Structure and Properties of Organic Molecules

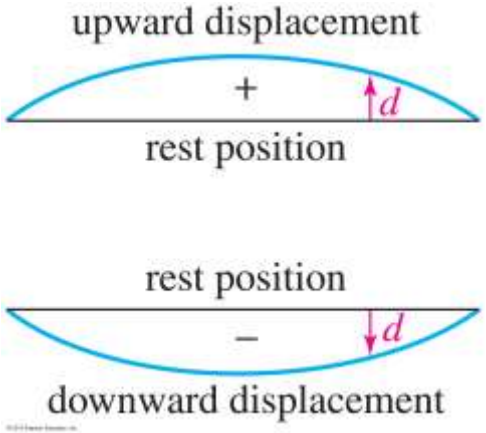
Electrons exhibit *wave-particle duality*.

There are 2 types of wave: **travelling** waves (ripples on a pond)
standing waves (guitar string, blow into beer bottle).

An electron in an atomic orbital can be described like a bound, stationary vibration – a standing wave.

Consider a guitar string being plucked in the middle

We get a standing wave, which at one moment has all of the string up, and then the next moment, all of the string down.

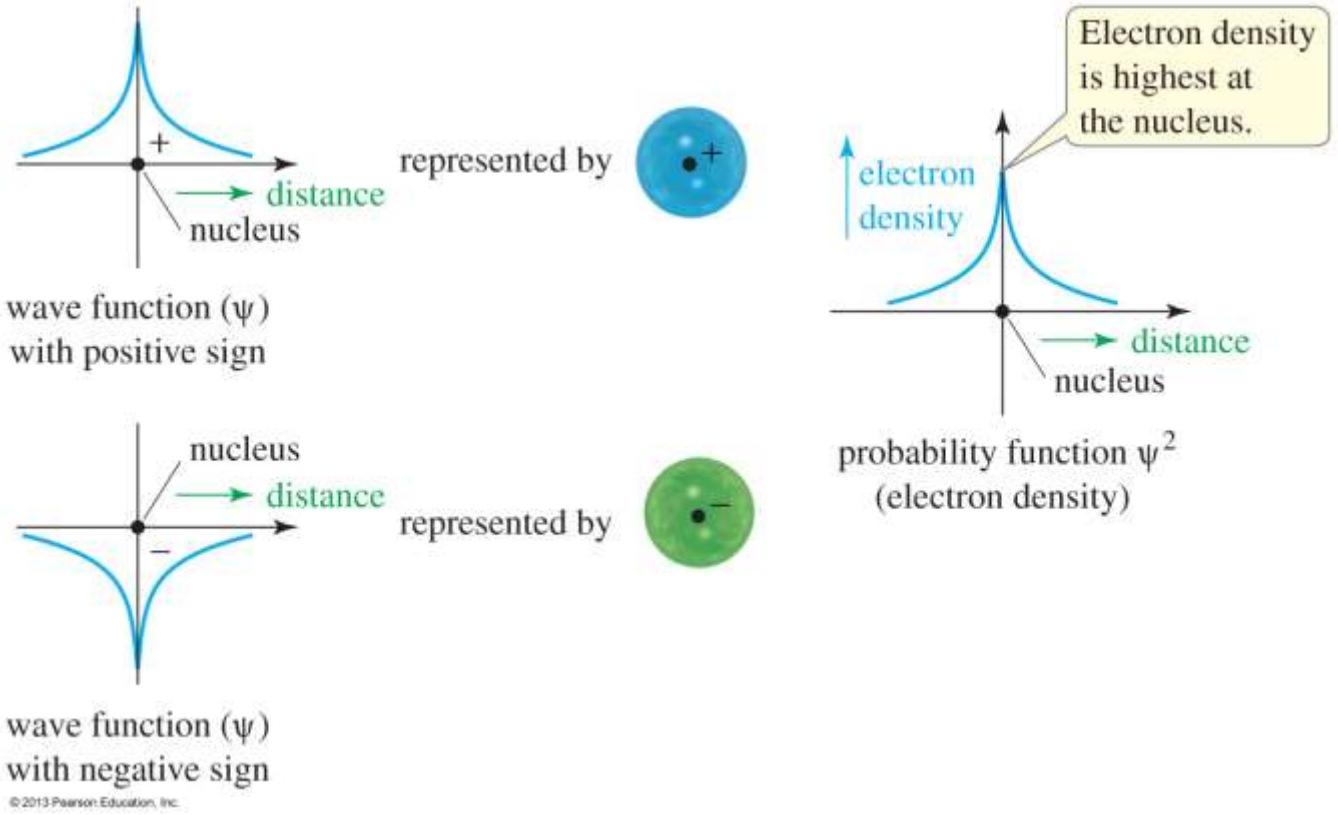


An instantaneous picture of the waveform would show the string in a smooth curve either displaced above or below the horizontal rest position.

