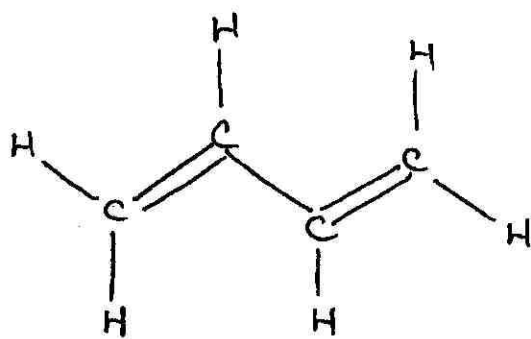


- ① We have a problem. We know MO's are eigenvectors. But we do not know a general procedure for finding eigenvectors. There are math courses which teach you how to solve this problem but the mathematical method is too involved.
- ② For this course we will use an iterative method of finding approximately correct M.O.'s. They will be good enough ^{M.O.s} for us to get answers about chemical questions.
- ③ We illustrate this method with a "simple" MO diagram for the π orbitals of butadiene



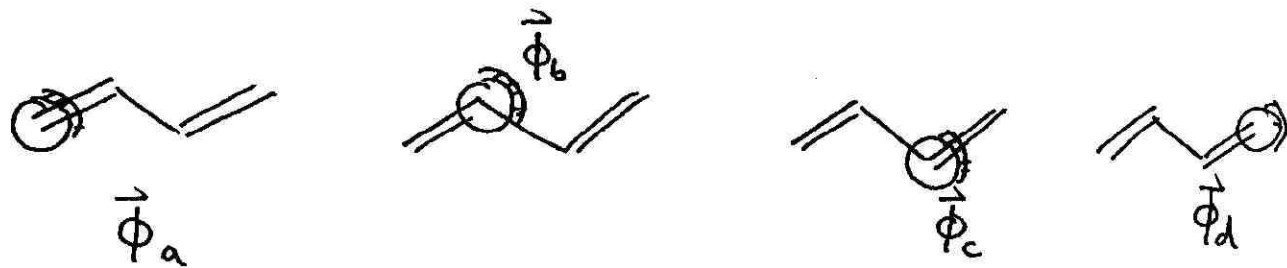
butadiene



abbreviated symbol.

④ The π orbitals of butadiene are

24.2



$$\vec{\phi}_a = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\vec{\phi}_b = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$

$$\vec{\phi}_c = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

$$\vec{\phi}_d = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

In Problem Set #7 we found the eigenvectors

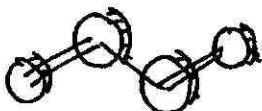
are

$$\begin{pmatrix} 1 \\ \frac{1+\sqrt{5}}{2} \\ \frac{1+\sqrt{5}}{2} \\ 1 \end{pmatrix}$$

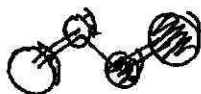
$$\begin{pmatrix} \frac{1+\sqrt{5}}{2} \\ 1 \\ -1 \\ -\frac{1+\sqrt{5}}{2} \end{pmatrix}$$

$$\begin{pmatrix} \frac{1+\sqrt{5}}{2} \\ -1 \\ -1 \\ \frac{1+\sqrt{5}}{2} \end{pmatrix}$$

$$\begin{pmatrix} +1 \\ -\frac{1+\sqrt{5}}{2} \\ +\frac{1+\sqrt{5}}{2} \\ -1 \end{pmatrix}$$



