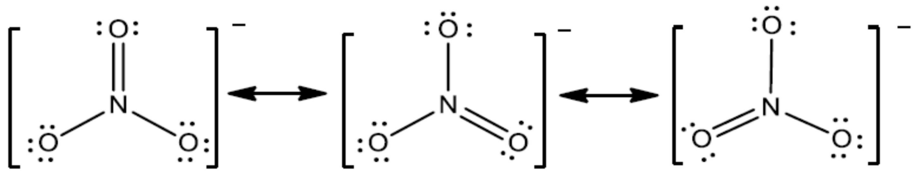
Solutions to suggested end-of-chapter problems for Ch. 8
Question numbers correspond to the 9th edition. The number in parentheses corresponds to the 10th edition.

9 (11). 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 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, sp^2, sp^3, dsp^3 or d^2sp^3. 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 sp^2 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 sp^3 hybridization, the s and all the p orbitals are hybridized; no unhybridized p atomic orbitals are present, so no π bonds form with sp^3 hybridization. For dsp^3 and d^2sp^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 (14). 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).

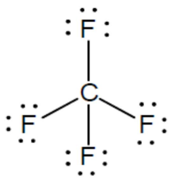
14 (18). From experiment, B_2 is paramagnetic. If the σ_{2p} MO is lower in energy than the two degenerate π_{2p} MOs, the electron configuration for B_2 would have all electrons paired. Experiment tells us we must have unpaired electrons. Therefore, the MO diagram is modified to have the π_{2p} orbitals 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.

16 (20). NO_3^-, $5 + 3(6) + 1 = 24\ e^-$



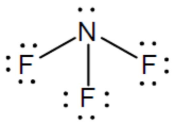
When resonance structures can be drawn, it is usually due to a multiple bond that can be in different positions. This is the case for NO_3^-. Experiment tells us that the three N–O bonds are equivalent in length and strength. To explain this, we say the π electrons are delocalized in the molecule. For NO_3^-, the π 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 π 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 π electrons situated above and below two specific nuclei, we think of the π 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 π bonding system in NO_3^-.

29 (33). a.



tetrahedral sp^3
109.5° nonpolar

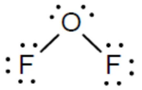
b.



trigonal pyramid sp^3
<109.5° polar

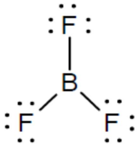
The angles in NF_3 should be slightly less than 109.5° because the lone pair requires more space than the bonding pairs.

c.



V-shaped sp^3
<109°.5 polar

d.



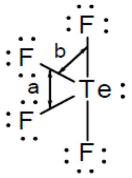
trigonal planar sp^2
120° nonpolar

e.

H—Be—H

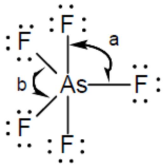
linear sp
180° nonpolar

f.



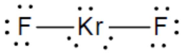
see-saw dsp^3
a) ≈120°, b) ≈90° polar

g.



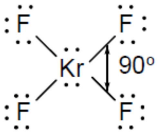
trigonal bipyramid dsp^3
a) 90°, b) 120° nonpolar

h.



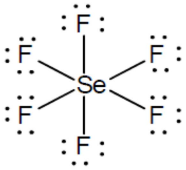
linear dsp^3
180° nonpolar

i.



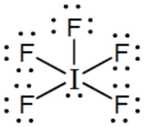
square planar d^{2}sp^3
90° nonpolar

j.



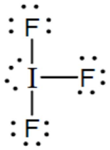
octahedral d^{2}sp^3
90° nonpolar

k.



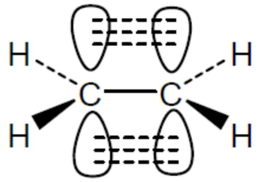
square pyramid d^{2}sp^3
≈90° polar

l.



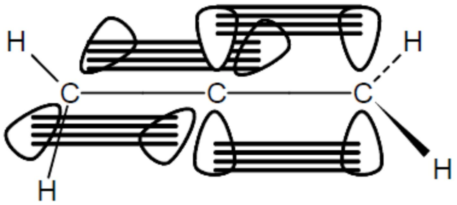
T-shaped dsp^3
≈90° polar

31 (35).



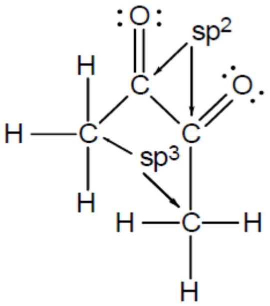
For the p orbitals to properly line up to form the π bond, all six atoms are forced into the same plane. If the atoms are not in the same plane, then the π bond could not form since the p orbitals would no longer be parallel to each other.

32 (36). No, the CH_2 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 CH_2 planes to be perpendicular.



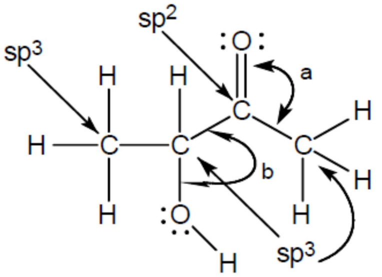
35 (39). To complete the Lewis structures, just add lone pairs of electrons to satisfy the octet rule for the atoms with fewer than eight electrons.

