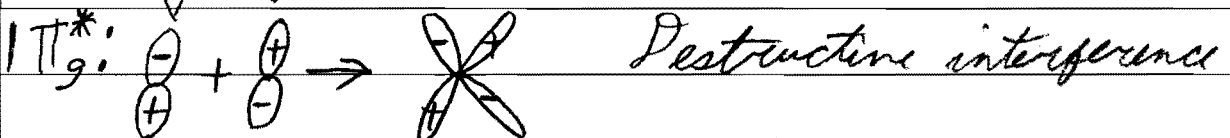
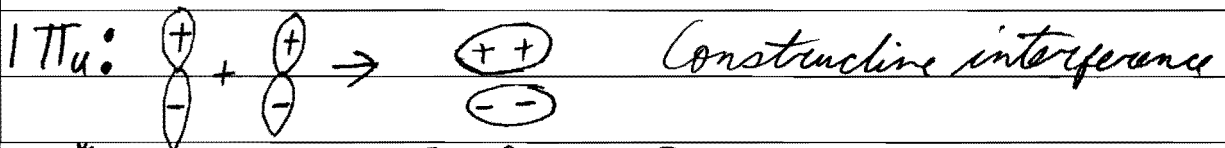
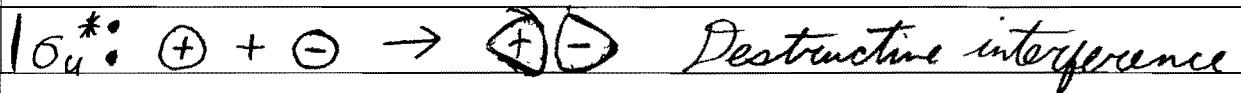
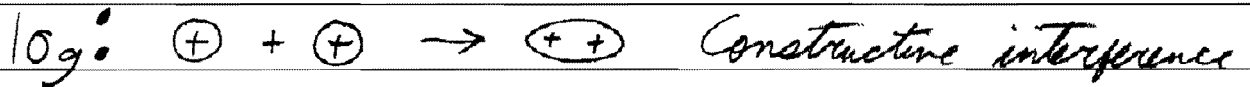


# HW #6 Key

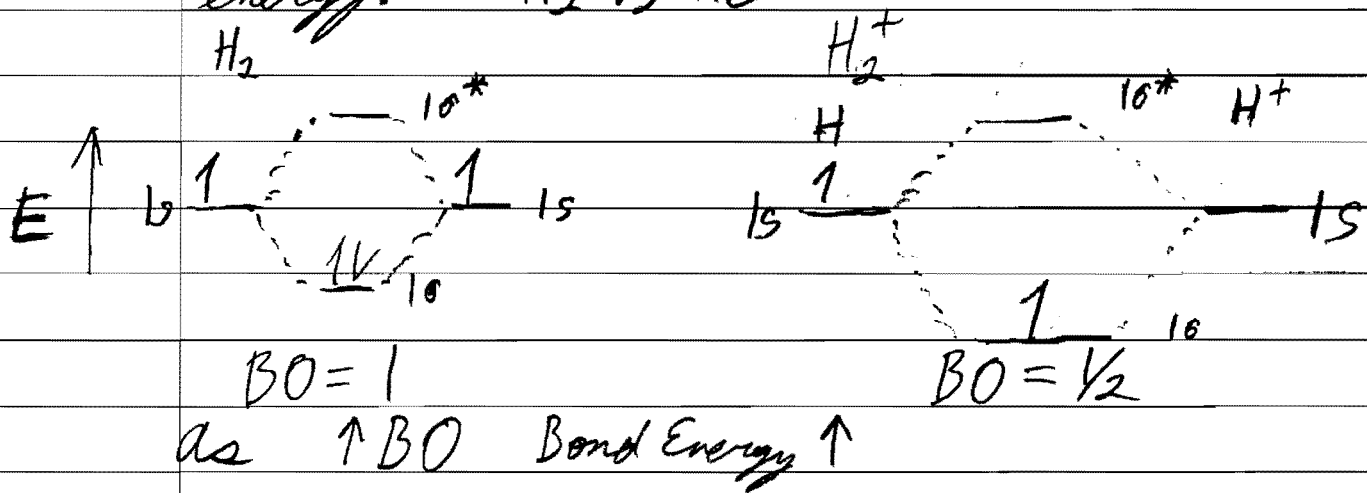
8, 10, 12, 16, 18, 26, 30, 34

⑧ Explain the different behavior of the two sets of MO.



