CHEM-457: Inorganic Chemistry

Midterm II – April 17th, 2014

NAME Solution Set

This exam is comprised of five questions and is 13 pages in length. Please be sure that you have a complete exam and place your name on each page.

Answer each question to the best of your ability. Partial credit will be awarded where appropriate. You are not permitted to use any supplemental materials other than what is included in this test booklet. Calculators are not needed and their use is not permitted for this exam. **PLEASE DO NOT REMOVE ANY PAGES FROM THIS EXAM EXCEPT FOR THE TWO APENDICIES.**

Write all your answers directly in this test booklet and show all work where necessary.

Good Luck!

1. _____ (12 pts)
2. _____ (20 pts)
3. _____ (10 pts)
4. _____ (24 pts)
5. _____ (34 pts)

Total _____

Name: _____

1. **(12 Total Points)** Please give definitions and an example for each of the following (1 point for each definition & 1 point for each example).

(a) Arrhenius Acid – An H^+ Donor in Water (i.e. H-Cl)

(b) Arrhenius Base - An OH^- Donor in water (i.e. NaOH)

(i.e. CH_3CO_2H)

(c) Brønsted-Lowry Acid - Species with ability to donate a H^+

(i.e. H_2CO_3)

(d) Brønsted-Lowry Base - Species with ability to accept a H^+

(i.e. OH_2)

(e) Lewis Acid - An e^- pair acceptor

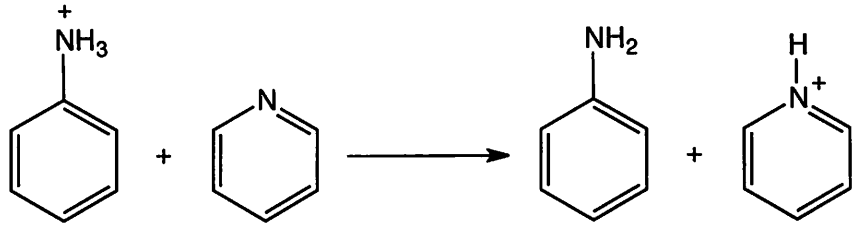
(i.e. BF_3)

(f) Lewis Base - An e^- pair donor

(i.e. NH_3)

Name: _____

2. **(20 Total Points)** Consider the following proton transfer reaction and corresponding proton affinities. For this problem, you may assume that entropic factors are negligible such that $\Delta G° \approx \Delta H = \Delta PA$.



$pK_a = 4.6$ aqueous | PA = 953 kJ/mol gas phase | PA = 899 kJ/mol gas phase | $pK_a = 5.2$ aqueous

(a) (3 Points) Is the above reaction spontaneous in aqueous solution? Please explain you answer.

$\Delta pK_a = 4.6 - 5.2 = -0.6$ Since pKa of pyridinium is greater than that of ammonium the reaction will lie to the right. ∴ Spontaneous

(b) (3 Points) Is the above reaction complete in aqueous solutions? Please explain you answer.

$\Delta pKa = 4.6 - 5.2 = -0.6$

ΔpK is not less than -6 ∴ reaction is not complete

(c) (8 Points) Determine the free energy change for the proton transfer in the gas phase. Is the above reaction spontaneous in the gas phase? Please explain your answer?

$Py_{(g)} + H^+_{(g)} \longrightarrow Py^+\text{-}H_{(g)}$ $\quad \Delta H = -PA_{Py} = -953 \frac{kJ}{mol}$ (2 pts)

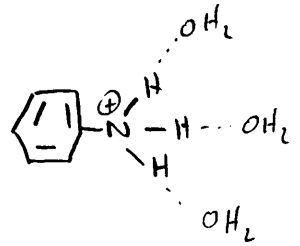
$An^+\text{-}H \longrightarrow An_{(g)} + H^+_{(g)}$ $\quad \Delta H = PA_{An} = 899 \frac{kJ}{mol}$ (2 pts)

$An^+\text{-}H_{(g)} + Py_{(g)} \longrightarrow Py^+\text{-}H_{(g)} + An$ $\quad \Delta H \sim \Delta G = -54 \frac{kJ}{mol}$ (4 pts)

↑ negative ∴ Spontaneous

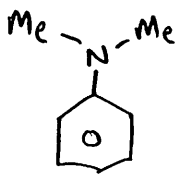
Name: _____

(d) (3 Points) Which of the four species in the acid-base reaction will be best solvated/stabilized in water? Please explain your answer.



