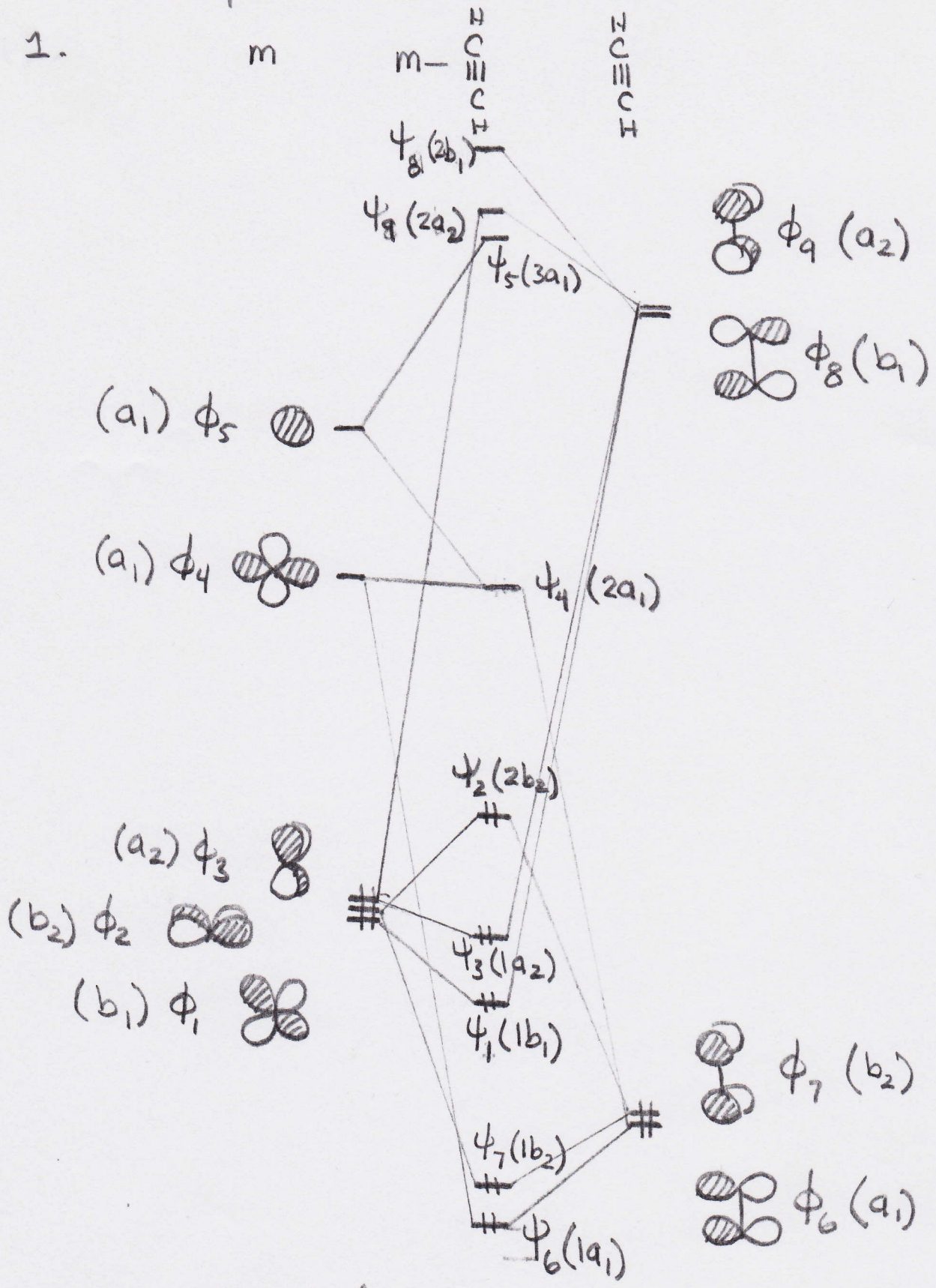
Answers - Chapter 10

1.



Only orbitals of the same symmetry interact! Notice that

$S_{46} \approx S_{56} > S_{18} \approx S_{27} > S_{39}$ (overlaps are $\sigma > \pi > \delta$!)

Notice that <u>all</u> $S_{ij} = (+)$ in the drawing.

$e_1 = e_1^\circ + e_1^{(2)}$ $\quad e_1^{(2)} \propto \frac{S_{18}^2}{e_1^\circ - e_8^\circ} = \frac{(+)}{(-)} = (-)$ stab.

$e_2 = e_2^\circ + e_2^{(2)}$ $\quad e_2^{(2)} \propto \frac{S_{27}^2}{e_2^\circ - e_7^\circ} = \frac{(+)}{(+)} = (+)$ destab.

$e_3 = e_3^\circ + e_3^{(2)}$ $\quad e_3^{(2)} \propto \frac{S_{39}^2}{e_3^\circ - e_9^\circ} = \frac{(+)}{(-)} = (-)$ stab.

$e_4 = e_4^\circ + e_4^{(2)}$ $\quad e_4^{(2)} \propto \frac{S_{46}^2}{e_4^\circ - e_6^\circ} = \frac{(+)}{(+)} = \underset{\text{(destab.)}}{(+)} + e_4^{(3)}$ (stab.)

$e_5 = e_5^\circ + e_5^{(2)}$ $\quad e_5^{(2)} \propto \frac{S_{56}^2}{e_5^\circ - e_6^\circ} = \frac{(+)}{(+)} =$ destab,

$e_6 = e_6^\circ + e_6^{(2)}$ $\quad e_6^{(2)} \propto \frac{S_{46}^2}{e_6^\circ - e_4^\circ} + \frac{S_{56}^2}{e_6^\circ - e_5^\circ} = \frac{(+)}{(-)} + \frac{(+)}{(-)} = (-)$ stab.

$e_7 = e_7^\circ + e_7^{(2)}$ $\quad e_7^{(2)} \propto \frac{S_{27}^2}{e_7^\circ - e_2^\circ} = \frac{(+)}{(-)} = (-)$ stab,

$e_8 = e_8^\circ + e_8^{(2)}$ $\quad e_8^{(2)} \propto \frac{S_{18}^2}{e_8^\circ - e_1^\circ} = \frac{(+)}{(+)} = (+)$ destab,

$e_9 = e_9^\circ + e_9^{(2)}$ $\quad e_9^{(2)} \propto \frac{S_{39}^2}{e_9^\circ - e_3^\circ} = \frac{(+)}{(+)} = (+)$ destab,

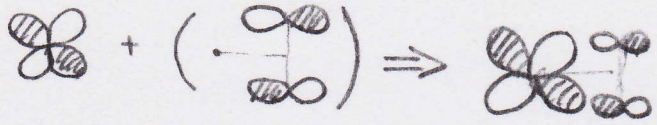
notice from what we have decided on the basis of overlaps:

$e_6^{(2)} < e_7^{(2)} \approx e_1^{(2)} < e_3^{(2)}$

and

$e_5^{(2)} > e_8^{(2)} \approx e_2^{(2)} > e_9^{(2)}$

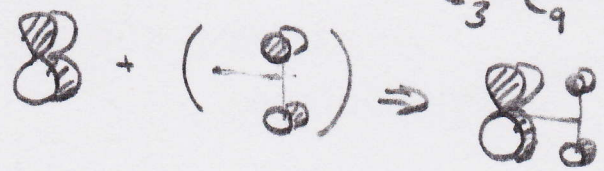
$$\psi_1 \approx \phi_1 + t_{81}^{(1)}\phi_8 \qquad t_{81}^{(1)} \propto \frac{-S_{18}}{e_1^\circ - e_8^\circ} = \frac{(-)}{(-)} = (+)$$