The resulting MO combinations are a consequence of constructive and destructive interference due to the combination of atomic orbitals in identical or opposite (-) orientations.

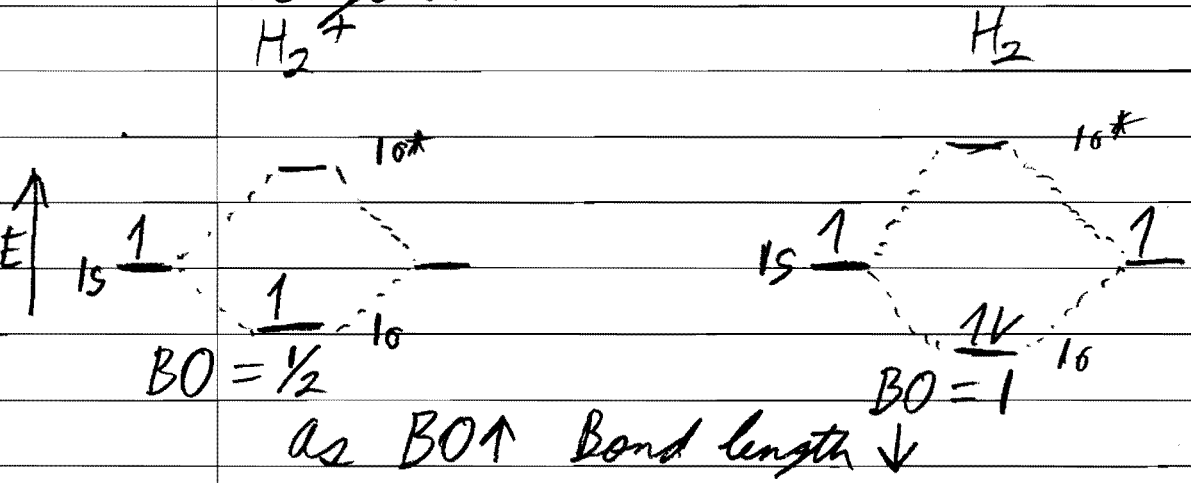
⑩ Which species has the higher bond energy?  
 $H_2$  vs  $He^{+2}$



