

# PROBLEM SET 6

P7. - USE MOLECULAR-ORBITAL THEORY TO EXPLAIN WHY THE DISSOCIATION ENERGY OF  $N_2$  IS GREATER THAN THAT OF  $N_2^+$ , BUT THE DISSOCIATION ENERGY OF  $O_2^+$  IS GREATER THAN THAT OF  $O_2$

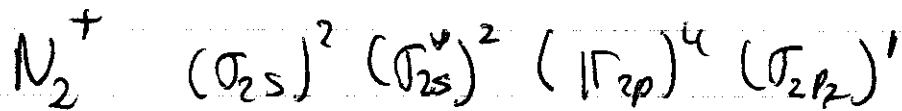
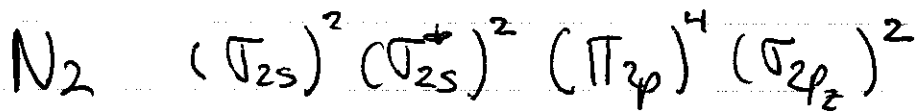
P8. - PREDICT THE RELATIVE STABILITIES OF THE SPECIES  $N_2$ ,  $N_2^+$ , AND  $N_2^-$ .

P9. - FOR A LINEAR  $XY_2$  MOLECULE, DRAW A SCHEMATIC REPRESENTATION OF THE  $1\pi_u$ ,  $2\pi_u$ , AND  $1\pi_g$  ORBITALS

P10. - EXPLAIN WHY THE DOUBLY DEGENERATE  $1\pi_u$  ORBITALS FOR A LINEAR  $XY_2$  MOLECULE DO NOT REMAIN DEGENERATE WHEN THE MOLECULE IS BENT

CH4 GRAY  
PROBLEMS  
2, 6, 10, 14. - d, e, f  
15, 16

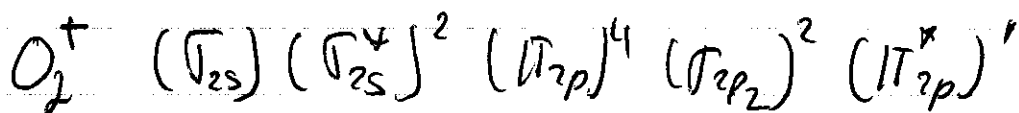
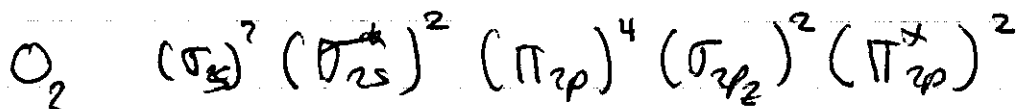
P7.-



BO  $N_2 = 3$

$$N_2^+ = 2\frac{1}{2}$$

Dis. ENERGY  $N_2 > N_2^+$



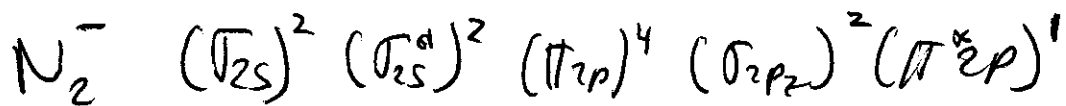
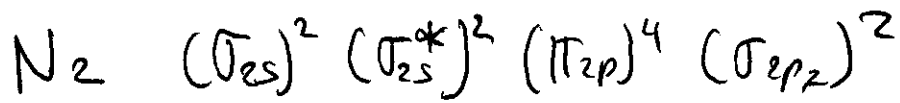
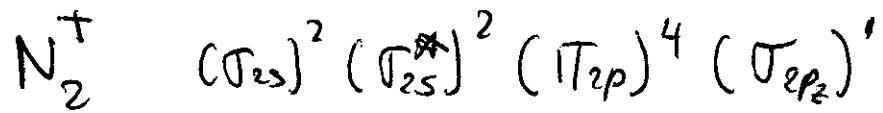
$O_2^+$  HAS less ANTIBONDING  $\sigma^-$  THAN  $O_2$

