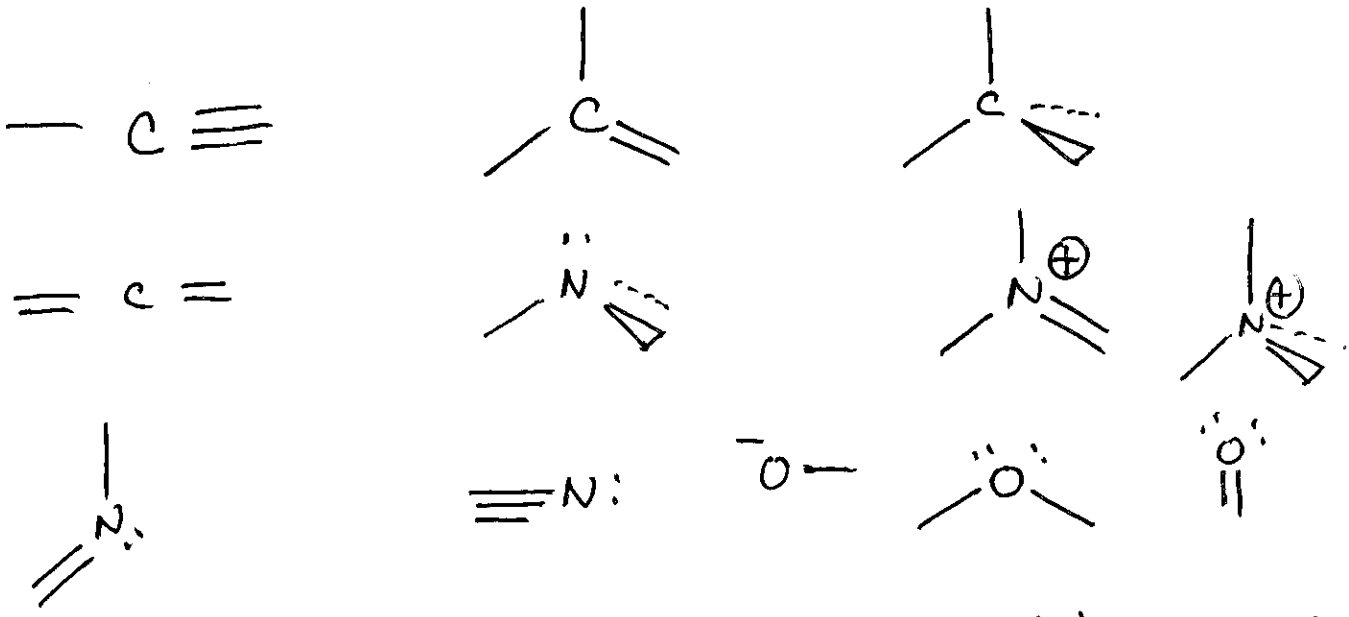
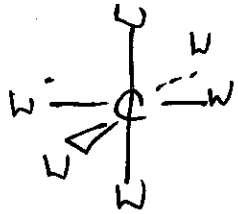
Review lect 40 (40) localized bonding & extended solids (REVIEW)

I think I went through the material a too fast on Monday/Wednesday. I would like to go over the points did I label in ~~that~~ those classes.

① In organic chemistry C, N, O, & H all have just a limited number of environments

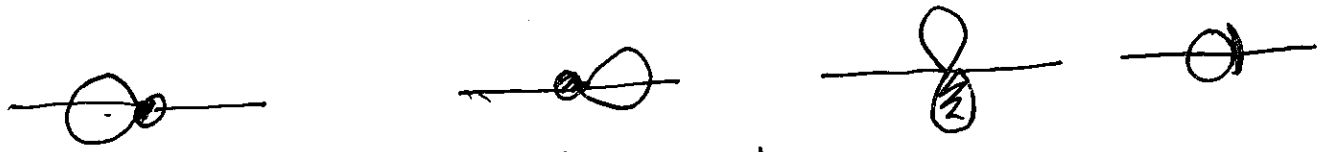


[By contrast C with most metal atoms often adopt 6 coordinate structures eg WC  etc...]

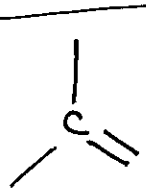
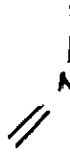
② We adopt the schemes sp, sp^2 & sp^3 to deal with the situations listed in ①. The point of these schemes is to place one orbital pointing along each σ bond.

