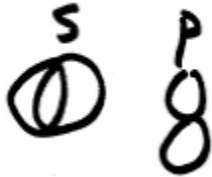


# LECTURE 12. VB THEORY: MAKING MOS FROM AOS

What is a bond? An overlap of e- density from 2 atomic orbitals.

Examples of atomic orbitals?

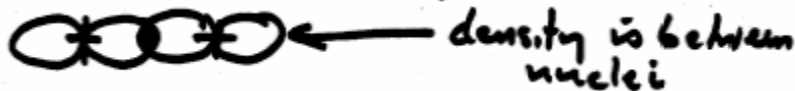


So, overlap them to make a VB:



So what are the types of molecular orbitals? There are only 2, sigma and pi.

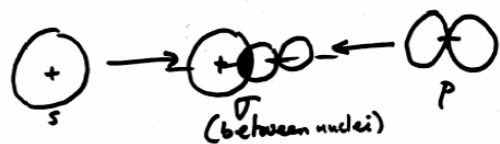
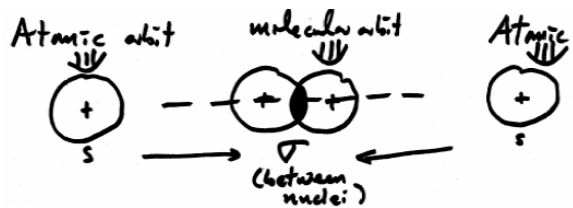
$\sigma$  → sigma, when e- density is between atoms



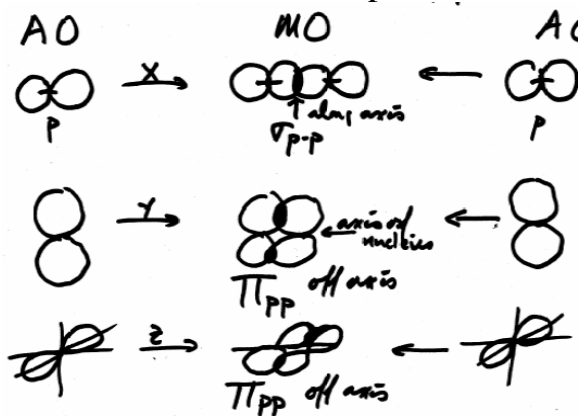
$\pi$  → pi, when e- density is off axis



So let's make sigma and pi bonds by mixing s and p atomic orbitals.



Note that since s orbit is in all directions, some overlap must be along axis of nuclei, so s orbitals are always sigma bonds. Now look at 3 orientations of p atomic orbitals:



## Summarizing:

- any bond involving s orbitals is sigma
- $s + s = \text{sigma}, \sigma$ ;  $s + p = \text{sigma}, \sigma$
- of 3 p orbitals overlapping, 2 will be pi,  $\pi$  and one will be sigma,  $\sigma$
  
- And that is almost it. Except that we need to consider the case where hybrid atomic orbitals:  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $dsp^3$ ,  $d^2sp^3$  are mixed. Note, happily, that every hybrid orbital has s character which means that they have some electron density along the axis and consequently:

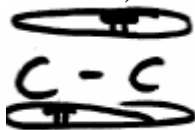
Every hybrid orbital that forms a valence bond with another atomic orbital is making a sigma,  $\sigma$ , bond.

Let's apply to 3 examples:  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ .

- sigma: bonds along the axis between atoms. It is the first bond formed and is from either atomic orbitals with s character or p orbitals, or hybrid orbitals. Example:



- pi: bond above and below nuclei axis; are formed by off-axis overlap of p-p orbitals.  $\pi$  bonding is always present when there are 1) double bonds 2) triple bonds 3) resonance. Example:



Now let's identify sigma and pi bonds in  $C_2H_6$ ,  $C_2H_4$ , and  $C_2H_2$ .

