

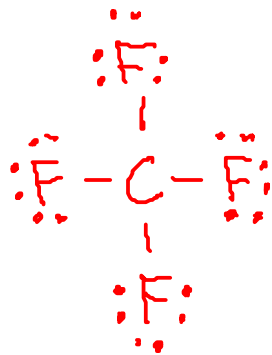
## Examples:



$$C: 4$$

$$F: 7 \times 4 = 28$$

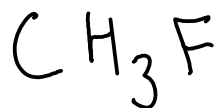
$$\hline 32$$



Polar?

\* POLAR BONDS? C-F bonds should be polar due to the electronegativity difference between C and F

\* GEOMETRY? TETRAHEDRAL. All these polar bonds are arranged around the center of the molecule symmetrically, so we don't have a "side" of the molecule that is positive (or negative) relative to the other. The molecule is NONPOLAR.

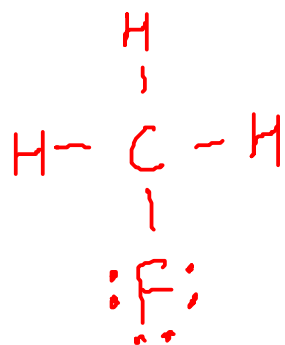


$$C: 4$$

$$F: 7$$

$$H: 1 \times 3$$

$$\hline 14$$



Polar?

\* POLAR BONDS? The C-F bond should be polar, but the C-H bonds are nonpolar.

\* GEOMETRY? TETRAHEDRAL. This molecule is polar, because the fluorine will pull electron density towards itself - at the expense of the rest of the molecule!

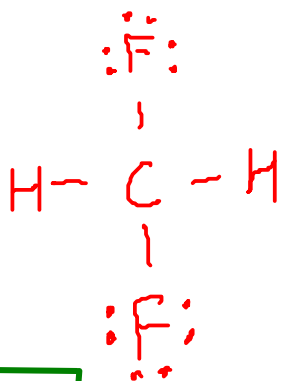


$$C: 4$$

$$F: 7 \times 2 = 14$$

$$H: 1 \times 2 = 2$$

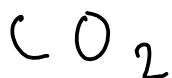
$$\hline 20$$



Polar?

\* POLAR BONDS? The C-F bonds should be polar, but the C-H bonds are nonpolar.

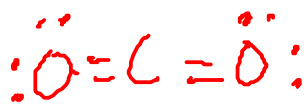
\* GEOMETRY? TETRAHEDRAL. This molecule is polar, because the fluorines will pull electron density towards their side of the molecule - at the expense of the hydrogen side!



$$C: 4$$

$$O: 6 \times 2 = 12$$

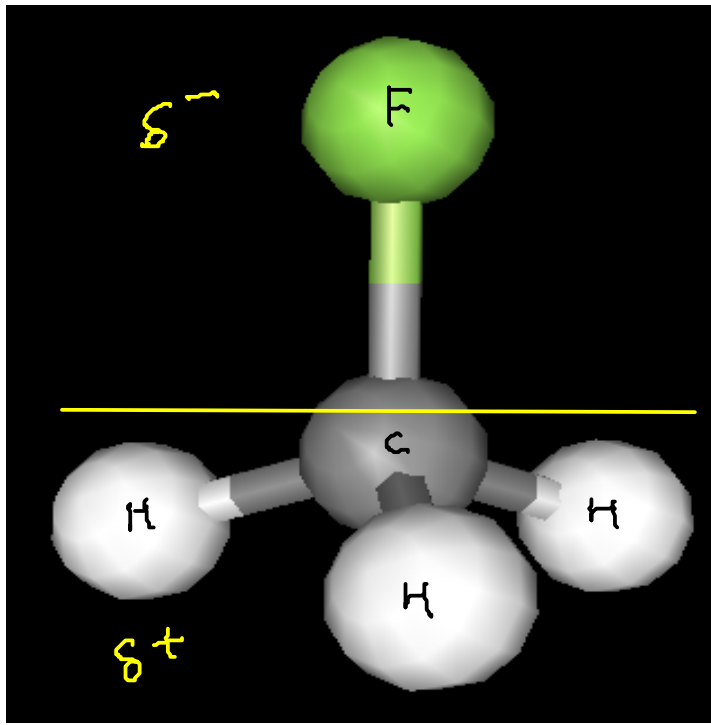
$$\hline 16$$



Polar?

\* POLAR BONDS? The C=O bonds should be polar.

\* GEOMETRY? LINEAR. This molecule is NONPOLAR, since the two C=O bonds are on opposite sides of the molecule!

