Structure and Properties of Organic Molecules

In order to take advantage of the great strides made in the 20th century in calculating properties of molecules, we must leave behind the 19th Century notions of "electron clouds" and orbitals as "regions of space". The image of a molecule on a computer screen, kinetics and thermodynamics calculations of a chemical reaction, and even simple rules that can be used as a guide to synthesis of larger molecules and of isomers all depend on the wave-like behavior of electrons.

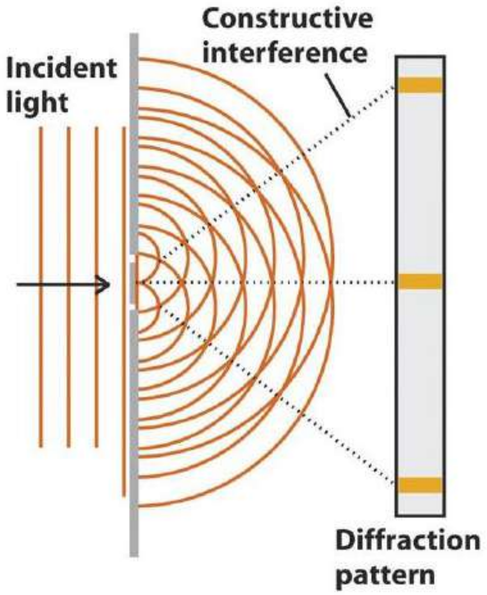
Let's start by considering where "90.9 on your FM dial" comes from. You need to supply work (energy) to change the electron flow (current) into (+) and out (-) of a radio antenna 90.9 million times per second.
1) Moving the electrons makes them emit "electromagnetic radiation". This is a wave traveling to the end of the Universe which can be described by a mathematical function that is as simple as a sine wave $f(x) \equiv y = \sin(x)$.
2) An electron in your radio captures some of this radiation and begins to move back and forth 90.9 million times per second.

3) Electrons and electromagnetic radiation both exhibit wave-particle duality.

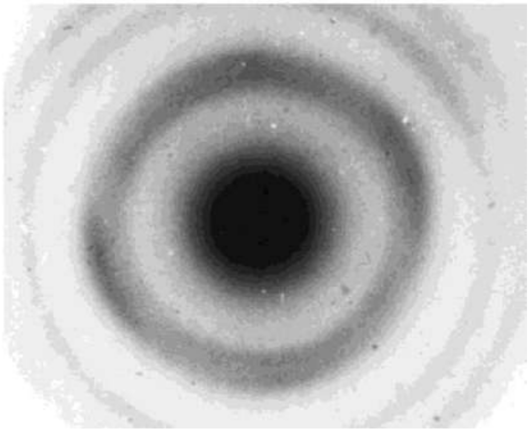
i. The *particle* property gives a meaning of "here at this spot at this time and going off in a particular direction with a certain speed (billiard ball)". The electromagnetic radiation that hits an electron at a certain point is called a *photon*.
Localized description Kinetic Energy = $\frac{1}{2} mv^2$.

ii. The *wave* property of both electro-magnetic radiation (e.g. X-rays) and of electrons (or even neutrons) can display diffraction (constructive and destructive interference) and can only be described by a mathematical function.
Delocalized description $\Psi(x) \equiv f(x) \equiv y = \sin(x)$

Diffraction patterns:



Light or surface of 'ripple tank'



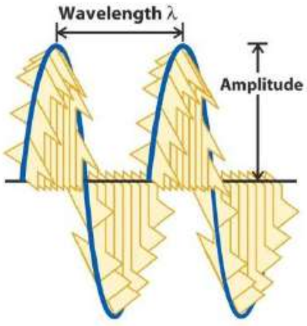
Diffraction pattern of X-rays on Ni surface

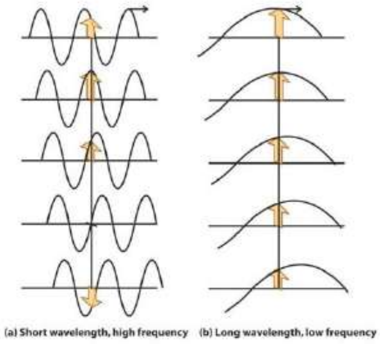
The pattern only appears if the two holes are placed by a distance n·λ apart (λ wavelength, n integer) i.e. if X-ray λ corresponds to internuclear distance in Ni crystal.

Types of waves

There are 2 types of wave: travelling (ripples on a pond, light wave)
standing waves (string, electron in an atom).

1) *Traveling:* $\Psi(x) \equiv f(x) \equiv y = \sin(x)$, where is any point in the Universe.





(a) Short wavelength, high frequency (b) Long wavelength, low frequency

- Velocity **v** = Wavelength **λ** times frequency **ν** $\mathbf{v} = \boldsymbol{\lambda} \cdot \boldsymbol{\nu}$

Standing:

An electron in an atomic orbital can be described like a bound, stationary vibration – a standing wave. There are some conditions on what values x can take in order to keep the electron on the atom.

The wave-like behavior of an electron bound in an atom can be very approximately described like the vibrations of a string on a guitar. This one dimensional orbital is the wave function, $\psi(x) = \sin(n \cdot x)$, where x is the position between the two attached points from 0 to π, and n = 1,2, ...
See Figure on the board:

If we don't pluck too hard, we get a standing wave with n =1 that is half of a sine wave. At one moment, all of the string is moving up to a maximum, and then the next moment, all of the string moves down to a minimum.

This corresponds to the Fundamental frequency of the wave / guitar string.

Next, if we place our finger exactly half way along the string and pluck harder, the string vibrates, we observe a standing wave, but the midpoint does not move. Now n = 2. This is the first Harmonic of the wave.

The value of $\psi(x)$ and the amplitude $\psi^2(x)$ at the midpoint are zero – a Node. The electron density at any point is equal to $\psi^2(x)$.

