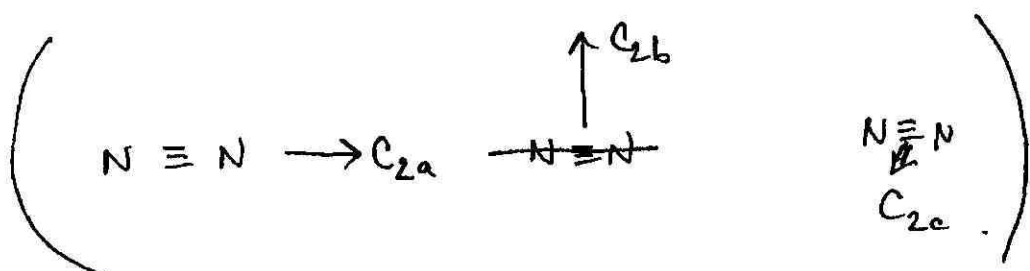
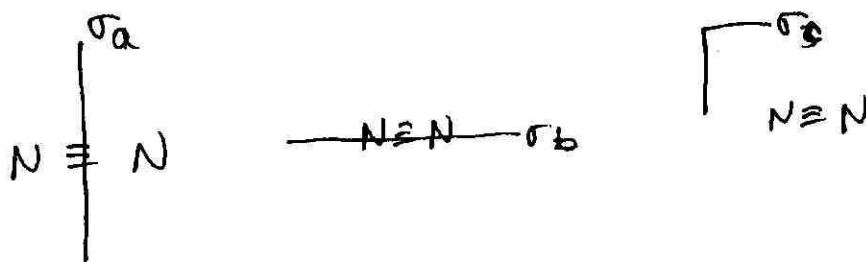


The 4th rule of MO theory

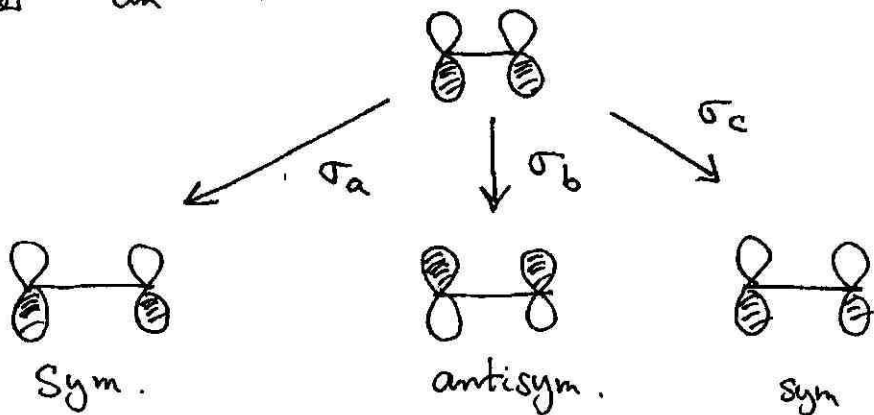
"If there are a set of perpendicular mirror planes and/or C_2 axes, the MO's are symmetric or antisymmetric with respect to these planes and/or C_2 axes."

Example 1

$N \equiv N$ has 3 mutually \perp mirror planes (& 3 mutually \perp C_2 axes).




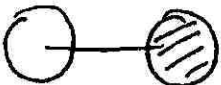

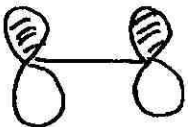

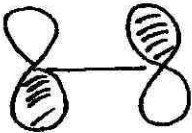
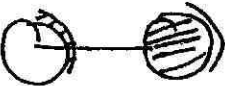

Consider an MO

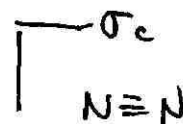
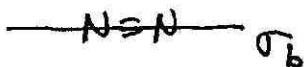


(We could add C_2 's here)

SAS
a b c

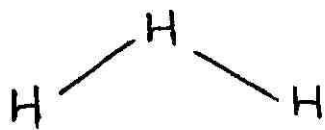
In exactly the same manner we can examine all the M.O.'s

	σ_a	σ_b	σ_c	<u>Combo</u>
	S	S	S	SSS
	A	S	S	ASS
	S	S	S	SSS
	S	A	S	SAS
	S	S	A	SSA
	A	A	S	AAS
	A	S	A	ASA
	A	S	S	ASS

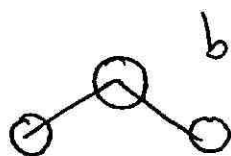


E

Example 2.



