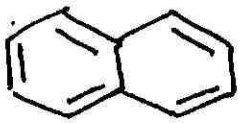
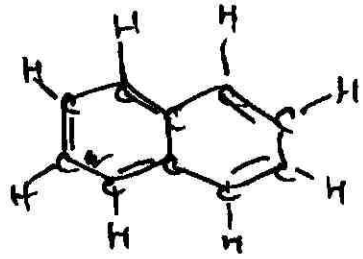
Week 10 Lecture 29 (skipped #28)

1. We can use MO theory to understand the results of many organic reactions. This week will study just a few examples.

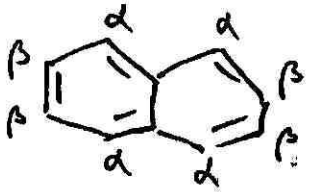


napthalene



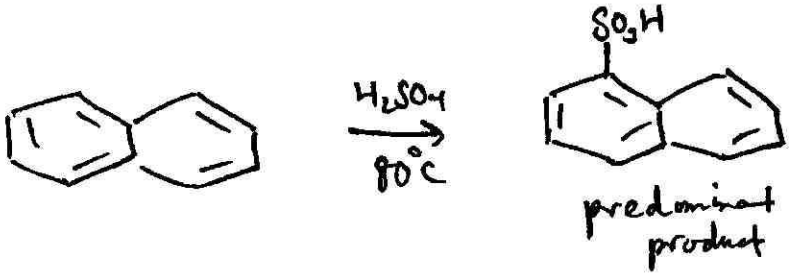
also undergoes aromatic electrophilic substitution.

Of the two sites

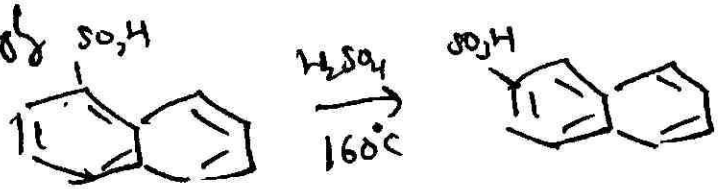


AES occurs preferentially first at the α site:

2. eg.



