
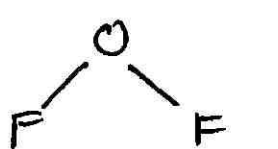


Lecture 32 Week 11

Inorganic chemistry

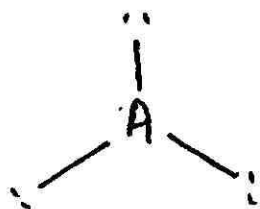
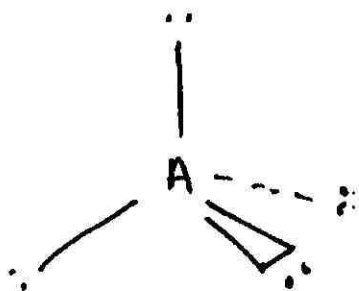
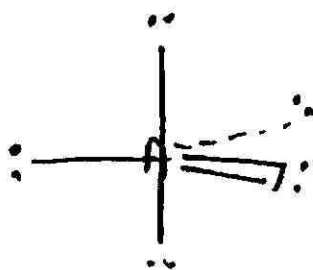
① The same MO ideas which are useful in organic chemistry are also useful when examining inorganic chemistry. As our first inorganic problem we consider the molecules and ion:

molecule:		geometry:
BeH_2	BeF_2	$\text{F}-\text{Be}-\text{F}$ linear
CH_2	CF_2	 bent
OH_2 (or H_2O)	OF_2	 bent
-	IF_2^-	$\text{F}-\text{I}^- - \text{F}$ linear

② Why are some molecules linear and other molecules bent?

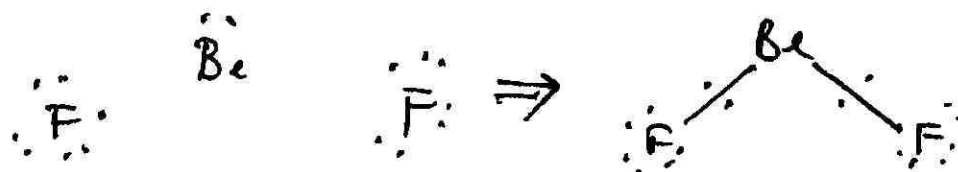
③ Let's first look at the way an inorganic chemist would view this problem. The inorganic chemist would count e^- and use the VSEPR model:

④

2 pairs e^- 3 pairs e^- 4 pairs e^- 5 pairs e^-

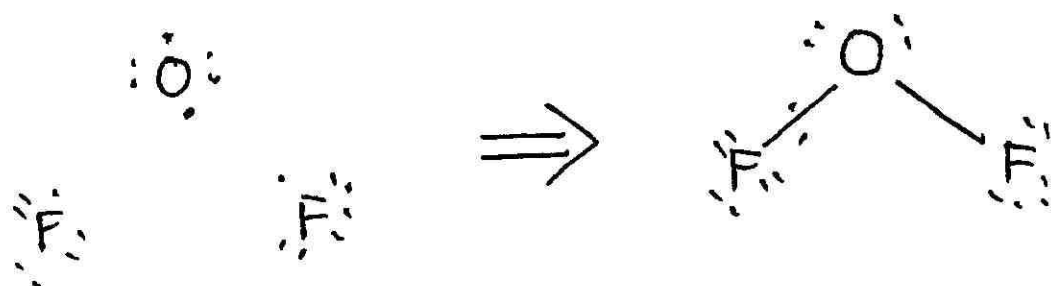
⑤

Consider BeF_2 . One draws a Lewis structure

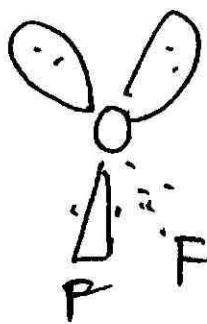


Be has 2 pairs of e^- and is \therefore by ④ linear.

⑥ By contrast OH_2 has the Lewis structure



O has 4 pairs e^- around it. Hence the e^- are in a tetrahedron & the structure of F_2O is



OF_2 is bent.

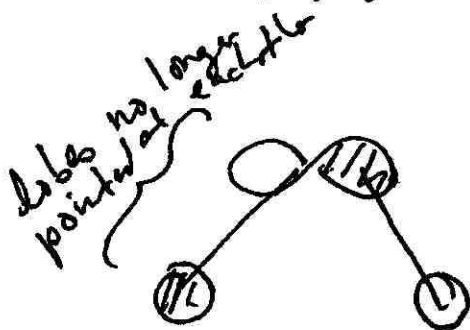
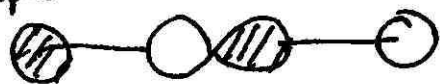
⑦ All of this is not an explanation, it is a rationalization. e^- after all are in orbitals or M.O.'s. Let's see if using MO theory we can come up with an explanation instead of a rationalization.