BO  $O_2 = 2$

$$O_2^+ = 2\frac{1}{2}$$

Dis ENERGY  $O_2^+ > O_2$

P8.-



BO	$N_2^+$	$2\frac{1}{2}$
	$N_2$	3
	$N_2^-$	$2\frac{1}{2}$

STABILITY  $N_2 > N_2^- \approx N_2^+$

Q9. - FOR A NON HYDROGEN TRIATOMIC MOLECULE

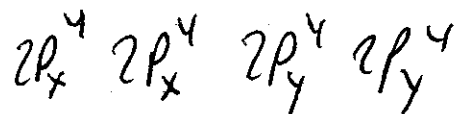
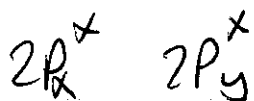
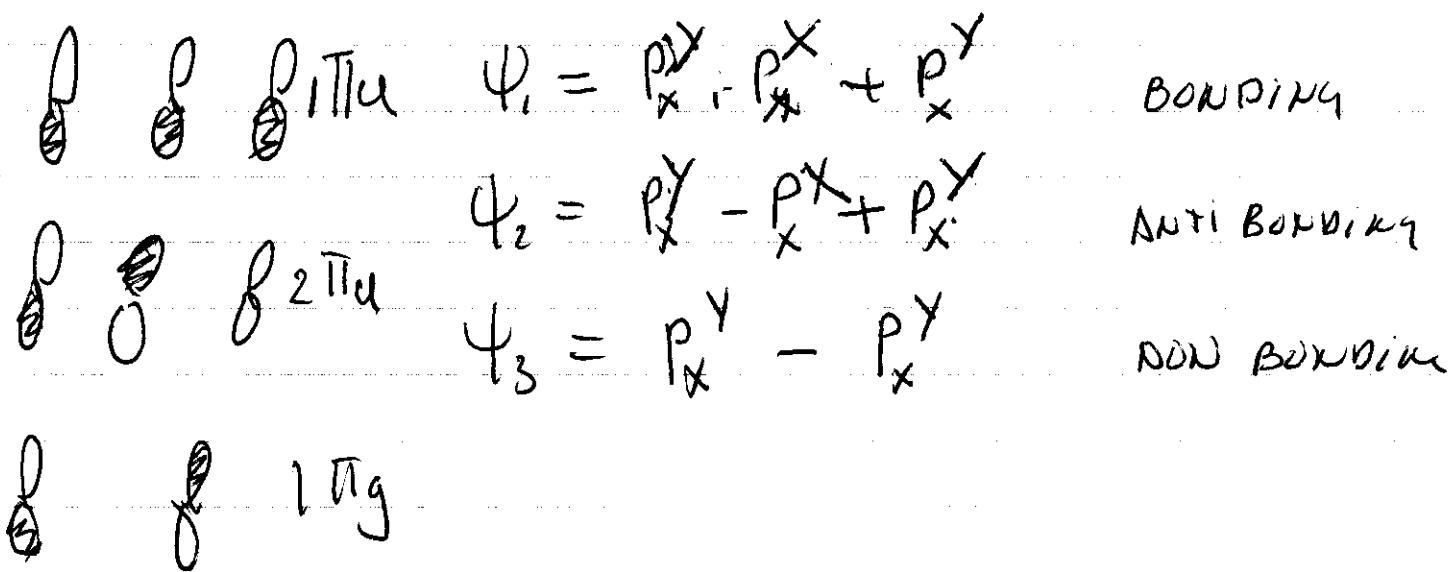
X CENTRAL ATOM HYBRIDIZE S AND P<sub>z</sub>