$\therefore \psi_1 =$ 

$$\psi_2 \approx \phi_2 + t_{72}^{(1)}\phi_7 \qquad t_{72}^{(1)} \propto \frac{-S_{27}}{e_2^\circ - e_7^\circ} = \frac{(-)}{(+)} = (-)$$

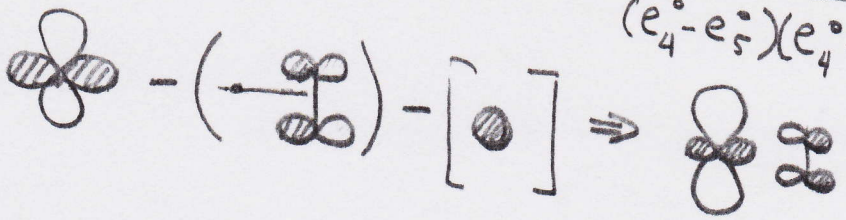
$\therefore \psi_2 =$ 

$$\psi_3 \approx \phi_3 + t_{93}^{(1)}\phi_9 \qquad t_{93}^{(1)} \propto \frac{-S_{39}}{e_3^\circ - e_9^\circ} = \frac{(-)}{(-)} = (+)$$

$\therefore \psi_3 =$ 

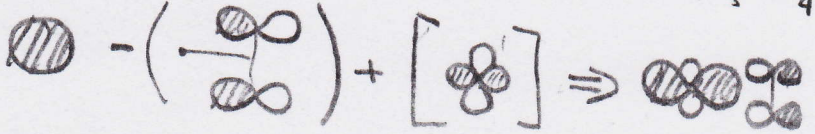
$$\psi_4 \approx \phi_4 + t_{64}^{(1)}\phi_6 + t_{54}^{(2)}\phi_5 \qquad t_{64}^{(1)} \propto \frac{-S_{46}}{e_4^\circ - e_6^\circ} = \frac{(-)}{(+)} = (-)$$

$$t_{54}^{(2)} \propto \frac{S_{46}\,S_{56}}{(e_4^\circ - e_5^\circ)(e_4^\circ - e_6^\circ)} = \frac{(+)(+)}{(-)(+)} = (-)$$

$\therefore \psi_4 =$ 

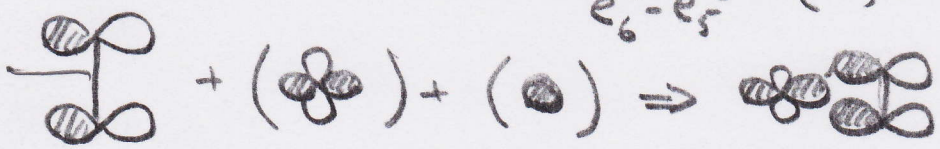
$$\psi_5 \approx \phi_5 + t_{65}^{(1)}\phi_6 + t_{45}^{(2)}\phi_4 \qquad t_{65}^{(1)} \propto \frac{-S_{56}}{e_5^\circ - e_6^\circ} = \frac{(-)}{(+)} = (-)$$

$$t_{45}^{(2)} \propto \frac{S_{56}\,S_{46}}{(e_5^\circ - e_4^\circ)(e_5^\circ - e_6^\circ)} = \frac{(+)(+)}{(-)(-)} = (+)$$

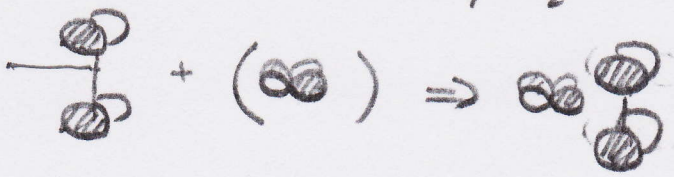
$\therefore \psi_5 =$ 

$\psi_6 \approx \phi_6 + t_{46}^{(1)}\phi_4 + t_{56}^{(1)}\phi_5$ $\quad t_{46}^{(1)} \propto \frac{-S_{46}}{e_6^\circ - e_4^\circ} = \frac{(-)}{(-)} = (+)$

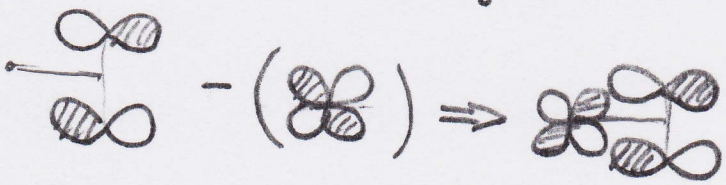
$t_{56}^{(1)} \propto \frac{-S_{56}}{e_6^\circ - e_5^\circ} = \frac{(-)}{(-)} = (+)$

$\therefore \psi_6 =$  $\Rightarrow$

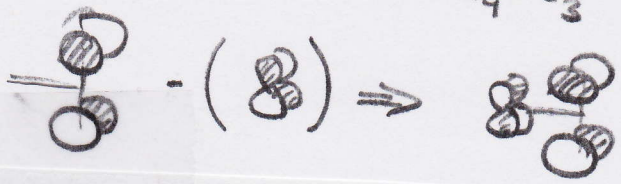
$\psi_7 \approx \phi_7 + t_{27}^{(1)}\phi_7$ $\quad t_{27}^{(1)} \propto \frac{-S_{27}}{e_7^\circ - e_2^\circ} = \frac{(-)}{(-)} = (+)$

$\therefore \psi_7 =$ 

$\psi_8 \approx \phi_8 + t_{18}^{(1)}\phi_1$ $\quad t_{18}^{(1)} \propto \frac{-S_{18}}{e_8^\circ - e_1^\circ} = \frac{(-)}{(+)} = (-)$