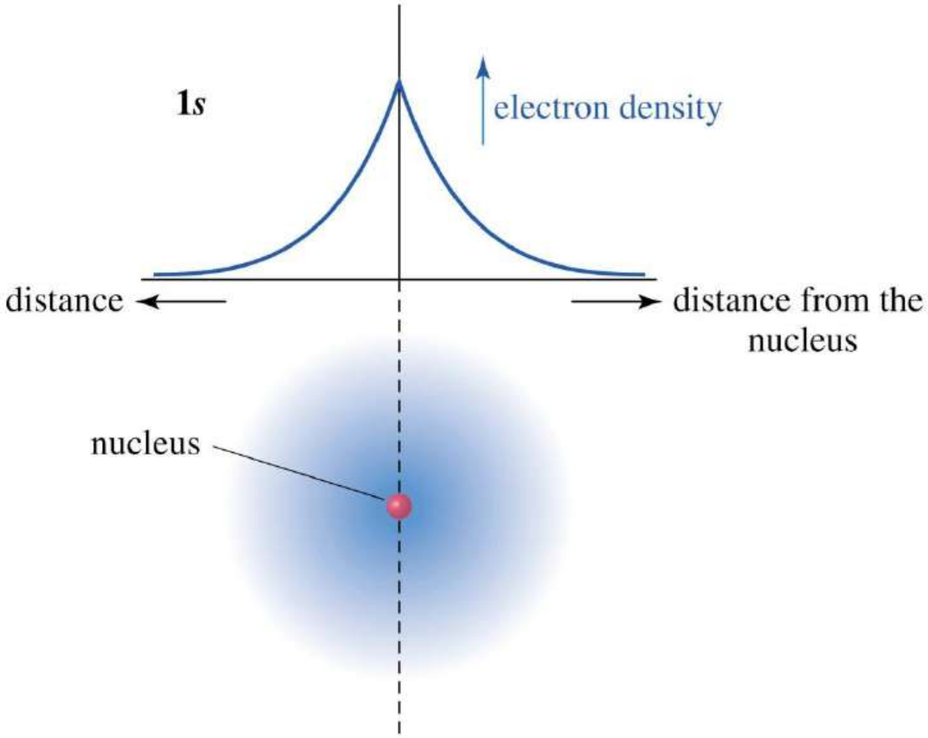
When one half of the string is up on one side, the other is down, and the two halves vibrate **out of phase** with one another.

N.B.!!! The +ve and –ve signs are **not** charges, just phases: values of y when distance equals x, i.e. $\Psi(x) \equiv f(x) \equiv y = \sin(x)$. Where are the 3 zero points?

This first harmonic with the +/- phases can be used to model either the 2s or 2p orbitals in hydrogen. (What can the second harmonic model?)
Imagine the amplitude (square of the displacement) in three dimensions – two out of phase lobes, separated by a nodal plane: a 2p orbital.

Now let’s explore a better orbital than a vibrating string. Better? By that we mean, when using the Schroedinger equation, the wave function gives calculated values that are closer to ones from experiment.
Imagine the shape of a 1s orbital, where the value of $\Psi(x,y,z)$ is the same anywhere on the surface of a sphere. This means we only need the radius to describe $\Psi(r)$ or $\Psi(x)$.

A better function is $\Psi(r) = e^{-|r|}$ or $\Psi(x) = e^{-|x|}$ This can be plotted on a graphing calculator:
$\Psi(x) \equiv f(x) \equiv y = \exp(-\mathrm{abs}((x)))$



A 2s orbital is $\Psi(x) = (2-x) \cdot e^{-|x/2|}$ and $2p_x$ $\Psi(x) = x \cdot e^{-|x/2|}$
Please plot these. You will need to adjust the boundaries so the orbitals are closer to those seen in General Chemistry.

Another point, electronegativity is introduced by putting the factor *alpha* into the exponent: $2p_x$ $\Psi(x) = x \cdot e^{-|\alpha \cdot x/2|}$. Try this for carbon $\alpha = 3$ and fluorine $\alpha = 7$. Remember which is bigger, the C or F atom?

Linear Combinations of Atomic Orbitals (LCAO)
1s, 2s, 2p,… orbitals are atomic orbitals.

Atomic orbitals can combine and overlap to give more complex standing waves (i.e. more complex orbitals).
This process is called linear combinations of atomic orbitals.

Molecular Orbitals are produced when mathematical functions (atomic orbitals or hybrid atomic orbitals) on different atoms interact.

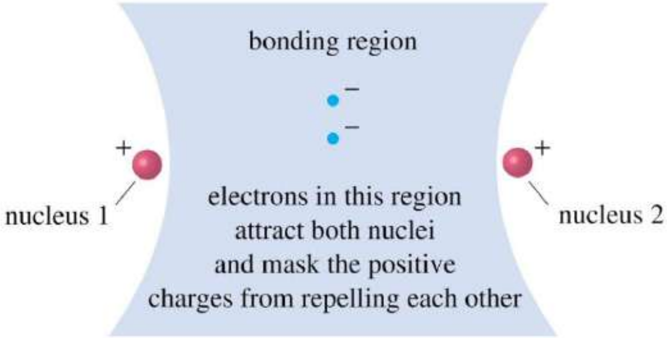
Hybrid Atomic Orbitals are produced when mathematical functions (atomic orbitals) on the same atom combined mathematically.

(The number of new orbitals produced always equals the original number of orbitals).

Molecular Orbitals
Two atoms bond together to attain a lower energy.

The stability of a covalent bond comes from the large electron density in the space between the space between the two nuclei (the bonding region).

The electrons shield the positive nuclei from each other, and allow them to get close.



There is an optimal distance for the nuclei to be separated: too close and the +ve nuclei will repel, too far and the electron sharing is weak.

This optimal distance is the Bond Length.

The Hydrogen Molecule

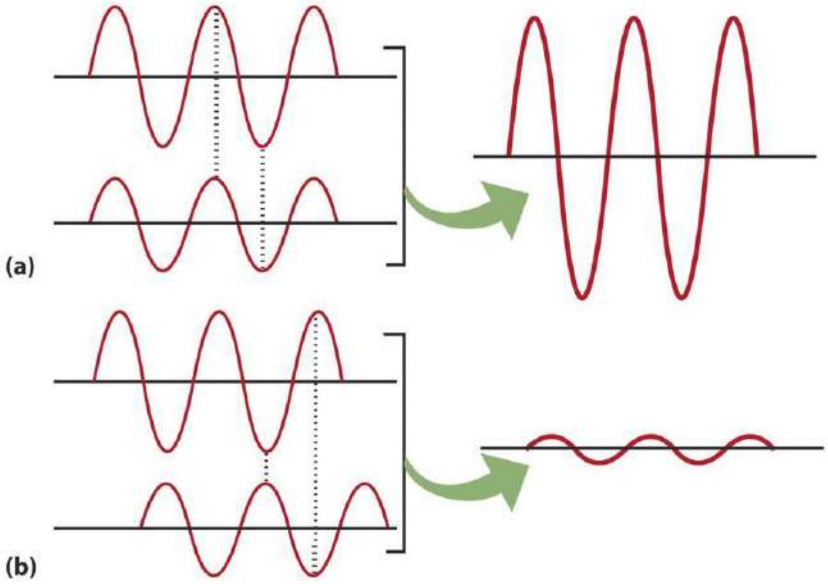
This is the simplest example of covalent bonding.

