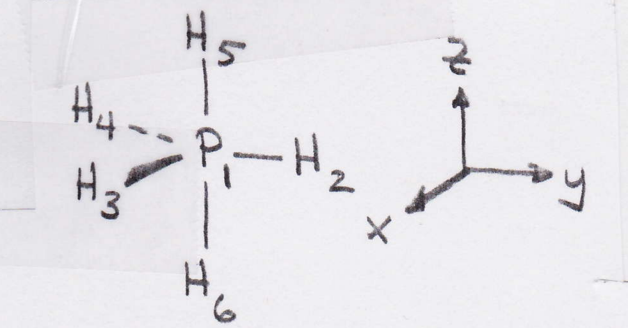
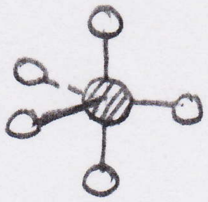
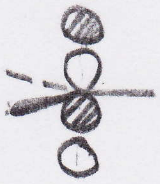
Answers - Chapter 14

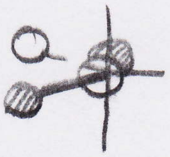
1. a)

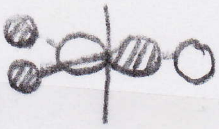


orbital energy (eV)

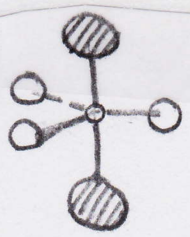
ψ_1 =

30.67

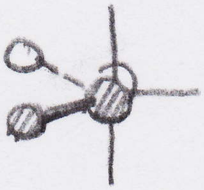
ψ_2 =

12.82

ψ_3 =


ψ_4 =


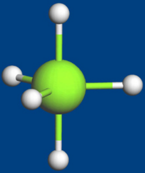
ψ_3, ψ_4: 4.36

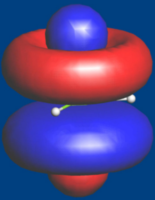
ψ_5 =

−11.17 (Homo)

ψ_6 =


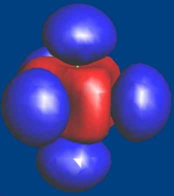
ψ_7 =


ψ_6, ψ_7: −17.66

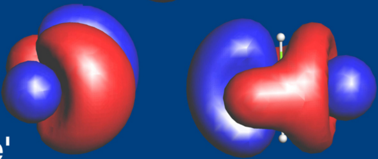




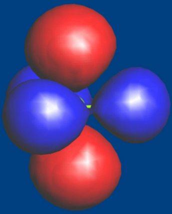
$2a_2''$



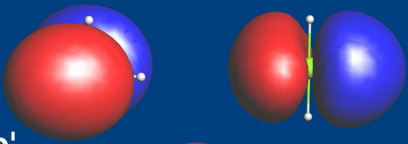
$3a_1'$



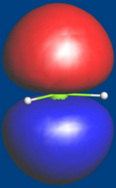
$2e'$



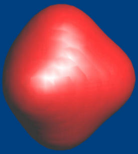
$2a_1'$



$1e'$



$1a_2''$

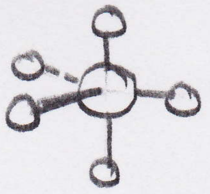


$1a_1'$

ψ_8 =

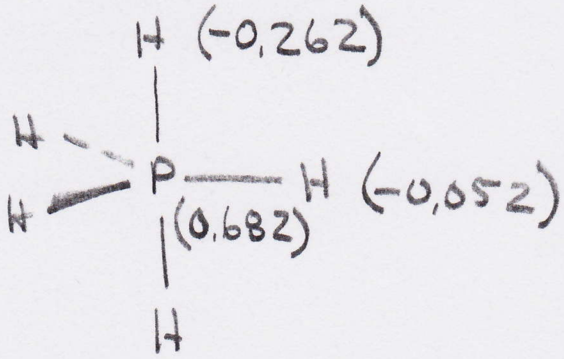
−18.06

ψ_9 =



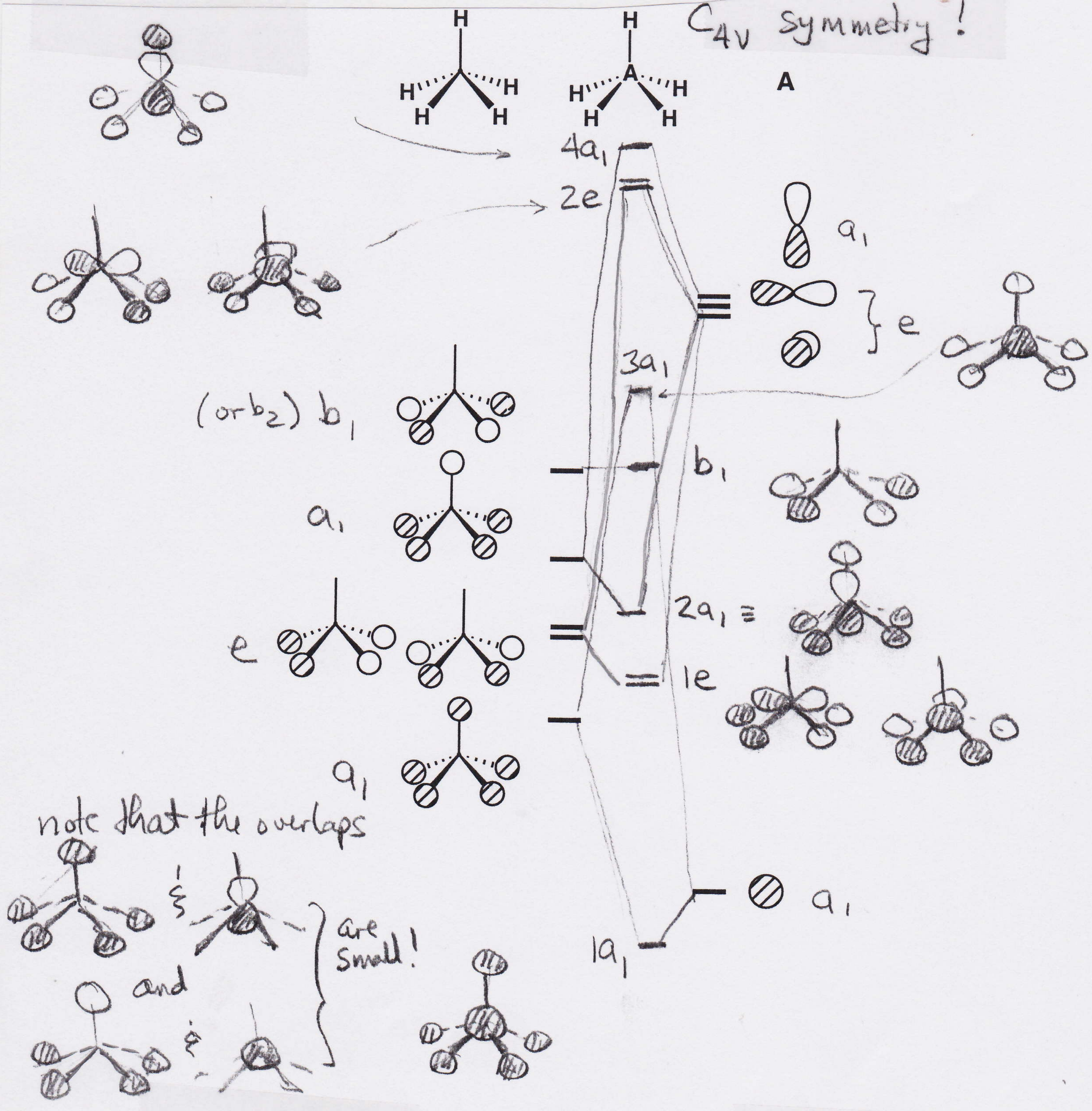
−22.43

(b) The charges on PH_5 are calculated to be:



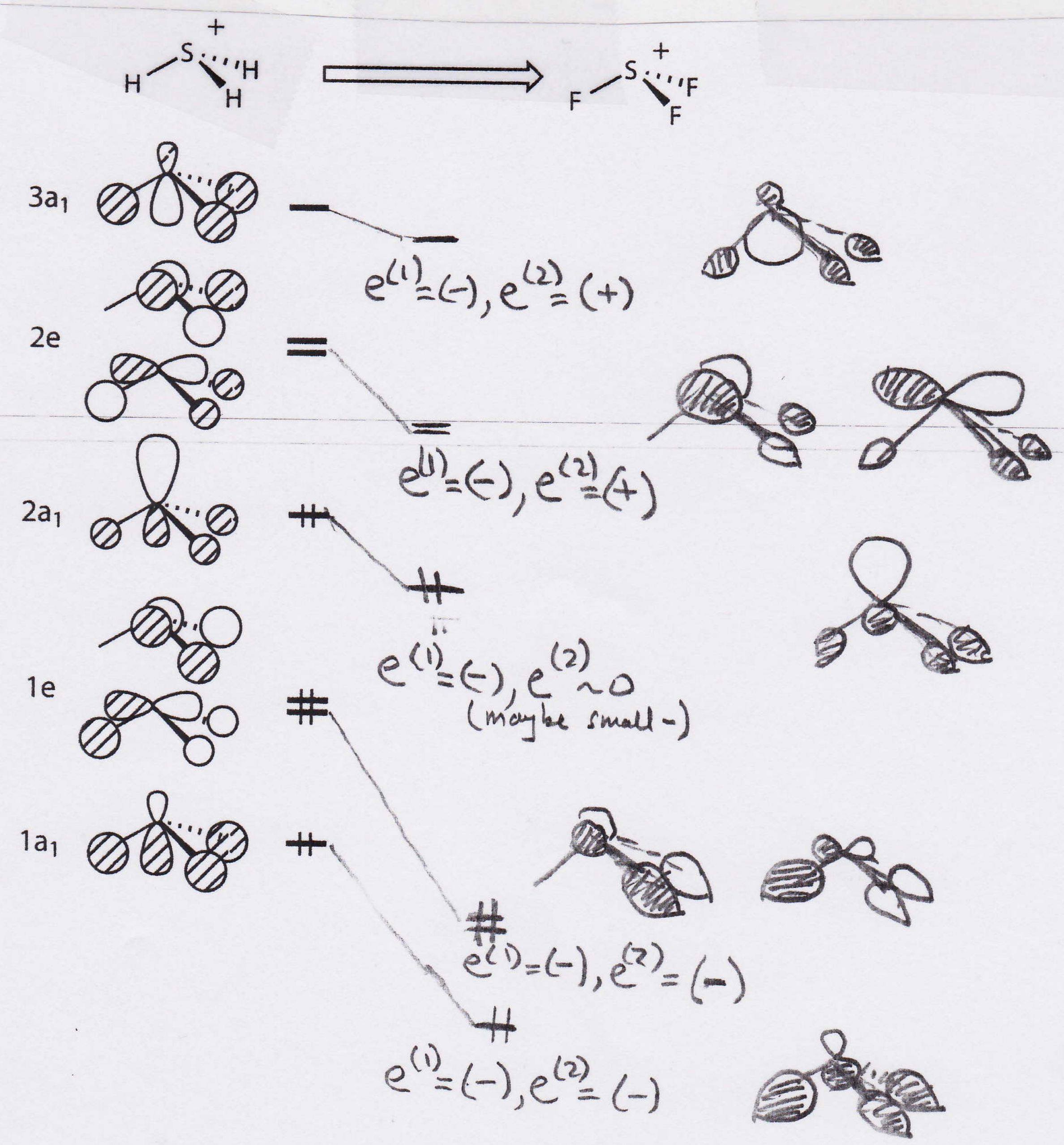
Electronegative substituents should go into positions of highest electron density, therefore the axial positions (H_5 and H_6) are prefered over the equatorial ones (H_2, H_3, and H_4). The $P\text{-}H_{axial}$ overlap population (1.152) is smaller than the $P\text{-}H_{equatorial}$ ones (1.398). Since the bonds were computed at the same lengths, the axial bond is predicted to be weaker than the equatorial one.

2.



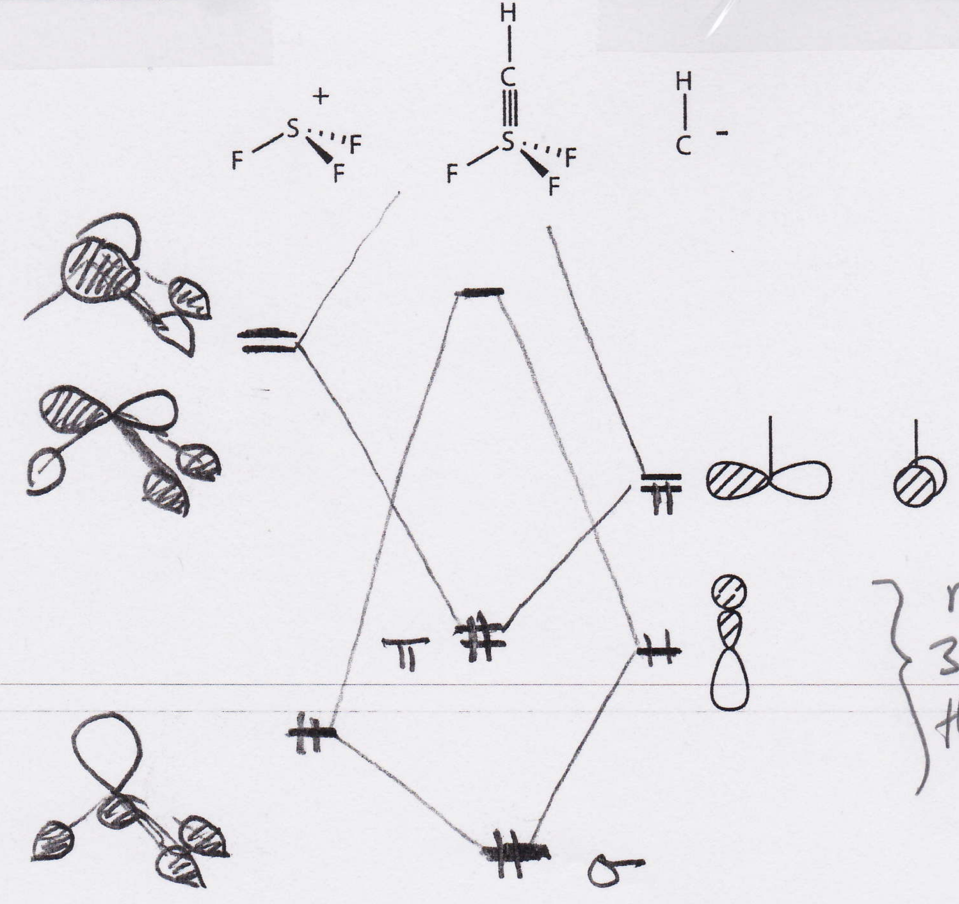
NOTE: The SALCS of H_5 are very easily constructed from a square H_4 and a capping H atom.

