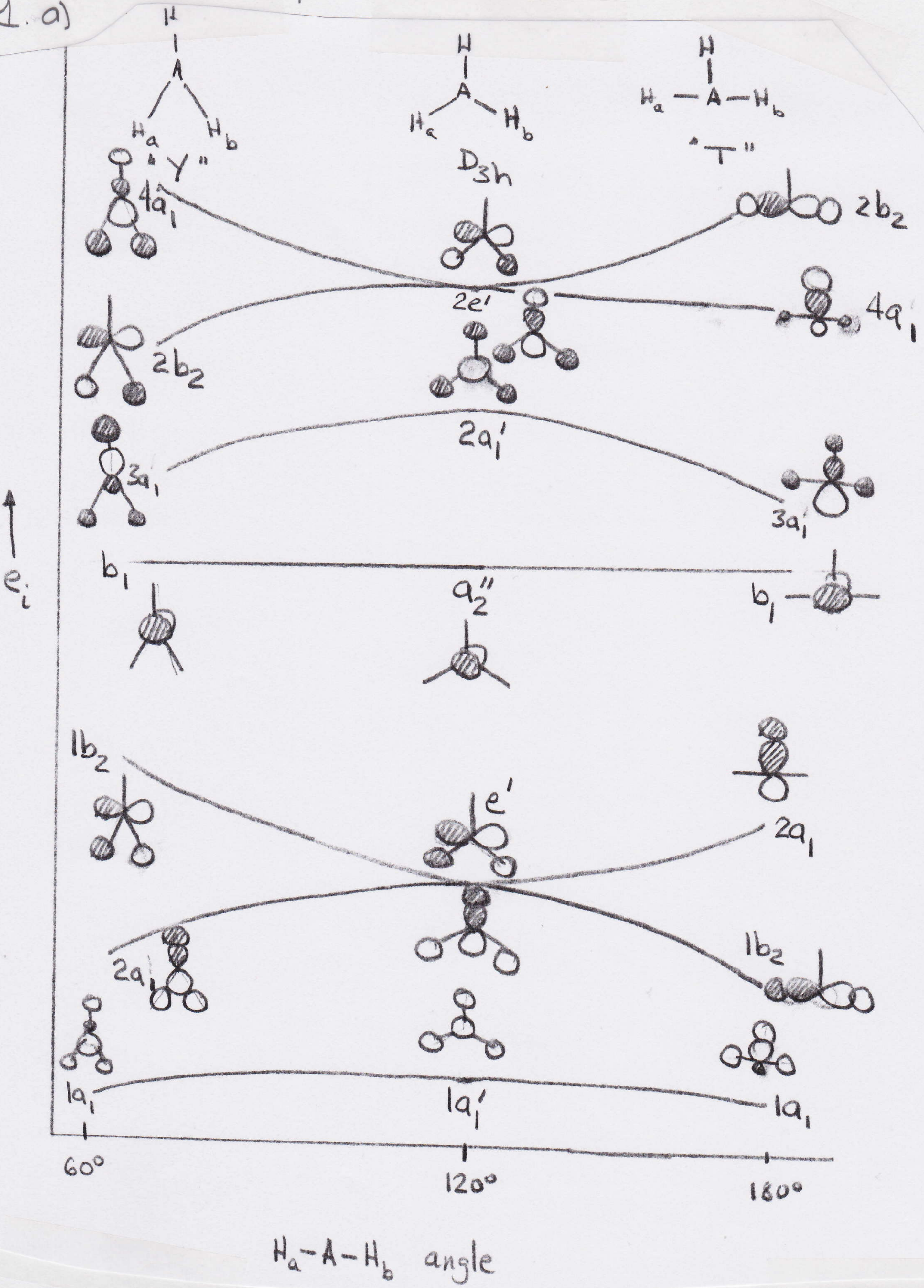
Answers - Chapter 9

1. a)



b) With $4e^-$ either C_{2v} geometry should be stable, i.e. $(1a_1)^2(2a_1)^2$ or $(1a_1)^2(1b_2)^2$

with $10e^-$ note that there will be a second order energy stabilization between $2a_1'$ and $2e'$ – large coefficients in these antibonding orbitals, thus either geometry should be stabilized.

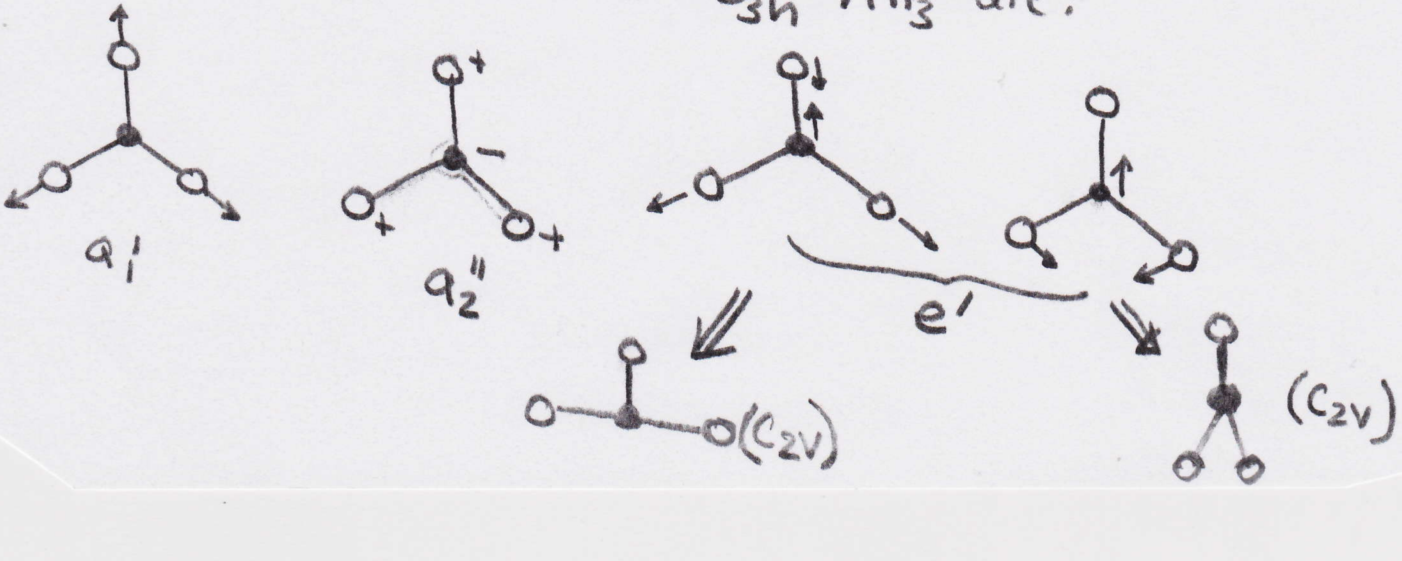
with $12e^-$ - only the C_{2v} geometry is stabilized - at the T geometry the 1st order stabilization of $4a_1$ is offset by the 2nd order destabilization with $3a_1$.