Consider bringing two Hydrogen atoms together: as they approach each other, their 1s orbitals will start to overlap.

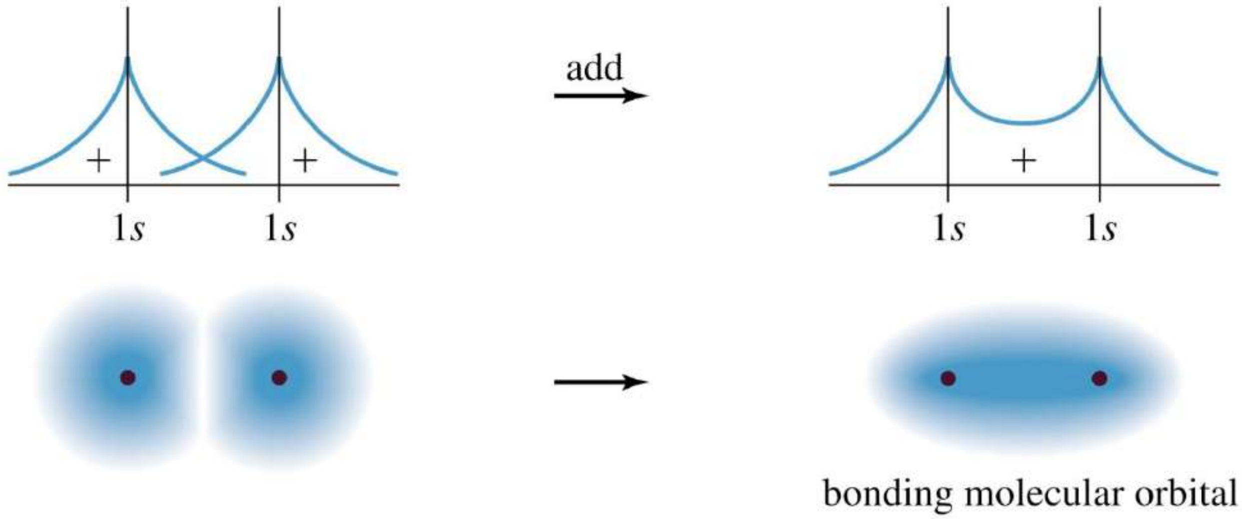
The orbitals (waves) will interfere constructively and destructively.

Constructive Interference

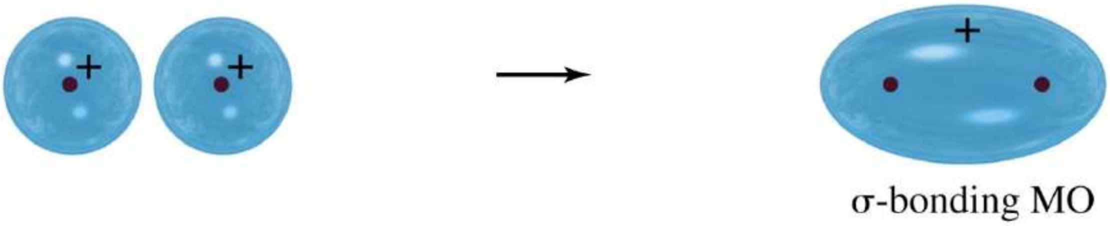
They interfere constructively when the orbitals are in phase (same sign).



- **a) Constructive interference**
- **b) Destructive interference**



represented by:



The wave functions reinforce one another, electron density is increased in this region: it is a Bonding Molecular Orbital (bonding MO).

Note the bonding MO has most of the electron density aligned along the axis of the two nuclei.

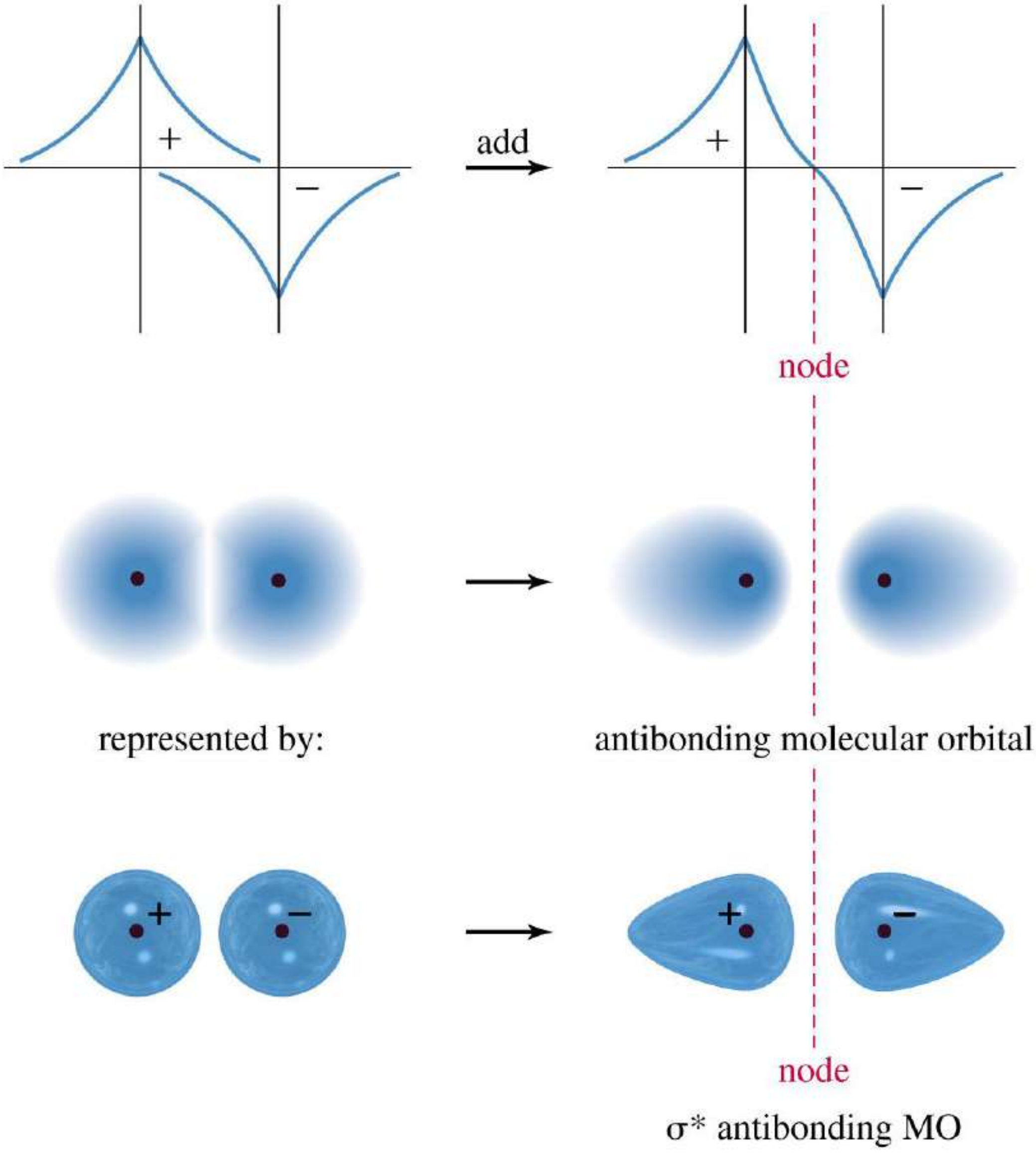
In three dimensions, this appears as a cylindrically symmetrical bond: this is a sigma (σ) bond.

