CH 221 Practice Problem Set #5

*This is a **practice problem set** and not the actual graded problem set that you will turn in for credit.*
Answers to each problem can be found at the end of this assignment.

Covering: **Chapter Five** *and* **Chapter Guide Five**
Important Tables and/or Constants: "**MO Diagram for B_2, C_2, and N_2**" *(Handout)*, "**MO Diagram for O_2, F_2, and Ne_2**" *(Handout),* "**Geometry and Polarity Guide**" *(Handout or here:* https://mhchem.org/geopo*)*

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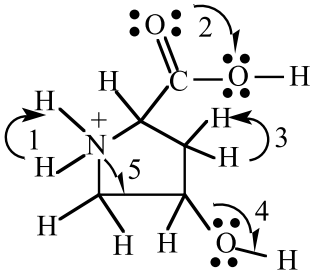
1. Draw the Lewis structure for chloroform, $CHCl_3$. What are its electron-pair and molecular geometries? What orbitals on C, H, and Cl overlap to form bonds involving these elements?
2. Specify the electron-pair and molecular geometry for each of the following. Describe the hybrid orbital set used by the central atom in each molecule or ion.
   a. BBr_3 b. CO_2 c. CH_2Cl_2 d. CO_3^{2-}
3. Draw the Lewis structure and then specify the electron- pair and molecular geometries for each of the following molecules or ions. Identify the hybridization of the central atom.
   a. SiF_6^{2-} b. SeF_4 c. ClF_2^{1-} d. XeF_4
4. The hydrogen molecular ion, H_2^+, can be detected spectroscopically. Write the electron configuration of the ion in molecular orbital terms. What is the bond order of the ion? Is the hydrogen–hydrogen bond stronger or weaker in H_2^+ than in H_2?
5. Calcium carbide, CaC_2, contains the acetylide ion, C_2^{2-}. Sketch the molecular orbital energy level diagram for the ion. How many net σ and π bonds does the ion have? What is the carbon–carbon bond order? How has the bond order changed on adding electrons to C_2 to obtain C_2^{2-}? Is the C_2^{2-} ion paramagnetic?
6. The simple valence bond picture of O_2 does not agree with the molecular orbital view. Compare these two theories with regard to the peroxide ion, O_2^{2-}.
   (a) Draw an electron dot structure for O_2^{2-}. What is the bond order of the ion?
   (b) Write the molecular orbital electron configuration for O_2^{2-}. What is the bond order based on this approach?
   (c) Do the two theories of bonding lead to the same magnetic character and bond order for O_2^{2-}?
7. Which of the homonuclear, diatomic molecules of the second-period elements (from Li_2 to Ne_2) are paramagnetic? Which have a bond order of 1? Which have a bond order of 2? Which diatomic molecule has the highest bond order?
8. Consider the three fluorides BF_4^{-1}, SiF_4, and SF_4.
   a. Identify a molecule that is isoelectronic with BF_4^{1-}.
   b. Are SiF_4 and SF_4 isoelectronic?
   c. What is the hybridization of the central atom in each of these species?
9. When is it desirable to use MO theory rather than valence bond theory?
10. Antimony pentafluoride reacts with HF according to the equation:

    $$2\ HF + SbF_5 \rightarrow [H_2F]^+[SbF_6]^-$$

    a. What is the hybridization of the Sb atom in the reactant and product?
    b. Draw a Lewis structure for H_2F. What is the geometry of H_2F^+? What is the hybridization of F in H_2F^+?

11. The CN molecule has been found in interstellar space. Using the appropriate molecular orbital energy level diagram, answer the following questions.
    a. What is the highest energy occupied molecular orbital (HOMO) to which an electron (or electrons) is (are) assigned?
    b. What is the bond order of the molecule?
    c. How many net σ bonds are there? How many net π bonds?
    d. Is the molecule paramagnetic or diamagnetic?
12. Draw the Lewis structure for ClF_3. What are its electron- pair and molecular geometries? What is the hybridization of the chlorine atom? What orbitals on Cl and F overlap to form bonds between these elements?
13. Hydroxyproline is an unusual amino acid with the structure shown to the right.
    a. What are the approximate values for the bond angles for *1*, *2*, *3*, *4* and *5*?
    b. Describe the hybridization around the central atom for *1*, *2*, *3*, *4* and *5*.