c) for LiH_3 at a D_{3h} geometry we have an electronic configuration $(1a_1)^2(1e')^2$. Therefore, a first order Jahn-Teller distortion is predicted, i.e.

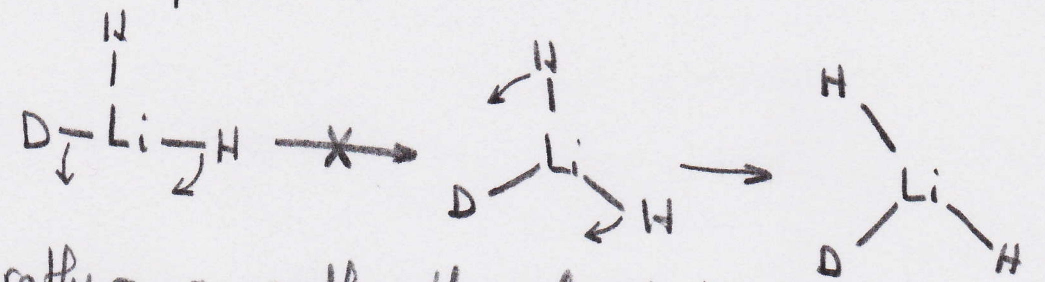
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
e'	2	-1	0	2	-1	0	
$e' \times e'$	4	1	0	4	1	0	$= a_1' + a_2' + e'$

$$T_Q = a_1' + a_2' + e'$$

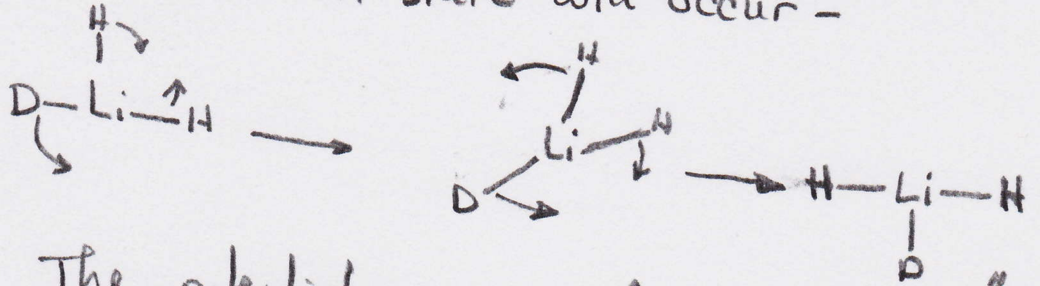
The normal coordinates for D_{3h} AH_3 are:



d) From the results above, a least motion path is <u>not</u> preferred, i.e.



<u>rather</u> a path through the "Y" C_{2v} geometry as the transition state will occur -

