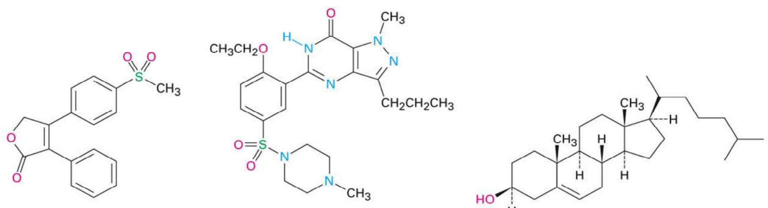
Chapter 1: Structure and bonding

Why do we study organic chemistry?

99% of known chemical compounds (over 30 million) are organic compounds.



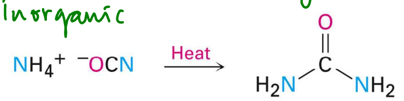
Rofecoxib (Vioxx) — Sildenafil (Viagra) — Cholesterol

What is an organic compound?

All organic compounds contain carbon!

Historically, it was thought that organic compounds were fundamentally different from inorganic compounds. They believed organic compounds had a "vital force" that inorganic compounds lacked.

inorganic organic

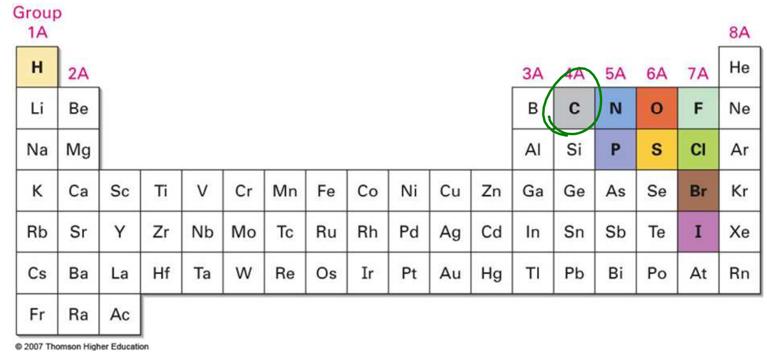


Ammonium cyanate Urea

No vital force!

Why carbon?

What's so special about carbon?



Group: IVA
Valence electrons: 4
\# Covalent bonds: 4

·Ċ·

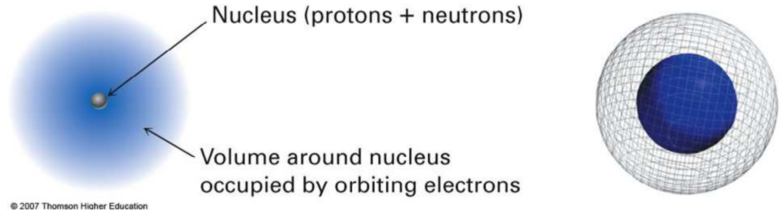
Ability to form chains:

C – C – C – C – C – C

C–C bond rel. strong

Organic compounds can be:
- formed by nature (natural products)
- created in a laboratory (synthetic)

1.1 The nucleus



Nucleus: dense center of atom

- **Protons:** pos. charge
- **Neutrons** no charge

approx same size

Electrons: negative charge
nearly massless

$\text{Å} = 10^{-10}$ m

Atom diameter: ~2 Angstroms (Å) = 2 x 10^{-10} m
Nucleus diameter: ~10^{-15} m   100,000 x smaller than atom

Atomic number (Z): number of: protons (which element)
Mass number (A): number of: protons + neutrons

Isotopes; same # of p^+ and different # of n°
(or, same Z (atomic #) and different A (mass #))   same element

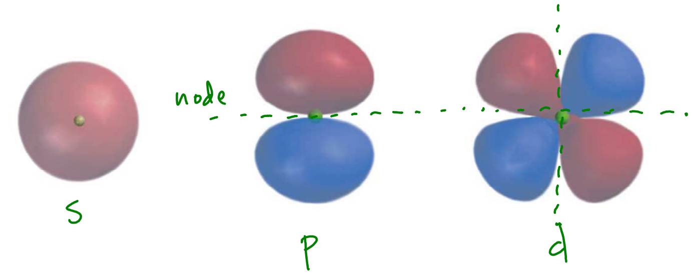
Atomic mass (amu): weighted average mass of natural isotopes

C : 12.01 amu
- C-14 (6p, 8n)
- C-13 (6p, 7n)
- C-12 (6p, 6n) >99%

1.2 Orbitals

Quantum mechanics uses mathematical wave equations to describe the behavior of electrons.

