# Answers - Chapter 5

## 1. a)



$\sigma_v$ $C_{4V}$

note: basis 1 : $x_1, x_2, x_3, x_4$    basis 2 : $x_5$

basis 2 : $\psi_{1a_1} = x_5$   $(a_1)$

basis 1 :

| $C_{4V}$ | E | $2C_4$ | $C_2$ | $2\sigma_v$ | $2\sigma_d$ |
|---|---|---|---|---|---|
| $\Gamma$ | 4 | 0 | 0 | 2 | $0 = a_1 + b_1 + e$ |

| | E | $C_4$ | $C_4^3$ | $C_2$ | $\sigma_v$ | $\sigma_v'$ | $\sigma_d$ | $\sigma_d'$ |
|---|---|---|---|---|---|---|---|---|
| $x_1$ | $x_1$ | $x_2$ | $x_4$ | $x_3$ | $x_1$ | $x_3$ | $x_2$ | $x_4$ |
| $x_2$ | $x_2$ | $x_3$ | $x_1$ | $x_4$ | $x_4$ | $x_2$ | $x_1$ | $x_3$ |

$\psi_{2a_1} \propto x_1 + x_2 + x_4 + x_3 + x_1 + x_3 + x_2 + x_4 = x_1 + x_2 + x_3 + x_4$

$\psi_{b_1} \propto x_1 - x_2 - x_4 + x_3 + x_1 + x_3 - x_2 - x_4 = x_1 - x_2 + x_3 - x_4$

$\psi_{1e'} \propto 2x_1 - 2x_3 = x_1 - x_3$  } they are already

$\psi_{1e''} \propto 2x_2 - 2x_4 = x_2 - x_4$  } orthogonal

Combining the two basis of $a_1$ symmetry

$\psi'_{1a_1} \propto \psi_{1a_1} + \psi_{2a_1} = x_1 + x_2 + x_3 + x_4 + x_5$

$\psi'_{2a_1} \propto \psi_{1a_1} - \psi_{2a_1} = -x_1 - x_2 - x_3 - x_4 + x_5$

b)

$$-\psi_{b_1} =$$



$\left.\right\}$ 4 antibnd.
$\left.\right\}$ 0 bnd.

$$=\psi'_{2a_1}$$



$\left.\right\}$ 4 antibond,
4 bond.
(antibonding destabilizes
more than bonding
stabilizes)

$$\#\psi_e$$



(0 bonding
0 antibonding)
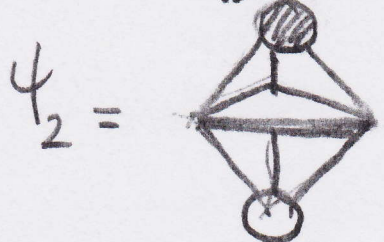
$$\#\psi'_{1a_1}$$



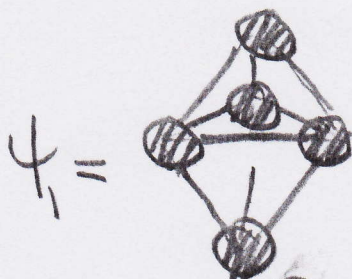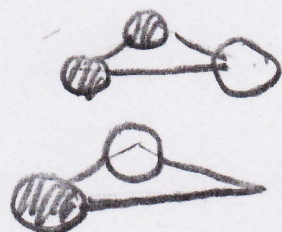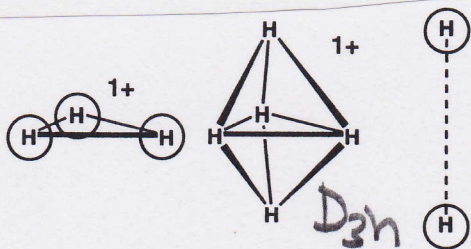$\left.\right\}$ 8 bonding
0 antibonding
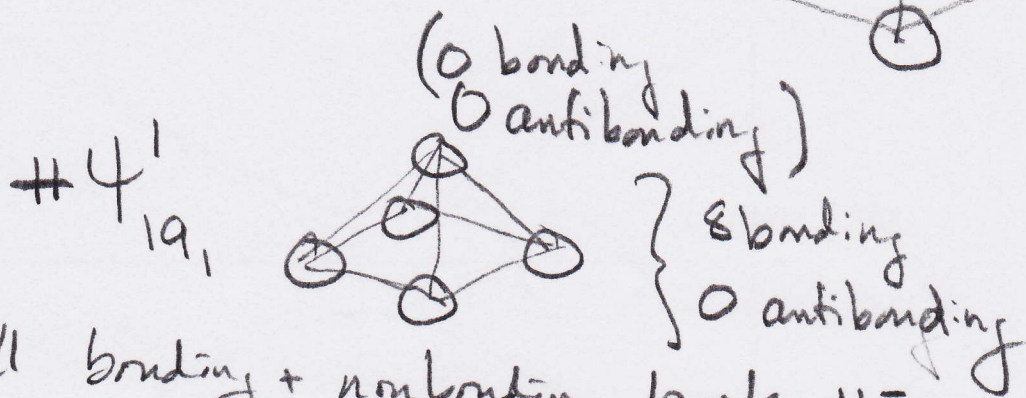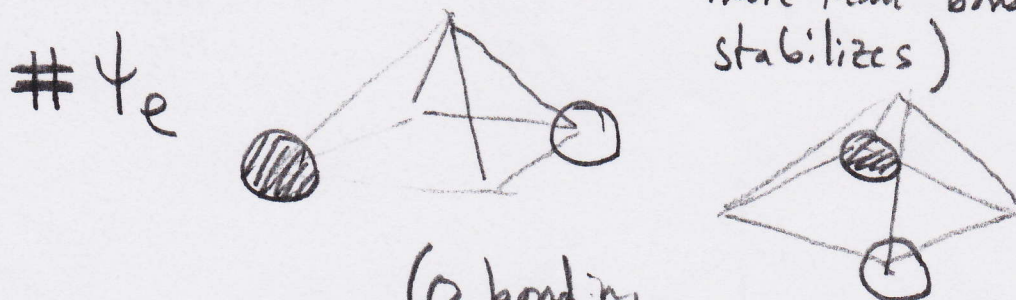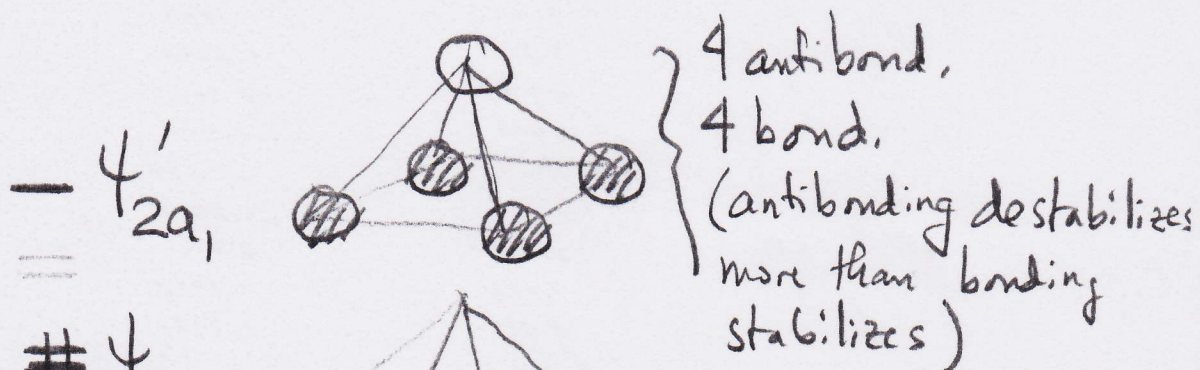
6 electrons fill bonding + nonbonding levels — $H_5^-$
actually $H_5^+$ (two less electrons) $\doteq$ stable — what is its structure?