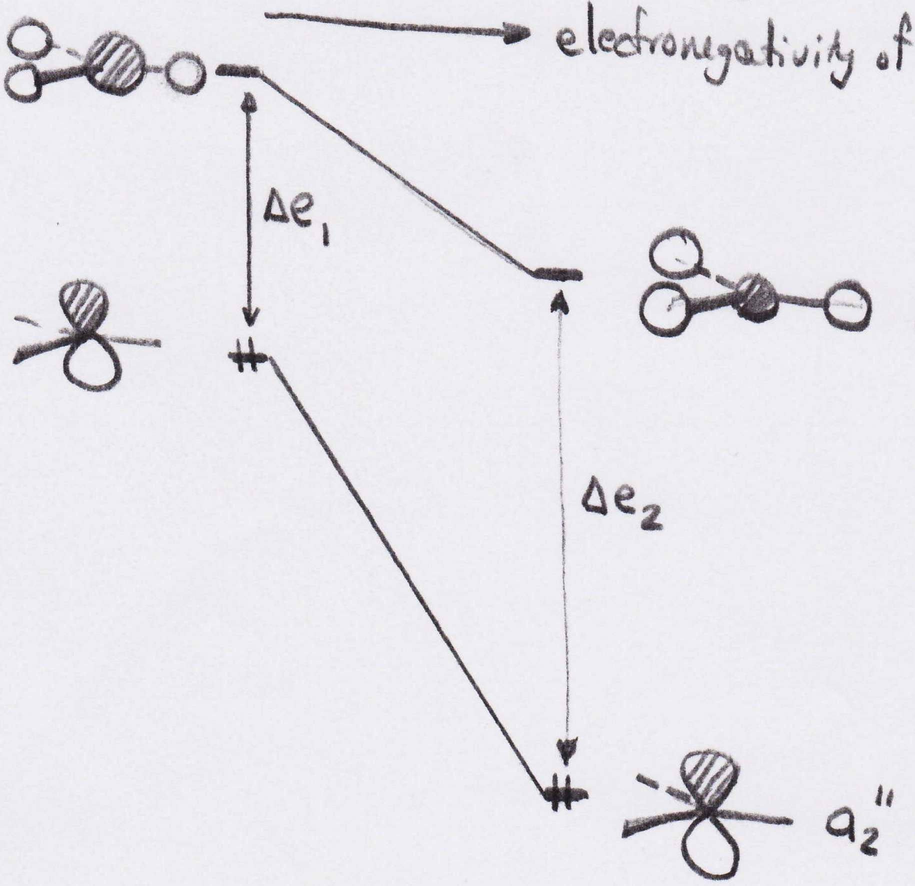


The potential energy surface will be a "Mexican-hat" surface like that on p. 101 of the book A, B & C are the three "T" geometries, D is the "Y" transition state and E is the D_{3h} mountain top.

2. On going from CH_3^- to NH_3 to OH_3^+ the central atom becomes more electronegative. The equilibrium H-A-H angle becomes <u>larger</u> and the inversion barrier drops, therefore, one might expect the mixing of $2a_1'$ into a_2'' to be energetically less stabilizing along this series. This 2^{nd} order energy stabilization is

$$e^{(2)} \propto \frac{\tilde{S}_{2a_1', a_2''}}{e^\circ_{a_2''} - e^\circ_{2a_1'}}$$

This is true for the following reason-



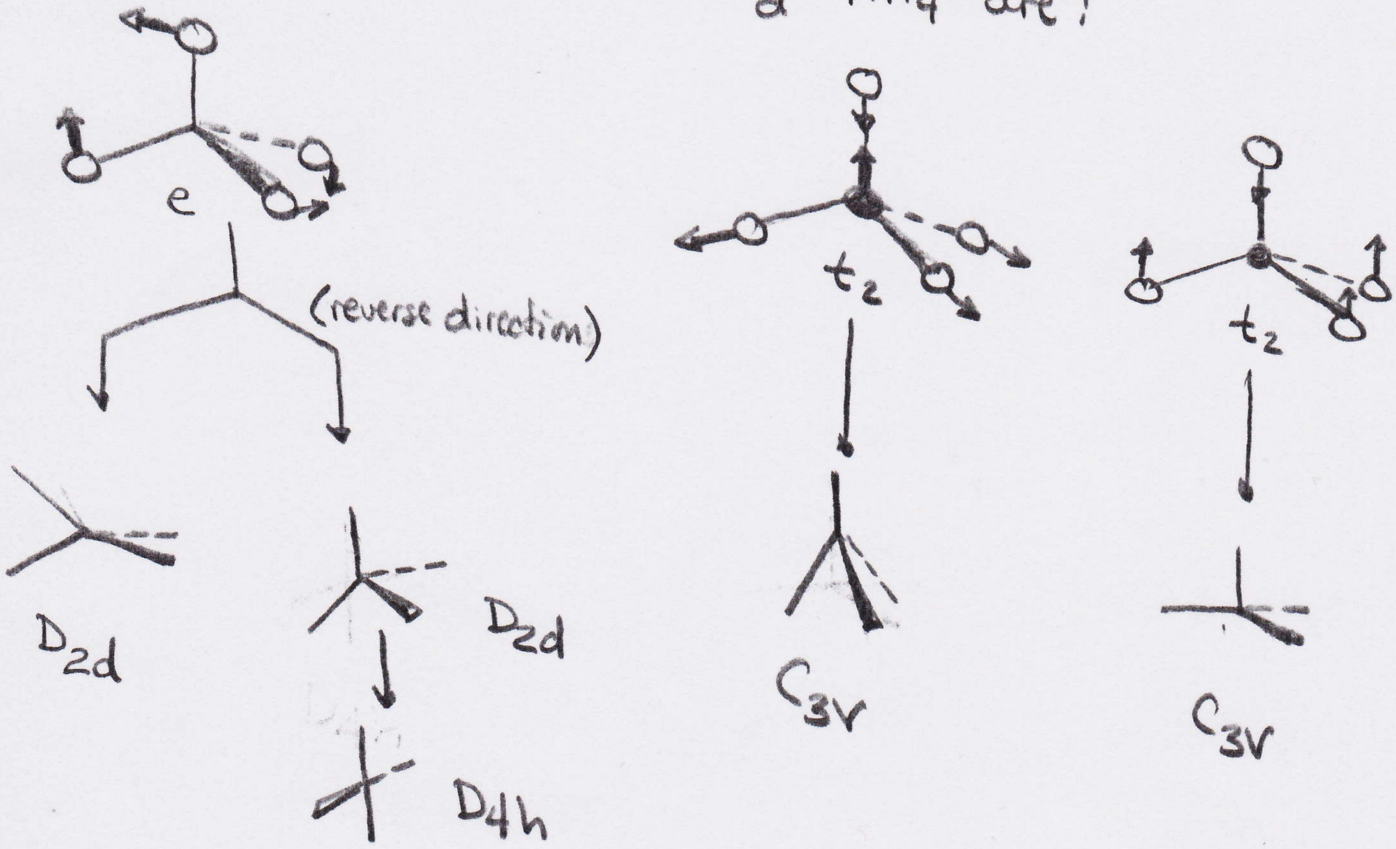
larger $e^{(1)}$ stabilization because a_2'' is totally localized on A which is becoming more electroneg., whereas, $2a_1'$ is delocalized over the whole molecule

$\therefore$ $\Delta e_2 > \Delta e_1$ as A becomes more electronegative. This will cause $e^{(2)}$ to decrease. On the other hand, note that as A becomes more electronegative the coefficients on the hydrogens increase and this will cause $\tilde{S}_{2a_1', a_2''}$ to increase as the electronegativity of A increases. The energy gap dominates in this case over overlap but this is why the effect is not a particularily larger one.

