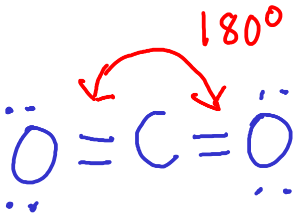
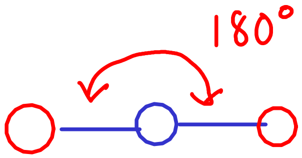
PREDICTING MOLECULAR SHAPE

The shape of simple molecules (and parts of larger molecules) can be easily predicted using the VSEPR model

VSEPR = Valence Shell Electron Pair Repulsion Model

- Each BOND or LONE PAIR OF ELECTRONS around an atom will try to move itself as far away from other bonds or lone pairs as possible!

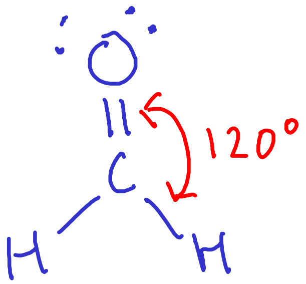


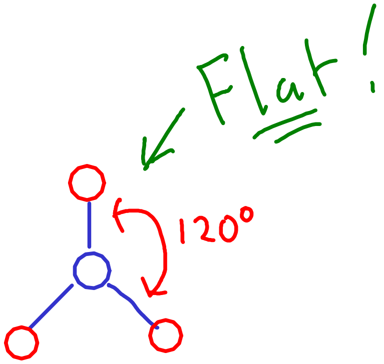


For the two red circles to be farthest apart, they must be 180 degrees apart

LINEAR MOLECULES

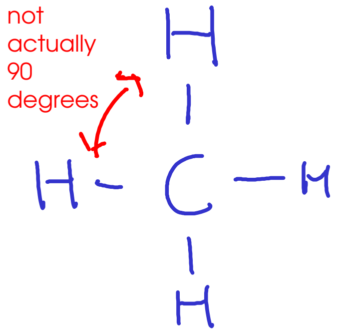
ANY diatomic (two-atom) molecule is linear, but only some three-atom molecules are!





For the three red circles to be farthest apart, they spread out so that each is 120 degrees from the others!

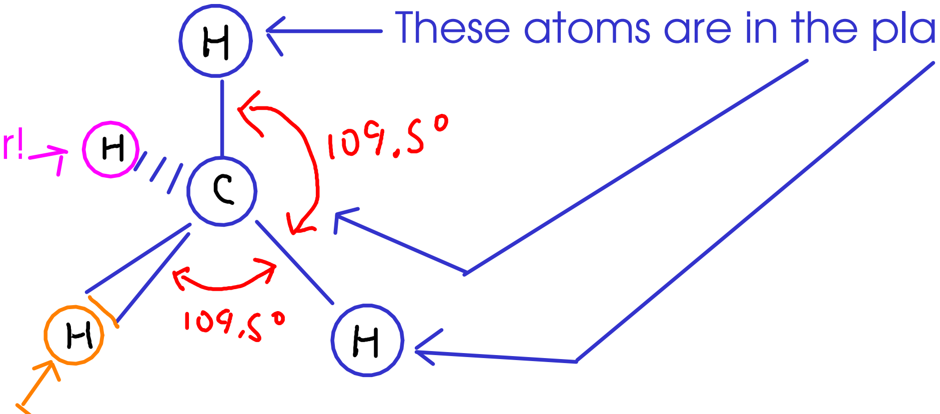
TRIGONAL
PLANAR
MOLECULES



not actually 90 degrees

These hydrogen atoms might appear at first glance to be 90 degrees apart, but remember that molecules exist in THREE DIMENSIONS, not two!

Each hydrogen atom is actually 109.5 degrees apart, forming a TETRAHEDRON.



These atoms are in the plane of the paper!

This atom is behind the paper!

This atom is pointing out at you!

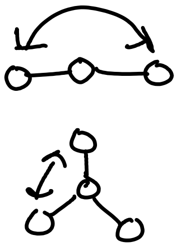
To see the tetrahedron in three dimensions WITHOUT buying a molecular model kit, just take four balloons, blow them up, and then tie them together. The knot will be the central atom, and the balloons will line themselves up to be 109.5 degrees apart.

VSEPR shapes

* "Groups" can be either BONDS or LONE PAIRS!

VSEPR shapes:

Groups* around central atom	Shape	Bond angle(s) in degrees
2	linear	180
3	trigonal planar	120
4	tetrahedral / pyramidal / bent	109.5
5	trigonal bipyramidal (and derivatives)	90 and 120
6	octahedral (and derivatives)	90

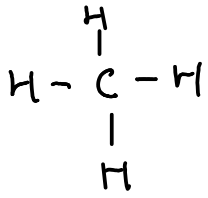


5 and 6 violate "octet rule"

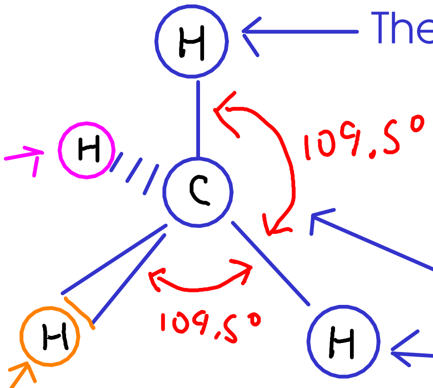
More on "4 things around a central atom":

- A compound that obeys the octet rule can have a maximum of four groups around its central atom. But we describe the molecular shape based on how ATOMS are arrnaged around the center. What if some of those groups aren't atoms, but pairs of UNSHARED electrons?

CH_4:



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$



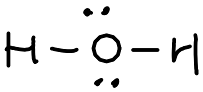
These atoms are in the plane of the paper!

This atom is behind the paper!

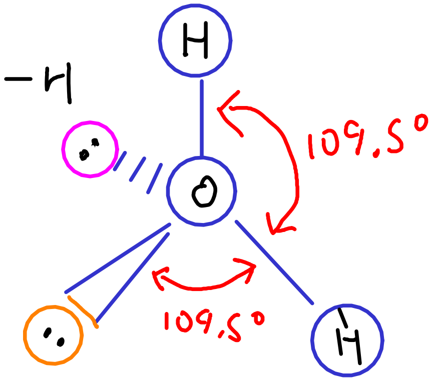
This atom is pointing out at you!

With four ATOMS around the center, we call the shape "TETRAHEDRAL"

H_2O:

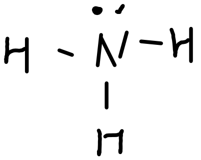


$$H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H$$

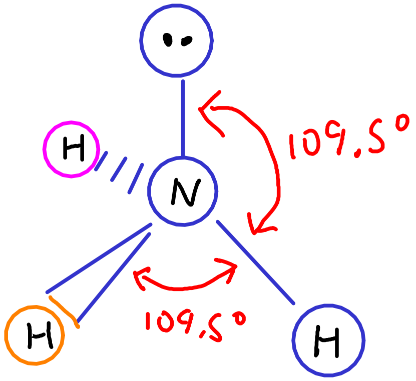


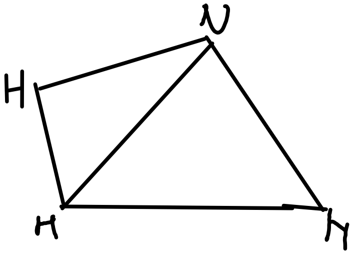
With two ATOMS and two LONE PAIRS, we call the shape "BENT"

NH_3:



$$\begin{array}{c} H-\overset{\cdot\cdot}{N}-H \\ | \\ H \end{array}$$

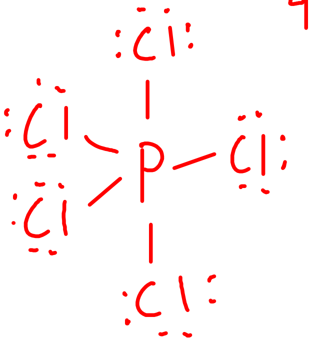




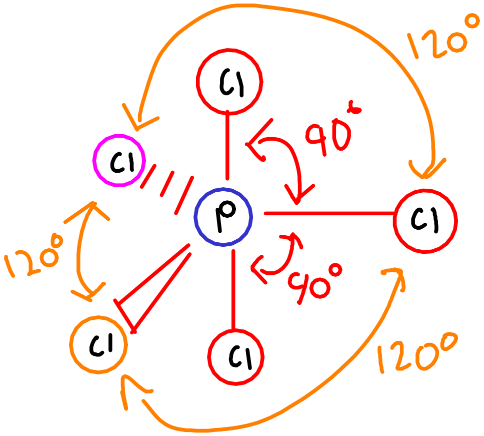
With three ATOMS and one LONE PAIR, we call the shape "PYRAMIDAL"

SHAPES OF EXPANDED VALENCE MOLECULES

PCl_5 : P : 5
Cl : 7 × 5
40

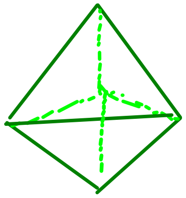


There are five atoms bonded to the central phosphorus atom, and they will attempt to get as far apart as possible from one another!



The top and bottom atoms are 90 degrees apart from the atoms around the center.

The atoms around the center are 120 degrees apart from each other.