③ For $-C\equiv$, $=C=$ or $\equiv N:$

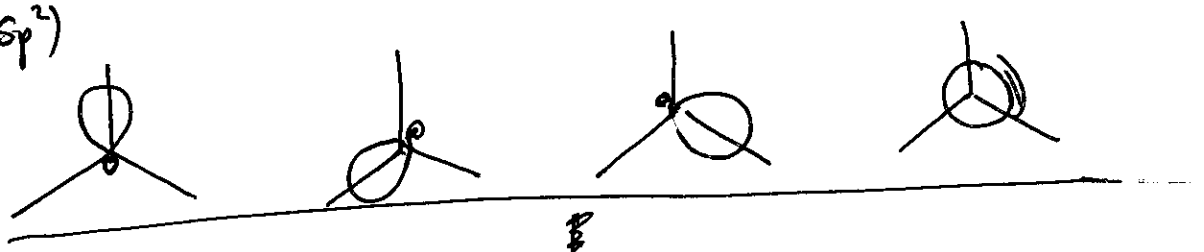
we can adopt the scheme (sp)

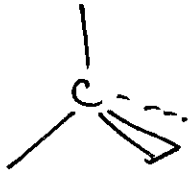
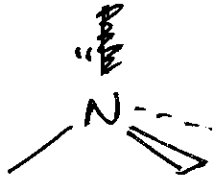


with ~~one~~ lobe pointed along each σ-bond.

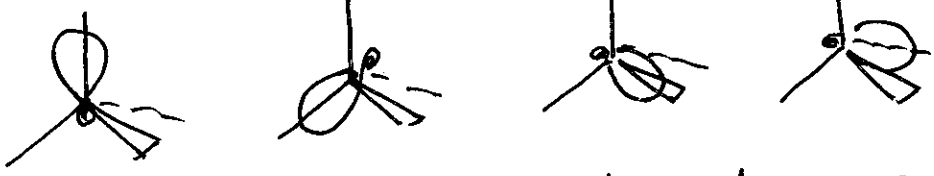
④ For  or  we can adopt the

scheme (sp^2)



⑤ For  &  we can adopt the

sp^3 scheme

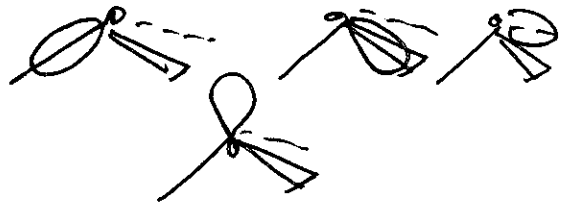


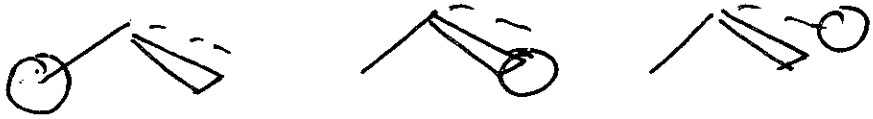
In all cases we point lobes along each of the bonds. [We deal with  later]

⑥ Let's use these simple schemes to make pictures of the orbitals in molecules & extended solids.

⑦ Let's consider ~~[illegible]~~ AsH_3 & As solid

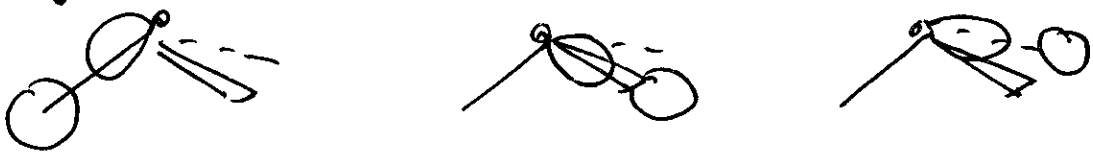
⑧ 

We take sp^3 

& mix with 

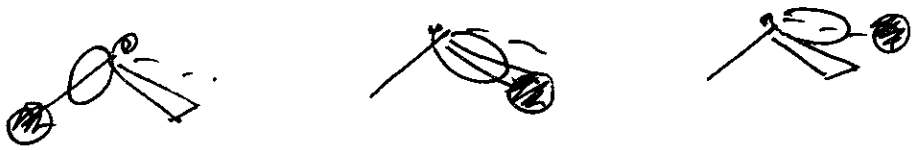
to make 3 binding orbitals, 3 antibinding orbitals & one non-binding orbital:

3 binding orbitals

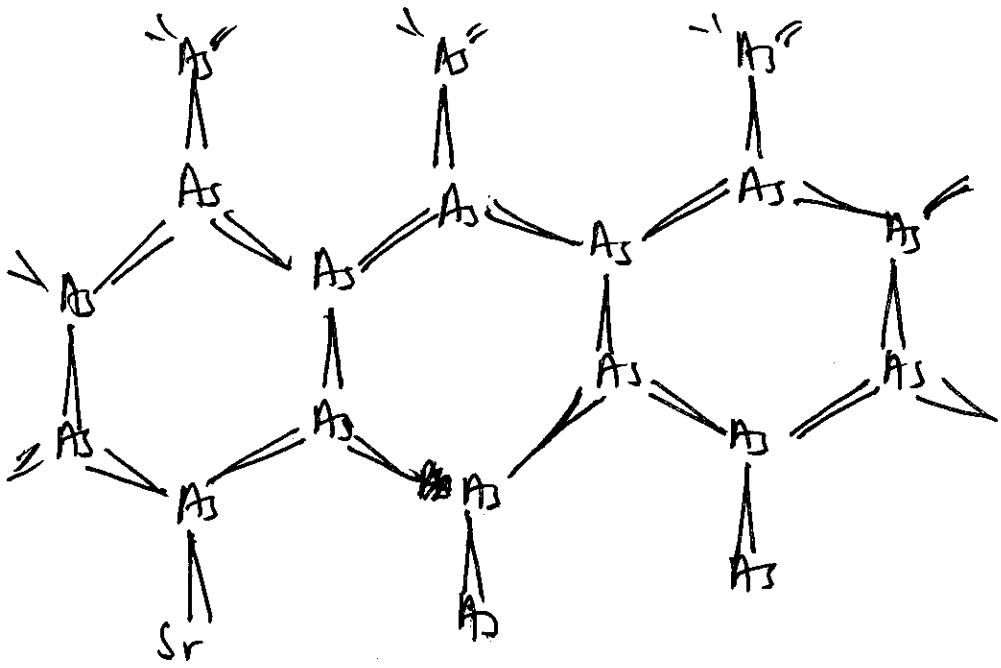


1 non binding orbital

3 antibinding orbitals

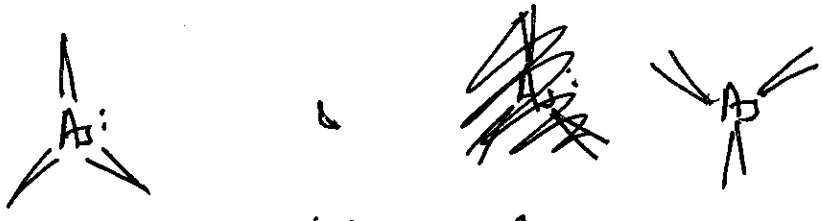


⑨ or consider As solid

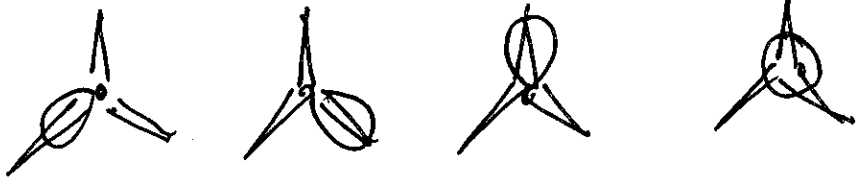


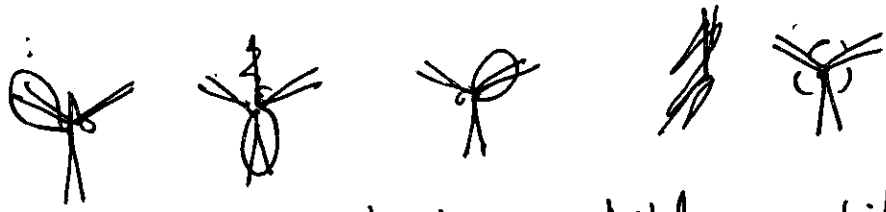
etc..

