

Week 9 Discussion Worksheet Answers

1) Let's consider the Born-Oppenheimer approximation.

a) Explain what the Born-Oppenheimer approx is and when it is valid.

Generally, nuclei move much slower than electrons and hence we can assume the nuclei are static; solve for the electronic wavefunction given a particular configuration of nuclei. That is we can separate the nuclear degrees of freedom from the electronic degrees of freedom. It is valid when the nuclei (ie potential generated by nuclei) moves much slower than the electrons.

b) Calculate the de Broglie wavelength of a hydrogen atom at 300K. Compare this to the diameter, 1 \AA . What can you conclude about quantum effects.

$$\frac{1}{2} m v^2 = \frac{3}{2} k_B T$$

$$\Rightarrow v = \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{(1.38 \times 10^{-23} \text{ J})(300 \text{ K})}{1.672 \times 10^{-27} \text{ kg}}} = 2725 \text{ m/s}$$

$$p = m v = (1.672 \times 10^{-27} \text{ kg})(2725 \text{ m/s}) = 4.55 \times 10^{-24} \text{ kg m/s}$$

$$\lambda_{DB} = \frac{h}{p} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{4.55 \times 10^{-24} \text{ kg m/s}} = 1.45 \times 10^{-10} \text{ m} = 1.45 \text{ \AA}$$

$\lambda_{DB} >$ diameter \Rightarrow we have quantum effects. Only if $\lambda_{DB} \ll$ objects size can we ignore quantum effects.

c) Compare the velocity to that of an electron, $\sim 2200 \text{ km/s}$. At what temperature would the hydrogen atom have to be at to be moving at around the same speed of an electron? Is this realistic?

At 300 K, $V = 2725 \text{ m/s} \ll \text{ speed of electron?}$

Now $2200 \text{ Km/s} = 2200000 \text{ m/s.}$

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T \Rightarrow \frac{mv^2}{k_B} = T$$

$$\frac{(1.672 \times 10^{-27} \text{ kg})(2200000)^2}{1.38 \times 10^{-23} \text{ J/K}} = 586411594 \text{ K}$$

$$\sim 5.8 \times 10^8 \text{ K}$$

Not a realistic temperature?

- d) Based upon the previous parts, does your analysis support or illustrate a flaw in the Born-Oppenheimer approximation?

This all supports the Born-Oppenheimer approx?
Speed of H < speed of electron.

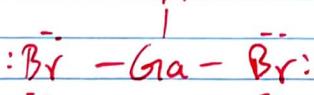
While we may have quantum effects of H, they will be much slower than in general.

Note, the BO approx does break down when there is strong coupling between the nuclear coordinates to the electronic wavefunction.

- 2) Consider GraBr_3

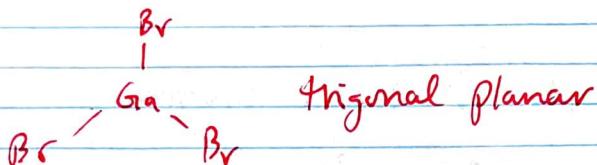
a) Draw the 2D Lewis dot structure

:Br:

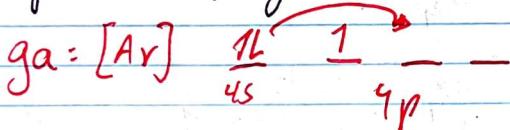


incomplete octet on Gra okay

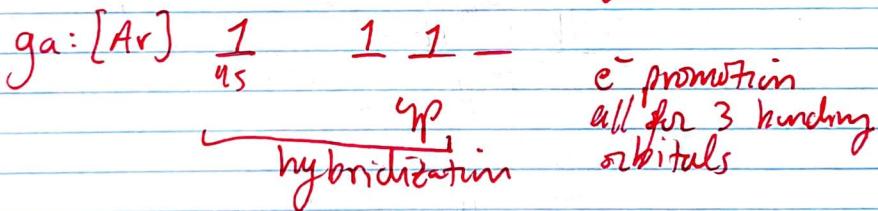
b) Draw the 3D VSEPR structure



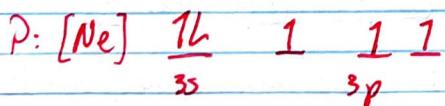
c) Using valence bond theory, determine the hybridization of the orbitals on the central atoms in GaBr_3 . Use noble gas shorthand orbital diagram to show any electron promotions / hybridization.