as  $\uparrow BO$  Bond Energy  $\uparrow$

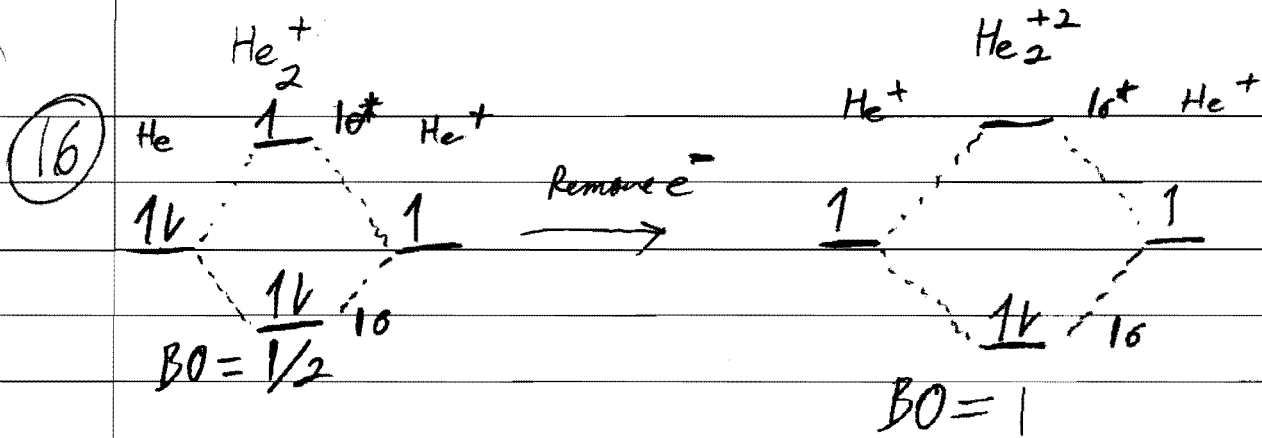
$H_2$  has higher Bond energy

⑫ Which species has the greater bond length?  
 $H_2^+$  vs  $H_2$



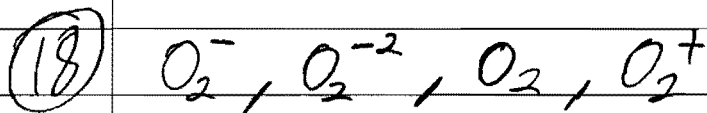
as  $BO \uparrow$  Bond length  $\downarrow$

$H_2^+$  has the greatest bond length

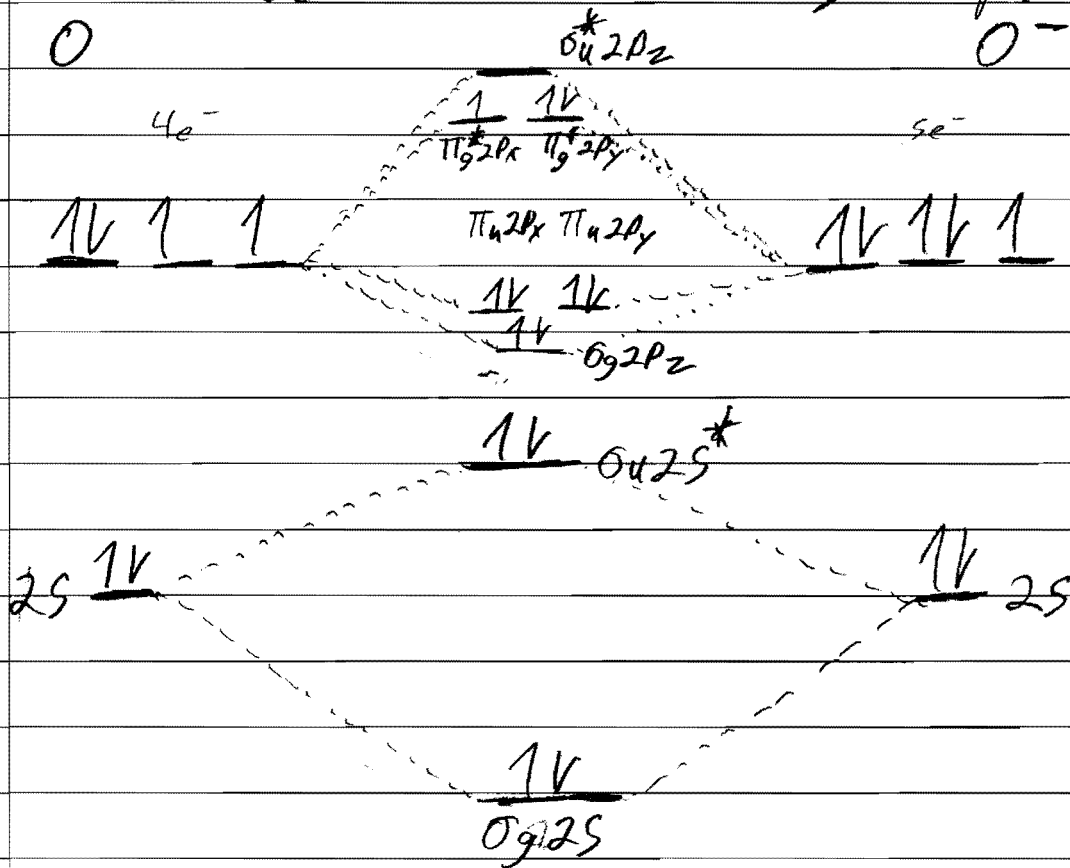


Is the Bond energy of  $\text{He}_2^{+2}$  higher or lower than  $\text{He}_2^+$ ?