We shall see in problem 4. Here with $2e^-$ less, $H_5^+$
will have a half-filled $e$ set. We shall see in
Chapter 7.4a that such situations are not stable —
that there will always (except in a diatomic molecule)
be a way to stabilize the singlet by a geometric
distortion. A triplet $H_5^+$ where the two electrons in $e$
are un-paired will be stable. $H_5^{3+}$ where only $1a_1$
is filled is also potentially stable. The MO's from an
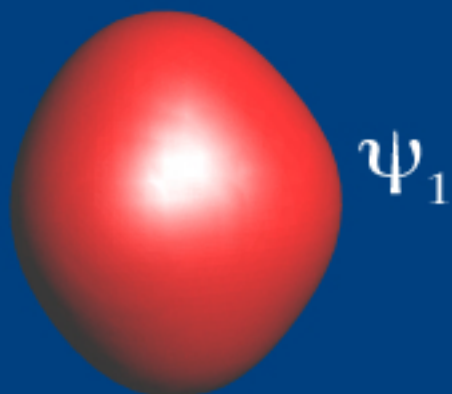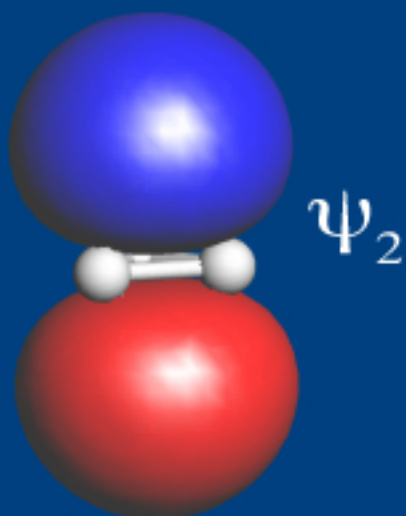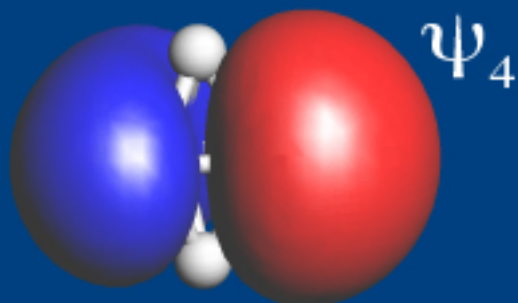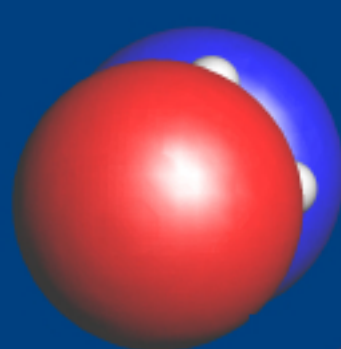extended Hückel calculation are plotted on the next page.

$b_1$

$2a_1$

$e$

$1a_1$

2.

$1+$

$D_{3h}$  $1+$

$\psi_5$

$e' = \quad\quad = \quad \begin{array}{c}\psi_3\\\psi_4\end{array}$

$a_2''$

$\psi_2$ ⇅ $\quad$ ⇅ $a_1'$

$a_1'$ ⇅

⇅ $\psi_1$

$\psi_1 =$

$\psi_2 =$

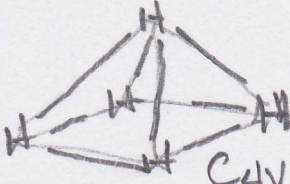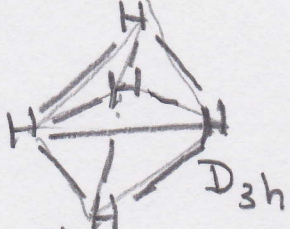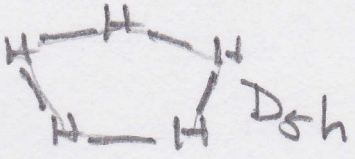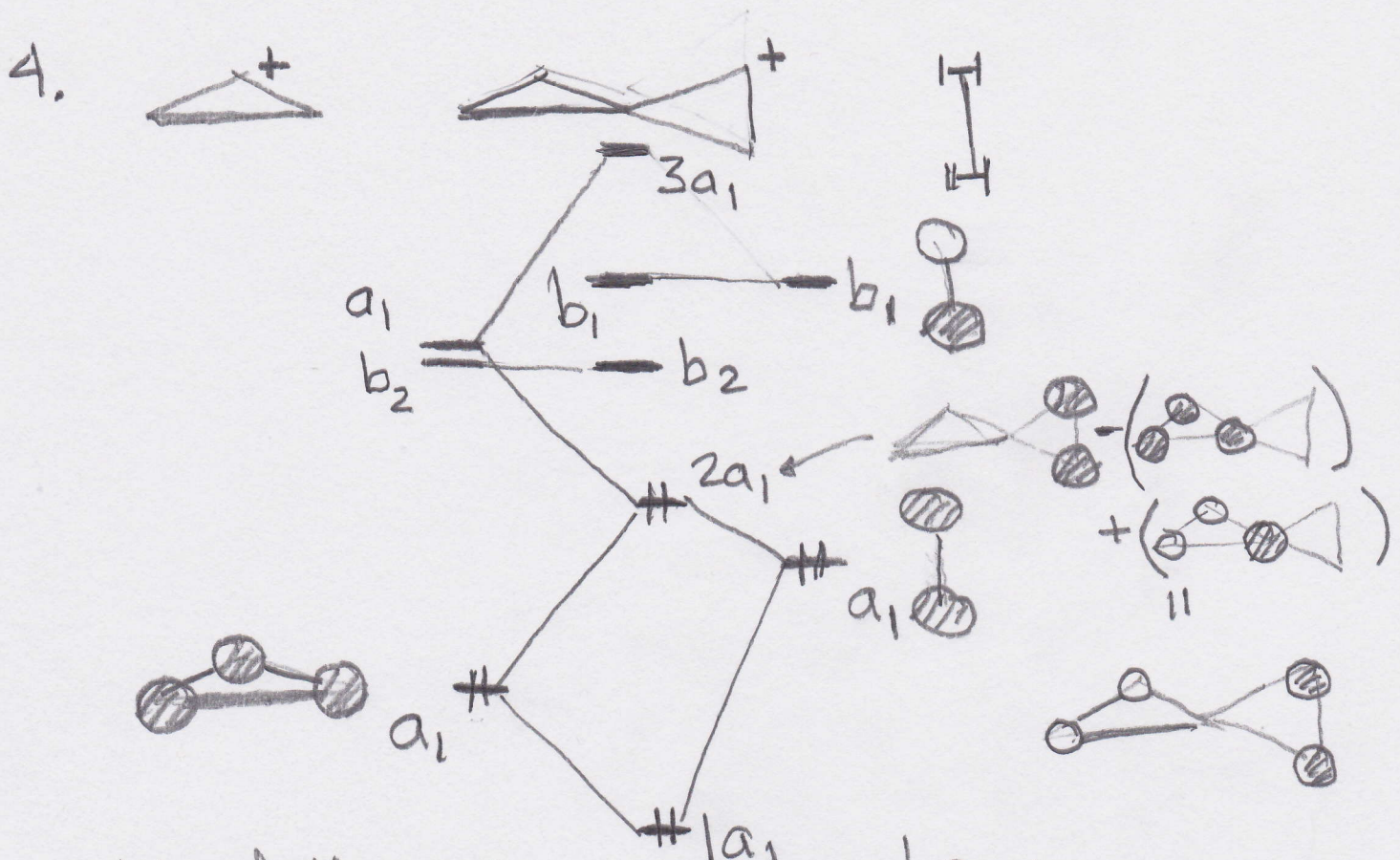$\psi_3 =$