⑧ We will make what is called, a Walsh diagram. We will draw the MO diagram of the high symmetry ^(linear) geometry. We will then distort the geometry to the bent (low symmetry geometry). We will see how this will affect MO's.

⑨ There will be two types of effects on MO, which we will call changes w/o mixing and changes w/ mixing.

(i) Orbital energy changes w/o mixing are the changes in energy from an orbital without considering interaction with other orbitals. An example will hopefully make this point clear:

Example

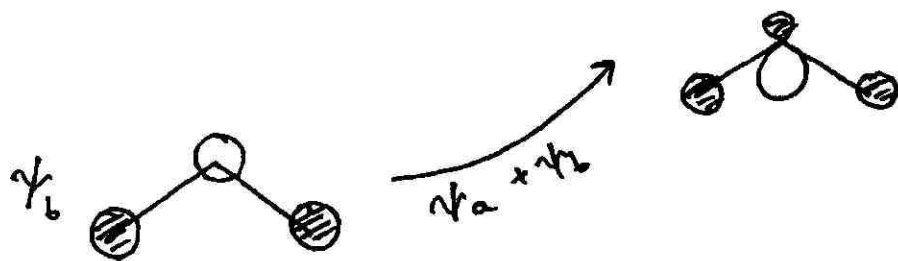


E ↑

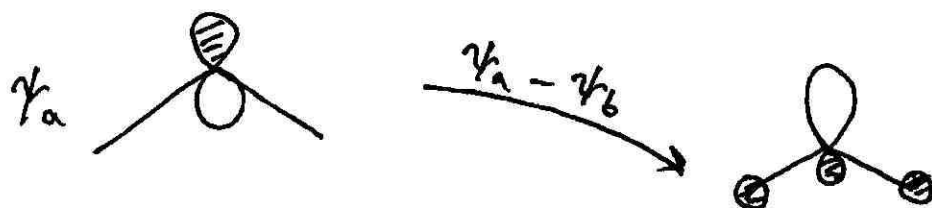
energy goes down as orbital becomes less antibonding

(ii)

Orbital energy change from mixing. Mixing here refers to the pairwise interaction of two orbitals.



