

Assignment 13 – Solutions

Problems: Ch.14: 28, 30, 34, 60, 61, 72, 74, 32, 36, 37, 38, 39, 40, 46, 48

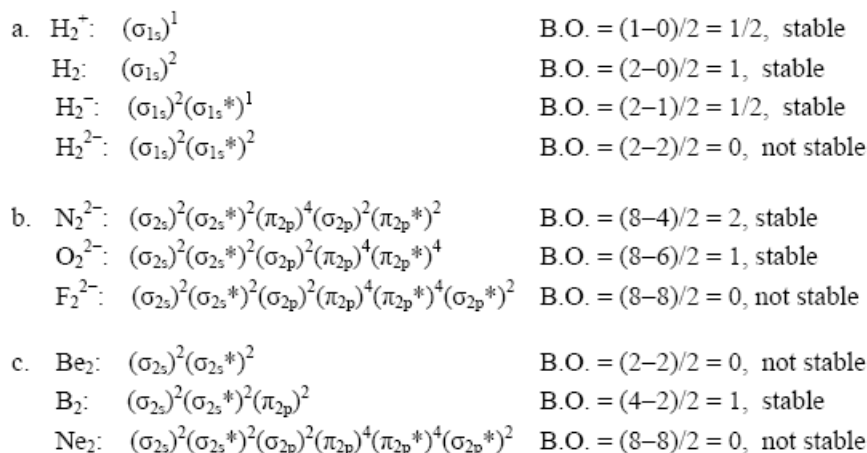
The Molecular Orbital (MO) Model

28. See Figure 14.34 for the 2s σ bonding and σ antibonding molecular orbitals, and see Figure 14.36 for the 2p σ bonding, σ antibonding, π bonding, and π antibonding molecular orbitals.
30. Bond energy is directly proportional to bond order. Bond length is inversely proportional to bond order. Bond energy and bond length can be measured; bond order is calculated from the molecular orbital energy diagram (bond order is the difference between the number of bonding electrons and the number of antibonding electrons divided by two).

Paramagnetic: a kind of induced magnetism, associated with unpaired electrons, that causes a substance to be attracted into an inducing magnetic field. Diamagnetic: a type of induced magnetism, associated with paired electrons, that causes a substance to be repelled from the inducing magnetic field. The key is that paramagnetic substances have unpaired electrons in the molecular orbital diagram, whereas diamagnetic substances have only paired electrons in the MO diagram.

To determine the type of magnetism, measure the mass of a substance in the presence and absence of a magnetic field. A substance with unpaired electrons will be attracted by the magnetic field, giving an apparent increase in mass in the presence of the field. A greater number of unpaired electrons will give a greater attraction and a greater observed mass increase. A diamagnetic species will not be attracted by a magnetic field and will not show a mass increase (a slight mass decrease is observed for diamagnetic species).

34. If we calculate a nonzero bond order for a molecule, then we predict that it can exist (is stable).



Additional Exercises

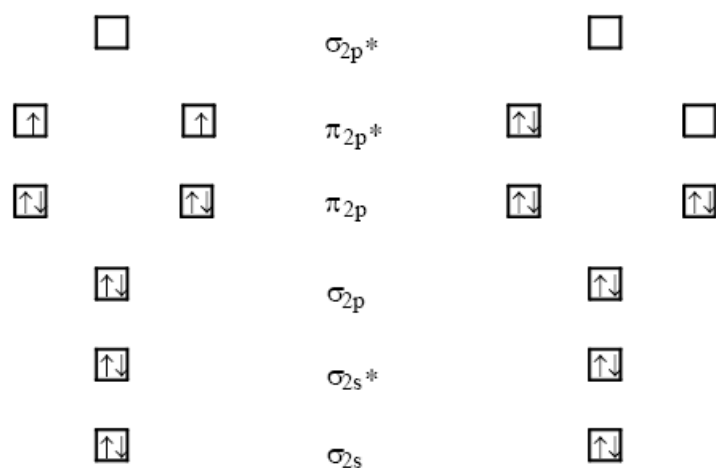
60. N_2 (ground state): $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$, B.O. = 3, diamagnetic (0 unpaired e^-)

N_2 (1st excited state): $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1(\pi_{2p}^*)^1$

B.O. = $(7 - 3)/2 = 2$, paramagnetic (2 unpaired e^-)

The first excited state of N_2 should have a weaker bond and should be paramagnetic.