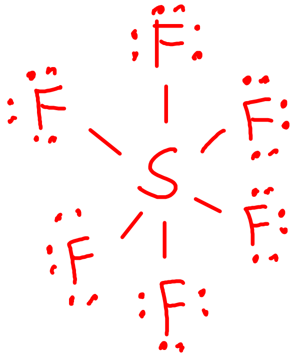


There are acually two DIFFERENT bond angles in this structure. It's called TRIGONAL BIPYRAMIDAL.

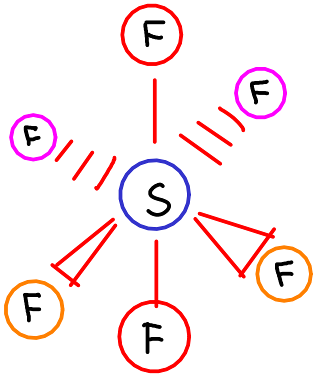
There are several derivatives of the trigonal bipyramidal shape (like the tetrahedral shape) - depending on how many things around the central atom are atoms!

SF_6:

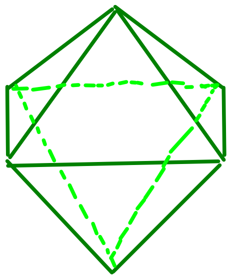
S: 6
F: 7x6
48



There are six atoms bonded to the central sulfur atom, and they will attempt to get as far apart as possible from one another!



All bond angles in this arrangement are 90 degrees!



This shape is called OCTAHEDRAL, since it has eight sides.

Like the tetrahedral and trigonal bipyramidal arrangements, there are several derivatives of the octahedron - depending on how many of the six things around the center are atoms!

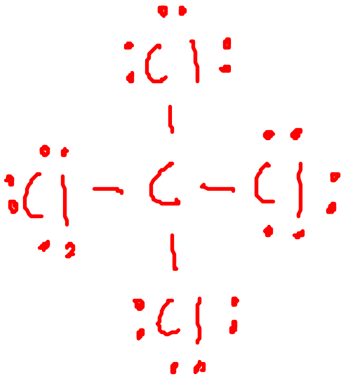
Examples:

CCl_4

$C: 1 \times 4$

$Cl: 4 \times 7$

$32\ e^-$



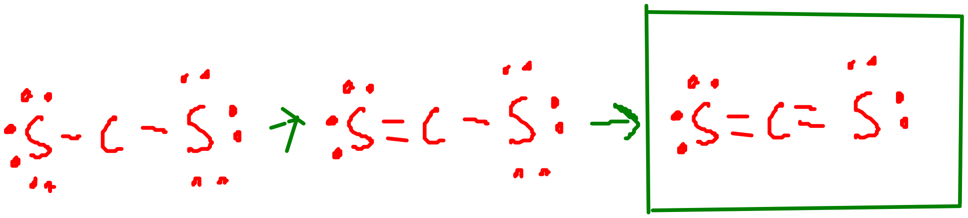
Shape and geometry? There are FOUR things around the central carbon (tetrahedral geometry), and all four are atoms (tetrahedral shape).

CS_2

$C: 1 \times 4$

$S: 2 \times 6$

$16\ e^-$



skeletal structure

final structure

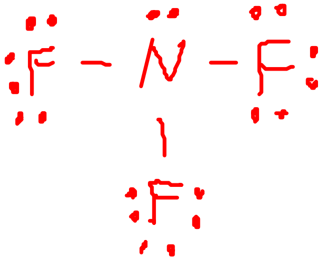
Shape and geometry? There are TWO things around the central carbon (linear geometry) and both are atoms (linear shape)

NF_3

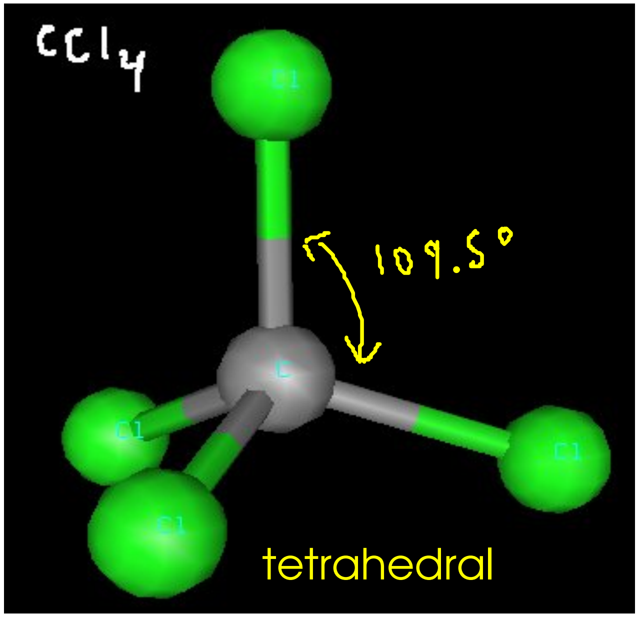
$N: 1 \times 5$

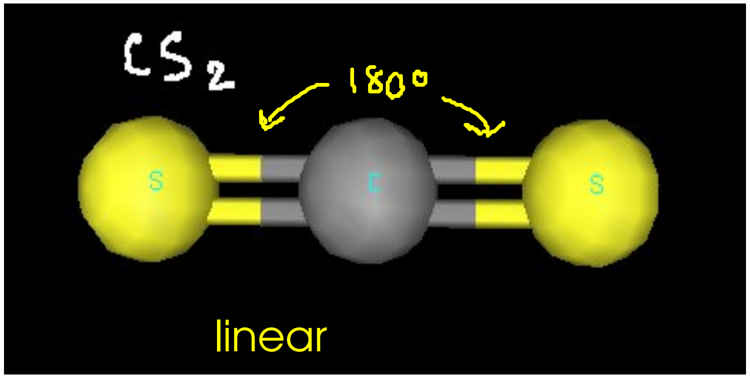
$F: 3 \times 7 = 21$

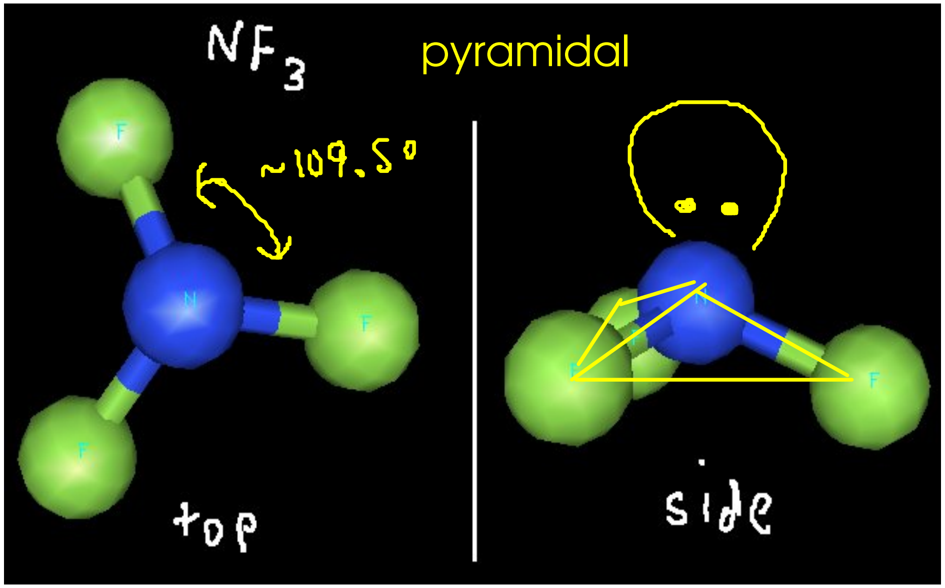
$26\ e^-$



Shape and geometry? There are FOUR things around the central nitrogen (tetrahedral geometry), but only three are atoms (pyramidal shape).

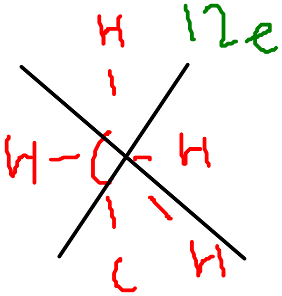

CCl4
Cl
109.5°
C
Cl
Cl
Cl
tetrahedral


CS2
180°
S
C
S
linear

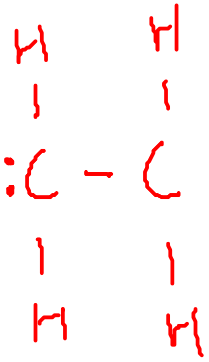

NF3
pyramidal
F
~109.5°
N
F
F
top
N
F
F
side

C_2H_4

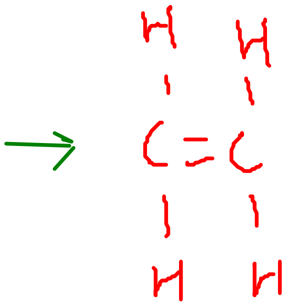
C: 2 × 4
H: 4 × 1
$12e^-$



Structure tip: Multiple carbon atoms mean multiple "central atoms"

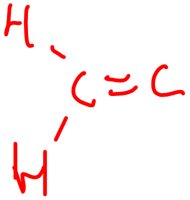


skeletal structure



final structure

Geometry and shape for each of the two carbon centers?

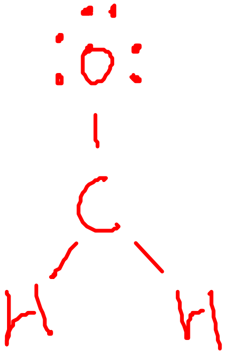


The carbon on the left has THREE things attached, and all are atoms: TRIGONAL PLANAR.