3. a)

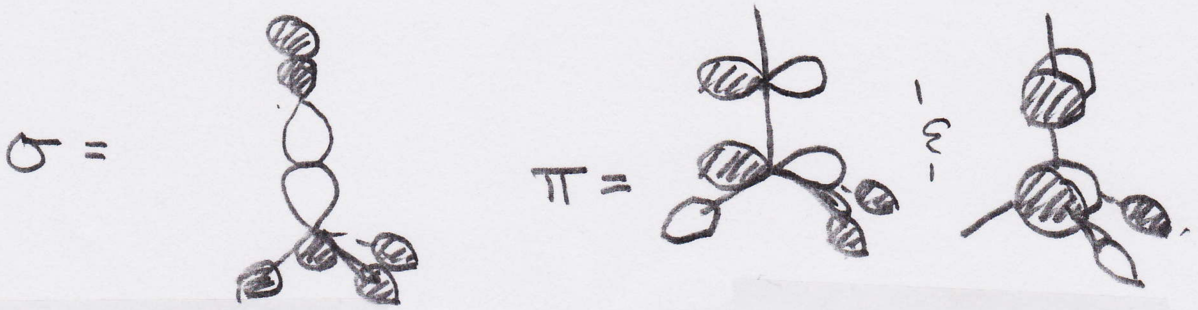


Notice that $1a_1$ & $1e$ are centered on the more electronegative F atoms. The $3a_1$ MO is hybridized towards the S–F region. Therefore, interaction of $F_3\overset{+}{S}$ with A ($F_3\overset{+}{S}$---A) will occur via $2a_1$ & $2e$.

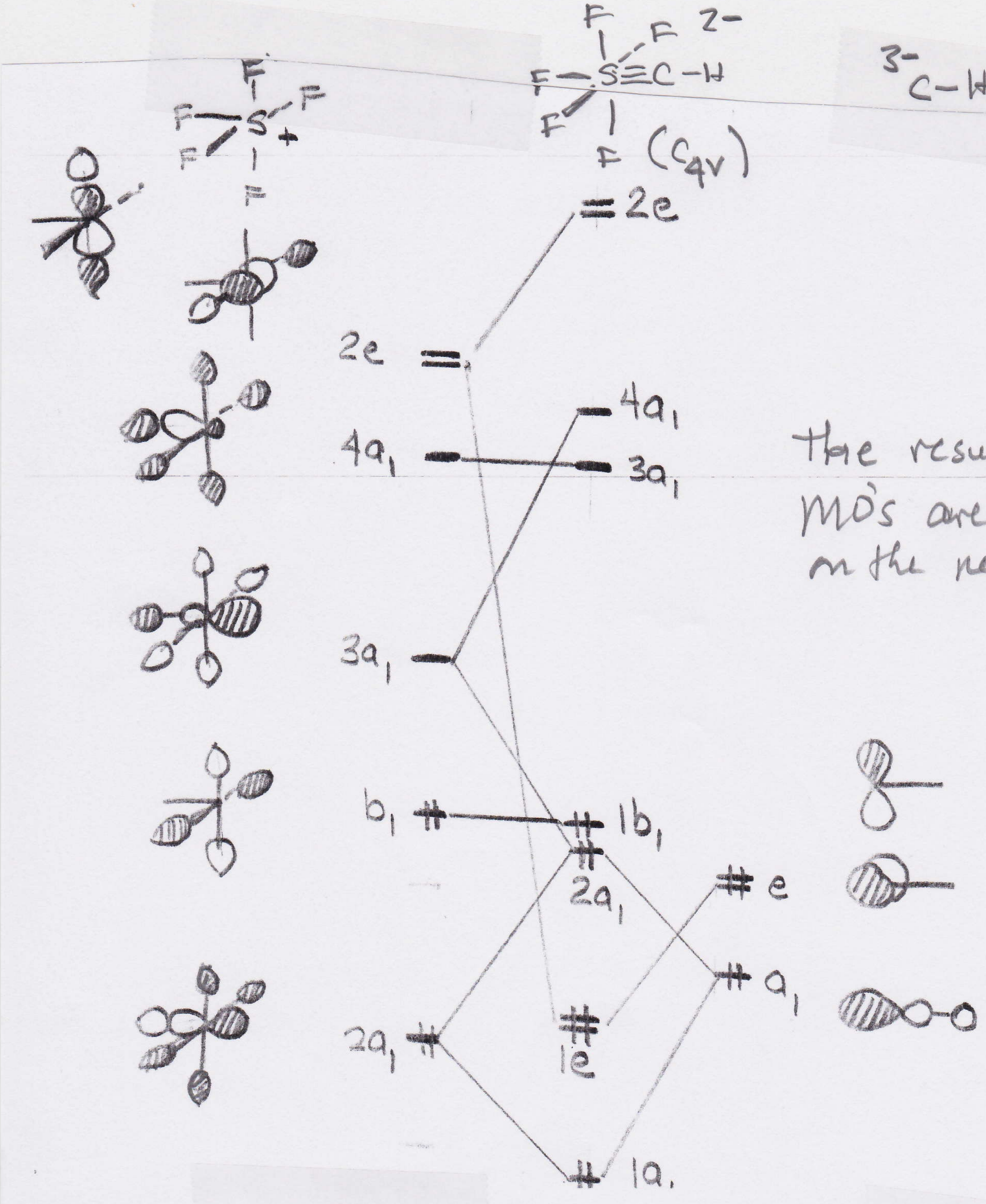
b)



note the 3 S-C bonds that are formed



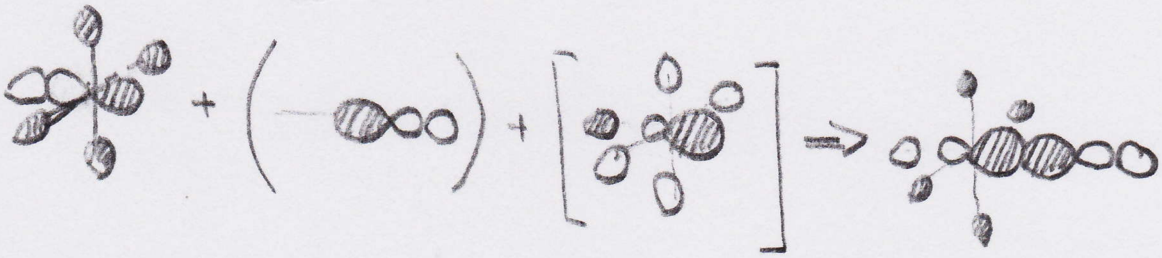
4. a) Here again one could use the orbitals of H_5S at a square pyramidal geometry and then "perturb" the H atoms to F. The most important - for S-C bonding will be $2a_1 \rightarrow 4a_1$ from problem 2:



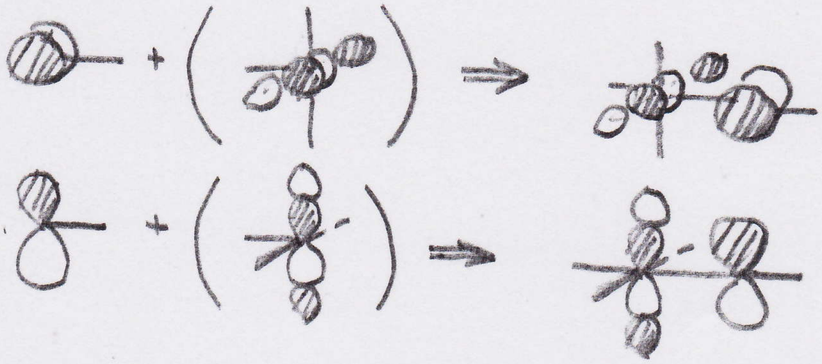
the resultant MO's are drawn out on the next page.

b) the $2a_1$ & $1b_1$ MOs are identical to the e_g in H_6A. Thus, there is little difference in the σ system. this is *not* true for the π system. See 1e on the next page - therefore the *cis* C-F bonds are weaker and longer than the *trans* C-F one.

$\psi_{1a_1} \propto$

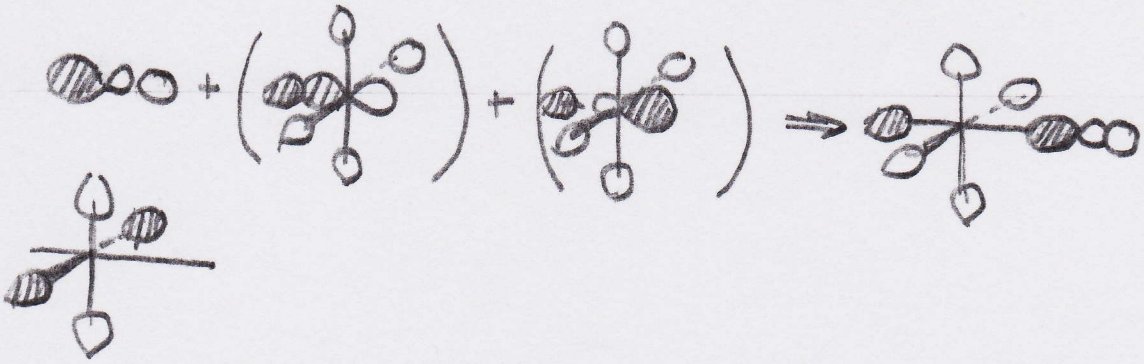


$\psi_{1e} \propto$

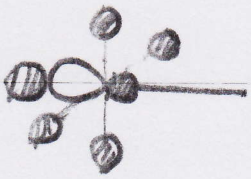


$\psi_{2a_1} \propto$

$\psi_{1b_1} =$

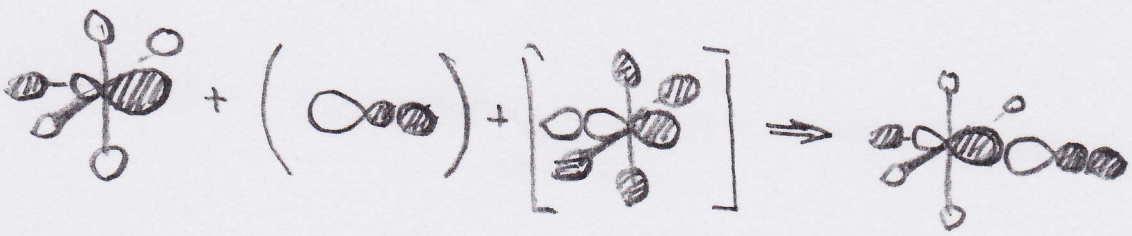


$\psi_{3a_1} \approx$

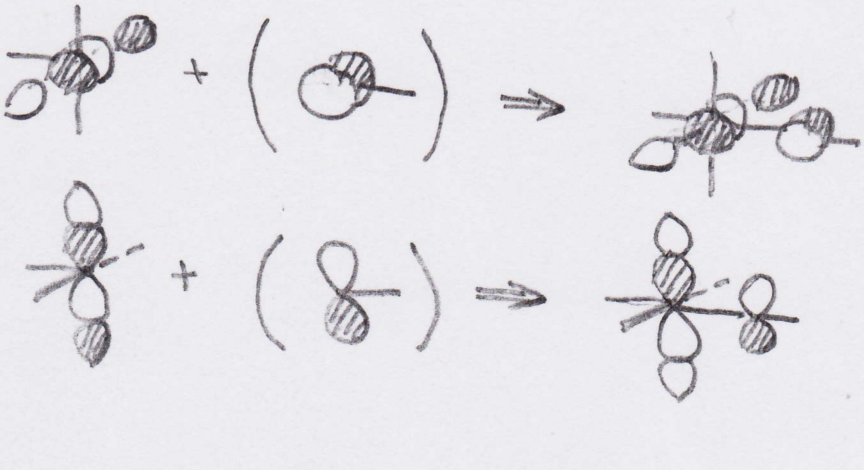


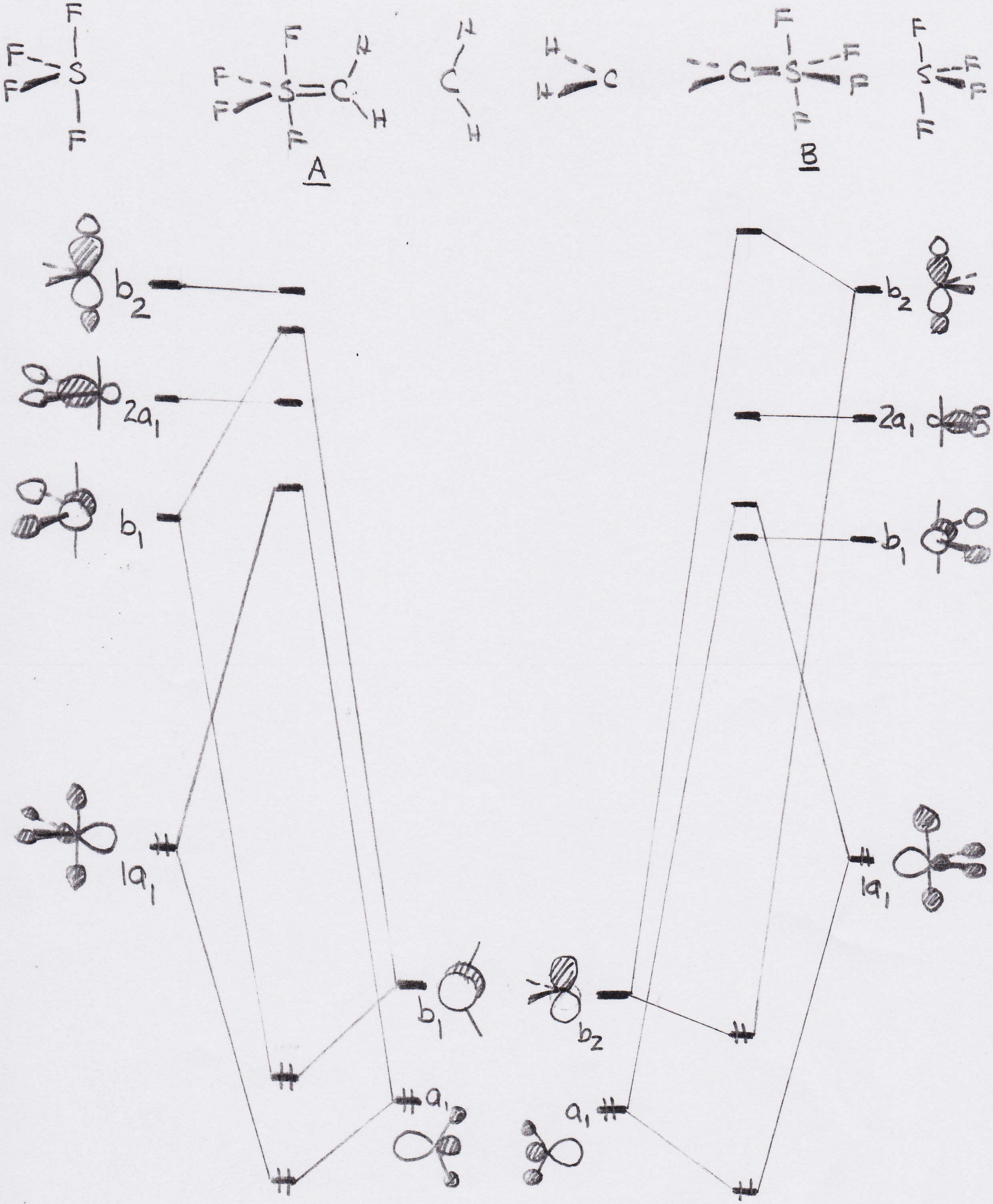
the overlap of the $4a_1$ orbital on F_5S^+ with a_1 on CH^{3-} is very small; its hybridized in the wrong direction

