CHAPTER 8 & 9 PROBLEMS



All questions listed below are problems taken from old Chemistry 121 exams given here at The Ohio State University. Read Chapters 8 and 9 and complete the following problems. These problems will not be graded or collected, but will be very similar to what you will see on an exam.

Lewis Structures

For each of the following molecules complete the following:

- (a) Total # of valence electrons
- (b) Identify the Central Atom
- (c) Identify the Ligands
- (d) Indicate the number of bonding pairs on the central atom
- (e) Indicate the number of lone pairs on the central atom
- (f) Indicate the electron domain geometry of the molecule
- (g) Indicate the molecular geometry of the molecule
- (h) Determine the hybridization of the central atom
- (i) Draw the molecule
- (j) Determine if the molecule is polar or non-polar
- 1. SiCl₄
- 2. PF₃
- 3. ClF₃
- 4. VF₅
- 5. SiH₄
- 6. SF₂
- 7. BeCl₂
- 8. NH₃
- 9. SF₄
- 10. BrF₃
- 11. XeF₂
- 12. SF₄
- 13. ICl₃
- 14. XeF₄
- 15. BrF₅
- 16. BrF₄+
- 17. BrF₄-
- 18. ICl₂-
- 19. ICl₂+

Lewis Structures and Resonance Structures

For each of the following molecules complete the following:

- (a) Total # of valence electrons
- (b) Identify the Central Atom
- (c) Identify the Ligands
- (d) Indicate the number of bonding pairs on the central atom
- (e) Indicate the number of lone pairs on the central atom
- (f) Indicate the electron domain geometry of the molecule
- (g) Indicate the molecular geometry of the molecule
- (h) Determine the hybridization of the central atom
- (i) Draw the molecule
- (j) Predict the structure according to the octet rule
- (k) Predict the structure according to formal charges
- (l) Draw any appropriate resonance structures
- 1. NO₂-
- 2. NO₃-
- 3. CO₃²⁻
- 4. SO₄²-
- 5. SO₃2-
- 6. PO₃²-
- 7. PO₄³-
- 8. ClO₃-
- 9. ClO₂-
- 10. SOCl₂
- 11. XeOF₂
- 12. $XeOF_4$
- $13. \ XeO_3F_2$
- 14. XeF₄

Hybrid Orbitals

- 1. List and sketch the five different electron domain geometries using 3-dimensional wedges and dashed lines when needed. Also indicate the hybridization and bond angles for each model.
- 2. Sketch one s orbital and one p orbital (be sure to include shading when needed) and add the two wave functions together to sketch an "sp" hybrid.
- 3. Sketch one s orbital and two p orbitals (be sure to include shading when needed) and add the three wave functions together to sketch an "sp²" hybrid.
- 4. Sketch one s orbital and three p orbitals (be sure to include shading when needed) and add the four wave functions together to sketch an "sp³" hybrid.
- 5. (a) Draw a σ bond between two s orbitals. (b) Draw a σ bond between two p orbitals. (c) Draw a π bond between two p orbitals.
- 6. Figure 9.15 listed on page 356 of the textbook shows the potential energy of two hydrogen atoms as a function of the distance between them. (a) To what does a zero energy correspond in the diagram?

- (b) According to valence bond theory, why does the energy decrease as the H atoms move from a large separation to a small one? (c) What is the significance of the H-H bond distance at the minimum point in the plot? (d) Why does the energy rise at the H-H distances less than the minimum point in the plot?
- 7. The molecule difluoromethane (CH_2F_2) is used as a refrigerant. Sketch the Lewis structure and determine if the molecule has a non-zero dipole moment. If the molecule is polar, in what direction does the overall dipole moment vector point in the molecule?
- 8. Consider the hydrocarbon shown below.