E_1



E_2



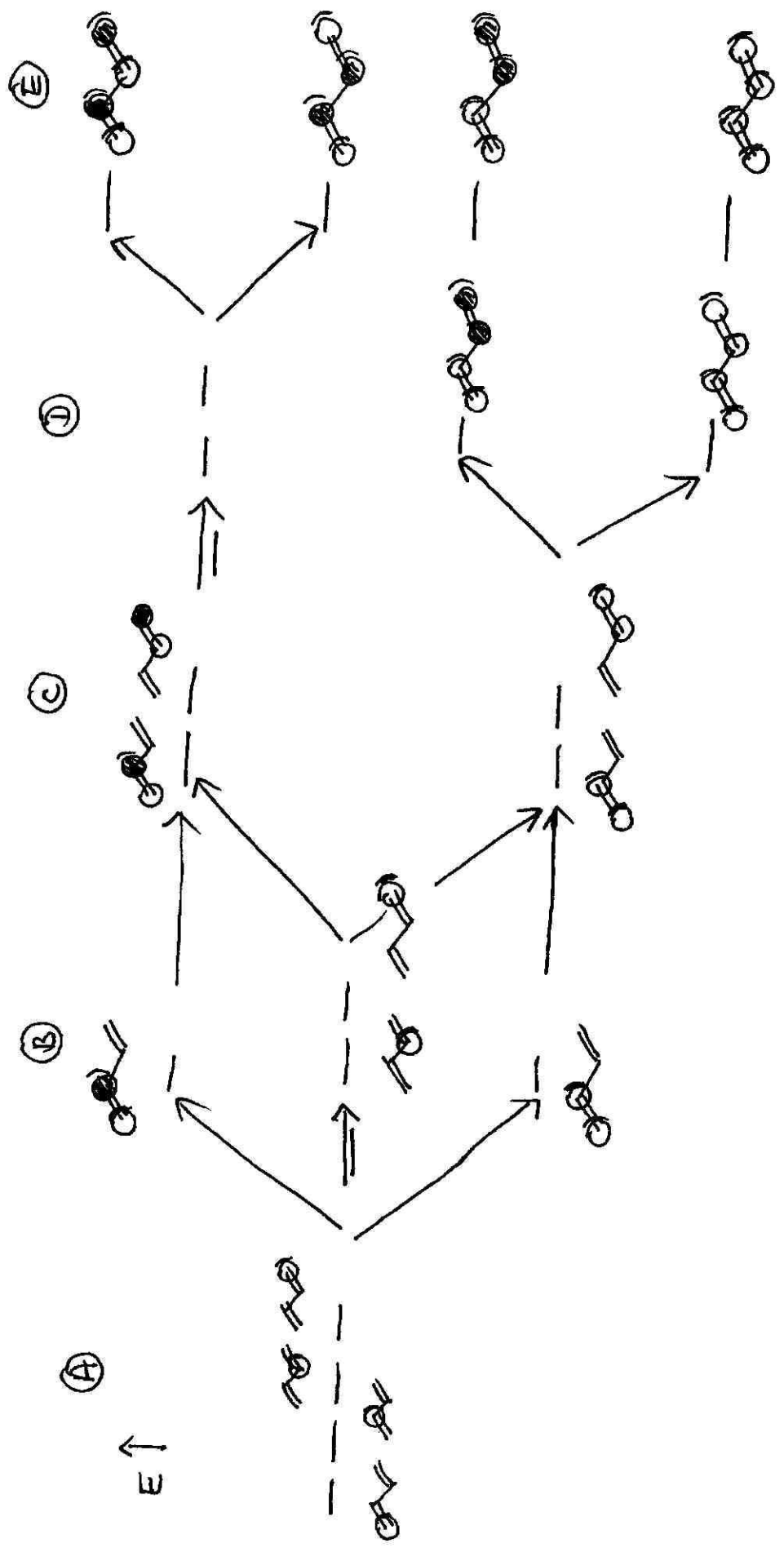
E_3



E_4

⑤ Now let's find an iterative procedure which will lead to the approximately correct answer. In this approach we ALWAYS CONSIDER JUST ONE PAIR OF ORBITALS AT A TIME.