The anilinium is the most stable species in water since it can hydrogen-bond with three equivalents of water, whereas anilinium can only hydrogen-bond w/ one.

(e) (3 Points) Do you predict the gas phase proton affinity of N,N-dimethylaniline (Ph–NMe_2) to be larger or smaller than that of aniline? Please explain your answer.



Should have a larger PA than aniline since the methyl groups increase the e⁻ density on nitrogen + hydrogen bonding to the protonated base is not important in the gas phase.

Name: _____

3. **(10 Total Points)** The sol-gel synthesis of oxide materials is accomplished using hydrated metal ions such as that of titanium.

$$[Ti(OH_2)_6]^{4+} + H_2O \rightarrow [Ti(OH_2)_5(OH)]^{3+} + H_3O^+$$

(a) (4 Points) Label each of the four species in the above reaction as either an acid or base. Please place your labels directly in the boxes below.

Reactants		**Products**	
$[Ti(OH_2)_6]^{4+}$	H_2O	$[Ti(OH_2)_5(OH)]^{3+}$	H_3O^+
Acid	Base	Base	Acid

(b) (4 Points) Using hard-soft acid base principles, explain whether H_2O or OH^- will be a better base toward Ti^{4+}.

OH^- will be a better base toward Ti^{4+}.
Ti^{4+} is a highly charged + small Lewis acid + will therefore form the strongest Lewis Acid-Base adduct w/ a hard Lewis base, such as hydroxide

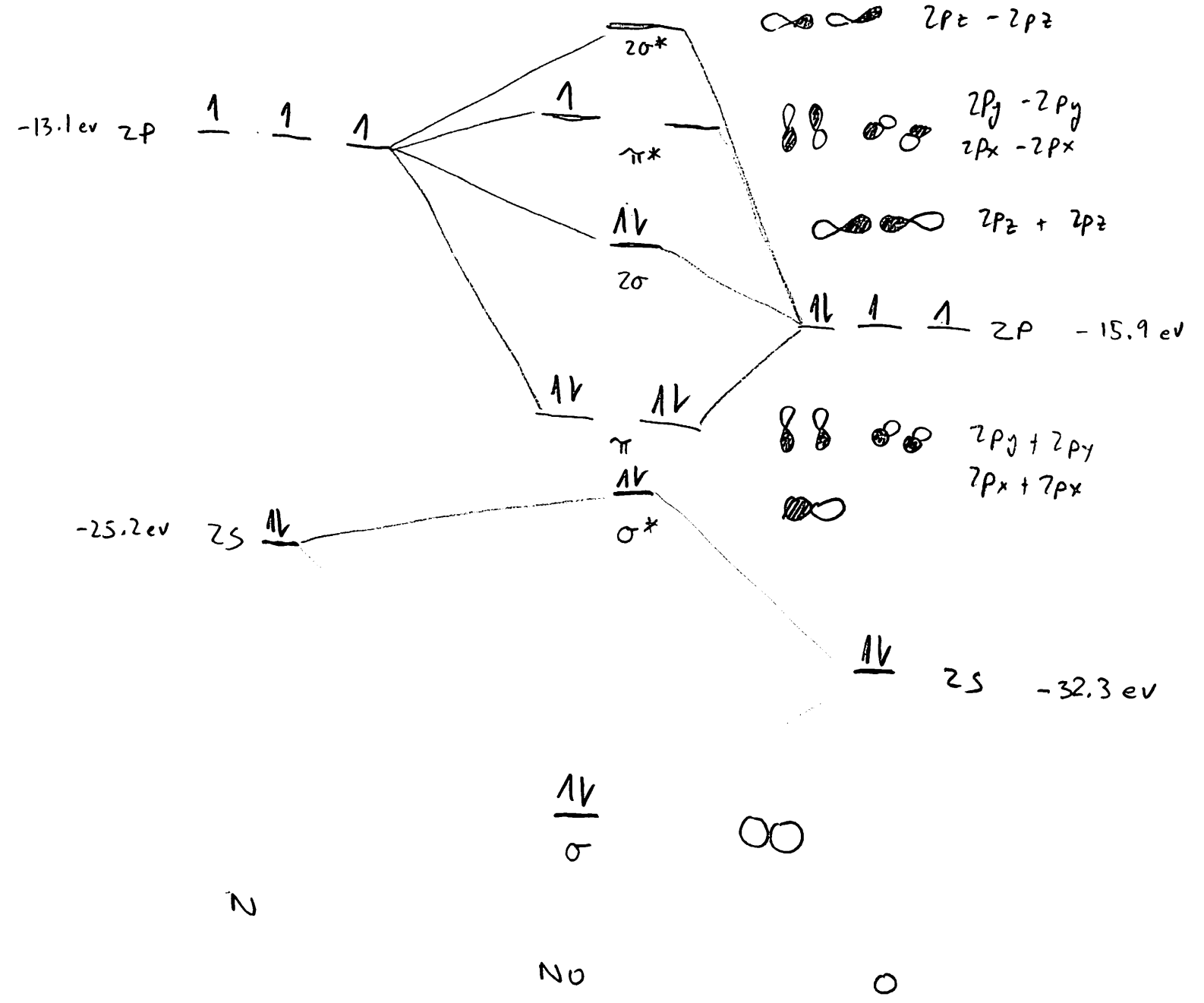
(c) (2 Points) Do you expect the equilibrium constant (K) for the above reaction to be greater than or less than 1.0? Please explain your answer.