Sigma bonds are the most common bonds in organic chemistry.
All single bonds are sigma bonds.
All multiple bonds contain one sigma bond.

Calculator Exercise:
Plot Function = $e^{-|x+1|} + e^{-|x-1|}$ exp(-abs(x+1)) + exp(-abs(x-1))

Destructive Interference

They interfere destructively when the overlapping orbitals are out of phase.

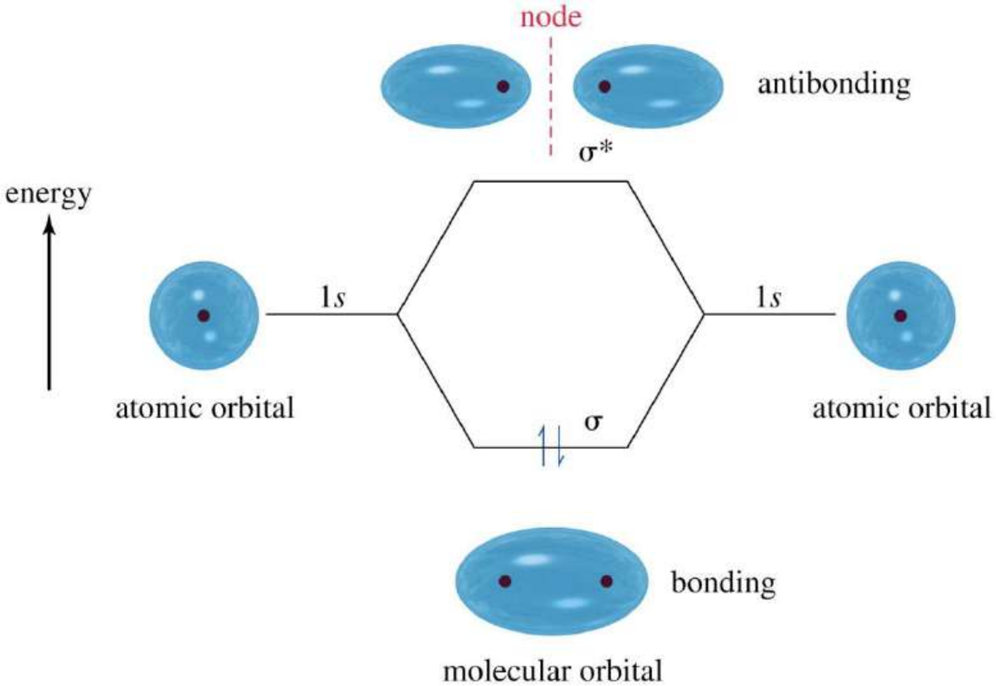


Calculator Exercise:

Plot Function = $e^{-|x+1|} - e^{-|x-1|}$ exp(-abs(x+1)) - exp(-abs(x-1))

The wavefunctions with opposite signs cancel each other out, resulting in a nodal plane between the atoms.

This results in an antibonding MO, in this case a sigma antibonding MO, σ*.



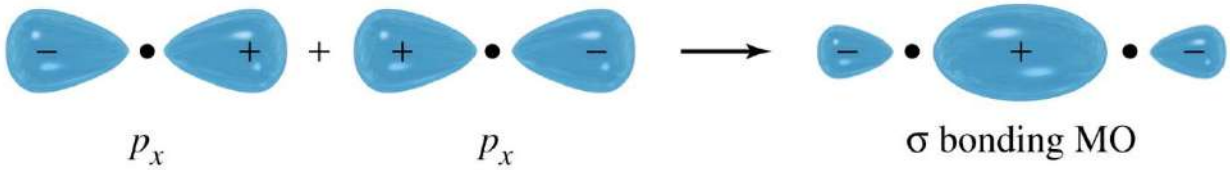
The energy diagram shows why the atoms bond – the overall new energy of the bonded system is lower than the energy of two separated atoms.

The two electrons (1 from each of the hydrogens) both go into the σ MO, representing a covalent σ bond.

Sigma Overlap with p Orbitals

Consider two p orbitals overlapping, again they can interfere constructively and destructively, giving bonding and antibonding MO's.

Constructively:



Destructively:

On the board

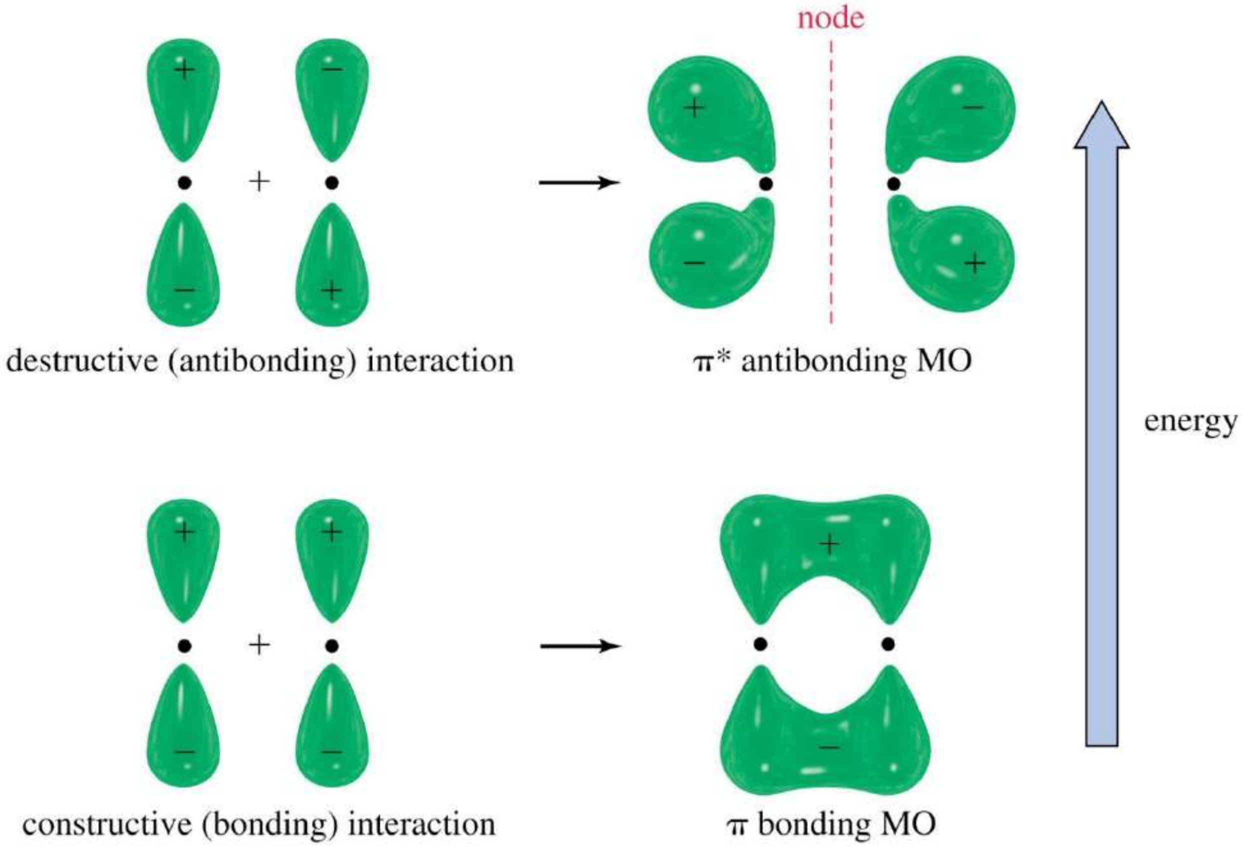
Sigma Overlap with an s and a p Orbital

Again, the s and p can overlap constructively or destructively, to give a bonding and a nonbonding MO.
Figure on board

Pi (π) Bonding

A π bond results from the overlap of two p orbitals that are oriented **perpendicular** to the axis of the nuclei.

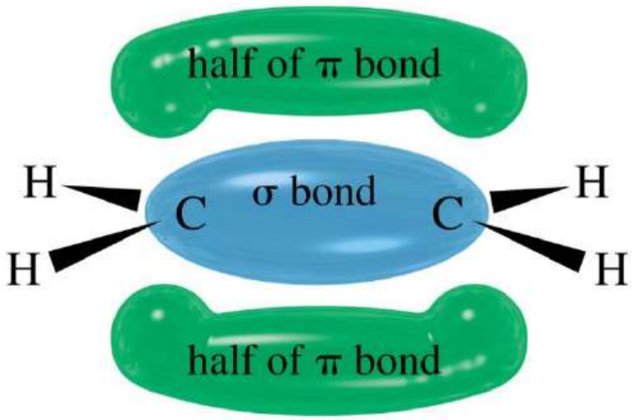
The parallel p orbitals overlap **sideways**, and most of the electron density is located above and below the line joining the 2 nuclei.

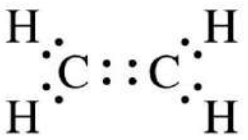


A π bond is **not** cylindrically symmetrical.

Single and Double Bonds

A double bond always consists of one σ and one π bond.
A σ bond is stronger than a π bond, due to better overlap.





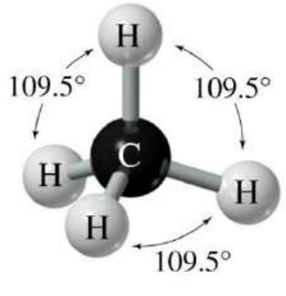
Lewis structure of ethylene

Hybrid orbitals

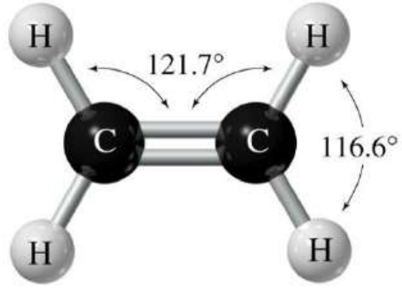
Hybrid atomic orbitals result from the mixing of atomic orbitals on the ***same*** *atom.* The mixing conforms to the molecular shape.

If organic molecules simply used s and p orbitals to form bonds, all bond angles would be 90^o or 180^o.

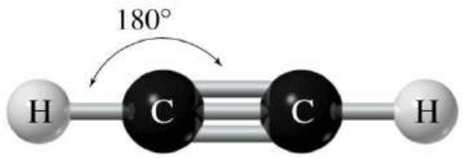
Molecules are found to have bond angles typically of 109.5, 120 and 180^o.



methane, 109.5°



ethylene, close to 120°



acetylene, 180°

Electron pairs (bonds) **repel** one another, and so they want to orient themselves in 3 dimensional space to get as **far away** from each other. (Valence Shell Electron Pair Repulsion Theory – VSEPR theory).

To separate 4 pairs, the best bond angle is 109.5^o.
To separate 3 pairs, the best bond angle is 120^o.
To separate 2 pairs, the best bond angle is 180^o.

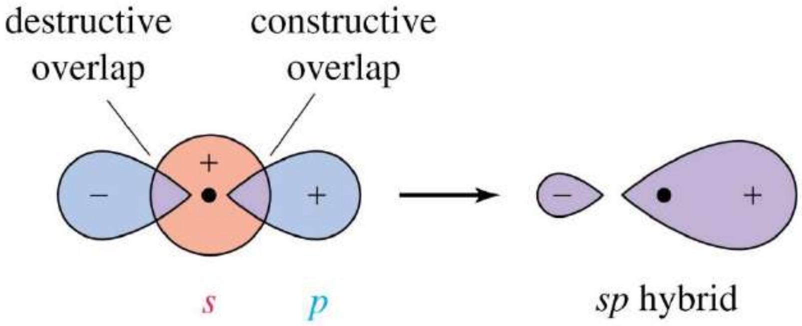
These cannot be attained using separate s and p orbitals for bonding - hybrid orbitals are required.

