Localized electron model for bonding

1. Determine the Lewis Structure for the molecule

2. Determine resonance structures

3. Determine the shape of the molecule

4. Determine the hybridization of the atoms

What does hybridization mean? Why hybridize?

Look at the shape of many molecules, and compare this to the shape of the orbitals of each of the atoms.

Shape of orbitals

Orbitals on atoms are **s**, **p**, **d**, and **f**, and there are certain shapes associated with each orbital.

an **s** orbital is a big sphere

the **p** orbitals looks like "8" 's
each one points in along an axis

four of the **d** orbitals look like four leaf clovers
one **d** orbital looks like an "8" with a doughnut around the middle

the **f** orbitals look like two four leaf clovers
three **f** orbitals look like weird "8"'s with two doughnuts around each one

Shape of molecules

Remember we determine the shape of molecules by determining the number of sets of electrons around the atom. count double and triple bonds as one set, count single bonds as one set of electrons and count lone pairs as a set

2 sets—each pair of electrons points 180° away from the other

3 sets—each pair points toward the corner of a triangle

4 sets—each pair points toward the corner of a tetrahedron

5 sets—each pair points toward the corner of a trigonal bipyramid

6 sets—each pair points toward the corners of an octahedron

To make bonds we need orbitals—the electrons need to go some where.

the **s**, **p**, **d**, and **f** do not point in the right directions (compare the lists which describe the shapes) so they cannot be the orbitals that are used.

The atomic orbitals must combine to form hybrids; these hybrids are the orbitals which will be used in bonding.

Making hybrid orbitals

In chemistry when orbitals are combined to form hybrids the number of orbital going in equals the number of orbitals that come out.

for example...

1 **s** orbital + 3 **p** orbitals ——> 4 **sp**^{3} orbitals

1 **s** orbital + 2 **p** orbitals ——> 3 **sp**^{2} orbitals there is 1 **p** orbital left over

1 **s** orbital + 1 **p** orbitals ——> 2 **sp** orbitals there are 2 **p** orbitals left over

remember the numbers listed above are amounts—1 orbital, 2 orbitals—the numbers do not represent principal quantum numbers **n**. We could add them in though if we wanted.

for example...

1 **2s** orbital + 3 **2p** orbitals ——> 4 **2sp**^{3} orbitals

1 **2s** orbital + 2 **2p** orbitals ——> 3 **2sp**^{2} orbitals there is 1 **2p** orbital left over

1 **2s** orbital + 1 **2p** orbitals ——> 2 **2sp** orbitals there are 2 **2p** orbitals left over

How do you tell what the hybridization around a given atom is?

The easy one....**H**

what orbitals are available to form hybrids? there is 1 **1s** orbital

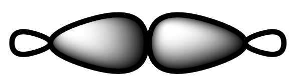
So what hybrids can form? ahhhh nothing to hybridize with

H will always use the **1s** to bond with other atoms

The others...some rules to make life simple...

All **single bonds** are made with **hybrid orbitals** (except H uses **s**)
All **lone pairs** go into **hybrid orbitals**.

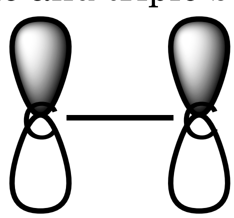
a C C single bond looks something like

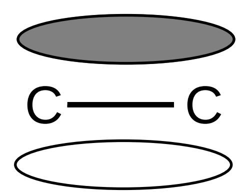


A bond that forms a cylinder around a line connecting the two atoms is called a **sigma σ** bond.

Almost all **double and triple bonds** are made with **p orbitals**

double and triple bonds would look something like





A bond that has electrons density on either side of the line connecting the atoms is called a **pi π** bond.

So, the first bond that forms is a **σ** bond, the second bond is a **π** bond—now there is a double bond—and the 3rd bond is also a **π** bond—now there is a triple bond. Notice both bonds which form the double and triple bonds are **π** bonds.