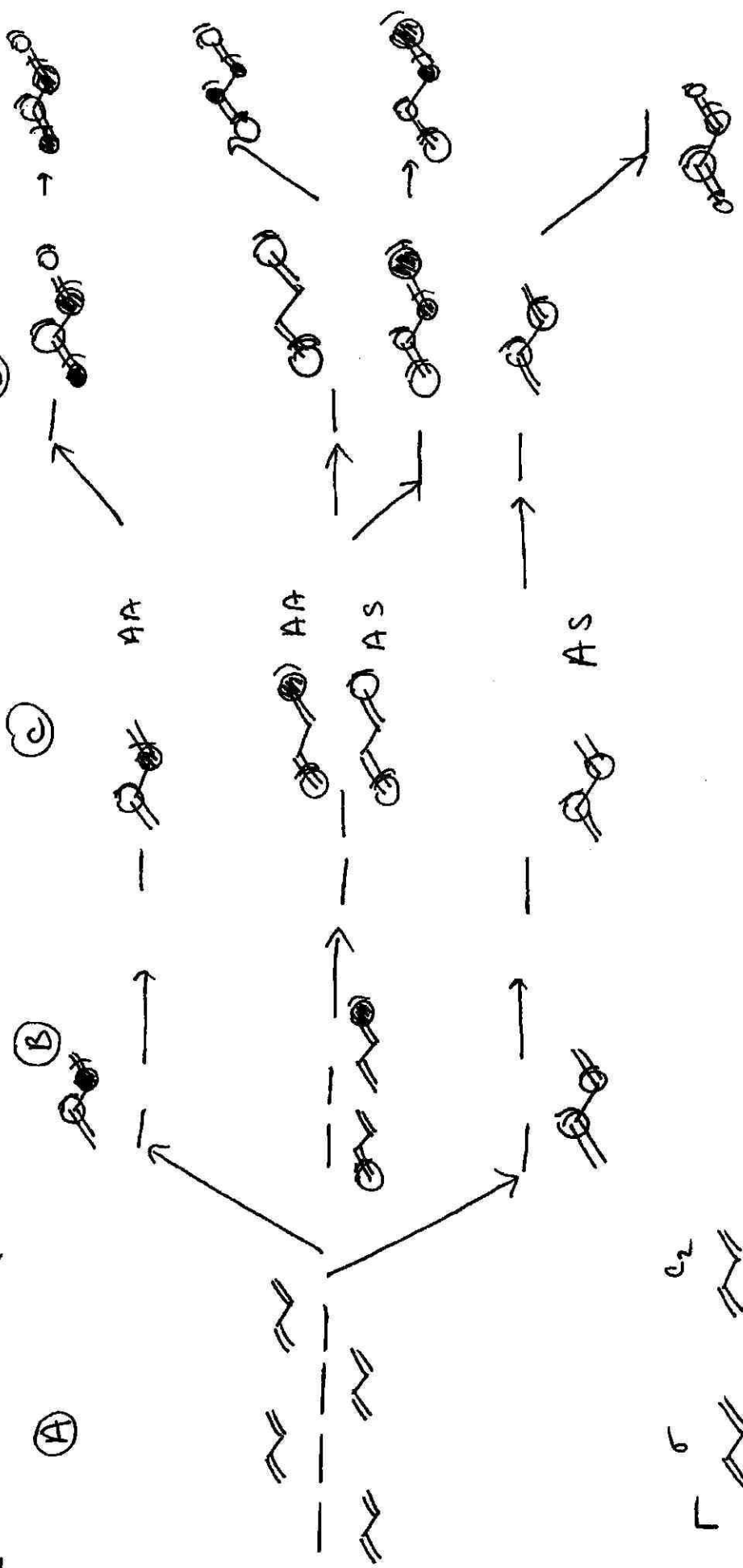
Starting Point



We see that (E) is very close to the final answer.
 How do we know when to stop? We stop when we can not find any more combinations which raise or lower the other energy. (Some thought will show (E) is the not quite the best set of M.O.'s)

24/7

Let's now use ideas of S & A to find MO's. (1)

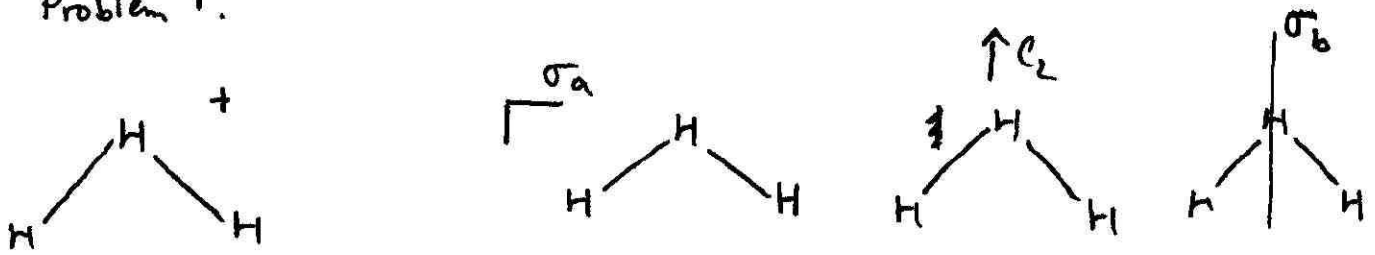


Note using S & A in 5 steps we get even a better answer than without S & A.

