

Homework #5

October 6 (for weekly quiz on October 15)

from Averill -- Chapter 9: 71, 93, 95, 96, 100, 103, 108(a & b); Chapter 11: 15, 17, 20, 26, 30,

Also, the following questions:

- Show that green light ($\lambda = 5 \times 10^{-7}$ m) can excite electrons across the band gap of silicon.
- (a) Electromagnetic radiation of frequency 3.091×10^{14} Hz illuminates a crystal of germanium. Calculate the wavelength photoemission generated by this interaction. Germanium is an elemental semiconductor with a band gap, E_g , of 0.7 eV.
(b) Sketch the absorption spectrum of germanium, i.e., plot % absorption vs wavelength, λ .

Solution outlines to supplemental questions

$$1. \quad \lambda_{\text{crit}} = \frac{hc}{E_g} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{1.1 \times 1.6 \times 10^{-19}} = 1.13 \times 10^{-6} \text{ m}$$

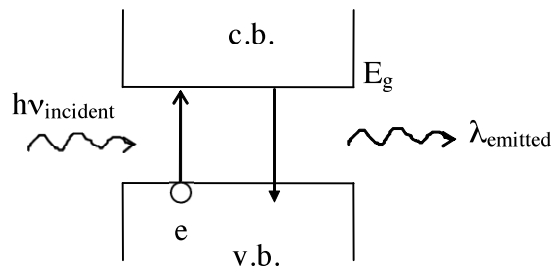
The critical λ for silicon is 1.1×10^{-6} m; thus radiation of $\lambda = 5 \times 10^{-7}$ m $= 0.5 \times 10^{-6}$ m has even more energy than that required to promote electrons across the band gap.

- (a) First compare E of the incident photon with E_g :

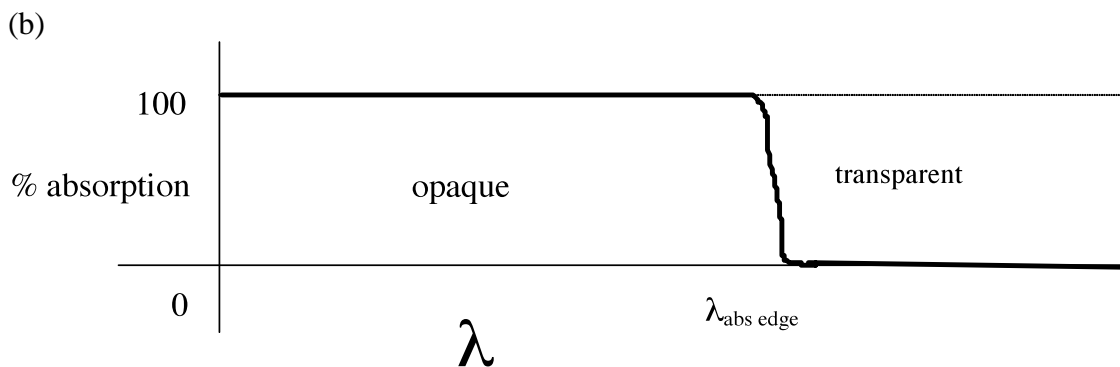
$$E_{\text{incident photon}} = h\nu = 6.6 \times 10^{-34} \times 3.091 \times 10^{14} = 2.04 \times 10^{-19} \text{ J}$$

$$E_g = 0.7 \text{ eV} = 1.12 \times 10^{-19} \text{ J} < E_{\text{incident photon}}$$

\therefore electron promotion followed by emission of a new photon of energy equal to E_g
- energy in excess of E_g is dissipated as heat in the crystal



$$\lambda_{\text{emitted}} = \frac{hc}{E_g} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{0.7 \times 1.6 \times 10^{-19}} = 1.77 \times 10^{-6} \text{ m}$$



$$\lambda_{\text{abs edge}} = \lambda_{\text{emitted}} \text{ as calculated in part (a)} = 1.77 \mu\text{m}$$