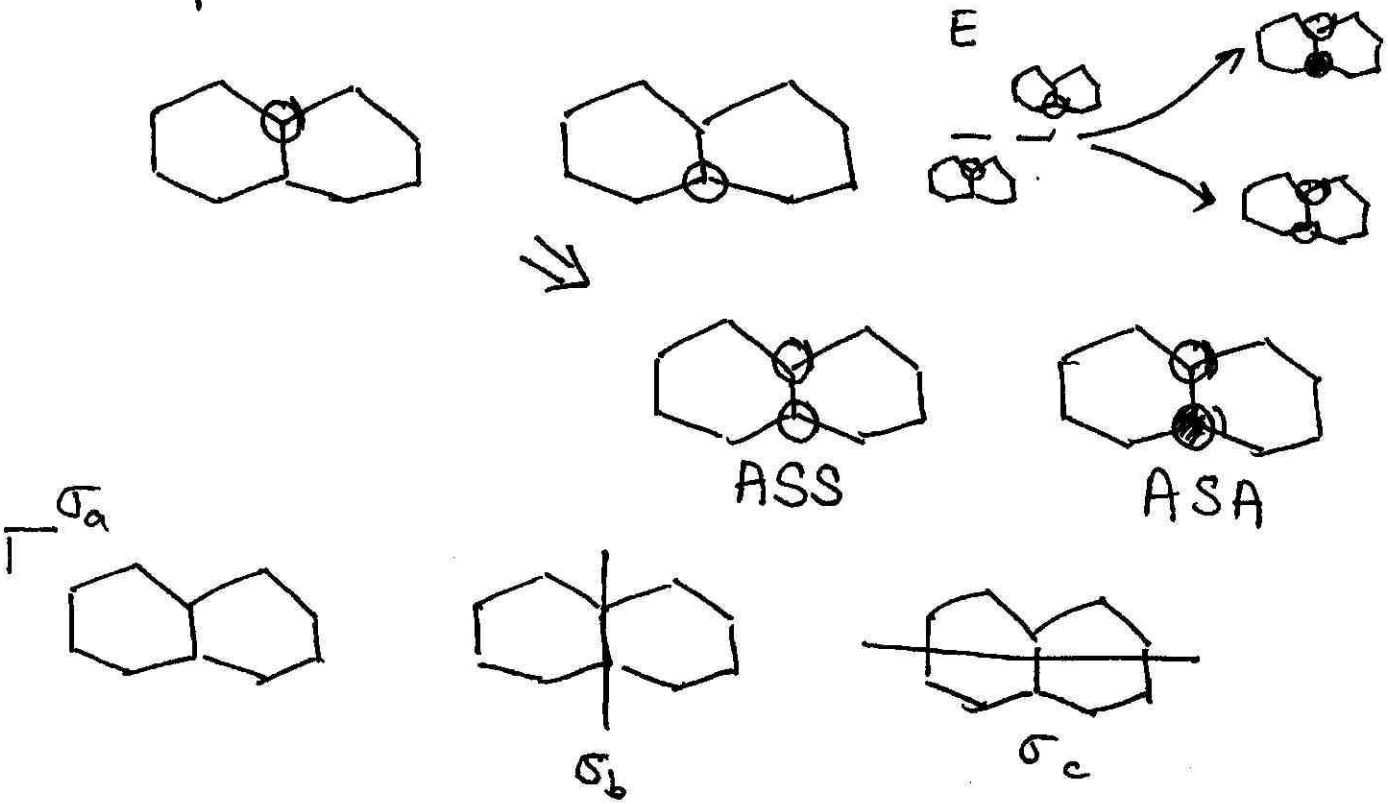
Interestingly

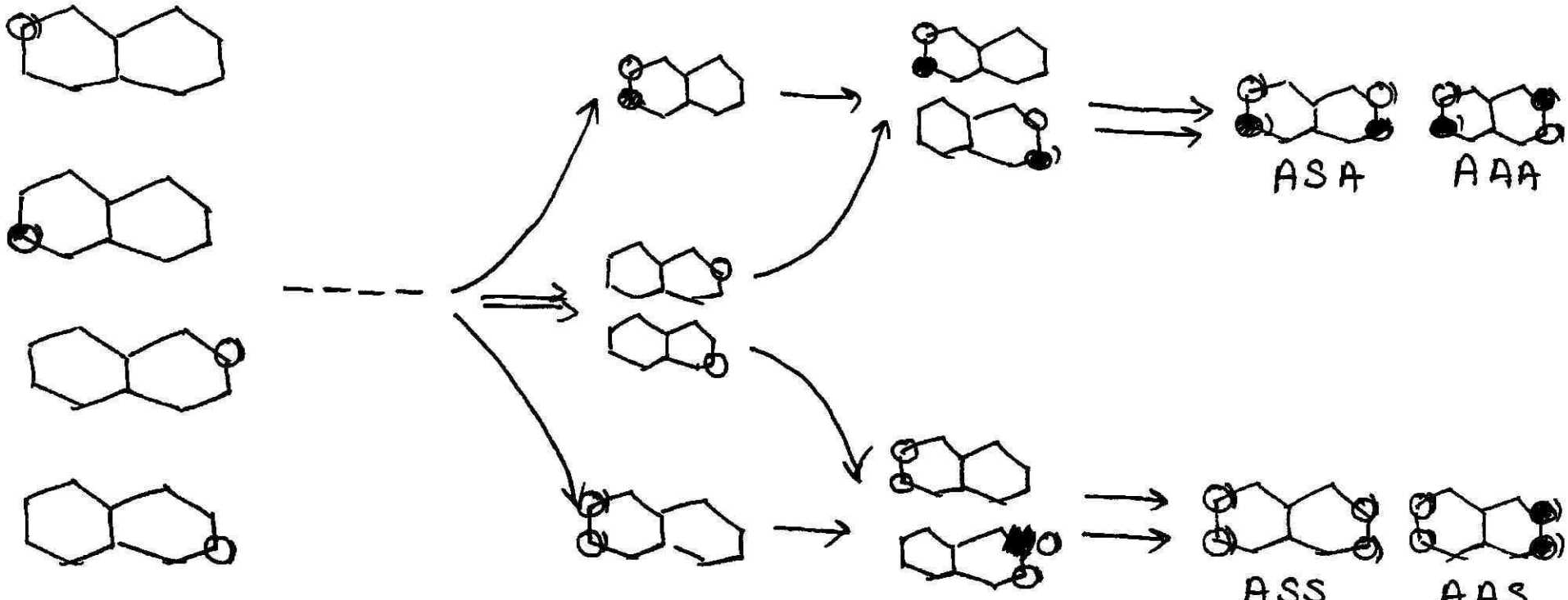


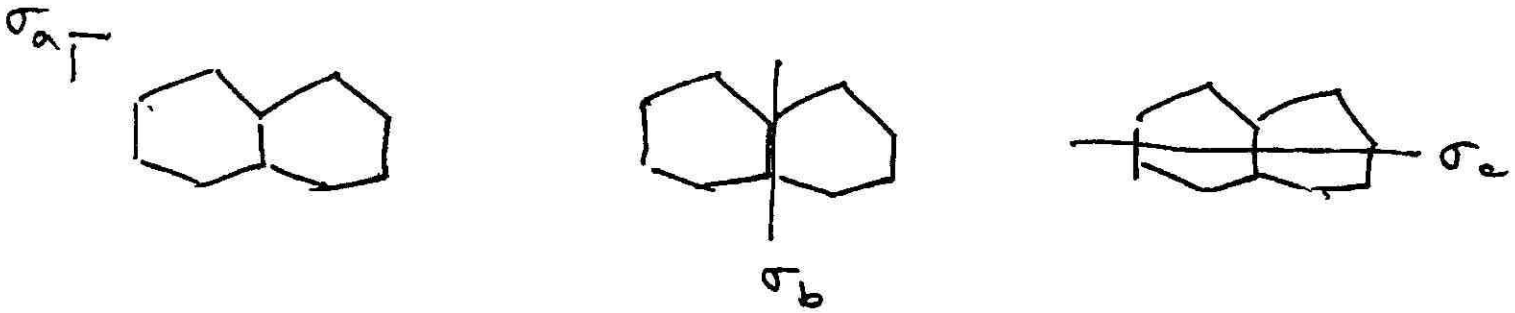
3. Why does attack first occur at α-position?

To answer this question we should look at the MO diagram of napthalene. In particular we should look at HOMO. If