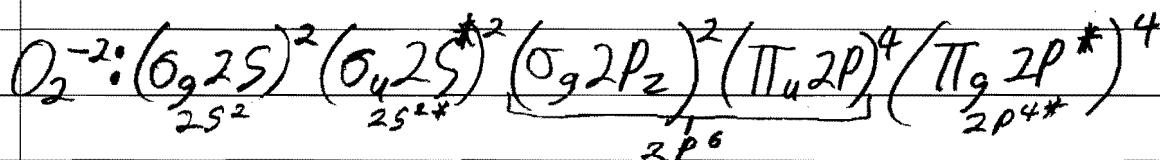
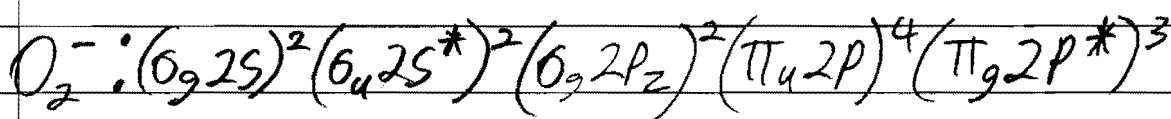
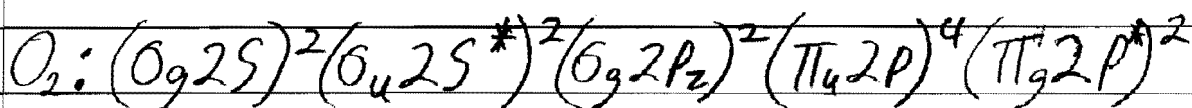
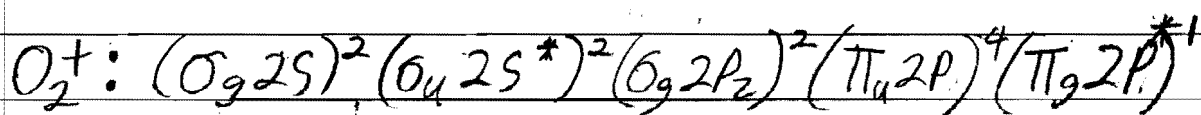
BE of  $\text{He}_2^{+2}$  is  $\uparrow$  than  $\text{He}_2^+$



(A) Construct the correlation diagram for  $\text{O}_2^-$



(18) (B) Molecular  $e^-$  configuration for:  $O_2^+$ ,  $O_2$ ,  $O_2^-$ ,  $O_2^{2-}$



It is easy to think of this style of configurations as just combining 2 electron configurations and arranging them into bonding & antibonding.

(C) Bond Order of each species:

$$O_2^+ : (6 \text{ Bonding} - 1 \text{ antibonding}) / 2 = 2.5$$

$$O_2 : (6 \text{ Bonding} - 2 \text{ antibonding}) / 2 = 2$$

$$O_2^- : (6 \text{ Bonding} - 3 \text{ antibonding}) / 2 = 1.5$$

$$O_2^{2-} : (6 \text{ Bonding} - 4 \text{ antibonding}) / 2 = 1$$

18 (D) Predict Which Species are Paramagnetic.

Paramagnetic = Unpaired  $e^-$

$O_2^{-2}$ : non-Paramagnetic or diamagnetic

$O_2^-$ : Paramagnetic

$O_2$ : Paramagnetic

$O_2^+$ : Paramagnetic.

(E) Predict the order of increasing bond dissociation energy.

