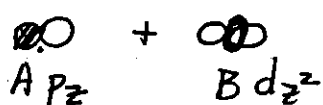
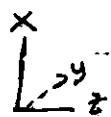


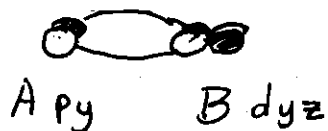
Ch. 5 HW: #1, 3a, 4, 8, 10 + additional problems

5.1 Interact  $p_x, p_y, p_z$  on atom A with  $d_{xy}, d_{xz}, d_{yz}, d_{z^2}, d_{x^2-y^2}$  on atom B.

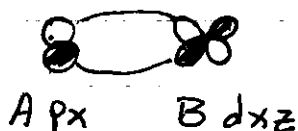
$z$  is the bonding axis (i.e. A and B come together by approaching along  $z$ ).



$\sigma$  and  $\sigma^*$  bonding + antibonding  
 $\uparrow$  overlap same sign       $\uparrow$  overlap opposite signs



$\pi$  and  $\pi^*$

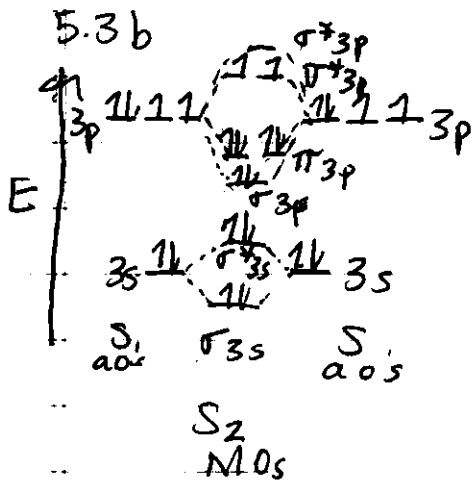


$\pi$  and  $\pi^*$

5.3 a) MO diagrams for  $P_2, S_2$  and  $Cl_2$  are similar to those for  $N_2, O_2$  and  $F_2$  in Period 2 above (except that the 3s and 3p valence orbitals are used).  $P_2$  has a bond order of 3 (like  $N_2$ );  $S_2$  has b.o. = 2 (like  $O_2$ ) and  $Cl_2$  has b.o. = 1 (like  $F_2$ ).

$P_2$  has the strongest bond;  $Cl_2$  is weakest.

#5.3 b, c  
 NOT  
 assigned  
 for 2014.  
 I refer to  
 the 3b  
 diagram  
 below,  
 though.



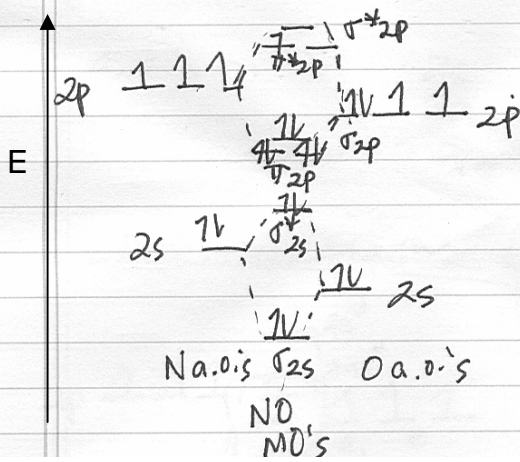
$$S_2 \text{ b.o.} = 2 = \frac{1}{2}(8-4)$$

$$S_2^+ : \text{b.o.} = \frac{1}{2}(8-3) = 2.5$$

$$S_2^- : \text{b.o.} = \frac{1}{2}(8-5) = 1.5$$

weakest bond

c)



$$NO: (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2 (\pi_{2p}^*)^1$$

$$\text{b.o.} = \frac{1}{2}(8-3) = 2.5 \text{ (for NO)}$$

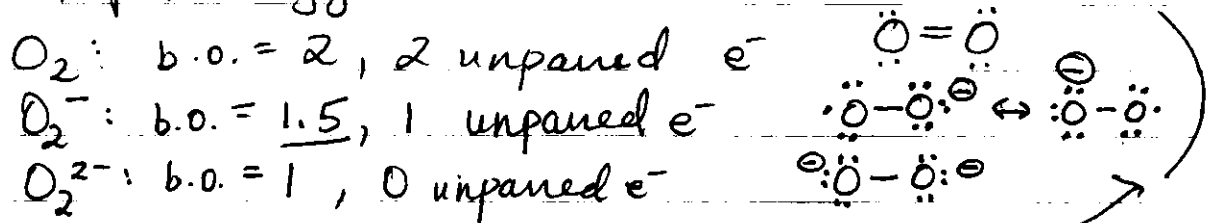
$$NO^+ : \text{b.o.} = \frac{1}{2}(8-2) = 3$$

$$NO^- : \text{b.o.} = \frac{1}{2}(8-4) = 2$$

$NO^+$  should have the  
 strongest bond (triple bond)

$NO^-$  is weakest.

4. Refer to diagram above for  $S_2$ , replacing  $3s, 3p$  with  $2s, 2p$  for oxygen. See #3b



strongest,  
shortest  
bond



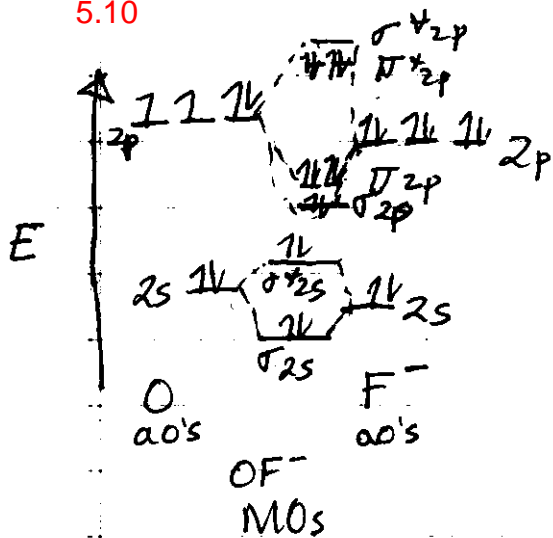
$O_2^{2-}$  weakest,  
longest  
bond

Note that Lewis structures cannot account for paramagnetism (unpaired  $e^-$ ) in  $O_2$ . Two resonance structures for  $O_2^-$  give the same bond order (on average) as predicted by MO theory.