$$H - C = C - C - C = C - C - H$$

- (a) What is the hybridization at each carbon atom in the molecule? (b) How many σ and how many π bonds are there in the molecule?
- 9. Consider the bonding in an MgH_2 molecule. (a) Draw the Lewis structure and predict its molecular geometry. (b) Before forming the hybrid orbitals on the central atom Mg, the Mg atom must exist in an excited state. Why does this excited state have to occur to allow the Mg to hybridize? (c) What is the hybridization on the Mg central atom? (d) Sketch the two bonds between the Mg hybrids and the two H 1s orbitals. Are these σ or π bonds?
- 10. (a) Draw a Lewis structure for SiH₄ and predict its molecular geometry. (b) What is the hybridization of the central atom Si in SiH₄? (c) What must happen to a ground state Si atom in order for hybridization to occur? (d) Sketch the four bonds that occur between the hybrid orbitals on the Si central atom and the four H 1s orbitals. (e) What is the bond angle that forms between each bond?
- 11. (a) If the valence atomic orbitals on an atom are sp hybridized, how many unhybridized p orbitals remain in the valence shell? How many π bonds can the atom form? (b) If the valence atomic orbitals on an atom are sp^2 hybridized, how many unhybridized p orbitals remain in the valence shell? How many π bonds can the atom form? (c) If the valence atomic orbitals on an atom are sp^3 hybridized, how many unhybridized p orbitals remain in the valence shell? How many π bonds can the atom form?
- 12. (a) Draw Lewis structures for methane (CH₄) and formaldehyde (H₂CO). (b) What is the hybridization at the carbon atom in CH₄ and H₂CO? (c) The carbon atom in H₂CO can form multiple bonds, whereas CH₄ can only form single bonds. Explain this observation using the hybridization at the central carbon atom.
- 13. The nitrogen atoms in N_2 form multiple bonds, while the nitrogen atoms in N_2H_4 do not. How can you explain this observation?

14. Ethyl acetate, C₄H₈O₂, is shown below.

- (a) What is the hybridization at each of the carbon atoms in this molecule? (b) How many σ and how many π bonds are there in the molecule? (c) What are the bond angles about each carbon atom?
- 15. Consider the Lewis structure for glycine shown below.

- (a) What are the approximate bond angles and hybridizations about each of the carbon and nitrogen atoms in the molecule? (b) How many σ and how many π bonds are there in the molecule?
- 16. (a) What is the difference between a localized and delocalized π bond in a molecule? (b) How can you determine whether a molecule or ion will exhibit delocalized π bonding? (c) Is the π bond in NO₂-localized or delocalized?
- 17. (a) What are the similarities and differences between atomic orbitals and molecular orbitals? (b) Why are the electrons in a bonding molecular orbital of H_2 at lower energy than the electron in a ground state hydrogen atom? (c) How many electrons can be placed in each molecular orbital of a molecule?
- 18. (a) Why is the anti-bonding molecular orbital in an H_2 molecule at a higher energy than the 1s orbital in a ground state hydrogen atom? (b) If two p orbitals on one atom combine with two p orbitals on another atom, how many molecular orbitals result?
- 19. (a) Sketch the σ and σ^* molecular orbitals resulting from the combination of two p_z atomic orbitals. (b) Sketch the π and π^* MOs resulting from the combination of two p_y orbitals. (c) Assuming no mixing of the s and p orbitals, arrange the MOs from part (a) and (b) in order of increasing energy.
- 20. (a) What is the relationship between bond order, bond length, and bond energy? (b) According to molecular orbital theory, would Be₂ or Be₂+ be more stable? Why? Would you expect either molecule to exist?
- 21. (a) What is meant by the term diamagnetism? (b) How does a diamagnetic substance respond to a magnetic field? (c) Which of the following would you expect to be diamagnetic: N_2 , O_2^2 , Be_2^+ , C_2^- ?
- 22. (a) What is meant by the term paramagnetism? (b) How can you determine experimentally whether a substance is paramagnetic? (c) Which of the following would you expect to be paramagnetic: O_2^+ , N_2^{2-} , Li_2^+ , O_2^{2-} ?
- 23. Draw out the molecular orbital diagram for B_2^+ , Li_2^+ , N_2^+ , and Ne_2^+ . Would the addition of an electron stabilize or destabilize the resulting molecule?

- 24. Predict the bond order and magnetism of CO+, NO-, OF+, and NeF+.
- 25. Calculate the bond order and determine the magnetism for CN+, CN, and CN-. Which molecule/ion would molecular orbital theory predict to be the most stable?
- 26. The nitric oxide molecule readily loses one electron to form the NO+ ion. (a) Using molecular orbital theory, explain why this observation makes sense chemically. (b) Arrange the following in order of increasing bond strength: NO, NO+, NO- and indicate if each molecule/ion is paramagnetic or diamagnetic. (c) Isoelectronic species have the same number of electrons. With what neutral homonuclear diatomic molecule are the NO+ and NO- ions isoelectronic?
- 27. (a) Draw the molecular orbital diagram for IBr and determine its bond order. (b) Are the atomic orbitals for I or Br lower in energy? Why?
- 28. The molecules SiF_4 , SF_4 , and XeF_4 all have the same molecular formula AX_4 yet they have different geometries. Predict the shapes of each molecule and explain why the shapes are different.
- 29. The PF₃ molecule has a dipole moment of 1.03 D, but the BF₃ molecule has a dipole moment of zero. How can you explain this difference?
- 30. It is often observed that σ bonds involving an sp hybrid are shorter than those involving sp² or sp³ hybrid orbitals. Can you propose a reason for this?
- 31. The magnetic properties of a compound can be measured using an instrument called a Guoy balance. When the magnetic measurements are made, the sample is generally covered by an atmosphere of pure nitrogen gas rather than in air? Why do you suppose chemists go through the hassle of using a nitrogen atmosphere in these measurements?

