

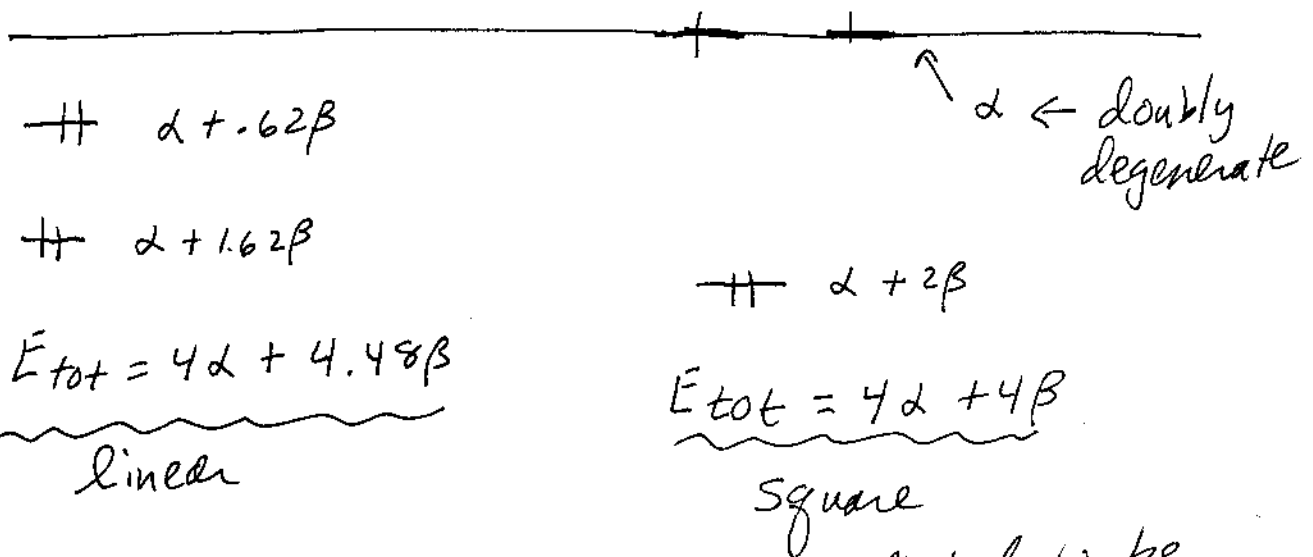
Chem 1410 HW #8 Answers

1. Would you expect  $H_4$  to be more stable as a linear or cyclic structure?

—  $\alpha - 1.62\beta$

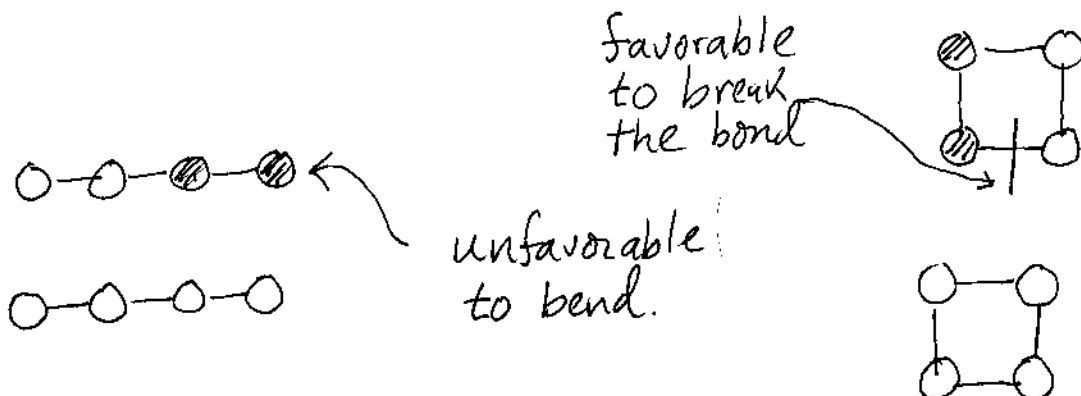
—  $\alpha - 2\beta$

—  $\alpha - .62\beta$



So the linear structure is predicted to be more stable than the square structure by  $0.48\beta$ .

The same conclusion is reached upon examining the MO's.



2. Do you expect the geometry of  $H_2O$  to change appreciably upon removal of an electron from the HOMO?

No. The HOMO is a non-bonding p orbital localized on the O atom.

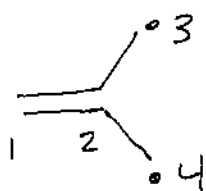
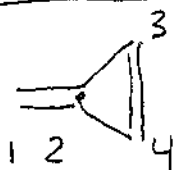
What about addition of an electron to the LUMO?



← sketch of the LUMO.

The  $H_2O$  molecule will distort to a smaller H-O-H angle upon addition of an electron to the HOMO.

3.



$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & \beta \\ 0 & \beta & \alpha & \beta \\ 0 & \beta & \beta & \alpha \end{pmatrix}$$

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & \beta \\ 0 & \beta & \alpha & 0 \\ 0 & \beta & 0 & \alpha \end{pmatrix}$$

Hückel matrices for these two problems.

$$\alpha - 1.48\beta \quad \text{---}$$

$$\alpha - \beta \quad \text{---}$$

$$\alpha + 0.31\beta \quad \text{++}$$

$$\alpha + 2.27\beta \quad \text{++}$$

$$E_{tot} = 4\alpha + 4.96\beta$$

$$\alpha - 1.73\beta \quad \text{---}$$

$$\alpha \quad \text{++}$$

$$\alpha + 1.73\beta \quad \text{++}$$

$$E_{tot} = 4\alpha + 3.46\beta$$

⇒ is the more stable molecule.