$\psi_4 =$

$\psi_5 =$
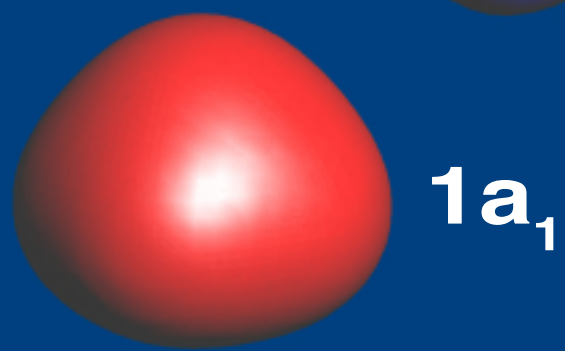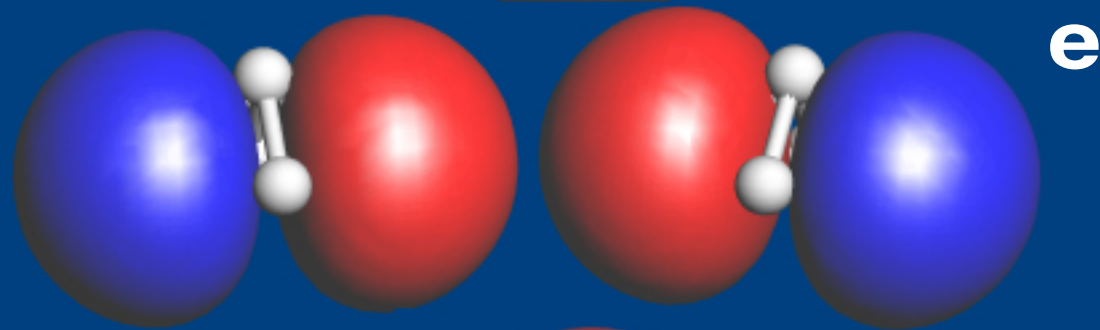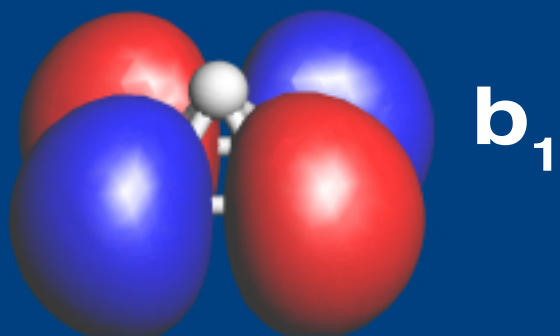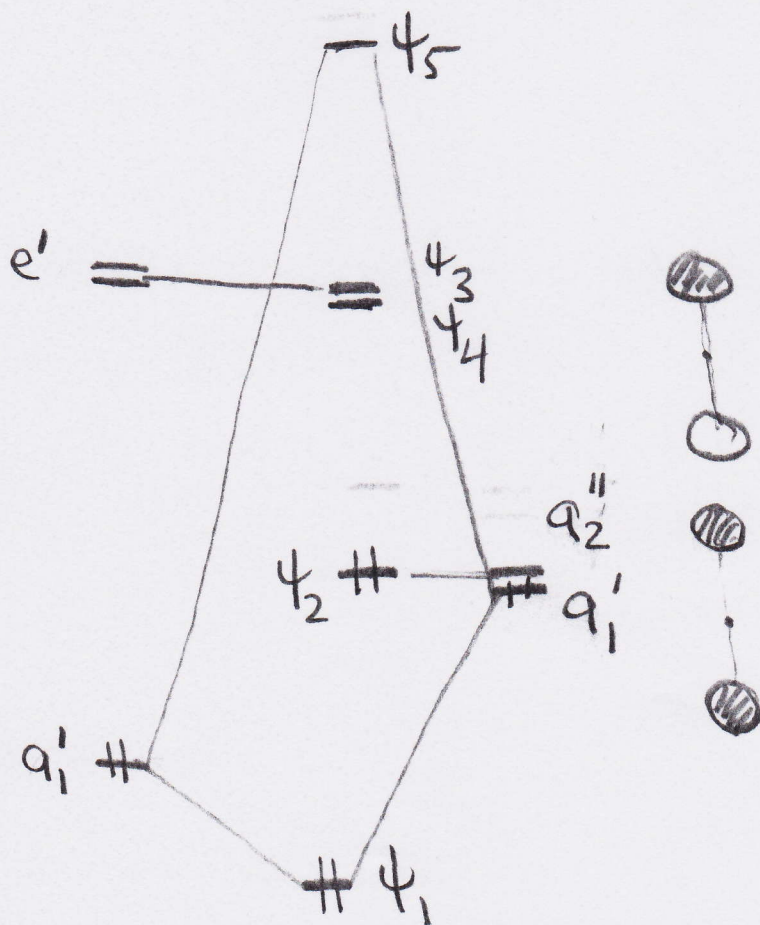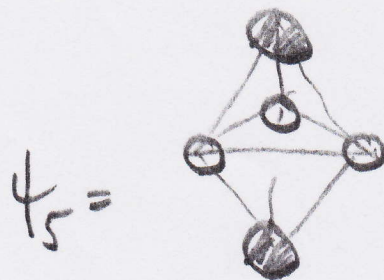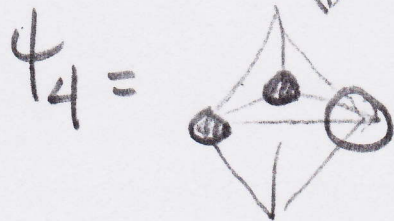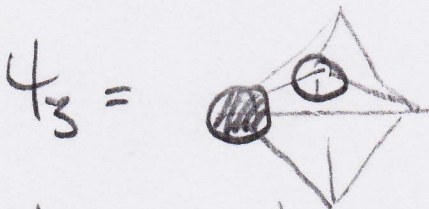
Either with 2 electrons, $H_5^{3+}$, or four electrons, $H_5^+$, are expected to be stable. MO's are plotted on the next page
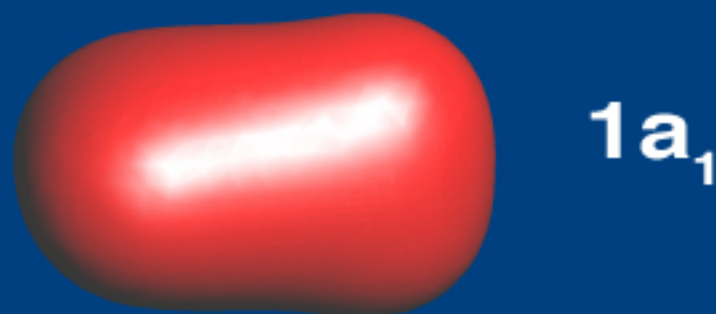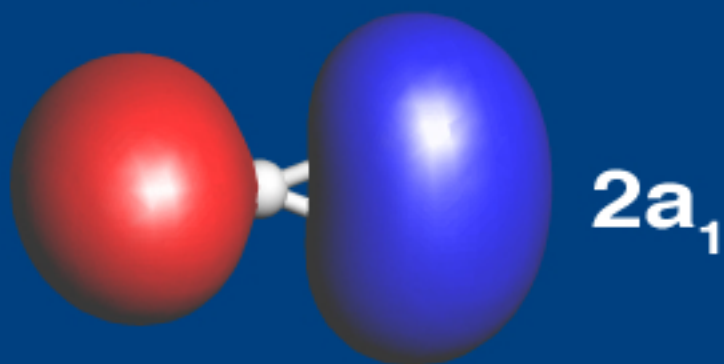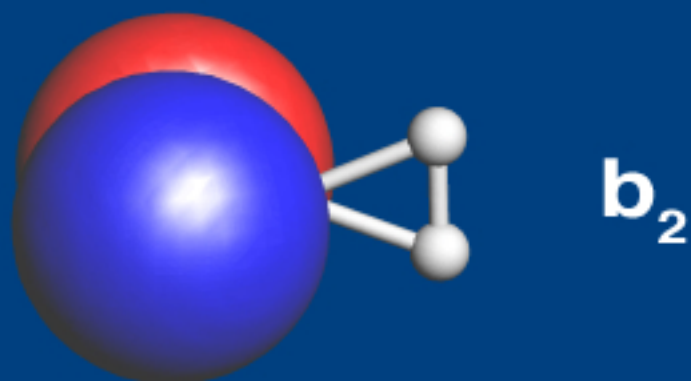
3. A rough way to guess at the relative stability
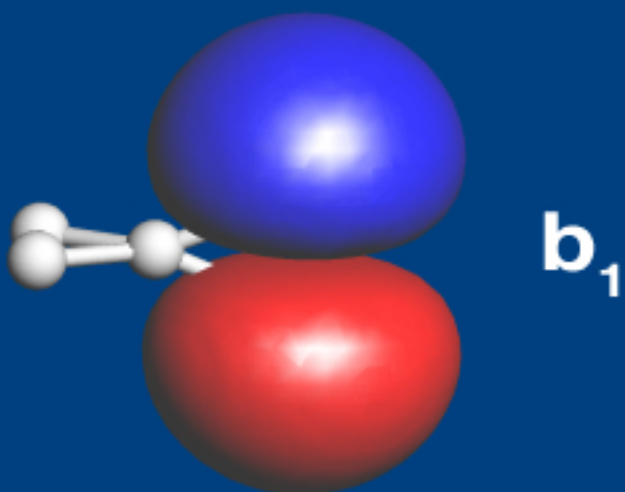
$\psi_5$