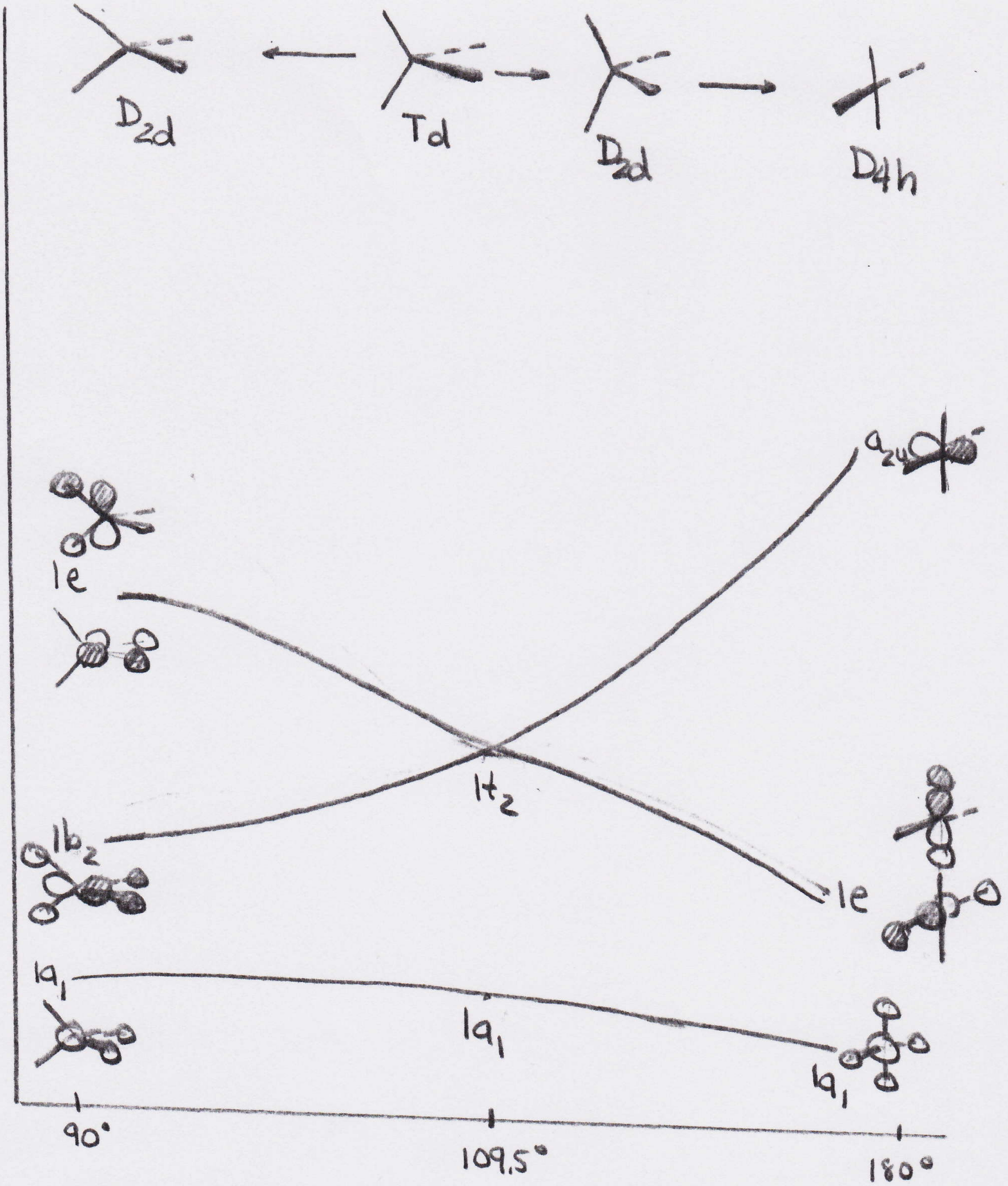
3. We start from the T_d geometry where the electronic configuration would be $(1a_1)^2(1t_2)^4$ thus a first order Jahn-Teller effect is predicted -

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
t_2	3	0	-1	-1	1
$t_2 \times t_2$	9	0	1	1	1 $= a_1+t_1+t_2+e$