HOMO is more on α-site, first attach should be at α.

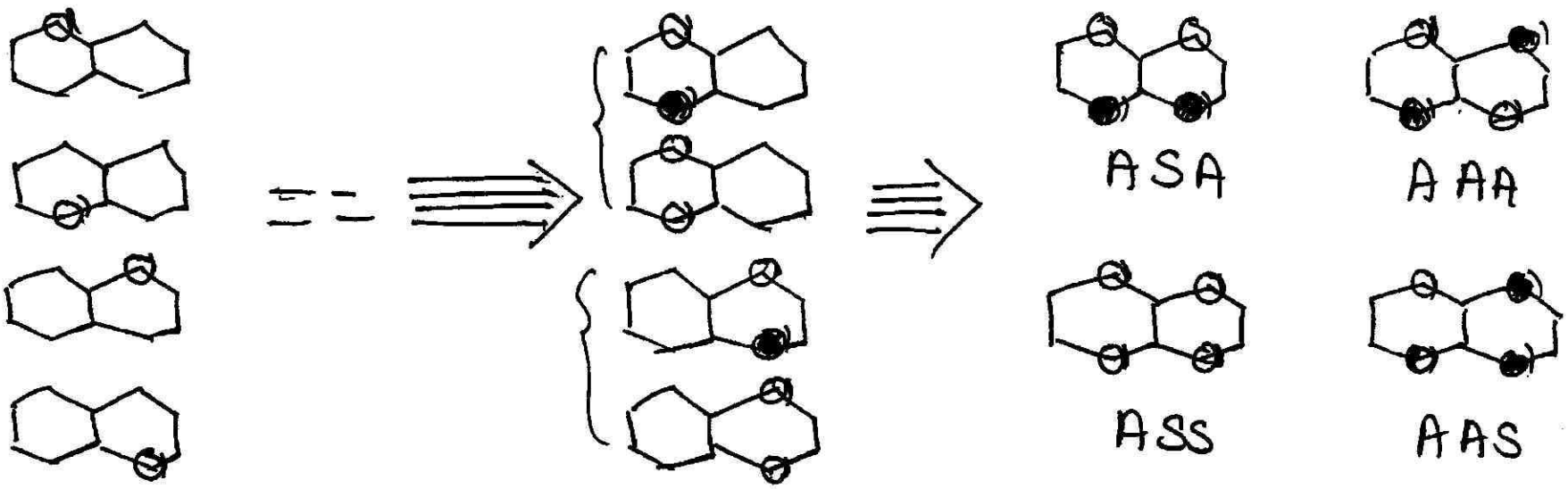
4. There are 10 π A.O.s in napthalene $\therefore$ 10 M.O.'s. Let's use symmetry. We will combine π A.O's so that they are symmetric & antisymmetric with respect to the mirror plane in this molecule.