**Example  $C_2H_6$ :**



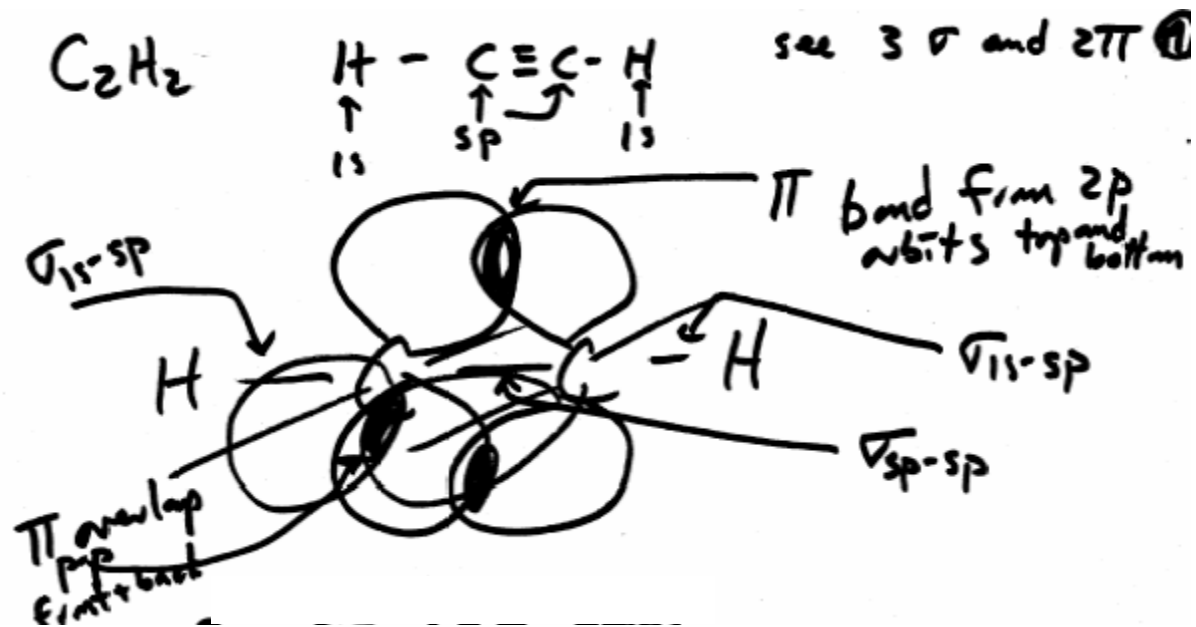
- note that there are 7 sigma bonds. 6 are C-H and 1 is C-C.
- C-H bond is H 1s overlap with Csp<sup>3</sup> orbit →  $\sigma_{1s-sp^3}$
- C-C bond is C sp<sup>3</sup> overlap with Csp<sup>3</sup> →  $\sigma_{sp^3-sp^3}$

#### Example C<sub>2</sub>H<sub>4</sub>:



- first bond type is seen 4 times: C-H →  $\sigma_{sp^2-1s}$
- second bond type is seen 1 time: C-C →  $\sigma_{sp^2-sp^2}$
- third bond type is pi bond seen once: C-C →  $\pi_{p-p}$

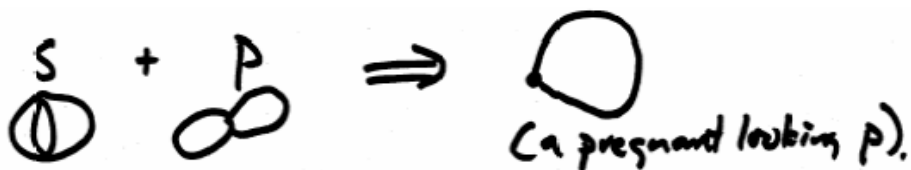
#### Example C<sub>2</sub>H<sub>2</sub>:



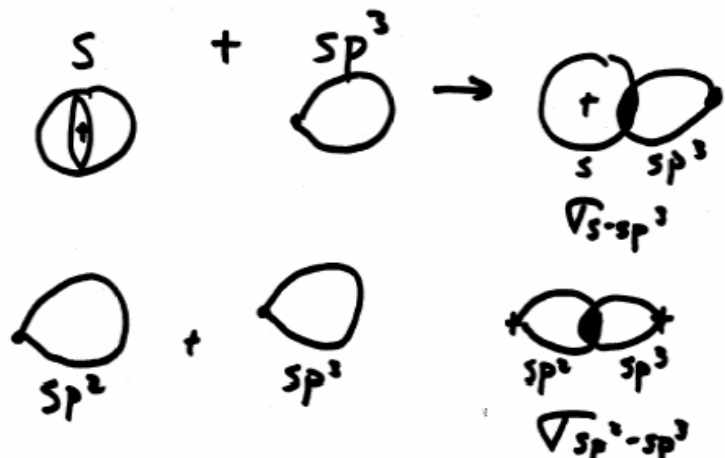
- 2 sigma C-H bonds  $\rightarrow \sigma_{1s-2p}$  from H and C
- 1 sigma C-C is  $\rightarrow \sigma_{sp-sp}$  from C and C
- 2 pi C-C is C-C  $\rightarrow \pi_{p-p}$  from overlap of p orbitals above and below, from and back

The bad news is that VB (valence bond) theory is needed to explain hybrids.

The good news is that all hybrid orbitals look pretty much the same.