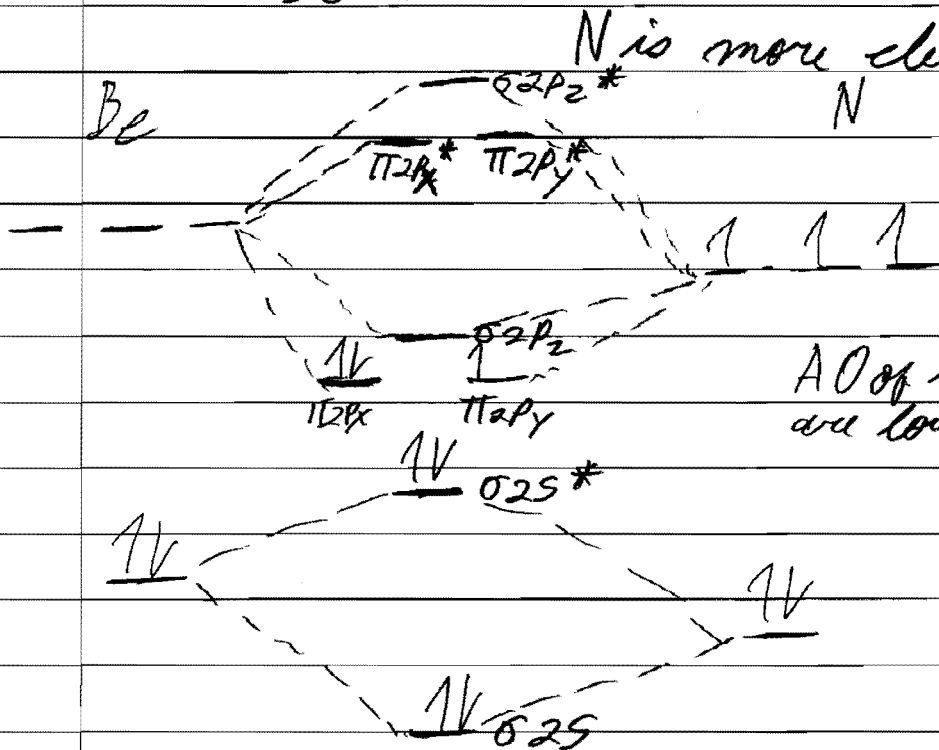
least  $O_2^{-2}$ ,  $O_2^-$ ,  $O_2$ ,  $O_2^+$  most  $E_D$

BO = 1 1.5 2 2.5

As bond order increases the bond energy increases and therefore the energy required to separate the atoms from each other also increases.

(26)

Follow Fig 6.19 Write the diagram for Be N

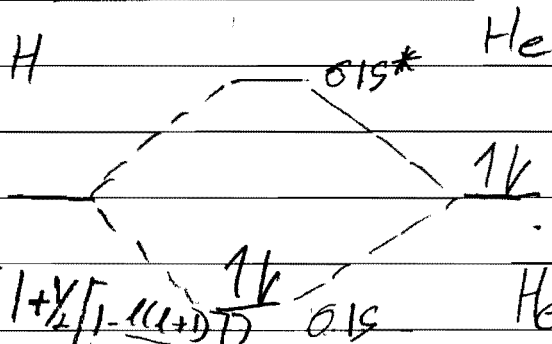


N is more electronegative.

AO of the more E-neg are lower in E.

(30)

He  $H^+ = 2e^-$



He  $H^+$  is diamagnetic.

$$\bar{r}_{nl} = \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left[ 1 - \frac{l(l+1)}{n^2} \right] \right\}$$

