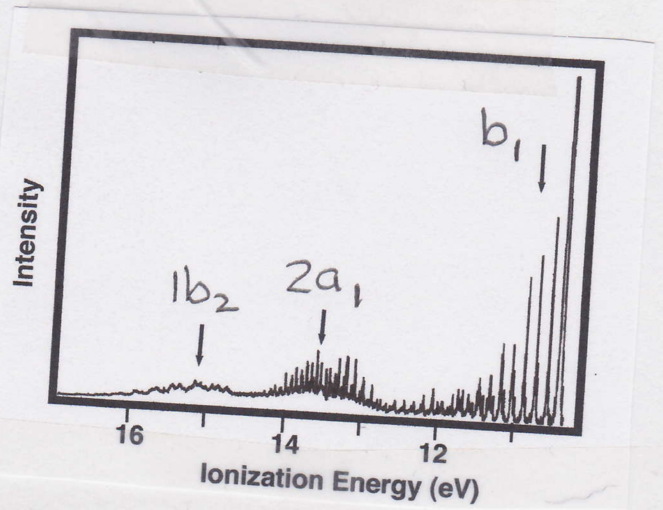
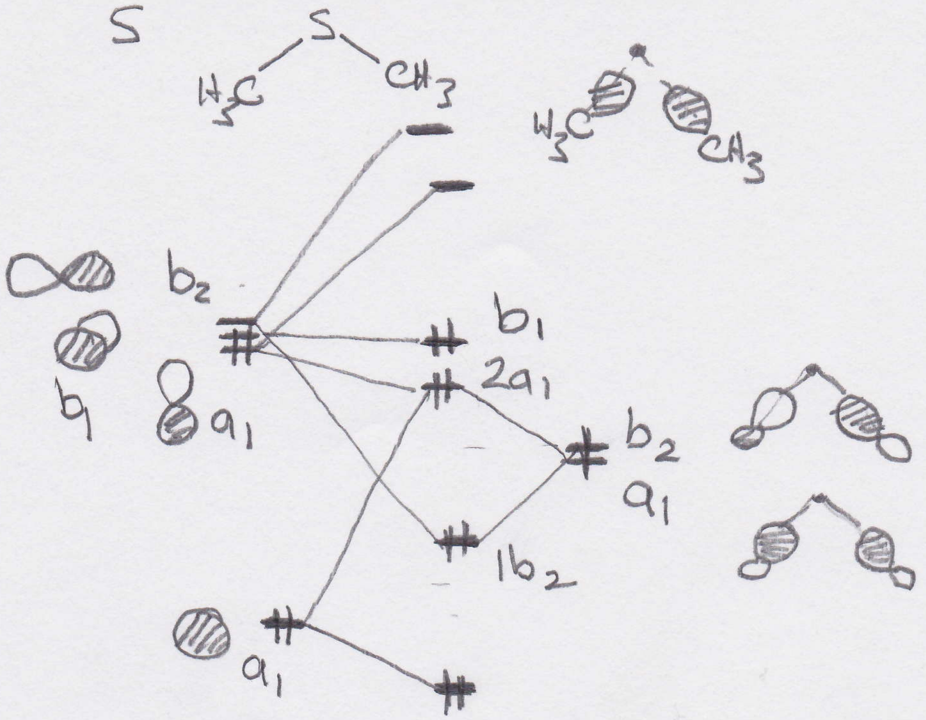
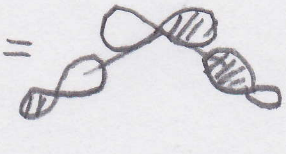
Answers - Chapter 7

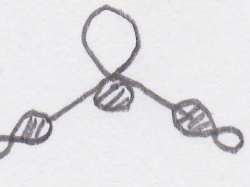
1. a) the orbitals of H_2S should qualitatively be similar to those for H_2O – the PE spectrum is shown in Figure 7.9. Therefore,