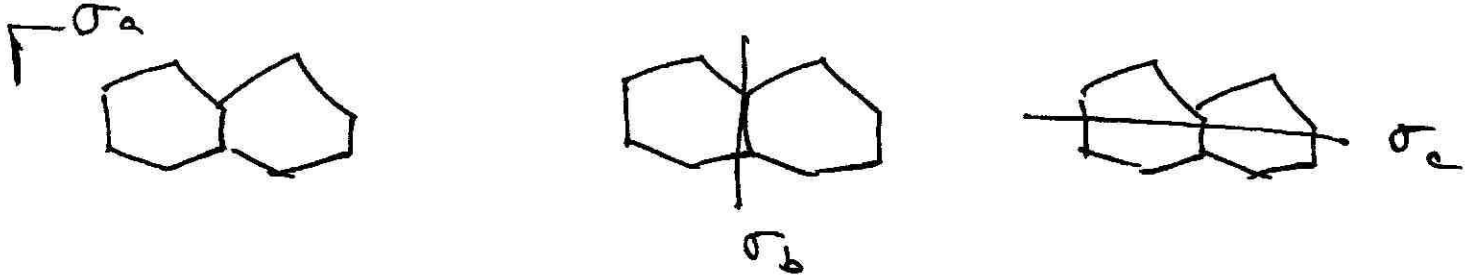



ASA
AAA
ASS
AAS


σ_a
σ_b
σ_c

Finally





Placing AAA. together, ASS togeth, ASA and, AAS:

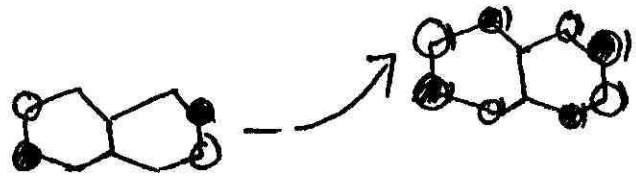
Et

AAA AAS ASA ASS

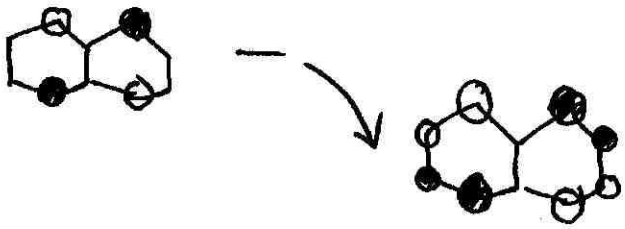
We know AAA orbitals can only mix with AAA orbitals, AAS w/ AAS etc...

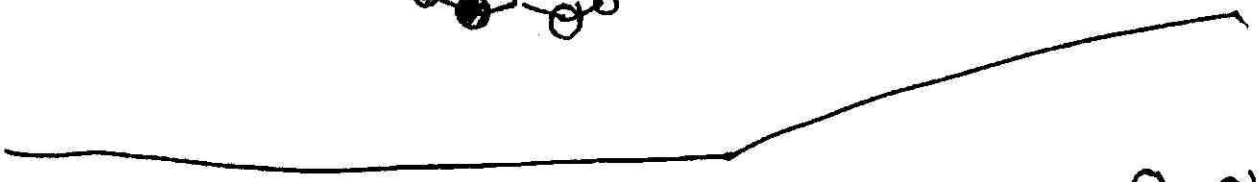
Let's consider the 4 sets separately & then add them together

AAA

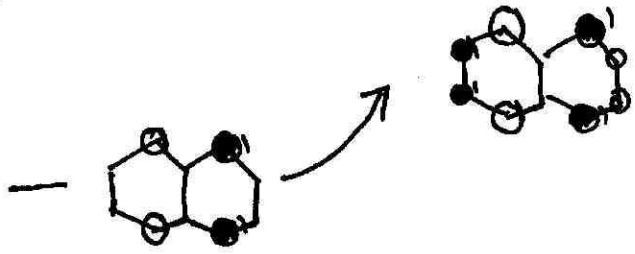


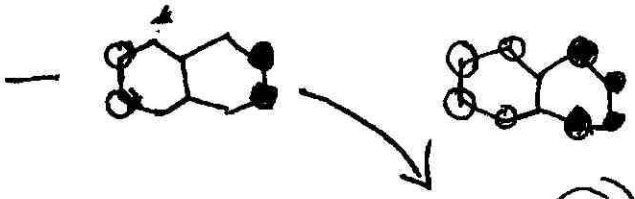
AAA





AAS



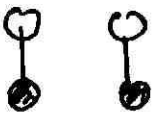


AAS

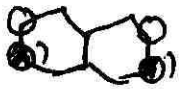
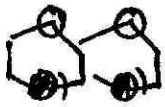
For ASA we observe the following point.