AND USE BOTH FOR BONDING WITH

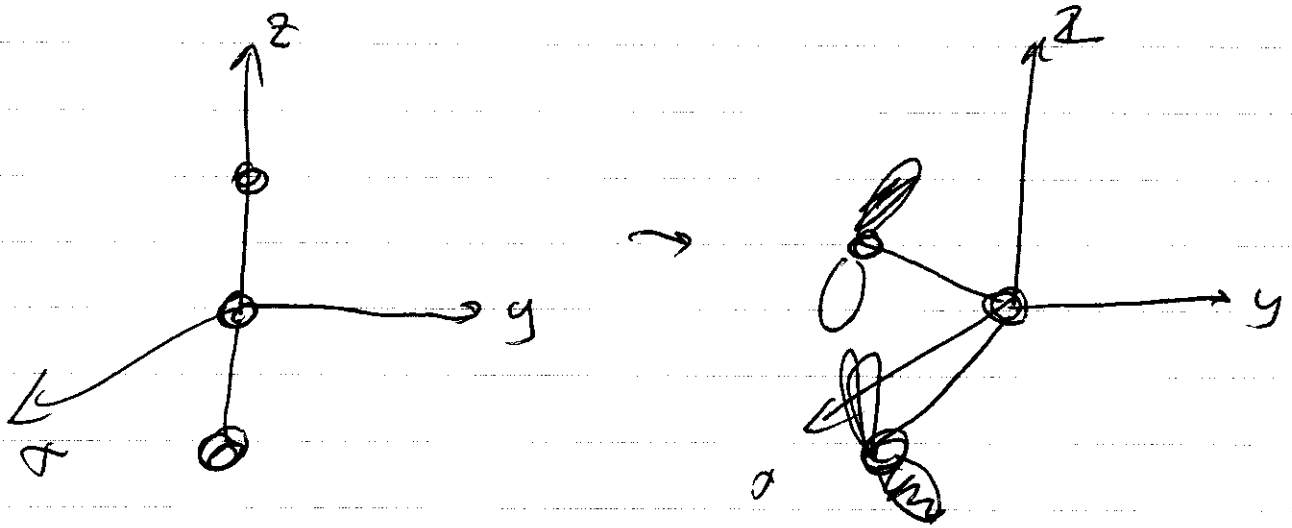
A P<sub>z</sub> FROM OUTER ATOM Y.

LEFT ARE THE P<sub>x</sub> AND P<sub>y</sub> ORBITALS

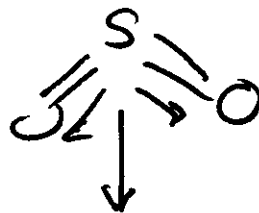
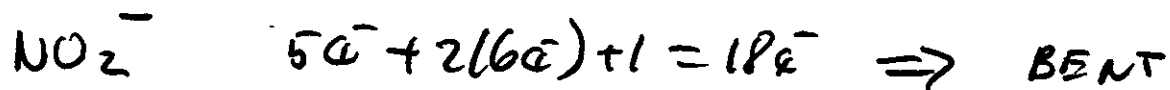
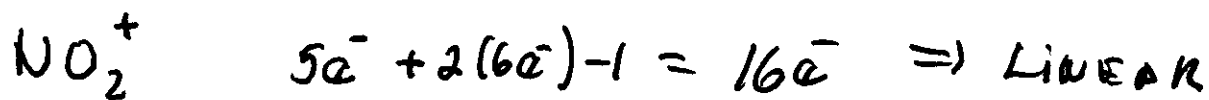
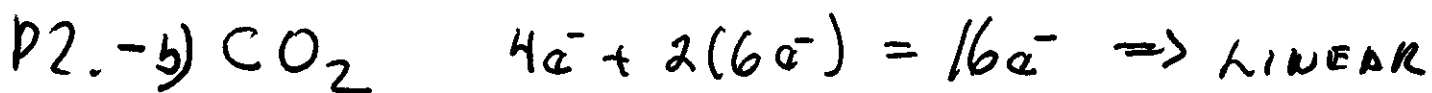
3 DELOCALIZED MO



P10



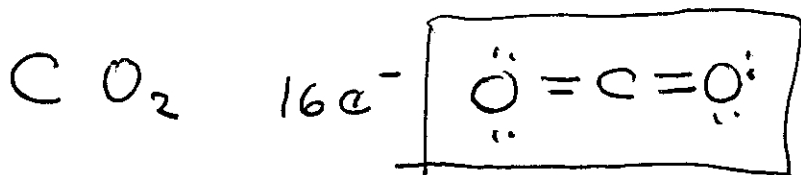
ONE OF THE  $1\pi_u$  LIES ON THE  
 $xz$  PLANE ( $2p_x$ ). THE OTHER IS  $\perp$   
BENDING INCREASES THE  $2p_z$  INTERACTION  
BUT LOWERS THE  $2p_y$ .  
THUS, ENERGY OF THE  $1\pi_u$   
DEPENDS ON THE ANGLE