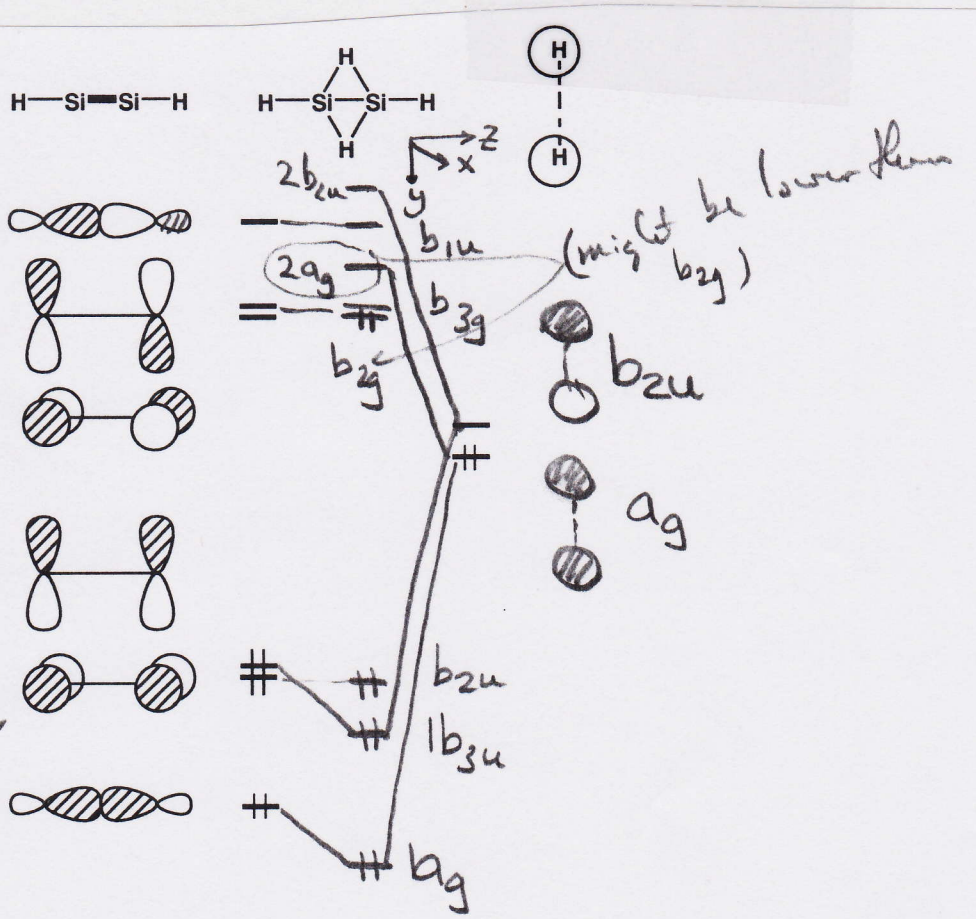
$\therefore \psi_8 =$ 

$\psi_9 \approx \phi_9 + t_{39}^{(1)}\phi_3$ $\quad t_{39}^{(1)} \propto \frac{-S_{39}}{e_9^\circ - e_3^\circ} = \frac{(-)}{(+)} = (-)$

$\therefore \psi_9 =$ 

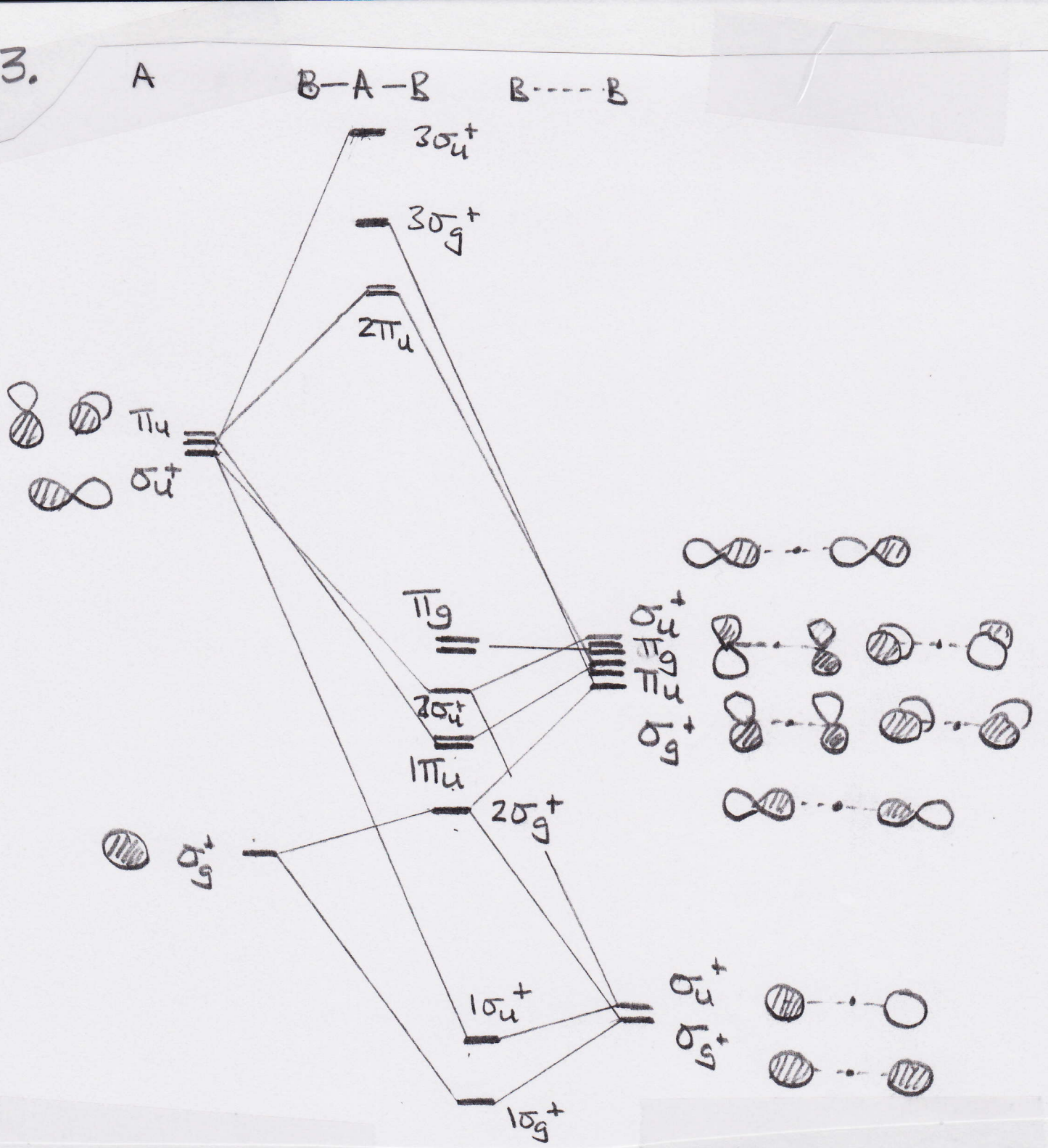
2.

using D_{2h} symmetry



Notice that b_{2g} and b_{3g} are at the same energy. Therefore, if the MO ordering is as given above, then the molecule should be a triplet. If $2a_g$ lies at lower energy (but notice that it is strongly Si–H antibonding) then one might have a singlet.

3.