There are two types of As :

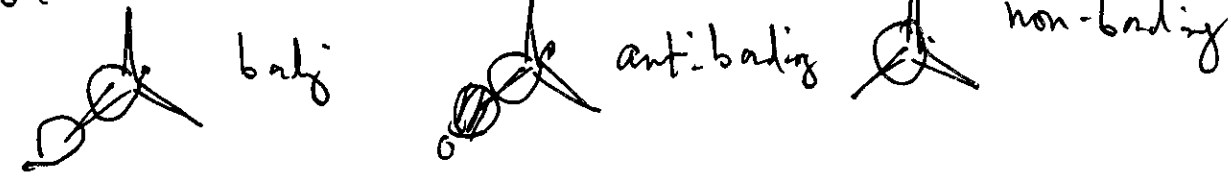


Both are modelled with sp^3





These combine to make bonding orbitals, antibonding & non bonding orbitals



Let's say we start with 10^{17} As atoms (a small piece of solid As (pretty much the smallest speck we can see)

There would be 1.5×10^{17} σ bonds in the As piece.

We would have 1.5×10^{17} bonding σ orbitals

1.5×10^{17} antibonding σ orbitals

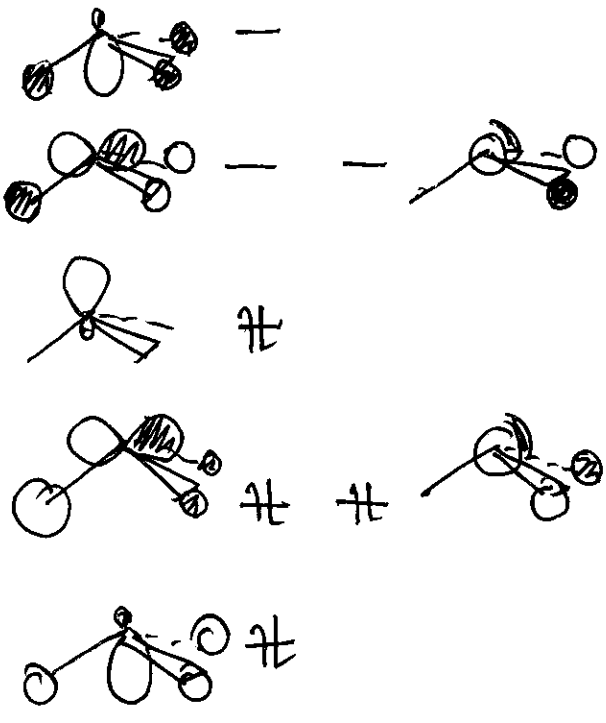
& 1.0×10^{17} non-bonding σ orbitals.

As there are 4×10^{17} orbitals in the chunk of As this accounts for all the orbitals in the system.

(10) BUT these localized orbitals are not MOs.

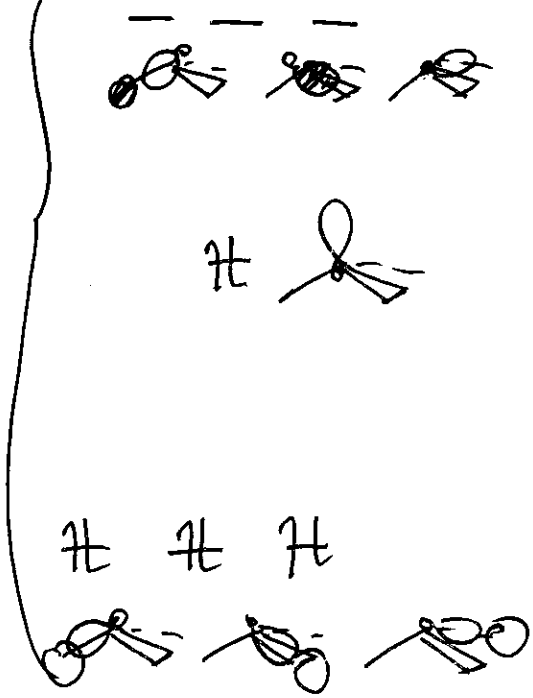
They are not the orbitals which result from any measurement.