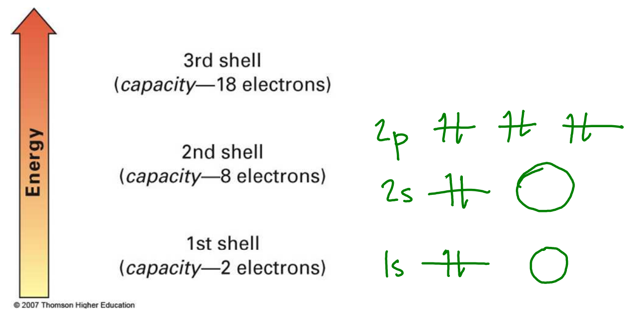
Wavefunction or **orbital**: A solution to a quantum mechanical wave equation that describes a 3-dimensional space where an electron is likely to be



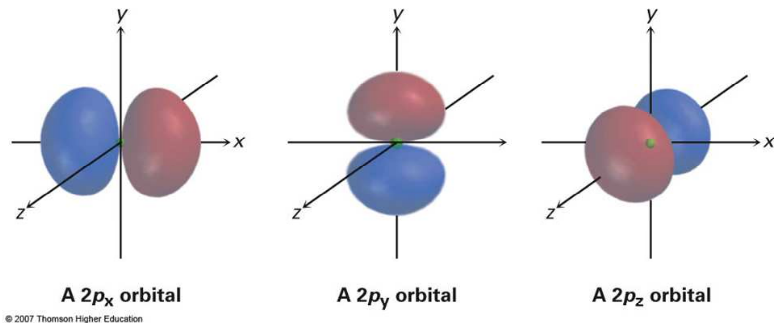
(we will be mostly concerned with *s* and *p* orbitals)

1 orbital holds 2 e⁻

Shells: groupings of orbitals. Higher shells have orbitals that are larger in size and higher in energy.



1.3 Electron configurations



Electrons fill into available orbitals using the following rules:

- Aufbau principle: electrons fill in lowest energy orbitals first

  (transition)

  1s , 2s , 2p , 3s , 3p , 4s , 3d

- Pauli exclusion principle: electrons have an up or down spin - each orbital can hold no more than 2 electrons, one with an up spin and one down

  ↑↓

- Hund's rule: if there are equal energy orbitals, electrons fill one per orbital first (with parallel spins) before pairing

  2p ↑↓ ↑ ↑

  $2p_x$ $2p_y$ $2p_z$

Electron configurations practice

H: 1 e^- $1s^1$ ← # e^-

1s ↑

N: 7 e^-

$1s^2 2s^2 2p^3$

5 valence e^-

2p ↑ ↑ ↑
2s ↑↓
1s ↑↓

C: 6 e^-

$1s^2 2s^2 2p^2$

4 ve

2p ↑ ↑ _
2s ↑↓
1s ↑↓

O: 8 e^-

$1s^2 2s^2 2p^4$

6 ve

2p ↑↓ ↑ ↑
2s ↑↓
1s ↑↓

F: 9 e^-

$1s^2 2s^2 2p^5$

7 ve

2p ↑↓ ↑↓ ↑
2s ↑↓
1s ↑↓

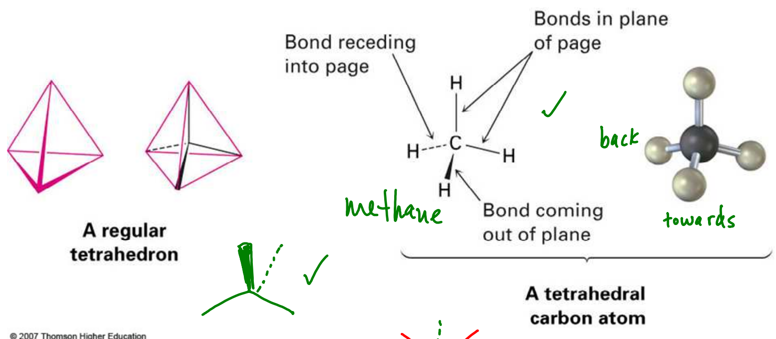
1.4 Development of chemical bonding theory