The *amplitude* of the wave is the *square of the displacement*.
Imagine the amplitude being 3 dimensional – this is the shape of a 1s orbital.

An orbital is described by its *wave function*, ψ, (psi), which is a mathematical description.
The electron density at any point is equal to ψ^2.

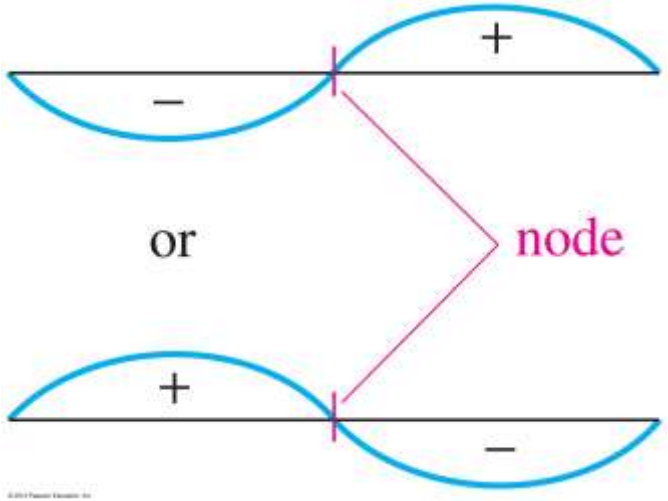
(The +ve and –ve signs are **not** charges, just *phases* of the wavefunction).



A 1s orbital is spherically symmetrical, and is often represented as a circle (meaning a sphere).

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

If we place our finger exactly half way along the string and pluck again, the string vibrates, we observe a standing wave but the midpoint does not move.