4) FOR  $\text{CO}_2$  AND  $\text{NO}_2^+$  SP HYBRIDS

FOR  $\text{NO}_2$   $\text{NO}_2^-$   $\text{SO}_2$   $\text{SP}^2$  HYBRIDS

Problem 2 b)



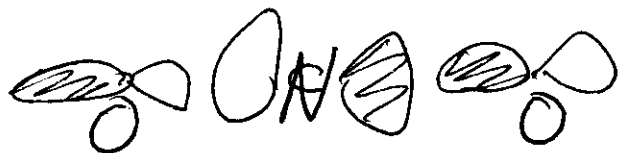
$SN = 2 \Rightarrow$  **LINEAR**  
 $sp$  FOR C



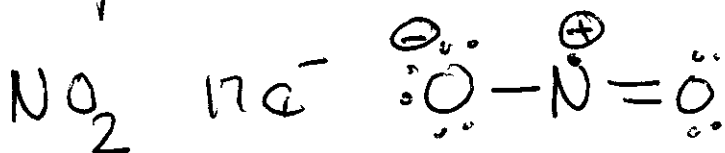
★ NO UNPAIRED  $e^-$  (LOWE  $e^-$ ) OR 4 UNPAIRED  
 NON POLAR (2 LOWE PAIRS)



$SN = 2$  **LINEAR**  
 $sp$  FOR N

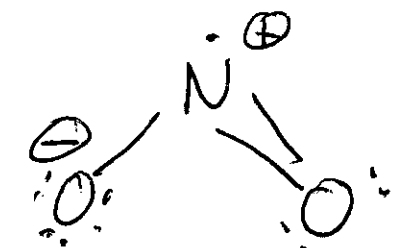


NO UNPAIRED  $e^-$  (1 LOWE  $e^-$ )  
 4 OR UNPAIRED  $e^-$  (2 ~~LOWE~~ PAIRS)



$SN = 3$   $sp^2$

THUS



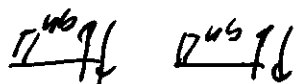
1 LOWE  $e^-$  ON N

**POLAR MOL**

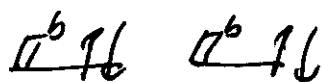
CO<sub>2</sub> 16e<sup>-</sup> LINEAR



ONLY 8e<sup>-</sup> FOR  $\pi$  ORBITAL

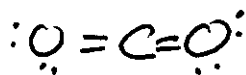


DIAMAGNETIC



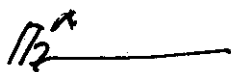
$$BO = 2\sigma + 2\pi = 4$$

4e<sup>-</sup> LOCALIZED ON O (2(2s) AND 2 FROM  $\pi^{nb}$ )

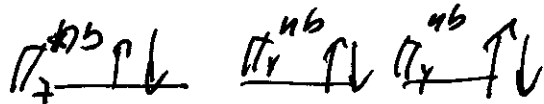


SO<sub>2</sub> 18e<sup>-</sup> BENT

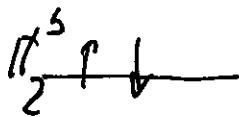
ONLY 8e<sup>-</sup> FOR  $\pi$  ORBITALS



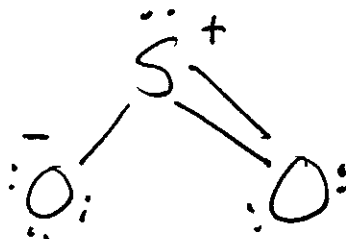
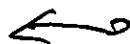
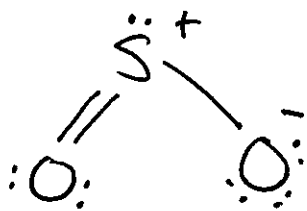
PARAMAGNETIC