61. Considering only the 12 valence electrons in O_2 , the MO models would be:



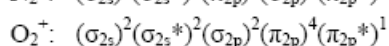
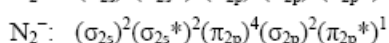
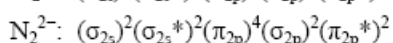
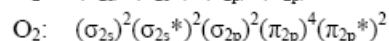
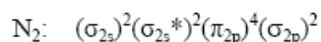
O_2 ground state

Arrangement of electrons consistent with the Lewis structure (double bond and no unpaired electrons).

It takes energy to pair electrons in the same orbital. Thus the structure with no unpaired electrons is at a higher energy; it is an excited state.

Challenge Problems

72. The electron configurations are:

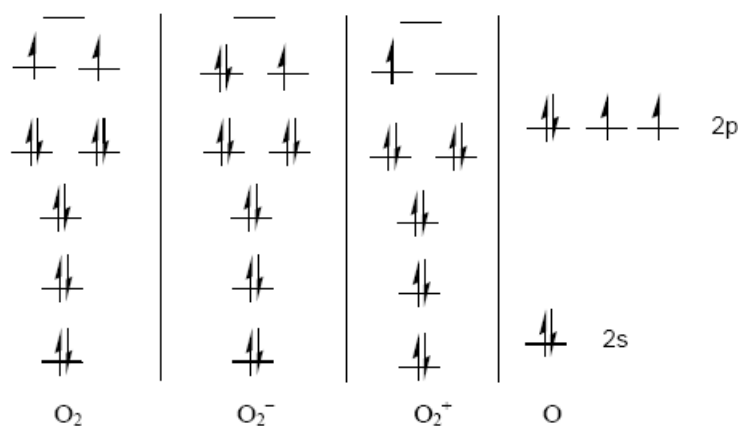


Note: The ordering of the σ_{2p} and π_{2p} orbitals is not important to this question.

The species with the smallest ionization energy has the electron that is easiest to remove. From the MO electron configurations, O_2 , N_2^{2-} , N_2^- , and O_2^+ all contain electrons in the same higher-energy antibonding orbitals (π_{2p}^*), so they should have electrons that are easier to remove as compared to N_2 , which has no π_{2p}^* electrons. To differentiate which has the easiest π_{2p}^* to remove, concentrate on the number of electrons in the orbitals attracted to the number of protons in the nucleus.

N_2^{2-} and N_2^- both have 14 protons in the two nuclei combined. Because N_2^{2-} has more electrons, one would expect N_2^{2-} to have more electron repulsions, which translates into having an easier electron to remove. Between O_2 and O_2^+ , the electron in O_2 should be easier to remove. O_2 has one more electron than O_2^+ , and one would expect the fewer electrons in O_2^+ to be better attracted to the nuclei (and harder to remove). Between N_2^{2-} and O_2 , both have 16 electrons; the difference is the number of protons in the nucleus. Because N_2^{2-} has two fewer protons than O_2 , one would expect the N_2^{2-} to have the easiest electron to remove which translates into the smallest ionization energy.

74.



The order from lowest IE to highest IE is: $O_2^- < O_2 < O_2^+ < O$.

The electrons for O_2^- , O_2 , and O_2^+ that are highest in energy are in the π_{2p}^* MOs. But for O_2^- , these electrons are paired. O_2^- should have the lowest ionization energy (its paired π_{2p}^* electron is easiest to remove). The species O_2^+ has an overall positive charge, making it harder to remove an electron from O_2^+ than from O_2 . The highest energy electrons for O (in the 2p atomic orbitals) are lower in energy than the π_{2p}^* electrons for the other species; O will have the highest ionization energy because it requires a larger quantity of energy to remove an electron from O as compared to the other species.