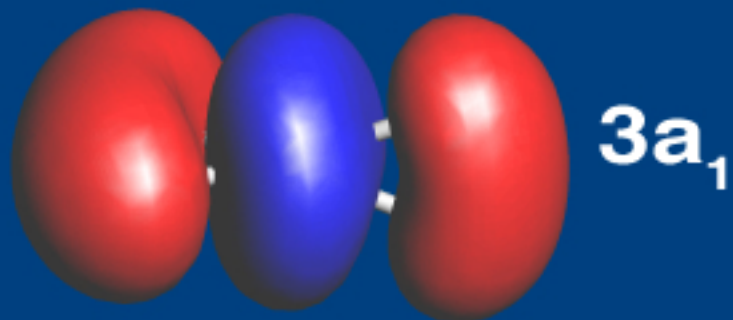$\psi_3$

$\psi_4$

$\psi_2$

$\psi_1$
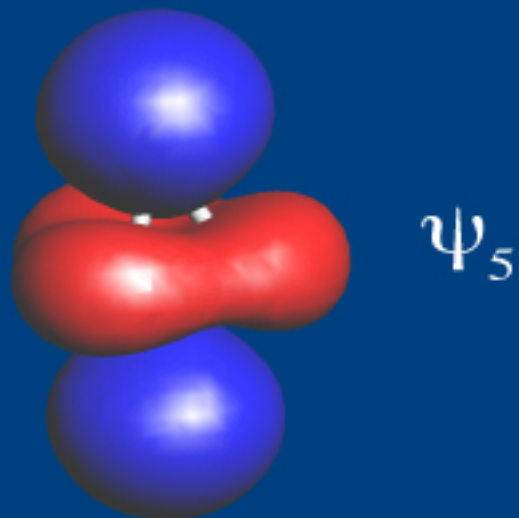
is to examine the nearest neighbor interactions
in the HOMO for each structure: are they bonding,
b, or antibonding, a. Furthermore, the HOMO
should be "closed shell", i.e. if there is a
degenerate pair of MO's, then there should be
four electrons in it. So for



|  | $C_{4v}$ | $D_{3h}$ | $D_{5h}$ |  |
|---|---|---|---|---|
| $H_5^{3+}$: | 8b; 0a | 9b; 0a | 5b; 0a | $\therefore D_{3h}$ |
| $H_5^{+}$: | ½ filled e | 0b; 0a | ½ filled e | $\therefore D_{3h}$ |
| $H_5^{-}$: | 0b; 0a | ½ filled e | 2b; 1a | $\therefore D_{5h}$ |

4.



Plots of these MOs are on the next page

$3a_1$

$b_1$

$b_2$

$2a_1$

$1a_1$

5.



$$\psi_1 = \phi_1 + (\phi_1') = \quad + \quad \Rightarrow \quad a_{1g} - 0 \text{ nodes}$$

$$\psi_2 = \phi_2$$
$$\psi_3 = \phi_3$$
$$\psi_4 = \phi_2'$$
$$\left. \right\} t_{1u} - 1 \text{ node}$$

$$\psi_5 = \phi_5 =$$
$$\psi_6 = \phi_1' - (\phi_1) = \quad - \quad = \quad \left. \right\} e_g - 2 \text{ nodes}$$

$\psi_8 - \psi_{10}\ (2t_{1u})$

$\psi_7\ (2a_{1g})$

$e_g$

$\psi_5$
$\psi_6$
$(e_g)$

$t_{1u}$

$\psi_2 - \psi_3$

$t_{1u}$

$a_{1g}$

$(1t_{1u})$

$a_{1g}'$

$\psi_1\ (1a_{1g})$

$\psi_1 =$    $\psi_2 =$    $\psi_3 =$    $\psi_4 =$

$\psi_5 =$    $\psi_6 =$

$\psi_7 =$    $\psi_8 =$    $\psi_9 =$    $\psi_{10} =$

Orbitals $\psi_1 - \psi_4$ are bonding, therefore a compound with $8 e^-$ will be stable. Also $\psi_5$ & $\psi_6$ are <u>nonbonding</u>, so molecules with $8 + 4 = 12$ electrons will also be stable.

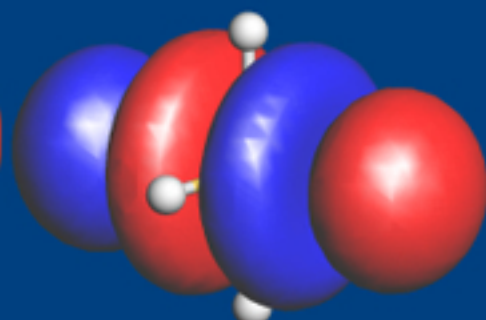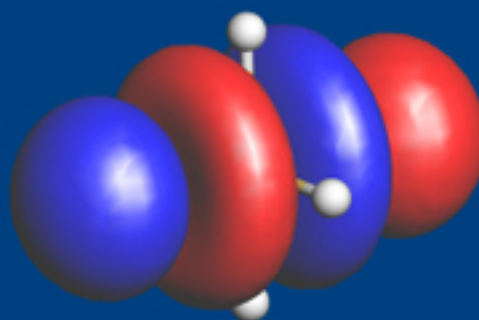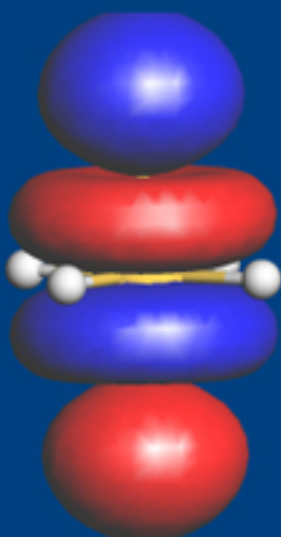The MO's of $SH_6$ from an extended Hückel calculation are plotted on the next page.

$2a_{1g}$

$2t_{1u}$

$e_g$

$1t_{1u}$

$1a_{1g}$

6.