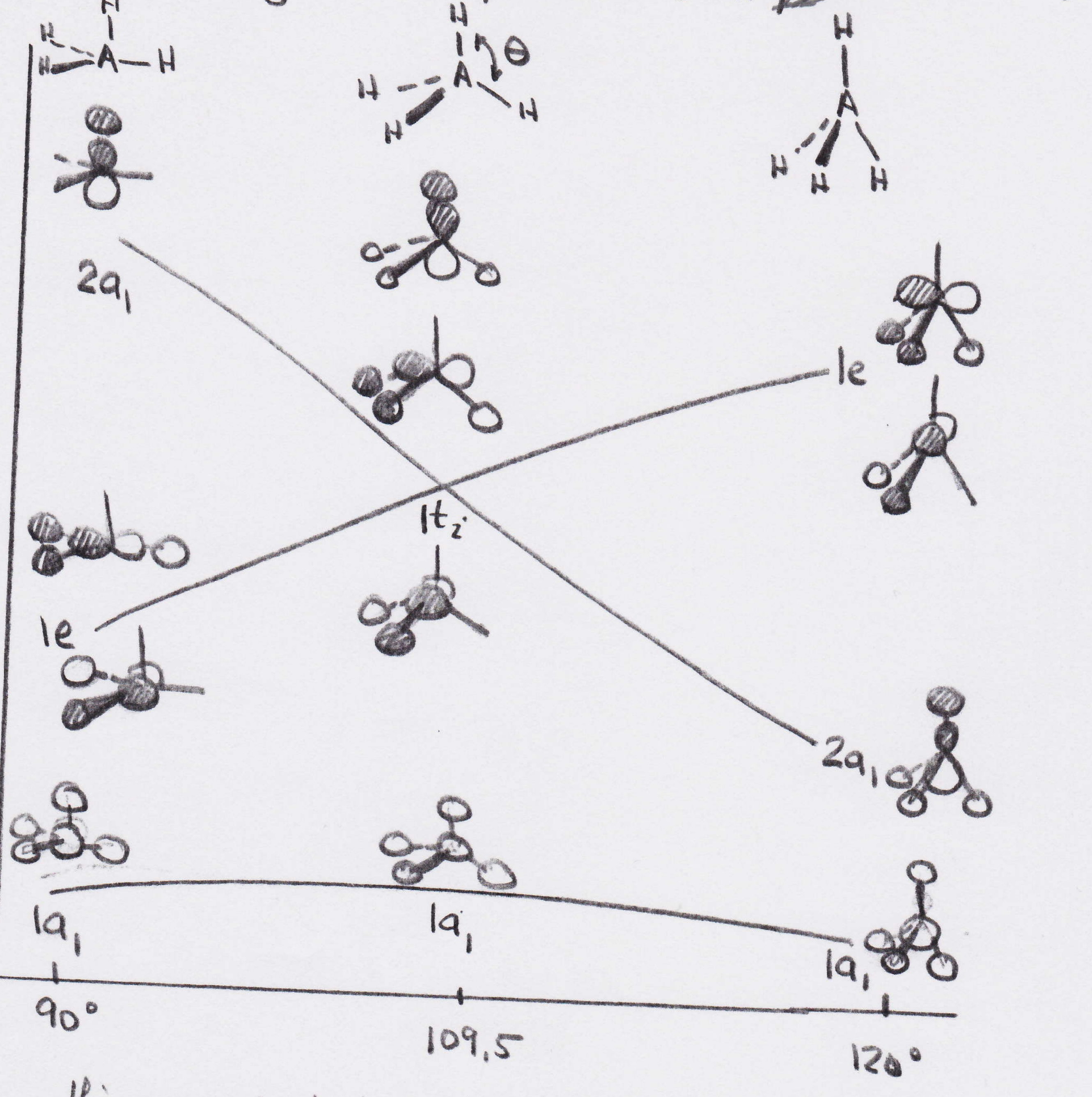
The normal modes for a T_d AH_4 are:



We've covered the $T_d \rightarrow D_{4h}$ distortion before:
(see Figure 9.11)