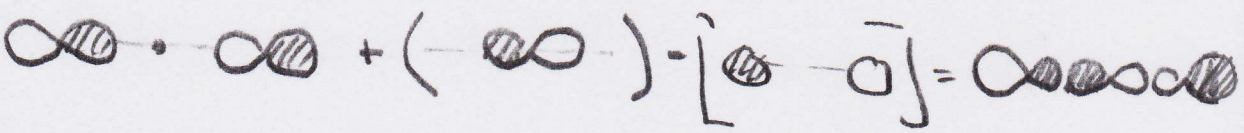
$1\sigma_g^+ \propto$ + ( ) + [ ] =

$1\sigma_u^+ \propto$ − + ( ) + [ ] =

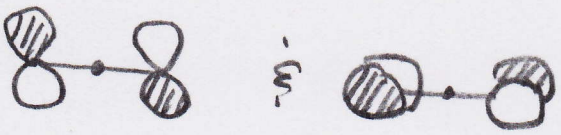
$2\sigma_g^+ \propto$ − (−) + ( ) =

$1\pi_u$ ∝

$2\sigma_u^+$ ∝

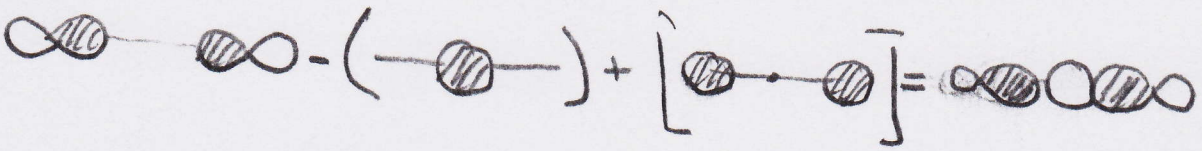


π_g =

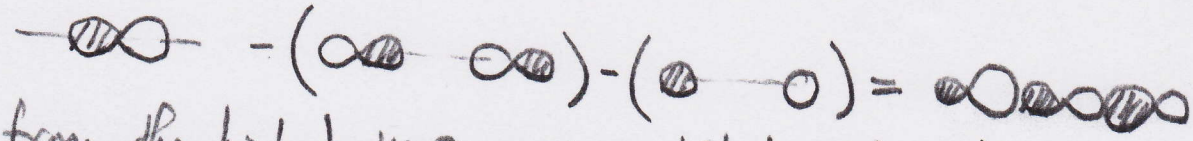


$2\pi_u$ ∝

$3\sigma_g^+$ ∝

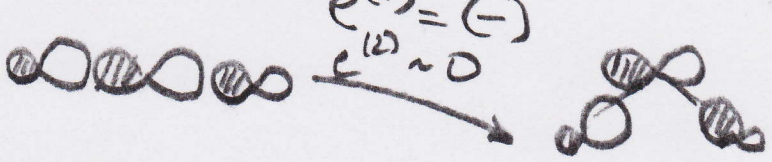


$3\sigma_u^+$ ∝



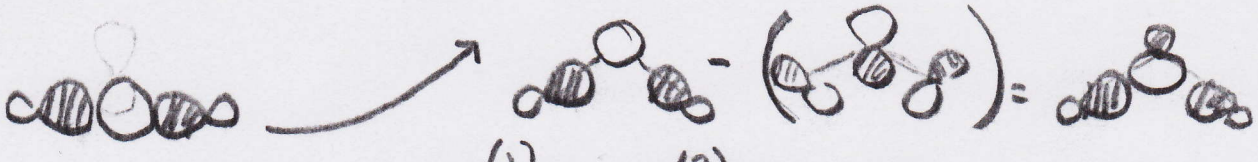
(b) Starting from the highest MO-only orbitals close to eachother in energy will be considered for the $e^{(2)} \neq t^{(1)}$ terms:

