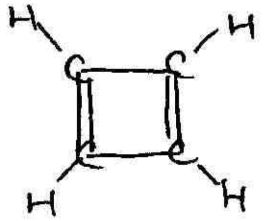
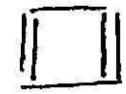
Problem Set #8

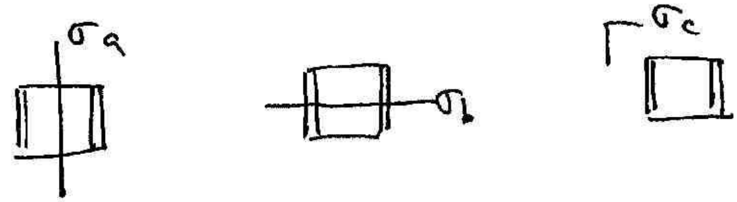
1. (i) Consider the molecule square cyclobutadiene



abbreviated



Consider the 3 mutally ⊥ σ's



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

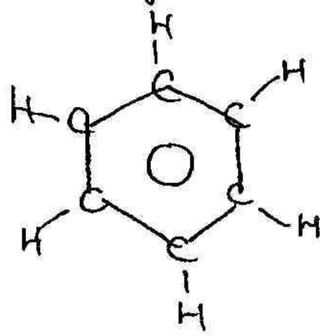
(ii) Write the $\mathbb{H}$. Assume:

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

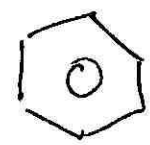
$$\vec{\phi}_a^{\,+} \mathbb{H} \vec{\phi}_c = \vec{\phi}_b^{\,+} H \vec{\phi}_d = 0$$

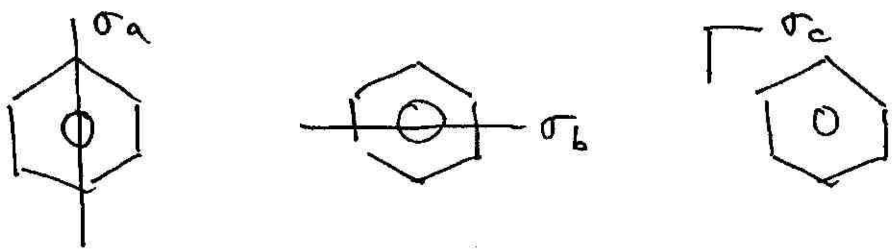
(iii) Show the MO's derived in i are indeed the eigenvectors of (ii). Find the corresponding eigenvalues.

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

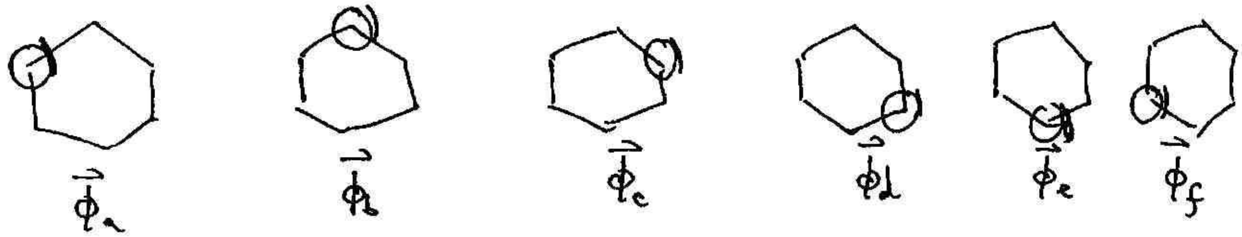


benzene

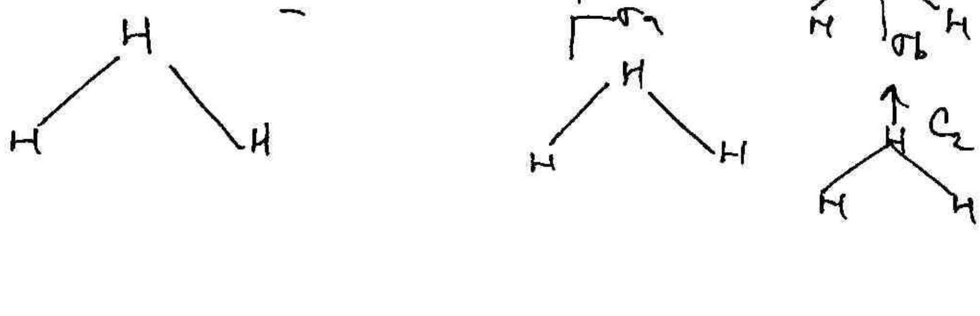
abbreviated 

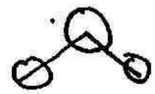


The six π A.O's are



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
$\vec{\psi}_1 + \vec{\psi}_2 = \vec{\psi}_{new}$ 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 pair-wise mixing is always done keeping the
vectors orthogonal to one another.