Determining hybridization

1. Count the number of lone pairs and single bonds

2. For each **σ** bond and lone pair a hybrid orbital is needed.

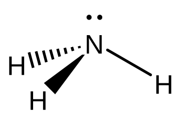
   If...

   a. four orbitals are needed all valence orbitals need to be hybridized.

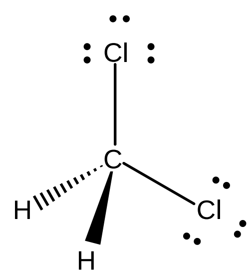
   1 **s** orbital + 3 **p** orbitals ——> 4 **sp³** orbitals

   Each orbital is an sp³ orbital; there are four of them. Sometimes chemists say the atom is **sp³** hybridized.

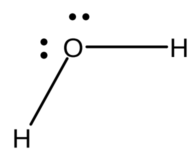
examples...



N is sp³



C and Cl are sp³



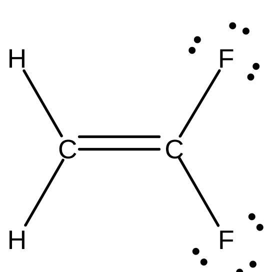
O is sp³

   b. three orbitals are needed only three valence orbitals will be hybridized.

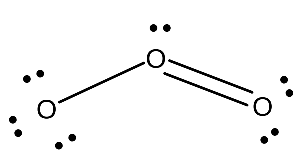
   1 **s** orbital + 2 **p** orbitals ——> 3 **sp²** orbitals   1 **p** orbital left over

   There are three sp² orbitals; the fourth is a **p** orbital. Sometimes chemists say the atom is **sp²** hybridized.

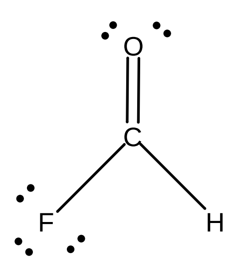
examples...



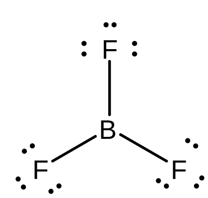
C's are sp²,
F's are sp³



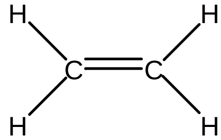
middle & right O sp²,
left O sp³



C and O sp²,
F sp³

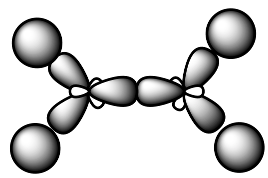


B sp²,
F sp³

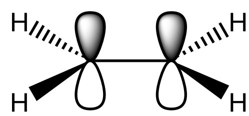


How would one draw the orbitals used in $H_2C{=}CH_2$?

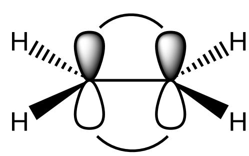
Since there are 3 σ bonds 3 hybrid orbitals are needed. 3 sp^2 orbitals form the σ bonds (σ bonds are regular single bonds).



There is a left over p orbital on each C.



Electrons in these orbitals can overlap and form a π bond.

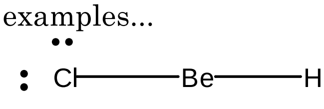


c. two orbitals are needed only two valence orbitals will be hybridized.

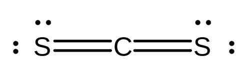
1 **s** orbital + 1 **p** orbitals ——> 2 **sp** orbitals 2 **p** orbitals left over

There are two sp^2 orbitals; the fourth is a **p** orbital. Sometimes chemists say the atom is **sp^2** hybridized.

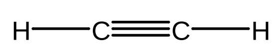
examples...



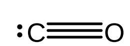
Be is sp
Cl is sp^3



C is sp
S's are sp^3



both C's are sp

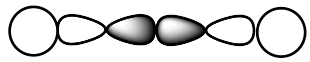


C & O are sp

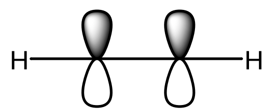
How would one draw the orbitals of HC≡CH?