$\psi_{4a_1} \propto$



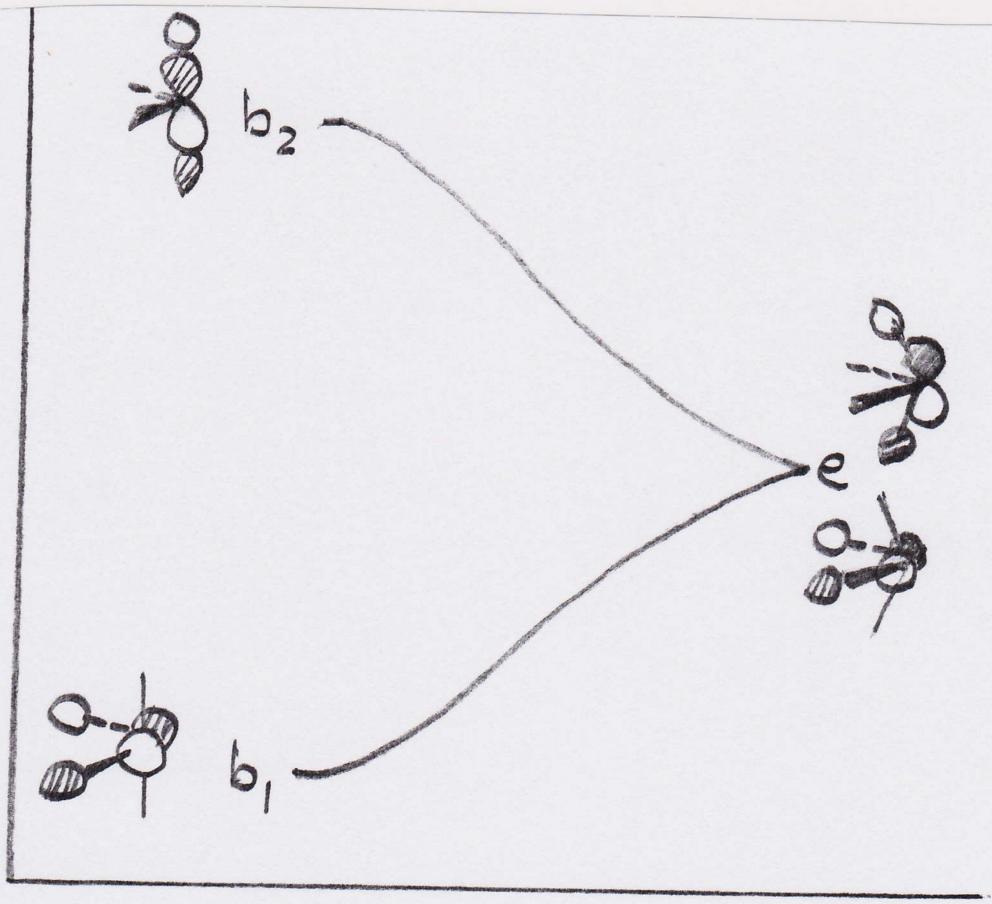
$\psi_{2e} \propto$

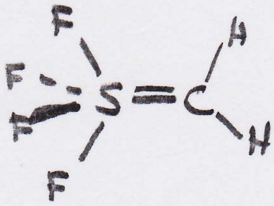
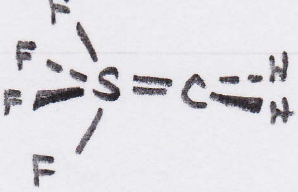


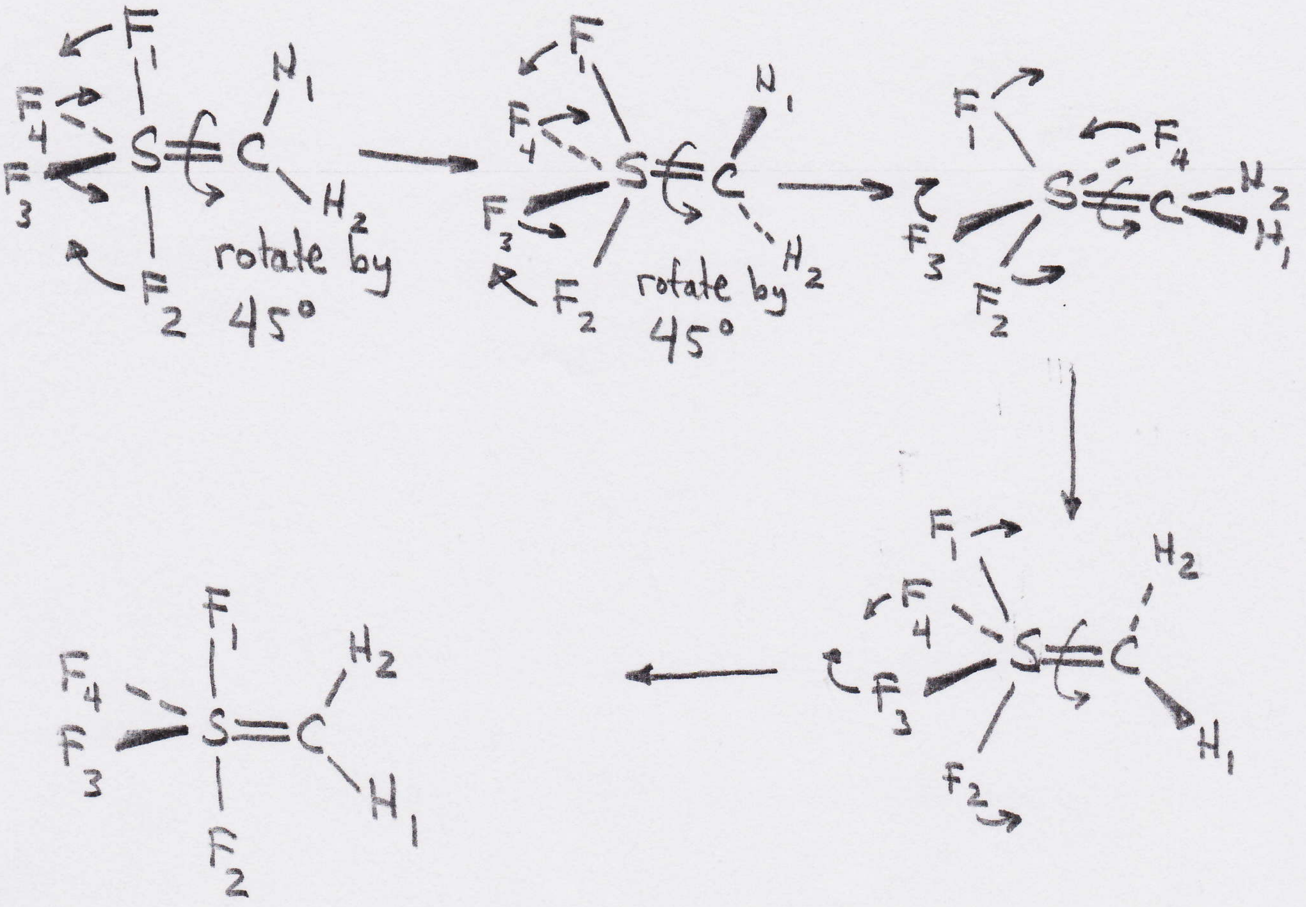

F
S
F
F
F
A
F
S
C
F
F
F
H
H
H
C
H
H
C
H
B
C
S
F
F
F
F
F
S
F
F
F
b2
2a1
b1
1a1
b2
2a1
b1
1a1
b1
a1
b2
a1

In both conformations a σ and π bond between S and C is filled. However, the π bond lies at lower energy in conformation A because the b_1 orbital in SF_4 lies lower in energy that the b_2 orbital does.

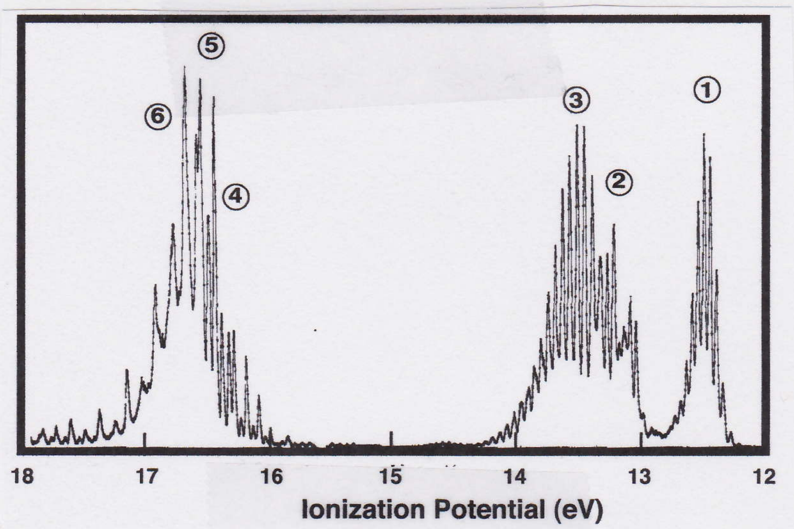
(b). The rotation barrier around the S–C bond is set up because of the b_2-b_1 energy difference in SF_4. This in turn is due to the fact that the axial F–S–axial F angle is 180° while the equatorial F–S–equatorial F angle is 109°. If one could make the b_2-b_1 energy difference zero, then there should not be a rotational barrier. The way to do this is to make both F–S–F angles identical, i.e. distort the SF_4 portion of the molecule from C_{2v} to C_{4v}. The b_2 orbital then is stabilized and the b_1 is destabilized, i.e. for SF_4 itself :



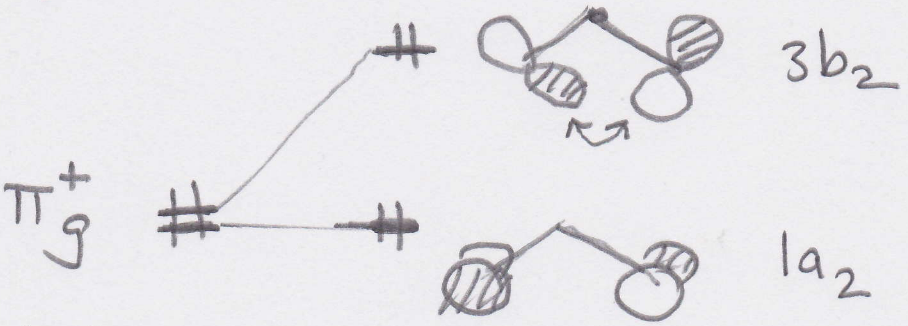
Therefore, the energy difference between  and  must now be zero since the p A.O. on CH_2 overlaps equally with either member of the e set. Likewise, when the CH_2 group is rotated 45° between each structure, the p A.O. on CH_2 will interact with a linear combination of the two members of the e set. Thus, there is free rotation in this structure. It is important to realize, however, that this structure cannot be at the same energy as conformation $\underline{A}$. The b_1 orbital is destabilized along this distortion path, thus, its interaction with the p A.O. on CH_2 is diminished. What we have done here is to combine psuedorotation ($F_4S{=}CH_2$ resembles structurally and electronically a trigonal bipyramid) at SF_4 with rotation around the S–C bond, i.e. for one complete rotation

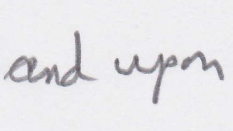


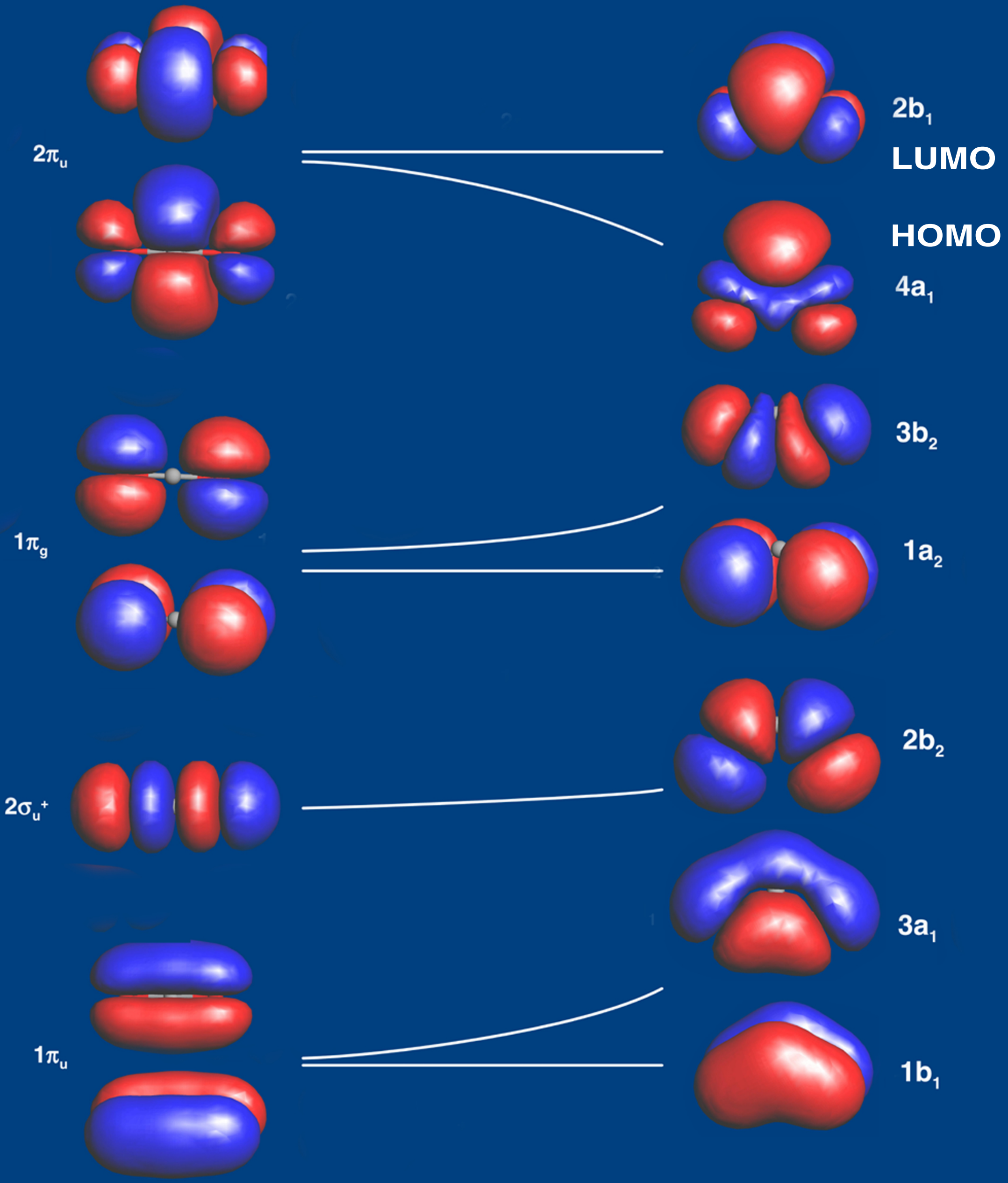
6.