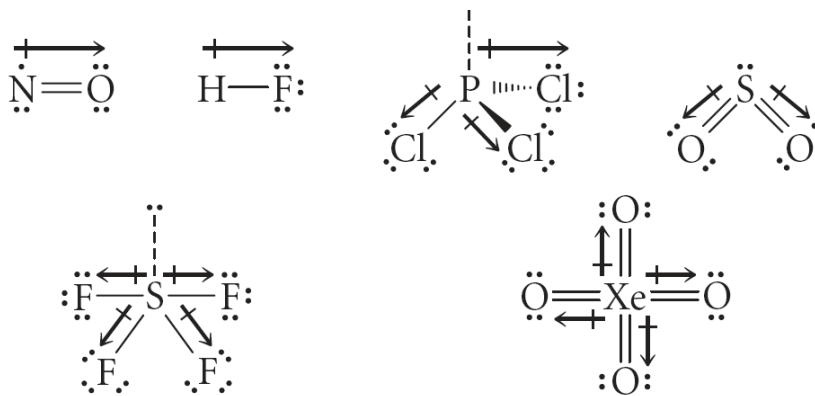
solution outlines to problems from the text

71. For diatomic molecules, we expect that a dipole moment will exist as long as $\Delta\chi \neq 0$. A triatomic or larger molecule will have a net dipole moment if the individual bond dipole moments do not cancel by symmetry. See, for example, Figure 9.5 which shows that the individual bond dipoles do cancel for CO_2 but not for H_2O . Thus, CO_2 is nonpolar, but H_2O is polar. We handle each molecule individually, and the Lewis structures with individual bond dipole directions follow. All actual bond dipole data are from the *CRC Handbook of Chemistry and Physics* (2004).

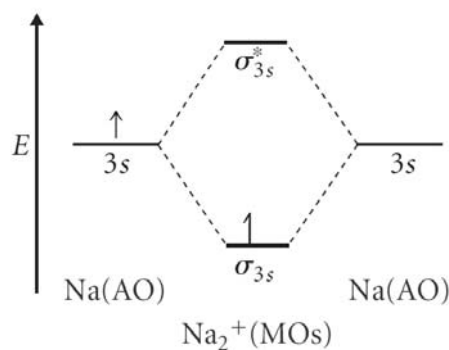
- (a) Based on $\Delta\chi$, we expect that every *heteronuclear* diatomic molecule will have a dipole moment. (The dipole moment of NO is 0.159 D.)
- (b) Based on $\Delta\chi$, we expect that every *heteronuclear* diatomic molecule will have a dipole moment. (The dipole moment of HF is 1.83 D.)
- (c) The Lewis structure for PCl_3 is below. From VSEPR it is a trigonal pyramidal molecule. The individual bond dipoles will not cancel, and we predict that PCl_3 will have a dipole. (The dipole moment of PCl_3 is 0.56 D.)
- (d) See Figure 9.5 for dipole individual directions and structure. CO_2 does not have an overall dipole movement.

- (e) The Lewis structure of SO_2 is below. It is a bent molecule; the individual $\text{S}=\text{O}$ bond dipoles will not cancel. Thus, we predict that SO_2 possesses a dipole moment. (The dipole moment of SO_2 is 1.63 D.)
- (f) SF_4 is discussed in detail on pages 390 to 392. Its seesaw structure is not symmetric, and the individual $\text{S}-\text{F}$ bond dipoles will not cancel. We predict that SF_4 will possess a dipole moment. (The dipole moment of SF_4 is 0.632 D.)
- (g) The Lewis structure with a formal charge of zero on all atoms for XeO_4 is below, showing that Xe *really* violates the octet rule! The VSEPR model treats single and double bonds equally. Thus, XeO_4 has tetrahedral geometry, and all of the individual bond dipoles will cancel. XeO_4 is predicted to be nonpolar.

The Lewis structures with individual bond dipole directions are below:

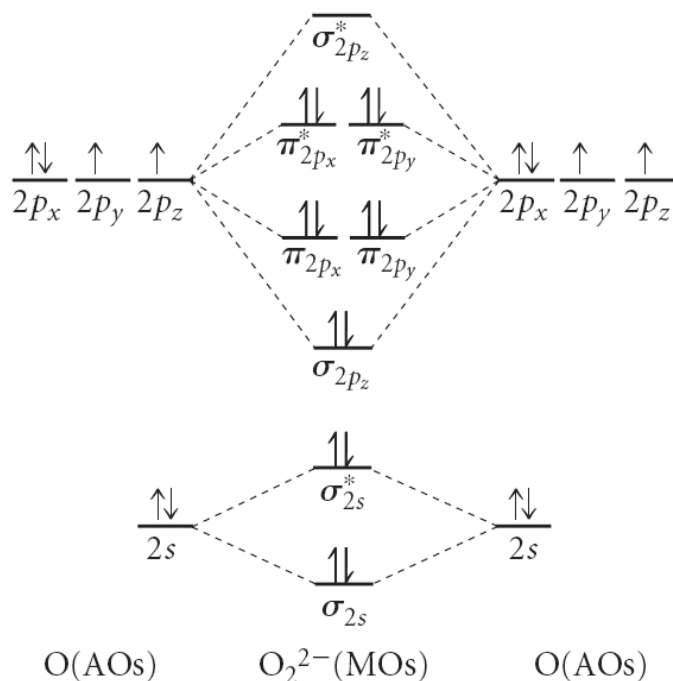


- *93.** Each Na atom contributes a $3s$ orbital to the molecular orbital diagram. Note that we do not show any of the electrons below the valence level. These electrons are held very tightly by each atom, and they do not participate in bonding in a significant way. Further, we do not worry about the $3p$ orbitals since they are not needed to accommodate the lone electron. Since the ion is $1+$, and each Na atom initially possesses a single $3s$ electron, there will only be one electron in the molecular orbital diagram. The diagram is:



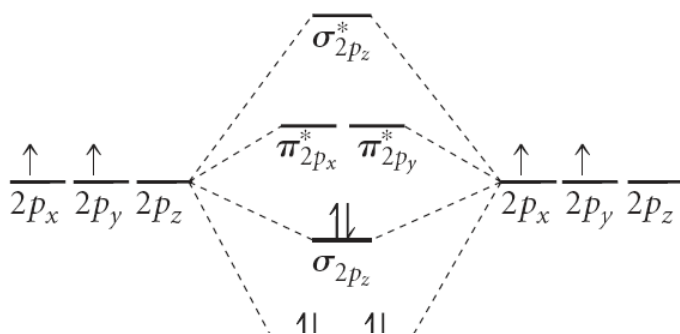
We have made the arrows different to show that the lone “atomic electron” becomes a shared electron in the molecule. Equation 9.5 gives the bond order as $(1-0)/2 = 1/2$, indicating that this molecule should be stable. The stability could be increased by a one electron reduction, which would add an electron to a bonding orbital and increase the bond order to 1. The bond orders for the three proposed species are $1/2$, 1, and $1/2$, respectively. Since Na₂ has the largest bond order, it should be the most stable.

95. In the molecular orbital diagram below, the “extra” electrons are added after the molecular orbitals are formed; each O atom brings 6 valence electrons to the ion. As usual, we omit any electrons below the valence level. To distinguish the valence electrons that the atoms bring from those in the molecule, we give the “atomic electrons” full arrowheads and the “molecular orbital electrons” half arrowheads. The molecular orbital diagram is



This indicates a valence electron configuration of $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi_{2p_{x,y}}^*)^4$. The bond order, therefore, is $(8 - 6)/2 = 1$, and we predict that O₂²⁻ is a stable ion.

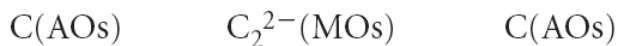
96. In the molecular orbital diagram below, the “extra” electrons are added after the molecular orbitals are formed; each C atom brings 4 valence electrons to the ion. As usual, we omit any electrons below the valence level. To distinguish the valence electrons that the atoms bring from those in the molecule, we give the “atomic electrons” full arrowheads and the “molecular orbital electrons” half arrowheads. The energy ordering for the molecular orbital diagram below is given in Figure 9.25:



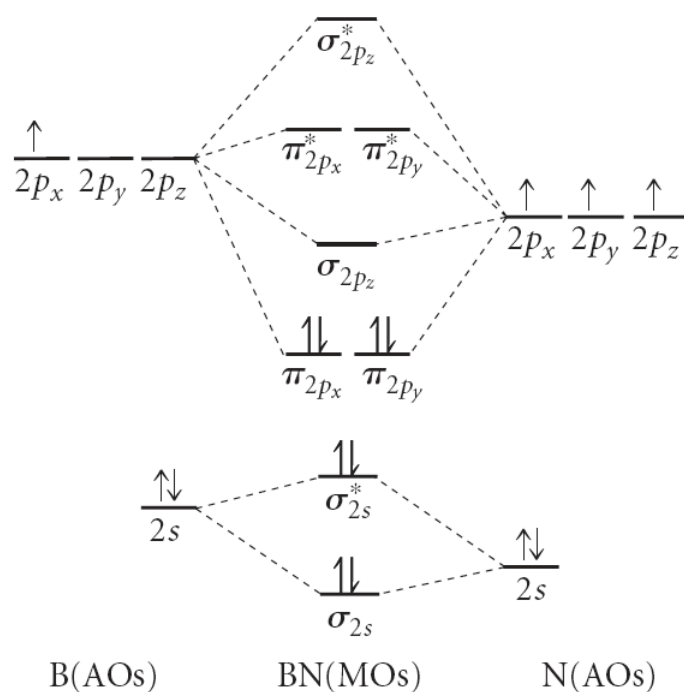
Note the reversal of the energy ordering of the $\pi_{2p_{x,y}}$ and σ_{2p_z} molecular orbitals from the order seen in Figure 9.23, giving the valence electron configuration