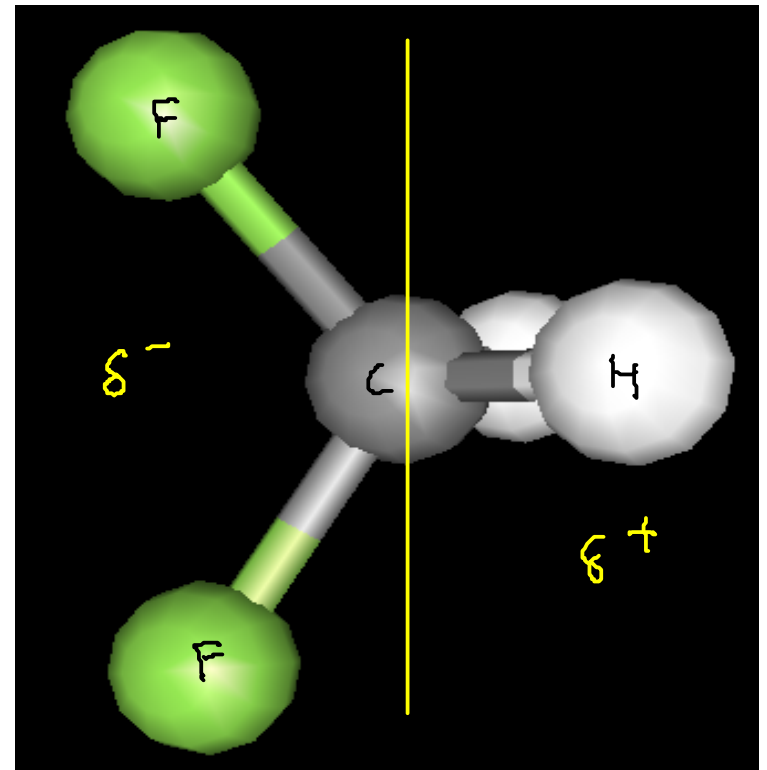
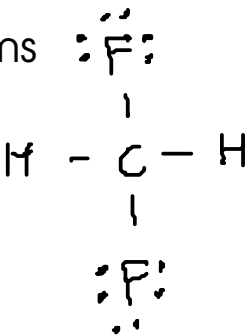


←  $\text{CH}_3\text{F}$  "fluoromethane"

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

"difluoromethane"  $\text{CH}_2\text{F}_2$  →

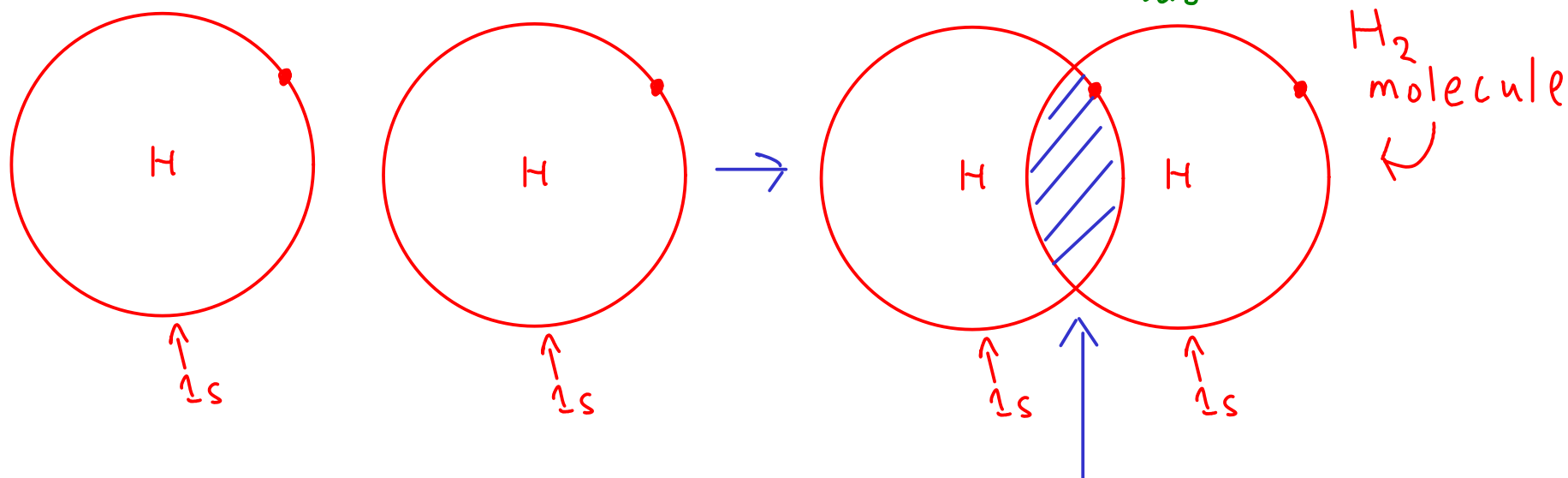
In 2D, the fluorine atoms appear to be on the opposite sides of the molecule, but in 3D they are on the same side.



## 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.

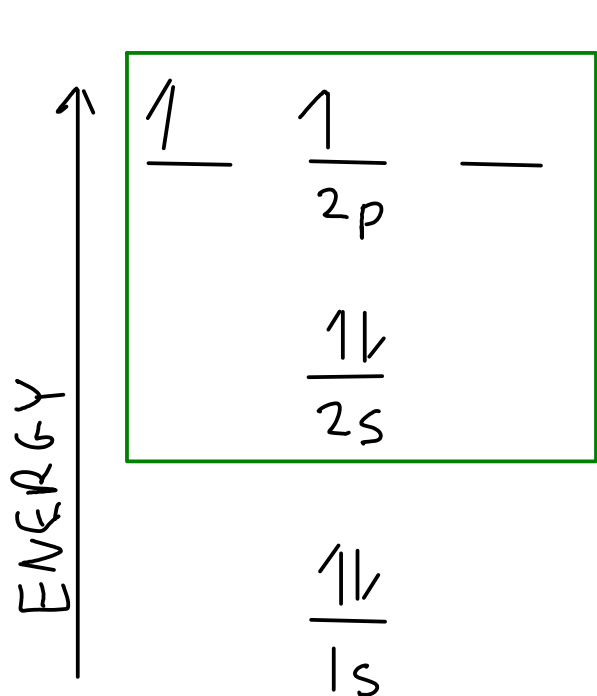
- 1 Bonds are formed when two atoms are close enough together so that their ORBITALS OVERLAP (share the same space).
- 2 Each SET of overlapping orbitals can contain at most a total of TWO electrons. So, two orbitals with one electron each may bond. An orbital with two electrons can only bond with an EMPTY orbital (This is called a COORDINATE COVALENT BOND.) *\*Ag<sup>+</sup> with :NH<sub>3</sub>... 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.