$3\sigma_u^+$

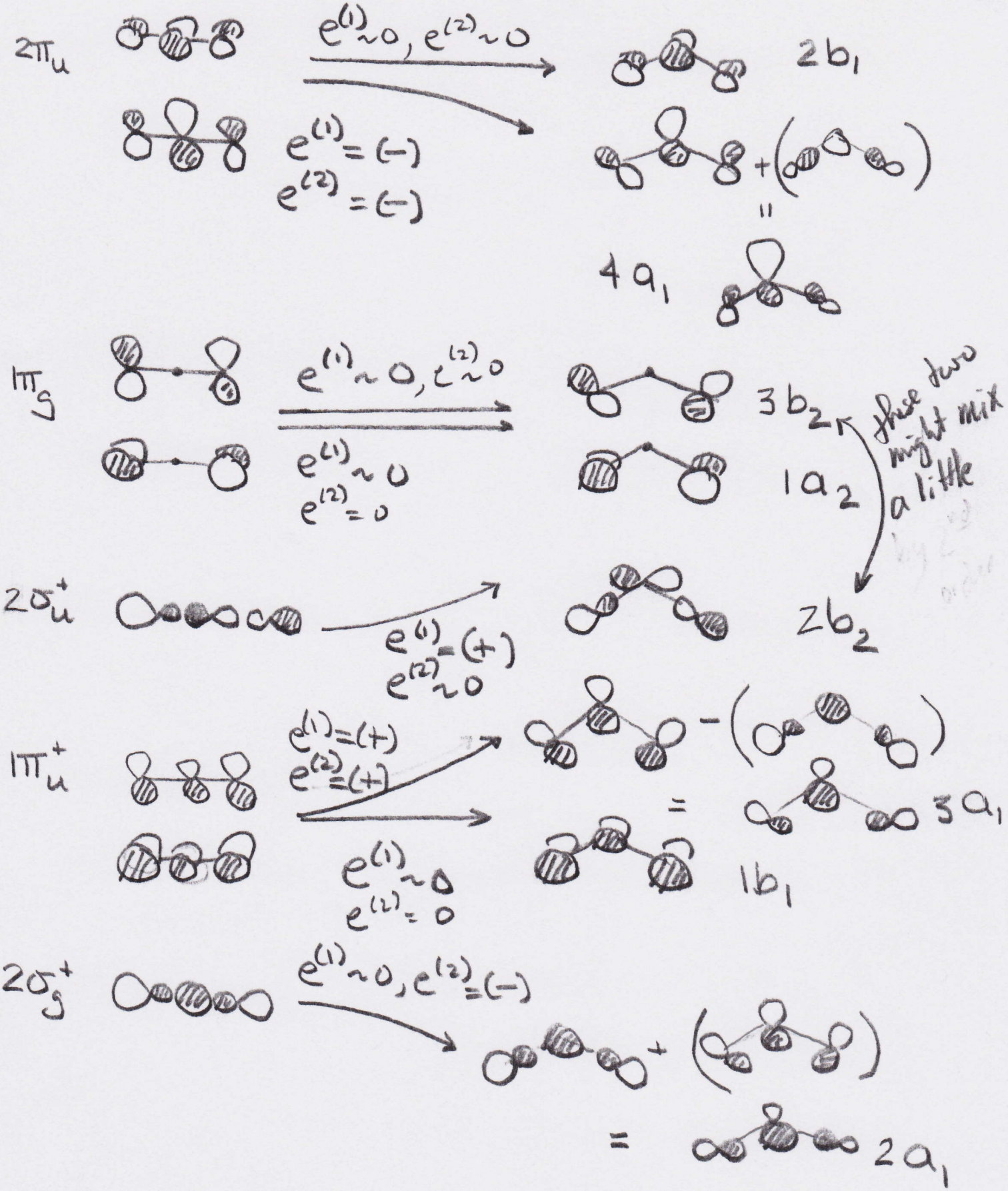


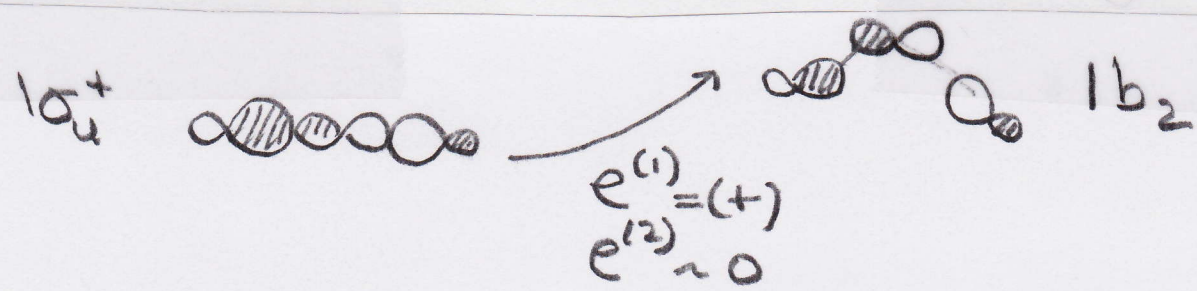
$4b_2$

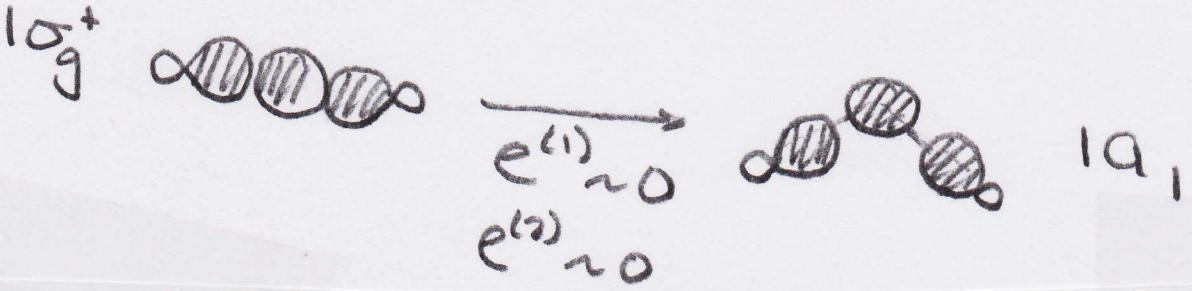
$3\sigma_g^+$



$e^{(1)} \sim 0, e^{(2)} = (+)$ $5a_1$


$2\pi_u$
$e^{(1)} \sim 0,\ e^{(2)} \sim 0$
$2b_1$
$e^{(1)} = (-)$
$e^{(2)} = (-)$
$4a_1$
$1\pi_g$
$e^{(1)} \sim 0,\ e^{(2)} \sim 0$
$e^{(1)} \sim 0$
$e^{(2)} = 0$
$3b_2$
$1a_2$
these two might mix a little
$2b_2$
$2\sigma_u^+$
$e^{(1)} = (+)$
$e^{(2)} \sim 0$
$1\pi_u^+$
$e^{(1)} = (+)$
$e^{(2)} = (+)$
$e^{(1)} \sim 0$
$e^{(2)} = 0$
$3a_1$
$1b_1$
$2\sigma_g^+$
$e^{(1)} \sim 0,\ e^{(2)} = (-)$
$2a_1$





The MO's for both geometries are displayed on the next page. These are extended Hückel calculations.

$B_2C = 10e^-$: $\ldots (1\pi_u)^4 - D_{\infty h}$

$CN_2 = 14e^-$: $\ldots (1\pi_u)^4(\pi_g)^2 - D_{\infty h}$ (triplet)

$CO_2 = 16e^-$: $\ldots (\pi\pi_u)^4(\pi_g)^4 - D_{\infty h}$

$CF_2 = 18e^-$: $\ldots (1\pi_u)^4(\pi_g)^4(2\pi_u)^2$ – triplet.

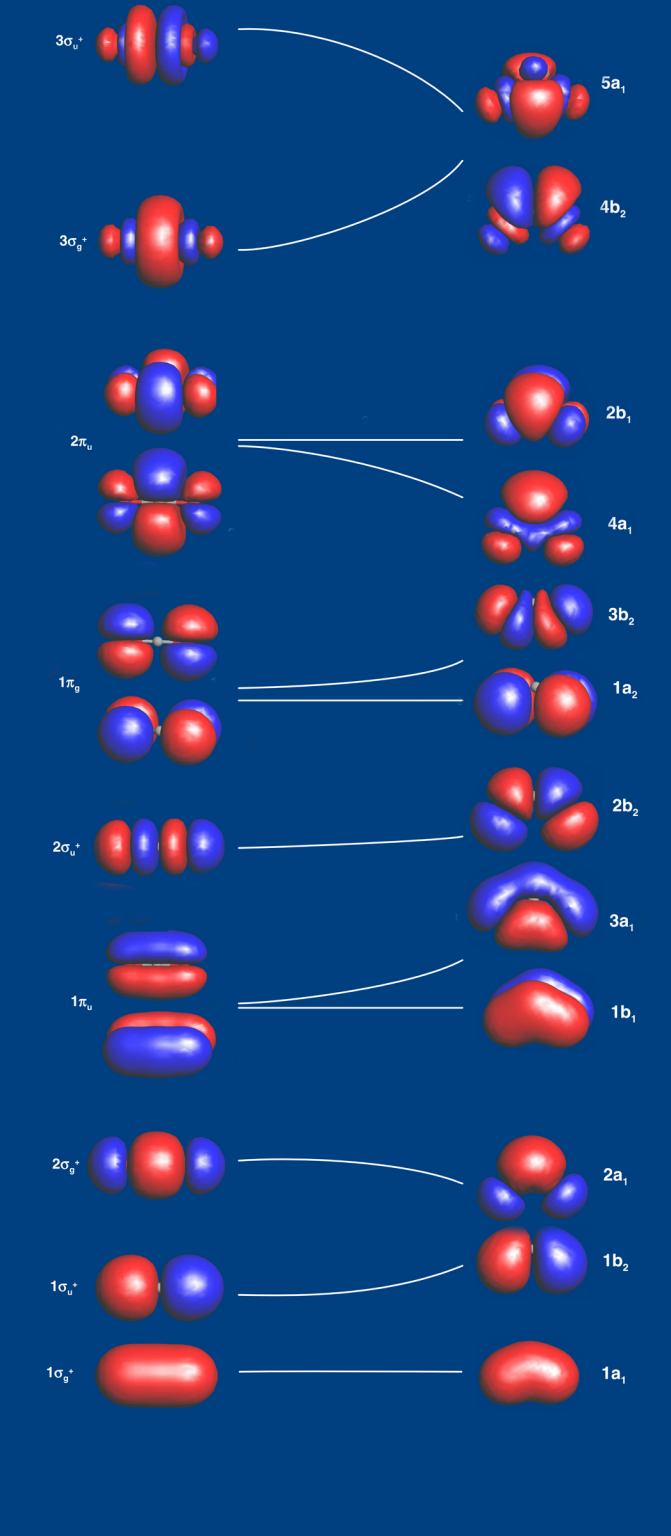
but C_{2v} $\ldots (4a_1)^1(2b_1)^1$ triplet

more stable $\ldots (4a_1)^2(2b_1)^0$ singlet

$O_3 = 18e^-$ → just like above

$OF_2 = 20e^-$: $\ldots (1\pi_u)^4(\pi_g)^4(2\pi_u)^4$ ∴ C_{2v} $\ldots (4a_1)^2(2b_1)^2$

$F_3^- = 22e^-$: $\ldots (\pi_g)^4(2\pi_u)^4(3\sigma_g^+) - D_{\infty h}$


$3\sigma_u^+$
$5a_1$
$3\sigma_g^+$
$4b_2$
$2\pi_u$
$2b_1$
$4a_1$
$3b_2$
$1\pi_g$
$1a_2$
$2b_2$
$2\sigma_u^+$
$3a_1$
$1\pi_u$
$1b_1$
$2\sigma_g^+$
$2a_1$
$1\sigma_u^+$
$1b_2$
$1\sigma_g^+$
$1a_1$