$\psi_1 = $ 

$\psi_2 = $ 

$\psi_3 = $ 

$\psi_4 = $ 

$\psi_5 = $ 
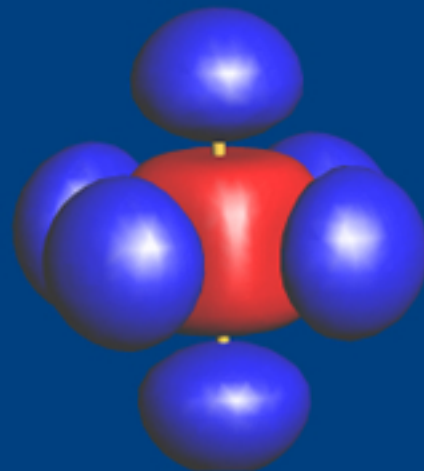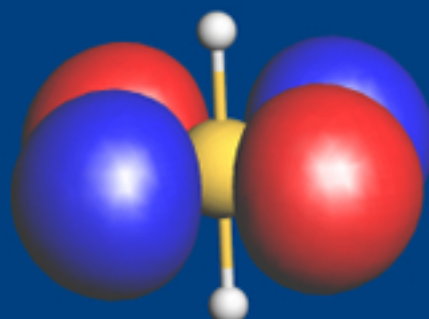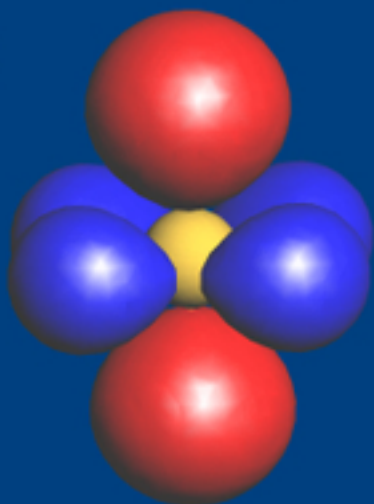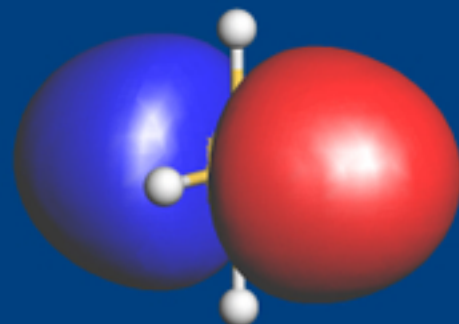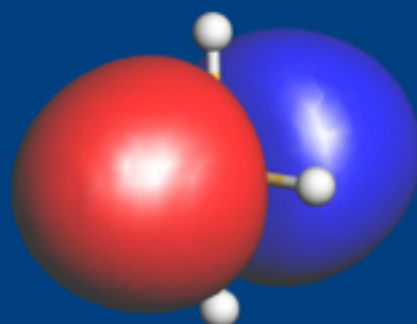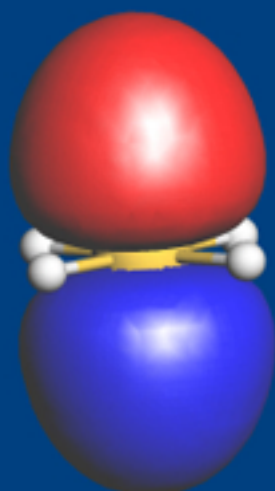
$\psi_6 = $ 
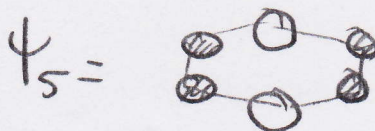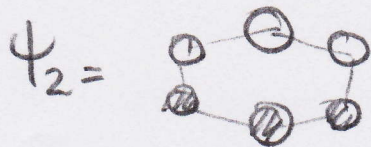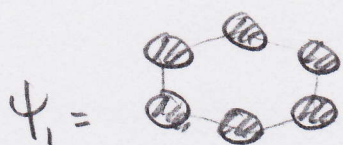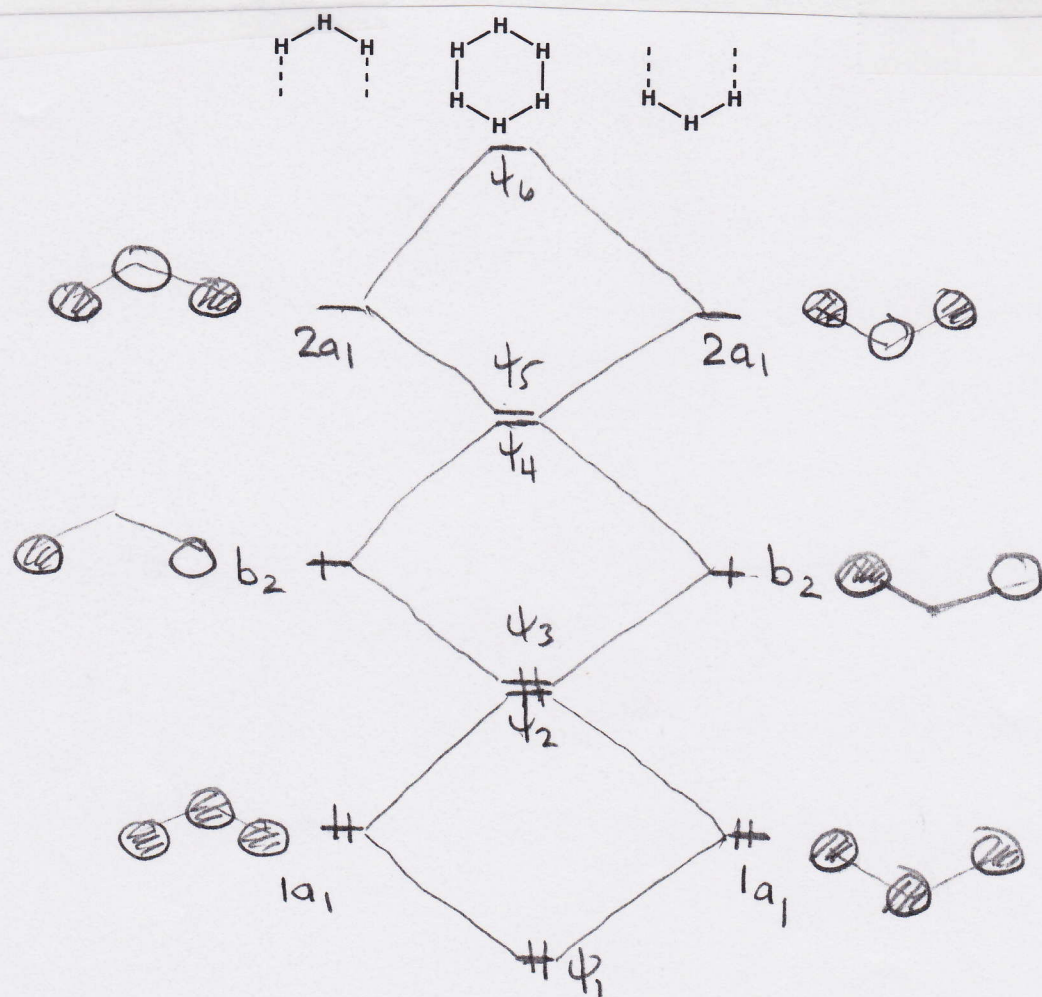
What is shown here are three degenerate interactions. In fact there are further non-degenerate mixings which give the resulting MOs $D_{6h}$ symmetry. The MO's for $D_{6h}$ $H_6$ are plotted on the next page

$\psi_6$

$\psi_4$

$\psi_5$

$\psi_3$

$\psi_2$

$\psi_1$

7.



more stable !!

$b_{1u}$ —

$a_2'$
$2e'$

$e_{2g}$ =

an avoided crossing
occurs between $1e'$ & $2e'$ !!