Mid 1800s: August Kekulé (Germany) and Archibald Couper (Scotland) independently showed that carbon is **tetravalent**

4 ve , 4 covalent bonds

Kekulé suggested carbon can form chains and rings.

Late 1800s: Jacobus van't Hoff (Netherlands) and Joseph Le Bel (France) showed that carbon is **tetrahedral**



Why do bonds form?

- Atoms bonded together in a stable compound have _lower_ energy than individual atoms. Energy is **always** _released_ when a bond forms.
- Ionic bonds: transfer electrons, then ions attract $Na^+ \rightarrow \leftarrow Cl^-$
- Covalent bonds: e^- shared H••H

Structures

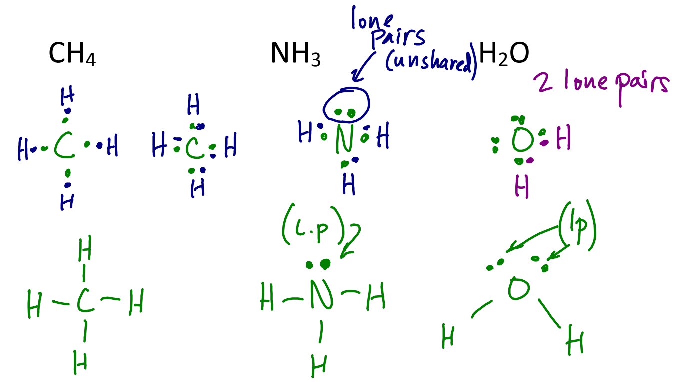
Lewis electron-dot structures show **valence** (group #) electrons as dots that can be shared between atoms in covalent bonds. H••H

Line-bond (Kekulé) structures represent a shared pair of electrons (covalent bond) as a line. H—H

CH_4 NH_3 H_2O

Lewis:

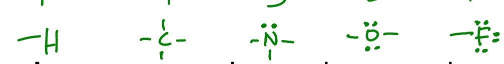
Kekulé:



Normal number of covalent bonds depends on the number of additional electrons required to reach noble-gas configuration.

octet rule

	H	C	N	O	F, Cl, Br, I
#v.e.	1	4	5	6	7
# c.b.	1	4	3	2	1



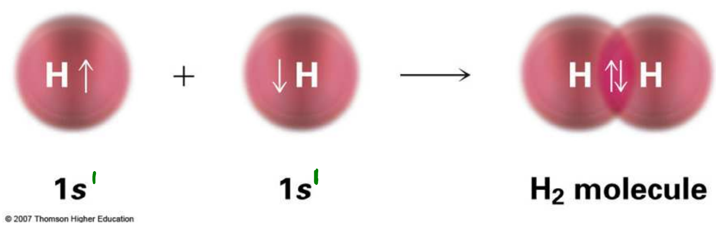
Nonbonding electrons are valence electrons that are not shared. * lone pairs

1.5 Valence bond theory

There are **two models** for describing covalent bonding:
- Valence bond theory
- Molecular orbital theory

Valence bond theory describes covalent bonding as the **overlap** between two single-electron orbitals so their electrons can be shared.

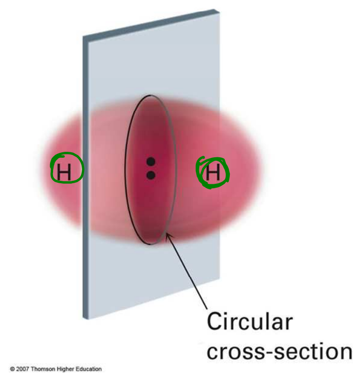
H• H• H—H



(Note the directions of the electron spins)

The new resulting orbital is cylindrically symmetrical. Bonds like this directly between two nuclei are called **sigma (σ) bonds**.