Since OH^- will be a better base toward Ti^{4+} than H_2O, it is expected that this equilibrium will lie to the right

Name: _____

4. **(24 total points)** Nitric oxide, which has the chemical formula NO, is a gaseous molecule that functions as a vasodilator in mammals.

   (a) (8 Points) Prepare a molecular orbital energy level diagram for NO. Please be sure to label all atomic orbitals and all molecular orbitals. Please be sure to provide sketches that clearly show how the atomic orbitals interact to form MOs. (Note: you may find the table of *Atomic Orbital Ionization Energies* on page 13 of this exam to be useful in constructing your MO diagram).



Name: _____

(b) (2 points) How does your diagram illustrate the difference in electronegativity between N and O?

The atomic orbitals of oxygen are lower in energy + ∴ lower on the diagram as compared to those of nitrogen

(c) (4 points) What are the bond order and multiplicity of NO?

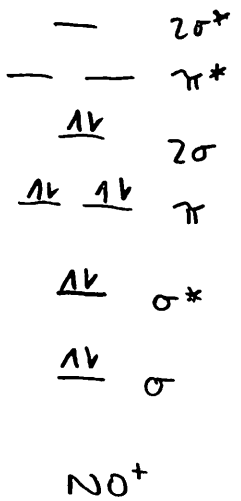
Bond Order = $\frac{1}{2}(8-3) = \frac{5}{2} = 2.5$ (2 pts)

↑ Bonding e⁻ ↑ Antibonding e⁻

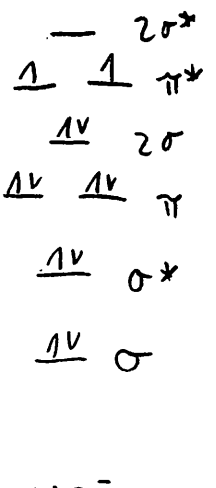
Multiplicity = 2 = Doublet (2 pts)

Name: _____

(d) (4 Points) NO^+ and NO^- are also known species. Calculate the bond orders of these species and compare these values with that of NO. Which of these three species would you predict to have shortest bond? Please explain your answer.



