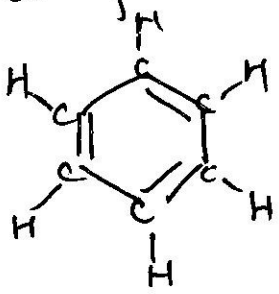
Counting σ & π orbitals & electrons

① Our goal today is to ~~count~~ ~~the~~ learn about localized orbitals. But we should first learn how to count σ & π electrons.

② What we know so far:

is



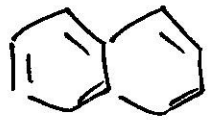
It has 3 π bonds & 12 σ-bonds.

With 2 e⁻/bond C_6H_6 has 30 valence e⁻.

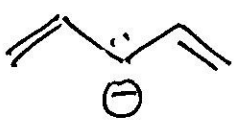
This works out $6 \times 4 + 6 \times 1 = 30$.

③ In the same way we see:

C_4H_6 has 4 π e⁻ & 18 σ e⁻

&  $C_{10}H_8$ " 10 π e⁻ & 38 σ e⁻.

④ But what about



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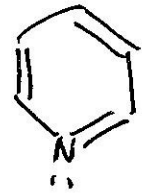
or



?

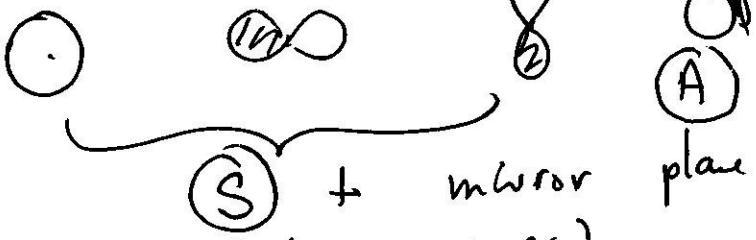
How do we count the lone pairs?

⑤ First, it's not the easiest thing in the world to think both lone pairs in H_2O are of σ-type. (In actual fact, one lone pair is σ, one lone pair is π).

⑥ The "secret to counting is recognizing that for counting we can assume for any bonding orbitals (MO) there is always [at least for organic chemists] one antibonding MO.

The second thing to realize is we can count in a straightforward way the # of σ-MOs & π-MOs (filled + unfilled)

⑦ Let's use these ideas in an example. Consider H_2O

O has 

+ mirror plane of molecule [plane of page]

H has 

$\therefore$ H_2O has 5 S-orbitals & 1 A-orbital.

⑧ S-orbital $\Rightarrow$ σ MOs

A-orbital $\Rightarrow$ π MOs

⑨ H_2O has 5 σ MOs, 1 π MO.

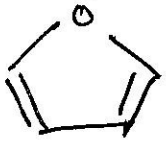
It has 2 bonding σ orbitals ∴ 2 antibonding σ-orbitals

& " O ∴ π-orbitals.

∴ H_2O has 2 bonding σ MOs
1 non-bonding σ MO
1 " π "
2 antibonding σ MO

H_2O has 4 pairs of valence e^- (6 + 2 = 8)
1O 2Hs 4 pairs.

⑩ ∴ H_2O has 2 bonding σ MOs, 1 non-bonding σ MO
1 non-bonding π-MO

⑪ Let's try 

1O	3S	1A
4C	(4×3)S	(4×1)A
H	4S	0A
Total	16S	5A.

 has 9 σ bonding MOs & $\frac{6+4+4\times4}{2} = 13$ pairs 1 valence e^-
9 " antibonding MOs
2 ~~then~~ Las π-bonding MOs
2 lews π-antibonding MOs

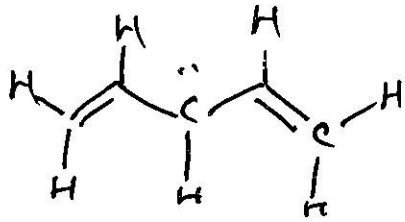
∴ 9 σ bonding MO — 2 π-bonding

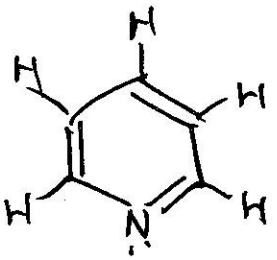
9 σ antibonding MO — 2 π antibonding

0 σ nonbonding — 1 π nonbonding.

∴ lone pair on O is non-bonding.

We count the lone pair as π e⁻.

(12) Try your hand at  



You'll find in  the lone pair is π

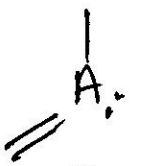
unlike in  it is σ.

(13) It turns out that for cases such as

 one lone pair is always σ

" " " " " π

for  one lone pair is always π

for  one lone pair is always σ.

To help in these costly cases we can use the concept of localized orbitals.