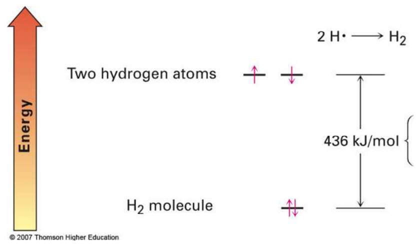
σ sigma



Energetics of bond formation

When bonds are formed, energy is <u>released</u>.

When two hydrogen atoms combine to make an H_2 molecule, 436 kJ/mol of energy is <u>released</u>.



released when forms
absorbed when broken

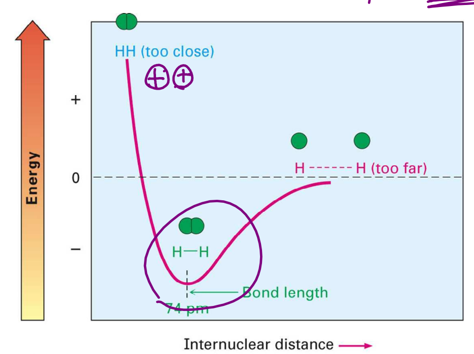
Which is more stable, the H_2 molecule or the two H atoms?

lower in energy

The **bond strength** of the H-H bond is 436 kJ/mol - the molecule would need to <u>absorb</u> 436 kJ/mol in order to break the bond.

100 kJ/mol weaker

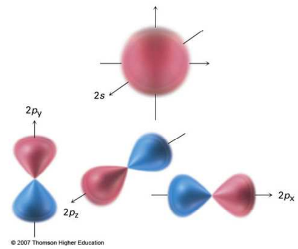
The nuclei in the H_2 molecule will sit at an optimal **bond length**



1.6 Structure of methane

Carbon has 4 valence electrons and forms 4 bonds.

Carbon's valence shell atomic orbitals:



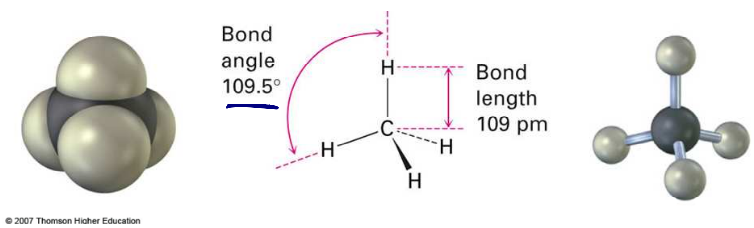
2p: ↿ ↿ ↿ ?

2s: ↿

Valence bond theory would suggest that each of carbon's orbitals would overlap with a hydrogen atom to make bonds.

So, does CH_4 have 3 of one kind of bond and 1of another?

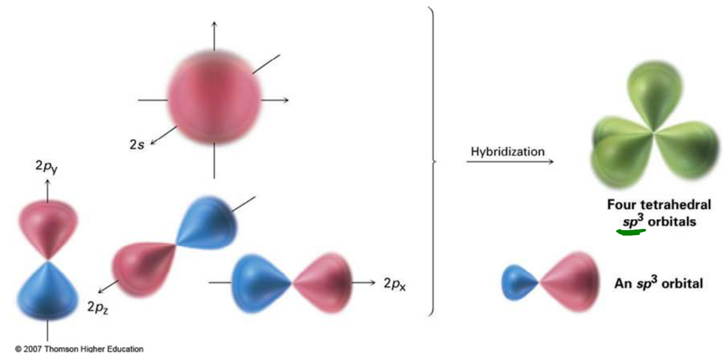
Actual structure of CH_4 is **tetrahedral** with **four identical bonds**:



tetrahedral bond angle 109.5° (sp^3)

sp^3 Hybrid orbitals

In order for carbon to make four equal bond the single s orbital and the three p orbitals must combine or **hybridize.**



See http://webs.anokaramsey.edu/aspaas/2061/molecules/C
orbitals.htm
for interactive 3D atomic and hybrid orbitals of C.