$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_{x,y}})^4(\sigma_{2p_z})^2$$

The bond order, therefore, is $(8 - 2)/2 = 3$, and we predict that the dicarbide ion C_2^{2-} is stable.

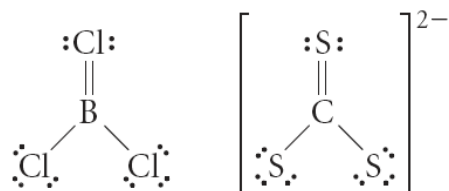


100. (a) B and N combine to give 8 valence electrons. With the given information we use the molecular orbital diagram for CN^- with the indicated orbital reversal. Thus,



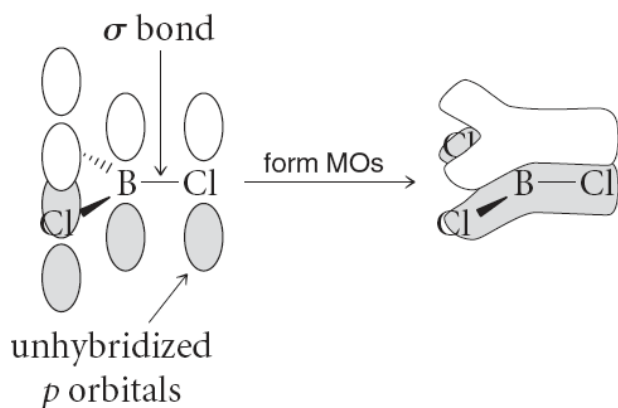
- (b) From Equation 9.5 the bond order is $(6 - 2)/2 = 2$.
 (c) Since the bond order is 2, this molecule should be stable.

103. BCl_3 is discussed before Example 8.8. While the text has argued that the best Lewis structure is the one with the lowest formal charges, we can still describe the bonding in the less important resonance structure shown below. (The Lewis structure with only single bonds in BCl_3 does not need molecular orbitals to rationalize the bonding.) The Lewis structures for both compounds (without the resonance structures) are

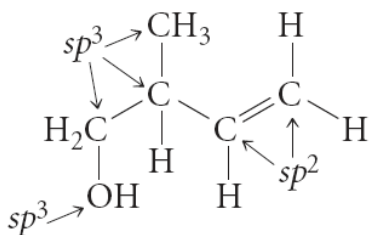


BCl_3 and CS_3^{2-} are isoelectronic, can be drawn with the same Lewis structure, and have the same molecular geometry, trigonal planar. For both molecules the σ bond framework consists of overlap between sp^2 hybrid orbitals on the central atom, and sp^2 hybrid orbitals on the terminal Cl and S atoms. (Hybridization of terminal atoms is not, however, necessary.) Thus, each atom possesses one unhybridized p orbital that is perpendicular to the plane of the molecule. The σ network accounts for 18 electrons of the 24 total electrons in

each structure, requiring us to place six electrons in the π molecular orbitals. From the Lewis structure, however, we know that only two of these will be in a bonding molecular orbital. The other four will be in two nonbonding molecular orbitals. The antibonding molecular orbital will be empty. (Note how this gives a total of four π molecular orbitals, in accord with the law of conservation of orbitals.) With only the bonding molecular orbital contributing to the bond order, we can account for the expected bond order of $1\frac{1}{3}$ for each bond. The bonding π molecular orbital, which is spread over the entire molecule, is shown below for BCl_3 . The shaded lobes indicate the change in sign of the orbital wave function. The BCl_3 plane lies in the nodal plane of the bonding π molecular orbital, and only the bonding π molecular orbital is shown. The same picture holds for CS_3^{2-} .