From assigned HW: SICI4, PF3, CIF3, VF5,
SiH4, SF2, BeCl2, NH3, SF4, BrF3, XeF2

From class assignment: SF4, ICl3, Xef4, BrF5
BrF4, BrF4, ICl2*, ICl2*

Sicly

(c) e-domain: Tetrahedral

(e) hybridization: 5p3

CA: Pa 5 vale 8e -> 4pales > 11p e-domain: tetrahedral hybridization: Sp3 CIFZ CA: Cl > 7 vale-10e-> 5 pairs > 21p > shape T-shaped e-Jonain = Trigonal Bypyramid Mybridization = 5p3d (... VF5 cA: V-> 5 vale-F> 5(le-) 10e - 5 pairs > 01p > molecular shape Trigonal By pyramid e-domain: Trigonal (For V-FI non-palar Pypyramid hybrid: sp32

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10e-> 5 pairs > 11p > shape = See-Saw F> 4(le-) e- Jonan: Trigoral By pyramid Whid: sp3d Brfz Br: 7 wle-F: 3(1e-) 10e-> 5 pairs > 21p > shape = T-Shape e- Jamain: Trigonal By pyramid hydrið: sp3d

XeFz (Xe: 8 vale-F: 2(le-) 10e-> 5 pairs > 3 lp > Modec.

Shape e-Journ = Trigonal Bypyramid Hybrid: 5p3d SFy: See above ICIZ I > 7 vale-(1-) 3(le-) e-Jomain: Trigonal Bypyrumil

hydrid: sp3d

 $\left(\frac{1}{2}\right)$

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5 bp 7 Modec = Square

12e- > 6 pours > 11p 5 shape = Pyramid

Br: 7 vale

F: 5(le)

12e-> 6 pairs > 1/p > shape = Square

Pyramid

e-domain = Octahedral

hybrid = 5p3d2

IF- Bri FI

(#)

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hybrid: sp3d

[F]

pdar

[E] BrFy Br: 7 vale-F: 4(1e-) charge + 1e 7 6pws 7 21p Shape

e-domain = Octatedral

hybrid: 5p3d2

IF-Br-FI

how

NO2

CA: N >5 Vale

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3prins John Johnson 0: (0e-)3 -: <u>ic</u> be->

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0: 4(0e)

7 Tetrahedral

2-: 2e

8e-> 4poirs > 01p 10-5-01 s can expand its octet!

This leads to DAFferent structures |O| = |O|Use formal Charge to determine the correct structure

A When an expanded octet is passible, formal charge rules will predict a structure in which the charge on the oxpanion is equal to the # of single bands formed by oxygen + the Central Atom. $\begin{array}{c|c}
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0:3(0e)

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\overline{10} - 5 - \overline{01}
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\overline{10} - 5 - \overline{01} \\
\overline{10} - 5 - \overline{01}
\end{array}\right)$

resonance

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 $3: 3e^{-}$
 $8e^{-} \Rightarrow 4pwis$

P can expand

 $10 - P - 01$
 $10 - P - 01$

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$$2(0e)$$

-: $1e^{-}$
 $8e^{-}$

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2 lp S

but C1 cam

expand its extet

 $10 - C1$
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 101

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$$|CII|$$

Xe OFz

Xe: 8 vale =

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5pd = edomini = Trigonal

Bypyramid

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17- Shaped

17|

Xe can expand

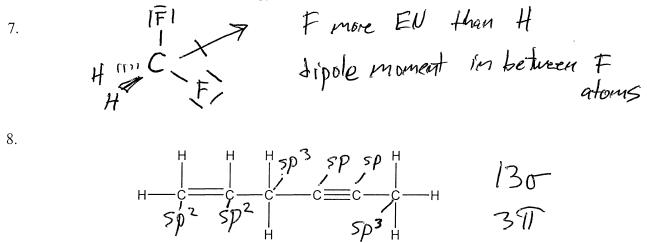
F.C. give:

17|

IFI IFI IFI Xe OF4 Xe: Svale 5p3d2 e Journin = Octahedron D= 1(0=) F: 4(le-) 12e > 6 pales > 1/p Pyramid Xe con expand F.C. predict: (F., 11. E)

Xe03/2 Xe: Sule sp³d = demain = Trigoral
Bypyramid 0 = 3(0e) 10e > 5 pairs > 0/p > Mdec = Trigonal
Bypyramis F: 2(le-) Xe con expand F.C. predict:

6. (a) The zero energy corresponds to the energies of the hydrogen atomic orbitals. (b) The overlap of the 1s orbitals increases. (c) It is the equilibrium bond distance. (d) The nucleus is positively charged and if the H – H distance gets too close the nuclei will repel each other and increase the overall energy.



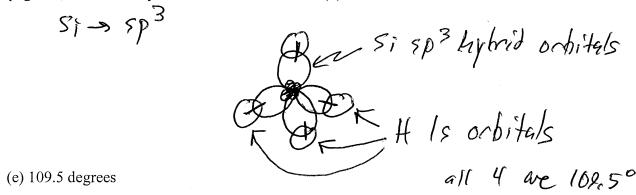
9. (a) H - Mg - H is linear in its electron domain and molecular geometry. (b) The Mg atom has 2 electrons in its 2s orbital; these electrons are paired. Without promotion to an sp excited state, Mg has no unpaired electrons available to form bonds with hydrogen. (c) sp (d)

(d)

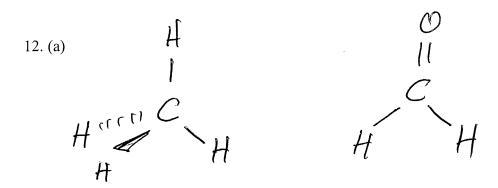
Has no unparted electrons available to form bonds with I sp hybrid on Mg

bond

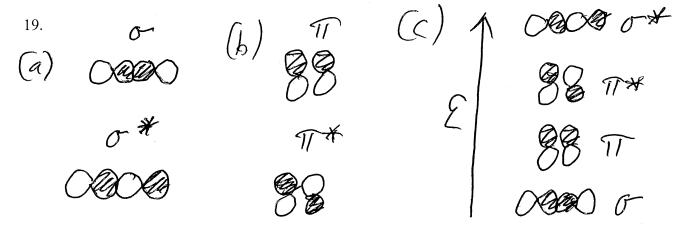
10. (a) SiH₄ has a tetrahedral electron domain and molecular geometries. (b) sp³ (c) See page 364. The same hybridization occurs in CH₄. (d)



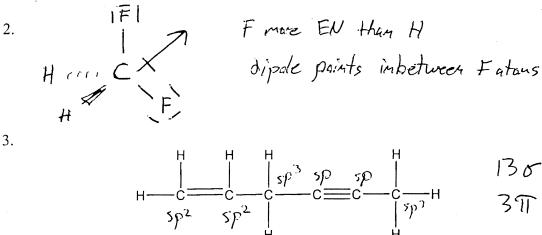
11. (a) There are two unhybridized p orbitals in an sp hybrid set. These two orbitals can form 2 π bonds. (b) There is one unhybridized p orbital in an sp² hybrid. This hybrid can form one π bond. (c) There are zero unhybridized p orbitals in an sp³ hybrid. This hybrid cannot form any π bonds.



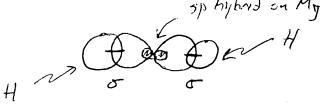
- (b) sp^3 and sp^2 (c) The C atom in CH₄ is sp^3 hybridized; there are no unhybridized p orbitals available for the π overlap required for a multiple bond. In CH₂O the C atom is sp^2 hybridized, which allows one of the π orbitals to form a multiple bond. In this case a carbon oxygen double bond.
- 13. In N_2 the hybridization is sp, while in N_2H_4 the hybridization is sp³. In an sp³ hybrid there are no p orbitals available for multiple bonding. In sp hybridization the two unhybridized p orbitals are available for multiple bonding.
- 14. (a) sp³, sp², sp³, and sp³ (b) 12 sigma and 1 pi (c) all the sp³ angles are 109.5 degrees and the sp² angles are 120 degrees.
- 15. (a) all the sp³ angles are 109.5 degrees and the sp² angles are 120 degrees. (b) 9 sigma and 1 pi bond
- 16. (a) In a localized π bond, the electron density is concentrated between the two atoms forming the bond. In a delocalized π bond, the electron density is spread over all the atoms that contribute p orbitals in the bonding network.
- 17. (a) Both atomic and molecular orbitals have a characteristic energy and shape; each can hold a maximum of two electrons; Atomic orbitals are localized with their energies resulting from the interactions between subatomic particles in a single atom. Molecular orbitals can delocalize and their energies are influenced by interactions between electrons on several atoms. (b) There is a net lowering in energy that accompanies bond formation because the electrons in H₂ are attracted to both H nuclei. (c) 2
- 18. (a) This stems from the law of conservation of energy. Each bonding interaction must be accompanied by an antibonding interaction. (b) 4