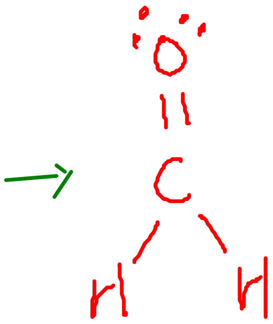
The carbon on the right is identical. Both centers are TRIGONAL PLANAR.

H_2CO

H : 2 × 1
C : 1 × 4
O : 1 × 6
$12e^-$

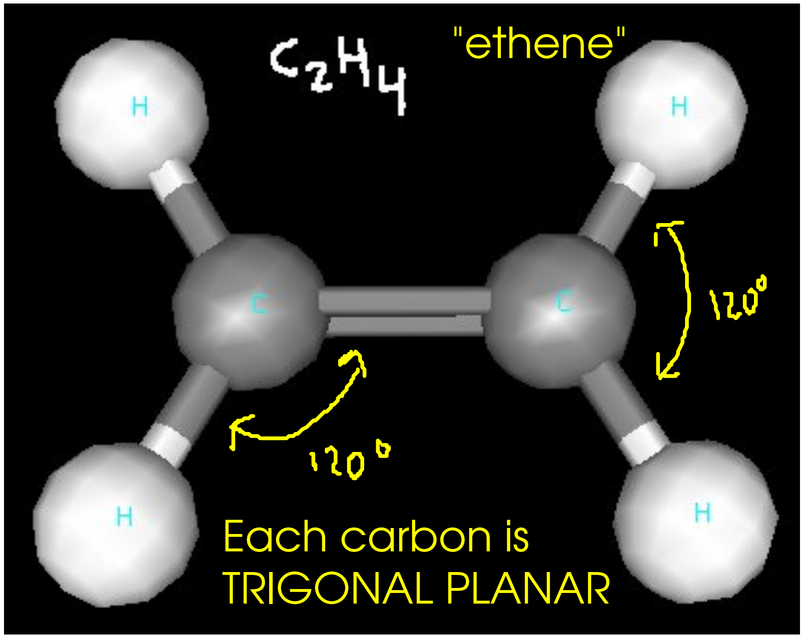


skeletal structure



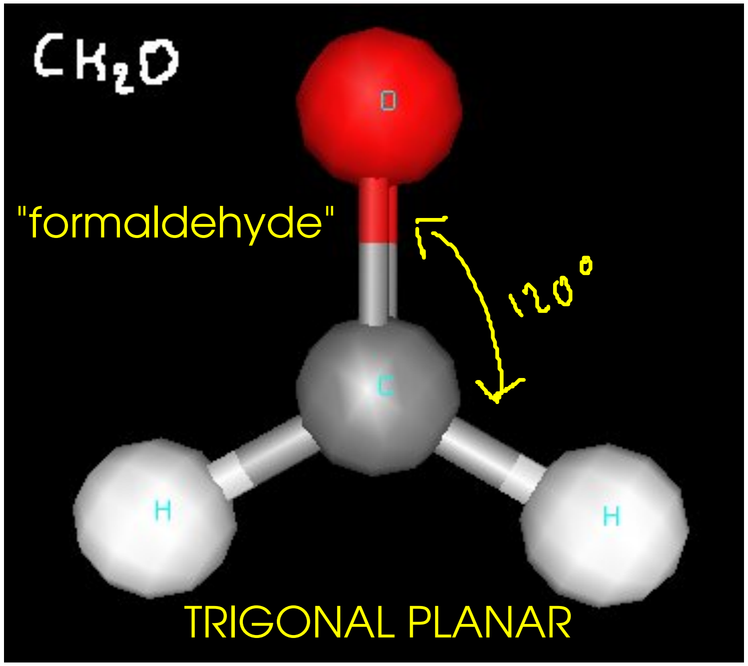
final structure

Geometry and shape? There are three things around the central carbon and all are atoms: TRIGONAL PLANAR.



C_2H_4 "ethene"

Each carbon is TRIGONAL PLANAR



CH_2O

"formaldehyde"

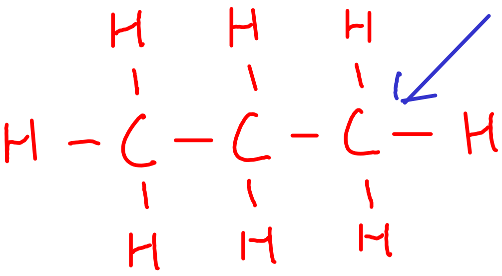
TRIGONAL PLANAR

VSEPR and large molecules

- Large molecules have more than one "center" atom

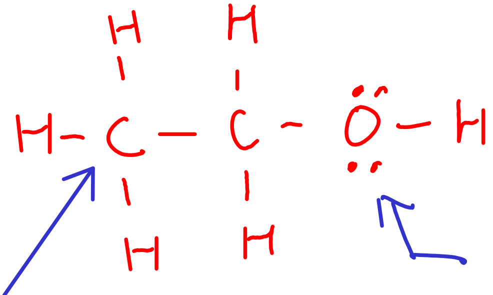
- Describe the molecule by describing the shape around each "center".

C_3H_8:



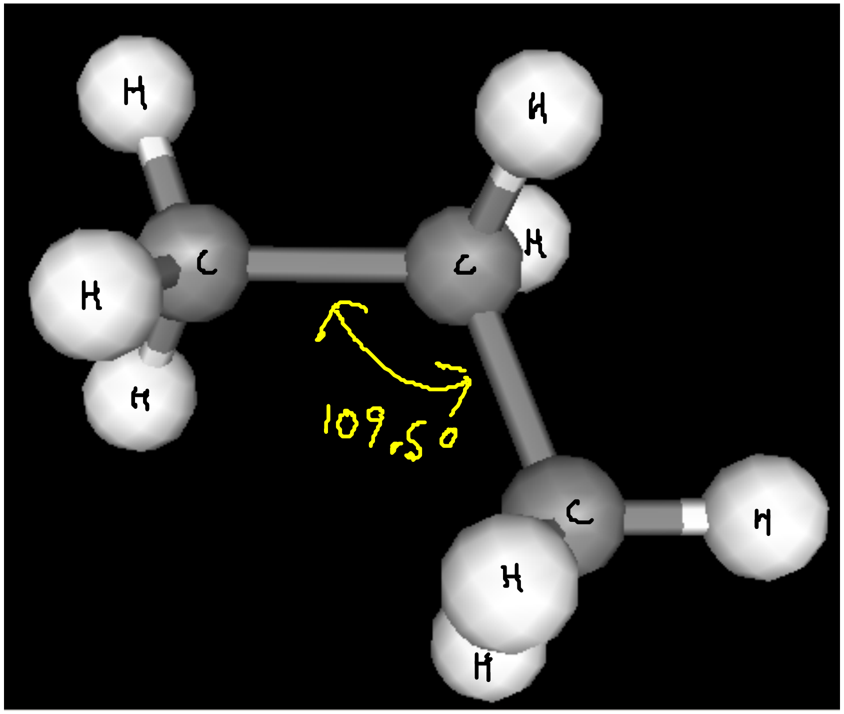
Each of the three carbon centers is TETRAHEDRAL, since each are surrounded by four groups.

CH_3CH_2OH:



The shape around this oxygen atom is BENT.

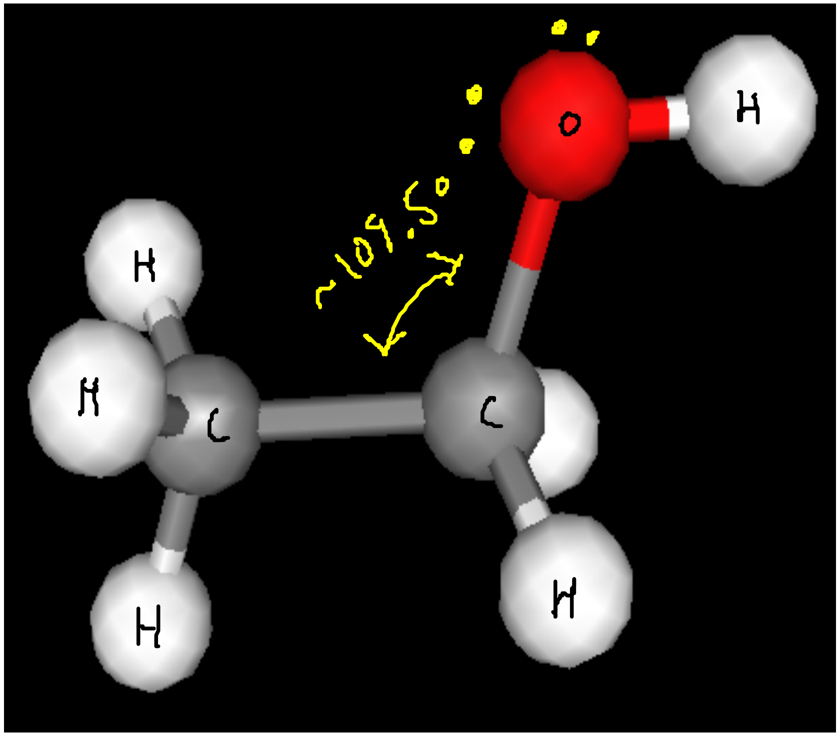
These carbon atoms have TETRAHEDRAL geometry.