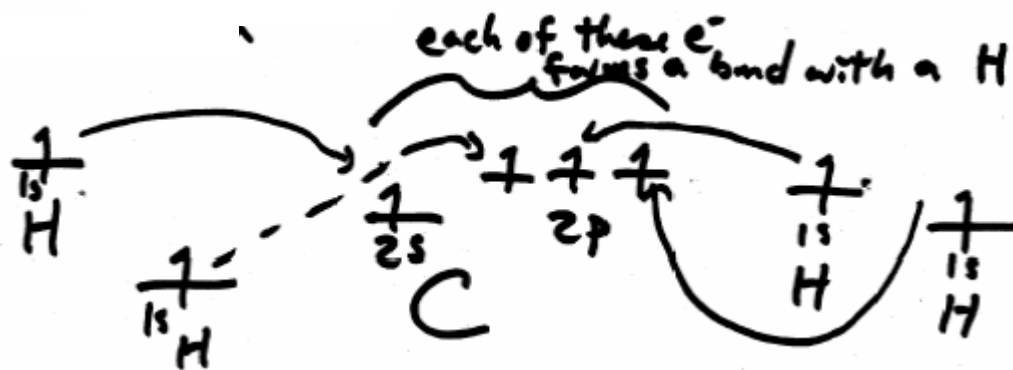
The reason they look the same is that all have s orbit in the mix ( $sp$ ,  $sp^2$ ,  $sp^3$ ,  $dsp^3$ ,  $d^2sp^3$ ). And the best news is that therefore all hybrids for sigma bonds.



So while we haven't learned why hybrids are needed, at least we know that they must form sigma bonds.

**Now let's see why Valence Bond (VB) Theory explains hybrids.**

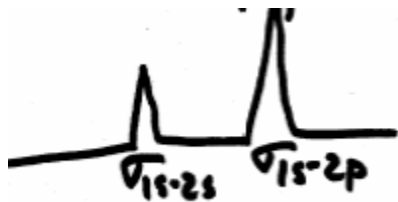
Imagine what CH<sub>4</sub> molecular orbits came from:



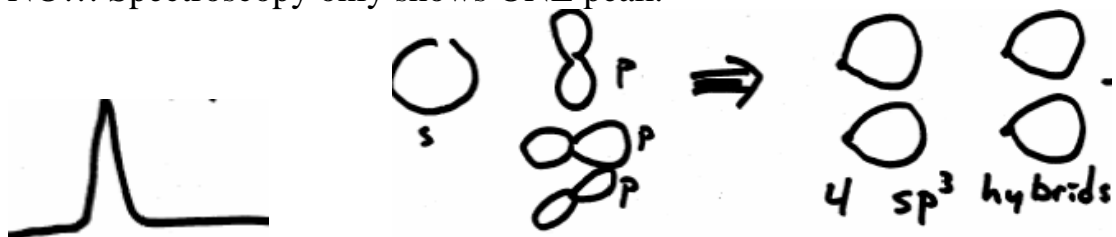
This means that we should have 4 bonds as shown to the right. They appear to be of two different types: sigma 1s-2s and sigma 1s-2p.

But the single  $\sigma_{1s-2s}$  is different from: the three  $\sigma_{1s-2p}$

So spectroscopy should show 2 peaks, right?


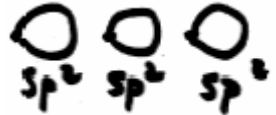

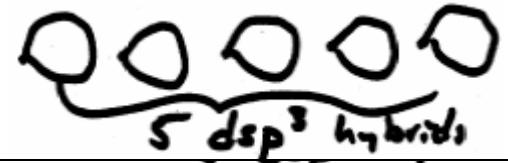



NO!!! Spectroscopy only shows ONE peak:



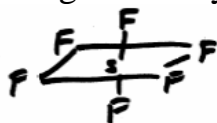
- so the 4 bonds must be the same. They must have mixed or hybridized orbitals
- The 4  $sp^3$  hybrids combine to form the one peak shown on the left.

So how many kinds of hybrids? They break down by # e- rich regions = # hybrid orbitals

# e- rich regions	Atomic orbits before mixing	Mixed Hybrid
2	s,p	
3	s,p,p	
4	s,p,p,p	
5	d,s,p,p	
6	d,d,s,p,p	

**Example:** What is hybridization of BeCl<sub>2</sub>?

Create Lewis structure → Cl-Be-Cl 2 e- rich regions so hybrid of two atomic orbitals = sp hybrid



**Example:** What is hybridization for SF<sub>6</sub> ?

6 e- rich regions means  
hybrid of six atomic orbitals  
= d<sup>2</sup>sp<sup>3</sup> hybrid



## Summarizing what you know: the 13 molecular shapes

Summarizing what you know:

# e- rich regions	Electronic geometry	Angle	Hybrid	Molecular geometry
2	Linear	180	Sp	AB2
3	Trigonal planar	120	Sp <sup>2</sup>	AB2 or AB3
4	Tetrahedral	109.5	Sp <sup>3</sup>	AB4, AB3U, AB3U2
5	Trigonal bipyramidal	120, 90, 180	Dsp <sup>3</sup>	AB5, AB4U, AB3U2
6	Octahedral	180, 90	D <sup>2</sup> sp <sup>3</sup>	AB6, AB5U, AB4U2

What starts it all, from 3D Lewis structure

3 things you know right away from # e- rich regions

Knowing bonding and unbonded pairs lets you determine molecular geometry