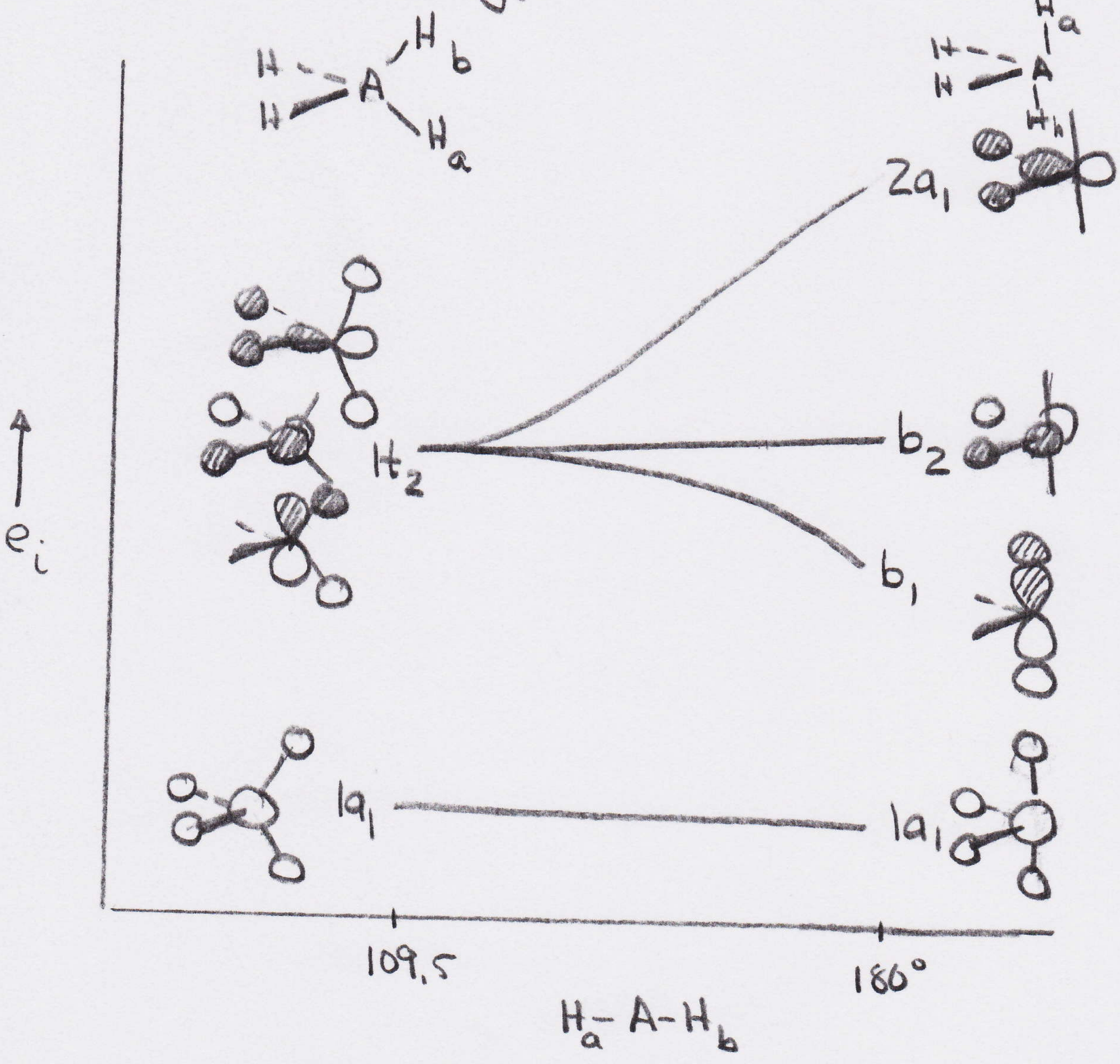


notice, that with 6 electrons distortion to small H–A–H angles is not preferred, the Jahn-Teller theorem does not tell us what direction the distortion will be stabilizing. Likewise, it does not tell us whether the distortion to large H–A–H angles will stop at an intermediate D_{2d} or all the way to D_{4h} although we would expect the latter. Also note that a **triplet** T_d geometry should be more stable than a triplet D_{2d} one distorting in either direction. The C_{3v} modes are (using the t_2 representations on 9,27 ~~p. 158~~ in the book)



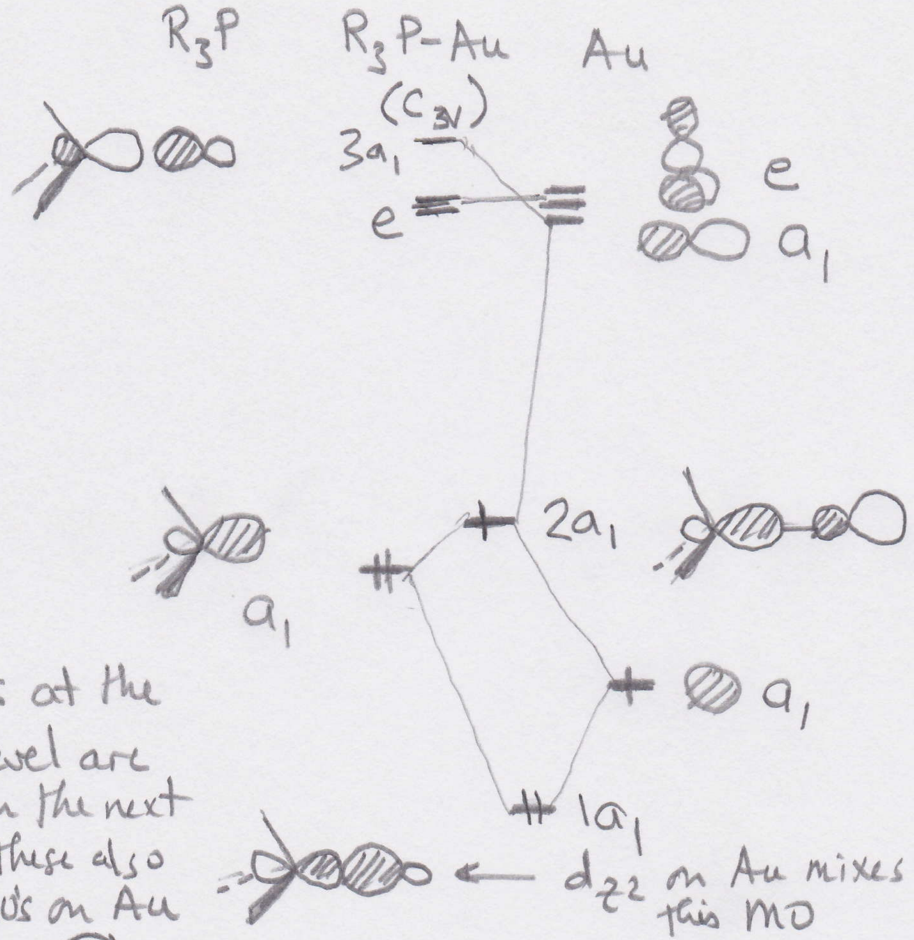
In this case distortion to small θ is stabilizing.

Yet another distortion to C_{2v} geometry is expected to be stabilizing, i.e.



Thus, a T_d triplet, a D_{4h} (or perhaps D_{2d}) singlet, a C_{3v} singlet and a C_{2v} singlet should be stable for CH_4^{2+}

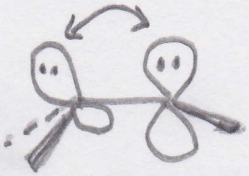
4.