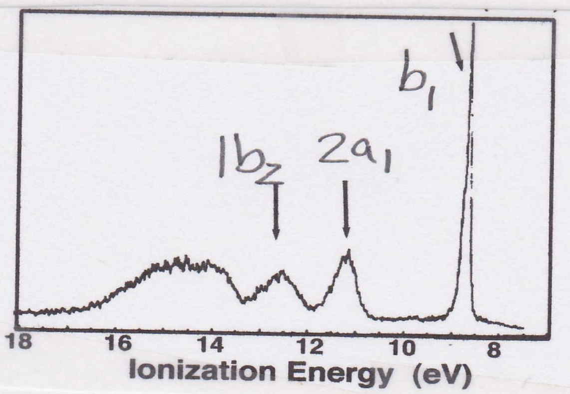
b)



$1b_2 =$ 

$2a_1 =$ 

$b_1 =$ 



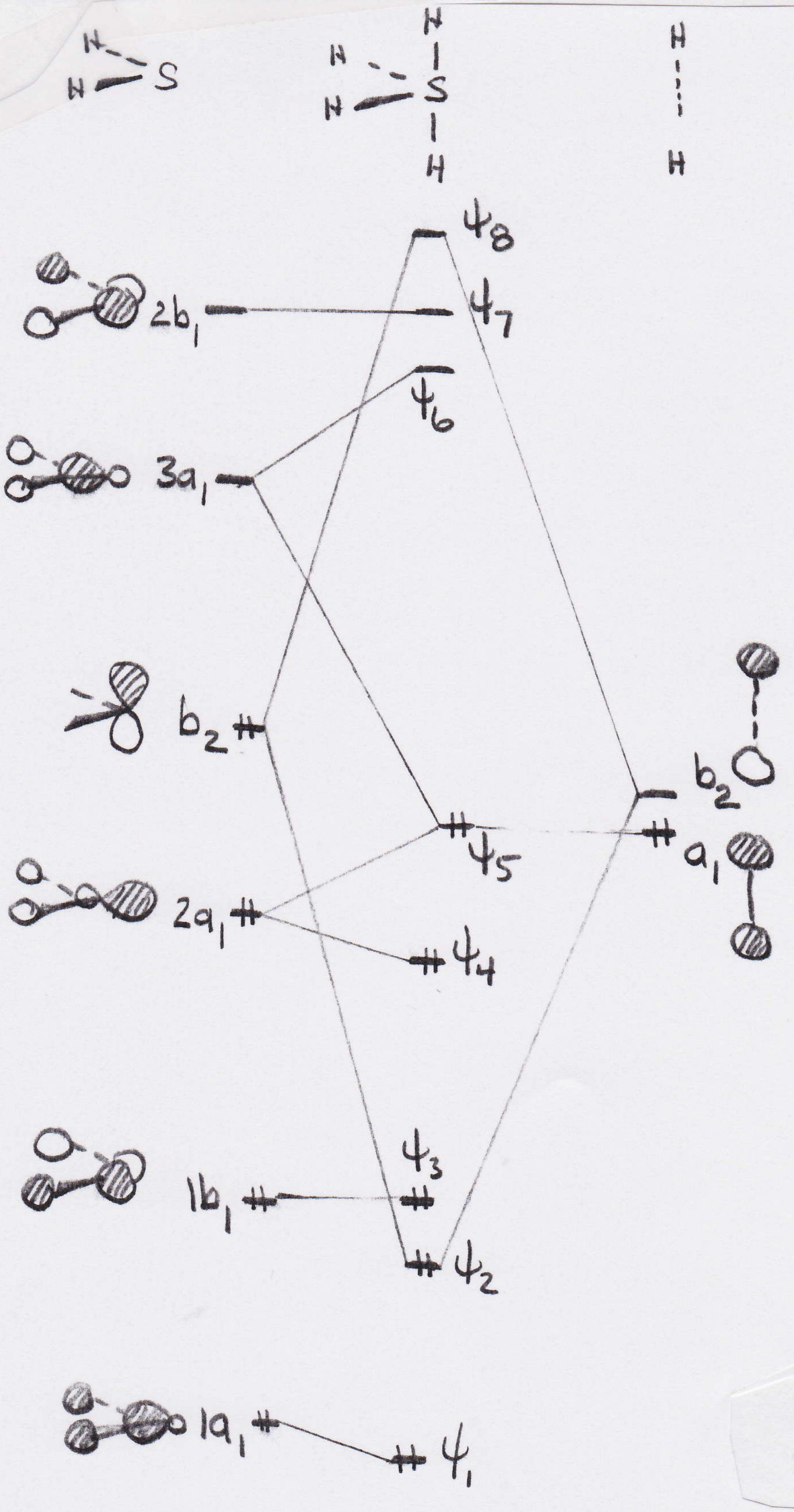
The first ionization is sharper (the vibrational progression is shorter) compared to the second ionization just as it is in H_2O and H_2S. This is consistent with b_1 MO being localized on S, as opposed to $2a_1$ which contains some CH_3 (or H) character and consequently the C-S-C (or H-S-H) bond angle changes in the radical ion state.

