

**Chem 370 - Spring, 2019**  
**Assignment 6**

**Reading Assignment**

As previously indicated, in Chapter 6 read sections 6.1 through 6.5 (sections 6.1, 6.2, and 6.4 in the 4<sup>th</sup> edition). We will skip section 6.6 (6.3 in the 4<sup>th</sup> edition) on Hard and Soft Acids and Bases.

Continue on to Chapter 7. (The section numbers are the same in both the 5<sup>th</sup> and 4<sup>th</sup> editions.) Read sections 7.1 (in subsection 7.1.2 concentrate on NaCl and just skim through the descriptions of other binary compound structures), 7.2 (you can skip subsection 7.2.2), and 7.5. We will skip sections 7.3, 7.4, 7.6 and 7.7 entirely.

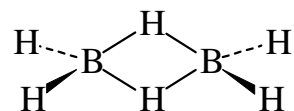
Rather than continuing on to descriptive chemistry (Chapter 8), we will next discuss the physical chemistry of transition metal complexes. Start by reading sections 9.1 and 9.2. Section 9.1 gives a little background on the history of coordination chemistry, and section 9.2 discusses nomenclature. I will not test you specifically on either of these topics. However, it is essential that you be familiar with the nomenclature of coordination compounds, because I will use it routinely as we cover the material in Chapters 10 through 12. Similarly, skim through all of section 9.3 on isomerism. I want you to be familiar with the terminology of isomerism and know the cases where certain types are possible, but I will not ask you, say, to list all of the isomers of some complex or otherwise specifically test you on isomerism. We will start by covering the material in Chapters 10 and 11, so you should be reading these. I will not discuss the angular overlap method (section 10.4), but we will talk about many of the topics in this section from a different perspective.

**Homework Assignment**

Do the following problems, which are adapted from Chapter 4 of my book. We will go over these in discussion on Friday, March 29<sup>th</sup>.

1. There is little evidence to support significant participation of  $3d$  orbitals in the bonding of  $\text{PF}_5$ . [cf. D. L. Cooper, T. P. Cunningham, J. Gerratt, P.B. Karadakov, and M. Raimondi, *J. Am. Chem. Soc.* **1994**, *116*, 4414.] Develop a qualitative MO scheme for trigonal bipyramidal  $\text{PF}_5$ , using only  $3s$  and  $3p$  orbitals on phosphorous and a single  $2p$  orbital on each of the five fluorine atoms. Make sketches of the bonding and nonbonding LCAOs formed from combining phosphorous AOs with fluorine SALCs.

2. Diborane,  $B_2H_6$  has a structure with bridging hydrogen atoms.



The terminal B–H bonds are conventional two-center, two-electron ( $2c-2e$ ) covalent bonds, but each B–H–B bridge is an electron-deficient, three-center, two electron ( $3c-2e$ ) bond. Develop a general MO scheme in diborane's point group,  $D_{2h}$ , for the pair of bridge bonds, assuming that each boron atom is  $sp^3$  hybridized. Although the choice of axes in  $D_{2h}$  is arbitrary, a typical orientation would have the two boron atoms along the  $z$  axis and the hydrogen bridges lying in the  $xz$  plane. In setting up the problem, use four  $sp^3$  hybrids, two on each boron atom, as the basis for a set of SALCs, and take the  $1s$  orbitals on the two bridging hydrogen atoms as a basis for a separate set of SALCs. Form MOs by matching boron SALCs with hydrogen SALCs. Draw sketches of the LCAOs of the bonding and nonbonding MOs.

3. Determine the sets of specific atomic orbitals that can be combined to form hybrid orbitals with the following geometries: (a) trigonal planar, (b) square planar, (c) trigonal bipyramid, (d) octahedral.
4. Hybrid orbitals are usually discussed in the context of perfect geometries. Yet in many cases the molecular structures for which these hybrids are postulated deviate significantly from the ideal. For example, consider an ideally tetrahedral  $MX_4$  molecule whose actual structure is slightly flattened along the  $z$  axis (a  $C_2$  axis in both the ideal and distorted structures). What sets of atomic orbitals could be combined to form hybrid orbitals with appropriate orientations to describe bonding in such a molecule? How do these results compare with the  $sp^3$  and  $sd^3$  hybrids appropriate for perfectly tetrahedral geometry?