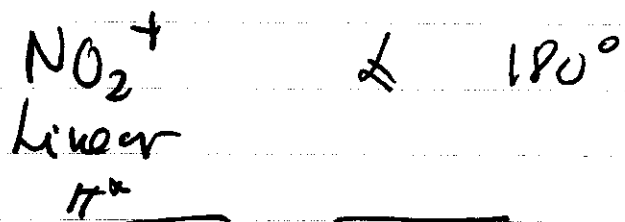
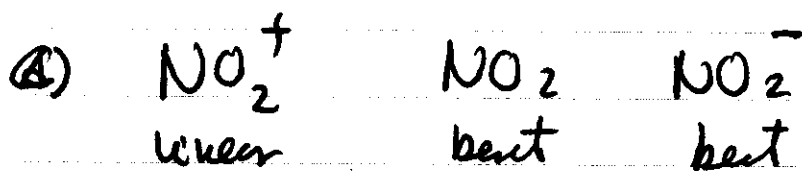
$$BO = 2\sigma + 1\pi = 3$$



S HAS A LOCALIZED LOWE PAIR AND O 2 1/2 PAIRS



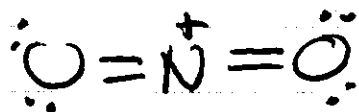




OF THE  $16e^-$  ( $\text{NO}_2^+$ ) 2 FROM N ARE USED FOR  $\sigma$  BONDING. EACH O PLACES 2E IN THE  $2s$  AND 1 IN THE  $\sigma$  BOND. WE ARE LEFT WITH  $8e^-$  FOR THE DELOCALIZED  $\pi$  ORBITALS

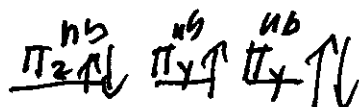
$$BO = 2\sigma + 2\pi = 4$$

WITH 2 PAIR OF UNPAIRED ELECTRONS ON THE  $Os$

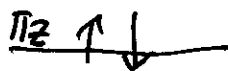


# NO<sub>2</sub> BENT MOLECULE

THE CENTRAL ATOM USES 3 e<sup>-</sup> FOR 3 SP<sup>2</sup> HYBRID WHICH ARE USED FOR  $\sigma$  BONDING. THE OUTER ATOM PLACES A PAIR OF e<sup>-</sup> IN THE 2S AND USES ONE ORB P ORBITAL FOR  $\sigma$  BONDING. THE CENTRAL ATOM PLACES A LONE PAIR ON THE THIRD SP<sup>2</sup> ORBITAL



PARAMAGNETIC

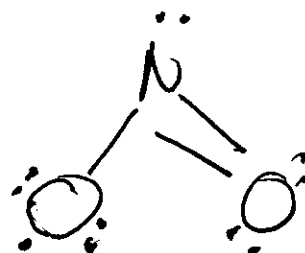
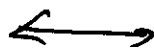
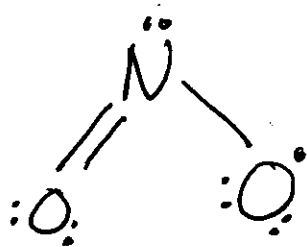


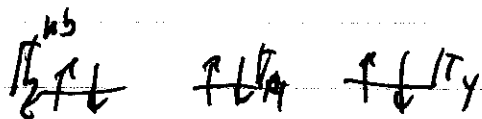
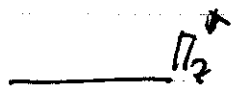
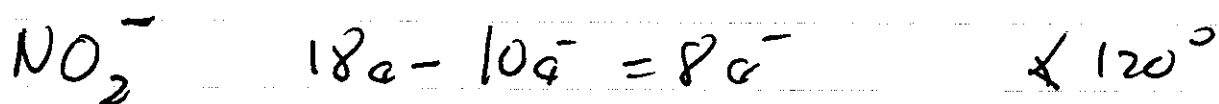
$$17e^- - 4e^- - 6e^- = 7e^-$$

$$BO = 2\sigma + 1\pi = 3$$

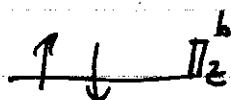
O'S HAVE 2 1/2 LONE PAIRS = 5 e<sup>-</sup>