108. (a) The hybridizations are indicated in the structure below



(b) There is only one double bond in this molecule. This is the location of the lone π bond. Every other bond in the molecule is a σ bond, a total of 15.

Chapter 11

- *15.** Stronger intermolecular attractions generally favor the formation of denser, more ordered states of matter. The Group 17 elements each exist as diatomic, nonpolar molecules, so only London dispersion forces need to be considered. Fluorine and chlorine are gases under standard conditions because their molecules are small and have small polarizability. Bromine molecules are heavier and more polarizable, resulting in stronger intermolecular attractions, making it a liquid under ambient conditions. The even larger molecular mass of iodine accounts for its existence as a solid.
- *17.** From a Lewis structure and the application of the VSEPR model, it is found that sulfur dioxide (SO_2) molecules are bent. Comparison of the electronegativity values of S and O ($\chi_{\text{S}} = 2.58$, $\chi_{\text{O}} = 3.44$) predict that the S = O bond is polar covalent, with greater electron density concentrated on the O atom. The SO_2 molecule will therefore have a net dipole moment and dipole–dipole interactions will be most important. Hydrogen fluoride (HF) also has a permanent dipole moment because of the electronegativity difference between the two atoms ($\chi_{\text{H}} = 2.20$, $\chi_{\text{F}} = 3.98$), but the dipole–dipole interactions are unusually strong because of the small size of H and the large polarity of the H–F bond. Such interactions are called hydrogen bonds and will be most important. From a Lewis structure and the VSEPR model, it is found that carbon dioxide (CO_2) is a linear molecule. Each C = O bond is polar ($\chi_{\text{C}} = 2.55$, $\chi_{\text{O}} = 3.44$) but the dipoles of the two bonds are oriented 180° apart and therefore cancel, resulting in zero dipole moment. London dispersion forces will be the most significant intermolecular interaction for CO_2 . Carbon tetrachloride (CCl_4), like CO_2 , is an example of a molecule with polar bonds ($\chi_{\text{C}} = 2.55$, $\chi_{\text{Cl}} = 3.16$) but no net dipole moment, since the Cl are arranged symmetrically about the C atom. London forces will be the most important for CCl_4 . Dichloromethane (CH_2Cl_2) has a distorted tetrahedral structure similar to CCl_4 . Each C–H bond is nearly nonpolar and each C–Cl bond is polar toward Cl ($\chi_{\text{C}} = 2.55$, $\chi_{\text{H}} = 2.20$, $\chi_{\text{Cl}} = 3.16$) resulting in a net dipole moment. Dipole–dipole interactions are the most important for this molecule. Chlorine atoms are also polarizable, so London dispersion forces will also be significant.

- 20.** Polarizability is the ease of deformation of the electron distribution of an atom or molecule. Heavier species tend to be more polarizable than lighter ones because the outer electrons are shielded from the attractive nuclear charge by electrons populating closed inner shells. The polarizability should, therefore, increase with molecular mass: H_2 (2 g/mol) < Ne (20 g/mol) < N_2 (28 g/mol) < O_2 (32 g/mol) < Cl_2 (71 g/mol) < Kr (84 g/mol).
- 26.** (a) NH_3 will have the higher boiling point because it is more polar and can form hydrogen bonds.
- (b) Ethylene glycol will have the higher boiling point because of its larger molar mass (stronger London dispersion forces) and larger number of hydrogen bonds per molecule.
- (c) N-butanol will have the higher boiling point because its shape is less compact and affords greater surface area for stronger London dispersion forces.
- 30.** (a) F is more electronegative than I ($\chi_{\text{F}} = 3.98$, $\chi_{\text{I}} = 2.66$), so the H–F bond is considerably more polar than the H–I bond. Additionally, the (larger) partial negative charge on the F atom is concentrated within a smaller volume than the partial negative charge on I, allowing closer approach of the partial positive charge of a H on a neighboring molecule. The greater separation of charge and closer approach results in stronger dipole–dipole interactions, called hydrogen bonds.
- (b) F is more electronegative than O, so each H–F bond will be more polar than each H–O bond. As a result, individual hydrogen bonds between HF molecules are stronger than hydrogen bonds between H_2O molecules.
- (c) H_2O can form twice as many hydrogen bonds per molecule, explaining why the boiling point of H_2O is greater than that of HF.