

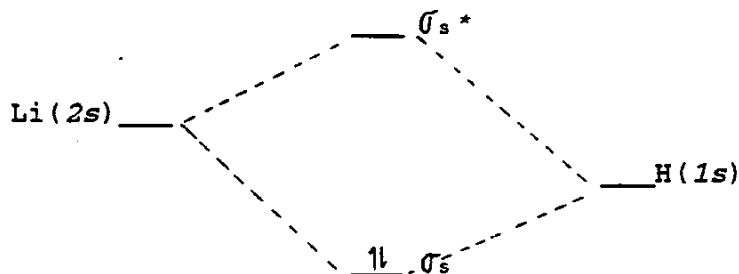
CHAPTER 3

3.2 σ -type bonding orbitals may contain as few as one lobe, and have no nodes between nuclei. π -type orbitals have a minimum of two lobes and one angular node, which passes through the nuclei. δ -type orbitals have a minimum of four lobes and two nodes.

3.3 (a) p_z ; (b) d_{z^2} ; (c) d_{xz} and d_{yz} ; (d) δ interaction.

3.4 The bond orders are 0.5 for BeH , 1.0 for BeH^+ , and 0 for BeH^- ; hence BeH^+ should be the most stable of the three.

3.5 (a)



Bond order = $(2-0)/2 = 1.0$; (b) The bond length and bond dissociation energy are reasonable in that they are intermediate between those of H_2 and Li_2 . (c) Hydrogen is partly negative, since $c_H > c_{Li}$ for the only occupied orbital.

3.6 (a) H_2 - bond order of 1.0 vs. 0.5; (b) C_2 - bond order of 2.0 vs. 1.5; (c) C_2^{2-} - bond order of 3.0 vs. 2.0; (d) F_2^+ - bond order of 1.5 vs. 1.0.

3.7 Chlorine is smaller than sodium; hence the Cl-Cl bond is

the shorter of the two, and chlorine's valence orbitals overlap more effectively than those of Na.

3.8 In addition to the bond order differential, there is a size effect. Since $B > C > N$ in size, this effect favors N-N and C-C vs. B-B interactions.

3.9 The bond is longer and weaker in O_2^{2-} , since oxygen is larger than fluorine. (Oxygen's nucleus has 8 protons, while fluorine's has 9.)

3.10 $s-p$ mixing causes the $\pi_{x,y}$ orbitals to lie lower in energy than σ_z . For Group 13 diatomics such as B_2 , the bond order is 1.0 regardless; however, those compounds are diamagnetic in the absence of strong mixing, but paramagnetic (two unpaired electrons) otherwise. For Group 14 diatomics the bond order is always 2.0, but such species are paramagnetic in the absence of mixing or diamagnetic if mixing is strong.

3.11 The $s-p$ energy differential is small (5.4 eV), so secondary mixing should be significant. Therefore, the $\pi_{x,y}$ orbitals should lie lower in energy than σ_z . This would cause Al_2 to have two unpaired electrons and be paramagnetic.

3.12 (a) Ionization of N_2 requires removal of a bonding electron, while ionization from N involves removal of a non-bonding electron. The former process requires more energy, so $IE_1(N_2) > IE_1(N)$. (b) The added electron enters an antibonding orbital in N_2 and a non-bonding orbital in N. Hence $EA_1(N) > EA_1(N_2)$.

- 3.13 Based on Figure 3.11, the bond orders are 1.0 for Cu_2 ($22 e^-$, occupancy through σ_z^*) and 0 for Zn_2 .
- 3.14 Overlap of a scandium $3d$ (or $4s$) orbital with $\text{H}(1s)$ should lead to a stable compound with a bond order of 1.0.
- 3.15 The σ bonding orbitals are filled in preference to the π bonding orbitals, which in turn are filled before the δ MO's.
- 3.16 The completed diagram should be generally similar to that of CO (Figure 3.13). (a) Assuming those relative orbital energies, the predicted bond order is 3.0. (b) The species is diamagnetic. (c) The HOMO is σ_s^* and the LUMO is $\pi_{x,y}^*$. (d) The HOMO is primarily boron in character.
- 3.17 $\text{NO} + \text{CN} \rightarrow \text{NO}^+ + \text{CN}^-$ is favored based on combined bond orders (the total number of bonds increases from 5 to 6).
- 3.18 The diagram should resemble that for HF (Figure 3.16), but with one fewer electron. (a) 1.0; (b) $\cdot\text{OH}$ should be comparable in stability to HF . (c) Yes, to fill the relatively stable $\text{O}(2p)$ non-bonding orbital. (d) No, since the second electron would enter an antibonding orbital.
- 3.19 The VSIE's of Li and F are more different from one another than those of Be and O (see Table 1.8). Therefore, the weighting coefficients are more lopsided (closer to 0.0 and 1.0 for any given molecular orbital) for LiF than for BeO . The charge distributions differ in the same manner.

3.20 The HOMO in CO is antibonding (Figure 3.13), while in N_2 it is a bonding orbital. Hence CO is more prone to electron pair donation than N_2 .

3.21 (a) The diagram should resemble Figure 3.19, but with six electrons. (b) The diagram should resemble Figure 3.18, but with six electrons.

3.22 Bent, in order to minimize the overall energies of the occupied valence orbitals. Note that NH_2^- is isoelectronic with H_2O .

3.23 The completed diagram should show three net bonds and one non-bonding electron pair. This is inferior to the tetrahedral option, in which all eight valence electrons reside in bonding orbitals.

3.24 (a) All six valence electrons occupy bonding orbitals. (b) p_z is non-bonding, as none of the SALC orbitals have the appropriate symmetry (A_2'') for overlap. (c) Lewis acid, because the LUMO (boron's non-bonding $2p_z$ orbital) is relatively stable. When BH_3 reacts with hydride ion, the electron pair of H^- moves to a more stable orbital. (A non-bonding orbital becomes bonding.)

3.25 The point group is C_{3v} . The relevant reducible representation is $\Gamma_r = 4 \quad 1 \quad 2$, which reduces to $2A_1 + E$. Central atom orbitals having the appropriate symmetry therefore include s (A_1), p_z (A_1), and $p_{x,y}$ (E). The resulting MO diagram shows all 8 valence electrons in bonding

orbitals, and is very similar to that given for silane (Figure 3.21).

3.26 (a) Using Figure 3.18(c) as a basis, there are four bonding, four non-bonding, and two antibonding electrons. The predicted bond order is $(4-2)/2 = 1.0$. (b) In the reaction $\text{H}_2\text{Ne} \rightarrow \text{Ne} + \text{H}_2$, there is one net bond for both the reactant and product side of the equation. However, the H-H bond should be much stronger than H-Ne, so this decomposition reaction is very exothermic. (The reaction is also favored by entropy.)

3.27 (a) Stable (although highly reactive) by analogy to the isoelectronic BeH_2 (Figure 3.18). (b) Stable according to either Figure 3.18 (if linear) or Figure 3.19 (if bent). (c) Unstable according to Figure 3.23 (no excess of bonding vs. antibonding electrons).

CHAPTER 4