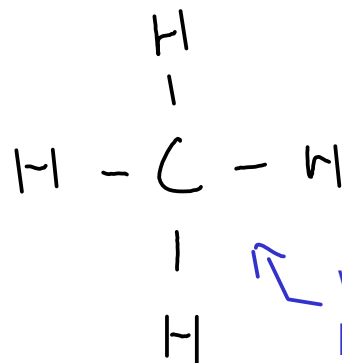
## Hybridization

- Look at carbon's electron configuration:



valence

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?

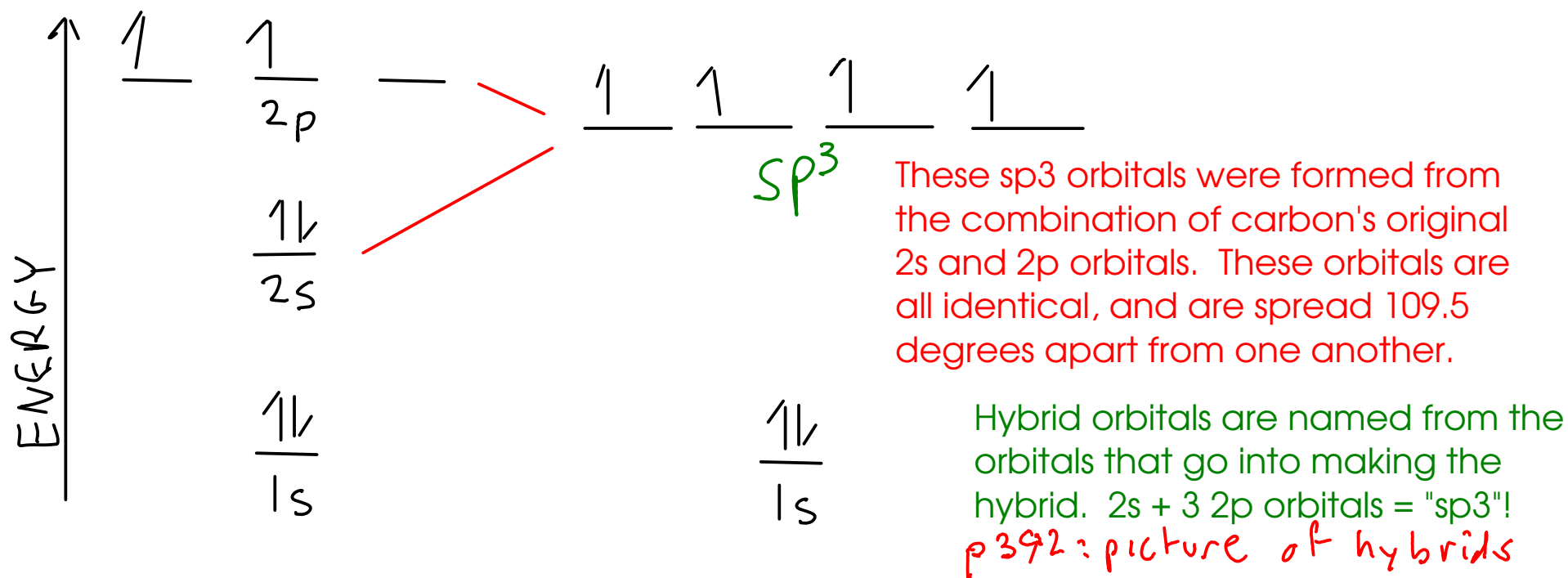


↙ We observe that these bonds are IDENTICAL! Same bond energy, distance, and angle.

- 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.



Types of hybrid orbitals:

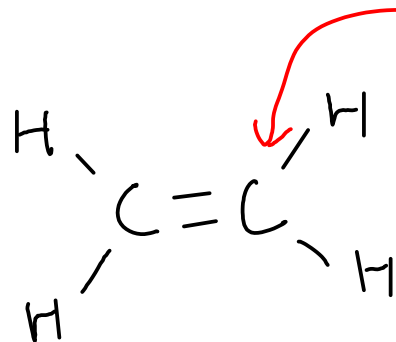
Hybrid type	Number of orbitals	Molecular shape
sp	2	linear
sp <sup>2</sup>	3	trigonal planar
sp <sup>3</sup>	4	tetrahedral (or derivatives)
sp <sup>3</sup> d	5	trigonal bipyramidal (or derivatives)
sp <sup>3</sup> d <sup>2</sup>	6	octahedral (or derivatives)