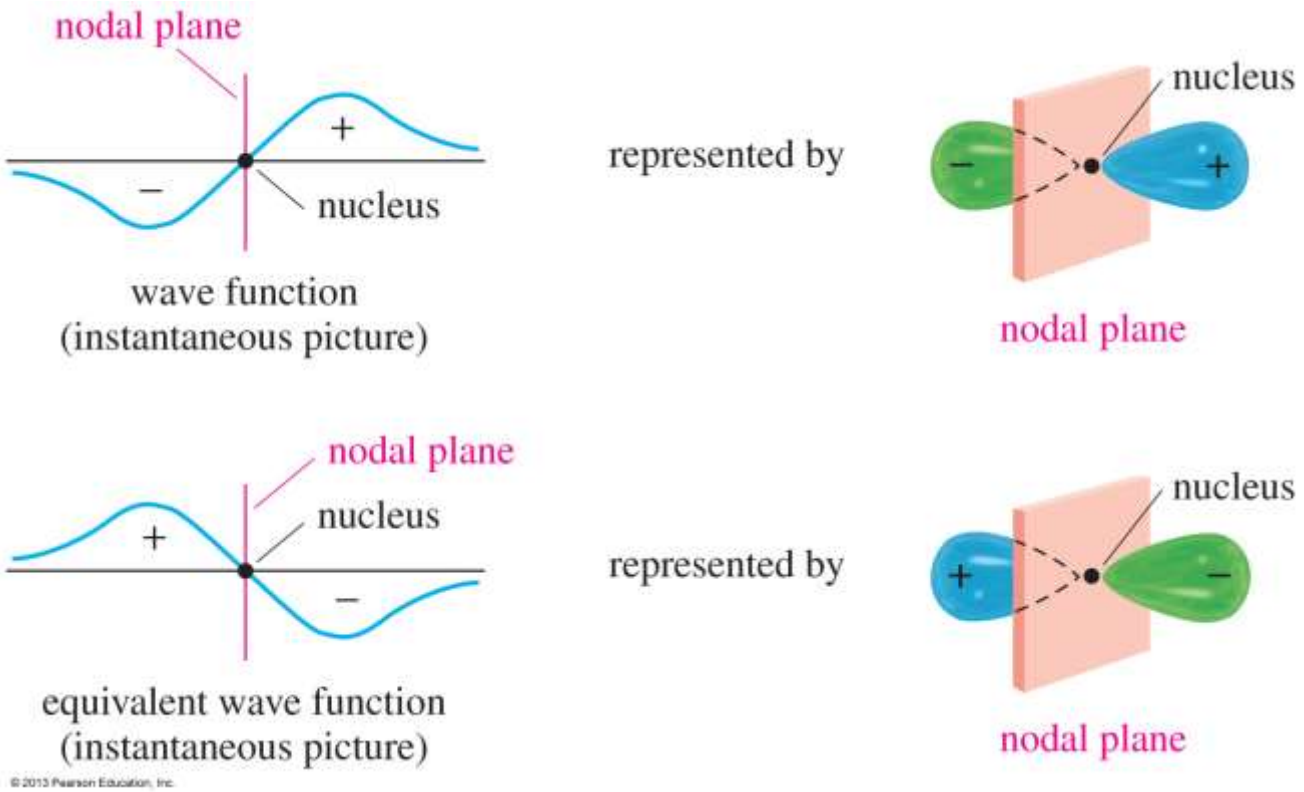


The amplitude at the midpoint is zero – a Node.

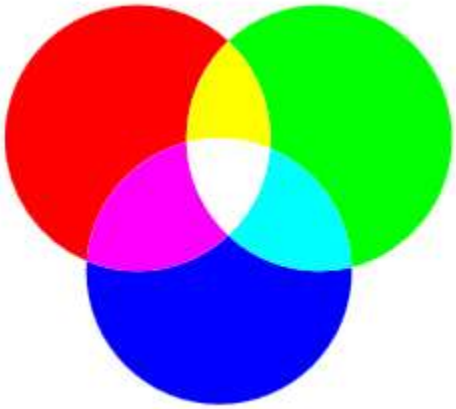
When one half of the string is up, the other is down, the two halves vibrate **out of phase** with one another.

This is the *first Harmonic* of the wave.

Imagine the amplitude (square of the displacement) in three dimensions – two out of phase lobes, separated by a nodal plane: a 2p orbital.



Waves can *interact* with other waves to produce something new or different.
E.g. multiple musical notes can give harmonies; multiple colours can give new colours.



This is also true for electrons / orbitals.

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*.

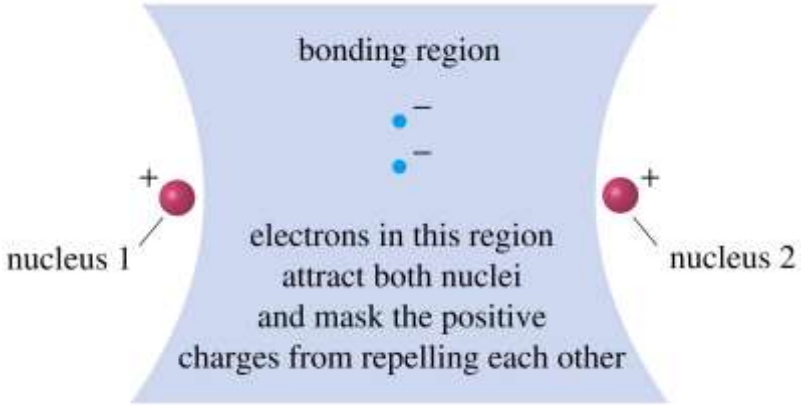
Molecular Orbitals are produced when orbitals on different atoms interact.