Any combination of  $\vec{\psi}_2$ &  $\vec{\psi}_1$

to say  does not change the energy

[Note  e^-'s have same antibonding energy as are H_2 antibonding orbital ]

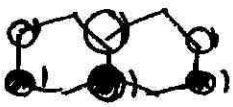
H_2 H_2

∴ Find a combination of the  &  which does not mix with  .

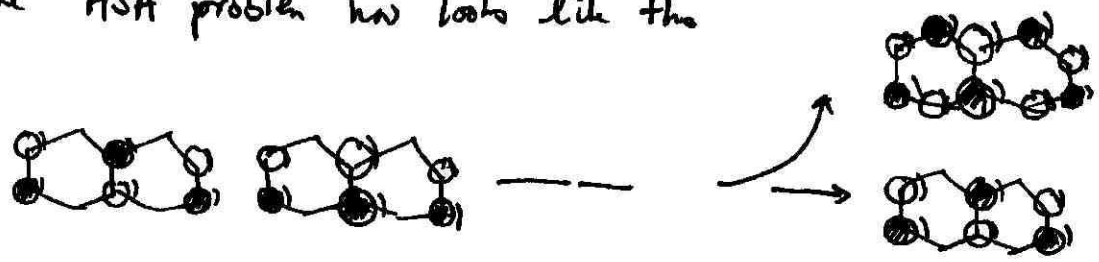
The combination is  $= \vec{\psi}_2 + a\vec{\psi}_1$

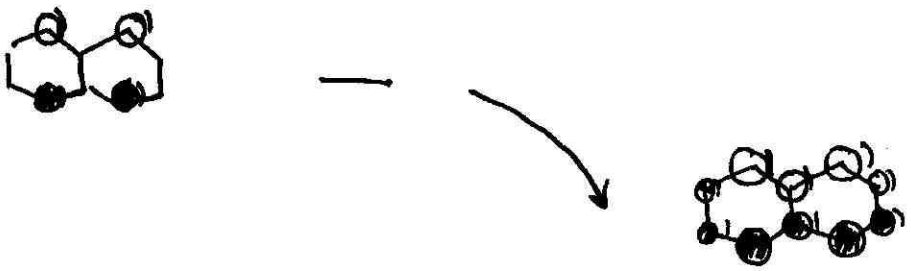
$\boxed{a < 1}$

The 2^{nd} orbital from pairwise mixing must be orthogonal to $\vec{\psi}_2 + a\vec{\psi}_1$. It must be $\vec{\psi}_1 - a\vec{\psi}_2$

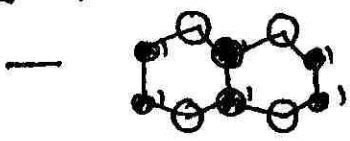


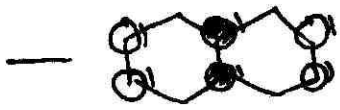
The ASA problem now looks like this

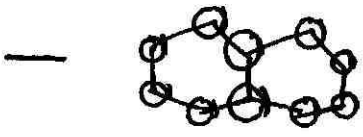




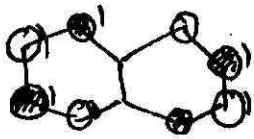
Exercise ASS. Using the same reasoning as we did for ASA show the 3 ASS π-MO's are



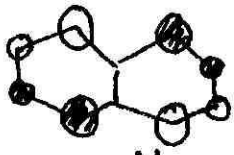




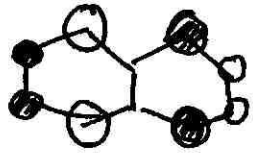
We now must place these 10 MO's from lowest to highest energy
twice # of bond. than anti.
[4 bonding, 2 antibonding]



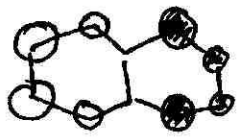
very antibonding



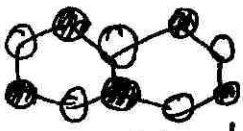
weakly bonding



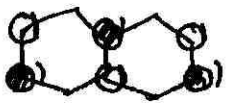
weakly antibonding



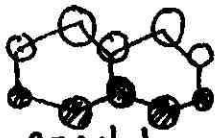
very bonding



very very antibonding

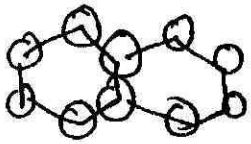


antibonding



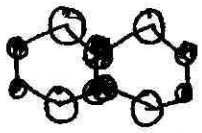
somewhat bonding

[8 bonding interactions
3 antibonding int.)
more than twice
# of bonding int.
than ant.