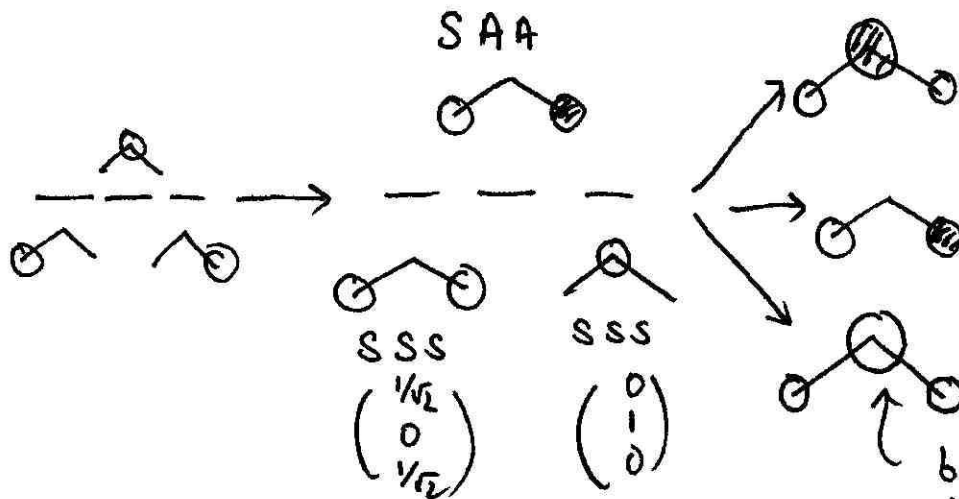
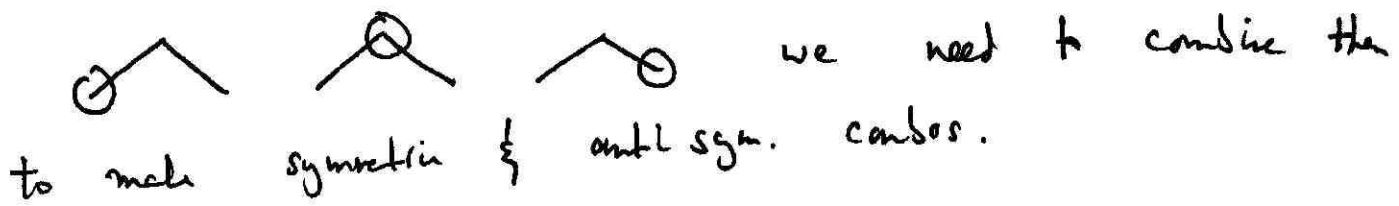
Addition to lecture 24 (N24)

N24.1

As an added example let's consider the two cases from Problem 1.



Taking the 3 orbitals:

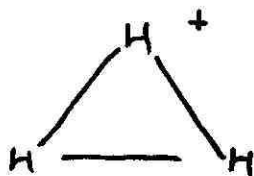


bigger a 1 is bigger than the $\frac{1}{\sqrt{2}}$ the system:

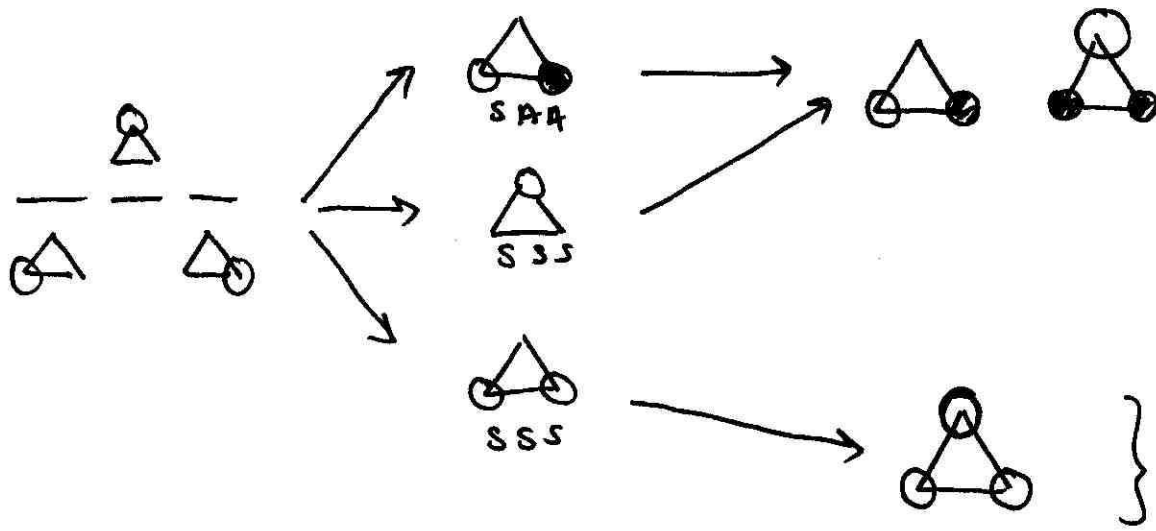
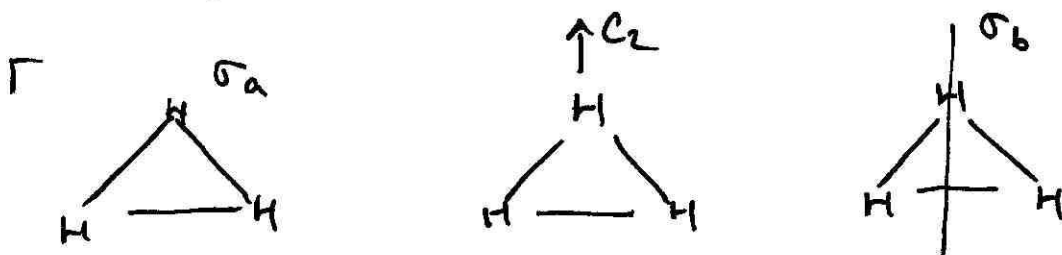
This corresponds to the 3 eigenvectors of the system:

$$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix} \text{ and } \begin{pmatrix} \frac{1}{2} \\ -\frac{\sqrt{2}}{2} \\ \frac{1}{2} \end{pmatrix}$$

We now consider



This molecule has lots of mirror planes & C_2 but we need only consider a \perp set.



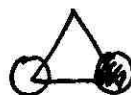
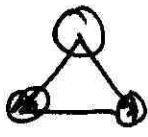
} two factors about size cancel:
 1. is lower in energy initially
 2. is a bigger lobe

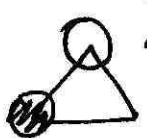

Question: What are the relative energies



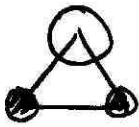
Note if $\vec{\psi}_1$ and $\vec{\psi}_2$ are eigenvectors
 w/ ^{the same} eigenvalue E , so $\vec{\psi}_1 + \vec{\psi}_2$ an eigenvector
 w/ eigenvalue E .

Pf. $H(\vec{\psi}_1 + \vec{\psi}_2) = E(\vec{\psi}_1 + \vec{\psi}_2)$

Apply this to  vs.  problem.

Note  $\vec{\psi}_1$ &  $\vec{\psi}_2$ have the same eigenvalue

status \Rightarrow .

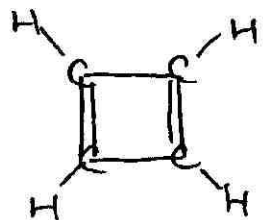
Now add $\vec{\psi}_1 + \vec{\psi}_2 =$ .

Conclusion  and  have the same

energy.