Hybrid Atomic Orbitals are produced when orbitals on the same atom interact.

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

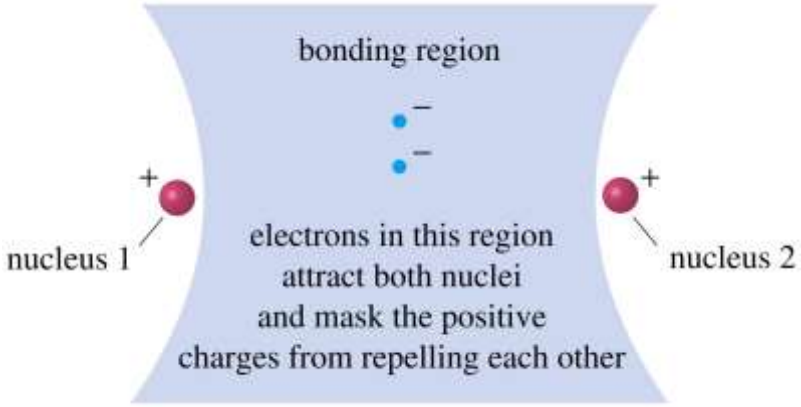
Molecular Orbitals
Two atoms bond together to attain a *lower* energy.
The stability of a covalent bond comes from the large electron density in the space between the two nuclei (the bonding region).

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*.



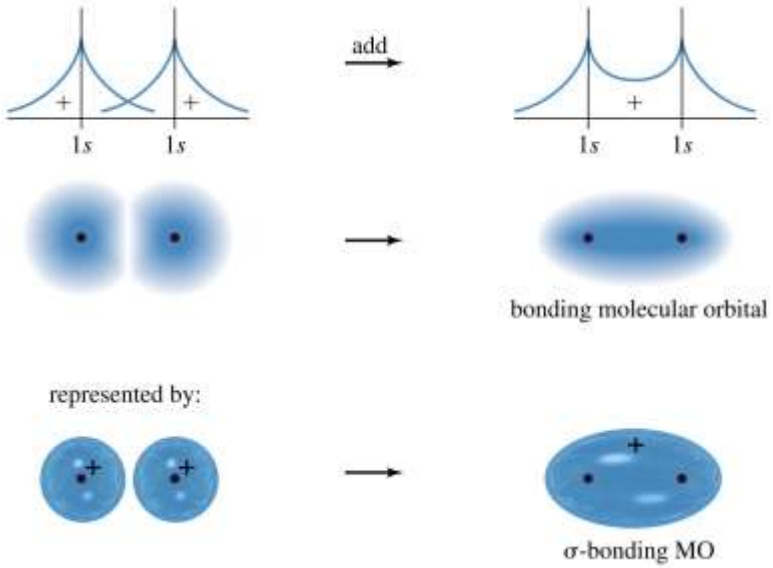
<u>The Hydrogen Molecule</u>
This is the simplest example of covalent bonding.

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).



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.