NO^+



NO^-

Bond order

$NO^+ > NO > NO^-$

$3 > 2.5 > 2$

NO^+ should have the shortest bond since it has the largest bond order

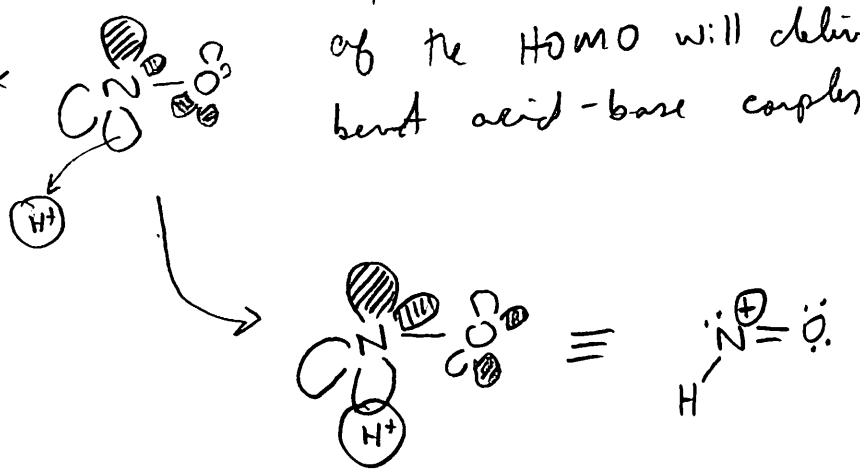
Bond Order $= \frac{1}{2}(8-2) = 3$

Bond Order $= \frac{1}{2}(8-4) = 2$

(e) (6 points) The ion NO^- can react with H^+ to form a chemical bond. Do you expect this protonation to occur on the oxygen or nitrogen atom of NO^-? Do you expect this acid-base adduct to be linear or bent? Please explain your reasoning.

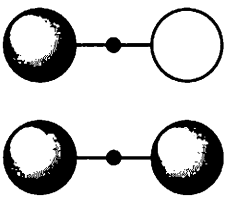
The HOMO of NO^- is π^*, which is closer in energy to the 2p orbitals of Nitrogen ∴ there should be more π^* density toward the nitrogen end of the molecule. Since the π^* does not align w/ the N-O internuclear axis, protonation of the HOMO will deliver a bent acid-base complex

HOMO = π^*

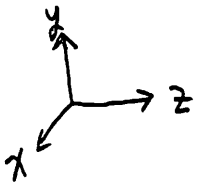


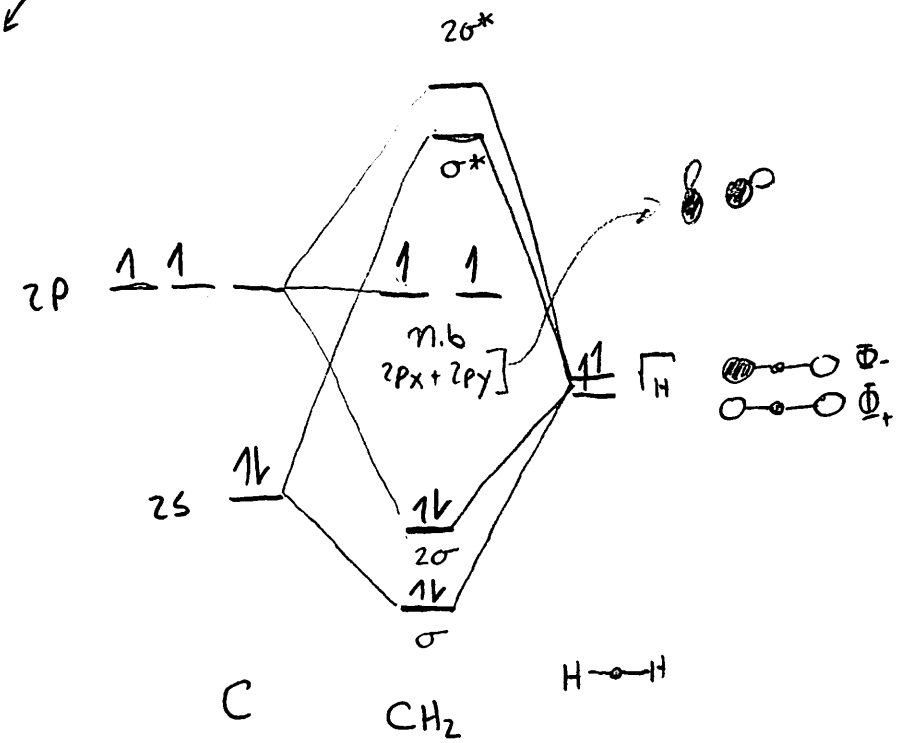
Name: _____

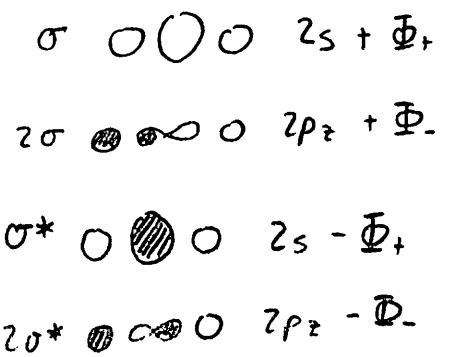
5. **(34 Total Points)** In this problem, let us consider the bonding for methylene (CH_2) using both the 2s and 2p valence orbitals of C and symmetry adapted linear combinations (SALCs) of H 1s orbitals as the basis set. The two H-atom SALCs are illustrated below.