C_3H_8

All bond angles in the propane molecule are 109.5 degrees

CH_3CH_2OH



Like propane, the bond angles in ethanol are also close to 109.5 degrees.

POLARITY and shape:

- A polar molecule has an uneven distribution of electron density, making it have ends (poles) that are slightly charged.

POLARITY influences several easily observable properties.

- Melting point. (Polar substances have higher melting points than nonpolar substances of similar molecular weight.)
- Boiling point. (Polar substances have higher boiling points than nonpolar substances of similar molecular weight.)
- Solubility. (Polar substances tend to dissolve in other polar substances, while being insoluble in nonpolar substances. Nonpolar substances dissove other nonpolar substances, and generally have poor solubility in polar solvents.)

- Polar molecules contain POLAR BONDS arranged in such a way that they do not cancel each other out.

... but how can we tell whether or not a bond will be POLAR? Use experimental data on ELECTRONEGATIVITY!

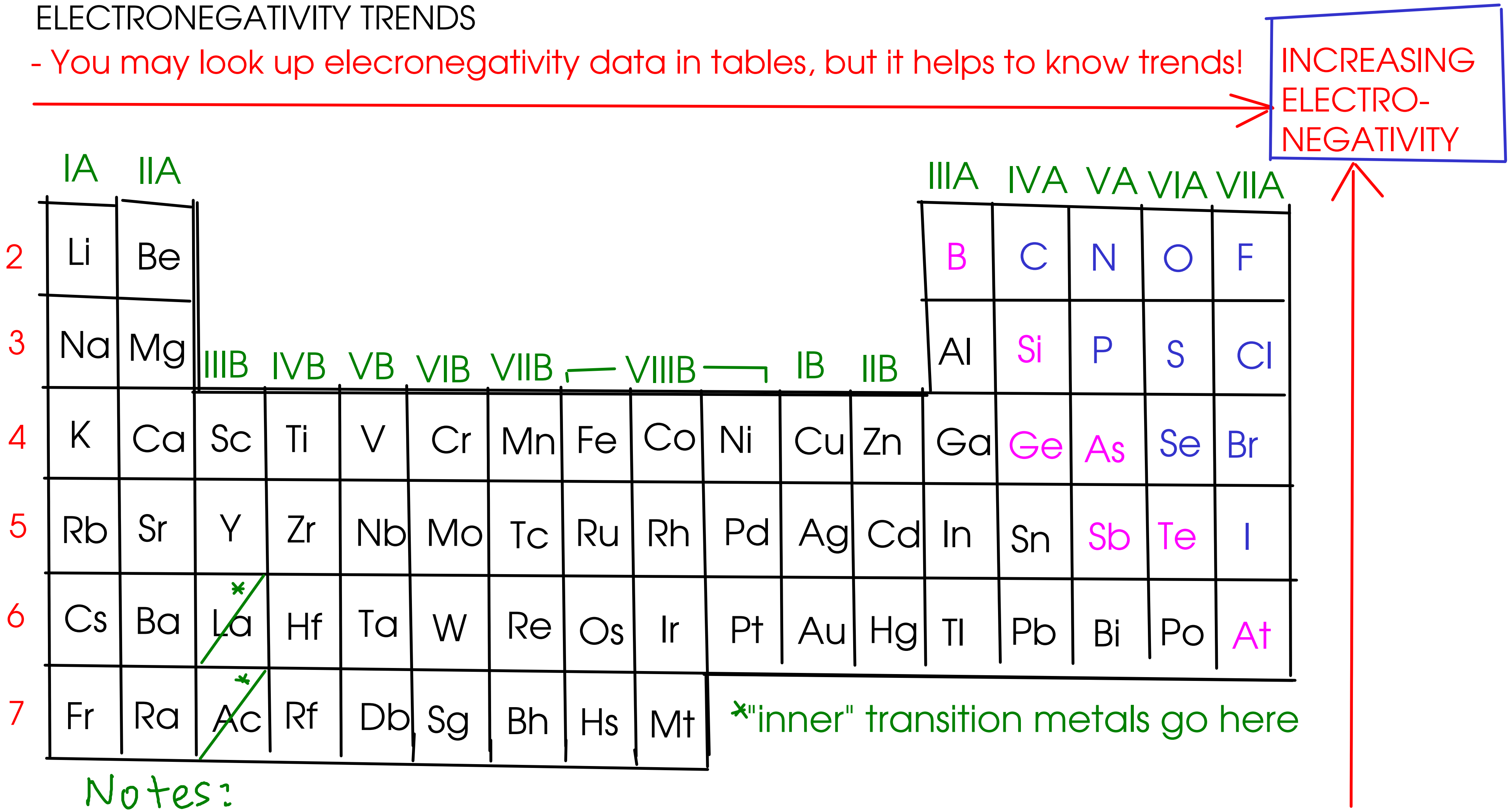
ELECTRONEGATIVITY:
-A measure of how closely to itself an atom will hold shared electrons

- A bond where there is a LARGE electronegativity difference between atoms will be either POLAR or (for very large differences) IONIC! (chart, p 352)

- A bond with little or no electronegativity difference between atoms will be NONPOLAR

ELECTRONEGATIVITY TRENDS

- You may look up elecronegativity data in tables, but it helps to know trends!



	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA
2	Li	Be											B	C	N	O	F
3	Na	Mg											Al	Si	P	S	Cl
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
6	Cs	Ba	* ~~La~~	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
7	Fr	Ra	* ~~Ac~~	Rf	Db	Sg	Bh	Hs	Mt								

*"inner" transition metals go here

Notes:

① - FLUORINE is the most elecronegative element, while FRANCIUM is the least!

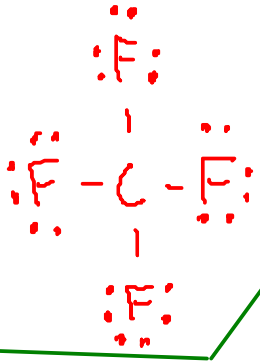
② - All the METALS have low electronegativity, and metal/nonmetal combinations form IONIC bonds

③ - HYDROGEN is similar in electronegativity to CARBON, so C-H bonds are considered NONPOLAR

Examples:

CF_4

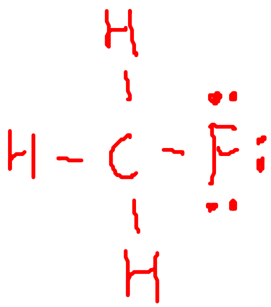
C: 1x4
F: 4x7
32e^-



Polar? (1) POLAR BONDS? Yes! C-F should be polar.
(2) GEOMETRY? TETRAHEDRAL. This molecule is symmetrical (fluorines at each site), so you can't get one side of the molecule positive and the other negative. It's NONPOLAR.

CH_3F

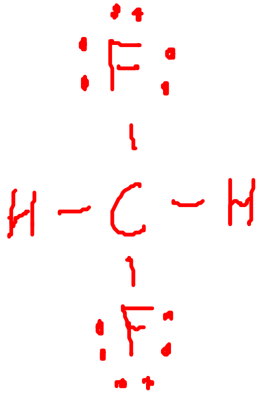
C: 1x4
H: 3x1
F: 1x7
14e^-



Polar? (1) POLAR BONDS? Yes! C-F should be polar, even though C-H isn't.
(2) GEOMETRY? TETRAHEDRAL. This molecule is POLAR, since the fluorines will pull electrons to their side of the molecule, leaving the hydrogen side positively charged.

CH_2F_2

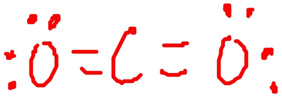
C: 1x4
H: 2x1
F: 2x7
20e^-



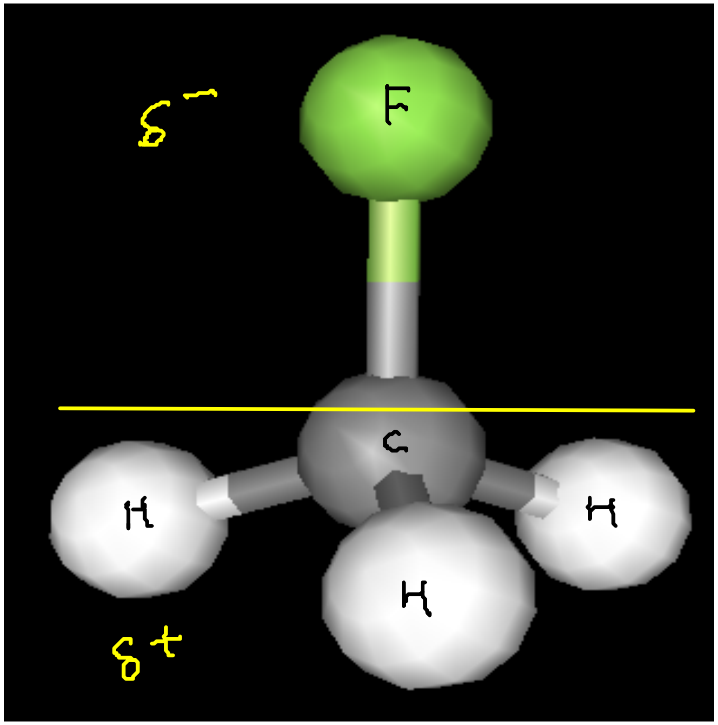
Polar? (1) POLAR BONDS? Yes! C-F should be polar, even though C-H isn't.
(2) GEOMETRY? TETRAHEDRAL. This molecule is POLAR, since the fluorines will pull electrons to their side of the molecule, leaving the hydrogen side positively charged.

