Quiz 9.2 – Molecular Orbital Theory: Diatomic Molecules

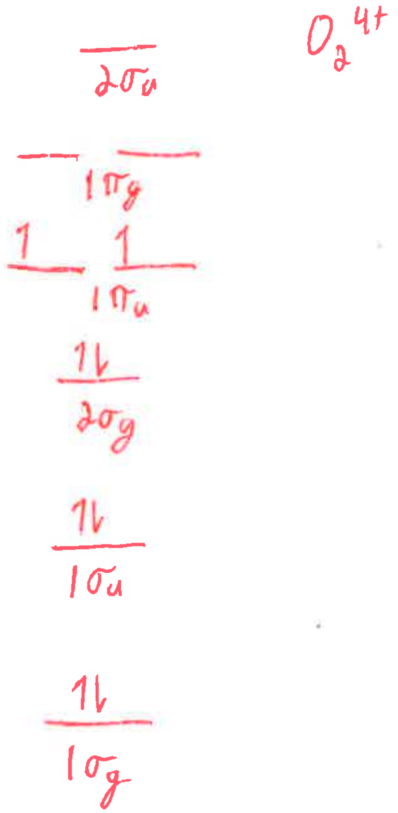
Name: *Key*

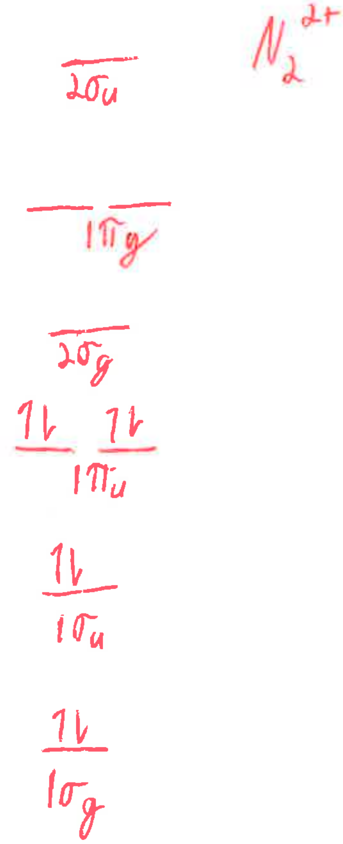
Homonuclear Diatomics

12 e's → ~~10~~ 8 valence e's

O_2^{4+} and N_2^{2+} have the same number of electrons, so you might expect them to have identical electronic structure

○ Draw the molecular orbital energy level diagram for these two molecules, filled with the proper number of electrons





○ Give the bond order of both molecules

2

○ Describe how both molecules might interact with a strong magnetic field

O_2^{4+} – Paramagnetic: Attracted to a magnetic field

N_2^{2+} – Diamagnetic: Repelled by a magnetic field

Heteronuclear Diatomics

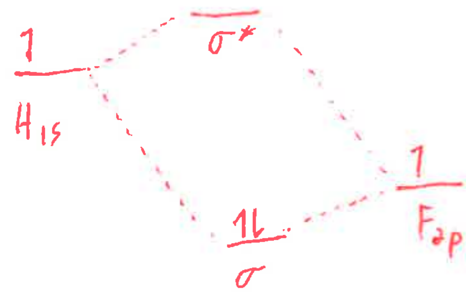
Consider the molecule HF. Because of the much higher nuclear charge on F, the H1s orbital actually aligns best energetically with the F2p_z orbital, so they are the two which combine to form a molecular orbital. $\alpha_{H1s} = -7.2eV$, $\alpha_{F2p} = -10.4eV$, and $\beta_{H1s-F2p} = -1.0eV$

o Calculate the energies of the two molecular orbitals, and draw an energy-level diagram which includes both the energies of the atomic orbitals and molecular orbitals. Remember that for heteronuclear diatomics we usually assume that the overlap integral $S = 0$

$$E_\pm = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}(\alpha_A - \alpha_B)\left[1 + \left(\frac{2\beta}{\alpha_A - \alpha_B}\right)^2\right]^{1/2}$$

$$E_+ = \frac{1}{2}(-17.6\ eV) + \frac{1}{2}(3.2\ eV)\left[1 + \left(\frac{-2\ eV}{3.2\ eV}\right)^2\right]^{1/2}$$

$$E_+ = -6.91\ eV$$



$$E_- = \frac{1}{2}(-17.6\ eV) - \frac{1}{2}(3.2\ eV)\left[1 + \left(\frac{-2\ eV}{3.2\ eV}\right)^2\right]^{1/2}$$

$$E_- = -10.69\ eV$$

o Calculate the coefficients for both MOs and sketch how they might look considering the unequal contributions from both atoms

σ

$$C_H = \left[1 + \left(\frac{\alpha_H - E_-}{\beta}\right)^2\right]^{-1/2}$$

$$C_H = \left[1 + \left(\frac{-7.2\ eV + 10.69\ eV}{-1.0\ eV}\right)^2\right]^{-1/2} = 0.275$$

$$C_F = -\left(\frac{\alpha_H - E_-}{\beta}\right)C_a = -\left(\frac{-7.2\ eV + 10.69\ eV}{-1.0\ eV}\right)\cdot 0.275$$

$$C_F = 0.960$$

σ^*

$$C_H = \left[1 + \left(\frac{\alpha_H - E_+}{\beta}\right)^2\right]^{-1/2}$$

$$C_H = \left[1 + \left(\frac{-7.2\ eV + 6.91\ eV}{-1\ eV}\right)^2\right]^{-1/2} = 0.960$$

$$C_F = -\left(\frac{\alpha_H - E_+}{\beta}\right)C_a = -\left(\frac{-7.2\ eV + 6.91\ eV}{-1\ eV}\right)\cdot 0.960$$

$$C_F = -0.278$$