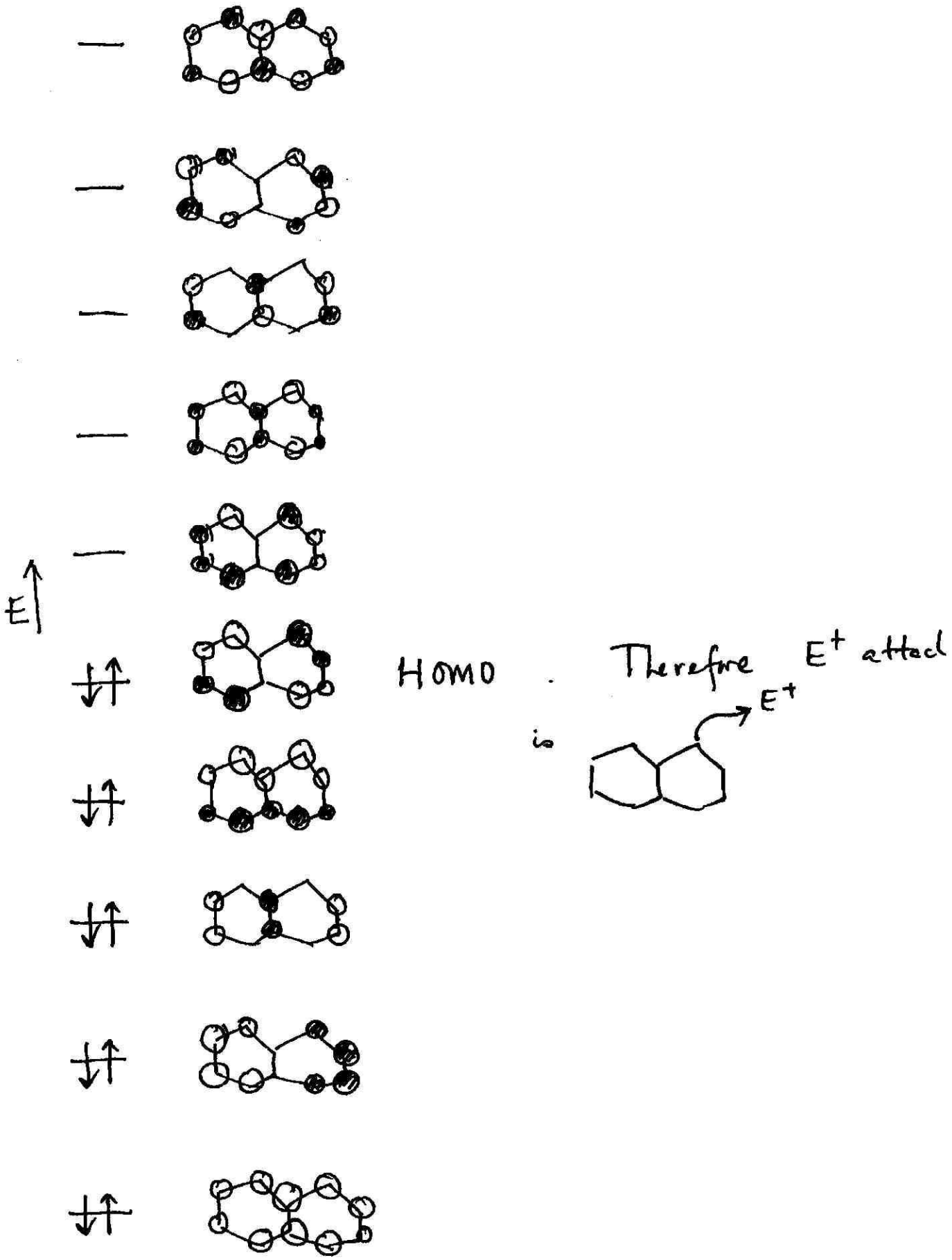
very very bonding

bonding



somewhat antibonding

On next page
we place
the 10 MO's in order.


E
HOMO
Therefore E+ attacl
is
E+