p392: picture of hybrids

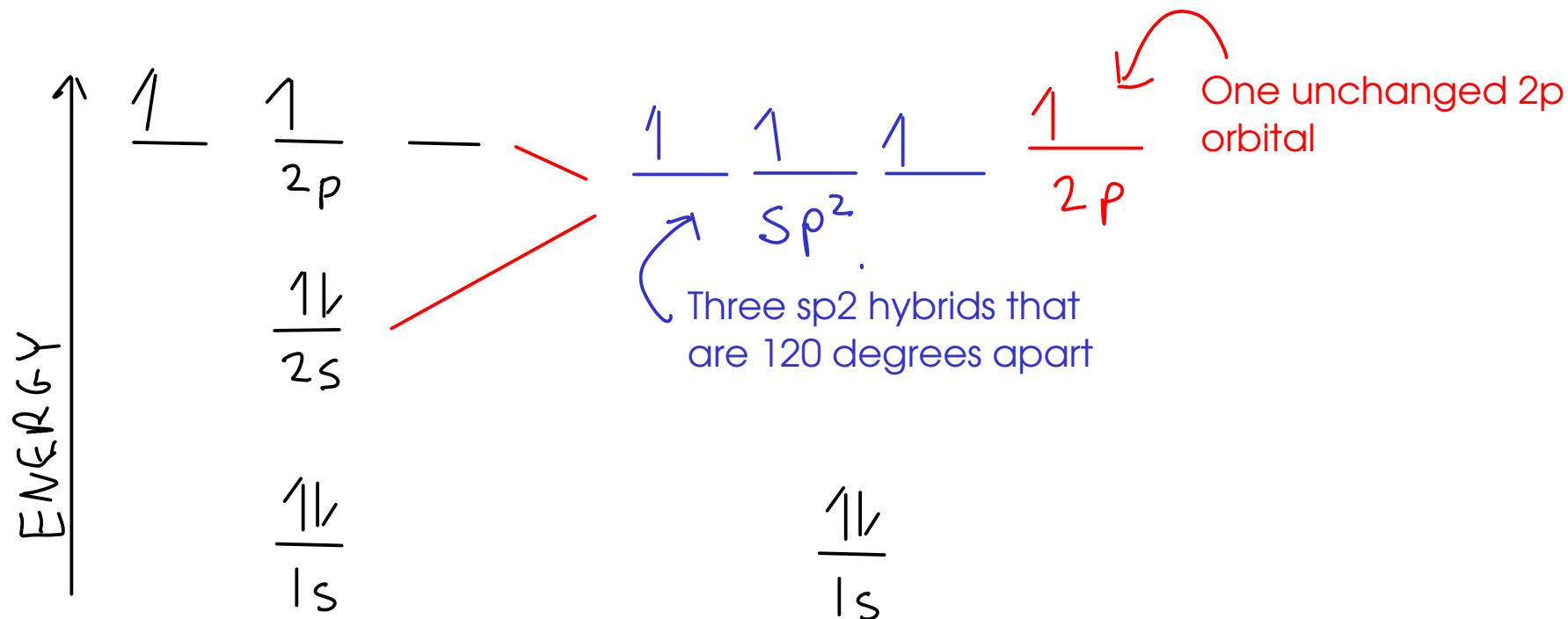
## MULTIPLE BONDS and VALENCE BOND THEORY

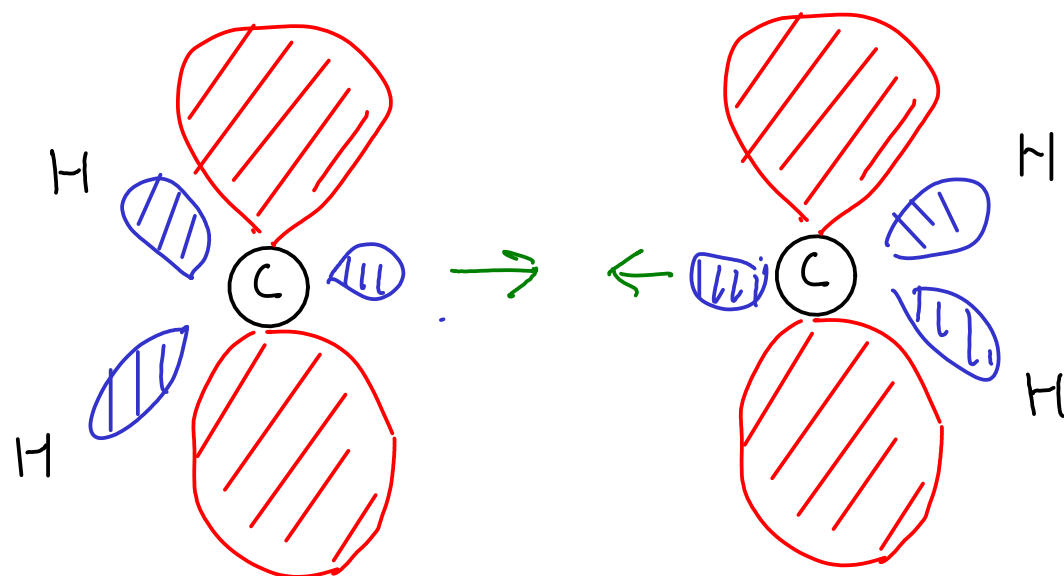
- Valence bond theory provides an explanation of multiple (double and triple) bonding that explains some interesting observations about these kinds of bonds.