skip 3d orbitals since they are not valence e^-



3) Use valence bond theory to explain why formation of hybrid orbitals in PBr_3 does not require $\cancel{1L}$ promotion of an electron to a higher energy orbital, but formation of hybrid orbitals in PBr_3^- does.



PBr_3 only needs 3 bonding opportunities (half-filled orbitals) so no e^- promotion is needed before hybridization

To get 5 bonding opp, promote 1 $3s \rightarrow 3d$ to get 5 bonding location \Rightarrow hybridization occurs.

4) Consider the molecule N_2 .

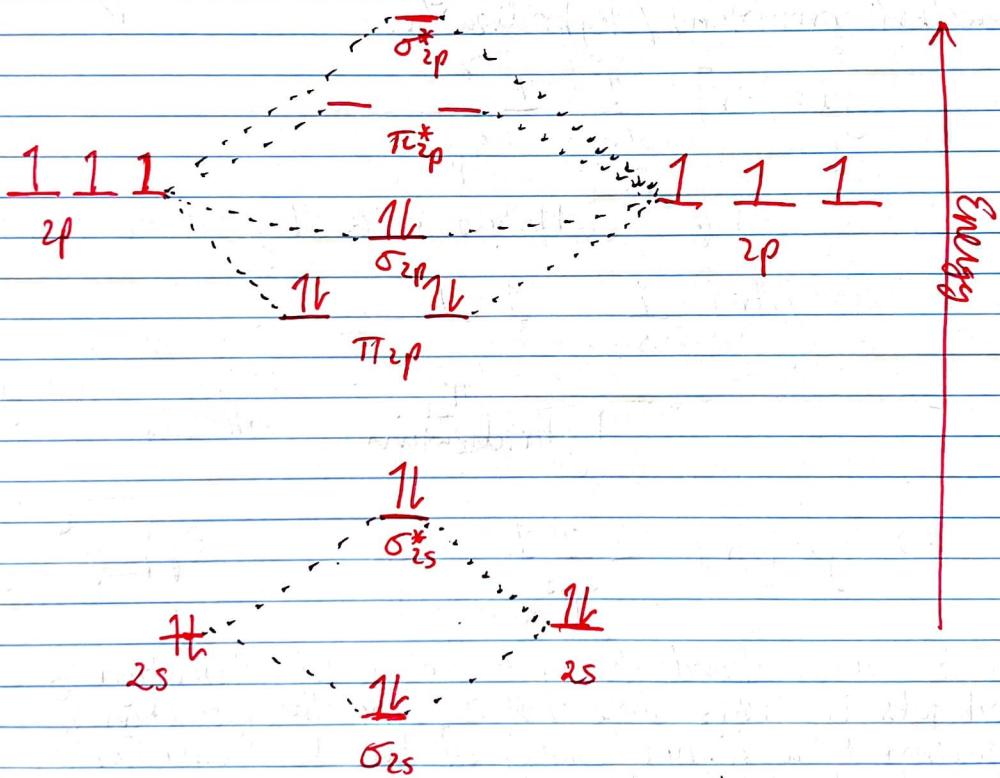
a) Draw the 2D Lewis dot structure.



b) Draw the 3D VSEPR structure.



c) Using an MO diagram, determine the bond order of N_2 .



$$BO = \frac{1}{2}(8 - 2) = 3 \Rightarrow \text{triple bond}$$

d) How many σ bonds does N_2 have? π-bonds?
label each bond.