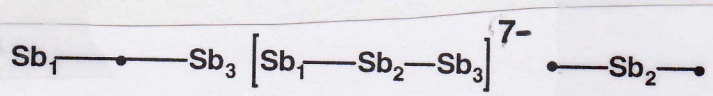
4. Both CO_2 and N_2O are 16e$^-$ molecules and, therefore, from prob. 3 both are linear molecules. Notice from the discussion around Figure 6.10, N_2O exists as NNO and not NON. From the interaction diagram for problem 3 the four sets of the highest occupied MO's are:

$$(2\sigma_g^+)^2(1\pi_u)^4(2\sigma_u^+)^2(\pi_g)^4$$

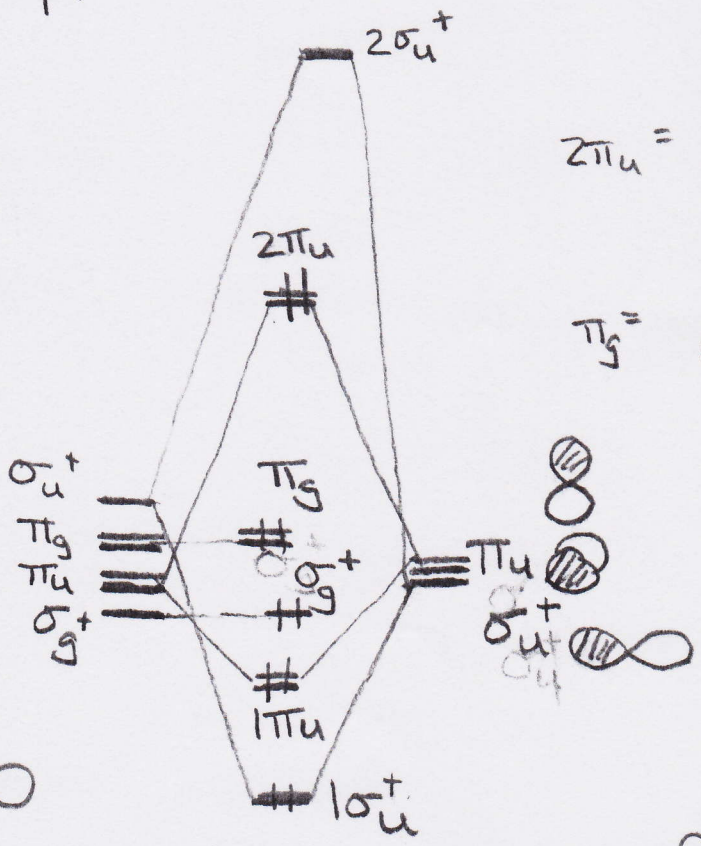
For CO_2 peaks ① & ③ have approximately twice the area compared to ② & ④ so this is in agreement with the ordering above. Notice that the ionizations from the two σ levels show vibrational progression whereas those in the π system are basically featureless.

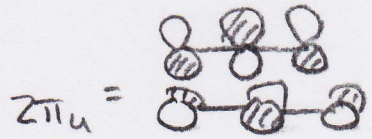
For N_2O peaks ① and ② correspond to the π sets (now $C_{\infty v}$ symmetry) so ③ & ④ are σ MOs. For yourself, work out what happens to the energies for these four MOs on going from O-C-O to N-N-O. For example, in π_g the density in CO_2 is localized on the two O atoms, so going to NNO, the $\pi_g \rightarrow 2\pi$ MO should go up in energy, therefore, a lower IP due to the electronegativity difference between N and O.

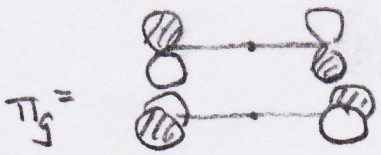
5.

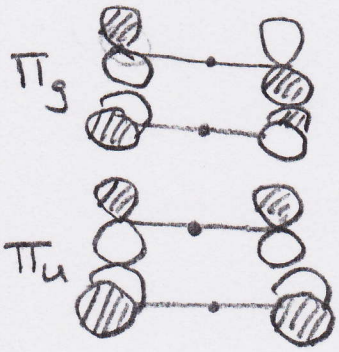


remember:
$\sigma > \pi$ overlap!









Sb = 5e⁻

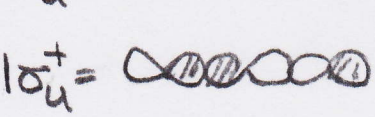
∴ Sb_3^{7-} = 3×5+7 = 22e⁻

− 6e⁻ from Sbs

16e⁻

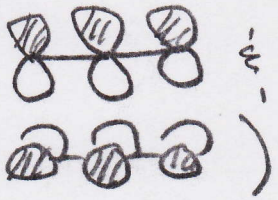
∴

$(1\sigma_u^+)^2(1\pi_u)^4(\sigma_g^+)^2(\pi_g)^4(2\pi_u)^4$

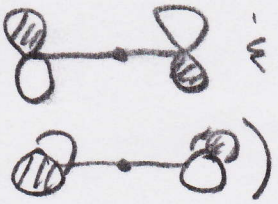


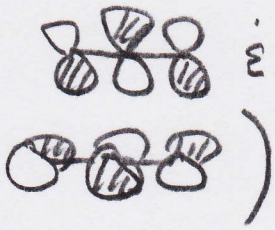
Sb_1-Sb_2 B.O. = Sb_2-Sb_3 B.O.

$1\sigma_u^+$ = bonding btwn Sb_1-Sb_2 (): BO = 1

π_u^4 = bonding btwn Sb_1-Sb_2 () : BO = 2

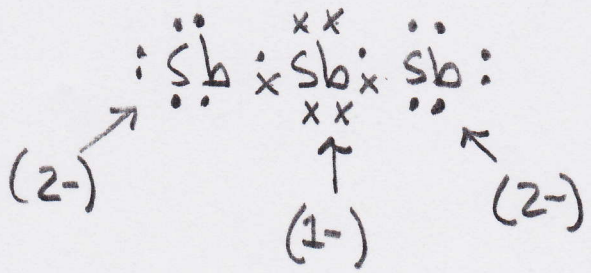
σ_g^+ = nonbonding btwn Sb_1-Sb_2 : () : BO = 0

π_g^4 = nonbonding btwn Sb_1-Sb_2 ( BO = 0

$2\pi_u$ = antibonding btwn Sb_1-Sb_2 ( BO = $\underline{-2}$

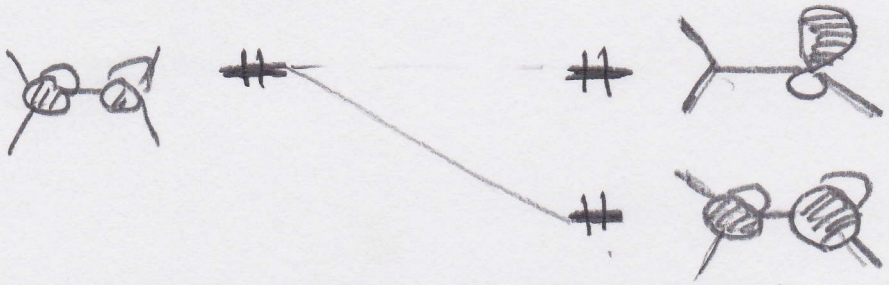
Tot = 1!