We have actually worked the level ordering before - problem 10.3! For SO_2 the HOMO is $4a_1$ (SO_2 is predicted and found to be bent) and this corresponds to peak ① Peak ② should be $3b_2$ and ③ should be $1a_2$. Actually the assignment is reversed. It is difficult to see why this should be the case. The MOs at the linear geometry are degenerate and upon bending:



The rest of the assignments follow the order given on the next page. SO_2 is typically drawn as  This does not correspond to the MO picture!


$2\pi_u$
$2b_1$
LUMO
HOMO
$4a_1$
$3b_2$
$1\pi_g$
$1a_2$
$2b_2$
$2\sigma_u^+$
$3a_1$
$1\pi_u$
$1b_1$

7. a)

either ① $[BrF_6]^+ \, [Sb_2F_{11} = F_5\text{-}Sb\text{-}F\text{-}SbF_5]^-$

12e⁻ around Br

12e⁻ around each $\left(F_5Sb \leftarrow :\ddot{F}:^{\ominus} \rightarrow SbF_5 \right)$

$$\begin{array}{c} 10e^- \\ +2 \\ \hline 12 \end{array} \qquad \begin{array}{c} 10e^- \\ +2 \\ \hline 12 \end{array}$$

-or- ② $[BrF_6]^- \, [Sb_2F_{11}]^+$

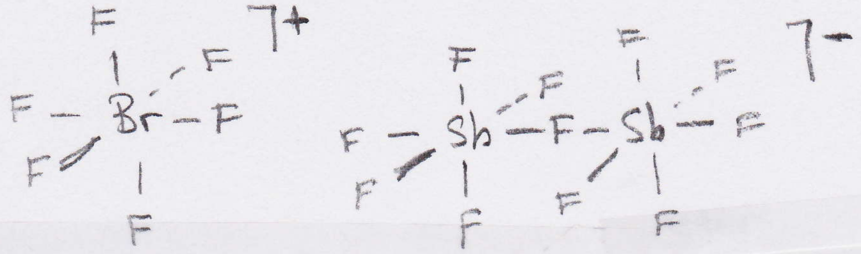
14e⁻ around Br

$F_5\overset{(+)}{Sb} \leftarrow :\overset{(-)}{\ddot{F}}: \rightarrow \overset{(+)}{SbF_5}$

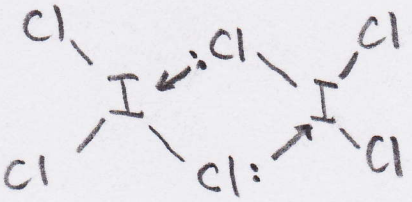
8+2= 10e⁻

① is more likely since VSEPR for 6 ligands around Sb → 12e⁻ not 10e⁻

∴



b) <u>note</u> each bridging Cl must use 4e⁻, i.e.



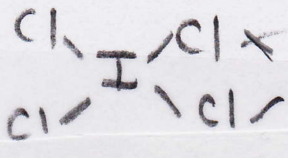
Therefore, we can count shared e⁻s around each I as either

$$\begin{array}{lcl} 3\,Cl\cdot & = & 3e^- \\ 1\,Cl: & = & 2 \\ I & = & 7 \\ \hline & & 12e^- \end{array}$$

or (using oxidation states)

$$\begin{array}{lcl} 3\,Cl^- & = & 6 \\ 1\,Cl: & = & 2 \\ I(3+) & = & 4 \\ \hline & & 12e^- \end{array}$$

With 12e⁻ around each I (6 pairs) an octahedron is expected, i.e.



so structure I is the most stable

c) Hg^{1-} has 4 less electrons than 1, therefore, there are 8e$^-$ (4 pairs) around each Hg so a tetrahedron at each Hg is preferred ($\frac{3}{2}$).

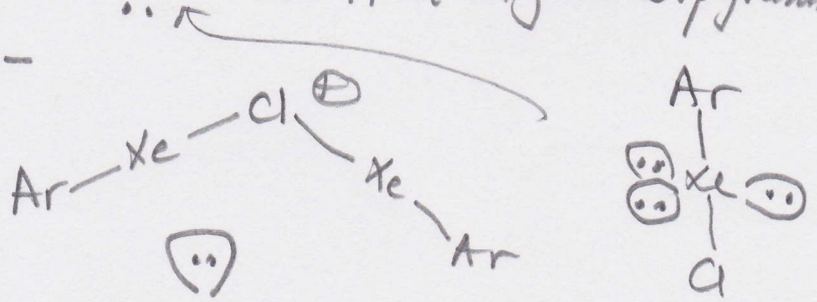
d) at Cl-count

∴ a tetrahedron around Cl

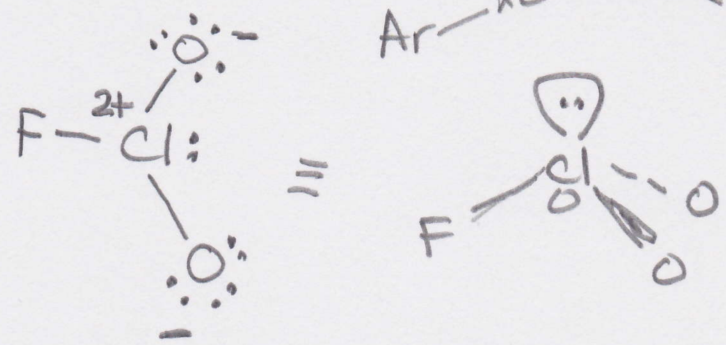
at Xe-count

∴ a trigonal bipyramid at Xe

so –

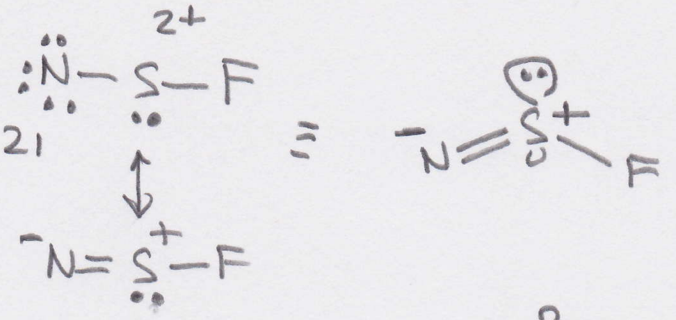


e)



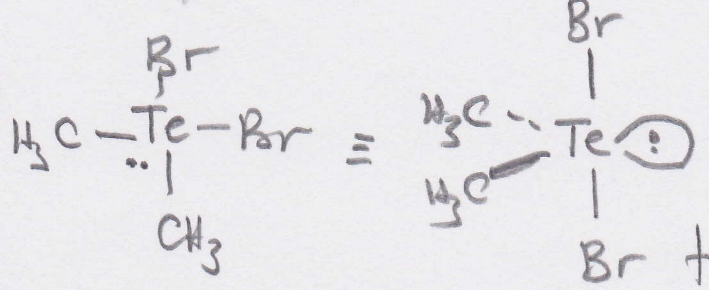
tetrahedral

f)



trigonal planar

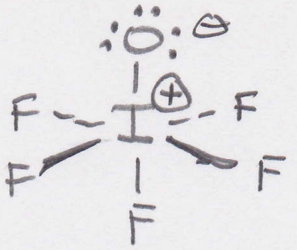
g)



(most electronegative atoms in the axial position)

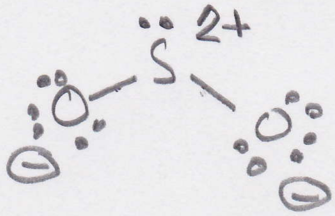
trigonal bipyramid

h)

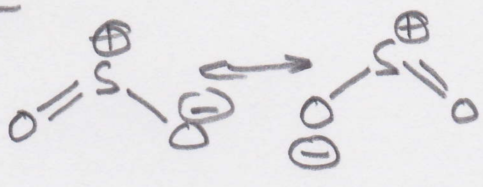


octahedral

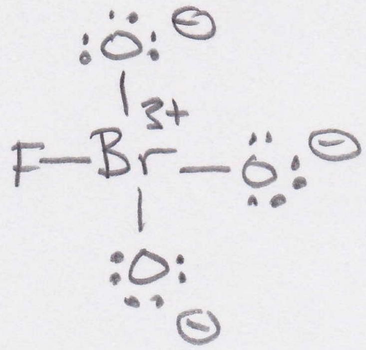
i)



∴ trigonal planar



j)



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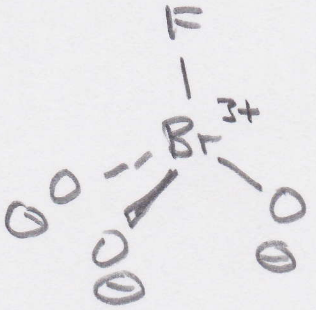
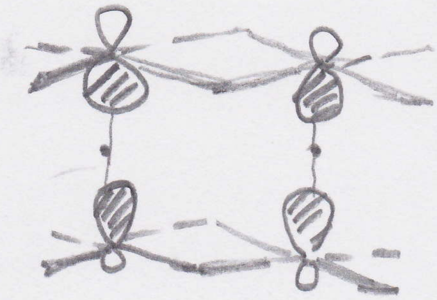


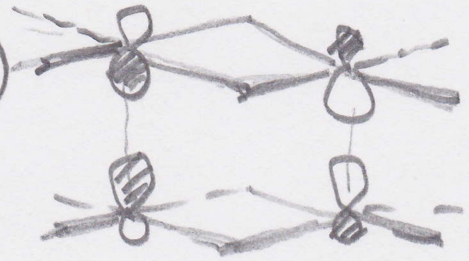
tetrahedral

8.

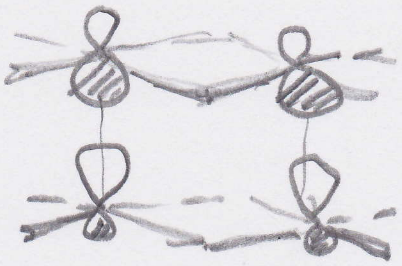
(D_{2h} symmetry)



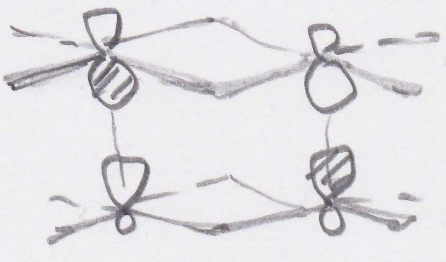
a_{1g}



b_{2u}

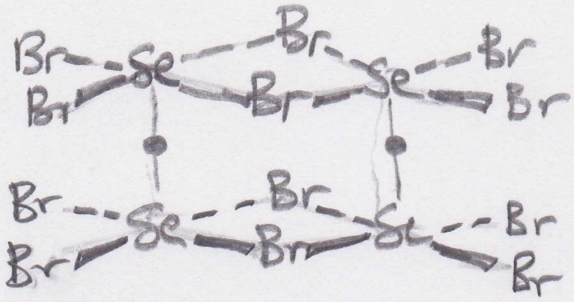


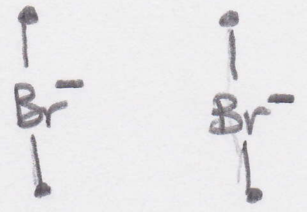
b_{3u}

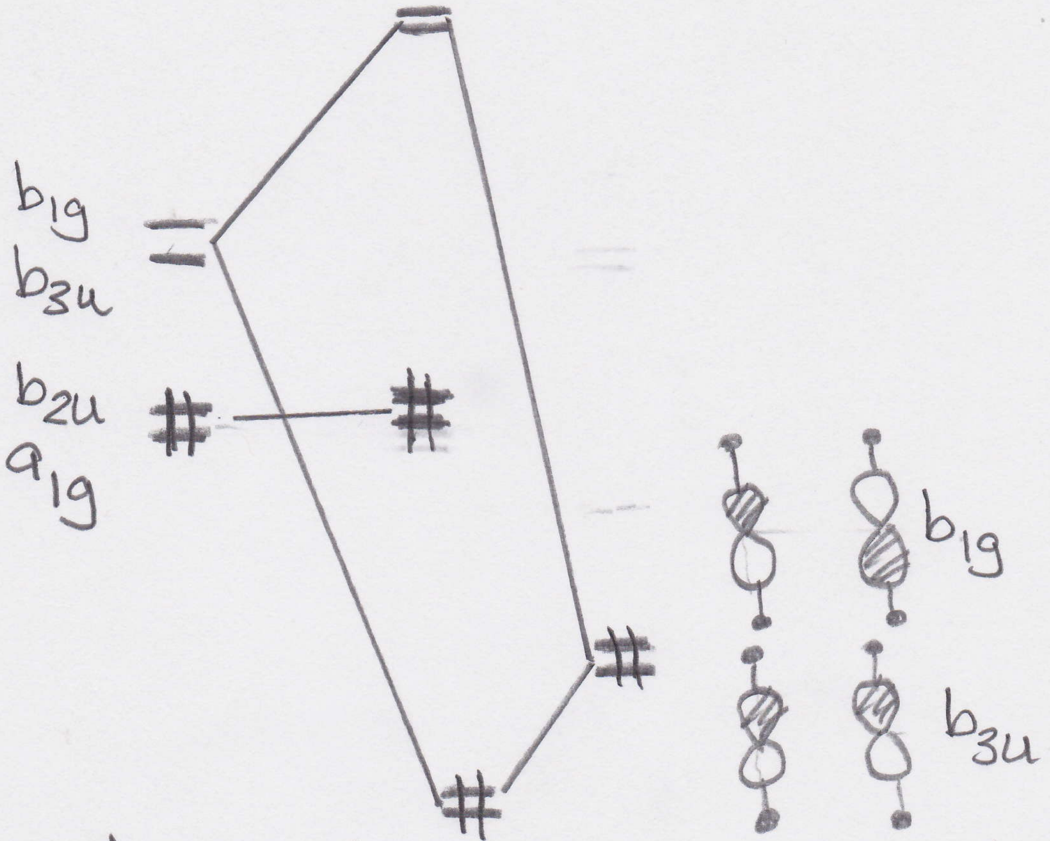


b_{1g}

Each Se has one "extra" electron so there are 4 electrons associated with the SALCs