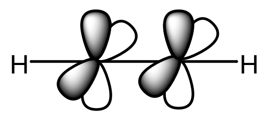
2 σ bonds so the carbon is sp hybridized.

The sp's form the σ bonds.

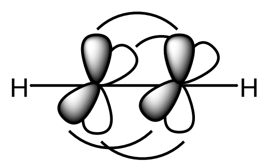


2P orbitals are left over on each carbon.



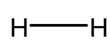


The left over p orbitals form the π bonds.



d. one orbital is needed then either someone made a mistake, or the atom in question is hydrogen.

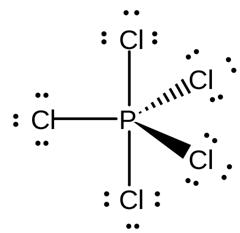
example...



H's not hybridized using s orbital

.We have described hybrids which can account for the formation of several geometries. We have not described hybrids which would allow for more than an octet of electrons.

The Lewis Structure of PCl_5 looks like....



There are 5 pairs of electrons around the P, but remember this is OK elements in the third row and higher can exceed an octet because of the presence of d orbitals.

Important points

There are 5 σ bonds present; our theory says that for each σ bond there is a hybrid orbital. We need five hybrid orbitals.

If the s and p orbitals are combined the maximum number of hybrids available is four.

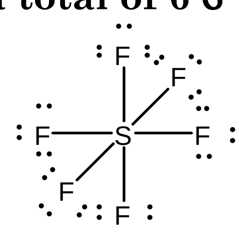
A fifth orbital has to be added to the so five hybrids can be produced.

The fifth orbital is a **d** orbital.

PCl_5 must be dsp^3

$d + s + p_x + p_y + p_z = sp^3d + sp^3d + sp^3d + sp^3d + sp^3d$

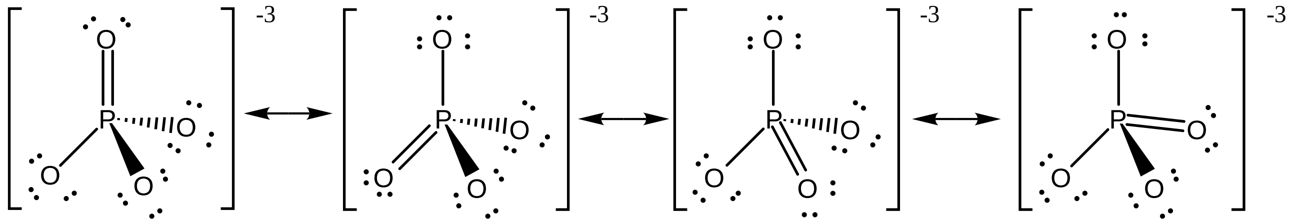
What about atoms with a total of 6 σ bond and lone pairs?



There must be six hybrids available.... so

$d + d + s + p_x + p_y + p_z = sp^3d^2 + sp^3\,d^2 + sp^3\,d^2 + sp^3\,d^2 + sp^3\,d^2 + sp^3\,d^2$

How about more complicated structures..



There are four σ bonds, so the hybridization at P must be sp^3, but how is the π bond formed?

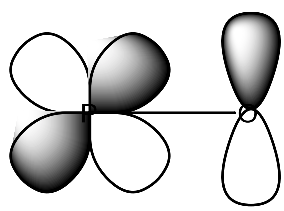
well what is the hybridization at O with the double bond?

2 p + 1 s = 3 hybrids

so,

sp^2 with a p left over

but P does not have a **p** left over so how does the π bond form? When an octet is expanded **d** orbitals become involved, so the π forms from a **d** orbital on the P and a **p** orbital on the O.



Well, now that you have figured out this new bonding model; it is time to show you how this model fails!