$e_{1u}$ ⌗

$1e'$
$a_1'$

$a_{1g}$ ⌗
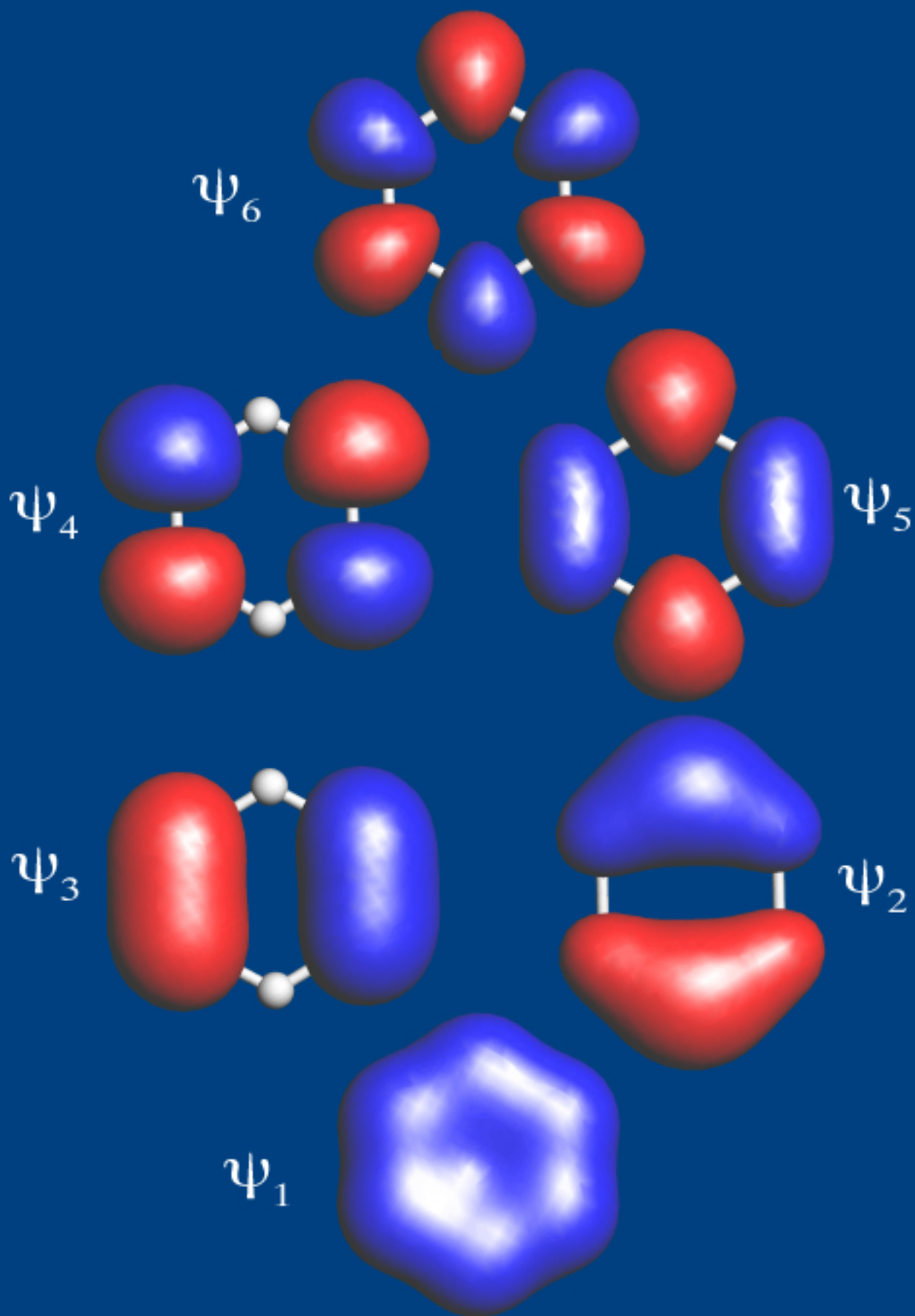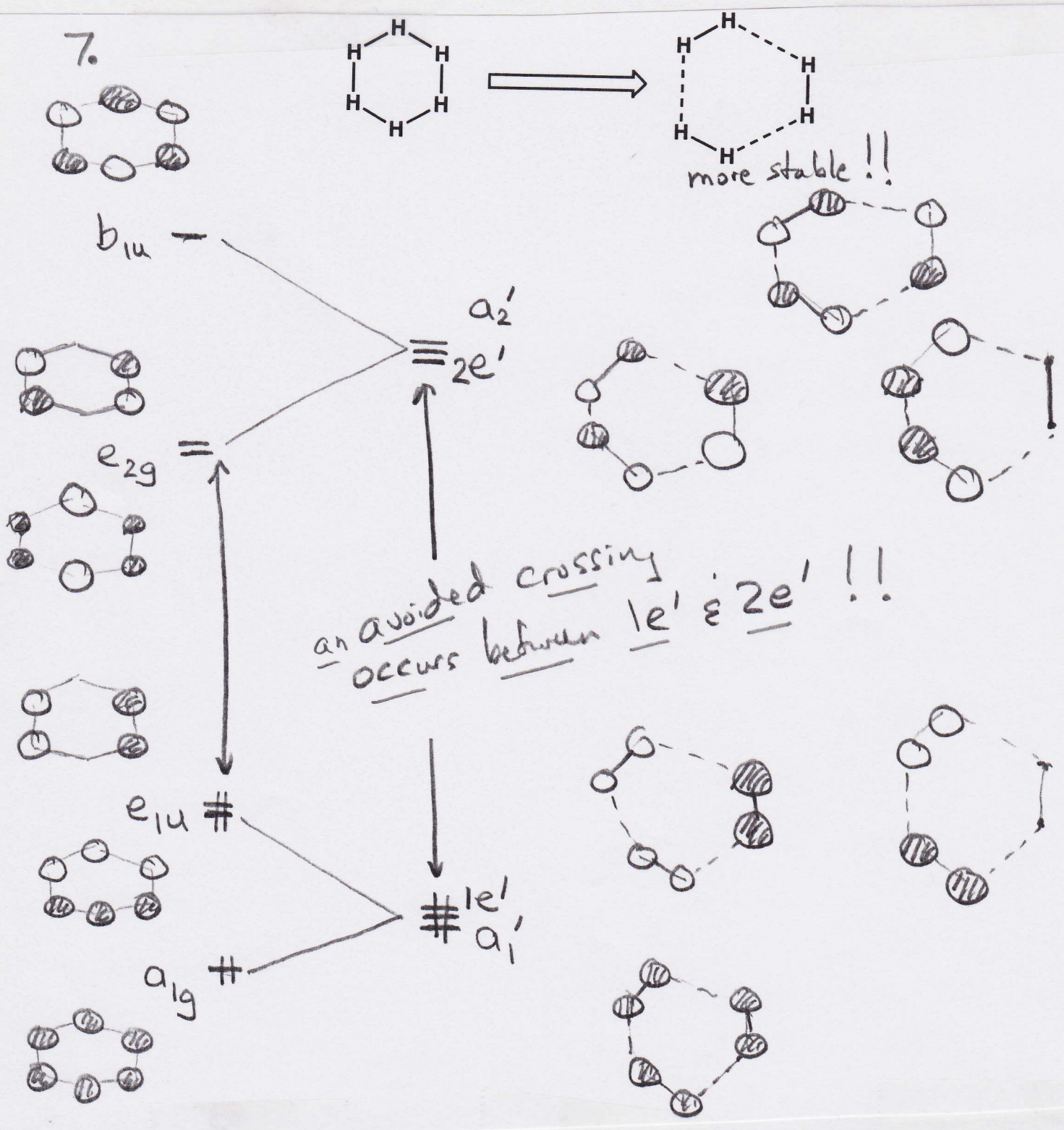
A cylinder of hydrogen gas does not contain rings of hydrogen atoms! The orbital structure of $D_{6h}$ $H_6$ seems perfectly reasonable although it is 67 Kcal/mol higher in energy than $3H_2$. The orbitals of $D_{6h}H_6$ have the same shape and orbital occupation as the $\pi$ orbitals of benzene. see Fig. 12.6. What does this say about the $\pi$-aromaticity in benzene. We return to this topic in Chapter 12.3

**8.** (a) There are a number of ways to determine the $H_{12}$ fragment. Perhaps the easiest is to take 6 $H_2$ $\sigma$ and 6 $H_2$ $\sigma^*$ type orbitals and split them according to the $D_{6h}$ symmetry in $H_{12}$ (see, in particular the relative energies in $H_6$ on p. 70-1)