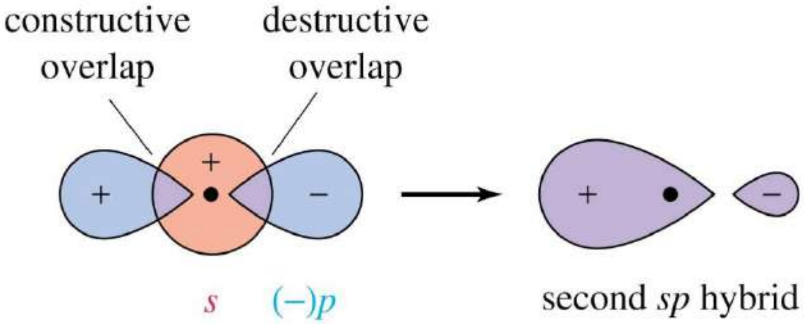
Hybrid Orbitals

Recall: **Molecular Orbitals** are produced when orbitals on **different** atoms combine.

Hybrid Atomic Orbitals are produced when orbitals on the same atom combine. Hybrid orbitals on one atom can be combined with hybrid orbitals on a neighboring atom to form a molecular orbital between the two atoms.

Consider the interaction of an s and a p orbital on the same atom.





This results in two sp hybrid orbitals.

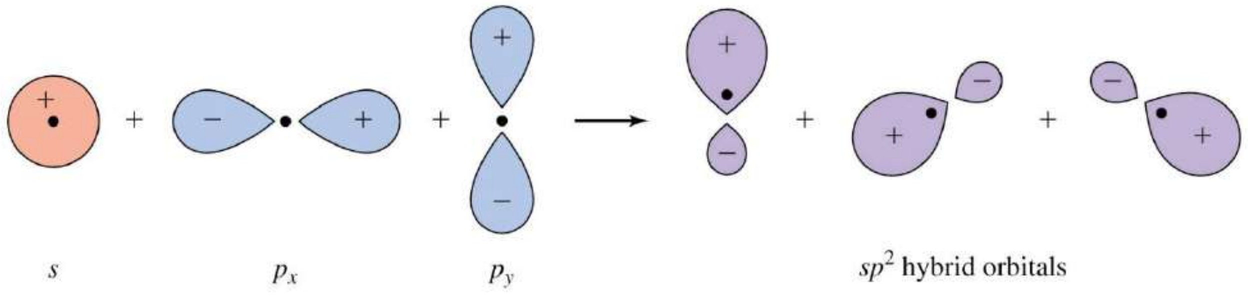
(Note: again **two** atomic orbitals give rise to **two** hybrid orbitals).

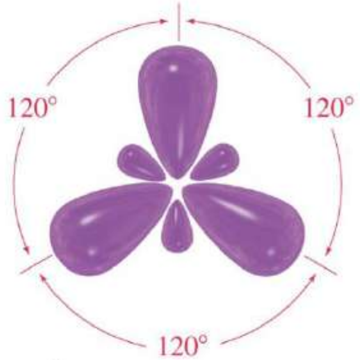
The hybrid orbitals have enhanced electron density oriented to either the left or right of the nucleus.

The sp hybrids provide bond angles of 180^{o}.

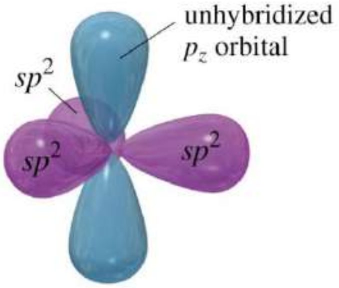
sp^2 Hybrid Orbitals

If we superimpose one s and two p atomic orbitals, we get 3 sp^2 orbitals.





three sp^2 hybrid orbitals superimposed



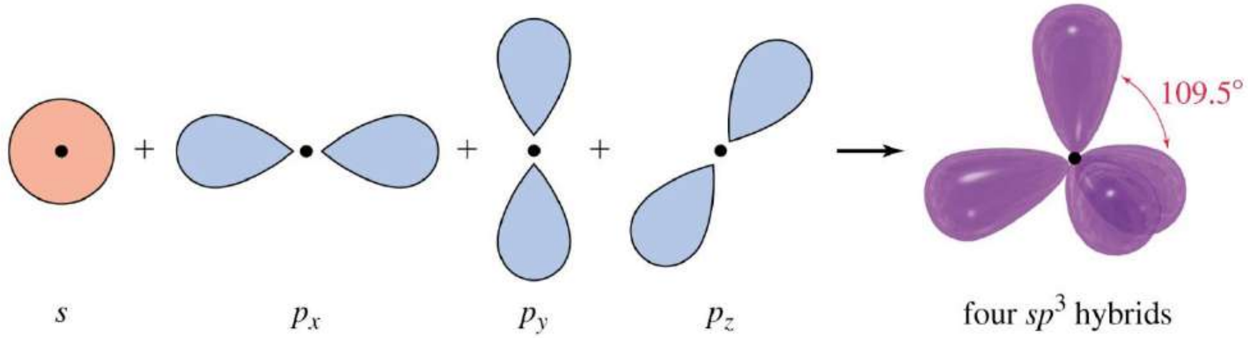
sp^2 hybrid carbon atom
(viewed from the side)

The sp^2 orbitals give rise to the necessary 120° bond angles required to most efficiently orient 3 bond pairs in space.

(Note: again **three** atomic orbitals give rise to **three** hybrid orbitals).

sp^3 Hybrid orbitals

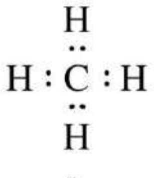
By combining one s and three p orbitals we achieve four sp^3 hybrids.



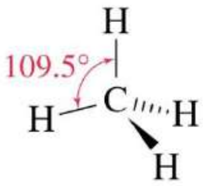
Notice that the combined four sp^3 orbitals give rise to a 3 dimensional tetrahedron shape.

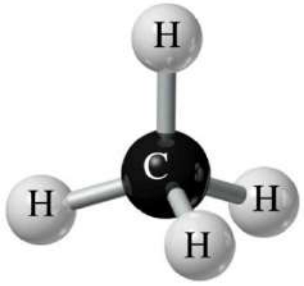
The bond angles are 109.5°.

