The bond strength will weaken if the electron removed comes from a bonding orbital. Of the molecules listed, \( \text{H}_2, \text{B}_2, \) and \( \text{C}_2^ {2-} \) would be expected to have their bond strength weaken as an electron is removed. OF has the electron removed from an antibonding orbital, so its bond strength increases.

66. a. The V-shaped (or bent) molecular structure occurs with both a trigonal planar and a tetrahedral arrangement of electron pairs. If there is a trigonal planar arrangement, the central atom is \( \text{sp}^2 \) hybridized. If there is a tetrahedral arrangement, the central atom is \( \text{sp}^3 \) hybridized.

b. The see-saw structure is a trigonal bipyramid arrangement of electron pairs which requires \( \text{dsp}^3 \) hybridization.

c. The trigonal pyramid structure occurs when a central atom has three bonded atoms and a lone pair of electrons. Whenever a central atom has four effective pairs about the central atom (exhibits a tetrahedral arrangement of electron pairs), the central atom is \( \text{sp}^3 \) hybridized.

d. A trigonal bipyramidal arrangement of electron pairs requires \( \text{dsp}^3 \) hybridization.

e. A tetrahedral arrangement of electron pairs requires \( \text{sp}^3 \) hybridization.
73. a. The Lewis structures for NNO and NON are:

\[
\begin{align*}
\text{N} & \equiv \text{N} \equiv \text{O} \quad \equiv \quad \text{N} \equiv \text{N} \equiv \text{O} \quad \equiv \quad \text{N} \equiv \text{N} \equiv \text{O} \\
\text{N} & \equiv \text{O} \equiv \text{N} \quad \equiv \quad \text{N} \equiv \text{O} \equiv \text{N} \quad \equiv \quad \text{N} \equiv \text{O} \equiv \text{N}
\end{align*}
\]

The NNO structure is correct. From the Lewis structures, we would predict both NNO and NON to be linear. However, we would predict NNO to be polar and NON to be nonpolar. Since experiments show N$_2$O to be polar, NNO is the correct structure.

b. Formal charge = number of valence electrons of atoms – [(number of lone pair electrons) + 1/2(number of shared electrons)].

\[
\begin{align*}
\text{N} & \equiv \text{N} \equiv \text{O} \quad \equiv \quad \text{N} \equiv \text{N} \equiv \text{O} \quad \equiv \quad \text{N} \equiv \text{N} \equiv \text{O} \\
-1 & \quad +1 & \quad 0 & \quad 0 & \quad +1 & \quad -1 & \quad -2 & \quad +1 & \quad +1
\end{align*}
\]

The formal charges for the atoms in the various resonance structures are below each atom. The central N is $sp$ hybridized in all the resonance structures. We can probably ignore the third resonance structure on the basis of the relatively large formal charges as compared to the first two resonance structures.

c. The $sp$ hybrid orbitals from the center N overlap with atomic orbitals (or appropriate hybrid orbitals) from the other two atoms to form the two sigma bonds. The remaining two unhybridized $p$ orbitals from the center N overlap with two $p$ orbitals from the peripheral N to form the two $\pi$ bonds.