$H_2\sigma^*$ ——— $b_{2g}$

$e_{2u}$

$e_{1g}$

$a_{2u}$

$b_{1u}$

$H\cdot$ ——— $e_{2g}$

$e_{1u}$

$H_2\sigma$ ——— $a_{1g}$
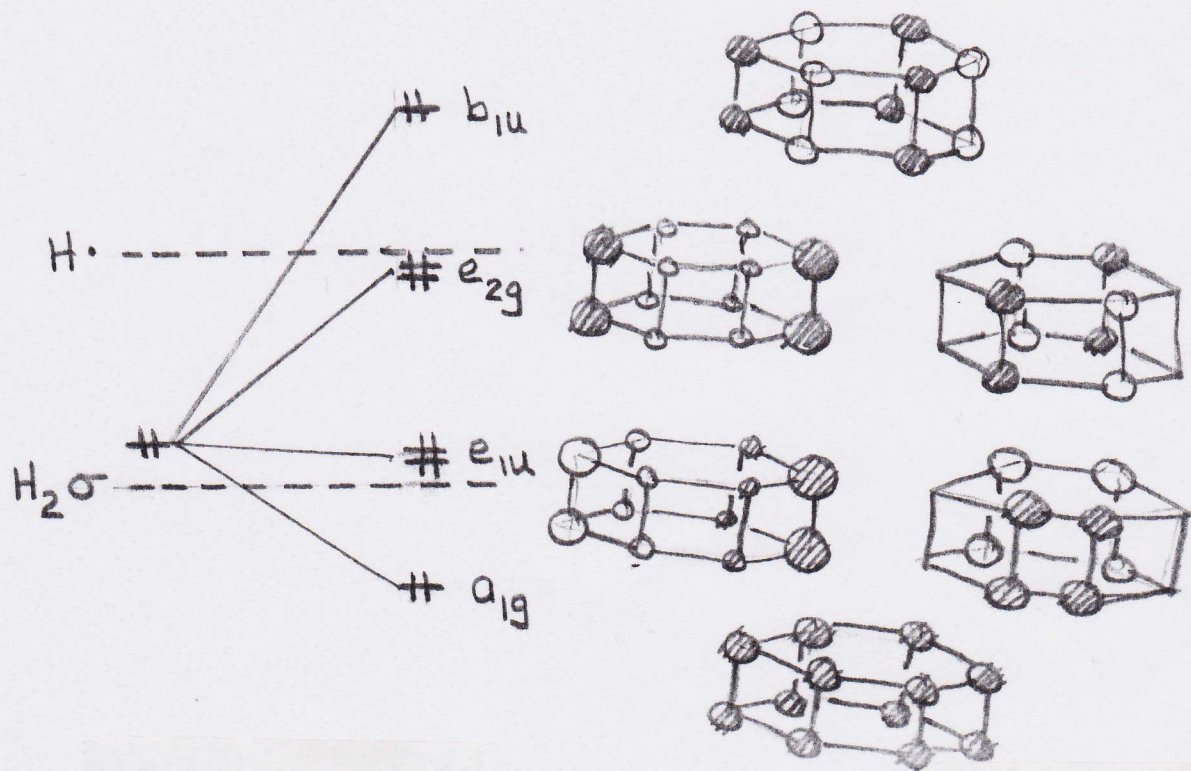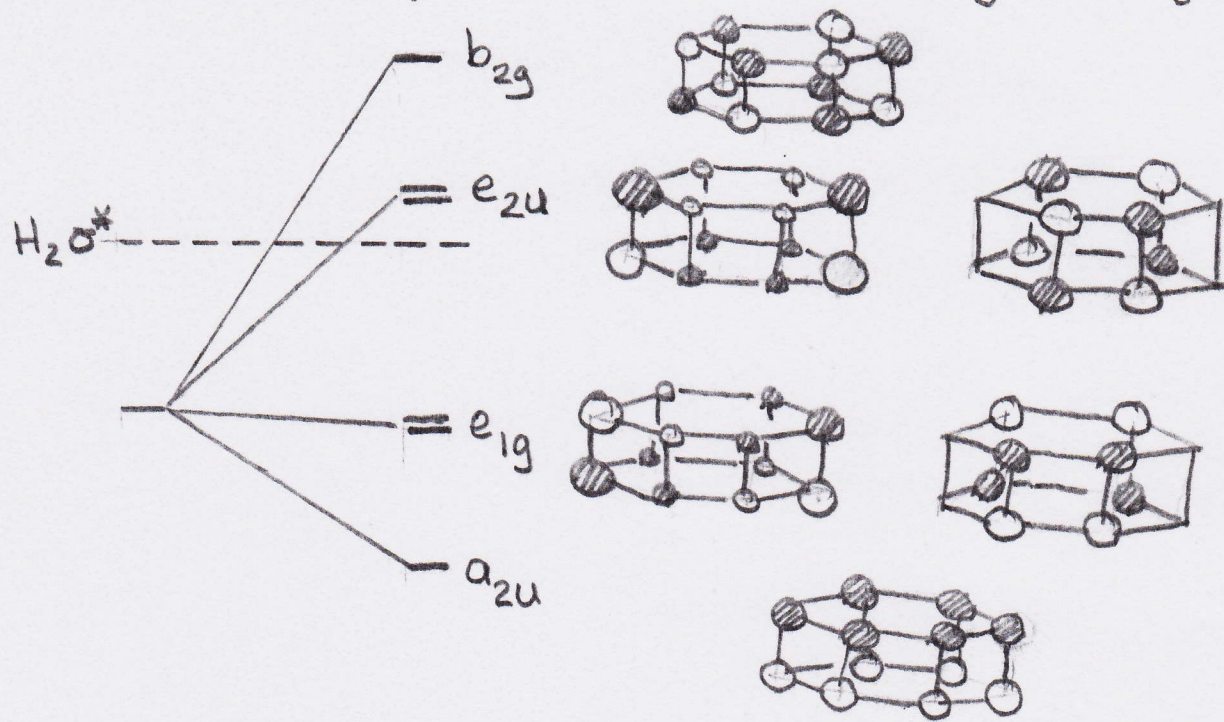
Notice that the irreducible representations in the $\sigma$ and $\sigma^*$ sets are all different. Therefore, there is no intermixing between them. The placement of the levels simply follows the H-H distances. The spread of the $a_{1g}$ to $b_{1u}$ orbitals will be smaller than that for $a_{2u}$ to $b_{2g}$ since the orbital coefficients in the $\sigma^*$ set are larger and hence lead to a larger overlap.