(a) (12 Points) Prepare a molecular orbital energy level diagram for CH_2 in a ***linear*** geometry. Please be sure to label all atomic orbitals, SALCs and molecular orbitals. Please be sure to provide sketches of the group orbitals and clearly show how they interact with the appropriate orbitals on carbon to form MOs. (Note: you may find the table of *Atomic Orbital Ionization Energies* on page 13 of this exam to be useful in constructing your MO diagram).





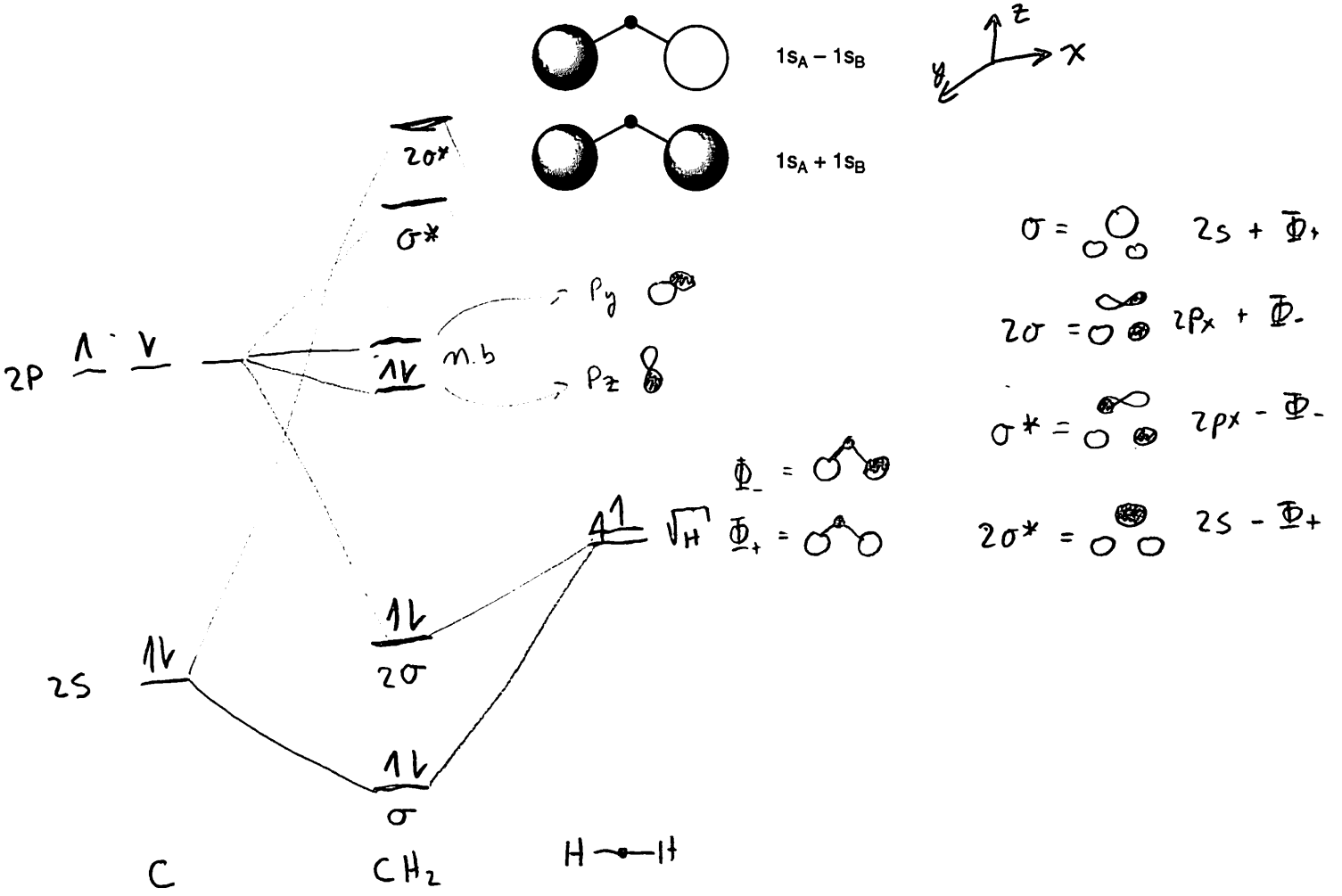


(b) (2 Points) What is the bond order of linear methylene? Is this species diamagnetic or paramagnetic?

Bond order = $\frac{1}{2}(4-0) = 2$ Molecule has 2 unpaired e⁻ ∴ it is paramagnetic

Name: _____

(c) (12 Points) Prepare a molecular orbital energy level diagram for CH_2 in a ***bent*** geometry. The appropriate two H-atom SALCs are illustrated below. Please be sure to label all atomic orbitals, SALCs and molecular orbitals. Please be sure to provide sketches of the group