N HAS 1 LONE PAIR

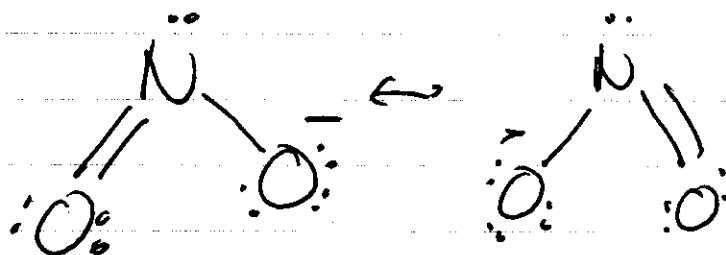




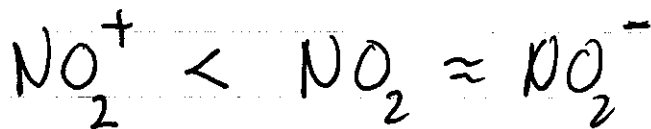
DIAMAGNETIC

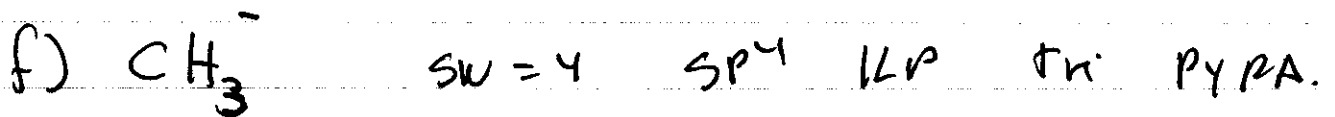
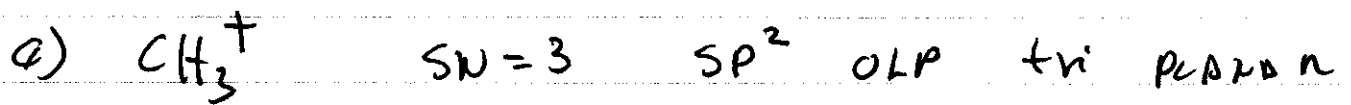
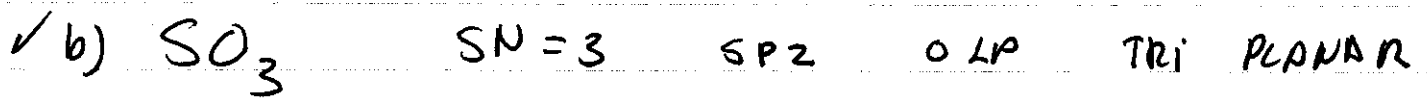
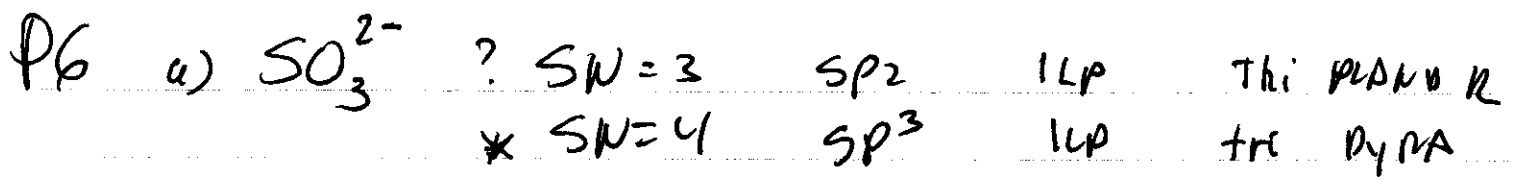


$BO = 3$



BOND LENGTH





P10

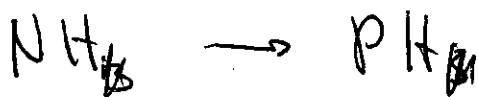
$$\text{NH}_3 \quad \mu = 1.47 \text{ D}$$

$$\text{PH}_3 \quad \mu = 0.55 \text{ D}$$

$$\text{NF}_3 \quad \mu = 0.23 \text{ D}$$

$$R_{\text{H}} = 0.37 \text{ \AA} \quad R_{\text{N}} = 0.70 \text{ \AA}$$

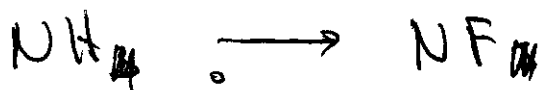
$$R_{\text{P}} = 1.10 \text{ \AA} \quad R_{\text{F}} = 0.64 \text{ \AA}$$



$$l = 1.07 \text{ \AA} \quad l = 1.47 \text{ \AA}$$

ELECTRO NEG  
 $N > P$

LESS CHARGE  
TRANSFER



$$l = 1.07 \text{ \AA} \rightarrow l = 1.37 \text{ \AA}$$

ELECTRO NEG.