The MO's at the EHT level are plotted on the next page - these also use d AO's on Au

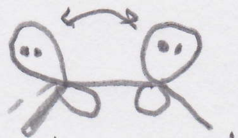
← d_{z^2} on Au mixes a fair amount in this MO

5. a)



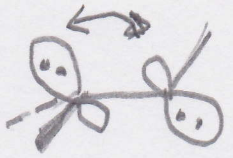
good overlap
4e⁻ repulsion maximized

vs



less overlap
smaller 4e⁻ repulsion

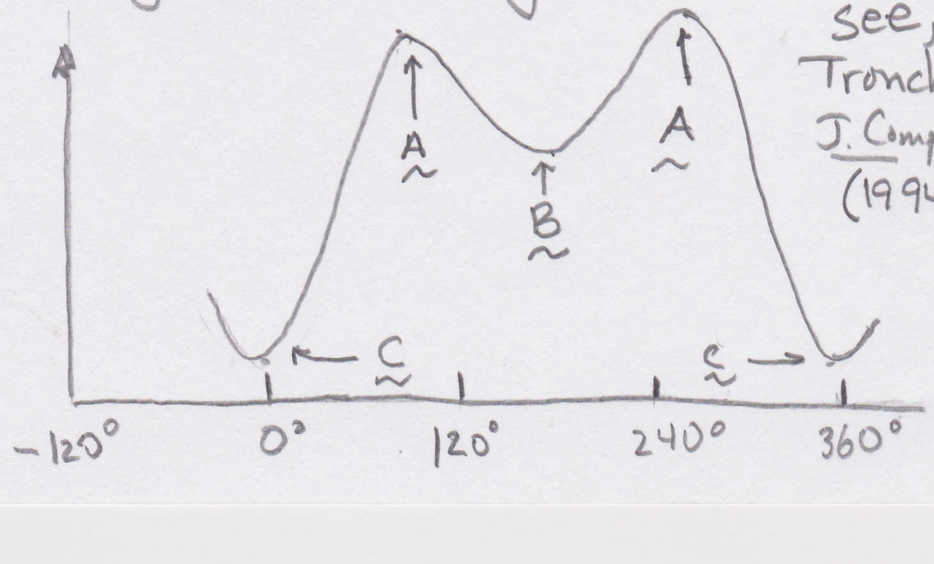
vs



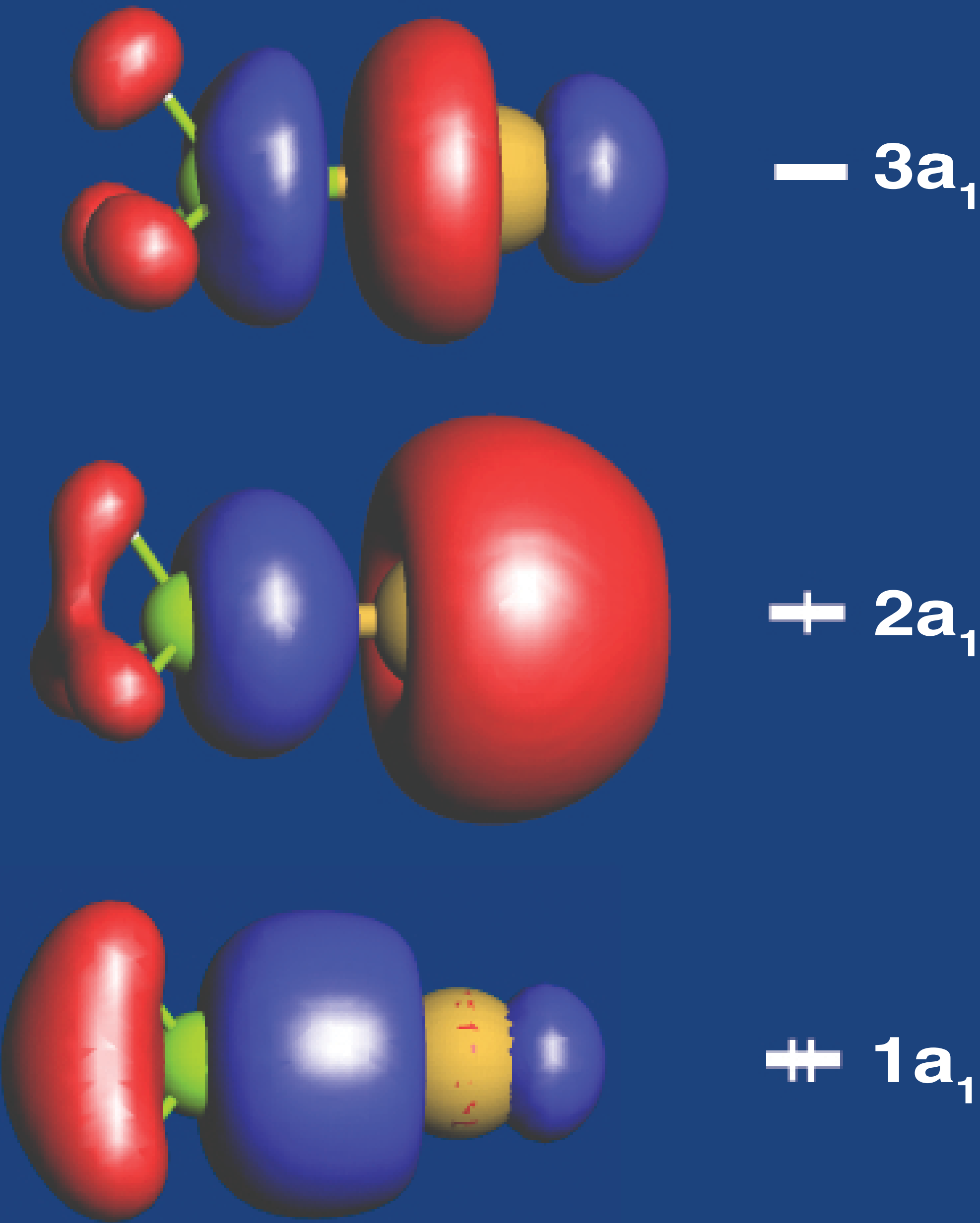
smallest overlap
least 4e⁻ repulsion

∴ stability order: C > B > A

all calculations on the internal rotation around the N–O bond in H_2N-OH give the following form:

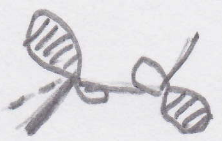


see, e.g., J.M.J. Tronchet & I. Komaromi, J. Comput. Chem., 15, 1091 (1994).