pair-wise interaction



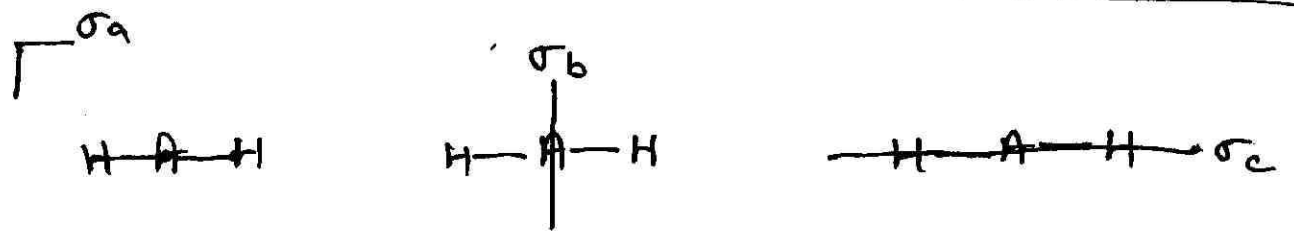
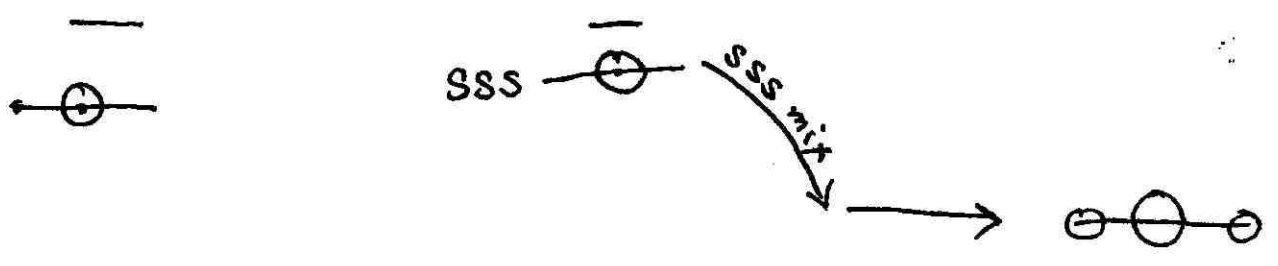
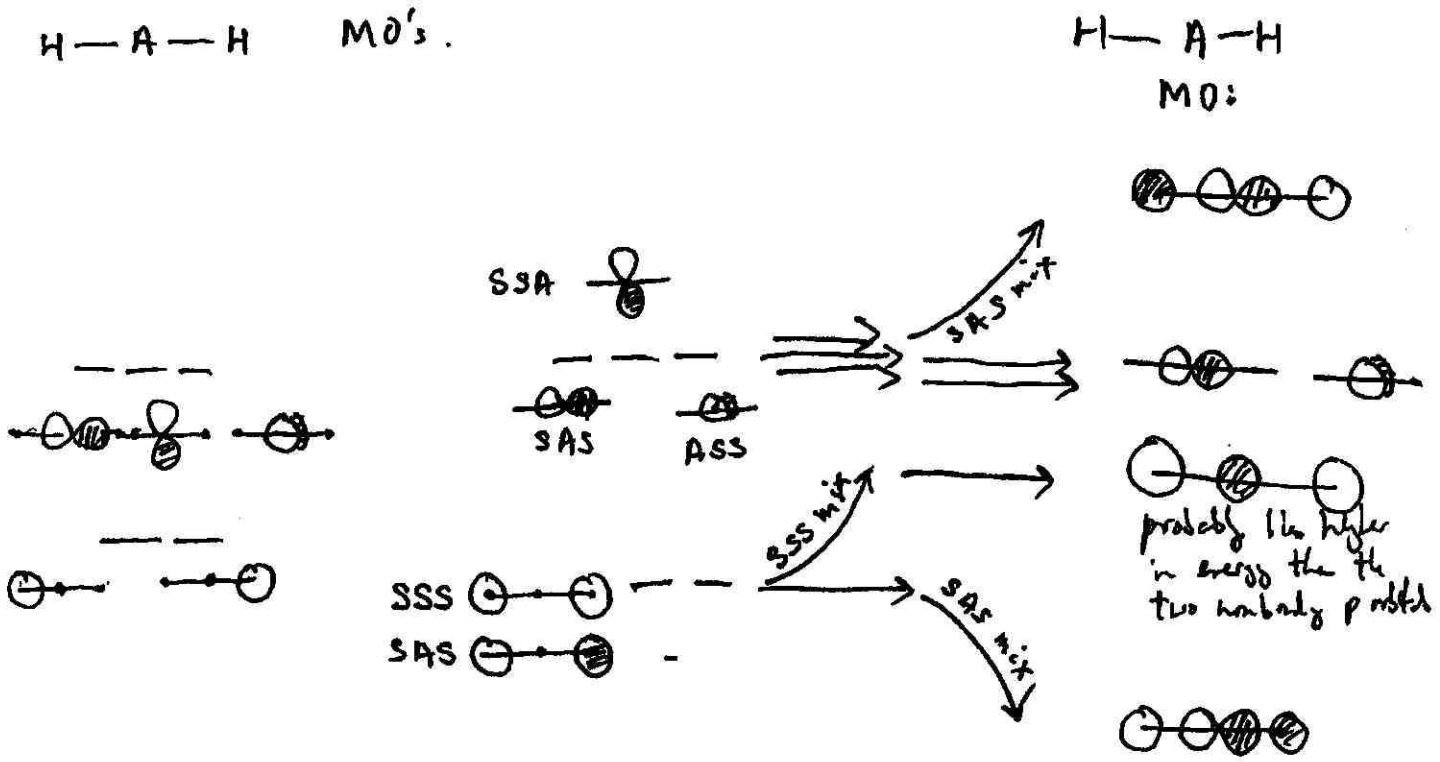
⑩ We will first make MO diagram of the linear AH_2 molecule. We pay attention to the following atomic energies:

	valence s	valence p
H	-13.6 eV	—
Li	-5.4	-3.5 eV
B	-15.2	-8.5
C	-21.4	-11.4
N	-26.0	-13.4
O	-32.3	-14.8
F	-40.0	-18.1