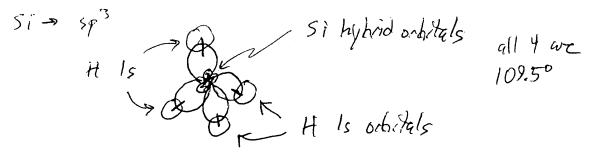
1. (a) The zero energy corresponds to the energies of the hydrogen atomic orbitals. (b) The overlap of the 1s orbitals increases. (c) It is the equilibrium bond distance. (d) The nucleus is positively charged and if the H – H distance gets too close the nuclei will repel each other and increase the overall energy.



4. (a) H - Mg - H is linear in its electron domain and molecular geometry. (b) The Mg atom has 2 electrons in its 2s orbital; these electrons are paired. Without promotion to an sp excited state, Mg has no unpaired electrons available to form bonds with hydrogen. (c) sp (d)

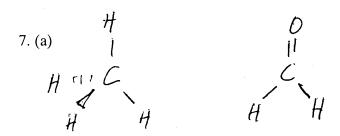


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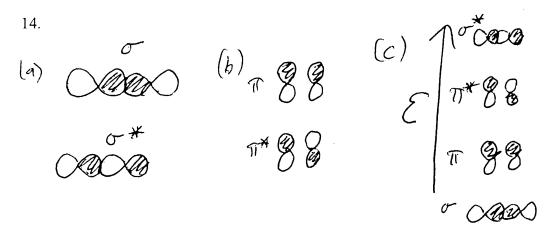


(e) 109.5 degrees

6. (a) There are two unhybridized p orbitals in an sp hybrid set. These two orbitals can form 2 π bonds. (b) There is one unhybridized p orbital in an sp² hybrid. This hybrid can form one π bond. (c) There are zero unhybridized p orbitals in an sp³ hybrid. This hybrid cannot form any π bonds.



- (b) sp³ and sp² (c) The C atom in CH₄ is sp³ hybridized; there are no unhybridized p orbitals available for the π overlap required for a multiple bond. In CH₂O the C atom is sp² hybridized, which allows one of the π orbitals to form a multiple bond. In this case a carbon oxygen double bond.
- 8. In N_2 the hybridization is sp, while in N_2H_4 the hybridization is sp³. In an sp³ hybrid there are no p orbitals available for multiple bonding. In sp hybridization the two unhybridized p orbitals are available for multiple bonding.
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- 13. (a) This stems from the law of conservation of energy. Each bonding interaction must be accompanied by an antibonding interaction. (b) 4



20. (a) When comparing the same two bonded atoms, bond order and bond energy are directly related, while bond order and bond length are inversely related. (b) Be₂ has a bond order of zero and it is not expected to exist. Be₂⁺ has a bond order of 0.5 and is slightly favored over isolated Be atoms and would most likely exist under extreme conditions.

21. (a, b) A diamagnetic substance does not have any unpaired electrons. These substances are not attracted to a magnetic field. (c) ${\rm O_2}^{2^-}$ and ${\rm Be_2}^{2^+}$

22. (a, b) A paramagnetic substance has unpaired electrons. These substances are attracted to a magnetic field. (c) O_2^+ , $N_2^{2^-}$, and Li^+