1 σ ; 2 π bonds

$N(sp) - N(sp)$ σ bond

$N(p) - N(p)$ π bond × 2

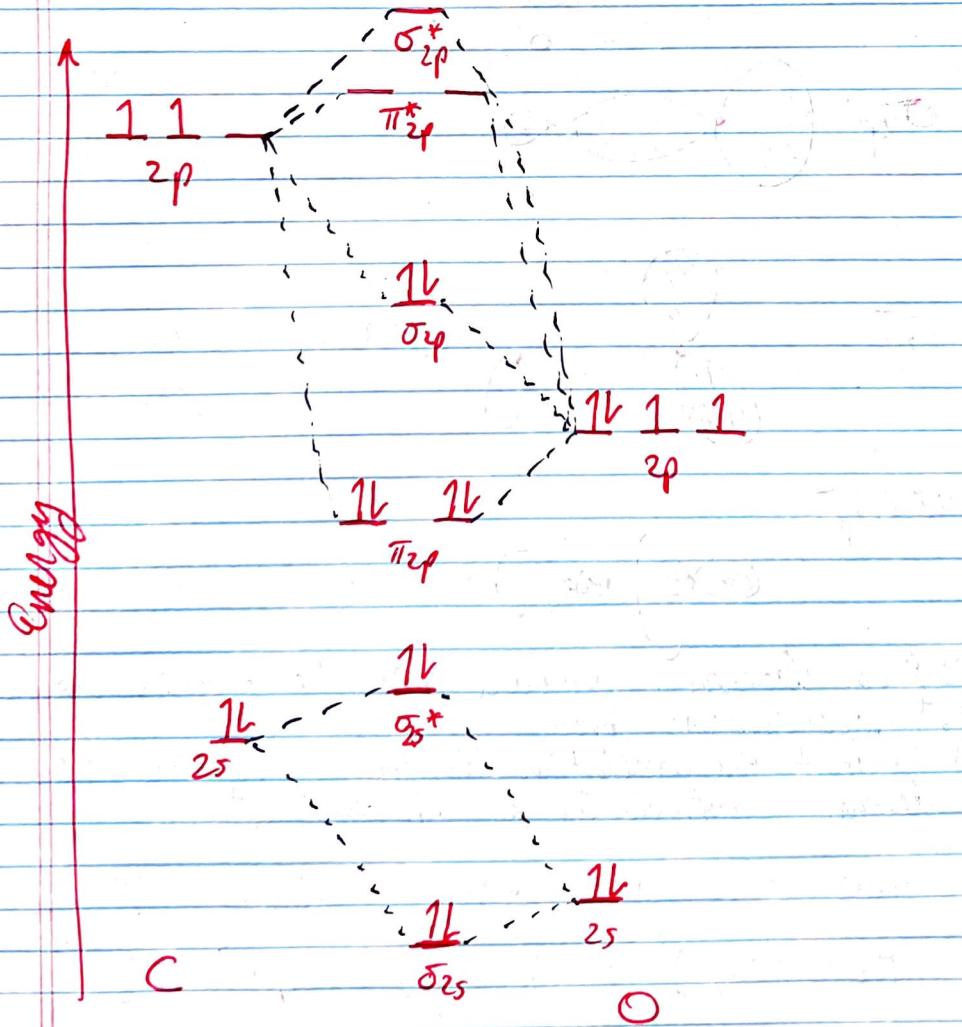
c) Which of the following should be diamagnetic?
 N_2 , N_2^+ , N_2^- . Why?

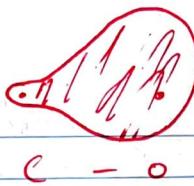
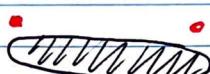
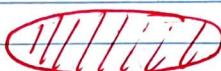
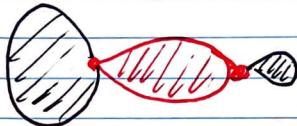
Diamagnetic \Rightarrow not magnetic \Rightarrow no unpaired e^- .

N_2 only to be diamagnetic.

N_2^+ : N_2^- will both have 1 unpaired e^- .

5) Draw the MO diagram for CO. Furthermore draw the rep. of each MO.