$C_2H_4$  :  
ethylene



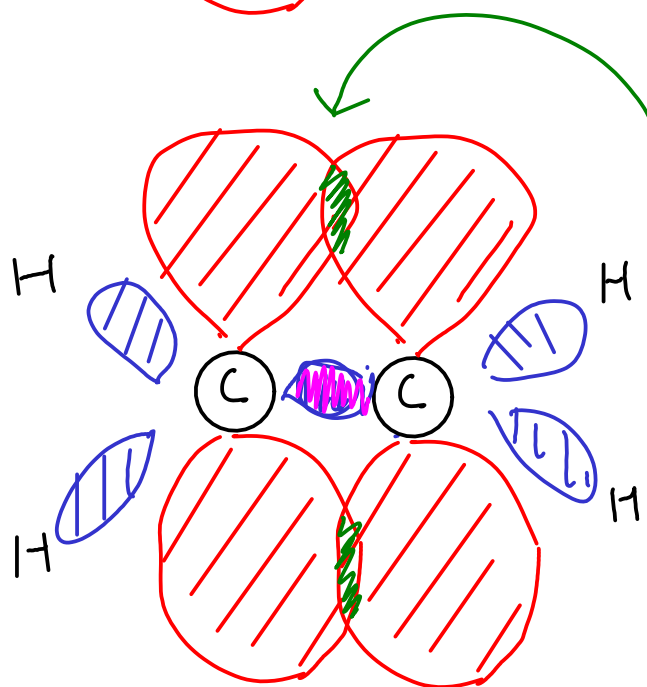
Each carbon has a TRIGONAL PLANAR geometry. This suggests that the carbons are "sp<sup>2</sup> hybridized".





$sp^2$  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  $sp^2$  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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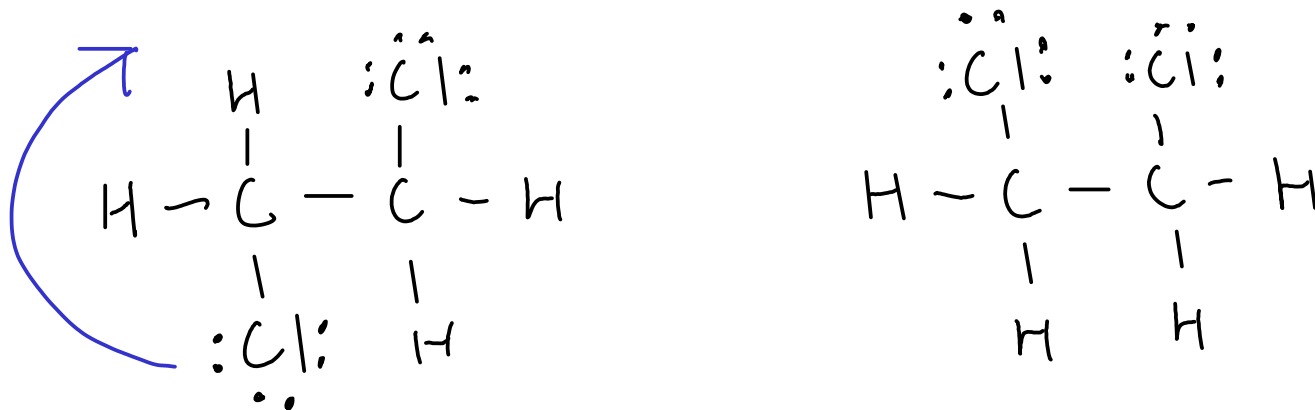
\*Experimentally, we observe that the bond energy of the C=C bond is less than the bond energy of two C-C bonds. This suggests that the second bond in a double bond is different from the first!

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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.

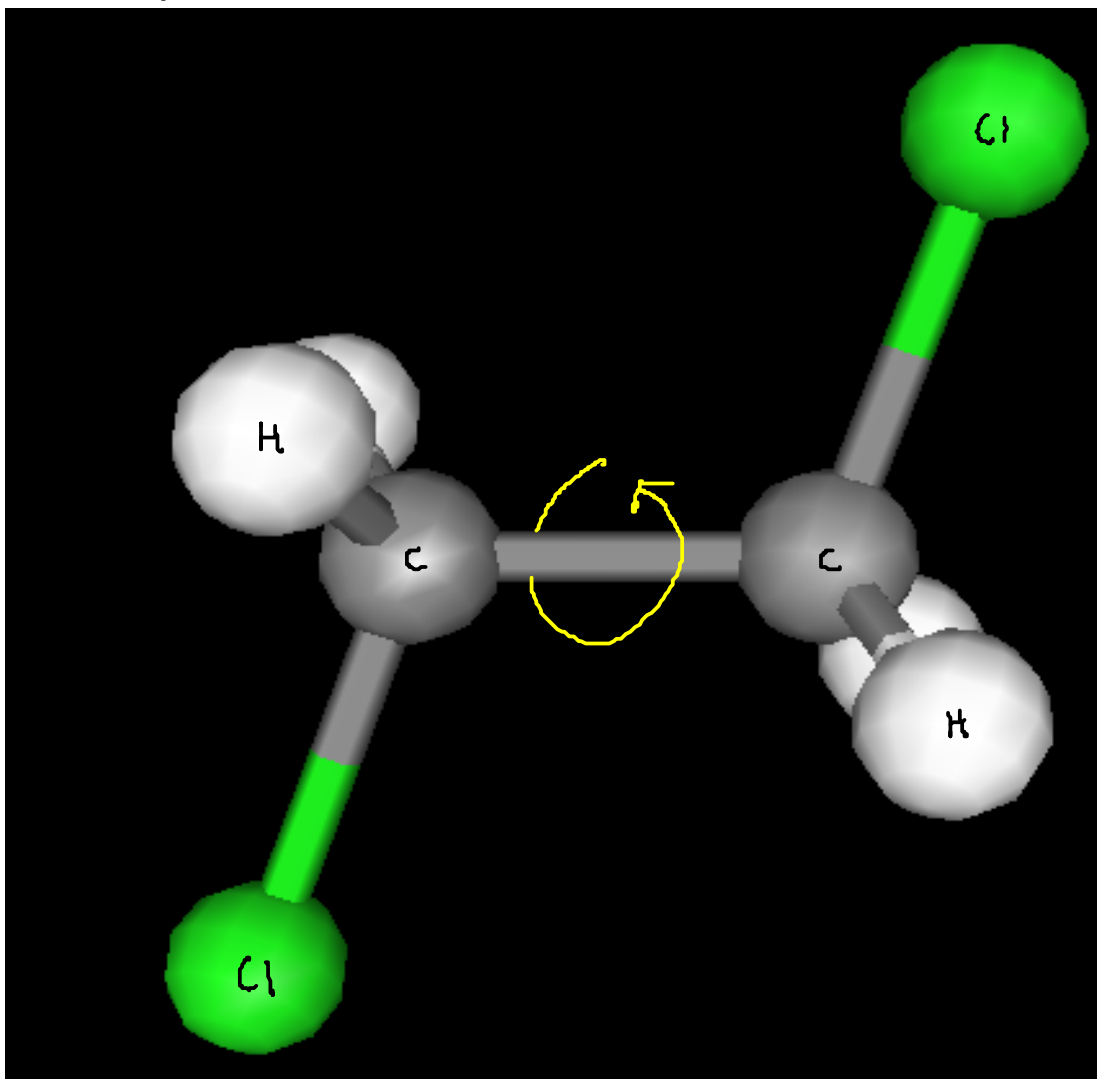
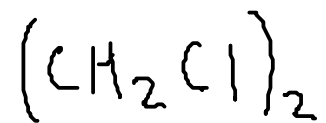
## ROTATION, ISOMERS, and VALENCE BOND THEORY