Biacetyl ($C_4H_6O_2$) has 4(4) + 6(1) + 2(6) = 34 valence electrons.



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.

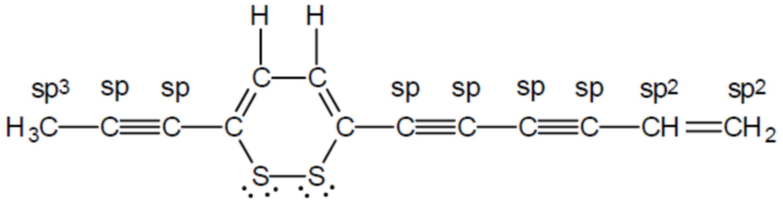
Acetoin ($C_4H_8O_2$) has 4(4) + 8(1) + 2(6) = 36 valence electrons.



The carbon with the doubly bonded O is sp^2 hybridized. The other three C atoms are sp^3 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.



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 σ and 9 π bonds. *Note*: CH_3 (H_3C), CH_2, and CH are shorthand for carbon atoms singly bonded to hydrogen atoms.

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

a. H_2^+: $(\sigma_{1s})^1$ B.O. = bond order = (1–0)/2 = 1/2, stable
H_2: $(\sigma_{1s})^2$ B.O. = (2–0)/2 = 1, stable
H_2^-: $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ B.O. = (2–1)/2 = 1/2, stable
H_2^{2-}: $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ B.O. = (2–2)/2 = 0, not stable

b. He_2^{2+}: $(\sigma_{1s})^2$ B.O. = (2–0)/2 = 1, stable
He_2^+: $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ B.O. = (2–1)/2 = 1/2, stable
He_2: $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ B.O. = (2–2)/2 = 0, not stable

44 (48). a. N_2^{2-}: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^2$ B.O. = bond order = (8–4)/2 = 2, stable
O_2^{2-}: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$ B.O. = (8–6)/2 = 1, stable
F_2^{2-}: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p}^*)^2$ B.O. = (8–8)/2 = 0, not stable

b. Be_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2$ B.O. = (2–2)/2 = 0, not stable
B_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2$ B.O. = (4–2)/2 = 1, stable
Ne_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p}^*)^2$ B.O. = (8–8)/2 = 0, not stable

45 (49). The electron configurations are:

a. Li_2: $(\sigma_{2s})^2$ B.O. = (2–0)/2 = 1, diamagnetic (0 unpaired e^-)

b. C_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$ B.O. = (6–2)/2 = 2, diamagnetic (0 unpaired e^-)

c. S_2: $(\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p})^2(\pi_{3p})^4(\pi_{3p}^*)^2$ B.O. = (8–4)/2 = 2, paramagnetic (2 unpaired e^-)

46 (50). 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 Cl_2, SCl^-, S_2^{2-}, and Ar_2^{2+}.

47 (--). O_2: $(\sigma_{2s})^2(\sigma_{2s}*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}*)^2$ B.O. = bond order = $(8-4)/2 = 2$

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

In O_2, 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 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 N_2.

48 (52). 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 $F_2^+ < F_2 < F_2^-$.

51 (55). The electron configurations are (assuming the same orbital order as that for N_2):

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 → longest bond length: $CO < CO^+ < CO^{2+}$

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

53 (57). a. H_2: $(\sigma_{1s})^2$

B_2: $(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^2$

b. C_2^{2-}: $(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^4(\sigma_{2p})^2$

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

The bond strength will weaken if the electron removed comes from a bonding orbital. Of the molecules listed, H_2, B_2, and 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 (70). 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 sp^2 hybridized. If there is a tetrahedral arrangement, the central atom is sp^3 hybridized.

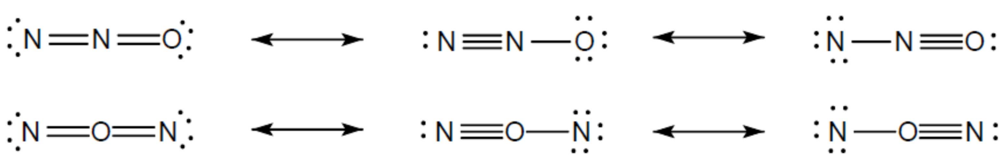
b. The see-saw structure is a trigonal bipyramid arrangement of electron pairs which requires dsp^3 hybridization.

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 sp^3 hybridized.

d. A trigonal bipyramidal arrangement of electron pairs requires dsp^3 hybridization.

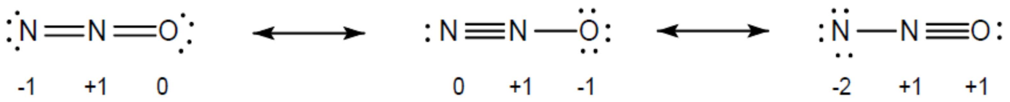
e. A tetrahedral arrangement of electron pairs requires sp^3 hybridization.

73 (77). a. The Lewis structures for NNO and NON are:



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_2O 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)].



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 π bonds.