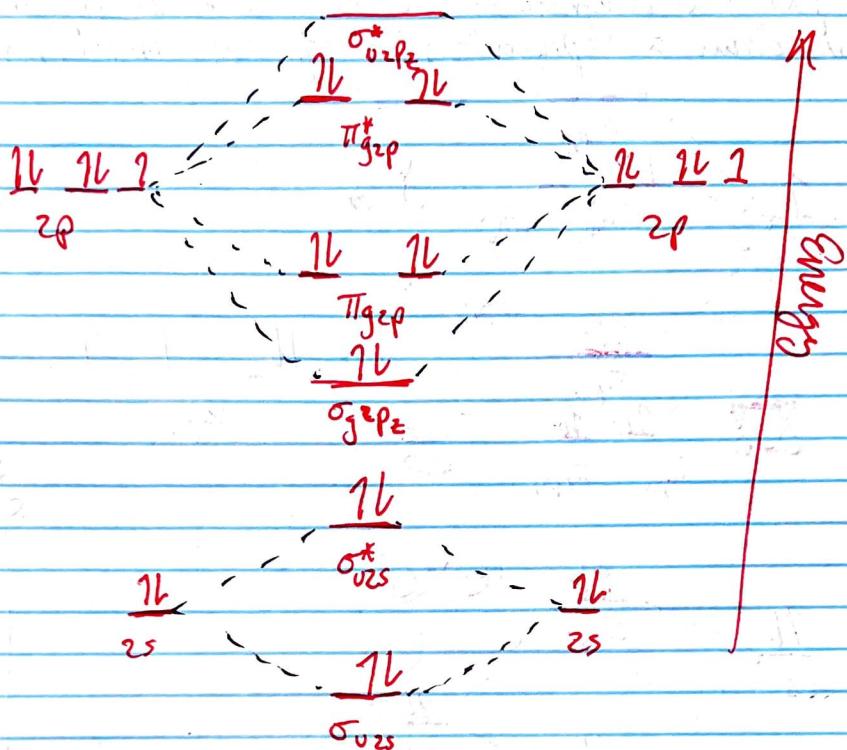
σ_{2s} : σ_{2s}^*  π_{2p}  $C - O$ σ_{2p}  π_{2p}^*  ~~σ_{2p}^*~~ 

- (e) If an electron is removed from the fluorine molecule, F_2^+ molecular ion forms
- Construct the correlation diagram and give the molecular electronic configurations for F_2 and F_2^+

Have 18 e⁻ in F_2 with 14 valence. F_2^+ has 13 valence

$$F_2: (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^1$$

$$F_2^+: (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^3$$



b) Give the bond order of each species.