- Consider this molecule:  $(\text{CH}_2\text{Cl})_2$   
 "1,2-dichloroethane"



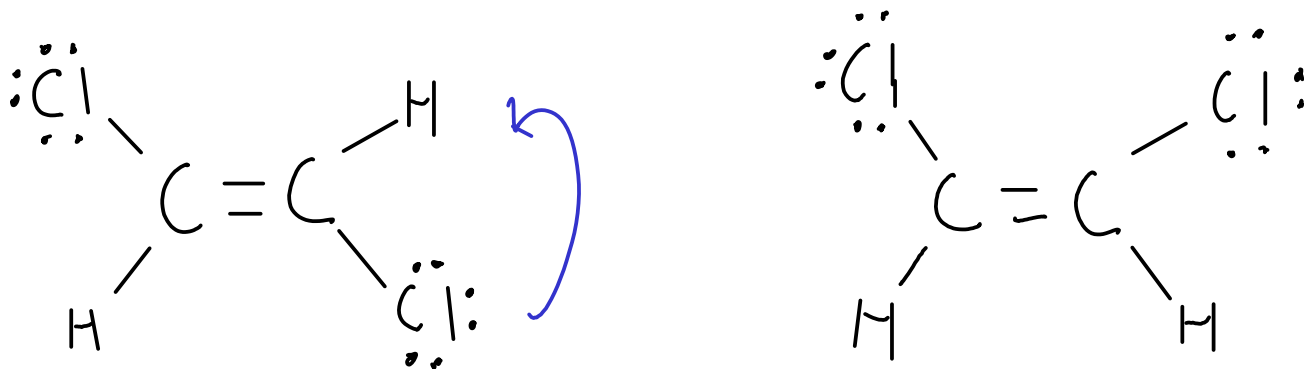
... are these two structures different?