c) The methyl group donates electron density compared to H. This pushes the MOs to higher energy or lower ionization potential in the PE spectrum.

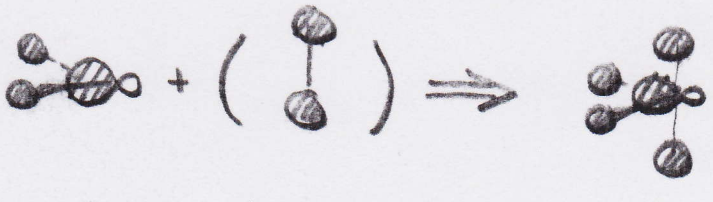
d) Going from $(CH_3)_2S$ to $[(CH_3)_3C]_2S$ the C-S-C bond angle is expected to open up. Recall from the Walsh diagram for H_2S in Figure 7.5; as the H-S-H angle increases, the $2a_1$ orbital is destabilized. Therefore, one would expect a lower ionization potential to be associated with it.

The actual mechanism for the destabilization of $2a_1$ & b_1 is documented more fully in Chapter 10.5.

2.



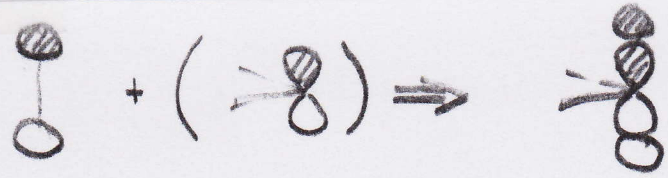
$\psi_1 \propto$



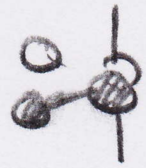
neglecting 2$^{\text{nd}}$ order mixings with 2a$_1$ and 3a$_1$

The MO's from an Extended Hückel calculation are on the next page

$\psi_2 \propto$

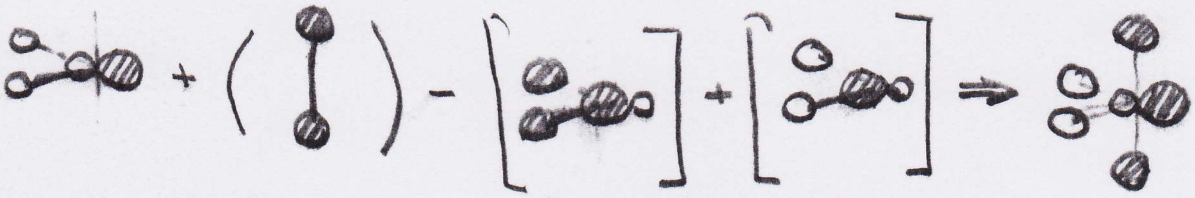


$\psi_3 =$



<u>note</u> this orbital must be higher in energy than ψ_2 is – why??