This same result, of course could have been obtained by a "brute force" approach with group theory using the s orbitals of $H_1$ to $H_{12}$ as a basis. A good way of approaching the problem would be to use the following fragmentation of orbitals :
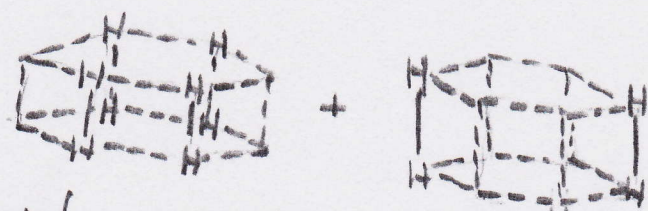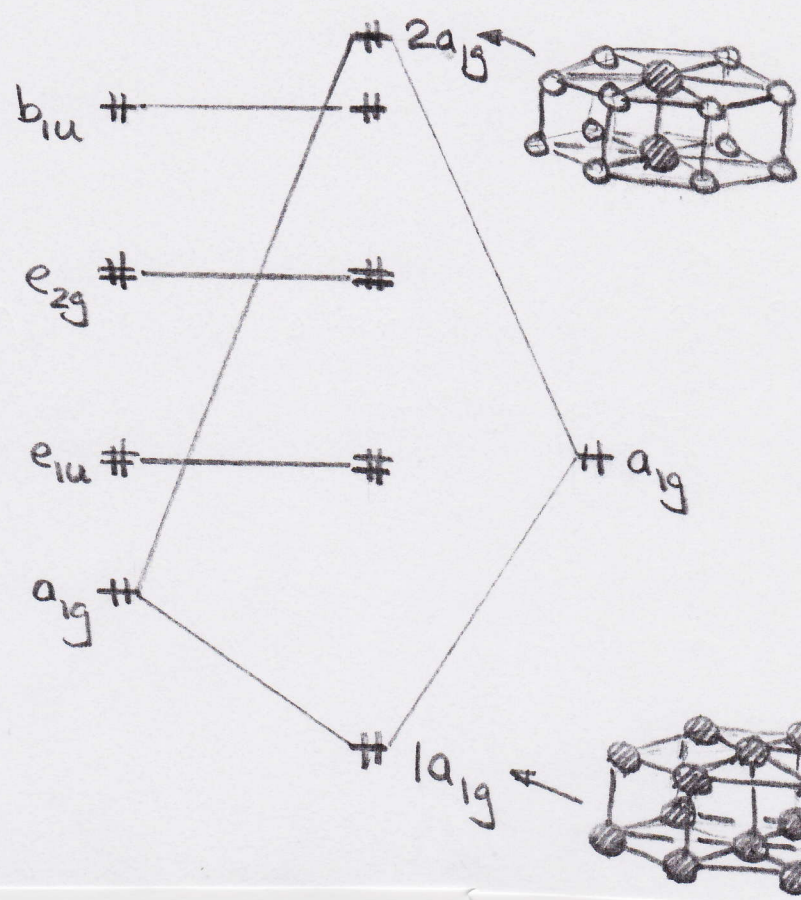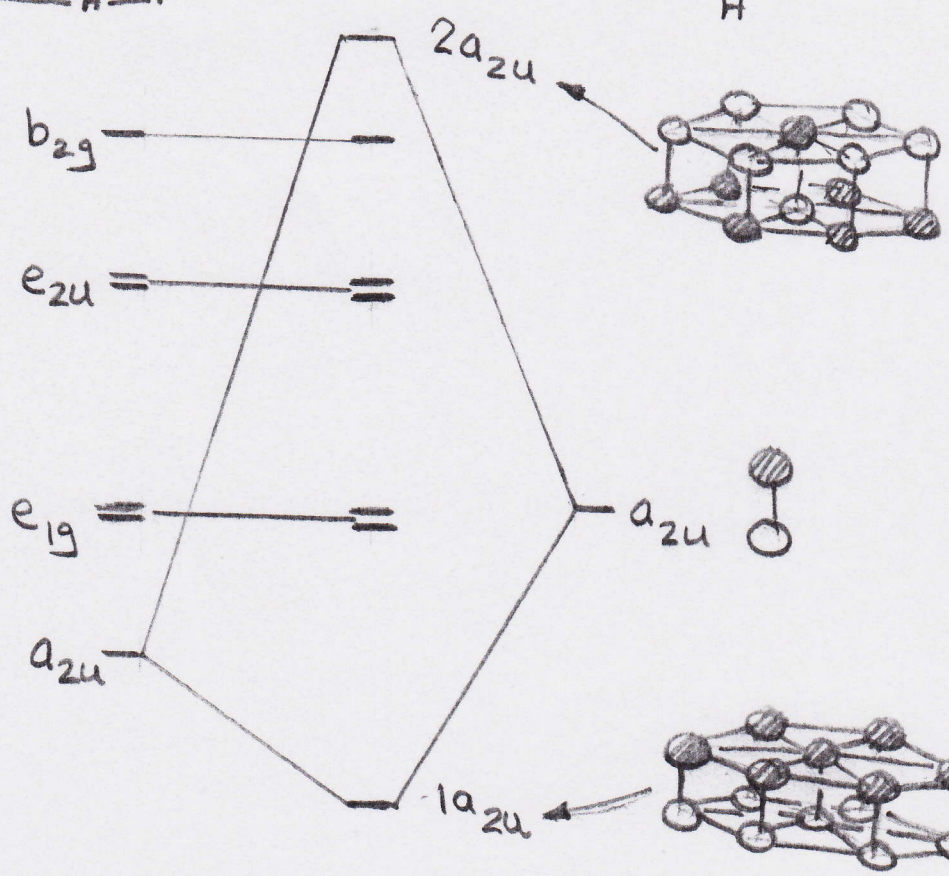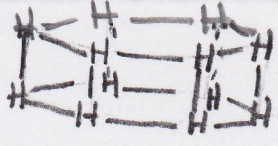


which is analogous to that given for $H_6$ in the book. Perhaps the <u>most</u> difficult is to interact one $H_6$ unit with another.

(b)

All of the other orbitals are exactly as drawn on the previous page

H—H

$2a_{2u}$

$b_{2g}$

$e_{2u}$

$e_{1g}$

$a_{2u}$

$a_{2u}$

$1a_{2u}$

$2a_{1g}$

$b_{1u}$

$e_{2g}$

$e_{1u}$

$a_{1g}$

$a_{1g}$

$1a_{1g}$

*The MO's for $b_{1u}$, $2a_{1g}$ and $1a_{2u}$ are plotted on the next page
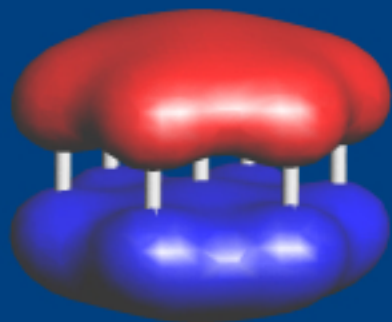
$1a_{2u}$ (LUMO)

$2a_{1g}$ (HOMO)

$b_{1u}$

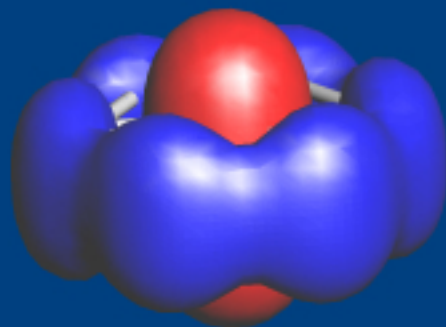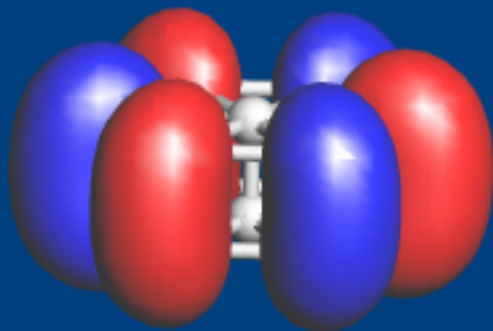Notice that $2a_{1g}$ and $2a_{2u}$ rise to very high energy. This is because in the $H_{12}$ unit each $H_2$ segment overlaps with only the two adjacent $H_2$ units on either side to any appreciable extent. The $H_2$ unit in the middle, however, overlaps with all $\underline{six}$ $H_2$ units around it.

(c) As additional $H_2$ units are added the $2a_{1g}$ orbital gets more and more destabilized – it will become maximally antibonding within each hexagonal layer and bonding between the two layers. Meanwhile $1a_{2u}$ becomes totally bonding within each layer and antibonding between them. So a large number of levels result with the pattern:
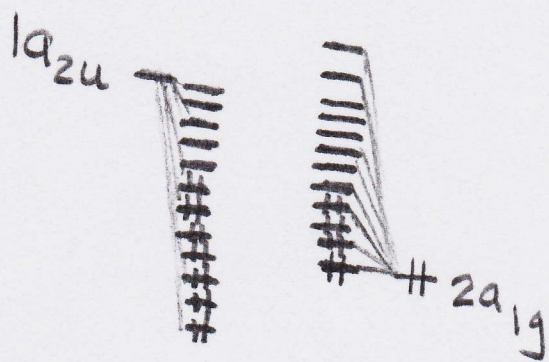


orbitals derived from $1a_{2u}$ become filled and some from $2a_{1g}$ become emptied.