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



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

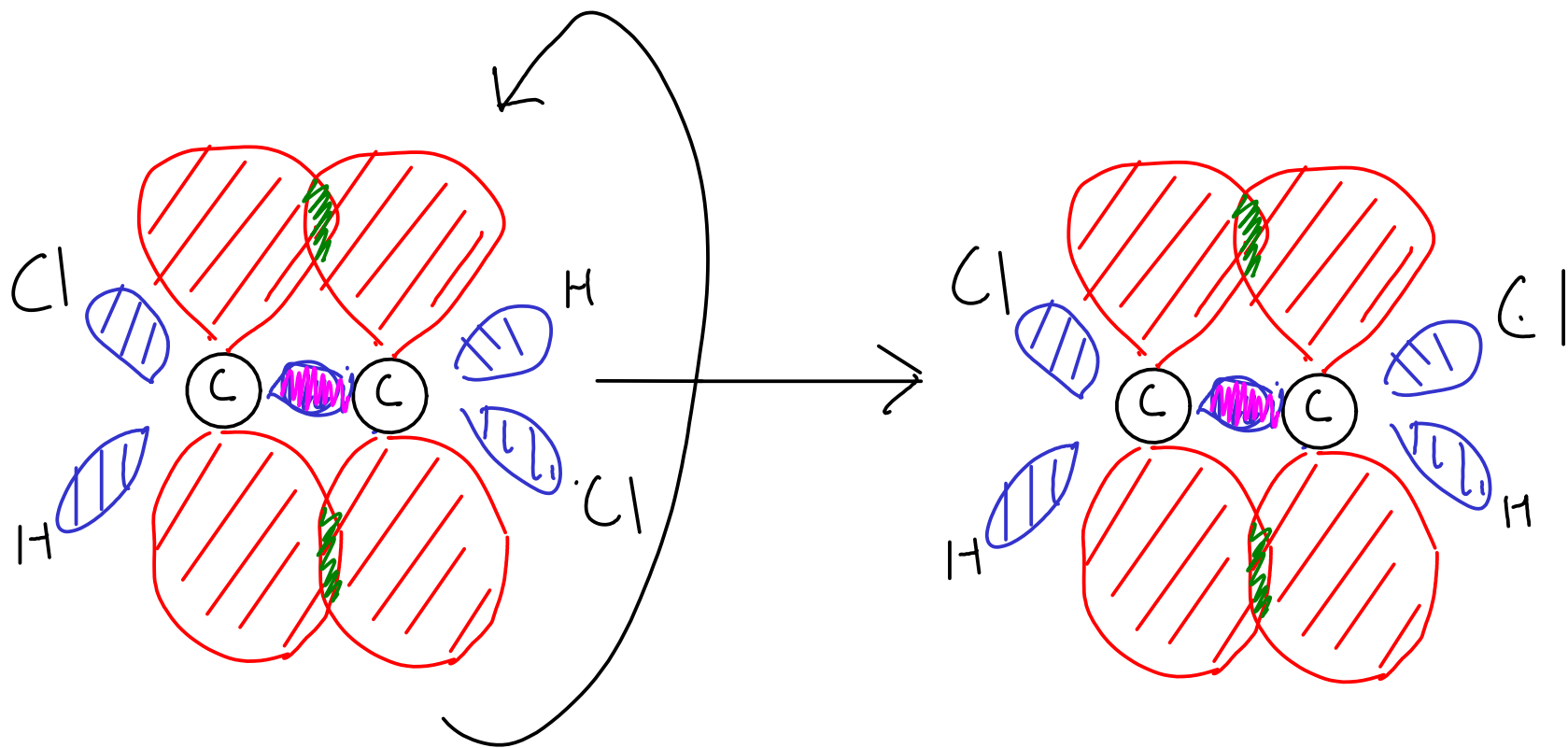
... now consider "1,2-dichloroethene":  $(\text{CHCl})_2$



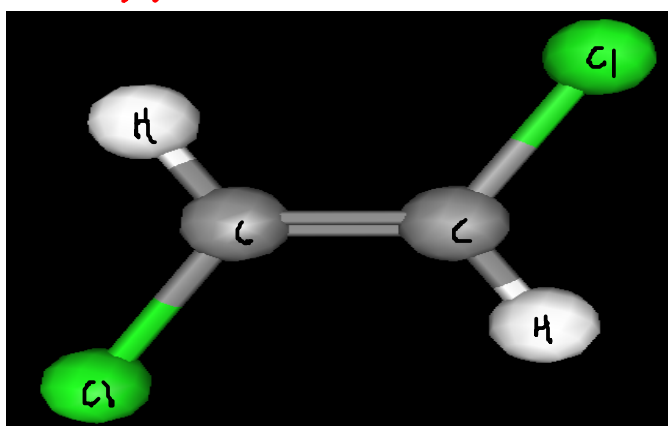
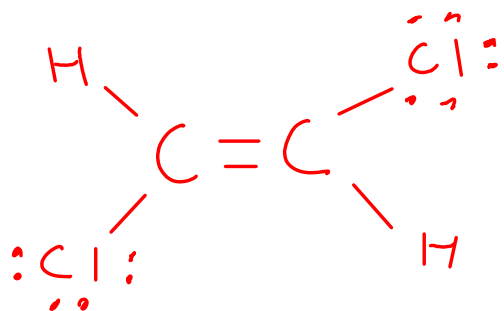
... are these two structures different?

YES ... The two carbon atoms in each structure are held together by a DOUBLE BOND, which contains both a sigma and a pi component. The molecule cannot rotate around the C=C bond without breaking the pi part of the bond, so the form with chlorine atoms on opposite sides of the bond cannot freely flip into the form with the chlorine atoms on the same side of the C=C bond!

So ... these two structures represent DIFFERENT MOLECULES. They're 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!

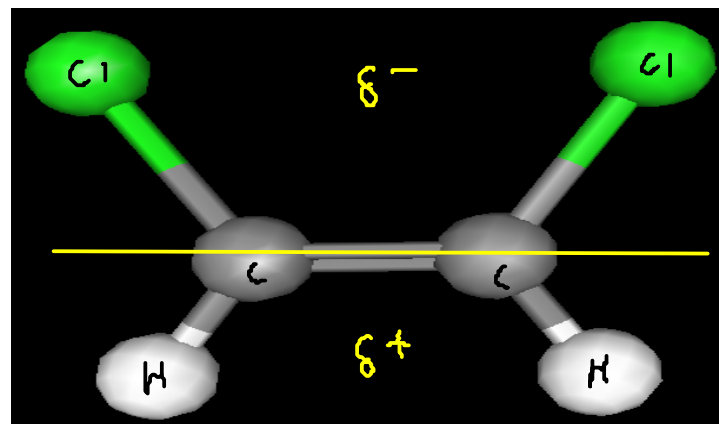
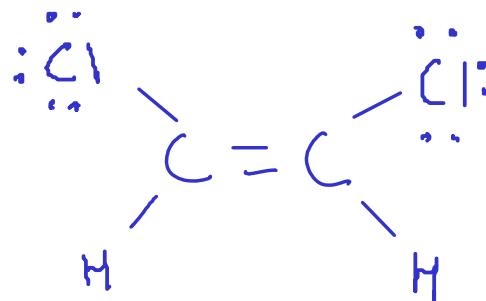