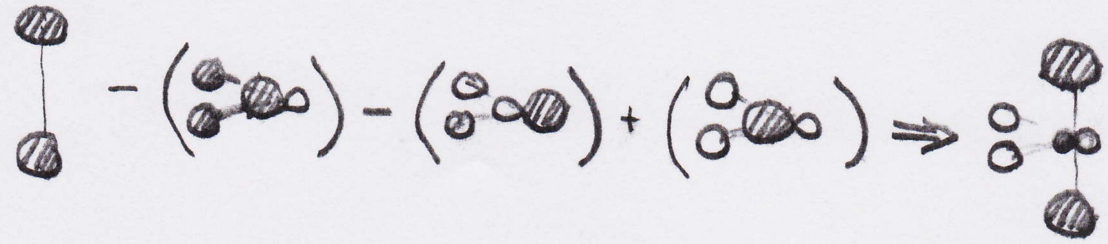
$\psi_4 \propto$



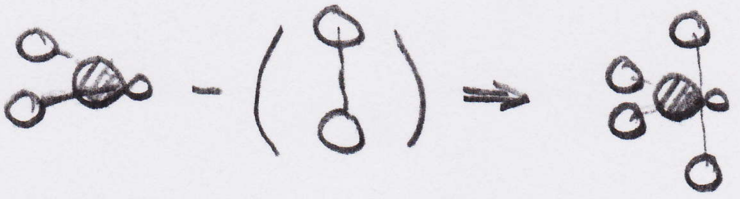
cancellation at S by these two 2nd order terms

<u>note</u> overlap between H_2 σ is determined by S A.O. at sulfur

$\psi_5 \propto$

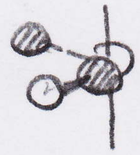


$\psi_6 \propto$

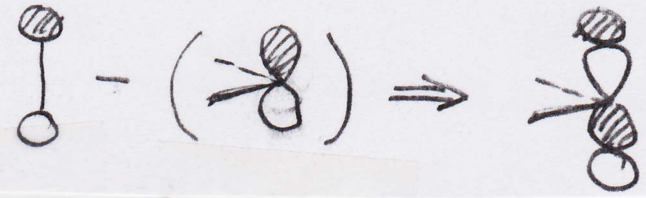


neglecting other 2nd order mixings

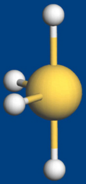
$\psi_7 =$

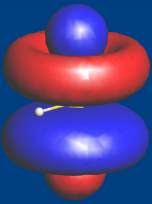


$\psi_8 =$

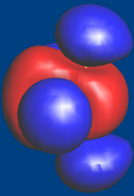


The MOs from an extended Hückel calculation are plotted on the next page.