We found MO's were non-bonding



bonding



non-bonding
 $\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$



antibonding

Consider σ 's & C_2 's.

 $\Gamma \sigma_a$  σ_b  C_2  σ_a

S

 σ_b

S

 C_2

S

Combo.

SSS



S

A

A

SAA



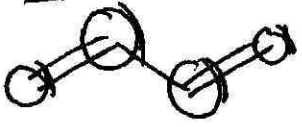
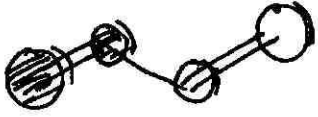

S

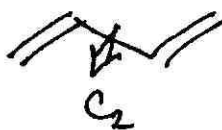
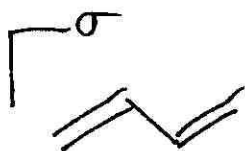
S

S

SSS

Exercise. We found in Problem Set #7 that the π M.O.s of butadiene are

	σ	C_2	conds
			
			
			



are symmetry operations.

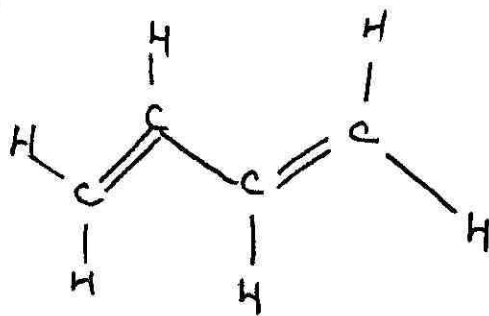
Complete the above table.

Conclusion. In all cases the MOs are either S or A with respect to mutually \perp σ & C_2 .

[Planar molecule A (MOs): called π -orbitals
 w/ respect to plane of molecule
 Planar molecule S (MOs) called σ -orbitals
 w/ respect to plane of molecule]

N23. The 4×4 Hamiltonian for butadiene
(π system only)

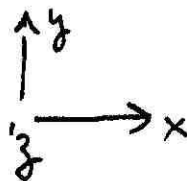
① The molecule butadiene is



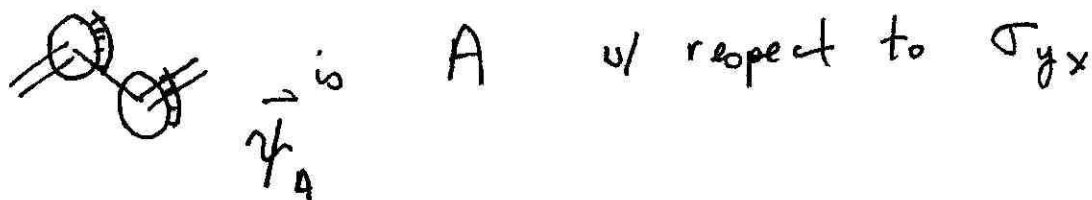
It is $\left\{ \begin{array}{l} \text{(always)} \\ \text{sometimes} \end{array} \right\}$ written



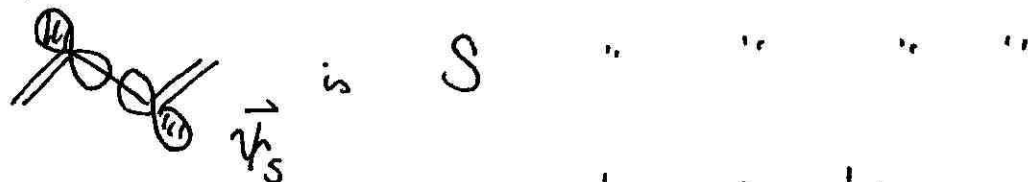
② We generally call the axes



Consider the σ_{yx} plane (σ_{yx} can be called σ_z)