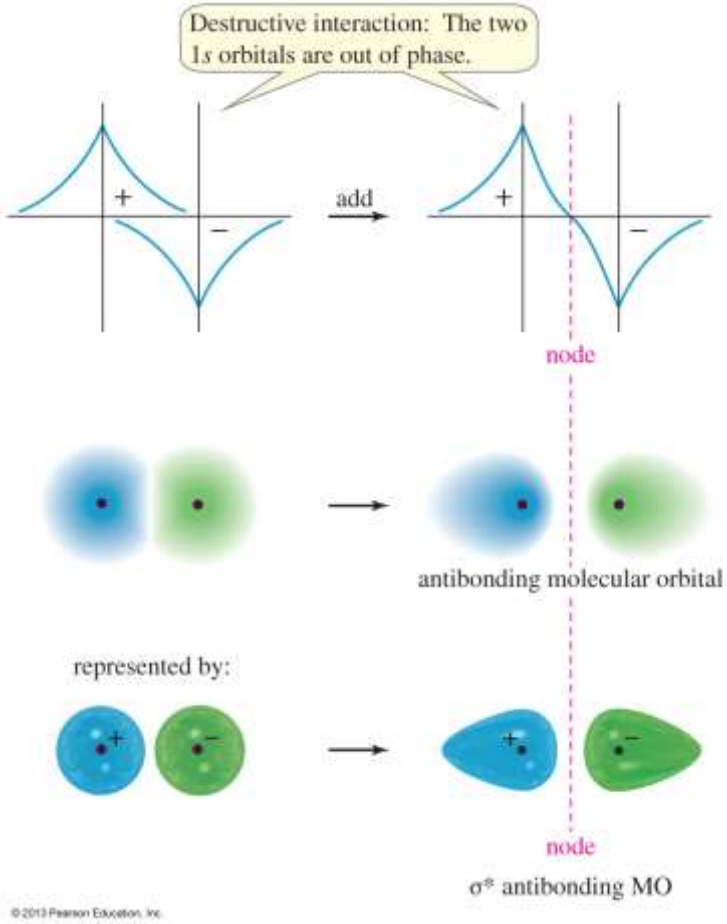
Sigma bonds are the most common bonds in organic chemistry.

All single bonds are sigma bonds.

All multiple bonds contain one sigma bond.

Destructive Interference

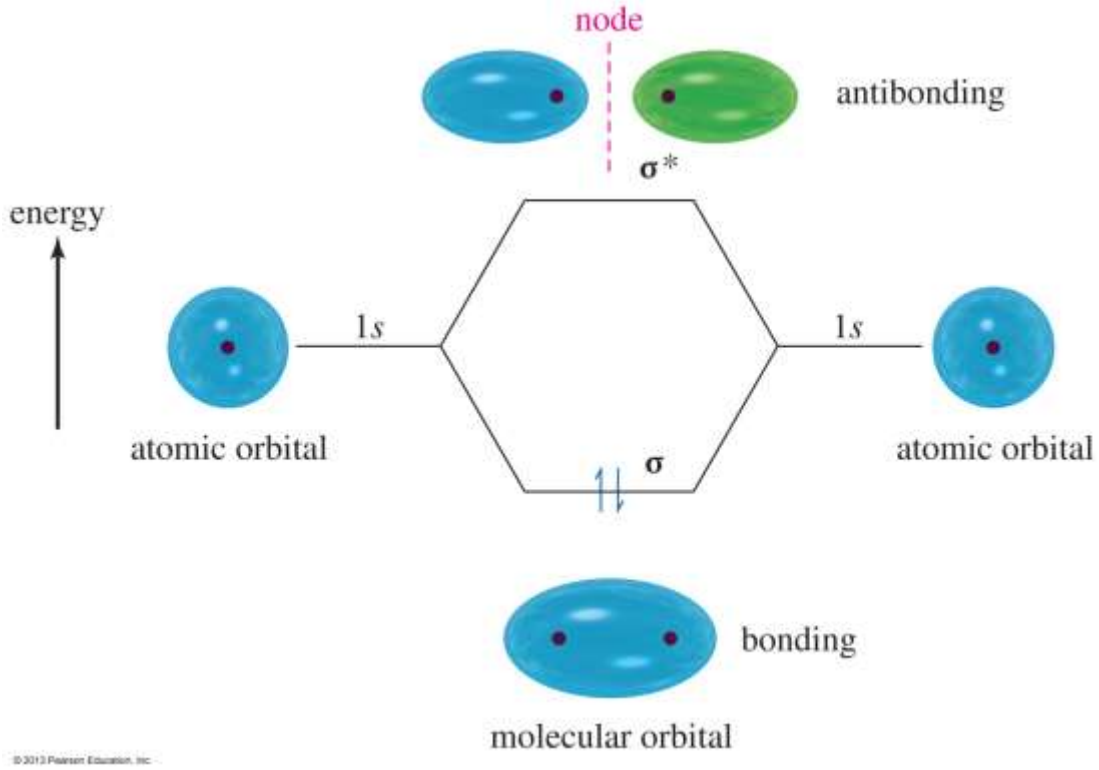
They interfere *destructively* when the overlapping orbitals are *out of phase*.



