

1. (10%) Explain why the bond order of N_2 is greater than that of N_2^+ , but the bond order of O_2 is less than that of O_2^+ .

Sol.

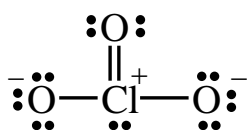
In forming the N_2^+ from N_2 , an electron is removed from the sigma *bonding* molecular orbital. Consequently, the bond order decreases to 2.5 from 3.0. In forming the O_2^+ ion from O_2 , an electron is removed from the pi *antibonding* molecular orbital. Consequently, the bond order increases to 2.5 from 2.0.

2. (10%) Draw three resonance structures for the chlorate ion, ClO_3^- . Show formal charges.

Sol.

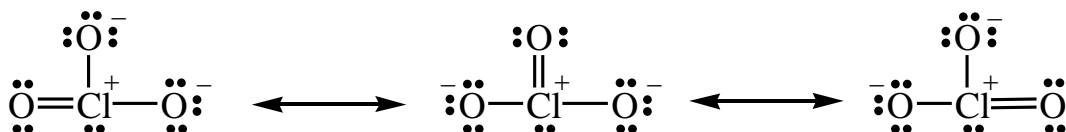
Strategy: We follow the procedure for drawing Lewis structures outlined in Section 3.4 of the text. After we complete the Lewis structure, we draw the resonance structures.

Solution: Following the procedure in Section 3.4 of the text, we come up with the following Lewis structure for ClO_3^- .

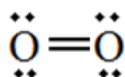


We can draw two more equivalent Lewis structures with the double bond between Cl and a different oxygen atom.

The resonance structures with formal charges are as follows:



3. (5%) Use the molecular orbital energy-level diagram for O_2 to show that the following Lewis structure corresponds to an excited state:



Sol.

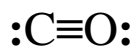
The Lewis structure shows 4 pairs of electrons on the two oxygen atoms. From Table 3.4 of the text, we see that these 8 valence electrons are placed in the

σ_{2p_x} , π_{2p_y} , π_{2p_z} , $\pi_{2p_y}^*$, and $\pi_{2p_z}^*$ orbitals. For all the electrons to be paired, energy is

needed to flip the spin in one of the antibonding molecular orbitals ($\pi_{2p_y}^*$ or $\pi_{2p_z}^*$).

According to Hund's rule, this arrangement is less stable than the ground-state configuration shown in Table 3.4, and hence the Lewis structure shown actually corresponds to an excited state of the oxygen molecule.

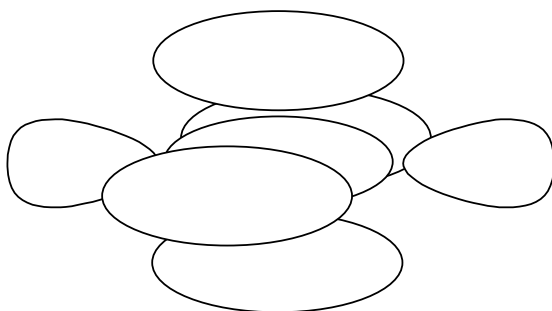
4. (10%) A reasonable Lewis structure for carbon monoxide (CO) is



Sketch the orbital overlap in the VB description corresponding to this Lewis structure. In this description, where do the lone pair reside?

Sol.

The bonding orbitals, depicted below, are due to the overlap of the p -orbitals. The lone pairs of electrons remain in the $2s$ orbitals on each atoms (not shown in the illustration below).

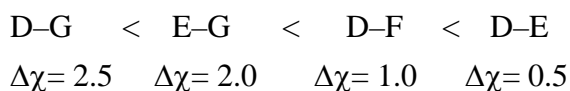


5. (5%) Four atoms are arbitrarily labeled D, E, F and G. Their electronegativities are as follows: D = 3.8, E = 3.3, F = 2.8 and G = 1.3. If the atoms of these elements form the molecules DE, DG, EG and DF, how would you arrange these molecules in order of increasing covalent bond character?

Sol.

The smaller the electronegativity difference between the atoms, the more covalent character the bonds have. Remember that the difference in electronegativity ($\Delta\chi$) is always positive.

Below the bonds are listed in order of increasing covalent character:



6. (10%) The dipole moment of HF is 1.92 D. Given that the H—F bond length is 91.7 pm, calculate the separated charge q , assuming the point charge model.
(1D = 3.336×10^{-30} C m)

Sol.

For the point charge model, the dipole moment is equal to the size of the charge times the distance between the charges (Equation 4.1). Hence, the charge is equal to the dipole moment divided by the distance between the charges. For this problem we also have to know that 1 Debye equals 3.336×10^{-30} C m and that a pm equals 10^{-12} m.

$$q = \frac{\mu}{r} = \left(\frac{1.92 \cancel{\text{D}} \left(\frac{3.336 \times 10^{-30} \text{ C m}}{1 \text{ D}} \right)}{91.7 \cancel{\text{pm}} \left(\frac{10^{-12} \text{ m}}{1 \text{ pm}} \right)} \right) = 6.98 \times 10^{-20}$$

Which is equal to 44% the charge of an electron. So, of the two bonding electrons, 22% stays on the fluorine giving the fluorine atom a negative charge, 22% is missing from the hydrogen, giving it a positive charge.