but

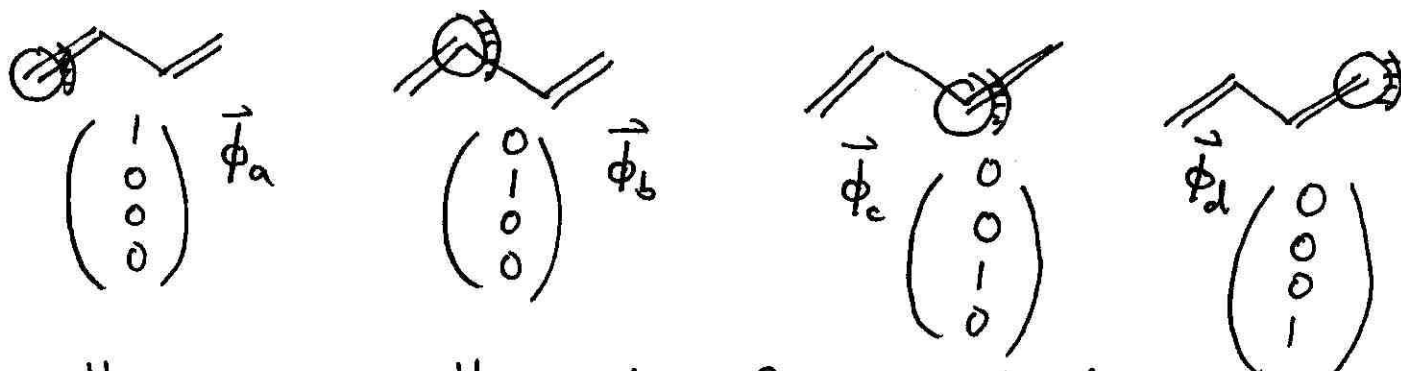


These orbitals can not mix because any combination
of $\vec{\psi}_A$ & $\vec{\psi}_S$ will be neither of A or S type.

③ We call A orbitals π -orbitals.

We call S " σ -orbitals.

④ Note there are four π A.O.s :



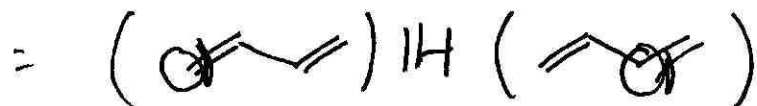
Note these are the only four π A.O.s & therefore all π M.O.s will be mixtures of these four orbitals.

⑤ We wish to find the Hamiltonian of these 4 A.O.s (the π -system)

$\begin{pmatrix} \text{orbital 1} \end{pmatrix}^\dagger$					= H
H_{11}	H_{12}	H_{13}	H_{14}		
$\begin{pmatrix} \text{orbital 2} \end{pmatrix}^\dagger$	H_{21}	H_{22}	H_{23}	H_{24}	
H_{31}	H_{32}	H_{33}	H_{34}		
$\begin{pmatrix} \text{orbital 3} \end{pmatrix}^\dagger$	H_{41}	H_{42}	H_{43}	H_{44}	
$\begin{pmatrix} \text{orbital 4} \end{pmatrix}^\dagger$					

$$\textcircled{6} \quad \vec{\phi}_a^+ H \vec{\phi}_a = \vec{\phi}_b^+ H \vec{\phi}_b = \vec{\phi}_c^+ H \vec{\phi}_c = \vec{\phi}_d^+ H \vec{\phi}_d = \alpha$$

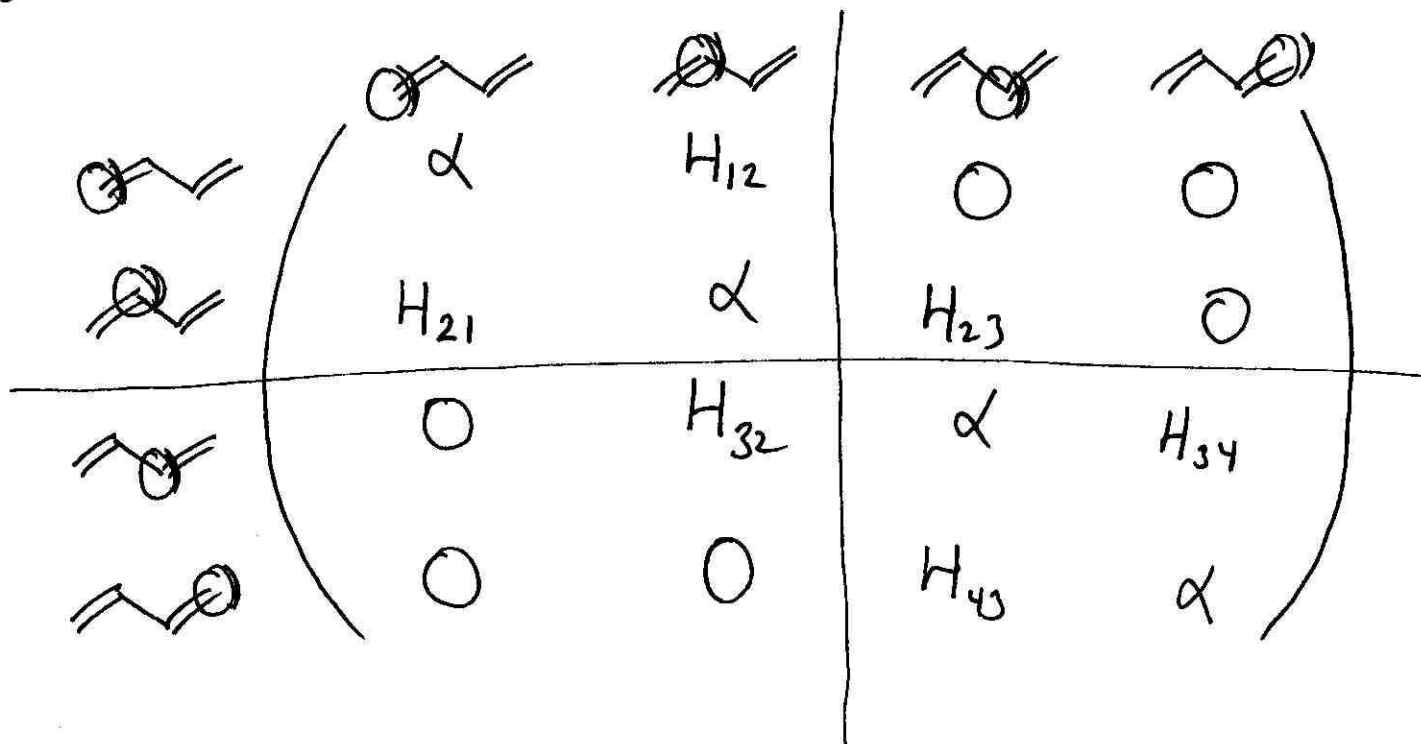
$$\textcircled{7} \quad \text{Now consider } \vec{\phi}_a^+ H \vec{\phi}_c$$