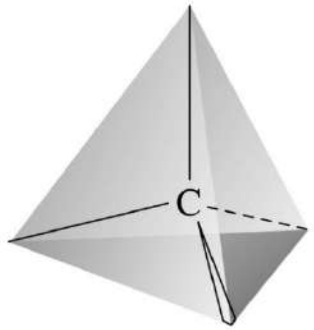
This tetrahedral arrangement of sp^3 orbitals is especially important for carbon, and is thus fundamental to organic chemistry.

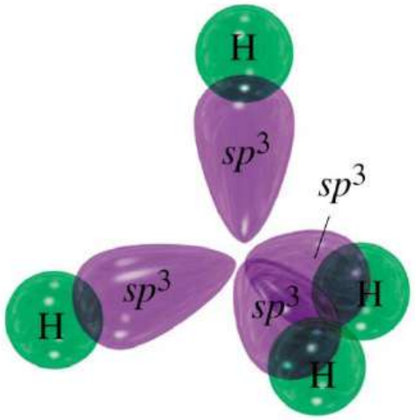


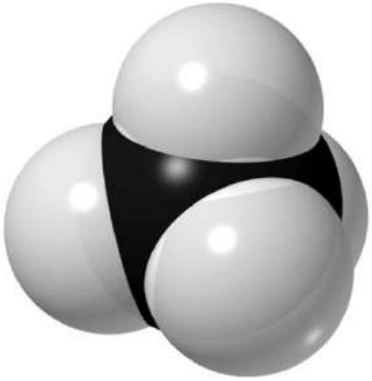
methane











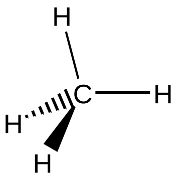
The line or double dot in the Lewis structure corresponds to an MO that is formed from the combination of a 1s AO on an H atom and an sp^3 HO on the C atom:

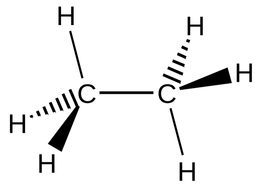
$$\text{Bonding MO, } \sigma = 1s_H + sp^3_C$$
$$\text{Antibonding MO, } \sigma^* = 1s_H - sp^3_C$$

Three Dimensional Structures

Organic molecules are 3 dimensional objects.

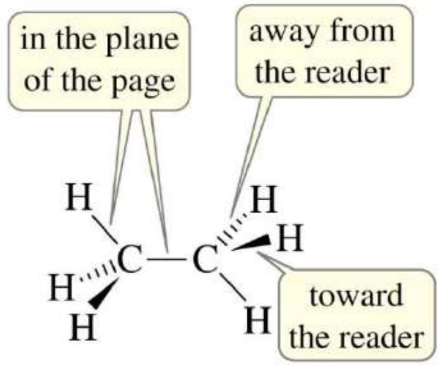
Shorthand notation for drawing 3D pictures:



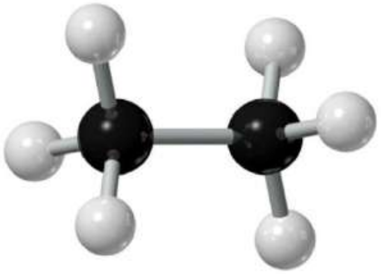


Straight lines are in the plane of the paper
Bold wedges are coming out of the plane of the paper

Dashed wedges are going into the plane of the paper.



ethane



ethane

ethane

<u>Summary of Hybridization</u>

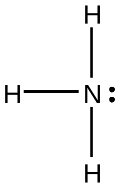
Rule 1: Both sigma bonding electrons and lone pairs occupy hybrid orbitals, so the number of hybrid orbitals is equal to the number of sigma bonds plus the number of lone pairs on the atom.

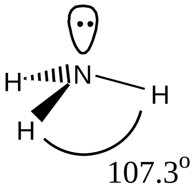
Rule 2: The hybridization must give rise to the best separation and geometry for the calculated number of sigma bonds and lone pairs. (Lone pairs occupy more space than a bond pair because they repel more strongly).

Rule 3: If 2 or more electron pairs are forming a multiple bond between 2 atoms, the first bond is always a σ bond using a hybrid orbital. The second is a π bond, with electron density above and below the σ bond. A triple bond will have another π bond perpendicular to the first π bond.

Consider ammonia, NH_3.

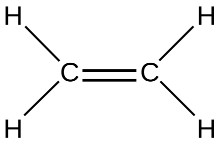
3 sigma bonds and 1 lone pair = 4 hybrid orbitals => sp^3





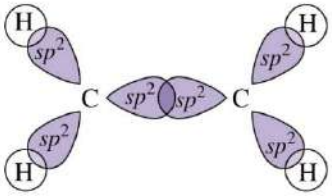
We predict a tetrahedral arrangement. The lone pair on the N forces the other three bonds away, and compresses the bond angles to 107.3° (c.f. 109.5° for a perfect tetrahedron).

Ethylene C_2H_4

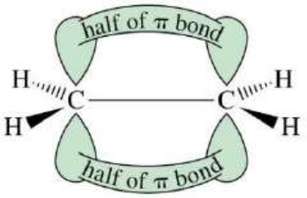


Each carbon is bound to 2 hydrogens, and a double bond to carbon
Each carbon has 3 sigma bonds, no lone pairs => sp^2.

The remaining p orbital is used for the π bond.



σ bond framework
(viewed from above the plane)

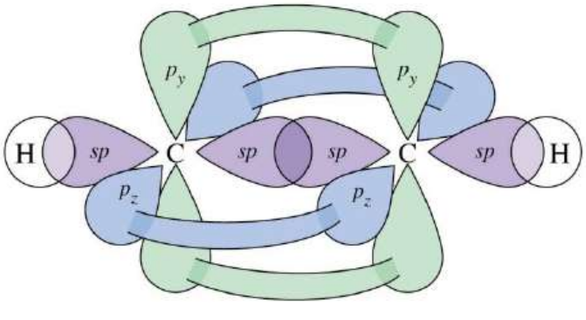


π bond
(viewed from alongside the plane)

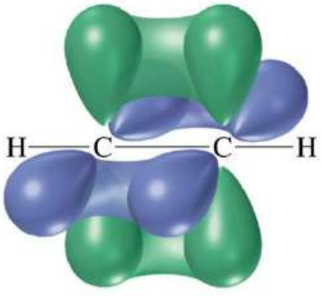
ethylene

Acetylene C_2H_2

$H-C\equiv C-H$



acetylene



acetylene

Carbon is bonded to 2 other atoms, with no lone pairs => sp

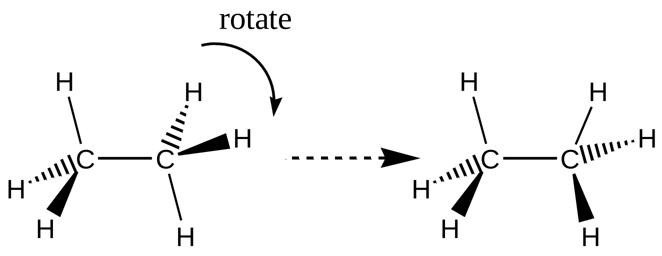
The remaining two p orbitals, form 2 perpendicular π bonds.

