Solutions to Suggested Problems From Chapter 4A

1. To overlap, two orbitals must be able to "join lobes" of electron density. This takes some imagination, but picture the two orbitals in the same Cartesian coordinate system (x-, y-, and z-axes) and try moving them together to see if they overlap. Of the choices given in this problem, the following will overlap

   $$2s + 2s \quad 2p_y + 2p_y \quad 2p_z + 2p_z$$

   and the following will not overlap

   $$2p_x + 2p_y$$

   The case of $2s + 2p_z$ depends upon how the orbitals approach each other; if the approach is along the z-axis, then they will overlap with each other.

5. To answer, draw a Lewis structure and use VSEPR to predict the electron domain geometry. (a) CH_4 has a tetrahedral geometry and has sp^3 hybridization; (b) H_2CO has trigonal planar geometry and has sp^2 hybridization; (c) HCO_2^- has trigonal planar geometry and has sp^2 hybridization.

8. (a) The Lewis structure has a triple bond between C and O. This triple bond includes a sigma bond from the overlap of sp hybrid orbitals on C and O, and two pi bonds, each from the overlap of p-orbitals on C and O.

   (b) The Lewis structure has double bonds between the C and O. Each double bond includes a sigma bond from the overlap of sp hybrid orbitals on C and O, a pi bond from the overlap of p-orbitals on C and O.

9. In a sigma orbital the electron density lies along the internuclear axis. For a pi orbital the electron density lies above and below the internuclear axis.

11. Stronger interactions lead to a greater difference between the energies of a bonding and antibonding pair. A sigma bond between two p-orbitals involves a stronger interaction as the electrons are more strongly attracted to each nucleus.

12. (a) σ_{2s} and σ_{2s}^*; (b) π_{2p} and π_{2p}^*; (c) π_{2p} and π_{2p}^*; (d) σ_{2p} and σ_{2p}^*; (e) $\sigma_{2s\text{-}2p}$ and $\sigma_{2s\text{-}2p}^*$

14. The molecule H_2 has two electrons and a MO configuration of $(\sigma_{1s})^2$ and a bond order of 1. The ions H_2^+ and H_2^- have MO configurations of $(\sigma_{1s})^1$ and $(\sigma_{1s})^2(\sigma_{1s}^*)^1$, and bond orders of 1/2 and 1/2, respectively.

16. Here we need only focus on the 2p electrons. For O_2 the MO configuration is $(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$ with a bond order of 2, whereas the MO configuration for O_2^-, which has one additional electron, is $(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$ with a bond order of 1.5; thus O_2 is the more stable species as it has the higher bond order and greater bond strength.

19. (a) HF has a single bond between H and F that is the overlap of an s-orbital and a p-orbital; thus, the MO configuration is $(\sigma_{sp})^2$ and it is diamagnetic. Note that because H has but on atomic orbital containing electrons, there is but one molecular orbital; the remaining electrons on fluorine remain in p-orbitals on the fluorine.

The remaining answers assume that Figure 4A.8 as a suitable MO diagram

(b) CO with 10 electrons is $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2px})^2(\pi_{2py})^2$ and is diamagnetic

(c) CN^- with 10 electrons is $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2px})^2(\pi_{2py})^2$ and is diamagnetic

(d) NO with 11 electrons is $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2px})^2(\pi_{2py})^2(\pi_{2px}^*)^1$ and is paramagnetic

(e) NO^+ with 10 electrons is $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2px})^2(\pi_{2py})^2$ and is diamagnetic