These A.O.'s do not overlap & do not change each other's De Broglie wavelength. $\therefore \vec{\phi}_a$ and $\vec{\phi}_c$ do not interact. $\therefore \vec{\phi}_a^+ H \vec{\phi}_c = 0$

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

$\textcircled{8}$ Using $\textcircled{6}$ & $\textcircled{7}$ H simplifies to:



⑨ Now consider $\vec{\phi}_b^+ H \vec{\phi}_c = (\text{diagonal}) H (\text{diagonal})$
 & compare to $\vec{\phi}_a^+ H \vec{\phi}_b = (\text{diagonal}) H (\text{diagonal})$

⑩ To a good approximation, these two interactions are equal. (Both interactions are for neighboring C atoms). Assume they are equal. Call $\vec{\phi}_b^+ H \vec{\phi}_c = \beta$

⑩ H becomes

	diagonal	diagonal	diagonal	diagonal
diagonal	α	β	0	0
diagonal	β	α	β	0
diagonal	0	β	α	β
diagonal	0	0	β	α

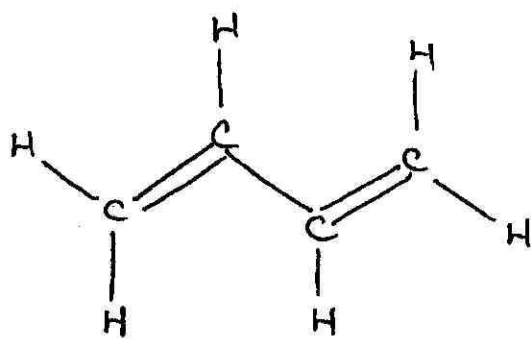
⑪ This H has the following 4 eigenvectors.

$$\begin{pmatrix} 1 \\ \frac{1+\sqrt{5}}{2} \\ \frac{1+\sqrt{5}}{2} \\ 1 \end{pmatrix}, \begin{pmatrix} \frac{1+\sqrt{5}}{2} \\ 1 \\ -1 \\ -\left(\frac{1+\sqrt{5}}{2}\right) \end{pmatrix}, \begin{pmatrix} \frac{1+\sqrt{5}}{2} \\ -1 \\ -1 \\ \left(\frac{1+\sqrt{5}}{2}\right) \end{pmatrix} \& \begin{pmatrix} 1 \\ -\left(\frac{1+\sqrt{5}}{2}\right) \\ -\left(\frac{1+\sqrt{5}}{2}\right) \\ 1 \end{pmatrix}$$

⑫ Problem set 7 asks you to find the corresponding eigenvalues.

P.S. $\frac{1+\sqrt{5}}{2} = \tau = \text{The golden mean} \approx 1.618$.

- 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 ^{MOS} 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.