Structure and Geometry

Rotation of Single Bonds

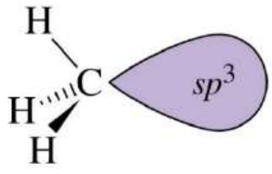
Ethane has both carbons sp^3 hybridized and tetrahedral.

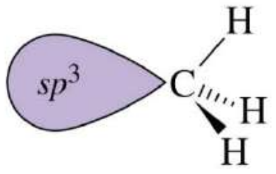
Ethane can exist in a variety of different orientations, through the rotation of one of the end methyl groups

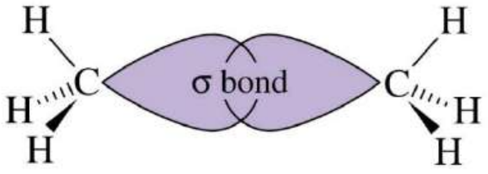


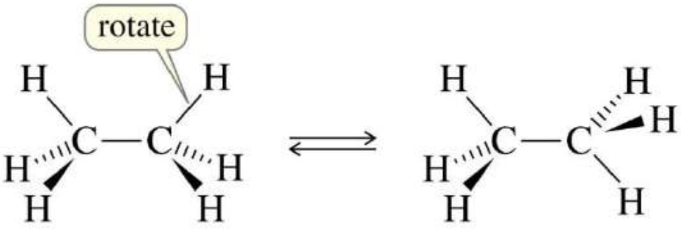
Structures that differ only in rotation about a single bond are called different CONFORMATIONS.

The sp^3 orbitals which overlap to form the C-C bond are shaped such that rotation about the bond axis does not interfere with their overlap.


methyl group


methyl group


ethane



eclipsed

staggered

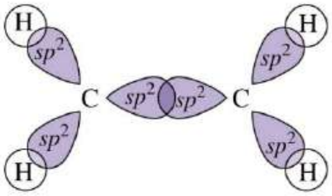
This bond can freely rotate.

(Notice that we use the double arrow <=> between conformations since we are moving atoms, the H’s.)

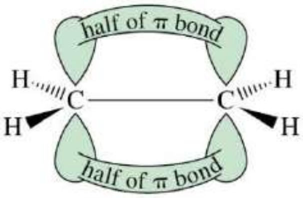
Rigidity of Double Bonds

Not all bonds can freely rotate.

Consider the bonding in ethylene: a sigma and a pi bond.



σ bond framework
(viewed from above the plane)



π bond
(viewed from alongside the plane)

ethylene

The sigma bond is **cylindrical**, and is unaffected by rotation of one of the CH_2 groups.

The pi bond is **different**. The overlap of the p orbitals would become adversely affected by rotation of one of the CH_2 groups.

Upon rotation, a pi bond would break.

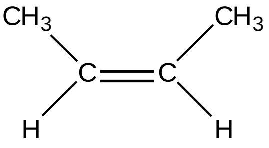
The same applies for a triple bond. The parallel overlap in a pi bond requires the atoms to be rigidly held in their conformation.

In general: Single bonds can rotate
Multiple bonds cannot.

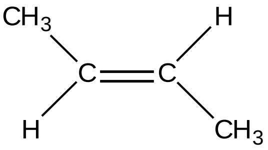
Isomers

An **isomer** is a compound that has the same molecular formula as another. The fact that there cannot be rotation around a double bond creates a situation where two compounds can differ only by the arrangement of substituents on a double bond.

Consider the following 2-butenes:



cis



trans

One molecule has the methyl groups on the same side of the double bond (cis isomer), whereas the other has the methyls on different sides (trans isomer).

The rigid double bond prevents the ends from rotating. They are two isomers of 2-butene.

When isomers differ only in their arrangement in space, and not in the order they are bonded, they are called **Stereoisomers**.

Cis and trans isomers are also known as **geometric isomers**.

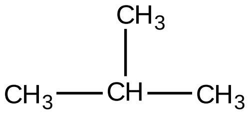
For geometric isomerism to exist, there must be 2 different groups on each end of the double bond.

Structural Isomers

These are isomers that differ in their bonding sequence. They have different bond connectivity.

$CH_3-CH_2-CH_2-CH_3$

n-butane



$CH_3-CH(CH_3)-CH_3$

isobutane

For example, these compounds have the same structural formula of C_4H_{10}, but are different compounds. They are **structural isomers** (or **constitutional isomers**).

The previous work was mainly organic chemistry background knowledge.

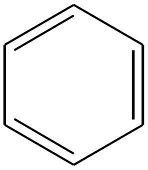
The rest of the course will deal with different types and classes of organic molecules, and their chemistry.
All molecules belong to certain classes or families, as determined by their functionality. (Reactive parts).

These are some of the most common functional groups:

$R-H$ alkane

$RHC=CHR$ alkene

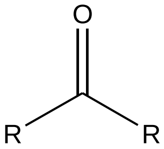
$R\text{-}C\equiv C\text{-}R$ alkyne



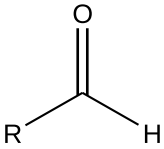
aromatic

$R-O\text{-}H$ alcohol

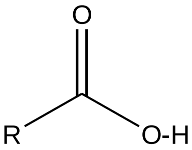
$R-O\text{-}R$ ether



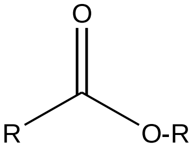
ketone



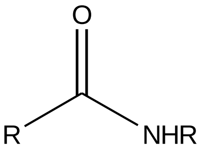
aldehyde



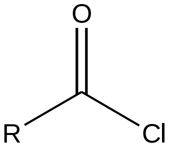
carboxylic acid



ester



amide



acid chloride

$R-NH_2$ amine

$RHC=NH$ imine

$R\text{-}C\equiv N$ nitrile

R = alkyl group, CH_3-, CH_3CH_2-, etc.