$$F_2 = 1$$

$$F_2^+ = \frac{3}{2}$$

c) Predict which species should be paramagnetic
 F_2 has 0 unpaired e⁻

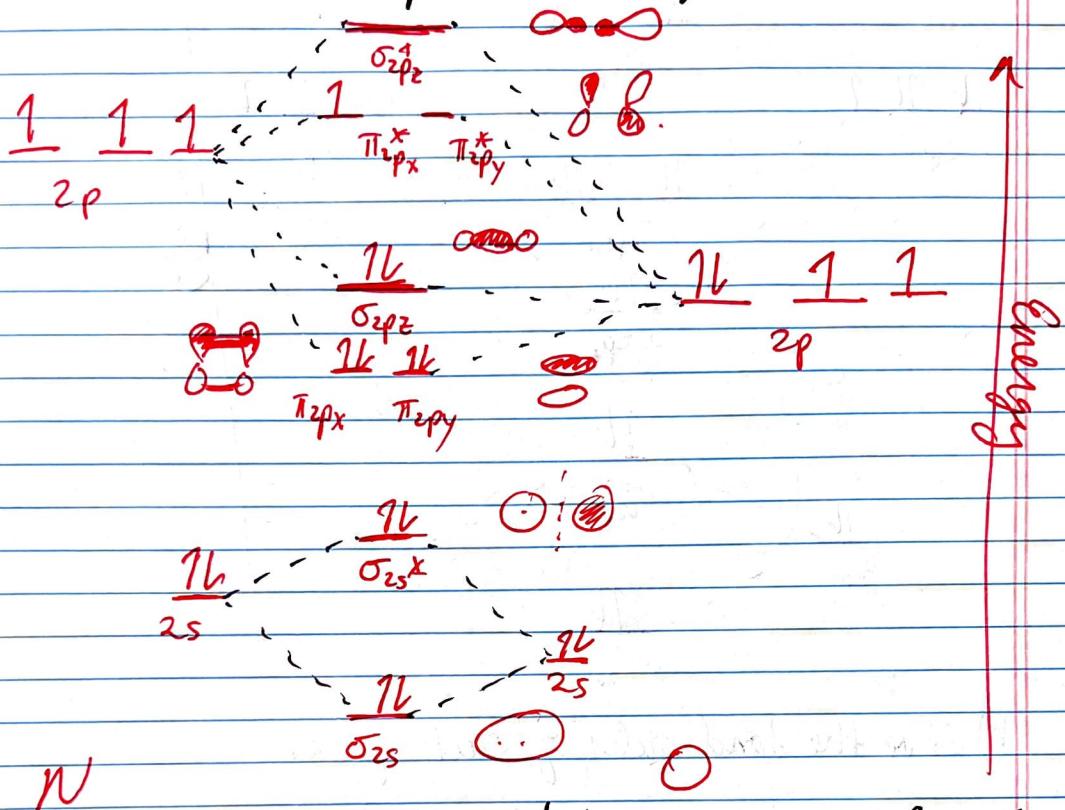
F_2^+ has 1 unpaired e⁻

F_2^+ should be paramagnetic.

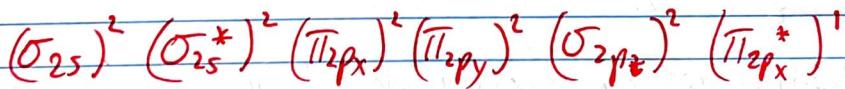
d) Predict which species has a greater BDE.

F_2^+ has larger bond order, hence it should have a larger BDE

7) a) Draw the MO diagram of NO. Next to each orbital or band, draw a representation of that orbital/band.



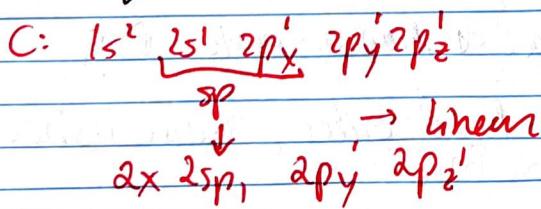
b) Write out the valence electron configuration for this molecule.



8) a) Draw the Lewis structure of HCN.



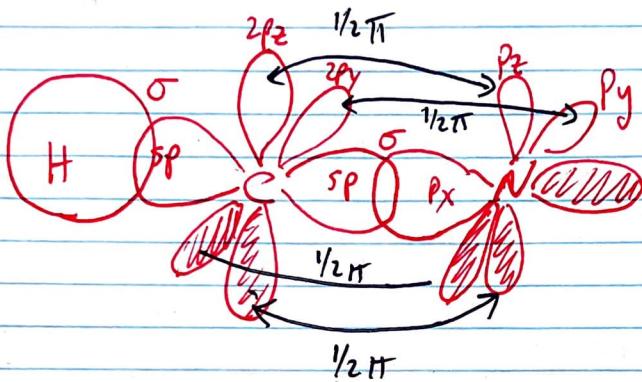
b) What is the hybridization of the central atom? How many of these hybrid orbitals does the central atom have?



Sp hybridization

2 sp orbitals

c) Draw the molecule showing the hybridized orbitals of the central atom and the atomic orbitals of the end atoms. Label each orbital; bond type, and each of the bonds formed.



d) What are the relevant bond angles ~~of~~ in this molecule?
The molecule is linear $\Rightarrow 180^\circ$ bond angles.