The Molecular Orbital (MO) Model

32. The localized electron model does not deal effectively with molecules containing unpaired electrons. We can draw all of the possible structures for NO with its odd number of valence electrons but still not have a good feel for whether the bond in NO is weaker or stronger than the bond in NO⁻. MO theory can handle odd electron species without any modifications. From the MO electron configurations, the bond order is 2.5 for NO and 2 for NO⁻ (see Exercise 14.31d for the electron configuration of NO⁻). Therefore, NO should have the stronger bond (and it does). In addition, hybrid orbital theory does not predict that NO⁻ is paramagnetic. The MO theory correctly makes this prediction.

36. H₂: (σ_{1s})²
 B₂: (σ_{2s})²(σ_{2s}*)²(π_{2p})²
 C₂²⁻: (σ_{2s})²(σ_{2s}*)²(π_{2p})⁴(σ_{2p})²
 OF: (σ_{2s})²(σ_{2s}*)²(σ_{2p})²(π_{2p})⁴(π_{2p}*)³

The bond strength will weaken if the electron removed comes from a bonding orbital. Of the molecules listed, H₂, B₂, and C₂²⁻ would be expected to have their bond strength weakened as an electron is removed. OF has the electron removed from an antibonding orbital, so its bond strength increases.

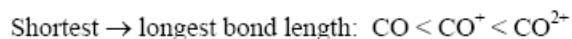
37. CN: (σ_{2s})²(σ_{2s}*)²(π_{2p})⁴(σ_{2p})¹
 NO: (σ_{2s})²(σ_{2s}*)²(π_{2p})⁴(σ_{2p})²(π_{2p}*)¹
 O₂²⁺: (σ_{2s})²(σ_{2s}*)²(σ_{2p})²(π_{2p})⁴
 N₂²⁺: (σ_{2s})²(σ_{2s}*)²(π_{2p})⁴

If the added electron goes into a bonding orbital, the bond order would increase, making the species more stable and more likely to form. Between CN and NO, CN would most likely form CN⁻ since the bond order increases (unlike NO⁻, where the added electron goes into an antibonding orbital). Between O₂²⁺ and N₂²⁺, N₂⁺ would most likely form since the bond order increases (unlike O₂²⁺ going to O₂⁺).

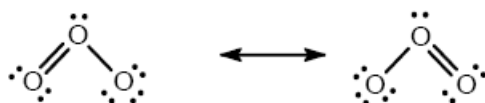
38. The electron configurations are (assuming the same orbital order as that for N_2):



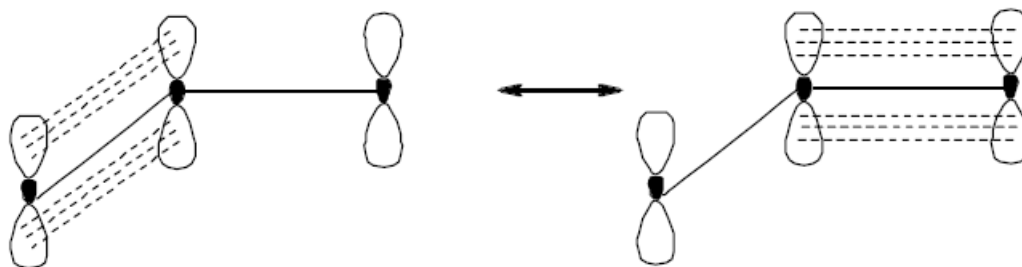
Because bond order is directly proportional to bond energy and, in turn, inversely proportional to bond length, the correct bond length order should be:



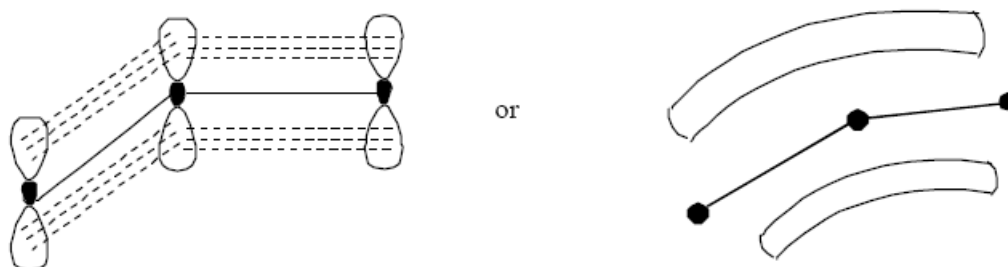
39. The π bonds between S atoms and between C and S atoms are not as strong. The atomic orbitals do not overlap with each other as well as the smaller atomic orbitals of C and O overlap.
40. There are 14 valence electrons in the MO electron configuration. Also, the valence shell is $n = 3$. Some possibilities from Row 3 having 14 valence electrons are Cl_2 , SCl^- , S_2^{2-} , and Ar_2^{2+} .
46. O_3 and NO_2^- are isoelectronic, so we only need consider one of them since the same bonding ideas apply to both. The Lewis structures for O_3 are:



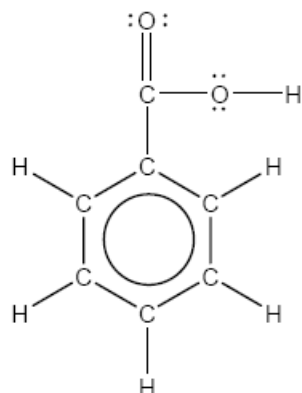
For each of the two resonance forms, the central O atom is sp^2 hybridized with one unhybridized p atomic orbital. The sp^2 hybrid orbitals are used to form the two sigma bonds to the central atom. The localized electron view of the π bond utilizes unhybridized p atomic orbitals. The π bond resonates between the two positions in the Lewis structures:



In the MO picture of the π bond, all three unhybridized p orbitals overlap at the same time, resulting in π electrons that are delocalized over the entire surface of the molecule. This is represented as:



48. Benzoic acid ($C_7H_6O_2$) has $7(4) + 6(1) + 2(6) = 46$ valence electrons. The Lewis structure for benzoic acid is:

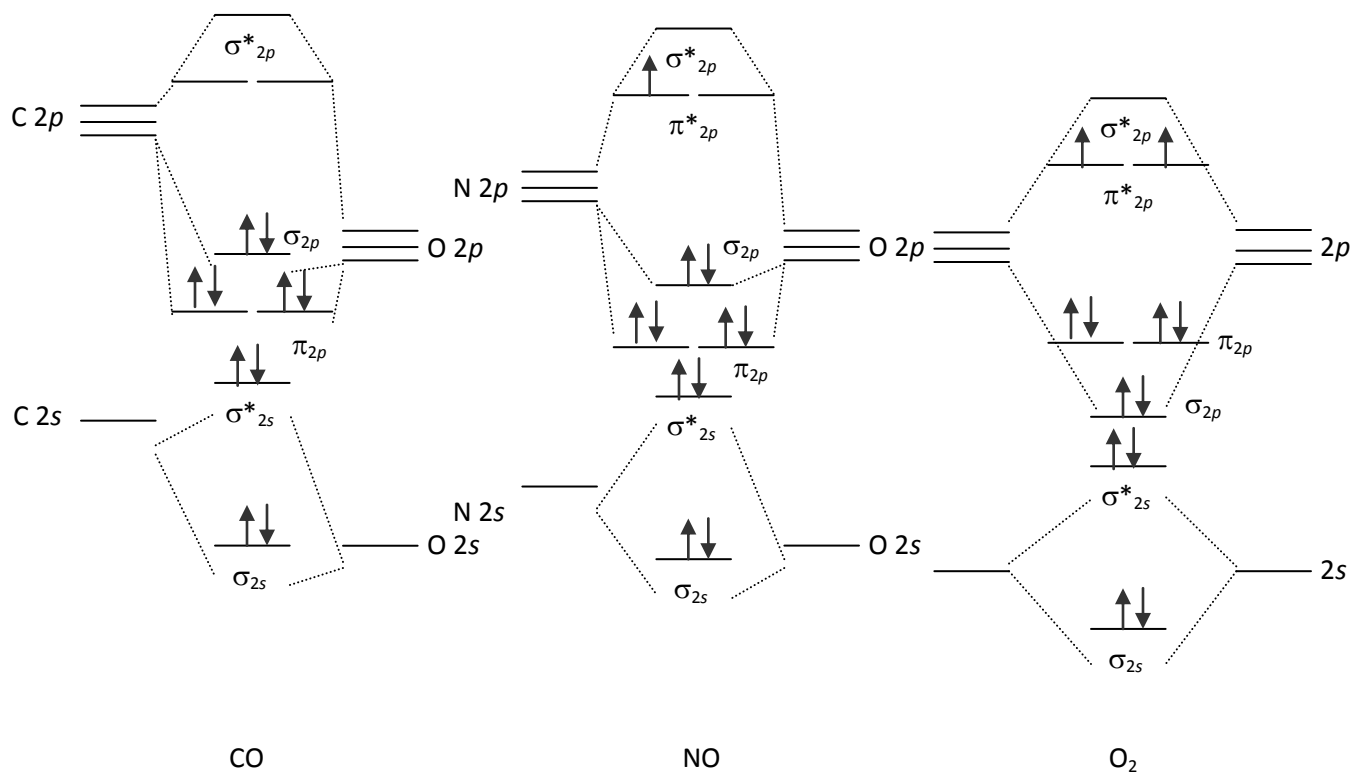


The circle in the ring indicates the delocalized π bonding in the benzene ring. The two benzene resonance Lewis structures have three alternating double bonds in the ring (see Figure 14.48).

The six carbons in the ring and the carbon bonded to the ring are all sp^2 hybridized. The five C-H sigma bonds are formed from overlap of the sp^2 hybridized carbon atoms with hydrogen 1s atomic orbitals. The seven C-C σ bonds are formed from head to head overlap of sp^2 hybrid orbitals from each carbon. The C-O single bond is formed from overlap of an sp^2 hybrid orbital on carbon with an sp^3 hybrid orbital from oxygen. The C-O σ bond in the double bond is formed from overlap of carbon sp^2 hybrid orbital with an oxygen sp^2 orbital. The π bond in the C-O double bond is formed from overlap of parallel p unhybridized atomic orbitals from C and O. The delocalized π bonding system in the ring is formed from overlap of all six unhybridized p atomic orbitals from the six carbon atoms. See Figure 14.50 for delocalized π bonding system in the benzene ring.

Assignment 12 Challenge Problem Solutions

1. a and b.



- c. CO: bond order = 3, diamagnetic.
 NO: bond order = 2.5, paramagnetic.
 O₂: bond order = 2, paramagnetic.
- d. CO has the strongest bond; O₂ has the weakest.
- e. We can order the ionization energies, from highest to lowest, as follows:
 CO > N > O > NO

Note that, based on the MO diagram (and trends in general), we might predict that the ionization energy of O is greater than that of N. But recall that there's an exception to the trend for N and O due to the electron configurations ($2s^22p^3$ for N vs. $2s^22p^4$ for O), so the IE of N is actually greater than that for O.

We also know $N > C$, and $O > O_2 > NO$, but we don't know how O₂ compares to N or how C compares to NO.

- f. The molecule with the smallest dipole moment is O₂. For this molecule, the electron density of all the MOs is distributed evenly between the two atoms. O₂ also displays no sp mixing, and the MO pictures should reflect that. The molecule with the largest dipole moment is CO. The orbital pictures should show sp mixing, and should show greater electron density around the O atom in the bonding MOs and greater electron density around the C atom in the antibonding MOs.