CO_2

C: 1x4
O: 2x6
16e^-



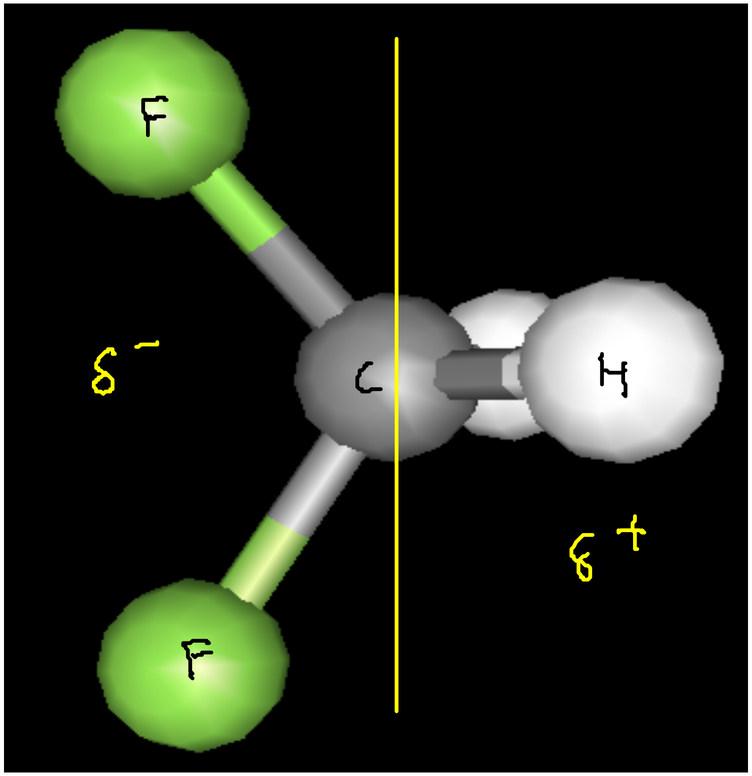
Polar? (1) POLAR BONDS? Yes! C=O is polar.
(2) GEOMETRY? LINEAR. This is a symmetric molecule, though. (Both polar bonds arranged opposite one another), so the molecule is NONPOLAR.



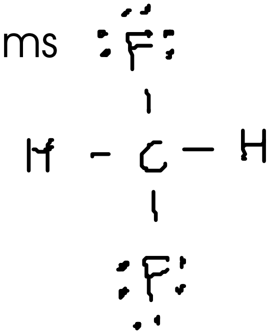
← CH_3F "fluoromethane"

Fluorine is able to pull electron density through the molecule, as it is being opposed by much less electronegative hydrogen atoms.

"difluoromethane" CH_2F_2 →



In 2D, the fluorine atoms appear to be on the opposite sides of the molecule, but in 3D they are on the same side.



$$\begin{array}{ccccc} & & :\ddot{F}: & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & :\ddot{F}: & & \end{array}$$

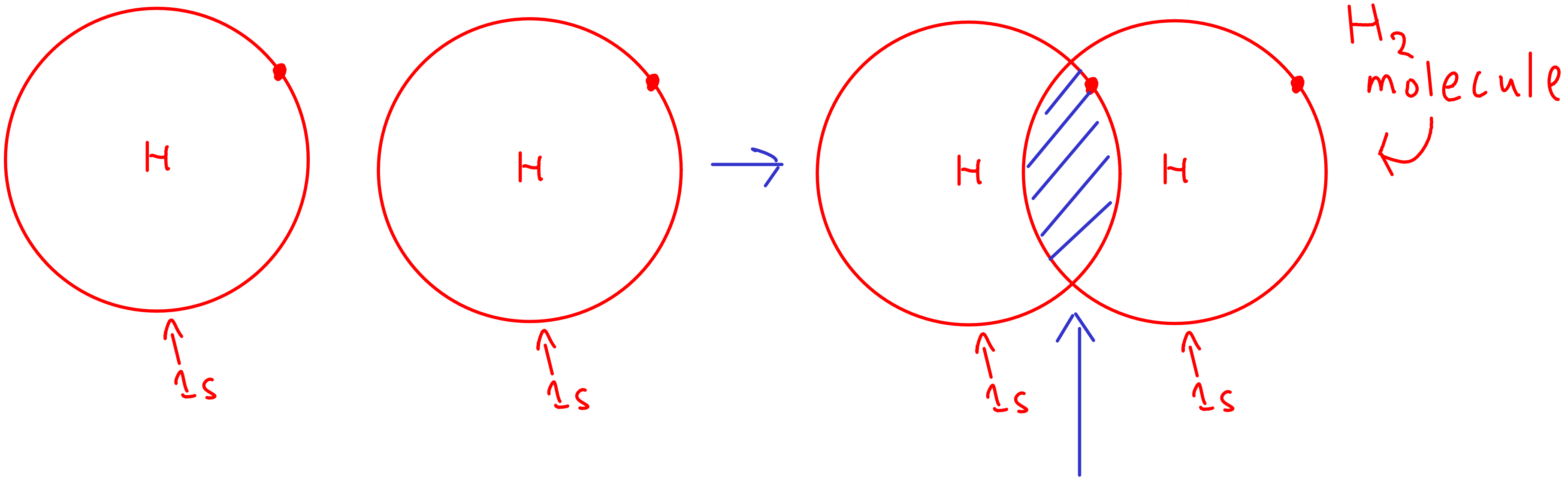
VALENCE BOND THEORY

- an attempt to explain why molecules behave in the way that the VSEPR model predicts.

- Describes the formation of bonds in terms of the OVERLAP of ORBITALS from the bonding atoms.

① Bonds are formed when two atoms are close enough together so that their ORBITALS OVERLAP (share the same space).

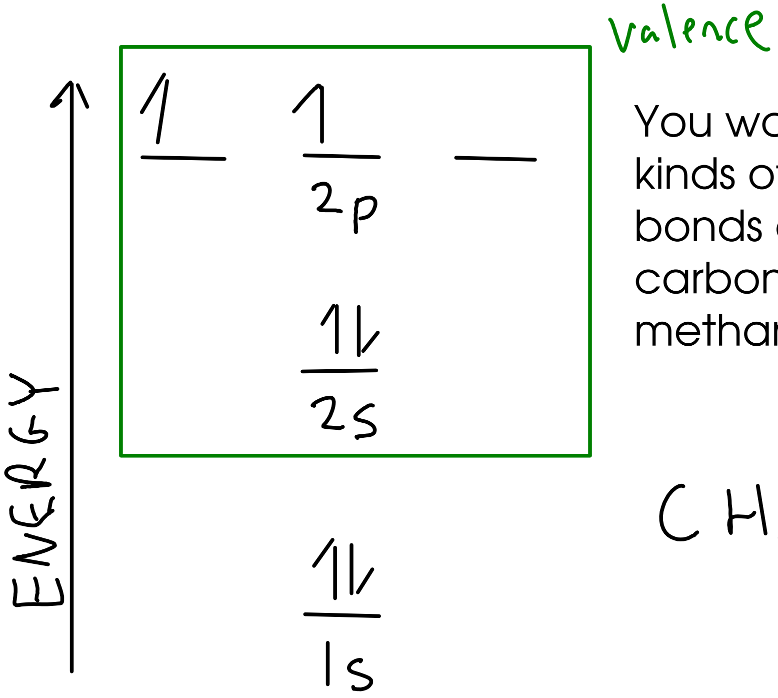
② Each SET of overlapping orbitals can contain at most a total of TWO electrons. So, two orbitals with one electron each may bond. An orbital with two electrons can only bond with an EMPTY orbital (This is called a COORDINATE COVALENT BOND.) *Ag^+ with $:NH_3$... the cleanup in the AgCl lab



These 1s orbitals overlap to form what we call a "sigma bond" with overlap BETWEEN the two atomic nuclei.

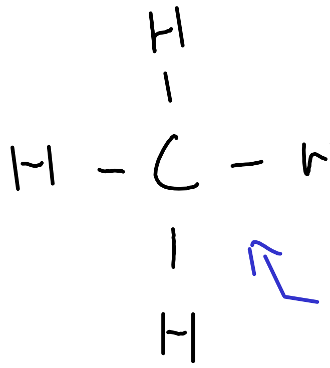
Hybridization

- Look at carbon's electron configuration:



You would expect that carbon would form several different kinds of bonds in a molecule like methane. But, methane's bonds are experimentally all identical. How does carbon form the four equivalent C-H bonds we see in methane?

CH_4 :



We observe that these bonds are IDENTICAL! Same bond energy, distance, and angle.