Example AsH_3 MO diagram



these orbitals are experimentally observed

Localized orbitals



NH_3 photoelectron spectra

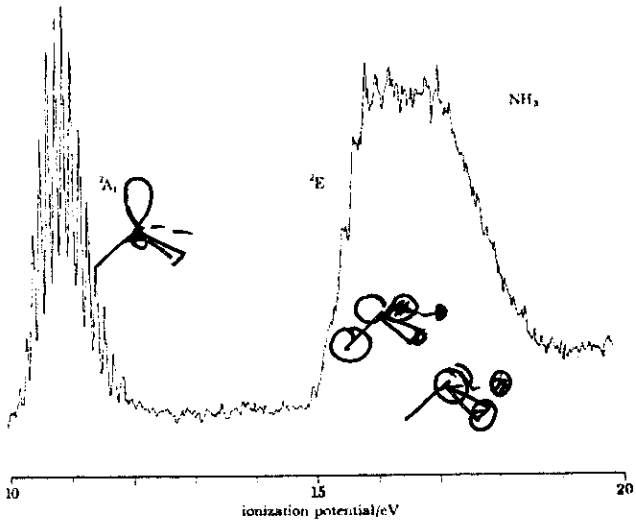
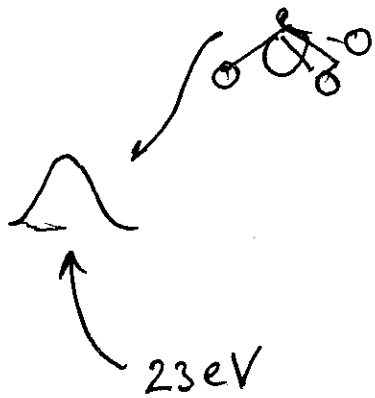


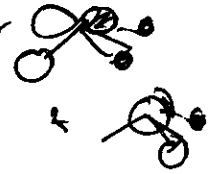
FIGURE 4. Photoelectron spectrum from ammonia obtained using the 584 Å helium resonance line.

Branston et. al
Phil Trans R S (Londa)
1970 A 268, 77-85



23eV

[from
Ellzey, M.L.
J. Mol Struct: THEO CHEM
530 (2000) 11-20]

Thus in NH_3 we observe 3 different energies for the filled orbitals: one for  , one for 

& lastly one for 

This is what we expect - MO theory, but for the localized picture there are only 2 energies expected.

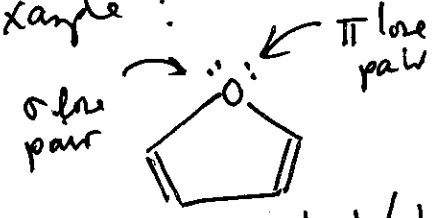
(11) So localized orbitals do not correspond to any measurable quantity. What are they good for?

(12) Localized orbitals can account for the number of σ, σ-nonbonding & σ antibonding orbitals. [They can account for the # of filled π-orbitals.]

(eg) Note both the MO diagram & localized picture have 3 bonding σ-orbitals, 1 non-bonding & 3 antibonding σ orbitals.

(13) Interestingly localized orbitals can not figure out the number of bonding, non-bonding & antibonding π orbitals.

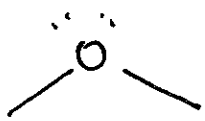
Example:



MO theory: 3 bonding MO's
2 antibonding MOs

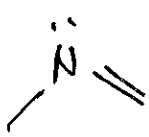
Localized/Lewis picture: 2 bonding MOs
1 nonbonding MOs
2 antibonding MOs

(14) BUT For π-~~electrons~~ orbitals, the localized picture [correctly used can be applied to get the correct number of π electrons.] We need to use the following scheme:

For  use sp^2

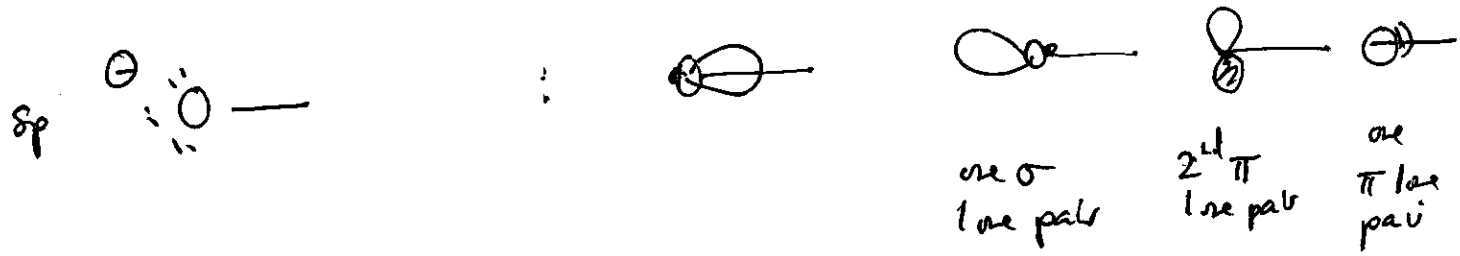
 use sp

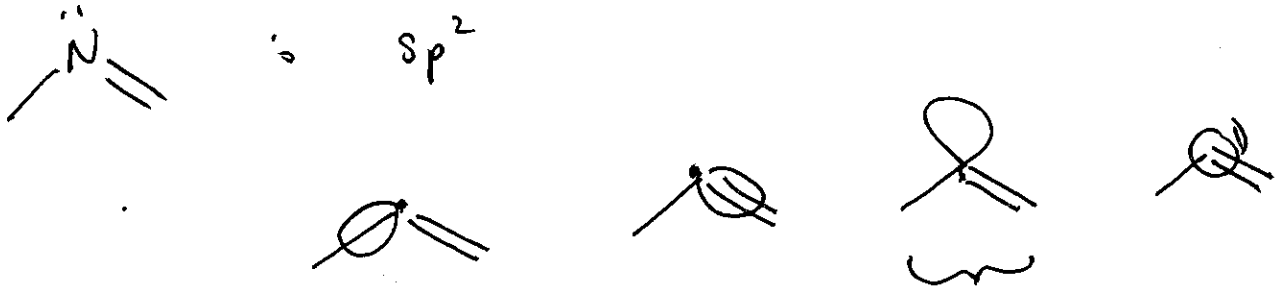
[Use scheme with smallest (sp^n) n compatible with structure]

 use sp^2

We assume all σ bonding & nonbonding orbitals are filled.

(15) Therefore





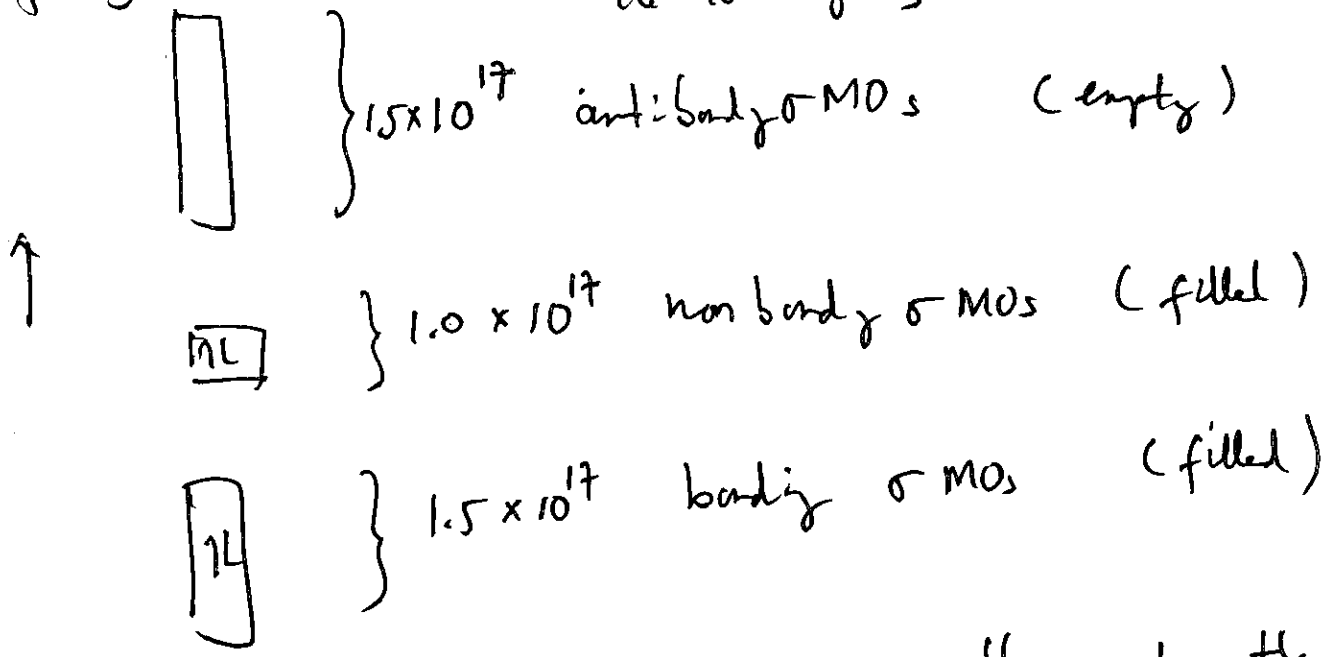
[Note all σ bonding & nonbonding orbitals are filled.]