5.8

- a), b) See lecture notes,  
 c) For  $CN^- + H^+ \rightarrow HCN$ ,  $CN^-$  is acting as a Lewis base;  $H^+$  is a Lewis acid. As such, the  $CN^-$  will donate  $e^-$  from its HOMO, the  $\sigma_{2p}$  MO, forming <sup>new</sup> bonding and antibonding interacting with the  $1s$   $H^+$  LUMO.

5.10



b)  $b.o. = \frac{1}{2}(8-6) = 1$

0 unpaired  $e^-$

- c)  $OF^-$  would act as the  $e^-$  donor, using <sup>one of</sup> the  $\pi^*_{2p}$  MOs. Because these are closer in energy to the O 2p a.o.'s (versus those for F), they have more  $e^-$  density on O. Thus,  $H^+$  should bond to O.

## Additional Problems

1.

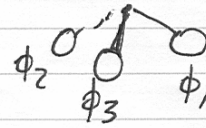
In  $\text{CN}^-$ ,  $\pi_{2p}$  orbitals lie below  $\sigma_{2p}$ ; in  $\text{OF}^-$ , the  $\sigma_{2p}$  orbital lies below the  $\pi_{2p}$  set. This difference arises due to the presence (in  $\text{CN}^-$ ) or absence (in  $\text{OF}^-$ ) of 2nd-order mixing. If they lie close enough in energy, the  $\sigma_{2s}$  and  $\sigma_{2p}$  MOs can engage in 2nd-order mixing (because they have the same symmetry). This lowers the energy of  $\sigma_{2s}$  and raises  $\sigma_{2p}$ , causing it to lie above  $\pi_{2p}$ . 2nd-order mixing therefore explains the ordering of MOs in  $\text{CN}^-$ . As we move farther to the right within a period, the energies of the 2s and 2p (or ns and np) orbitals grow farther apart (as  $Z^*$  increases and the 2s orbitals decrease significantly in E). As a result, in  $\text{OF}^-$ , the  $\sigma_{2s}$  and  $\sigma_{2p}$  do not undergo detectable 2nd-order mixing. When these orbitals are unaffected by 2nd-order mixing,  $\sigma_{2p}$  lies below  $\pi_{2p}$  as  $\sigma$ -type overlap is stronger and more stabilizing than  $\pi$ -type overlap.



2. NH3  $C_{3v}$  point group

SALCs - basis set = 1s orbitals on 3 H atoms

$C_{3v}$	E	$2C_3$	$3\sigma_v$	
$\Gamma_R$	3	0	1	$\{\phi_1, \phi_2, \phi_3\}$
$A_1$	1	1	1	
$A_2$	1	1	-1	
E	2	-1	0	
$\rho(\phi_i)$	$\phi_1$	$\phi_2, \phi_3$	$\phi_1, \phi_2, \phi_3$	



Decompose  $\Gamma_R$ :

$$\begin{aligned} \#A_1 &= \frac{1}{6}(3+3) = 1 \\ \#A_2 &= \frac{1}{6}(3-3) = 0 \\ \#E &= \frac{1}{6}(6) = 1 \end{aligned}$$

$$\Gamma_R = A_1 + E$$

symmetries of SALCs  
(one with  $a_1$ , two with e)

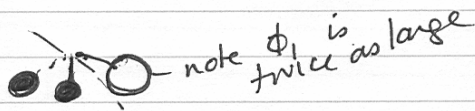
$$\hat{P}(A_1) = \phi_1 + \phi_2 + \phi_3 + \phi_1 + \phi_2 + \phi_3 = 2(\phi_1 + \phi_2 + \phi_3)$$

$$N = \frac{1}{\sqrt{3}}; \quad a_1 = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)$$



$$\hat{P}(e) = 2\phi_1 - \phi_2 - \phi_3 \quad N = \frac{1}{\sqrt{6}}$$

$$e = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)$$



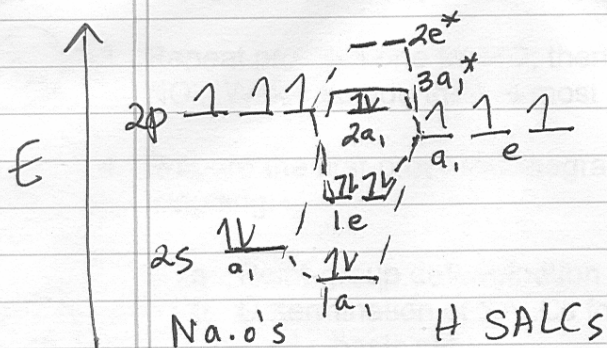
other e!  
( $\perp$  node)

$$e = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$



a.o.'s on N:  $2s \rightarrow a_1$   
 $2p_x, 2p_y \rightarrow e$   
 $2p_z \rightarrow a_1$

MO diagram (1st order)



Note:  
 $1a_1, 2a_1, 3a_1^*$  could undergo 2nd-order mixing here (as occurred for H2O).

NH3 MO's