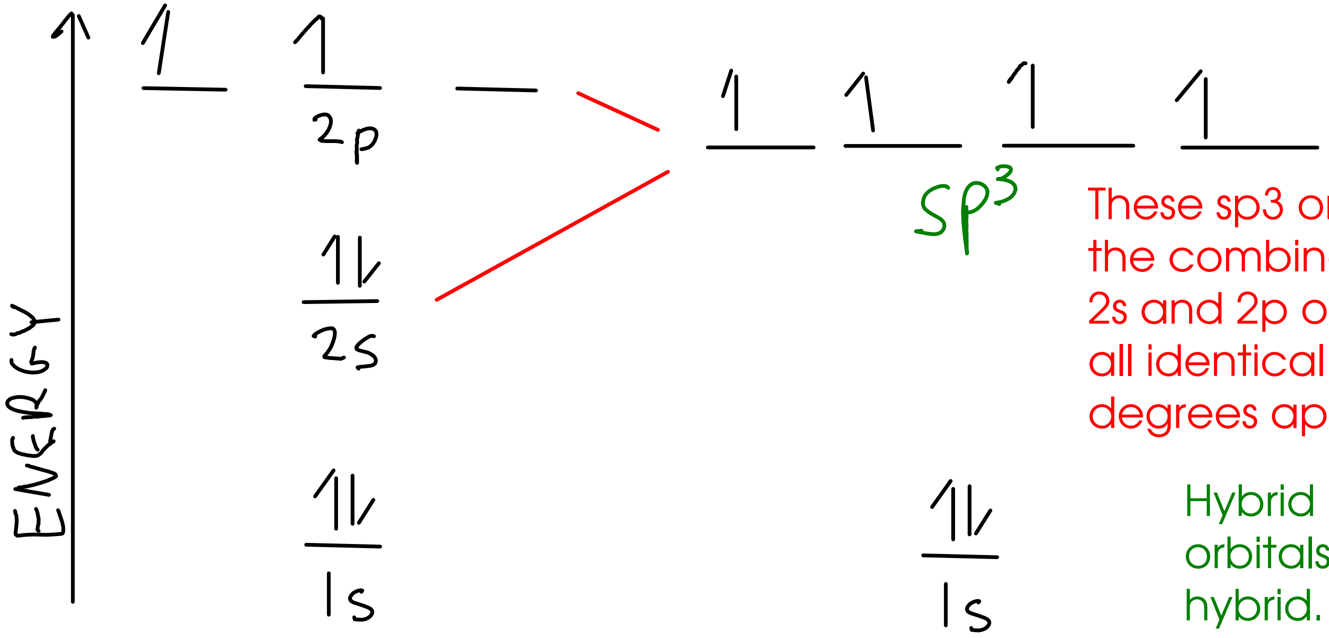
- In valence bond theory, atomic orbitals can COMBINE to make new orbitals that can then go on to bond with other molecules.

- When orbitals combine to make HYBRID ORBITALS, ...

① The overall NUMBER OF ORBITALS does not change.

② The overall NUMBER OF ELECTRONS around the atom does not change

③ The energy of the orbitals is between the energies of the orbitals that combine.



These sp3 orbitals were formed from the combination of carbon's original 2s and 2p orbitals. These orbitals are all identical, and are spread 109.5 degrees apart from one another.

Hybrid orbitals are named from the orbitals that go into making the hybrid. 2s + 3 2p orbitals = "sp3"!

p402: picture of hybrids (p401, 10th ed)

Types of hybrid orbitals:

Hybrid type	Number of orbitals	Molecular shape
sp	2	linear
sp2	3	trigonal planar
sp3	4	tetrahedral (or derivatives)
sp3d	5	trigonal bipyramidal (or derivatives)
sp3d2	6	octahedral (or derivatives)

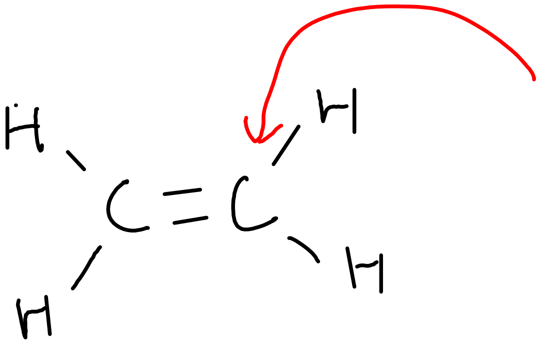
p402 : picture of hybrids
(p401, 104b)

MULTIPLE BONDS and VALENCE BOND THEORY

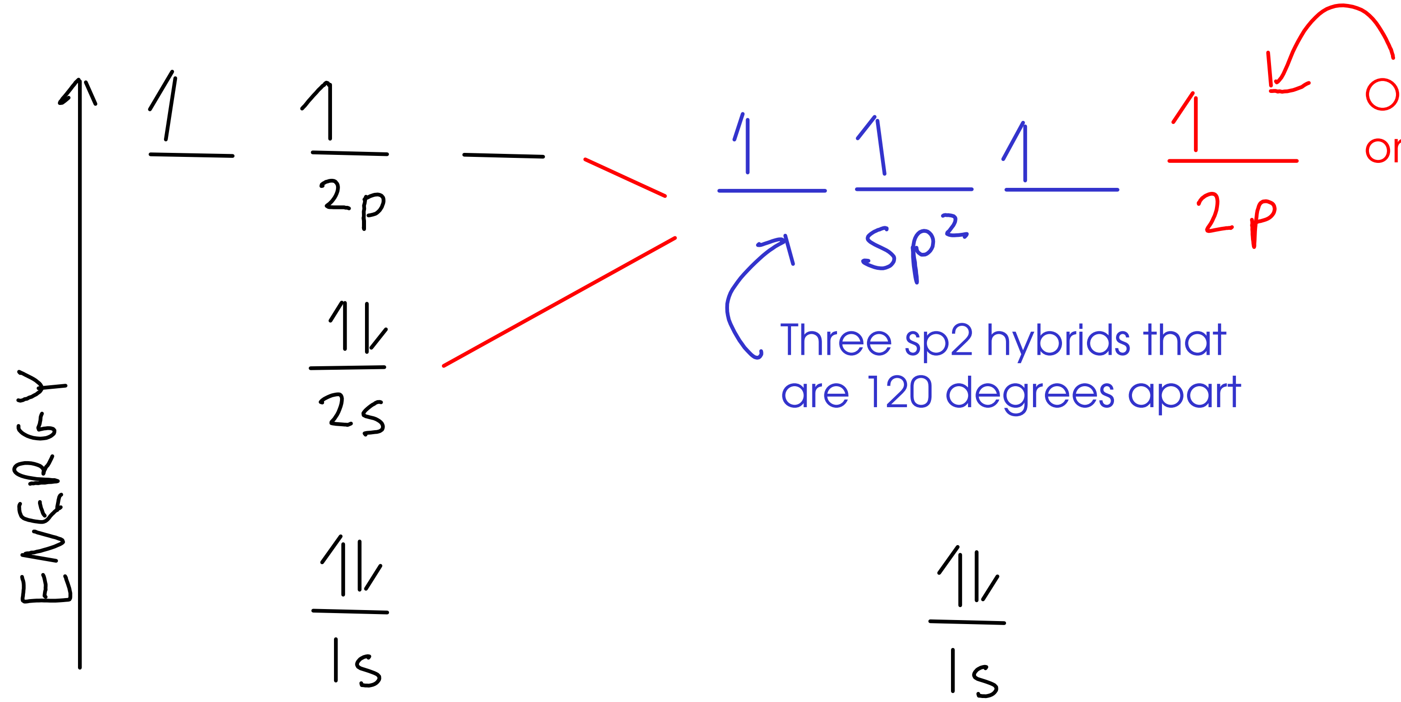
- Valence bond theory provides an explanation of multiple (double and triple) bonding that explains some interesting observations about these kinds of bonds.

C_2H_4 :

ethylene



Each carbon has a TRIGONAL PLANAR geometry. This suggests that the carbons are "sp2 hybridized".