So we will choose an average A atom. A represents \downarrow represents

(Be-I) $p = -13.0 \text{ eV}$ $s = -22.0 \text{ eV}$

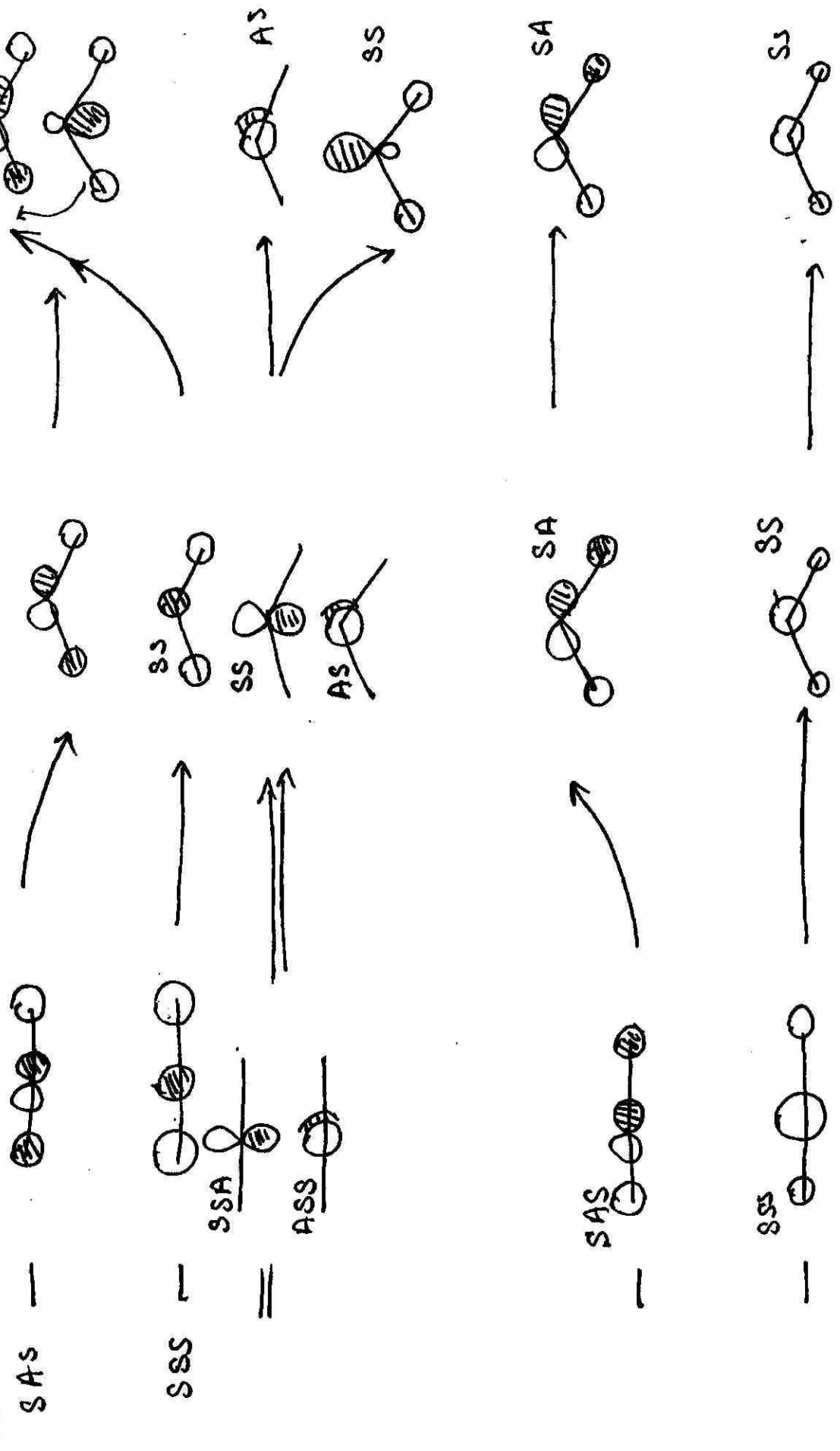
① We first make symmetry adapted orbitals & then intersect these sym. adapted orbitals in order to obtain MO's.



(12) Now consider energies under consider

the Walsh diagram, the change in the movement: H-A-H to mixing then we consider with mixing.

MOs & their first



σ_b H A H

W/o mixing

No σ_c after bonding of HAH angle.

W/ mixing. LOOK for orbitals close in energy which could not mix before in linear geometry.

⑬

Now we consider which MO is lower in energy.

# valence e^-	# filled orbitals	geometry	example
4 e^-	2 filled orbitals	linear	BeF_2
6 e^-	3 filled orbitals	bent	$\begin{cases} \text{CH}_2 \\ \text{CF}_2 \end{cases}$
8 e^-	4 filled orbitals	bent	$\begin{cases} \text{OH}_2 \\ \text{OF}_2 \end{cases}$
10 e^-	5 filled orbitals	linear	IF_2

⑭ Compare the MO explanation with the VSEPR explanation. Summarize in your mind the advantage and disadvantage of the two methods. Are the explanations based on the same chemical/physical ideas? If they are based on different physical ideas which one do you think may be more correct? Is there a way to test ^{experimentally} these ideas to find out which idea is correct?