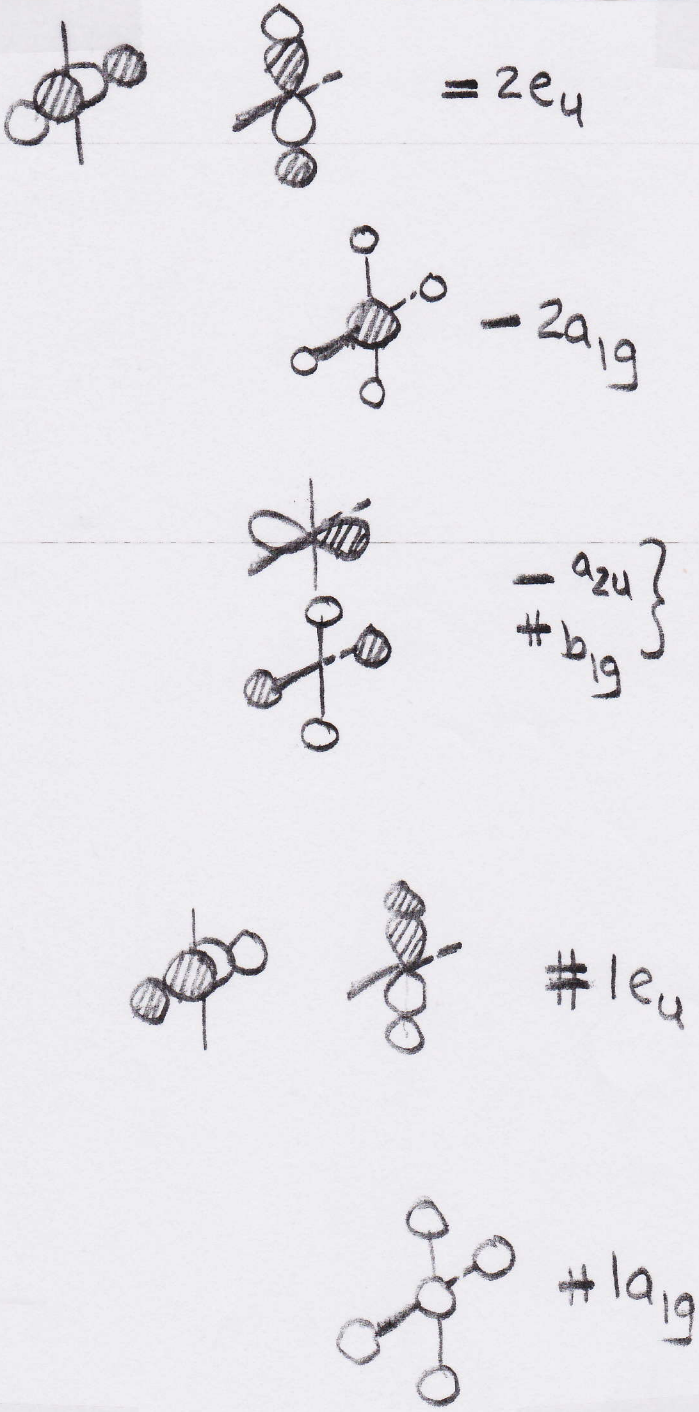






The picture is actually more complicated because the s AOs from Se and the bridging Br atom also mix into the a_{1g} and b_{2u} combinations, but the essense of the picture is still captured with the simplified model above. There is a large HOMO/LUMO gap if one does a calculation and not a diradical, etc.

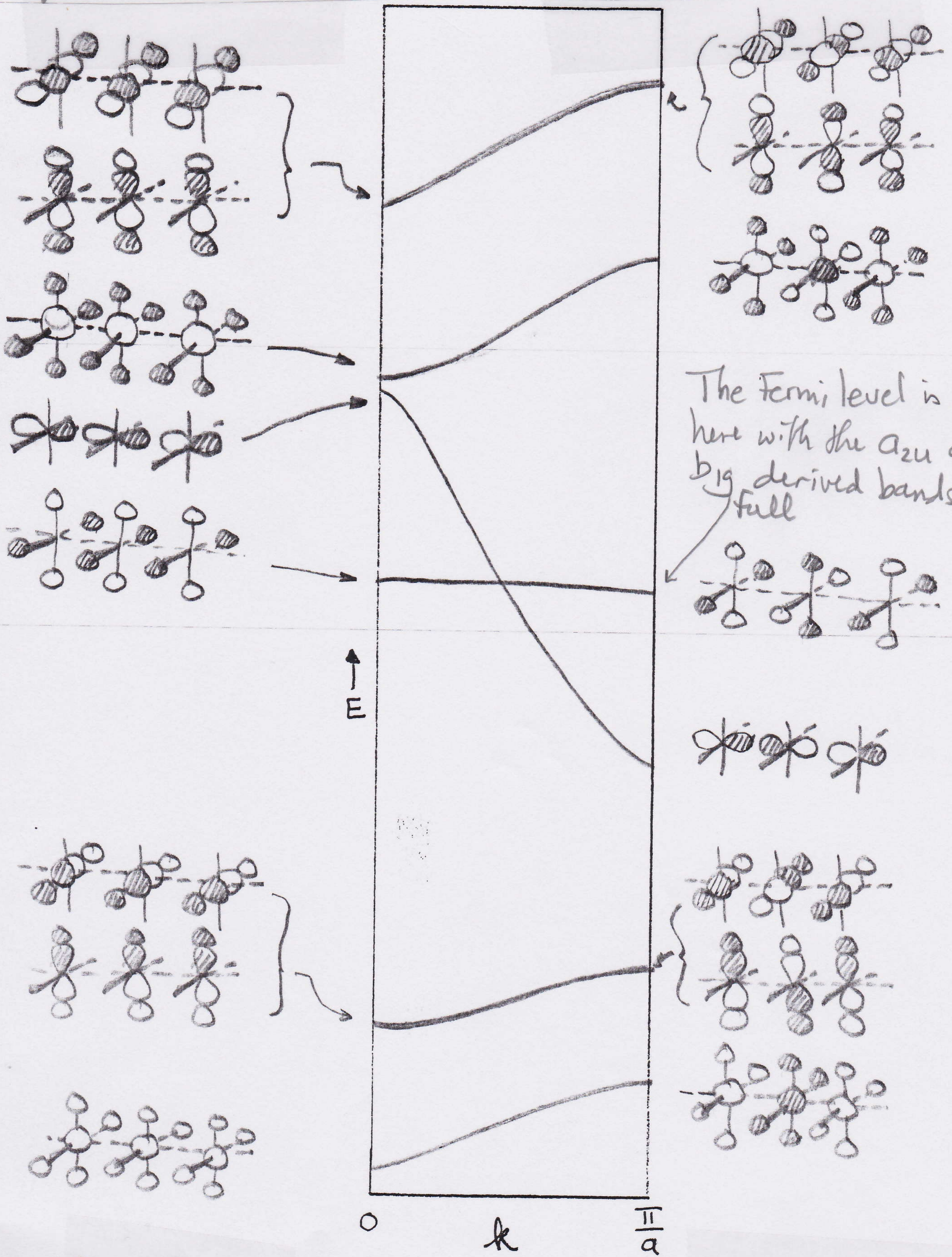
9. a) The MO's of square planar AH_4 are easy –



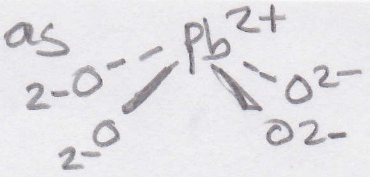
these two will be close and ordering could be inverted

I've put the a_{2u} level higher than b_{1g} because Sn is so electropositive. But this wouldn't matter when the MO's spread into bands:

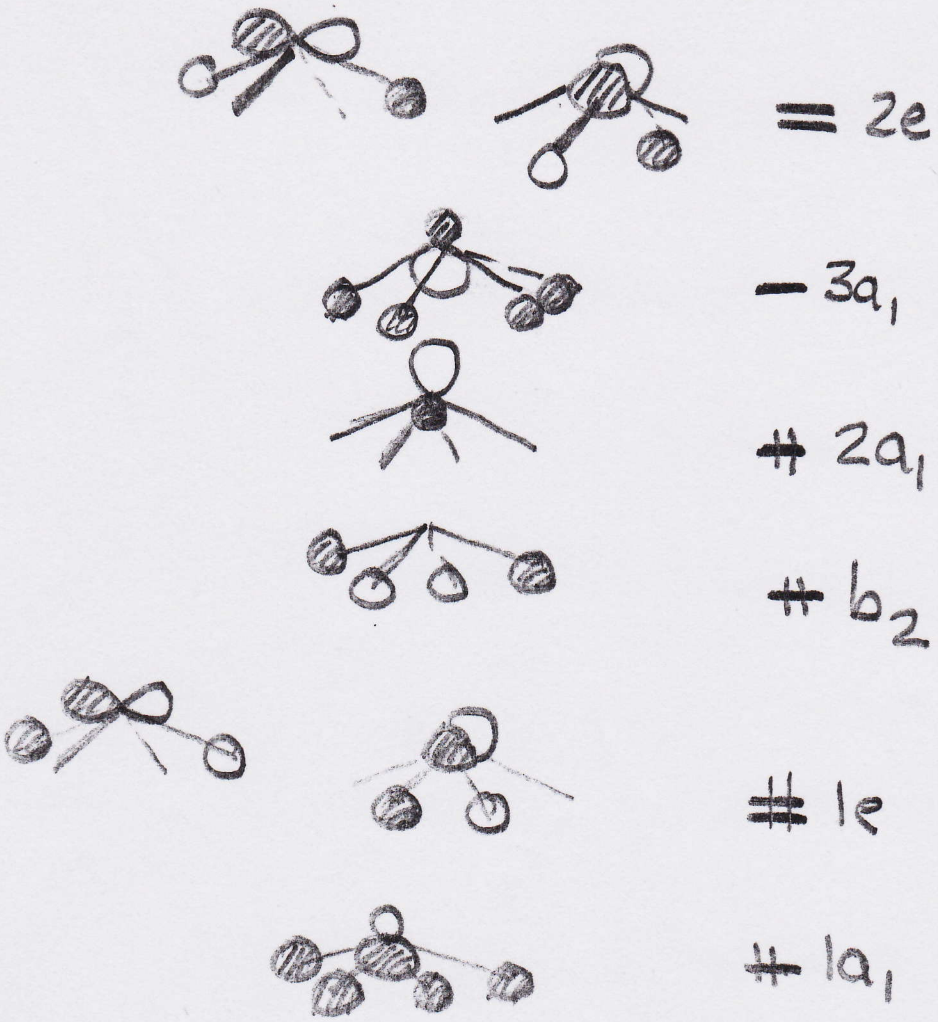
b)



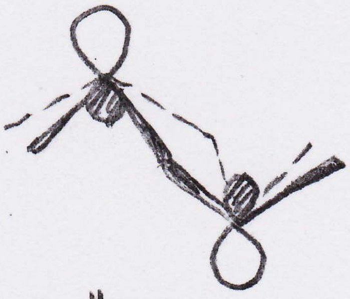
The Fermi level is around here with the a_{2u} and b_{1g} derived bands ~ half full

10. a) View PbO as 

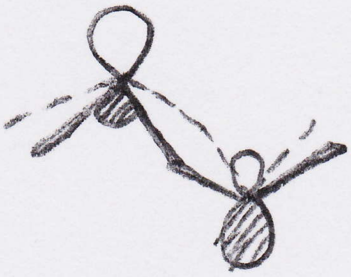
so Pb has $2e^-$ and each Oxygen $8e^-$. Let us forget about the lone pairs around oxygen and consider only the σ electrons. At each oxygen there is a σ type hybrid so the total electron count is $4 \times 2 = 8$ electrons plus the two on Pb (Pb^{2+}) give a total of 10 electrons at each square pyramid. For an AH_4 system where H is much more electronegative than A the order is:



b) The highest occupied bands then will be derived from the $2a_1$ orbital and there will be two of them since there are two Pb per unit cell. Their basic shapes will be



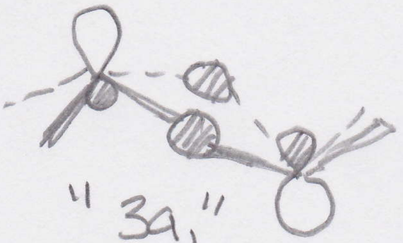
"$3a_1$"



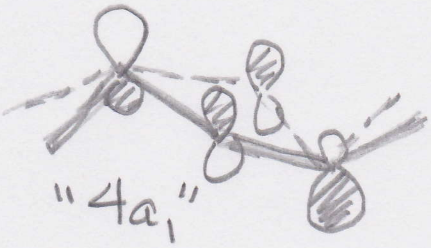
"$4a_1$"

(Notice that there are six bands labelled $2e$, $2b_2$, $1e$ and $2a_1$ are derived from the oxygen p A.O.'s and two at lower energy, not shown in Figure 3, that come from oxygen 2s.

c) When the PbO layers are stacked on top of eachother, not too much will happen to the six Oxygen p based bands. However, since "$3a_1$" and "$4a_1$" are directly pointed towards adjacent layers, they will spread out and become much more dispersive. It is the six bands in the energy range from ~ 17,3 to − 14,5 are derived from the oxygen p AOs. That the Pb-O COOP curve is positive in this region is consistent with this. From −13,5 to −10,5 the Pb-O COOP is negative, so the basic crystal orbital shape must be more like:

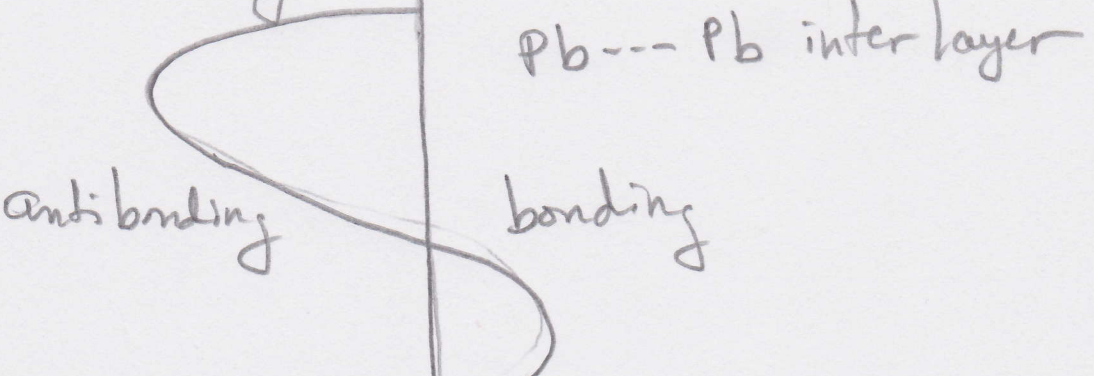


"3a₁"

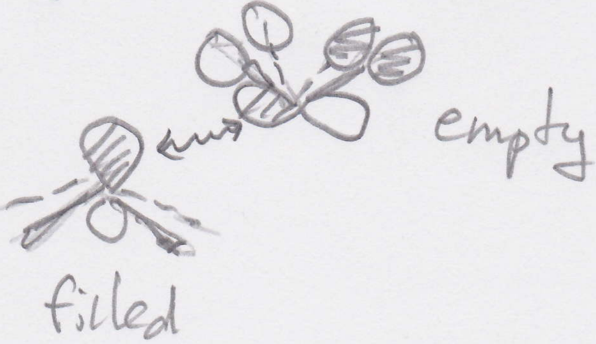


"4a₁"

what is peculiar is the shape of the Pb-Pb COOP in the −13,5 to −10,5 region, One should expect something like:

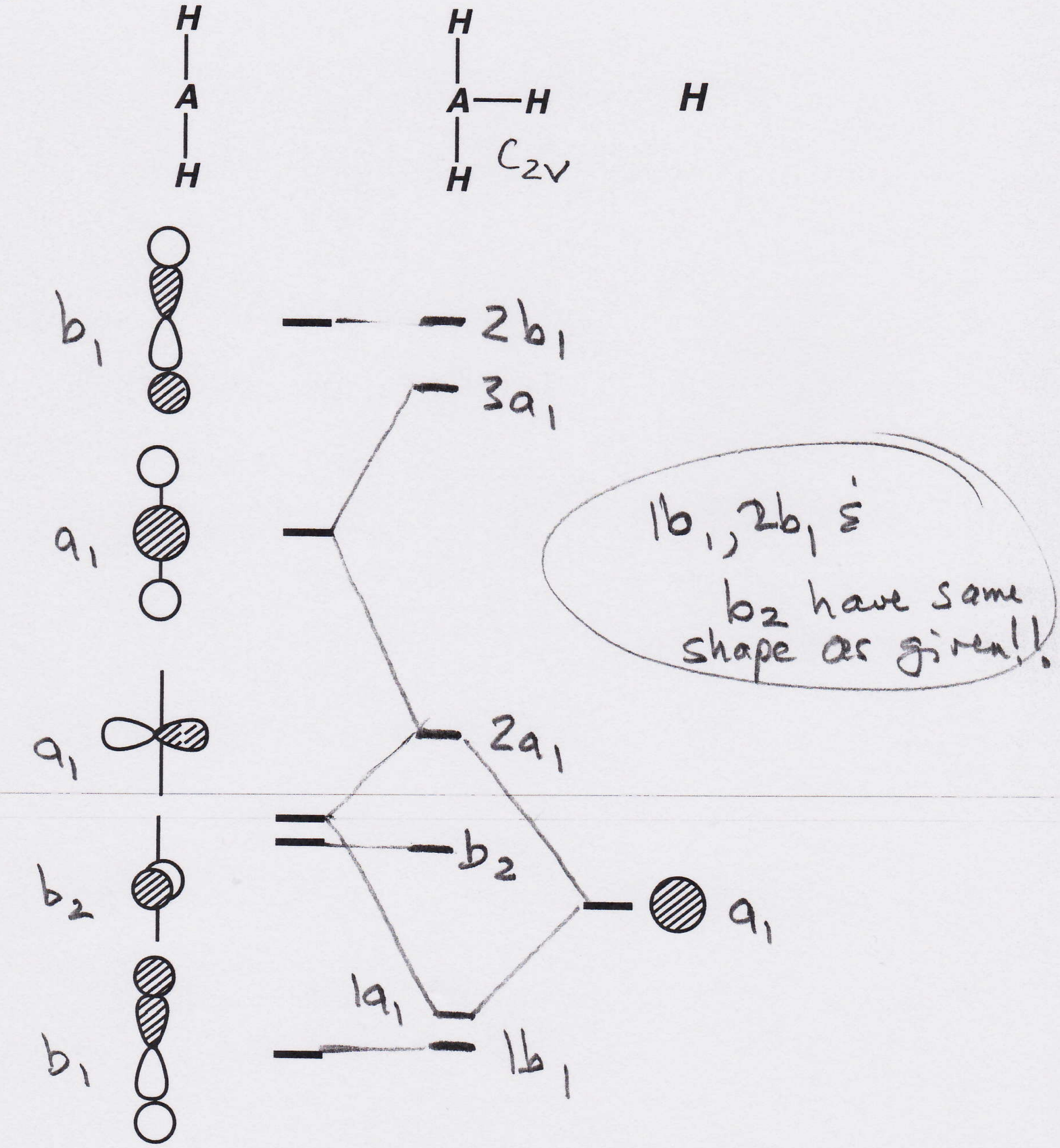


If it is just Pb lone pairs overlaping with each other then the antibonding should have a larger population and the interaction should be repulsive. This is not the case. the lone pairs do not lie directly over eachother. Consequently the lone pairs can overlap somewhat with empty orbitals centered on Pb corresponding to $3a_1$ and especially 2e in our O_4Pb unit cell picture. This makes the PbO layers slightly attractive to eachother. In other words



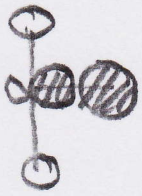
interactions like this are important and decrease the negative Pb...Pb interlayer overlap populations

11.

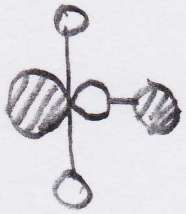


$1b_1, 2b_1$ & b_2 have same shape as given!!

$1a_1 =$

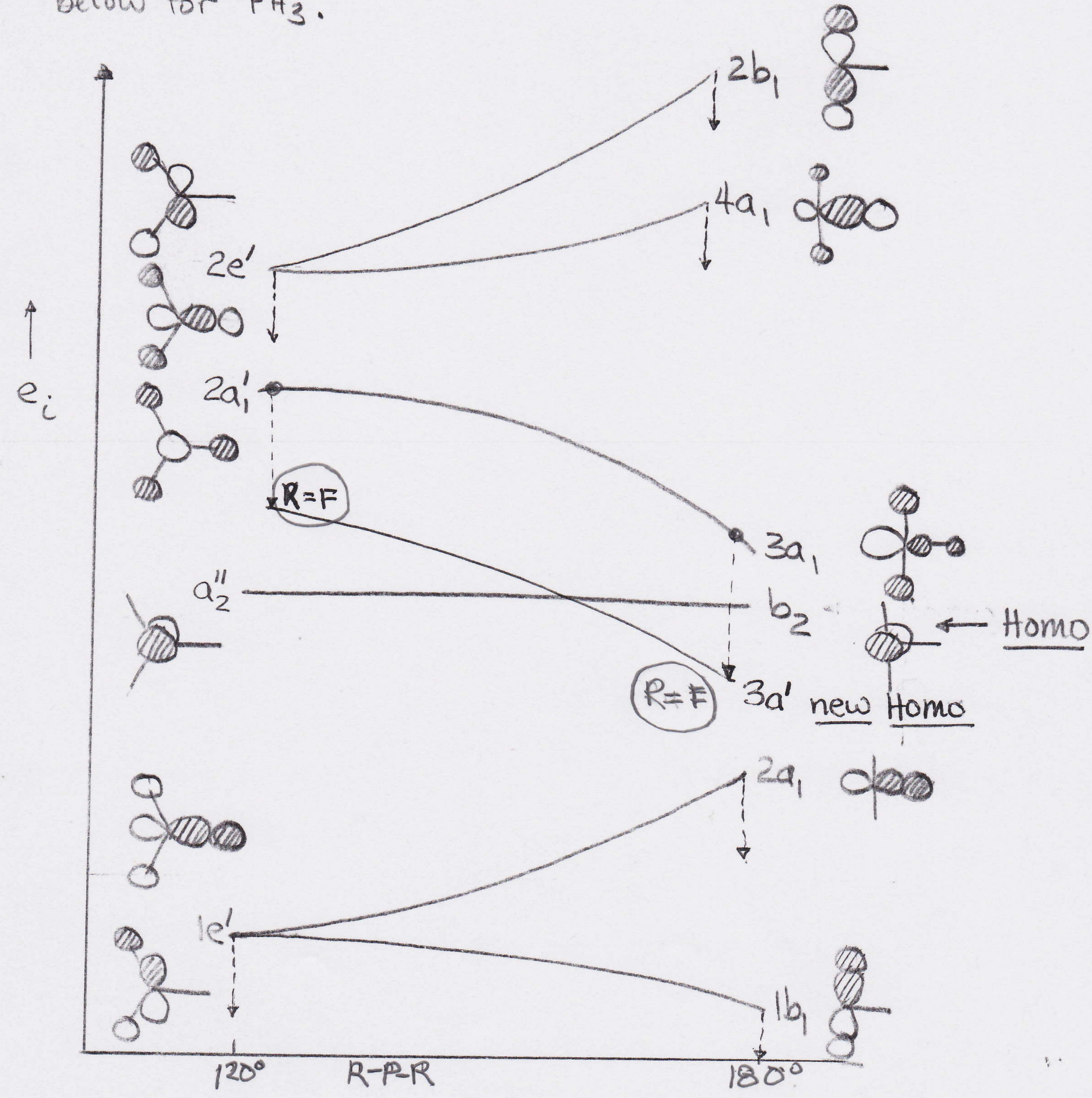


$2a_1 =$



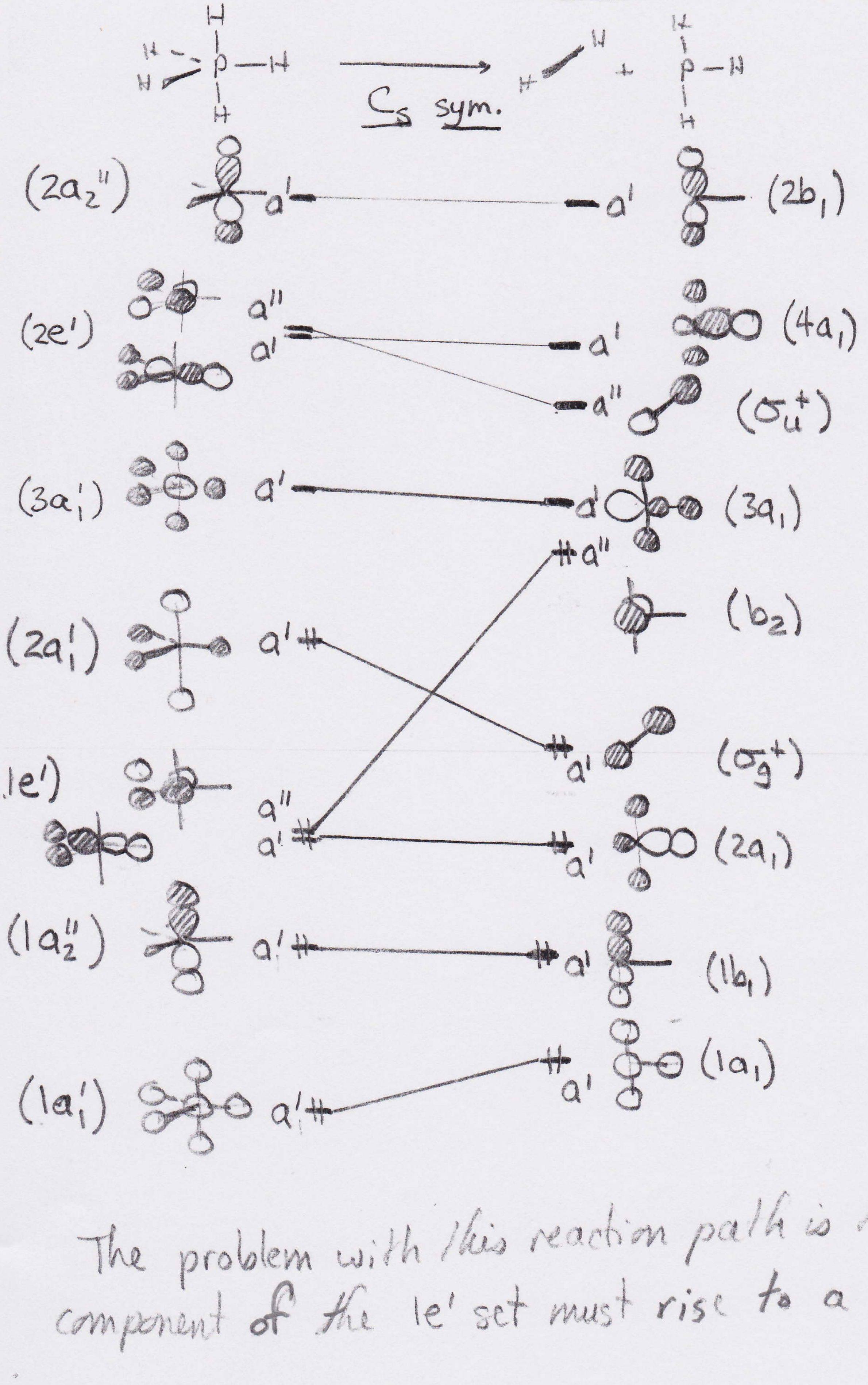
$3a_1 =$

12. what is critical here is to evaluate the energies of transition state A relative to B as a function of the electronegativity of R. A partial walsh diagram for A going to B is shown below for PH_3.

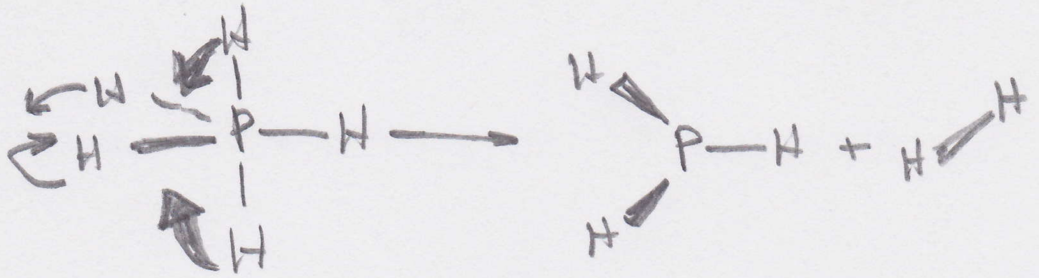


As shown in the Walsh diagram for R=H a D_{3h} geometry is more stable than C_{2v} ($2a_1$ is destabilized when the R-P-R angle increases and b_2 – the HOMO – remains at constant energy). However, for R=F all of the MO's are stabilized ($e^{(1)} < 0$) except a_2'' or b_2. Consequently, $3a_1$ can lie lower in energy than b_2 and the path B through TS_B is more stable than pyramidal inversion via TS_A.