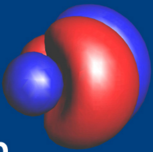




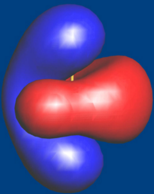
$2b_1$



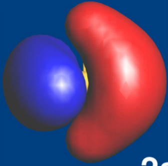
$4a_1$



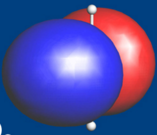
$2b_2$



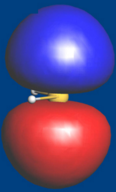
$3a_1$



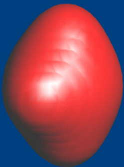
$2a_1$



$1b_2$

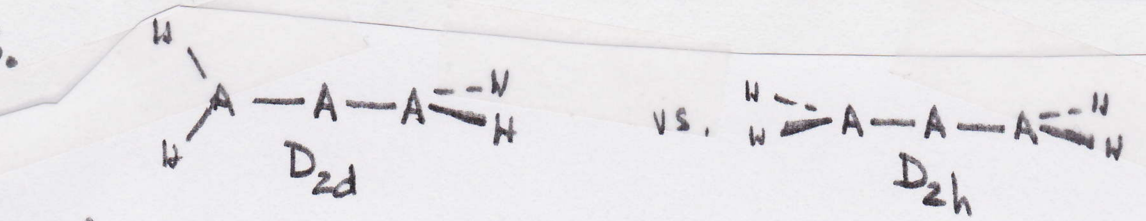


$1b_1$

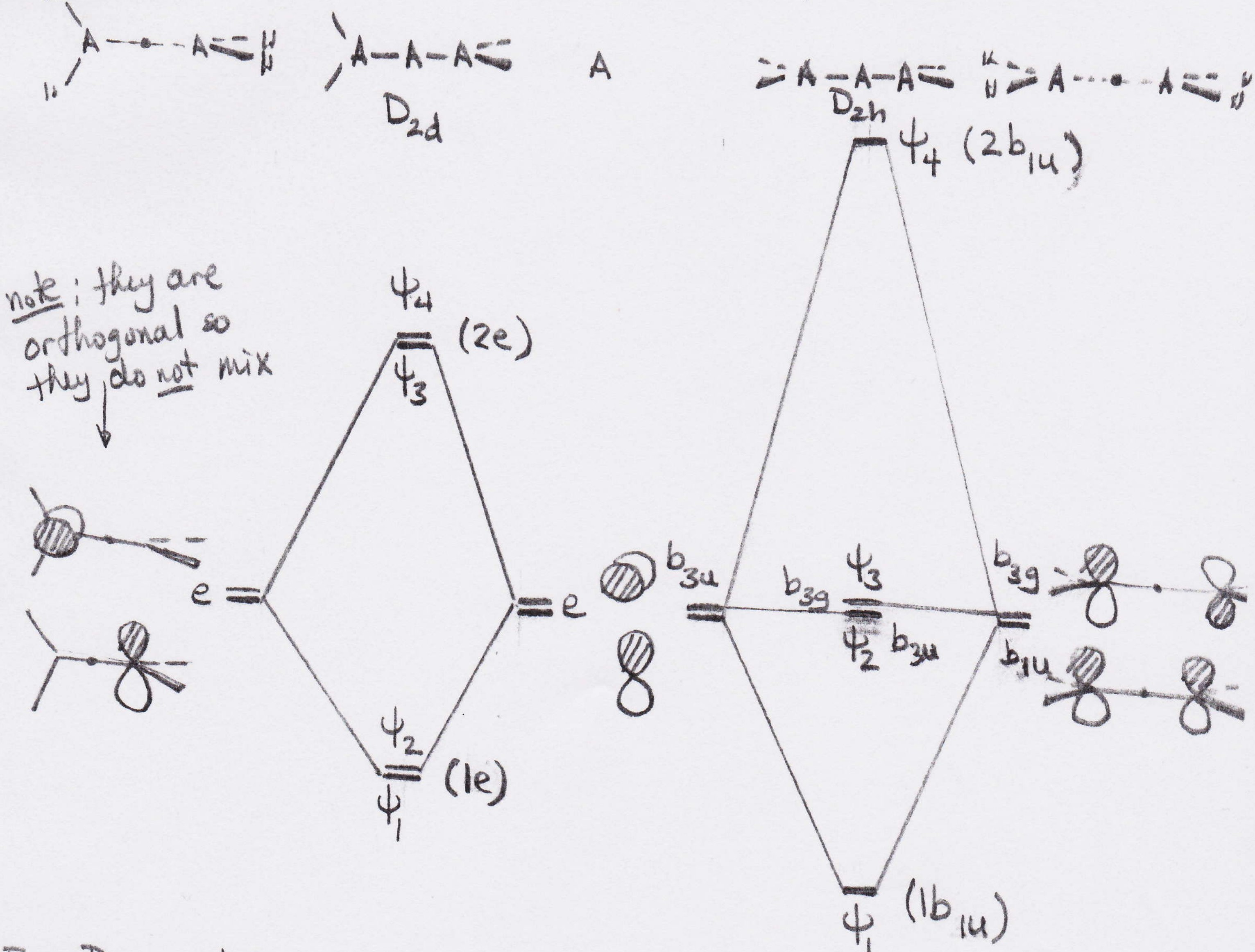


$1a_1$

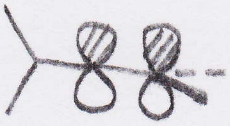
3.