orbitals and clearly show how they interact with the appropriate orbitals on carbon to form MOs. (Note: you may find the table of *Atomic Orbital Ionization Energies* on page 13 of this exam to be useful in constructing your MO diagram).



(d) (2 Points) What is the bond order of bent methylene? Is this species diamagnetic or paramagnetic?

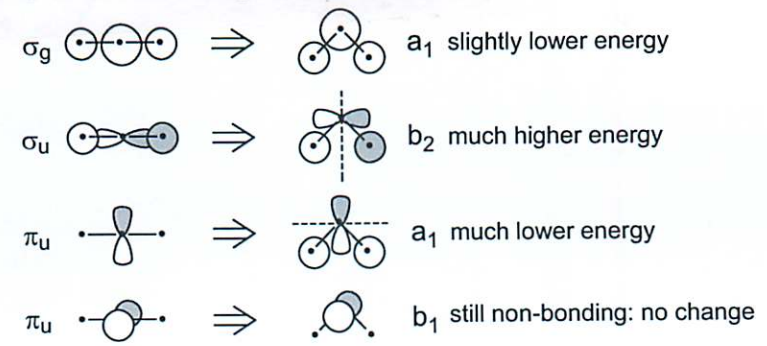
Bond Order = $\frac{1}{2}(4-0) = 2$

Molecule has no unpaired e^- ∴ it is diamagnetic

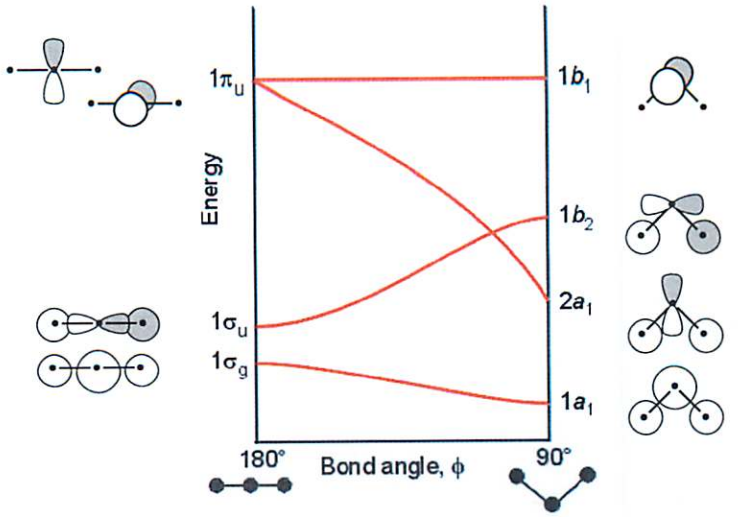
Name: _____

(e) (6 Points) Based on your MO diagrams for linear and bent methylene, which geometry of this species do you expect to be more stable? Please explain your answer.

EH_2: Qualitative Change to MOs with Varying Bond Angle



EH_2: Walsh Diagram, 90° – 180°



Since the first 3 MOs are occupied, the bent geometry should be more stable. This will place the highest energy e⁻ in a MO that is overall non-bonding, but is slightly stabilized by interaction of p_z w/ H_+.