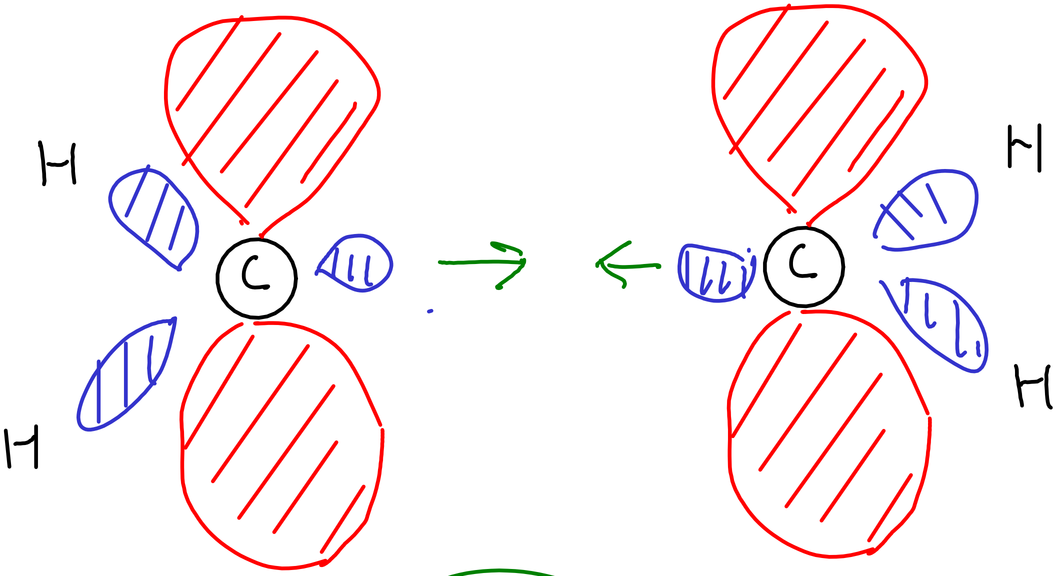


One unchanged 2p orbital

Three sp2 hybrids that are 120 degrees apart

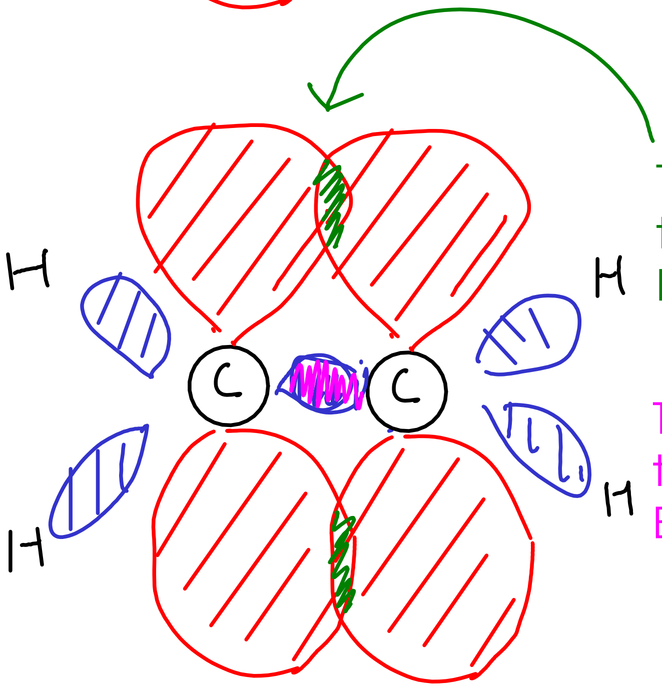
"Original" unbonded carbon atom

Carbon atom with sp2 hybrid orbitals



sp2 hybrid orbitals in BLUE

2p orbital in RED



The 2p orbitals overlap above and below the axis between the two carbon atoms. This OFF-AXIS overlap is called a PI BOND.

The sp2 hybrid orbitals overlap ON THE AXIS between the two carbon atoms. This bond is called a SIGMA BOND.

As you can see, the carbon-carbon double bond in ethylene is made up of TWO DIFFERENT KINDS OF BONDS!

Some notes on sigma and pi bonds:

① SIGMA bonds are formed when orbitals overlap along the axis between two atoms. These bonds have good overlap between the bonding orbitals, meaning that they are strong. Single bonds are always sigma bonds. Double and triple bonds contain one sigma bond each.

② PI bonds are formed when off-axis orbitals (usually p orbitals) overlap. Since the overlapping orbitals do not face each other as in the sigma bond, the overlap in pi bonds tends to be poorer than in sigma bonds, As a result, pi bonds tend to be weaker than sigma bonds. Double bonds contain a single pi bond, and triple bonds contain two pi bonds.*

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*Experimentally, we observe that the bond energy of the C=C bond is less than the bond energy of two C-C bonds. This suggests that the second bond in a double bond is different from the first!

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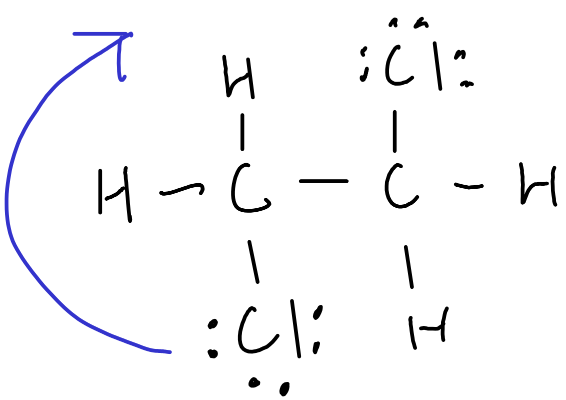
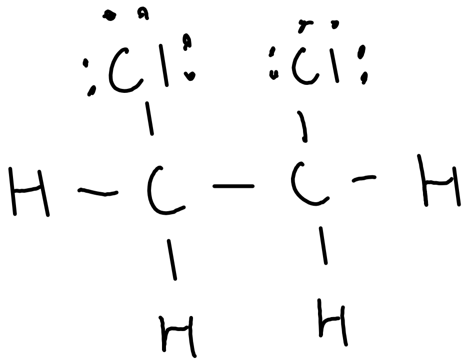
③ Molecules may rotate around SIGMA bonds, since rotation around the axis between two atoms will not affect the overlap and break the bond. Off-axis PI BONDS prevent rotation because rotation would break the pi bond.

ROTATION, ISOMERS, and VALENCE BOND THEORY

- Consider this molecule: $(CH_2Cl)_2$

"1,2-dichloroethane"

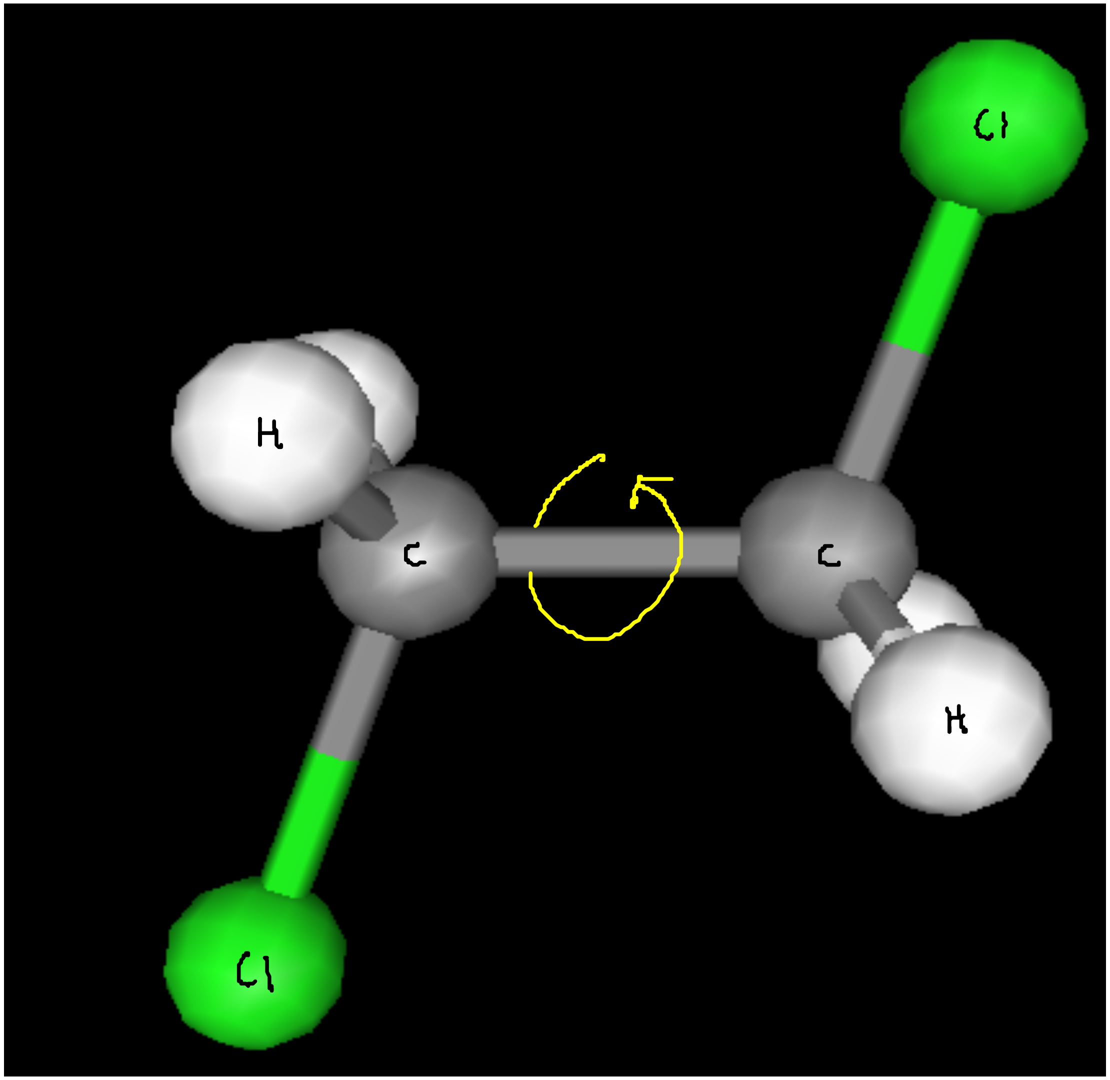




... are these two structures different?

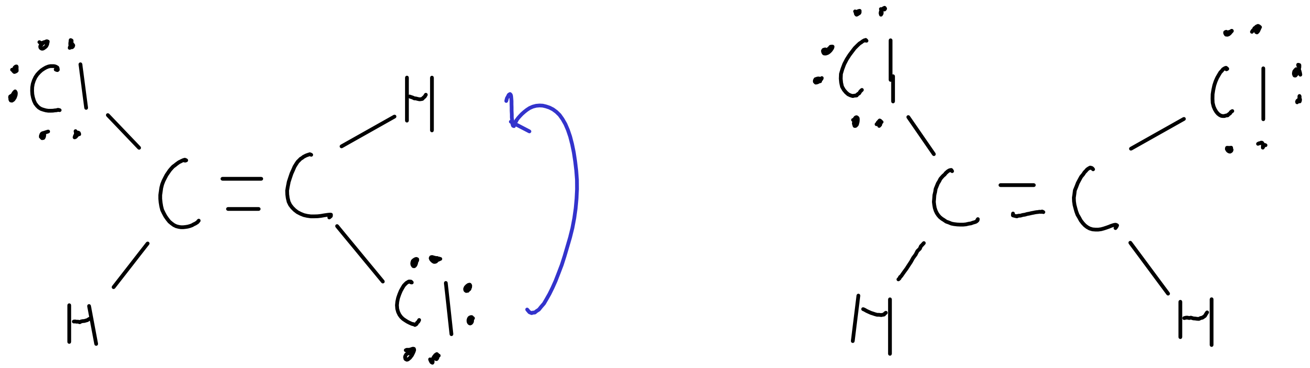
No! The molecule is free to rotate around the C-C single (sigma) bond, and we do not observe two different versions of 1,2-dichloroethane. Both of the forms drawn above are equivalent.