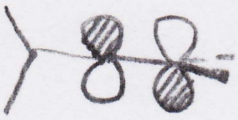


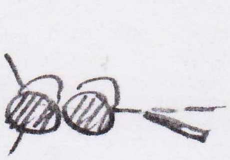
The easiest way to derive the π orbitals is via interacting $H_2A\text{-----}AH_2$ with the central A atom:

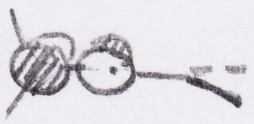


note: they are orthogonal so they do not mix

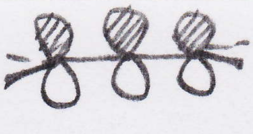
For D_{2d}: ψ_1 = 

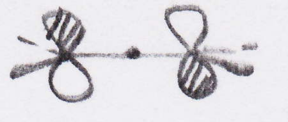
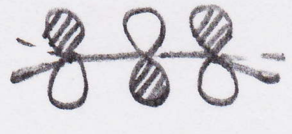
ψ_3 = 

ψ_2 = 

ψ_4 = 

just the simple π/π^* levels!

For D_{2h}: ψ_1 =  ψ_2 = 

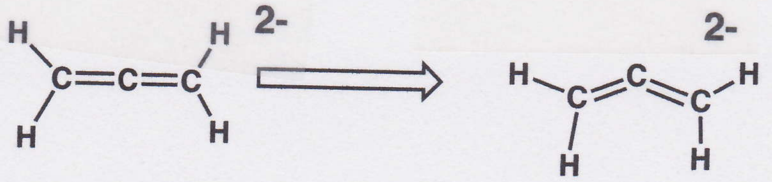
ψ_3 =  ψ_4 = 

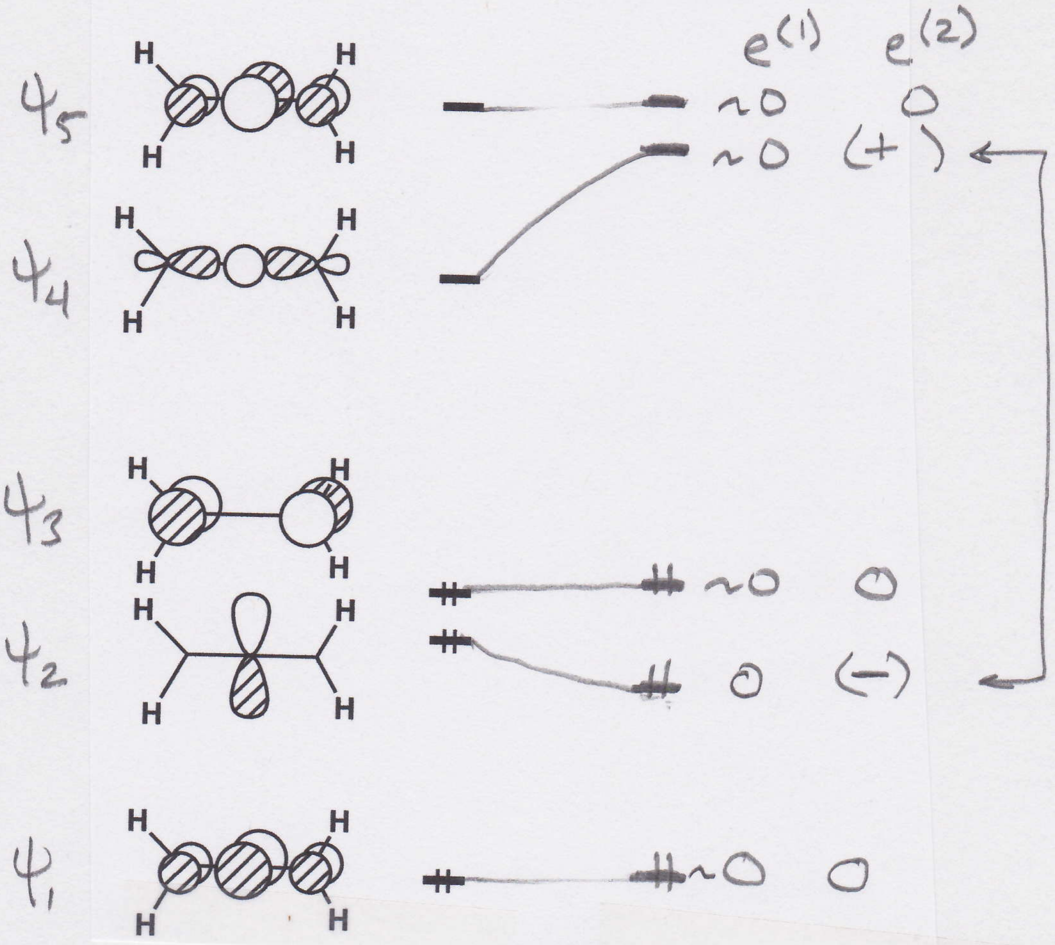
<u>note</u> ψ_1 ; ψ_3 & ψ_4 are the π orbitals of an allyl system