NOTE: electron rich "hypervalent"



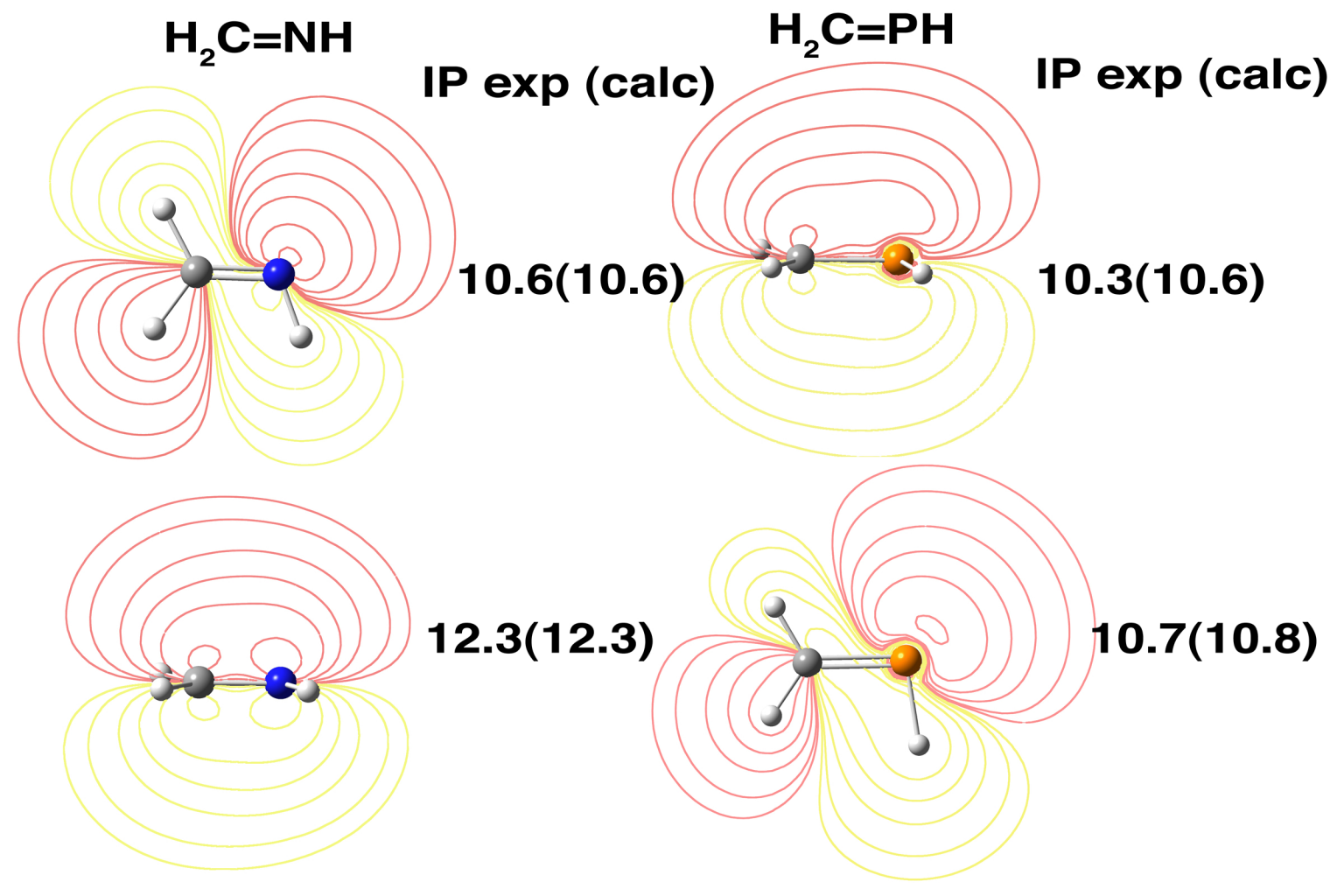
+ 2 more e⁻s!!

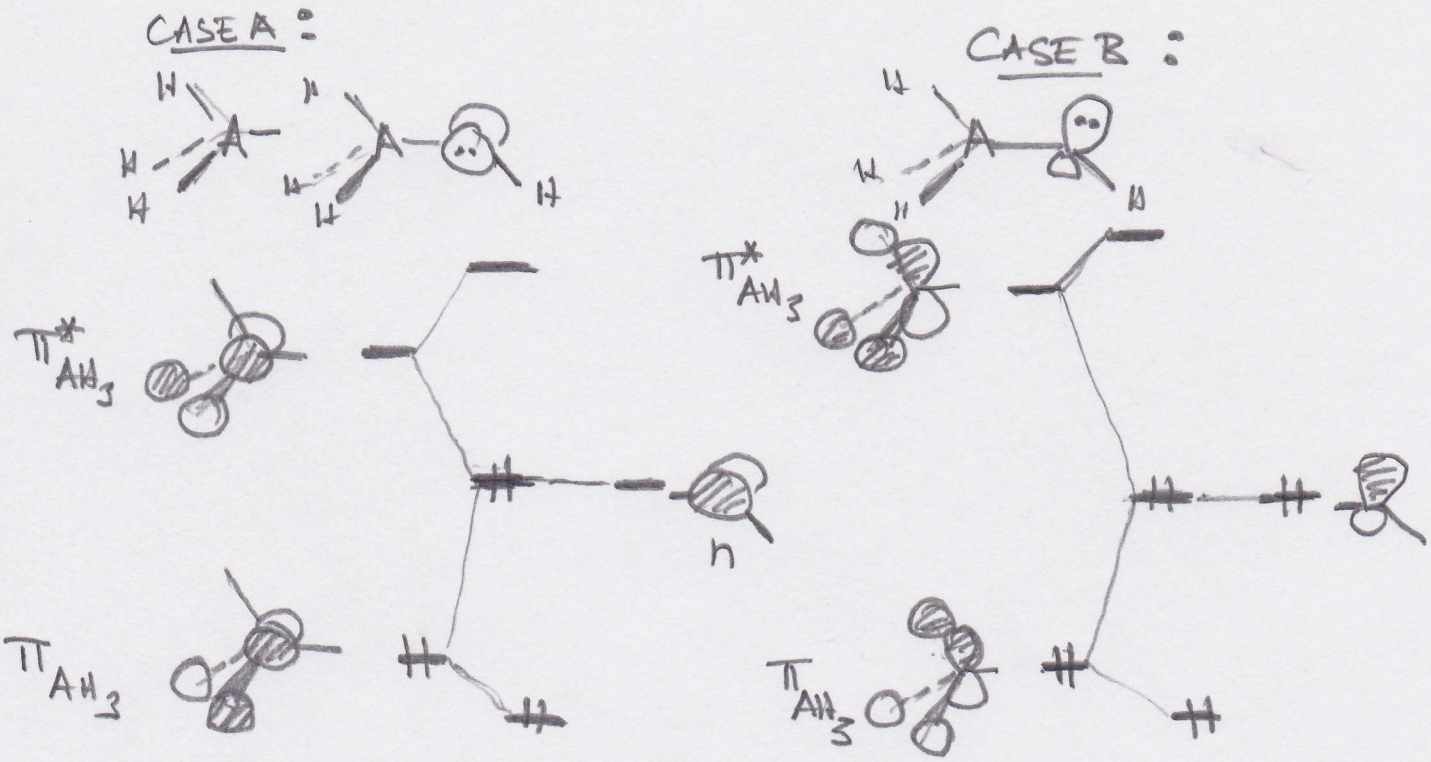
6. The ionization from the π orbital in ethylene is 10.5 eV. For $H_2C{=}NH$ the two ionizations are at 10.5 and 12.4 eV. Peak ① cannot possibly be the π ionization since N is more electronegative than C, the π ionization must increase in going from $H_2C{=}CH_2$ to $H_2C{=}NH$. So peak ② corresponds to the π and peak ① must be the lone pair on nitrogen, i.e.