$$\bar{r}_{nl} = \frac{n^2 a_0}{Z} \cdot \text{Constant}$$

$$\bar{r}_{nl} = \frac{1^2 a_0}{1} \cdot \text{Constant}$$

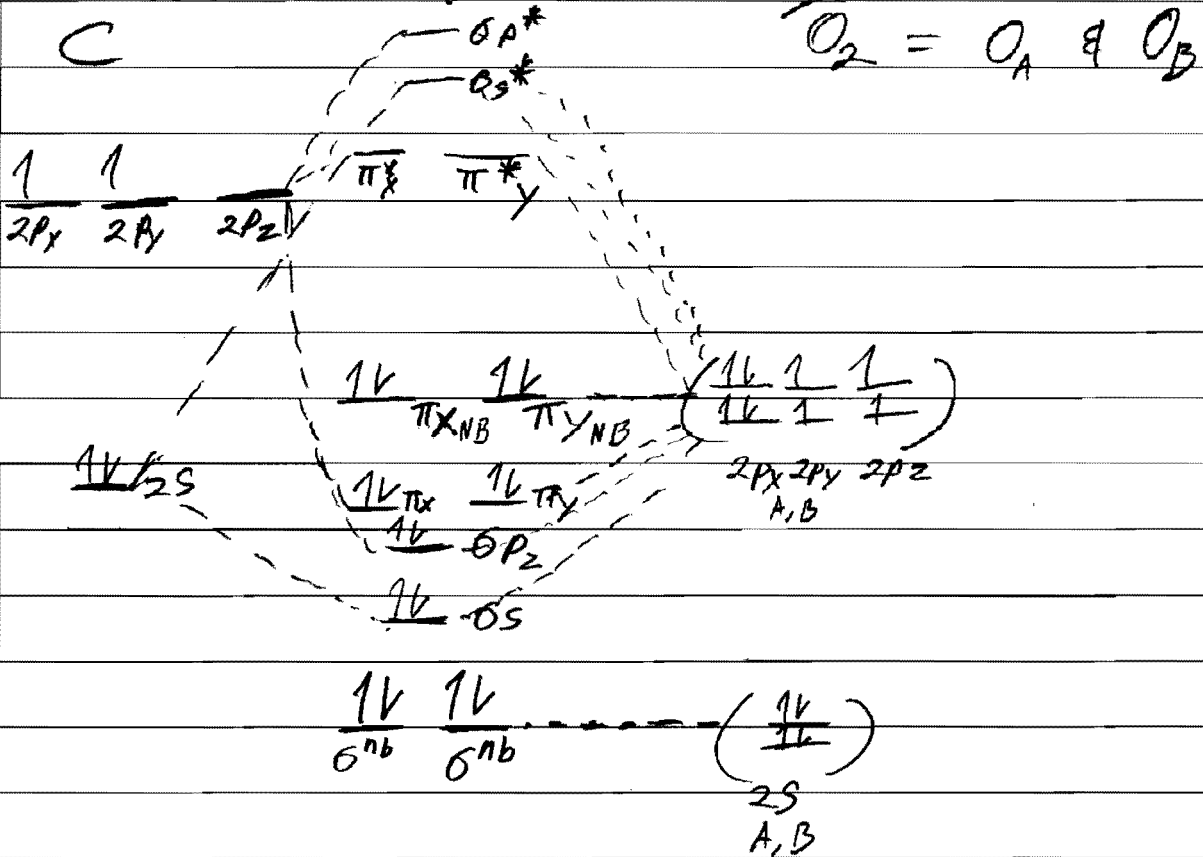
$$\bar{r}_{nl} = \frac{1^2 a_0}{4} \cdot \text{Constant}$$

$HeH^+ \rightarrow He + H^+$  is more stable because the electrons are more closely bound to He than to  $H^+$  indicating a stronger ~~bond~~ interaction.

(34)

$\text{CO}_2$  goes to  $\text{CO}_2^{3+}$ .

Is the dissociation energy of  $\text{CO}_2^{3+}$  larger or smaller than  $\text{CO}_2$ . How will the CO bonds change



The  $3e^-$  will be removed from the non-bonding region. Because the NB region does not contribute to bond order the BO does not change, the bond energy will not change, and the bond distance will not change.

# HW #6 Other Problems.

Explain why each of the following statements is false.

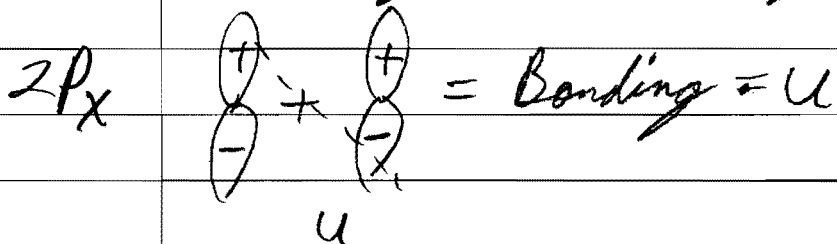
1. The Born Oppenheimer approximation assumes that the electronic wave function is independent of nuclear coordinates.