The hybrid orbitals are called *sp*^{3} because one *s* and 3 *p* orbitals are combining. The superscript 3 is the number of *p* orbitals that combined.

2p: ↿ ↿ ↿

2s: ↿

unhybridized

$\xrightarrow{\text{hyb.}}$ #

sp^3: ↿ ↿ ↿ ↿

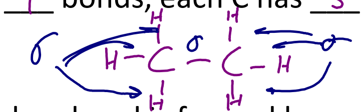
σ bonds

overlap w/

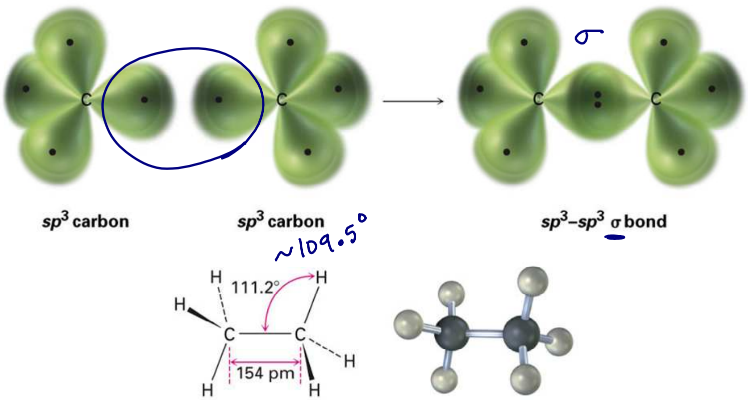
H· H· H· H·

1.7 Structure of ethane

Ethane, C_2H_6, contains a carbon-carbon bond. Since carbon makes 4 bonds, each C has 3 H atoms bonded to it.



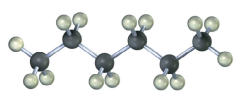
The carbon-carbon bond is formed by σ overlap of of an sp^3 hybrid orbital from each carbon.

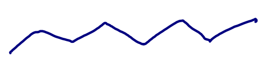


Ethane

See http://webs.anokaramsey.edu/aspaas/2061/molecules/ the 3D structures of all the molecules in this chapter.

Chains of carbons tend to form zig-zag shapes because of the tetrahedral angles of the sp^3 hybrid orbitals.

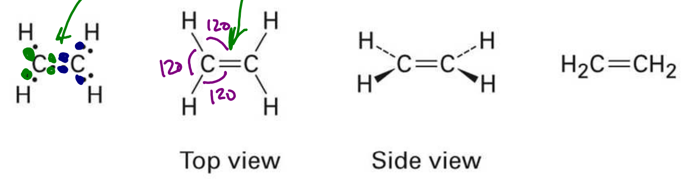

Hexane



1.8 sp^2 Hybrid orbitals and the structure of ethylene

Ethylene also has two carbons, but it has two fewer hydrogens than ethane: C_2H_4.

The only way for carbon to have four valence electrons is if the two carbons are **double bonded** (share four electrons).

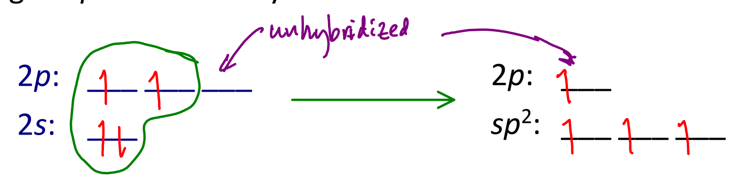


Some representations of ethylene

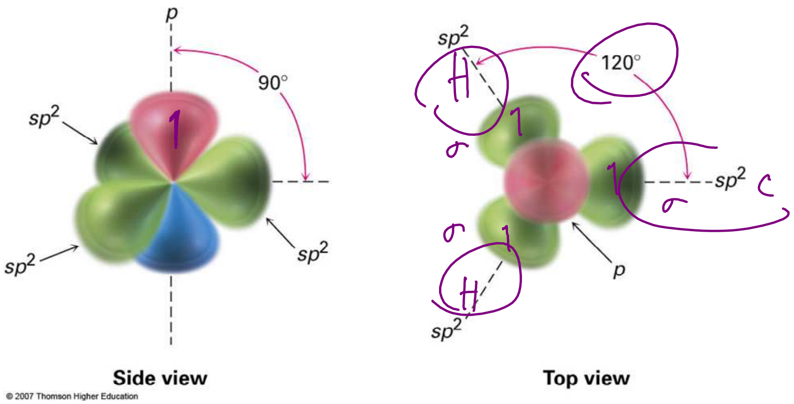
The structure of ethylene is much different than ethane:

- Its bond angles are approx 120° (not 109.5°)
- The molecule is **planar** (all of its atoms exist in a single, flat plane - it's flat!)

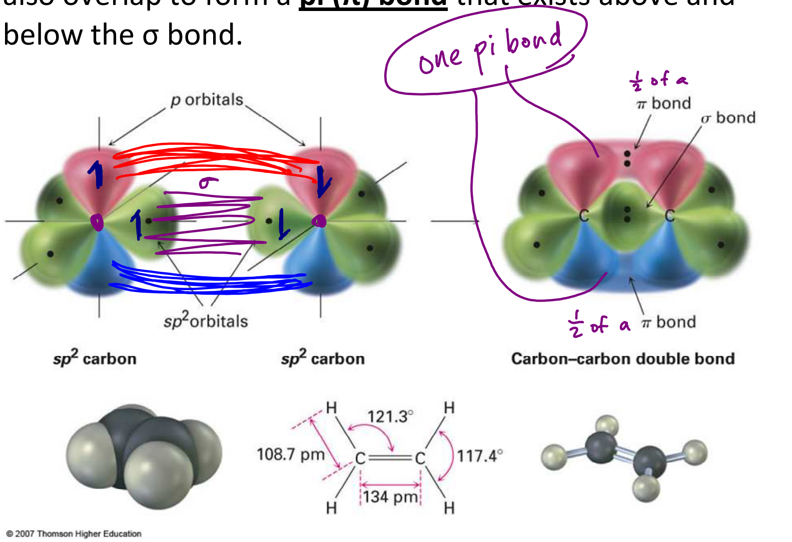
This arrangement can come from the formation of **three** ***sp*** **hybrid orbitals** instead of four, leaving one of the original *p* orbitals unhybridized.



sp^2 Hybrid orbitals and the structure of ethylene



One hybrid orbital from each carbon overlaps to form a bond just like in ethane, but the unhybridized *p* orbitals also overlap to form a **pi (π) bond** that exists above and below the σ bond.



C=C double bond

σ bonding only shares 2 electrons between 2 atoms.

More electrons can be shared by adding π bonds in addition to the σ bond, but that requires leaving one p orbital out of the hybridization for every π bond.

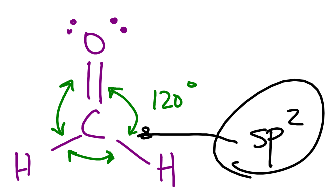
Each additional π bond adds two shared electrons. π bonds can only form by overlapping unhybridized p orbitals.

A **C=C double bond** consists of:

- **one σ bond** directly between the two nuclei, formed by two overlapping *sp*^{2} hybrid orbitals
- **one π bond** above and below the σ bond, formed by two overlapping unhybridized *p* orbitals

Carbon will be *sp*^{2} hybridized even if it's double bonded to an element other than carbon, like oxygen.

CH_2O, formaldehyde:



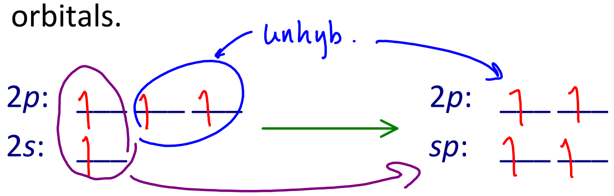
1.9 *sp* hybrid orbitals and the structure of acetylene