Problem Set #8

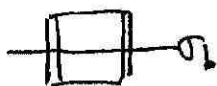
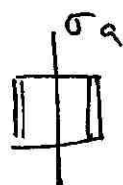
1. (i) Consider the molecule square cyclobutadiene



abbreviated

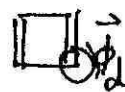
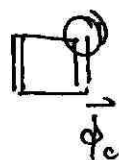
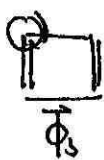
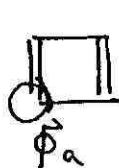


Consider the 3 mutually \perp σ 's



Use the ideas of S & A combination and pairwise orbital mixing to derive the π MO's of square cyclobutadiene.

(ii) Write the H. Assume:

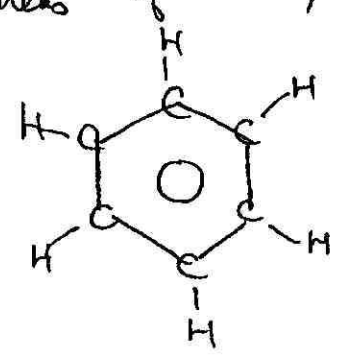


$$\vec{\phi}_a^+ H \vec{\phi}_b = \vec{\phi}_b^+ H \vec{\phi}_c = \vec{\phi}_c^+ H \vec{\phi}_d = \vec{\phi}_d^+ H \vec{\phi}_a = \beta$$

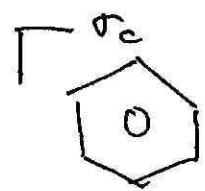
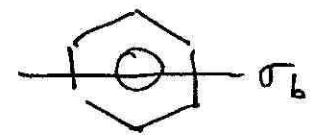
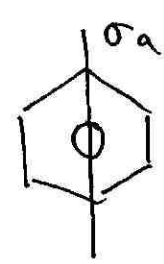
$$\vec{\phi}_a^+ H \vec{\phi}_c = \vec{\phi}_b^+ H \vec{\phi}_d = 0$$

(iii) Show the MO's derived in i are indeed the eigenvectors of (ii). Find the corresponding eigenvalues.

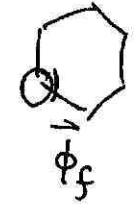
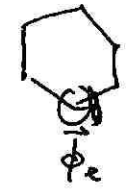
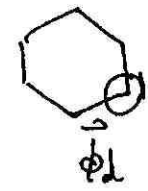
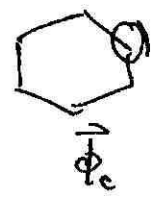
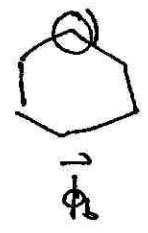
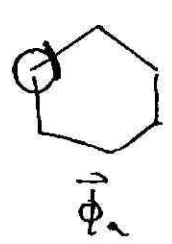
2. Perhaps the most important molecule in organic chemistry is benzene. Draw 6 π MO's of benzene using the ideas of S & A and pairwise orbital mixing.



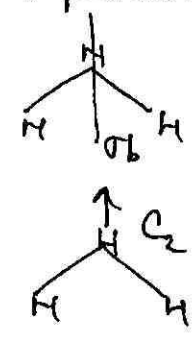
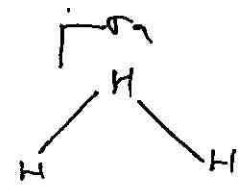
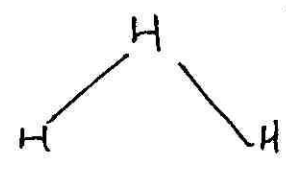
benzene





The six π A.O.'s are



3. Using the ideas of sym. & antisym MO's & pairwise mixing, derive the MO diagram for.



4. Consider the  = $\vec{\psi}_1$ and  = $\vec{\psi}_2$

M.O.'s The first orbital is of SSS type.

The 2nd MO is of SAA type. Draw the

$\vec{\psi}_1 + \vec{\psi}_2 = \vec{\psi}_{\text{new}}$ orbital. Show it is neither

SSS or of SAA type. Explain why this shows

we only need to pair-wise interact orbitals of

the same type if we are to obey our 4th

rule for making MO diagrams.

5. On p. 24.3 we show a first example

of pairwise mixing (for butadiene). Show that

at each step of the process the 4 vectors

are orthogonal. Confirm that the same is true on p. 24.4.

Note pairwise mixing is always done keeping the

vectors orthogonal to one another.