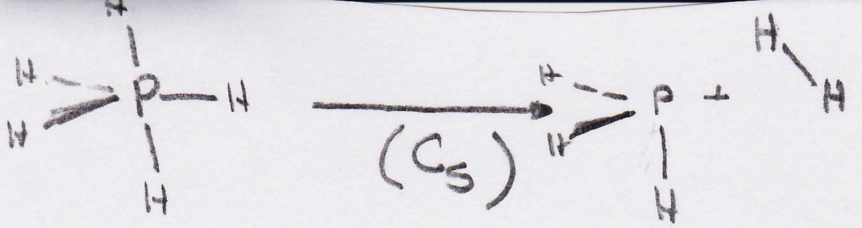
B. An orbital correlation diagram preserves a mirror plane of symmetry in Path 1 which bisects the H--H bond that is formed:

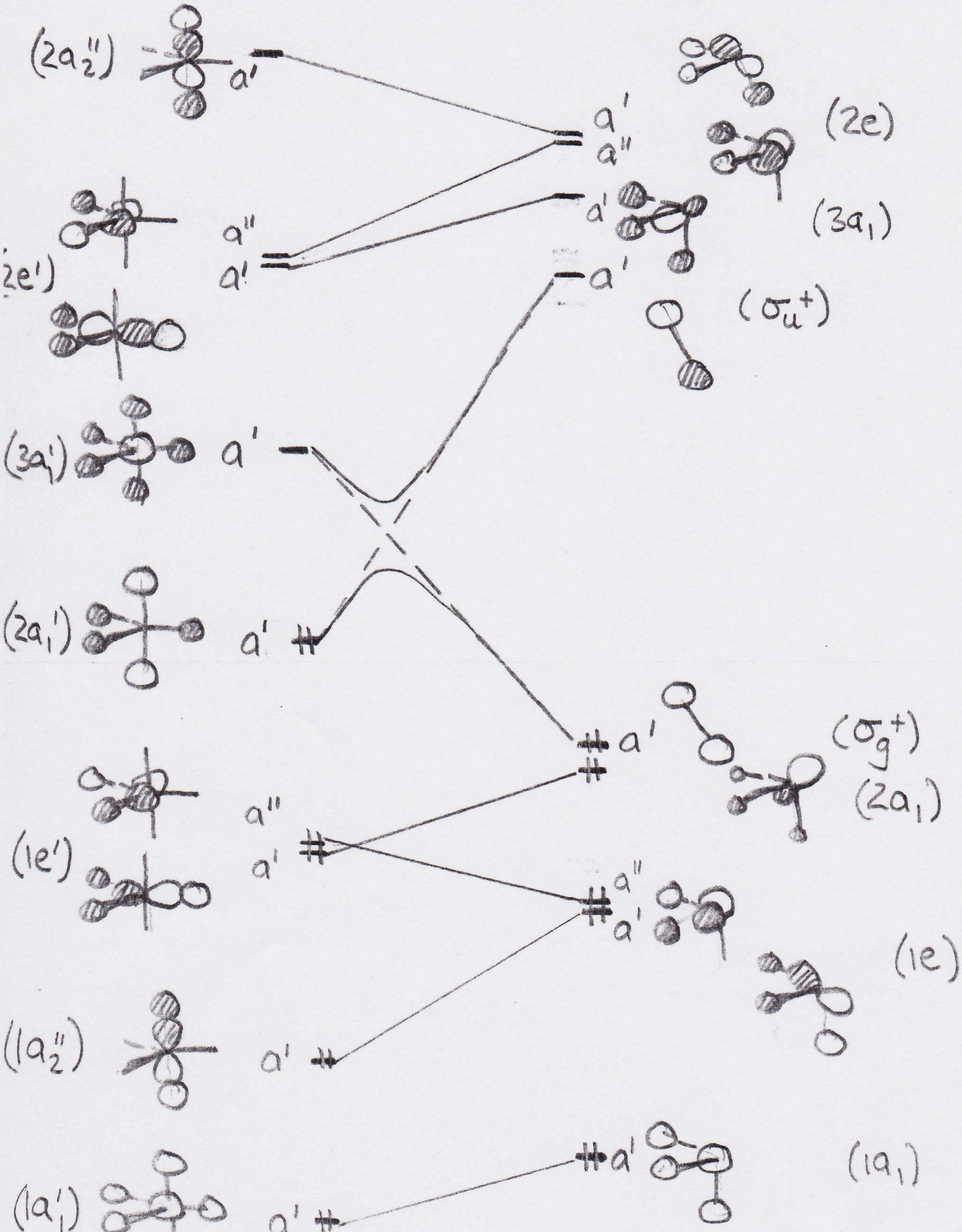


The problem with this reaction path is that one component of the 1e' set must rise to a very high energy and become the b_2 orbital in a C_{2v} PH_3 molecule; see the previous problem. C_{2v} PH_3 lies 159 Kcal/mol <u>above</u> the energy of C_{3v} PH_3. The only way to avoid this is to use the complicated motion shown below:

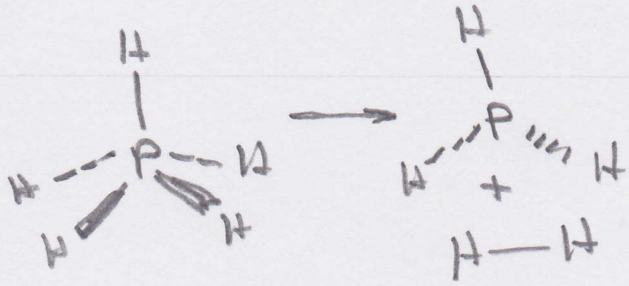


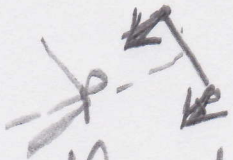
The orbital correlation diagram for path 2 is:


H
H
P
H
H
H
(Cs)
H
P
H
H
+
H
H


(2a$_2''$)
a'
a'
a''
(2e)
a'
(3a$_1$)
a''
a'
2e')
a'
(σ$_u^+$)
(3a$_1'$)
a'
(2a$_1'$)
a'
a'
(σ$_g^+$)
(2a$_1$)
a''
a'
(1e')
a''
a'
(1e)
(1a$_2''$)
a'
a'
(1a$_1$)
(1a$_1'$)
a'

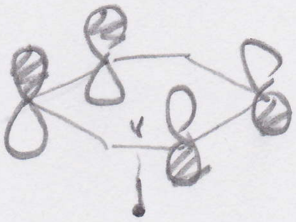
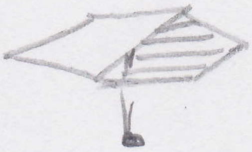
The problem with this path is that, at PH_5, the $2a_1'$ orbital should evolve into σ_u^+ of H_2 and $3a_1'$ should correlate to σ_g^+ of H_2. Instead of this happenning there is a weakly avioded crossing that will occur, but the energy if $2a_1'$ must rise substantially so there still will be a very high activation barrier. The reader can determine that a least motion path from the square pyramid:

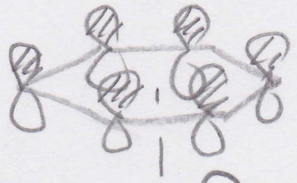


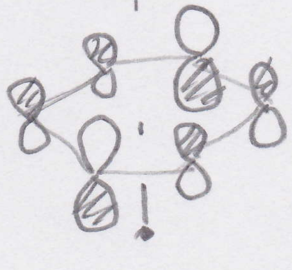
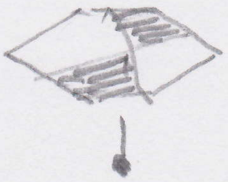
is symmetry forbidden, But one can ask if path 2 not being rigourously forbidden, might have a small barrier for PCl_5. In other words, perhaps the avoided crossing is much stronger than anticipated for PH_5. B3LYP Calculations were carried out using a large, 6-311G+(2d) basis set. The results are on the next page. The barrier is quite high, furthermore, keeping C_s symmetry gives two (not one!) immaginary frequencies. At 91i cm^{-1} the normal mode is  but at 345i cm^{-1} there is a normal mode that wants to break C_s symmetry if followed. 

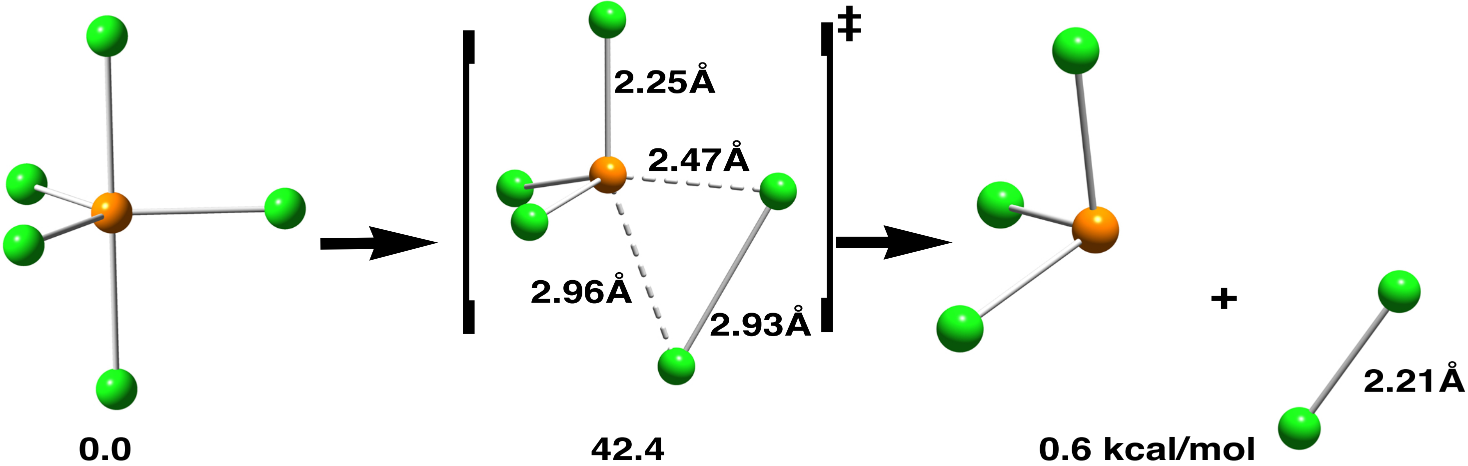
The HOMO & LUMO are also close together at the transition state, as shown on the next page. Their shapes are just what one expects from the correlation diagram.

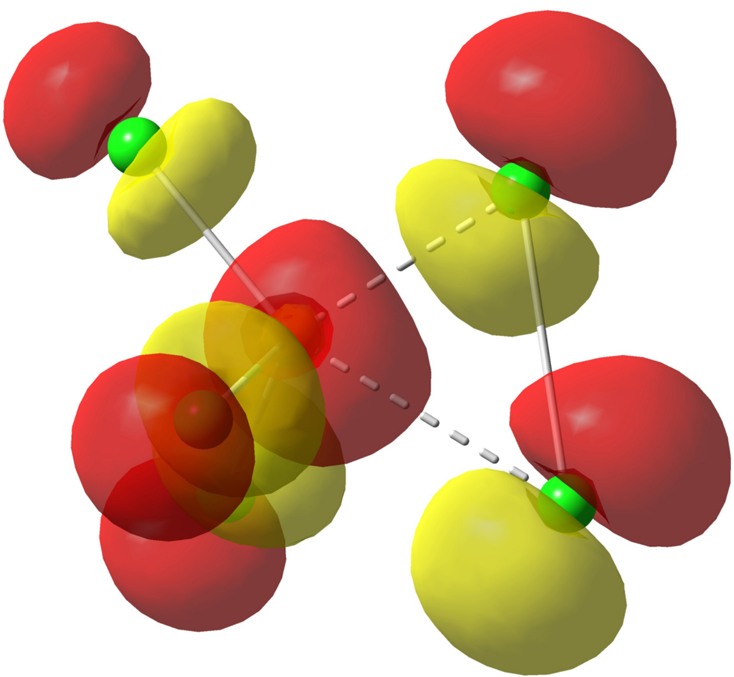
14. I will use the short hand notation for the π orbitals of benzene:

 ≡ 

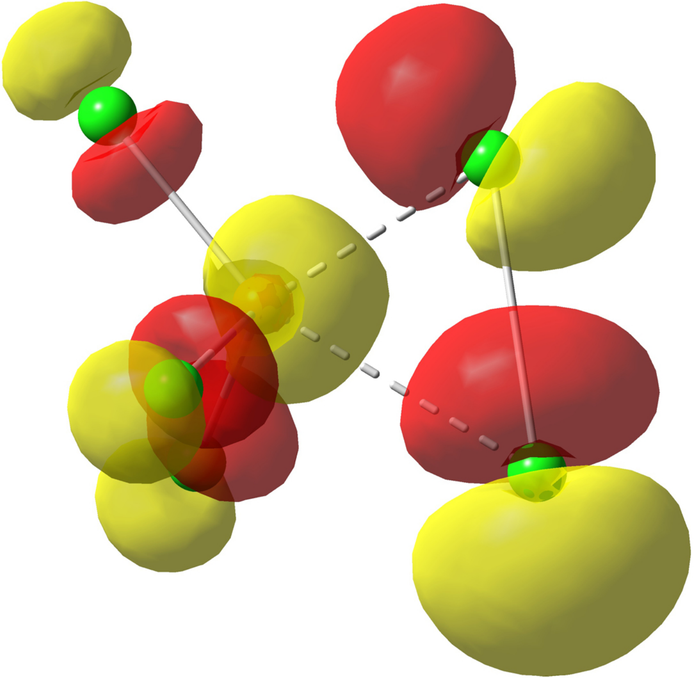
 ≡ 

 ≡  etc.

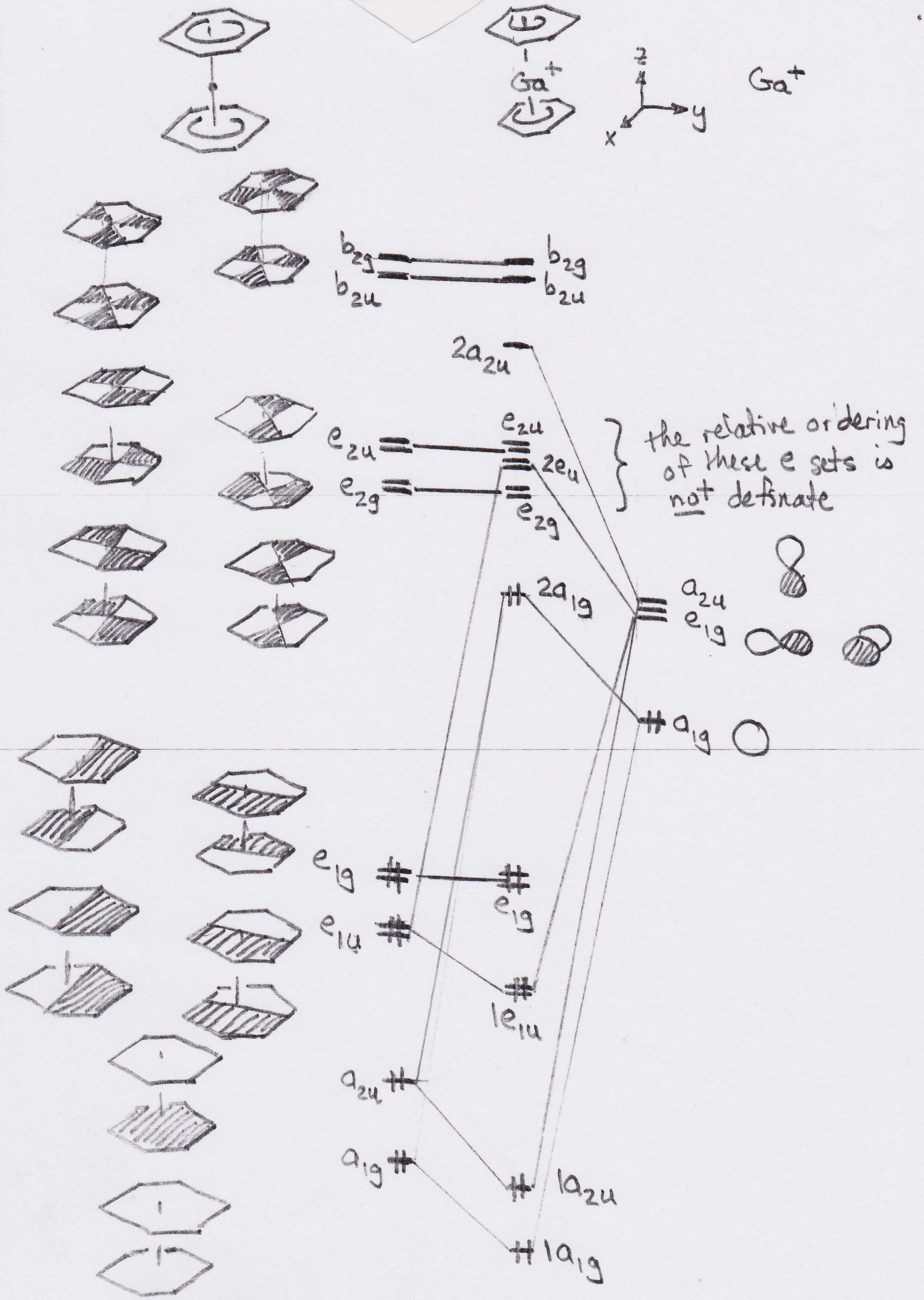

0.0
2.25Å
2.47Å
2.96Å
2.93Å
‡
42.4
+
2.21Å
0.6 kcal/mol



LUMO (-7.0 eV)