For $H_2C{=}PH$ the two ionizations are at 10.3 & 10.7 eV. Its pretty hard to tell which is which because of the lack of detail in the PE spectrum. The MO's for both molecules at the B3LYP 6-311G+2d level are plotted on the next page along with the calculated and experimental energies.

7. The basic ideas in this problem are covered in chapter 10.5. They can be summed up in 10.50 and 10.67. The AH_3 unit has two A–H bonding MO's, π_{AH_3}, and two antibonding MOs, $\pi^*_{AH_3}$. Both will interact with a filled p AO of sp hybridized orbital on an adjacent atom with a lone pair. So the interaction is like, Case A or Case B.

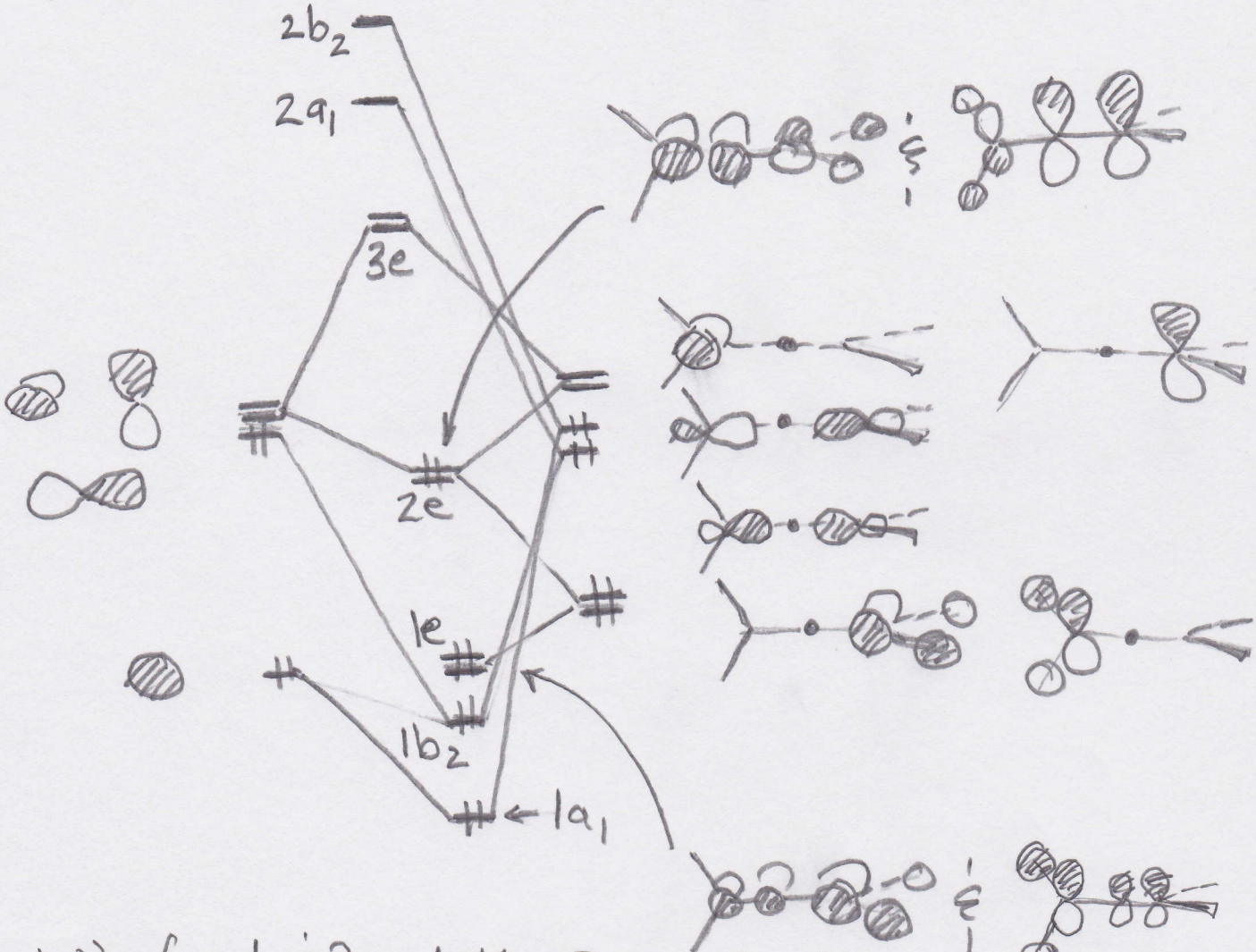

H2C=NH
IP exp (calc)
10.6(10.6)
12.3(12.3)
H2C=PH
IP exp (calc)
10.3(10.6)
10.7(10.8)



The ionization from the b_1 orbital in $(H_3A)_2S$ is an example of Case A. With CH_3 the interaction with π_{AH_3} is stronger than that with $\pi^*_{AH_3}$. Therefore, the IP is smaller for $(CH_3)_2S$ than for H_2S — see problem 7.1. But for SiH_3 the $\pi^*_{AH_3}$ interaction is much stronger — see 10.67. Consequently the IP increases. For the a_1' MO in $(H_3A)_3P$ one has an identical situation now using the three-orbital pattern in Case B. Again the IP increases going from $(CH_3)_3P$ to $(SiH_3)_3P$. Note: this is not because Si has empty d AO's! The IP for the b_2 MO in $(H_3A)_2S$ goes up on going from A = C to Si. This is a consequence of the fact that Si is more electropositive than C, i.e. H_3Si is a stronger

σ donor (its a_1 orbital lies at a higher energy). Precisely this same factor occurs for the e set in the $(H_3A)_3P$ series. The a_1 MO in $(H_3A)_2S$ contains both factors the a_1 lone pair on S is stabilized (compared to CH_3) for H_3Si by $\pi^*_{AH_3}$. On the other hand the σ donor effect also operates so the net effect is little change in the IP's.

8. a) C $H_2C\cdots\bullet\cdots CH_2$



The MO's for $1e_1$ & 2e at the B3LYP level are on the next page.

The shapes for a_1 & b_2 are straight-forward. The difference lies in the e sets - they are not just π & π^* as developed in problem 7.3 but also contain CH_2 σ character.

b) Ionization from the 2e set produces the radical cation with ^2E symmetry. Therefore, the molecule is subject to a Jahn-Teller distortion (Chapter 7.4). The symmetric direct product

$$e \times e = a_1 + b_1 + b_2.$$

The b_1 mode is especially interesting in that we determined from problem 7.3 that rotation around the C-C axis is stabilizing for molecules with 2 less electrons than in allene. This rotational mode is, in fact, the b_1 mode. Any one of the three b_2 modes will also lift the degeneracy of the ^2E state. Computations [see S. Mahapatra, L.S. Cederbaum and H. Köppel, J. Chem. Phys., 111, 10452 (1999) and references therein] have shown that the b_1 and the asymmetric stretching mode of b_2 symmetry (the middle one shown) are the major players. It is these large geometrical motions that create the unusual fine structure

in the PE spectrum of the 2e band.

c) There is a coupling between the $2a_1$ and one member of the 2e set. A careful discussion of this may be found in M. Kira, T. Iwamoto, S. Ishida, H. Masuda, T. Abe and C. Kabuto, J. Am. Chem. Soc, 131, 17135 (2009).