trans 1,2-dichloroethene

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

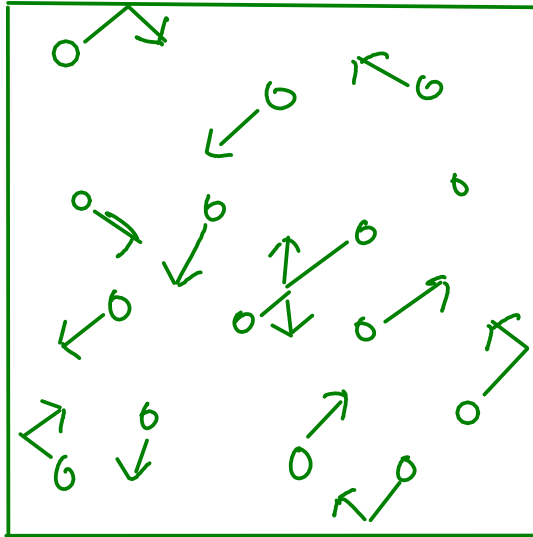
\* As you can see, some of the properties of these two molecules are very different! The presence of the pi bond (part of the double bond) in each of these molecules means conversion from one form to the other requires a chemical reaction instead of a simple rotation.

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

## SOLIDS AND LIQUIDS

- Here's a brief review of the atomic picture of gases, liquids, and solids

## GASES



## Kinetic theory says...

- \* Gas molecules are small compared to the space between them.
- \* Gas molecules move in straight lines until they hit another gas molecule or the walls of the container.
- \* There are no attractive or repulsive forces between gas molecules except during a collision.
- \* When gas molecules collide, energy may be transferred, but no energy is lost as heat.
- \* The temperature of a gas is proportional to the average kinetic energy of the gas molecules.

... kinetic energy depends on velocity of gas molecules!

$$E_K = \frac{1}{2}mv^2$$

Gases are FLUID, COMPRESSIBLE, and DIFFUSE (NOT DENSE)!

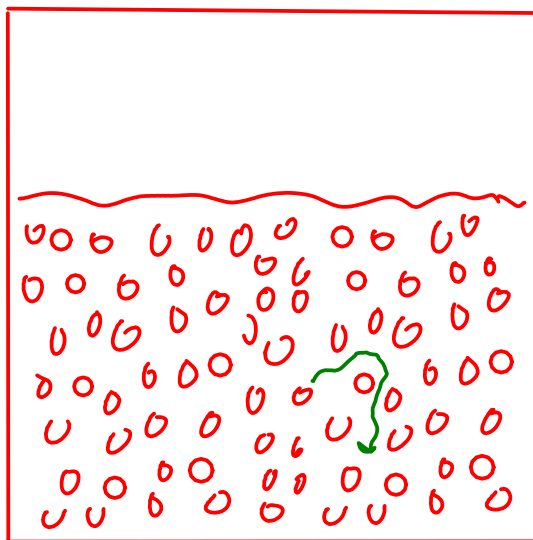


variable volume!

- The properties of different gases are very similar to one another. At moderate conditions, different gases obey the simple IDEAL GAS EQUATION.

$$PV = nRT$$

## LIQUIDS



- \* Molecules are much closer together than in the gas phase.
- \* Molecules are free to move around each other, but there is much less freedom of motion than in the gas phase
- \* Molecules in the liquid state are held together by attractive forces that we will call INTERMOLECULAR FORCES

Liquids are FLUID, DENSE, and INCOMPRESSIBLE!

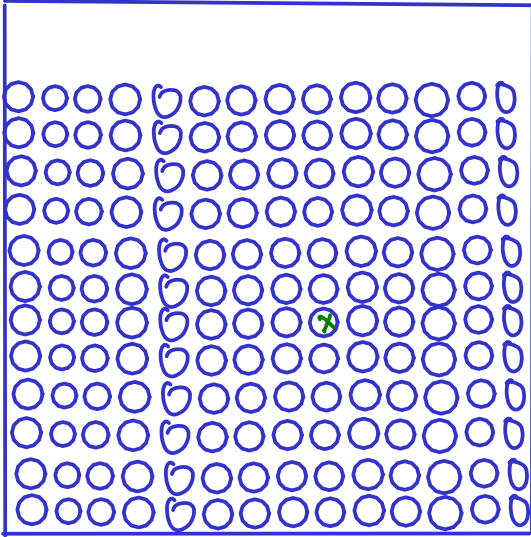
↑  
fixed volume!

- The properties of different liquids are often very different from one another, Compare liquids like water and motor oil, which are different enough so that they won't readily mix with one another!

no simple " $PV = nRT$ " for liquids.!



## SOLIDS



- \* Molecules are usually packed closer together in the solid phase than in the gas or liquid phases.
- \* Molecules are not free to move around each other as in the liquid phase. Molecular/atomic motion in the solid phase is limited to vibration.
- \* Most solids have a regular structure - unlike liquids or gases. This structure is called a **CRYSTAL LATTICE**.
- \* Molecules are held together by INTERMOLECULAR FORCES. These are usually stronger than in the liquid phase.

Solids are RIGID, DENSE, and INCOMPRESSIBLE!

- As for the liquids, the properties of different solids often differ considerably. Compare a sample of candle wax to a sample of quartz.