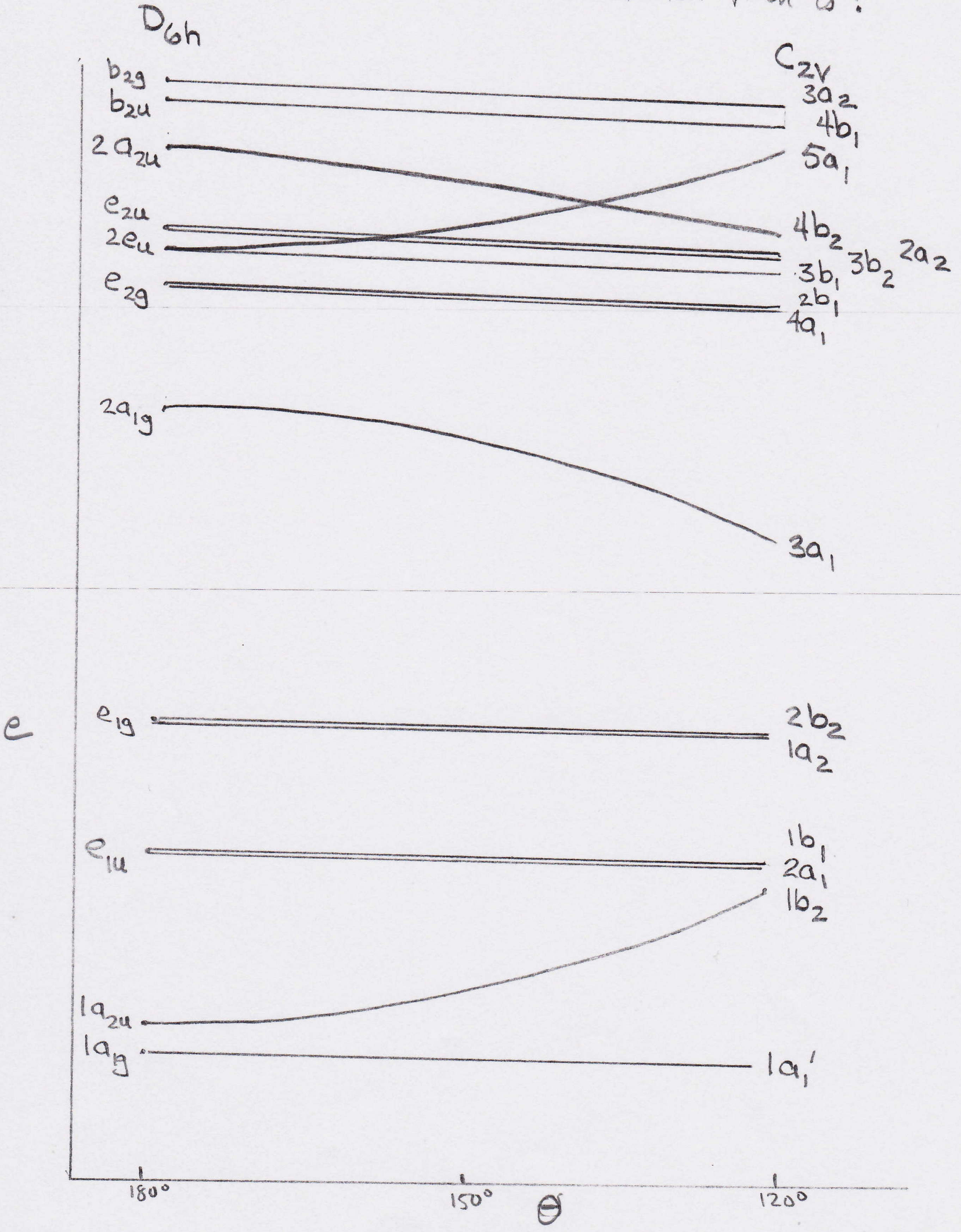


HOMO (-7.9 eV)



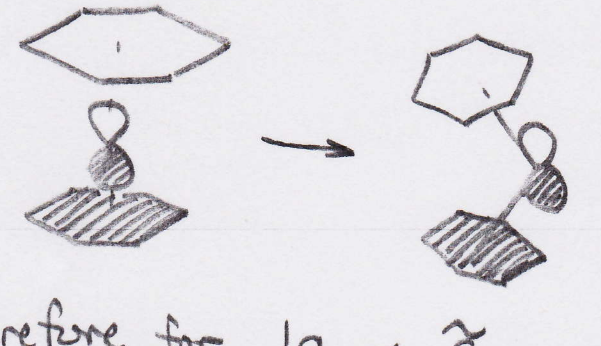
the relative ordering of these e sets is <u>not</u> definate

We will make the simplifying assumption that no interactions are turned on when θ = 120° (all C--C distances are still long). The form of the Walsh orbital then is:



Most orbitals are totally unperturbed! There are only 4 that are greatly changed:

overlap between the a_{2u} π combination and p_z is lost when θ decreases, i.e.,



Therefore, for $1a_{2u}$: $\tilde{S}_{ii} = (-)$ overlap decreases (bonding decreases

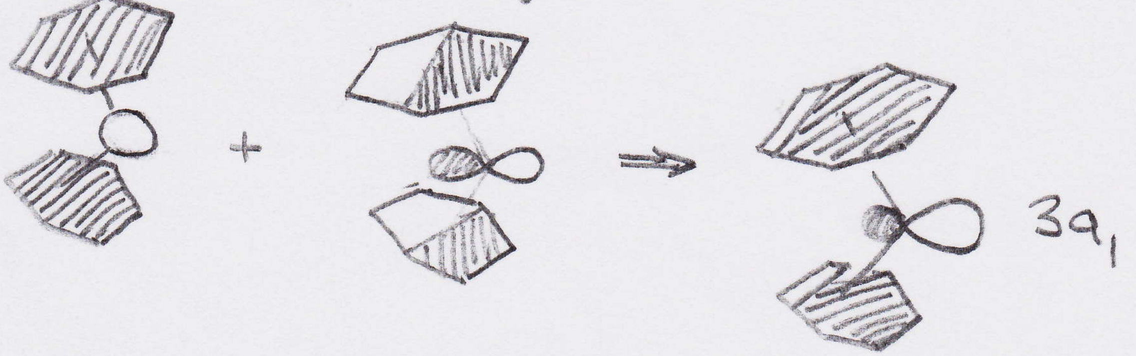
$e^{(1)} \propto -\tilde{S}_{ii} = (+)$; orbital is destabilized

for $2a_{2u}$: $\tilde{S}_{ii} = (+)$ overlap increases (antibonding decreases)

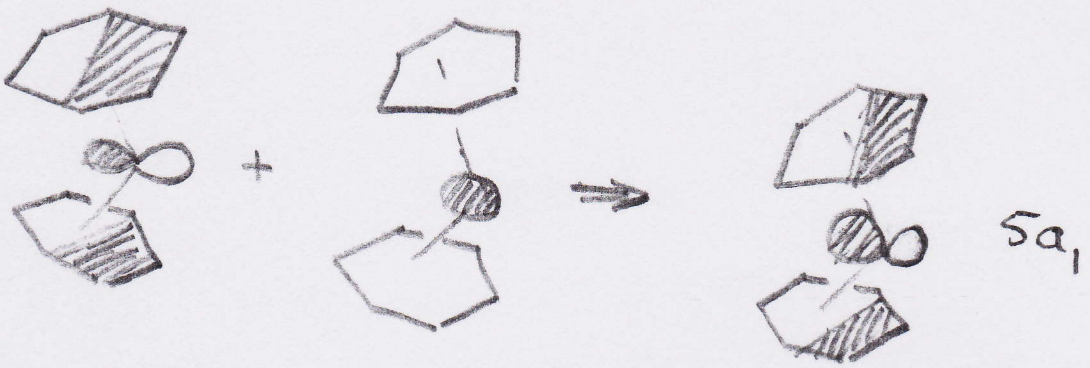
$e^{(1)} \propto -\tilde{S}_{ii} = (-)$; orbital is stabilized

The $2a_{1g}$ orbital lies close to the $2e_u$ set, consequently there can be a second order change

for $2a_{1g}$: $e^{(2)} \propto \frac{\tilde{S}_{ij}^{2}}{e_i^0 - e_j^0} = \frac{(+)}{(-)} = (-)$ stabilization

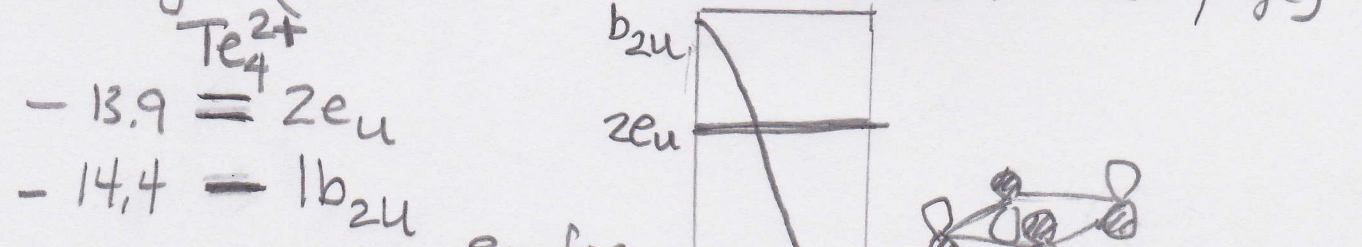


Likewise for $2e_u$ $\quad e^{(2)} = \frac{\tilde{S}_{ij}^2}{e_j^\circ - e_i^\circ} = \frac{(+)}{(+)} = (+)$ destabized

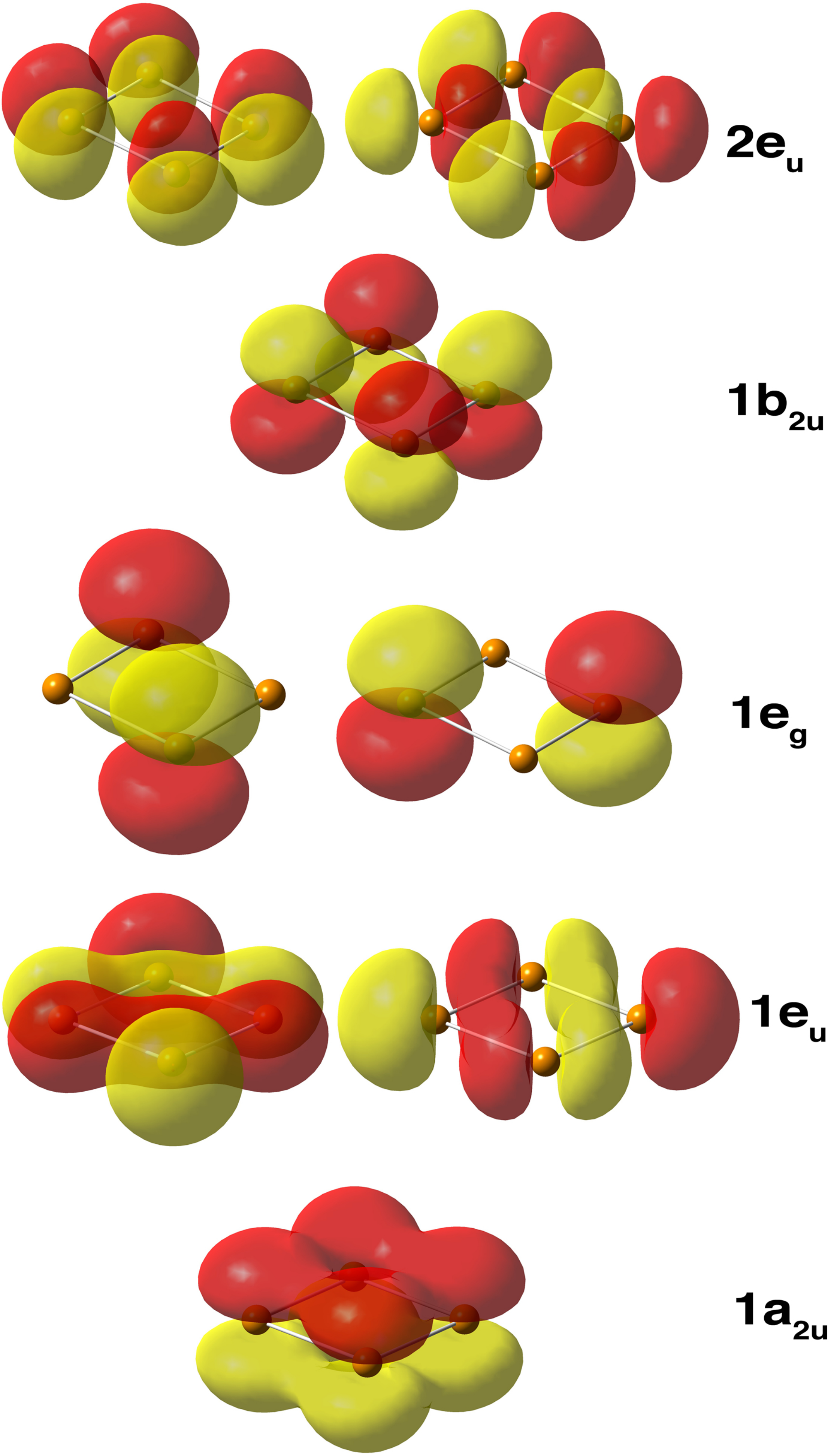


with $3a_1$ the HOMO, decreasing θ is stabilizing

15. For Te_4^{2+} B3LYP calculations give the following energies (the orbitals are shown on the next page)



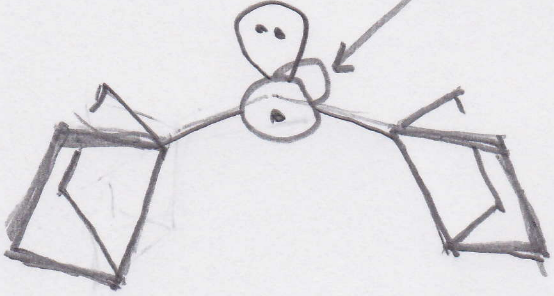
The e_u bands have no dispersion – there is essentially


$2e_u$
$1b_{2u}$
$1e_g$
$1e_u$
$1a_{2u}$

no intercell overlap. The π bands do overlap and give rise to essentially the same shape in each case. It is the top band which becomes partially filled upon reduction.

16. For Sr_3In_5 we can count the 4-coordinate In atoms as having 4 electron pairs around them (they are tetrahedral), so $Sr_3In_5 \equiv In_4^{4-}$ for the 4-coordinate atoms, leaving the 2 coordinate In atoms as In^{2-}. According to the Zintl-Klemm rules two coordinate In's should have 

} i.e. In^{3-}. So there is a problem with the electron counting. From the In DOS, the region around the Fermi level is primarily In(1) - the 2-coordinate In. Furthermore, from the second DOS plot, the region around the Fermi level is almost exclusively In px, i.e. it must be



forms a band $\sim 1/2$ filled, i.e.