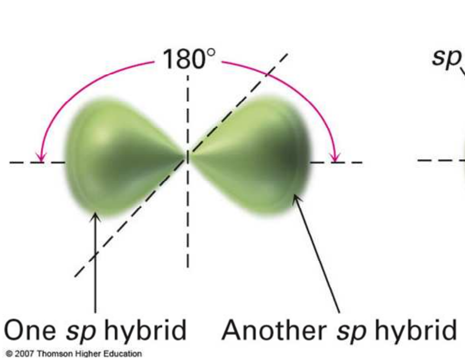
In **acetylene**, C_2H_2, the carbons are **triple bonded.**

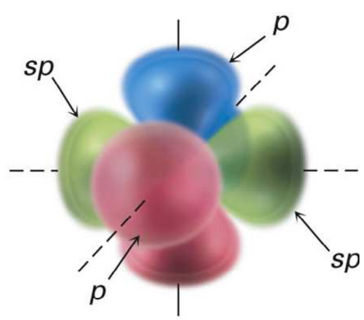
H—C≡C—H

A **triple bond** contains:

- One σ bond, from overlapping *sp* hybridized orbitals
- **Two** π bonds, from two pairs of unhybridized *p* orbitals.

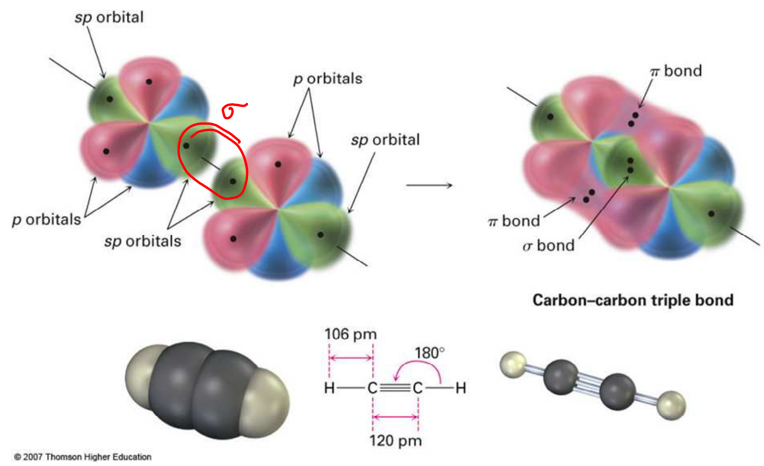






Structure of acetylene

sp hybrid orbitals are 180° apart since there are only two of them. The two unhybridized *p* orbitals occupy the other two axes.

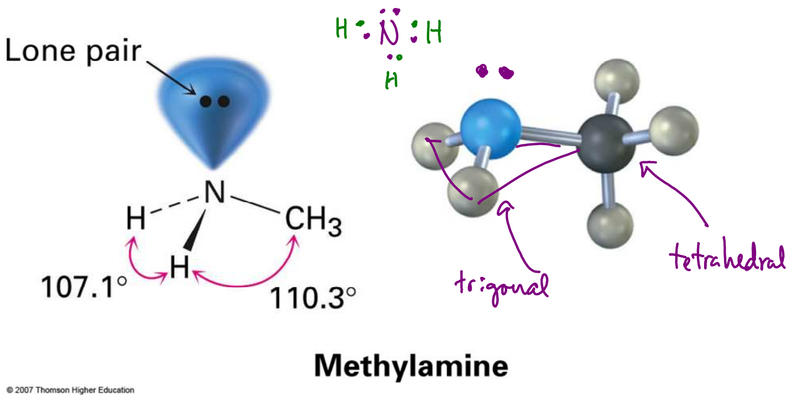


Review of carbon bonding:

Bonding	Hybridization	# σ	# π	Bond angle
4 single	sp^3	4	0	109.5°
2 single, 1 double	sp^2	3	1	120°
1 single, 1 triple	sp	2	2	180°

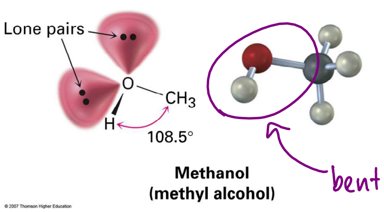
1.10 Hybridization of N and O

Nitrogen normally has one lone pair of electrons in order for it to share its 5 valence electrons and make 3 bonds.