7. (10%) In 1998 scientists using a special type of electron microscope were able to measure the force needed to break a single chemical bond. If 2.0×10^{-9} N was needed to break a C—Si bond, estimate the bond dissociation energy in kJ mol^{-1} . Assume that the bond had to be stretched by a distance of 2 Å (2×10^{-10} m) before it was broken.

Sol.

$$\begin{aligned} \text{Work done} &= \text{force} \times \text{distance} \\ &= (2.0 \times 10^{-9} \text{ N}) \times (2 \times 10^{-10} \text{ m}) \end{aligned}$$

$$\begin{aligned} \square\square\square\square\square\square\square &= 4 \times 10^{-19} \text{ N}\cdot\text{m} \\ &= 4 \times 10^{-19} \text{ J to break one bond} \end{aligned}$$

Expressing the bond enthalpy in kJ mol^{-1} :

$$\frac{4 \times 10^{-19} \text{ J}}{1 \text{ bond}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.022 \times 10^{23} \text{ bonds}}{1 \text{ mol}} = 2 \times 10^2 \text{ kJ mol}^{-1}$$

8. (10%) Compare the MO theory description for the H_2 molecule given by Equation

3.10 with the VB theory treatment given in Equation 3.1. Under what condition do they become identical?

$$(\text{Equation 3.1: } \psi_{VB} = N[\phi_{A,1s}(1)\phi_{B,1s}(2) + \phi_{B,1s}(1) + \phi_{A,1s}(2)])$$

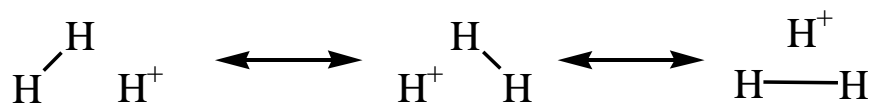
$$\text{Equation 3.10: } \psi_{H_2} \approx \sigma_{1s}(1) \sigma_{1s}(2) = \frac{1}{\sqrt{2}} [\phi_{A,1s}(1) + \phi_{B,1s}(1)] [\phi_{A,1s}(2) + \phi_{B,1s}(2)]$$

Sol.

The wavefunction determined from molecular orbital (MO) theory contains the same terms as the wavefunction determined from valence bond (VB) theory.

The wavefunction determined from MO theory also contains terms corresponding to both electrons being on the same atom. If the likelihood of the two electrons being on the same atom is negligible (such as for a homonuclear diatomic molecule), then the wavefunctions from the two theories are identical.

9. (5%) The species H_3^+ is the simplest polyatomic ion. The geometry of the ion is that of an equilateral triangle. Draw three resonance structures to represent the ion.
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10. (5%) Which of the following molecules has the shortest nitrogen-to-nitrogen bond: N_2H_4 , N_2O , N_2 , and N_2O_4 . Explain.

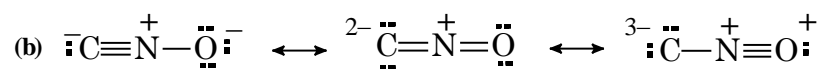
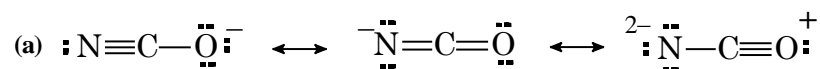
Sol.

Only N_2 has a triple bond. Therefore, it has the shortest bond length.

11. (10%) Write three resonance structures for (a) the cyanate ion (NCO^-) and (b) the isocyanate ion (CNO^-). In each case, rank the resonance structures in order of increasing importance.

Sol.

The resonance structures are:

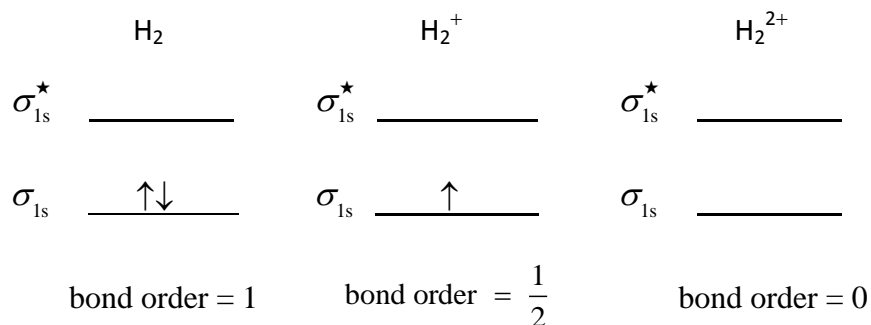


In both cases, the most likely structure is on the left and the least likely structure is on the right.

12. (5%) Explain in molecular orbital terms the changes in H—H internuclear distance that occur as the molecular H_2 is ionized first to H_2^+ and then to H_2^{2+} .

Sol.

The molecular orbital electron configuration and bond order of each species is shown below.



The internuclear distance in the +1 ion should be greater than that in the neutral hydrogen molecule. The distance in the +2 ion will be very large because there is no bond (bond order zero).

13. (5%) Which of the following species are tetrahedral? SiCl_4 , SeF_4 , XeF_4 , Cl_4 , or CdCl_4^{2-} .

Sol.

SiCl_4 , Cl_4 , and CdCl_4^{2-} would all be tetrahedral.