$(CH_2Cl)_2$



The molecule is free to rotate about the carbon-carbon bond!

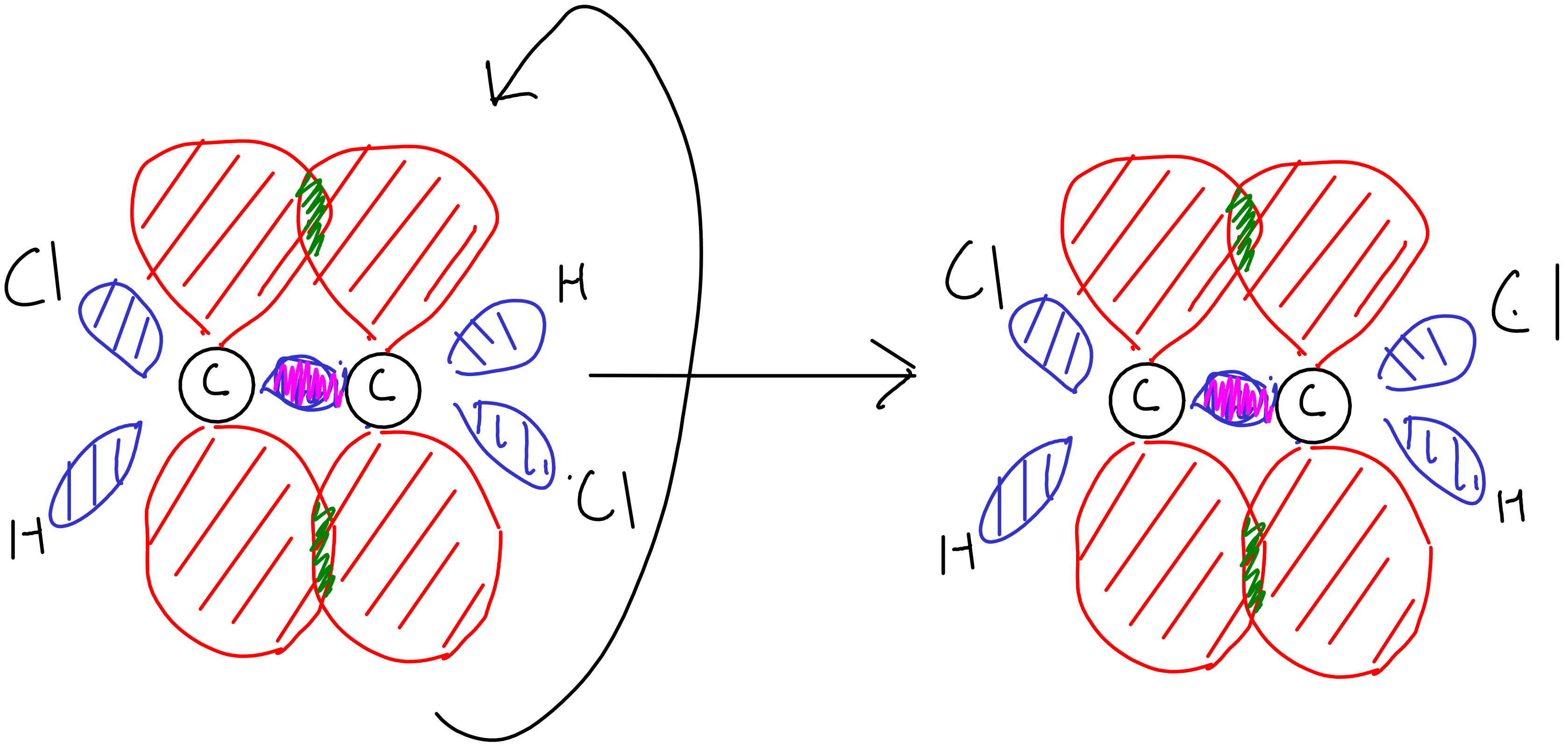
... now consider "1,2-dichloroethene": $(CHCl)_2$



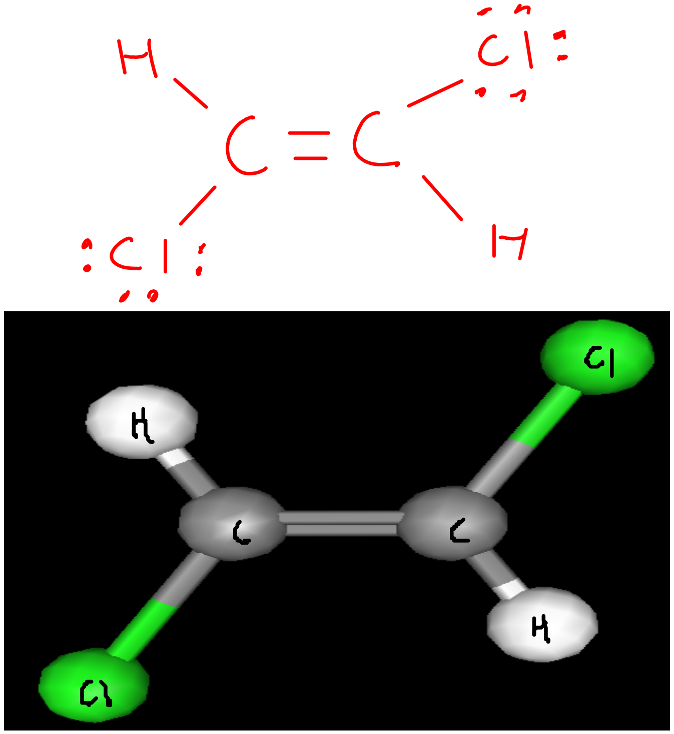
... are these two structures different?

YES! The two carbon atoms in these structures are held together by a DOUBLE BOND, which contains a pi bond. The molecule cannot rotate around the C=C double bond without breaking the pi bond, so the form with the two chlorine atoms on opposite sides cannot freely flip over to the form with the chlorine atoms on the same side.

These two Lewis structures actually represent DIFFERENT MOLECULES. They are called ISOMERS, since they have the same chemical formula but different arrangements of atoms.



For this rotation to take place, the PI BOND must break and then re-form!

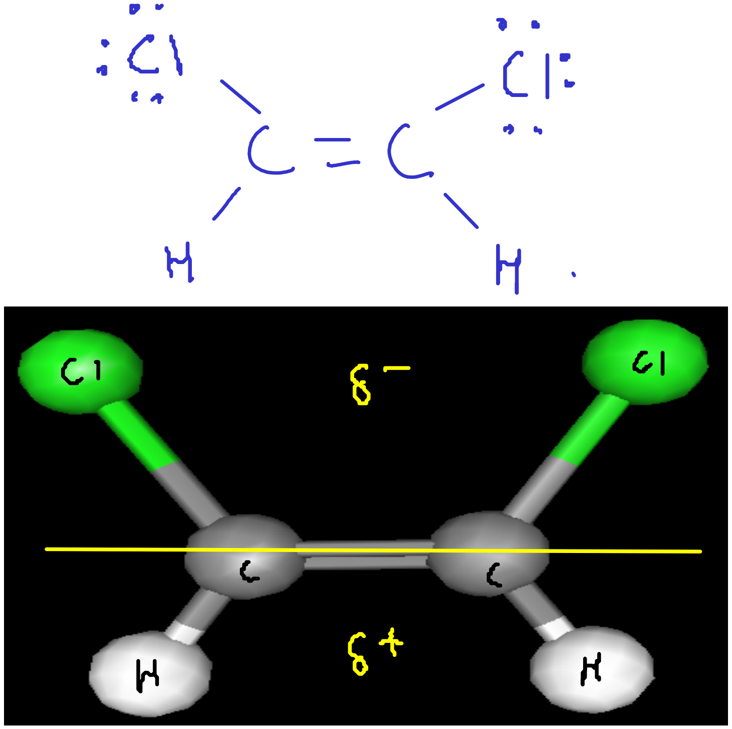


trans 1,2-dichloroethene

BOILING POINT: 47.5 C

POLARITY: NONPOLAR (0 D dipole moment)

DENSITY: 1.26 g/mL



cis 1,2-dichloroethene

BOILING POINT: 60.3 C

POLARITY: POLAR (1.9 D dipole moment)

DENSITY: 1.28 g/mL

* As you can see, some of the properties of these two molecules are very different! The presence of the pi bond (part of the double bond) in each of these molecules means conversion from one form to the other requires a chemical reaction instead of a simple rotation.

* Double (and triple) bonds prevent rotation and "fix" the structure of a molecule. This is easily explained by valence bond theory!