If the 3 bonds are single bonds, N is sp^3 hybridized much like carbon, except one sp^3 orbital is occupied by two nonbonding electrons. (lone pair)

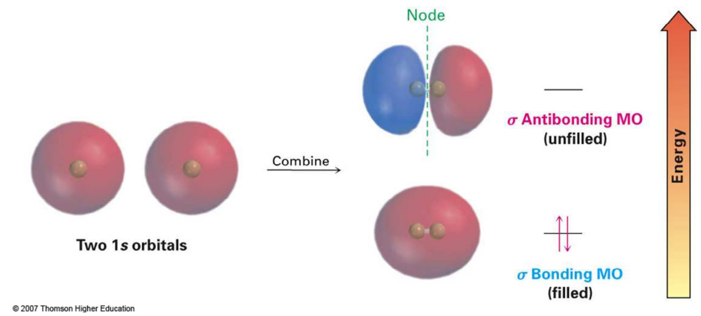
Oxygen normally has two lone pairs and makes two bonds. If they're single bonds, the oxygen is sp^3 hybridized, and the two lone pairs occupy two of the hybrid orbitals.

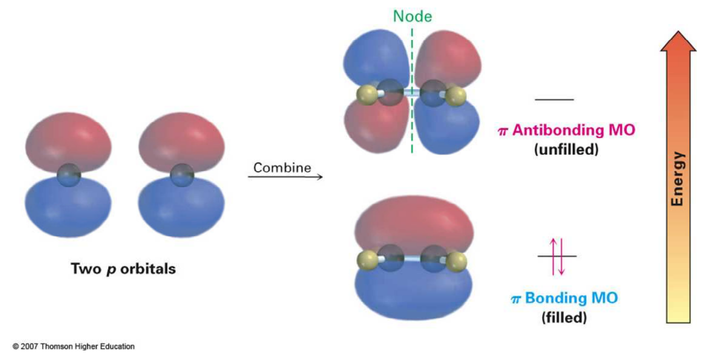


Lone pairs take up slightly more space than a σ bond, so they compress the remaining bond angles.

1.11 Molecular orbital theory

Molecular orbital theory is used often when describing the behavior of π bonds, especially when there are multiple π bonds in a molecule. We'll discuss it in detail in 2nd semester.

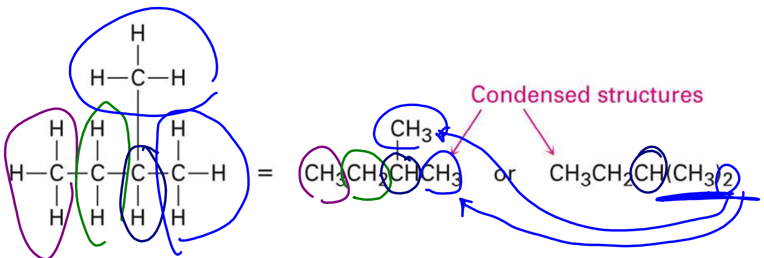




1.12 Drawing structures

We will **very rarely** draw organic molecules with every bond shown.

Condensed structures omit C-H and C-C single bonds, and combine together atoms or groups that are bonded to a common atom.



2-Methylbutane

$CH_3CH_2CH_2CH_2CH_2CH_3$ hexane

$= CH_3(CH_2)_4CH_3$

$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 = CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3$

$= CH_3CH_2COCH_3$

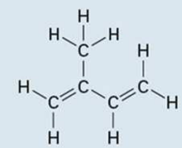
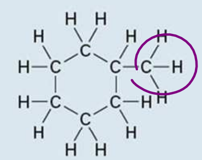
$CH_3CH_2CH_2O\,CH_3$

$CH_3CH_2CH_2-O-CH_3$

Line structures

Line structures or **skeletal structures** show the C-C bonds but not actual C or H atoms.

- C atoms are understood to be at the ends or the intersections of lines
- H's are not shown, and are understood to fill carbon's valence
- Atoms other than C and H are shown (as well as H's bonded to those atoms)

Compound	Kekulé structure
Isoprene, C_5H_8	
Methylcyclohexane, C_7H_{14}	
Phenol, C_6H_6O