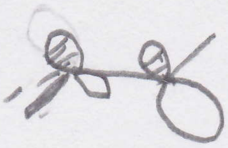

$3a_1$
$2a_1$
$1a_1$

b) The lone pair on NH_3 is at 11.0 eV; the b_1 lone pair in H_2O is at 12.6 and the a_1 lone pair is at 13.8 eV. We expect in geometry C that the N lone pair will mix with H_2O a_1 to give an antibonding combination, mainly on N that has a lower IP than 11 eV and a bonding combination mainly on O which has an IP larger than 13.8 eV, i.e.

both have a′ symmetry

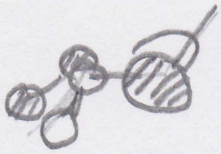


IP < 11 ∴ band ①

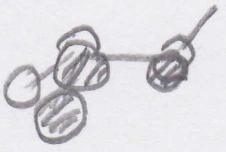


IP > 13.8 ∴ most consistent with band ③

The other lone pair on oxygen should be ~ 12.6, <u>however</u>, it can mix with one member of the e set in the NH_3 model - both have a″ symmetry, so

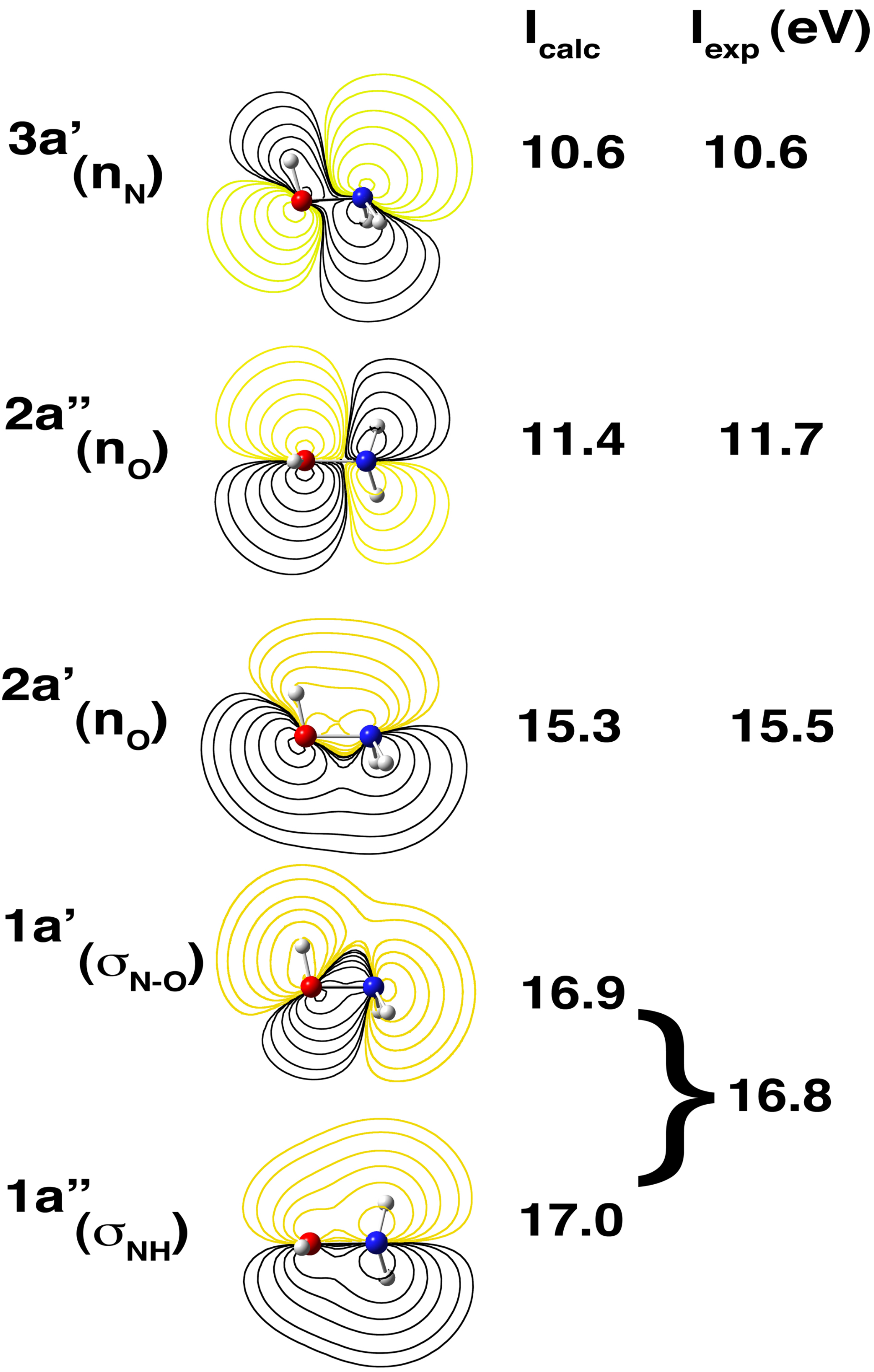


IP < 12.6 - consistent now with band ②



IP > 16.2 (the IP of the e set in NH_3) - consistent with band ④ or ⑤

So what about the other band in the ④/⑤ set? This turns out to be an N–O σ MO. The MO plots and calculated IP's (using Koopmanns theorem) at the B3LYP level using a 6-311G+2d basis set (really big with polarization functions is shown on the next page


I_{calc}
I_{exp} (eV)
3a' (n_N)
10.6
10.6
2a'' (n_O)
11.4
11.7
2a' (n_O)
15.3
15.5
1a' (σ_{N-O})
16.9
16.8
1a'' (σ_{NH})
17.0