Adding an e to Bz puts an e into a bonding M.D. La stabilization (1 B.O.) Lizt

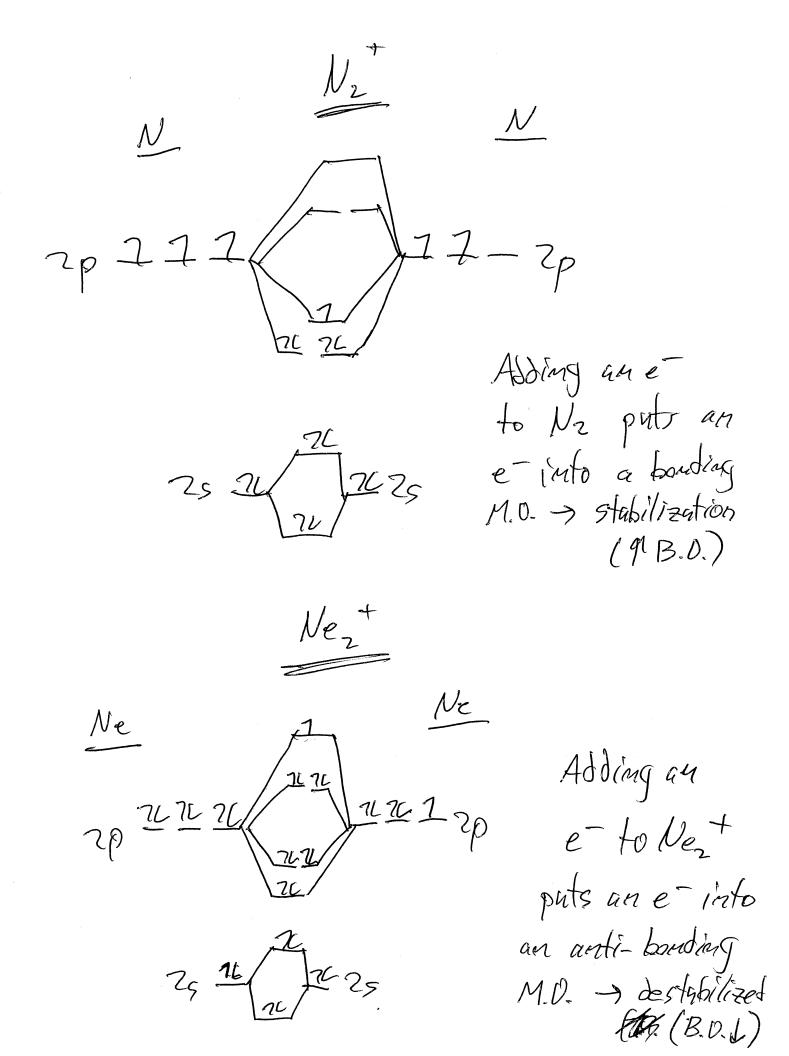
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Adding ame to Lizt

puts rue = into 9

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bonding M.O. Stabilization (MBU)



- 24. CO⁺ has a bond order of 2.5 and it is paramagnetic. NO⁻ has a bond order of 2 and it is paramagnetic. OF⁺ has a bond order of 2 and is paramagnetic. NeF⁺ has a bond order of 1 and it is diamagnetic.
- 25. CN^+ has a bond order of 2 and is paramagnetic. CN^- has a bond order of 3 and is diamagnetic. CN has a bond order of 2.5 and is paramagnetic. Molecular orbital theory predicts the following trend [most stable] $CN^- > CN > CN^+$ [least stable]
- 26. (a) The electron is taken away from an anti-bonding molecular orbital and upon removal the bond order increases, making NO^+ more stable. (b) [weakest bond] $NO^- < NO < NO^+$ [strongest bond]. NO and NO^- are paramagnetic and NO^+ is diamagnetic. (c) NO^+ is isoelectronic with N_2 and NO^- is isoelectronic with O_2 .
- 27. (a) Bond Order = 1 (b) The atomic orbitals for I are lower in energy because the I is more electronegative than the Br.
- 28. SiF₄ is tetrahedral, SF₄ is see-saw, and XeF₄ is square planar. The shapes are different because the number of pairs of electrons about the central atom is different leading to a difference in electron domain geometries.
- 29. The PF₃ molecule has a trigonal pyramid molecular geometry due to the lone pair on the central atom. This lone pair makes the PF₃ molecule polar, whereas in BF₃ the electron domain geometry is trigonal planar with no lone pairs of electrons around the B central atom and this molecule is non-polar.
- 30. In an sp hybrid the central atom can form a triple bond or two double bonds. An sp² hybrid can form one double bond, but never a triple bond, while and sp³ hybrid can only form single bonds.
- 31. Air contains O_2 , which is paramagnetic. Any measurements made in an oxygen atmosphere could potentially give false positive results for paramagnetism due to the presence of O_2 . N_2 is diamagnetic and would have a magnetic moment of zero and would have no influence on the Guoy balance measurements.