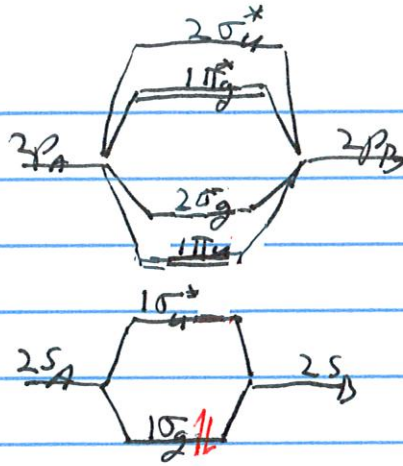


SOLUTIONS

PROBLEM SET 9

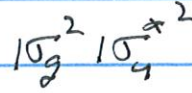
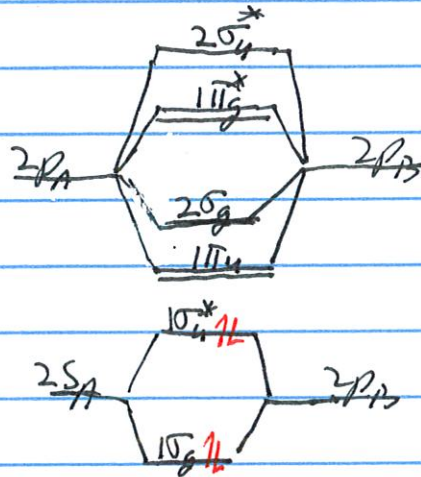
CHM 3411, Dr. Chatfield

1. (a) Li_2 

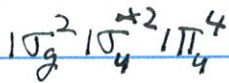
(Li $1s^2 2s^1 \Rightarrow 1$ valence el.
 $\Rightarrow \text{Li}_2$ has 2 valence el.)

$$b = \frac{1}{2}(n - n^*) = \frac{1}{2}(2 - 0) = 1$$

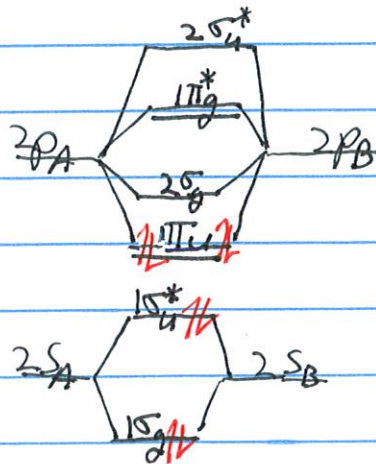
Be $1s^2 2s^2 \Rightarrow 2$ valence el.
 $\Rightarrow \text{Be}_2$ has 4 valence el.

 Be_2 

$$b = \frac{1}{2}(2 - 2) = 0$$

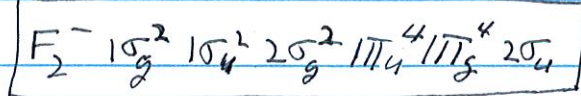
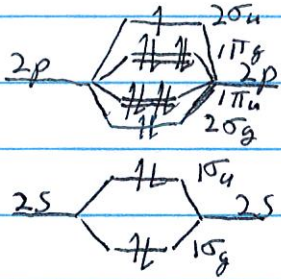
 $\text{C}_2 \Rightarrow 8$ valence el.

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



1. (b)

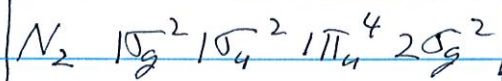
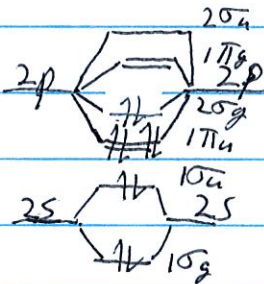
F_2^- : Each F has 7 valence electrons, so including the negative charge there are 15