$N < F$

LESS CHARGE TRANSFER

$$\epsilon_{\text{N}} = 3.04$$

$$\epsilon_{\text{F}} = 3.88$$

$$\epsilon_{\text{P}} = 2.19$$

$$\epsilon_{\text{H}} = 2.20$$

CAN NOT EXPLAIN  
GIVE US ACCURATE

USE PR  
ANGLES

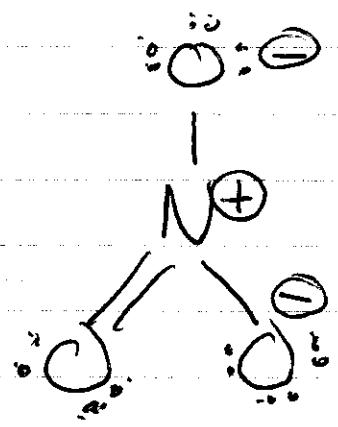
DOES NOT  
 $\text{H}_2\text{O} \quad \text{H}_2\text{S}!$

P14  $\text{NO}_3^-$   $24e^-$   $\text{sp}^2$  tri planar

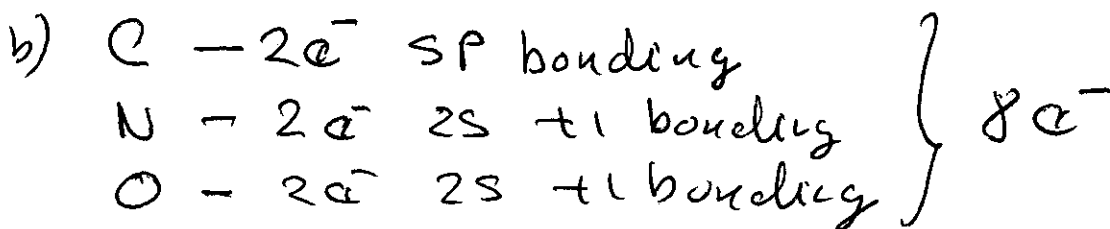
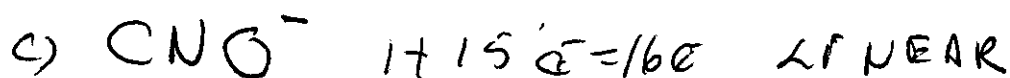
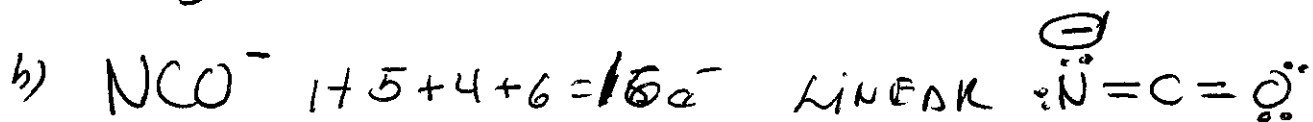
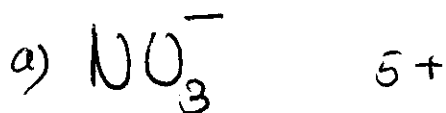
$\text{NCO}^-$   $16e^-$   $\text{sp}$  linear

$\text{CNO}^-$   $16e^-$   $\text{sp}^{\text{hyb}}$  linear

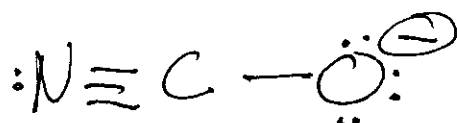
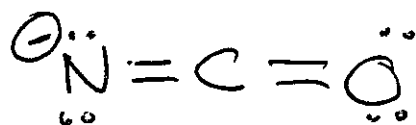
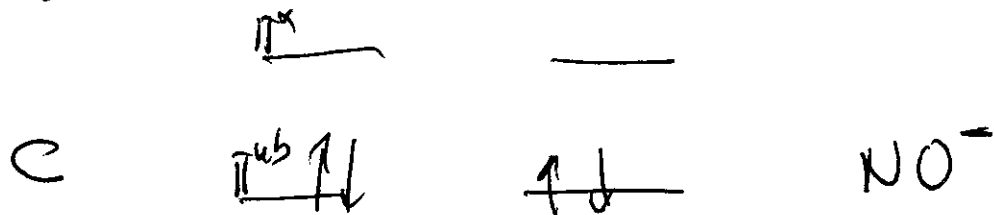
$\text{NO}_3^-$