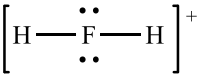
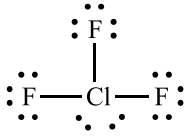
Hydroxyproline

14. Iodine and oxygen form a complex series of ions, among them IO_4^{-1} and IO_5^{-3}. Draw the Lewis structures for these ions and specify their electron pair and molecular geometries. What is the hybridization of the I atom in these ions?
15. Which of the following molecules or ions should be paramagnetic? What is the highest occupied molecular orbital (HOMO) in each one? Note that if an O, F or Ne is present in the molecule, you should use the molecular orbital diagram for O_2, F_2 and Ne_2 to construct the molecule.
    a. NO
    b. OF^{-1}
    c. O_2^{2-}
    d. Ne_2^{+1}
    e. CN

Answers to the Practice Problem Set:

1. The electron-pair and molecular geometries are tetrahedral. The C atom is sp^3 hybridized. Three of these hybrid orbitals each overlap with a chlorine 3*p* orbital to form three C—Cl sigma bonds. One hybrid orbital overlaps with a hydrogen 1*s* orbital to from a C—H sigma bond.
2. *Answers:*

(a) BBr_3	trigonal planar	trigonal planar	sp^2
(b) CO_2	linear	linear	sp
(c) CH_2Cl_2	tetrahedral	tetrahedral	sp^3
(d) CO_3^{2-}	trigonal planar	trigonal planar	sp^2

3. a) octahedral, octahedral, sp^3d^2 b) trigonal bipyramid, see-saw, sp^3d c) trigonal bipyramid, linear, sp^3d d) octahedral, square planar, sp^3d^2
4. H_2^+: $(\sigma_{1s})^1$ Bond order = $\frac{1}{2}(1 - 0) = \frac{1}{2}$, weaker H—H bond H_2: $(\sigma_{1s})^2$ Bond order = $\frac{1}{2}(2 - 0) = 1$, stronger H—H bond
5. C_2^{2-}: $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2\ (\pi_{2p})^4\ (\sigma_{2p})^2$ C_2^{2-} ion has a bond order of $\frac{1}{2}(8 - 2) = 3$ (one σ bond and two π bonds). The C_2 molecule has two fewer electrons and a bond order of $\frac{1}{2}(6 - 2) = 2$. The C_2^{2-} ion is diamagnetic.
6. (a) bond order = 1 (b) [core electrons]$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$ bond order = $\frac{1}{2}(8 - 6) = 1$ (c) The theories agree here.
7. B_2 and O_2 are paramagnetic, Li_2, B_2, and F_2 have a bond order of 1, C_2 and O_2 have a bond order of 2, and N_2 has the highest bond order, 3.
8. (a) CF_4 is isoelectronic with BF_4^- (32 valence electrons)
   (b) SiF_4 (32 valence electrons) and SF_4 (34 valence electrons) are not isoelectronic
   (c) BF_4^-: sp^3 SiF_4: sp^3 SF_4: sp^3d
9. Molecular orbital theory correctly predicts the electronic structures for odd-electron molecules and other molecules such as O_2 that do not follow the electron-pairing assumptions of the Lewis dot structure approach.
10. (a) sp^3d in SbF_5, sp^3d^2 in SbF_6^-
    (b)  The geometry of H_2F^+ is bent, and the F atom is sp^3 hybridized.
11. CN [core electrons]$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^1$
    (a) The HOMO is σ_{2p}
    (b) Bond order = $\frac{1}{2}(7 - 2) = 2\ \frac{1}{2}$
    (c) One-half net σ bond and two net π bonds
    (d) paramagnetic
12.  The electron-pair geometry is trigonal bipyramidal, and the molecular geometry is T-shaped. The Cl atom is sp^3d hybridized. Three of these hybrid orbitals each overlap a fluorine 2*p* orbital to form three Cl—F sigma bonds.

13. a - all angles 109° except angle 2 = 120°. b - all sp^3 except C(2) = sp^2

14. IO_4^{-1} = tetrahedral (EPG & MG), sp^3 IO_5^{-3} = trigonal bipyramid (EPG & MG), sp^3d

15.

(a)	NO	paramagnetic	π^*_{2p}	11
(b)	OF^-	diamagnetic	π^*_{2p}	14
(c)	O_2^{2-}	diamagnetic	π^*_{2p}	14
(d)	Ne_2^+	paramagnetic	σ^*_{2p}	15
(e)	CN	paramagnetic	σ_{2p}	9