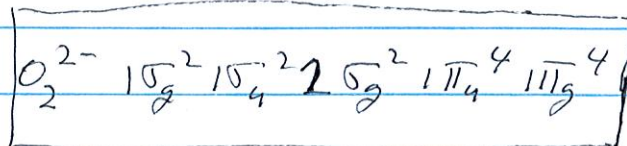
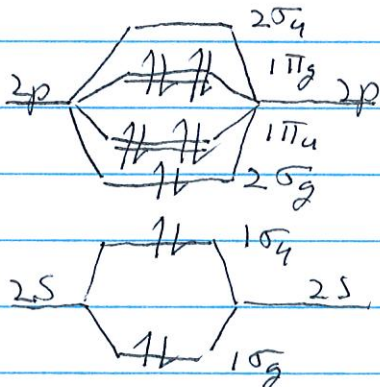
Note: $1\sigma_u^*$, $1\pi_g$, $2\sigma_u^*$ are antibonding orbitals

Note: Identifying antibonding orbitals with asterisks (*) is optional.

N_2 : Each N has 5 valence electrons \Rightarrow 10 total
Order of $2\sigma_g$ & $1\pi_u$ is different from F_2

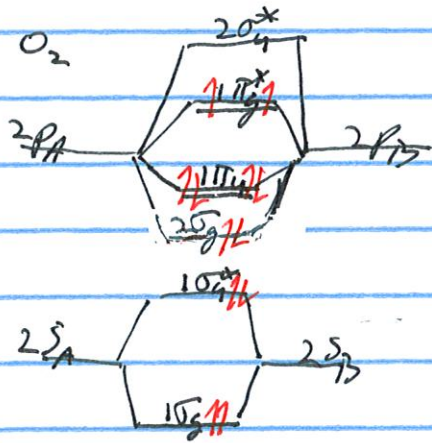


O_2^{2-} : 6 valence electrons for each O + 2 for charge
 \Rightarrow 14 total



- 2 (a) From problem 1, we see that $b=1$ for Li_2 and $b=0$ for Be_2 . Therefore Li_2 is expected to have the greater dissociation energy.

(b) O_2 has 12 valence electrons ($\text{O}: 1s^2 2s^2 2p^4$)



$$\text{O}_2: 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*2}$$

$$b = \frac{1}{2}(n - n^*) = \frac{1}{2}(8 - 4) = 2$$

$$\text{O}_2^+: 1\sigma_g^2 1\sigma_u^{*2} 1\sigma_g^2 1\pi_u^4 1\pi_g^{*1}$$

$$b = \frac{1}{2}(8 - 3) = \frac{5}{2}$$

$$\text{O}_2^-: 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*3}$$

$$b = \frac{1}{2}(8 - 5) = \frac{3}{2}$$

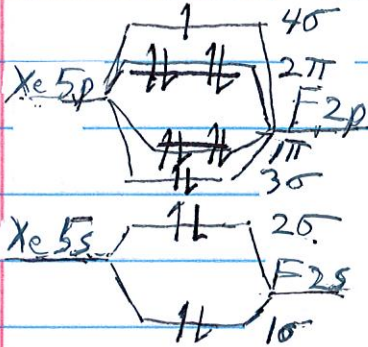
$$\text{O}_2^{2-}: 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*4}$$

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

Based on b , bond strength is: $\text{O}_2^+ > \text{O}_2 > \text{O}_2^- > \text{O}_2^{2-}$

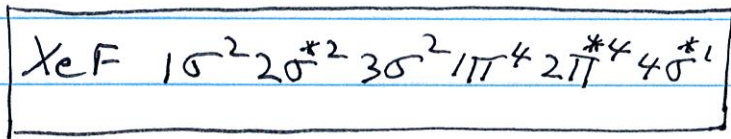
Bond length is inversely related to bond strength (strong bond \Rightarrow short bond), so bond length will follow orders: $\text{O}_2^{2-} > \text{O}_2^- > \text{O}_2 > \text{O}_2^+$