P15

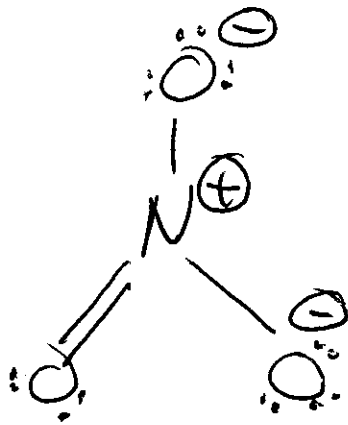


8 FOR  $\pi$  MO

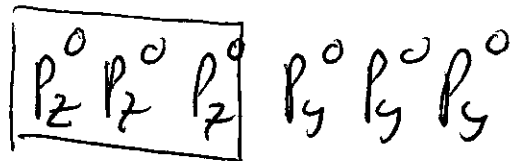
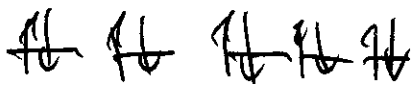
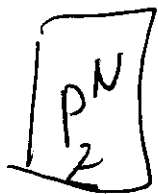




24e<sup>-</sup>



N      3 p<sub>x</sub> p<sub>y</sub>      => 3 sp<sup>2</sup> }  
 O      2e<sup>-</sup> 2s + 1e<sup>-</sup> bonding } 12e<sup>-</sup>



$$\text{BO} = 3\sigma + 1\pi = 4$$

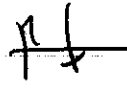
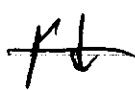
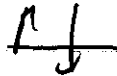
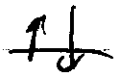


c)

N



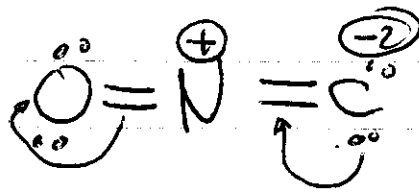
CO<sup>-</sup>



2 → 2s 1 bond

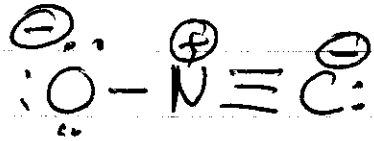
2 → 2s 1 bond

2 sp



?

low PROBABILITY

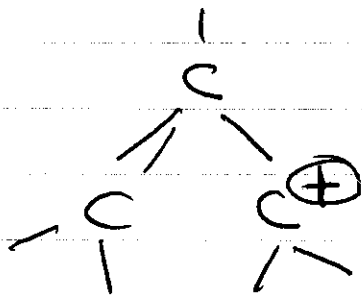


p16 ALLYL cation  $C_3H_5^+$

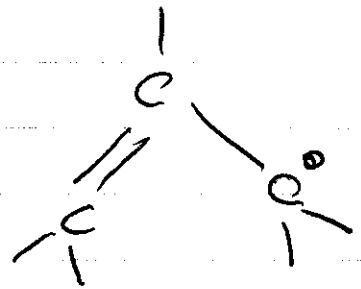
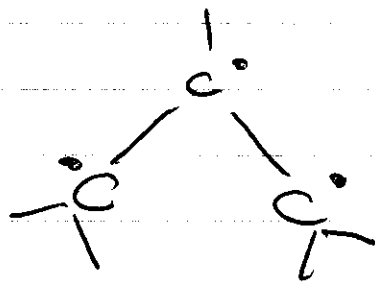
radical  $C_3H_5$

Anion  $C_3H_5^-$

$C_3H_5^+$   
 $sp^2$



$C_3H_5$



$C_3H_5^-$