The Born Oppenheimer approximation electronic wave function uses the nuclear coordinates as a parameter for the electronic wave function.

2. Solutions to  $H_2^+$  presented in the text are the exact wavefunctions for the  $H_2^+$  molecule.

The B-O approach is iterative, so the wave functions will be close, but never exact.

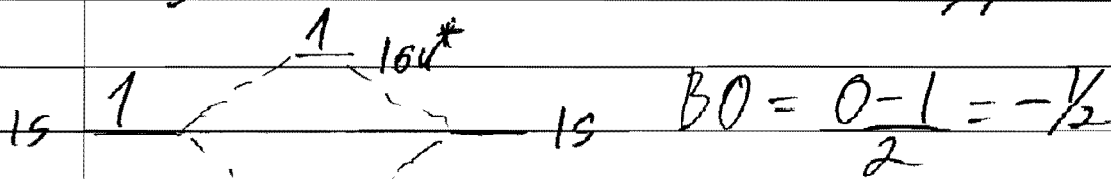
3. All molecular orbitals with even symmetry are bonding (9)





# Short Answers

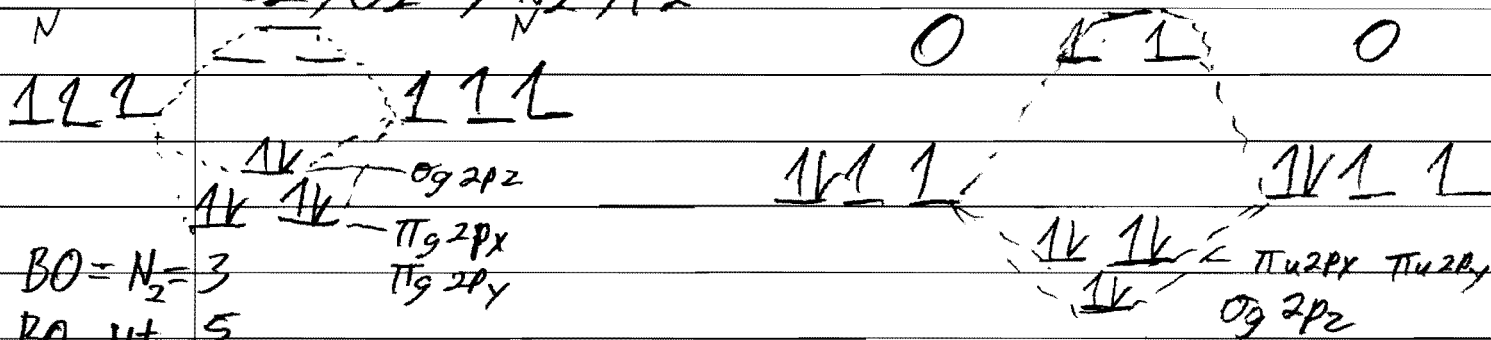
1. If you excited the electron in  $H_2^+$  from  $1\sigma_g$  to  $1\sigma_u^*$  what would happen



The molecule will dissociate.

2. Which has the highest bond order

$O_2, O_2^+, N_2, N_2^+$



$N_2 =$  highest BO

Short answer

② lower energy limit between  $\pi$  &  $\pi^*$  for  $N_2$ .

$N_2$  is invisible, so its absorption is in the UV<sup>(g)</sup>  $\sim 400\text{nm}$

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$c = v\lambda \quad \Delta E = hv$$

$$v = \frac{c}{\lambda} \quad \frac{\text{m/s}}{\text{m}}$$

$$E = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.99 \times 10^8 \text{ m/s})}{400 \times 10^{-9} \text{ m}} = 4.95 \times 10^{-19} \text{ J}$$

Because the range of absorption for  $N_2$  is 100nm to 400nm, 400nm is the lowest energy transition.