2(b) XeF: Xe has 8 valence electrons (5s, 5p) } 15 total
 F has 7 (2s, 2p)



F has larger electronegativity, so its atomic orbitals have lower energy

Because this is a heteronuclear diatomic, the orbitals do not have a parity symmetry (g or u). Therefore the numbering is different

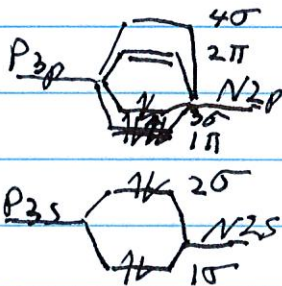


N.B.: 20, 40 + 2π

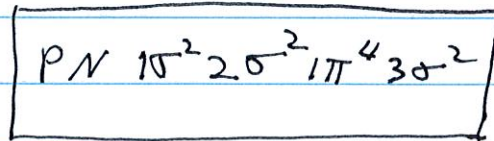
are antibonding.

Adding * is optional

PN: P has 5 valence electrons (3s, 3p) } 10 total
 N (2s, 2p)



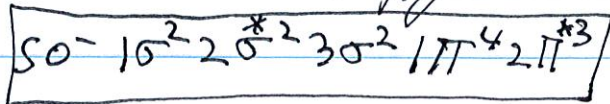
N has larger electronegativity



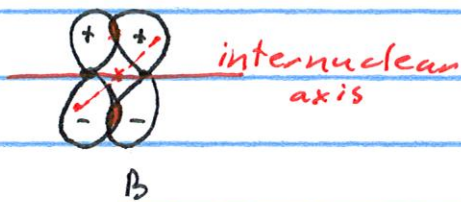
It is just a help

13 val. elect.

SO⁻: Same principle. We can determine electron configuration without correlation diag.



3. (a) $2p_{yA} + 2p_{yB}$

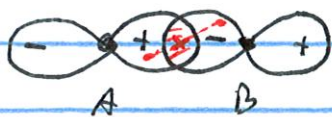


Π orbital (nodal plane through internuclear axis)

Π inversion through center of molecule changes sign (but not magnitude) of wavefunction

bonding interference is constructive (+ overlaps +, - overlaps -)

(b) $2p_{zA} - 2p_{zB}$



σ orbital electron probability density along internuclear axis

σ inversion through center of molecule changes sign of wavefunction

antibonding interference is destructive (+ overlaps -)

(C) $3d_{xy}(A) + 3d_{xy}(B)$

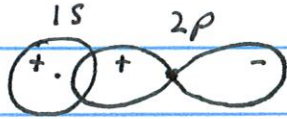


δ orbital (4 lobes, on 4 sides of internuclear axis)

Dotted lobes go
behind plane of paper;
Solid lobes come out
of plane of paper

δ
bonding

4.



| R/a_0 | S |
|---------|------|
| 0.0 | 0.00 |
| 0.1 | 0.10 |
| 0.2 | 0.20 |
| 0.3 | 0.30 |
| 0.4 | 0.39 |
| 0.5 | 0.48 |
| 0.6 | 0.57 |
| 0.7 | 0.65 |
| 0.8 | 0.72 |
| 0.9 | 0.79 |
| 1.0 | 0.86 |
| 1.1 | 0.92 |
| 1.2 | 0.97 |
| 1.3 | 1.01 |
| 1.4 | 1.05 |
| 1.5 | 1.09 |
| 1.6 | 1.12 |
| 1.7 | 1.14 |
| 1.8 | 1.15 |
| 1.9 | 1.17 |
| 2.0 | 1.17 |
| 2.1 | 1.18 |
| 2.2 | 1.17 |
| 2.3 | 1.17 |
| 2.4 | 1.16 |
| 2.5 | 1.15 |
| 2.6 | 1.13 |
| 2.7 | 1.11 |
| 2.8 | 1.09 |
| 2.9 | 1.07 |
| 3.0 | 1.05 |

MAX