(16) Recap: Localized orbitals are not measurable. BUT they count correctly

① # σ bonding, σ antibonding, σ nonbonding orbitals (all filled)

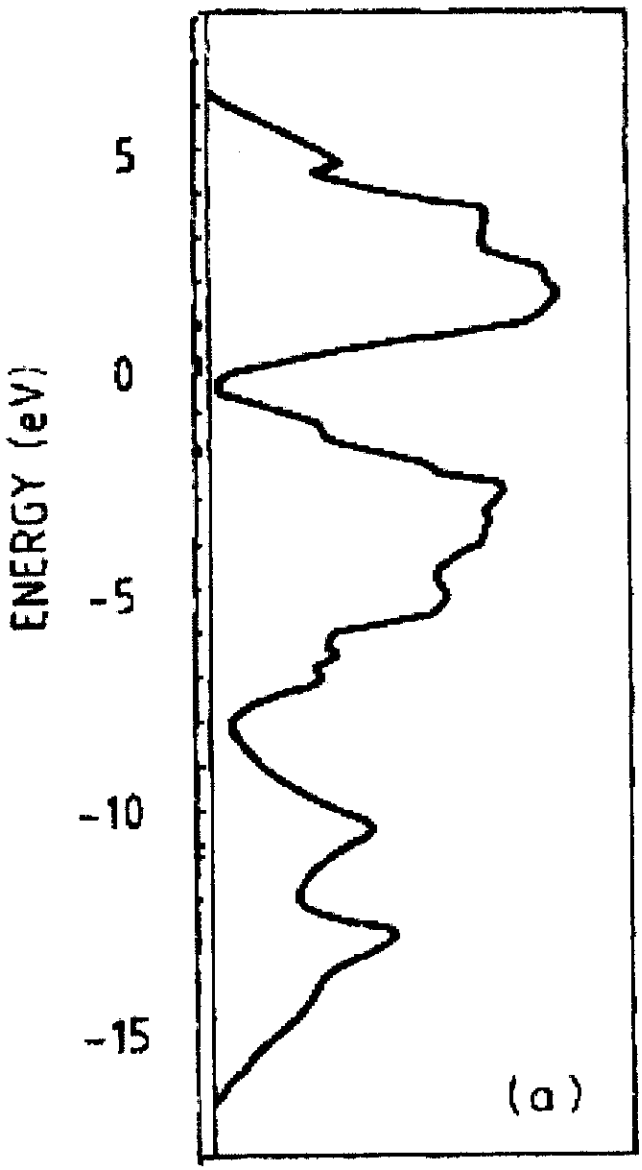
② # π filled orbitals.

(17) We may use the facts in (16) to get a picture of the MO banding picture in As solid [assume 10^{17} As atoms] (i.e. for systems where we do not know [at least from this class how to calculate the MO diagram].



(18) This picture bears some resemblance to the actual MO diagram for As. [Note as we are dealing with for all practical purposes almost an ∞ number of MOs, we just plot the number found at a certain energy.]

Robertson Phys. Rev. B 1983 (28) 4671



σ antibonding MOs

σ non-bonding MOs

σ bonding MOs

Note the localized scheme just gets the # of orbitals correct; it does not give us any sense of the actual spread of energies!