The π orbitals here are strictly analogous to the σ orbitals of H_2 and linear H_3. Notice that $1b_{1u}$ in D_{2h} is lower in energy than the 1e set is in D_{2d} and $2b_{1u}$ is much higher in energy than the 2e set. This is a straightforward application of Fig. 3.1. ~~on p. 36!~~ Therefore, the prefered structures are:

number of e⁻	structure	
2	D_{2h}	$(1b_{1u})^2$ vs. $(1e)^2$
4	D_{2d}	$(1b_{1u})^2(b_{3u})^2$ vs $(1e)^4$
6	D_{2h}	$(1b_{1u})^2(b_{3u})^2(b_{3g})^2$ vs. $(1e)^4(2e)^2$
8	D_{2d}	$(1b_{1u})^2(b_{3u})^2(b_{3g})^2(2b_{1u})^2$ vs $(1e)^4(2e)^4$

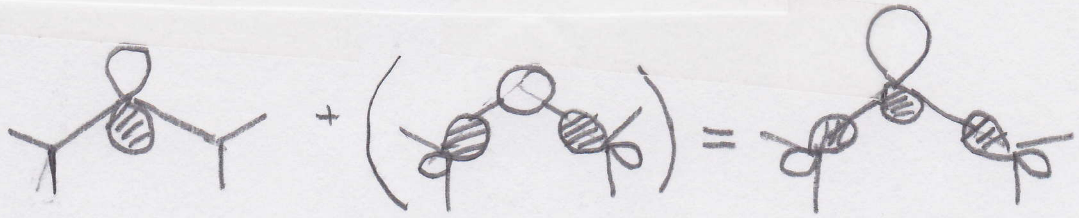
4. a)



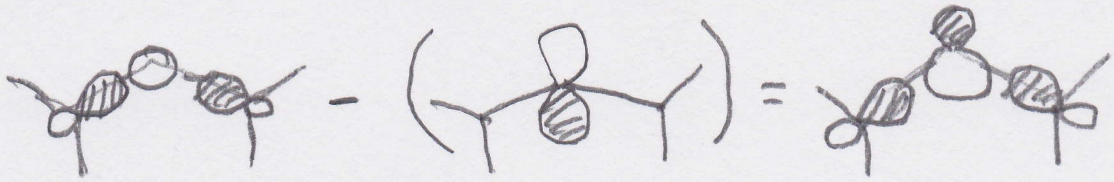


these two MO's mix strongly on bending

$\psi_2 =$

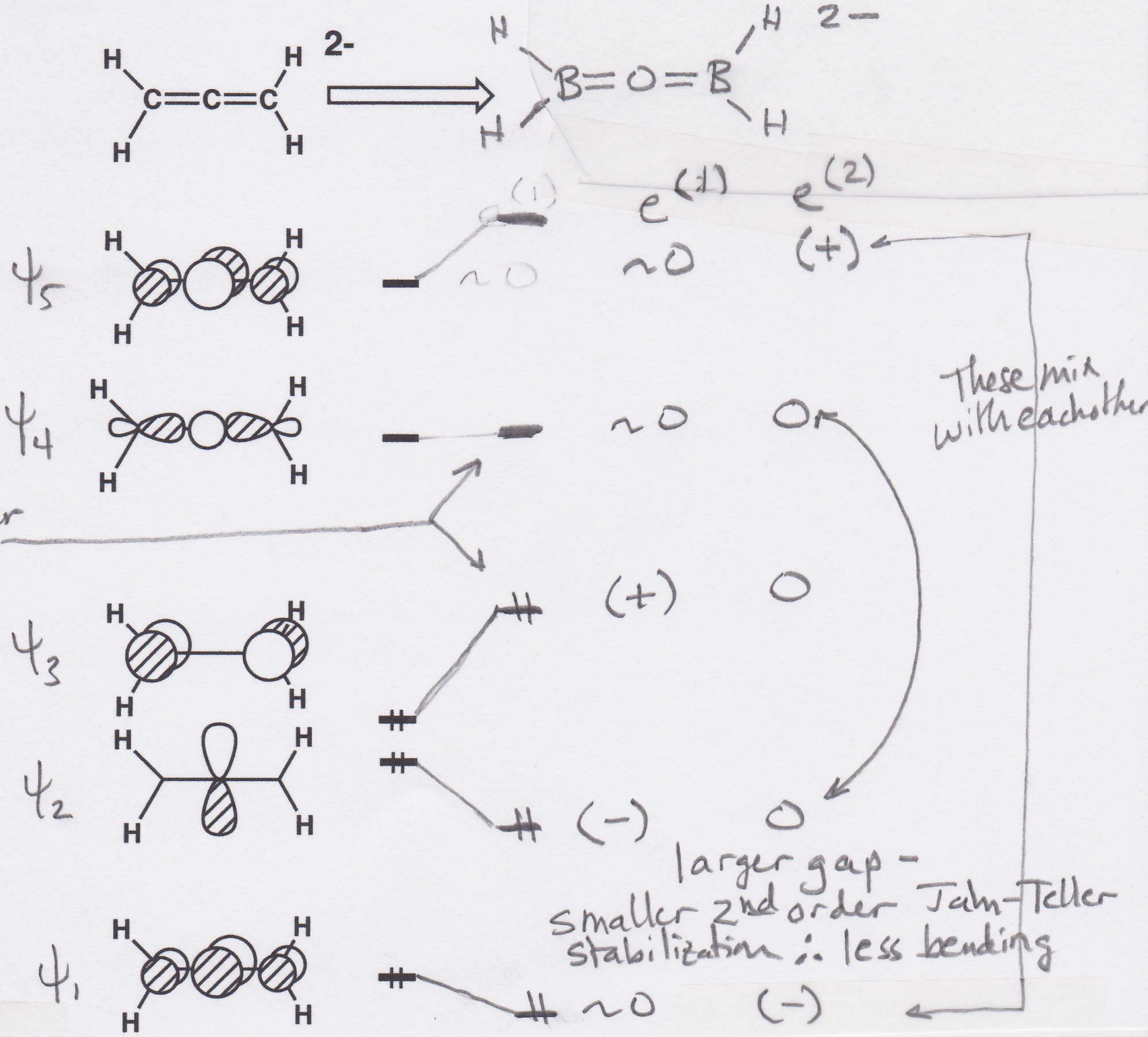


$\psi_4 =$



<u>note</u> $\langle \psi_2 | \psi_4 \rangle = (+)$ as drawn

b) For B $\delta\alpha = (+)$; for O $\delta\alpha = (-)$. Either $\delta\alpha$ for two B atoms is greater in absolute magnitude than one O atom or they will cancell. Lets assume the latter. Then



These mix with each other

note: a smaller Homo-Lumo gap does not always lead to a larger geometry change

larger gap - smaller 2nd order Jahn-Teller stabilization ∴ less bending

5. See Figure 9.12 and the discussion around it for the answer. We shall see another H_2 complex in 14.47 and in 15.25.