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*.

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

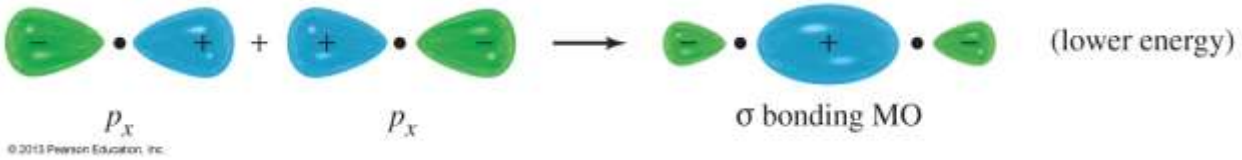


The two electrons (1 from each of the hydrogens) both go into the σ MO, representing a covalent σ bond.

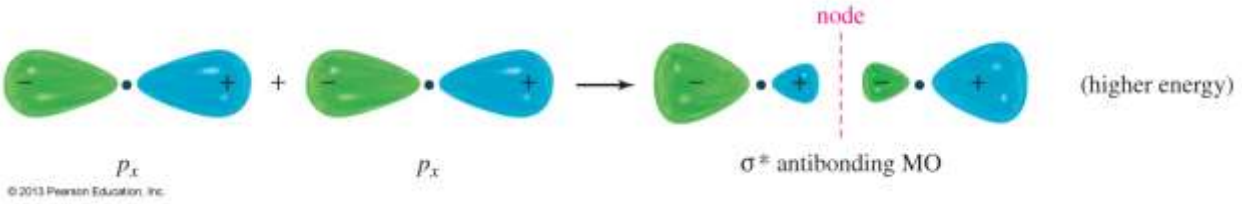
Sigma Overlap with p Orbitals

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

Constructively:

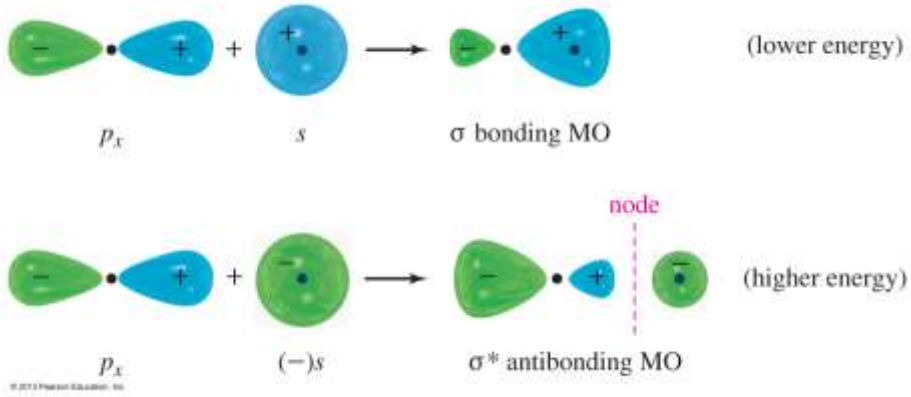


Destructively:



Sigma Overlap with an s and a p Orbital

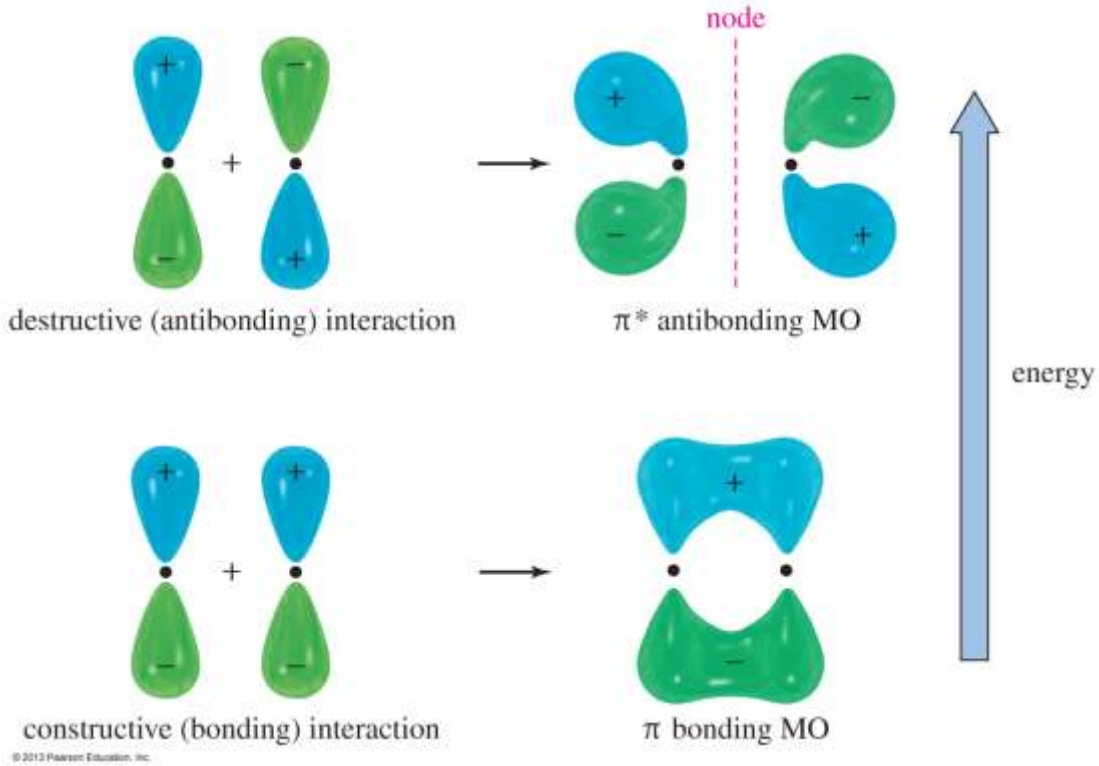
Again, the s and p can overlap constructively or destructively, to give a bonding and a nonbonding MO.



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.

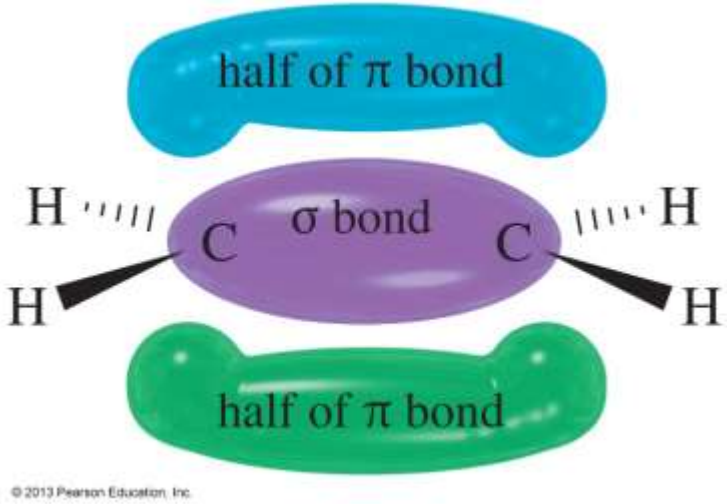


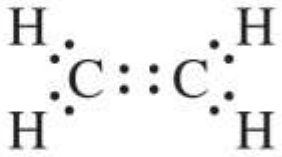
Notice that a π bond is **not** cylindrically symmetrical.

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, and electrons being closer to nuclei.





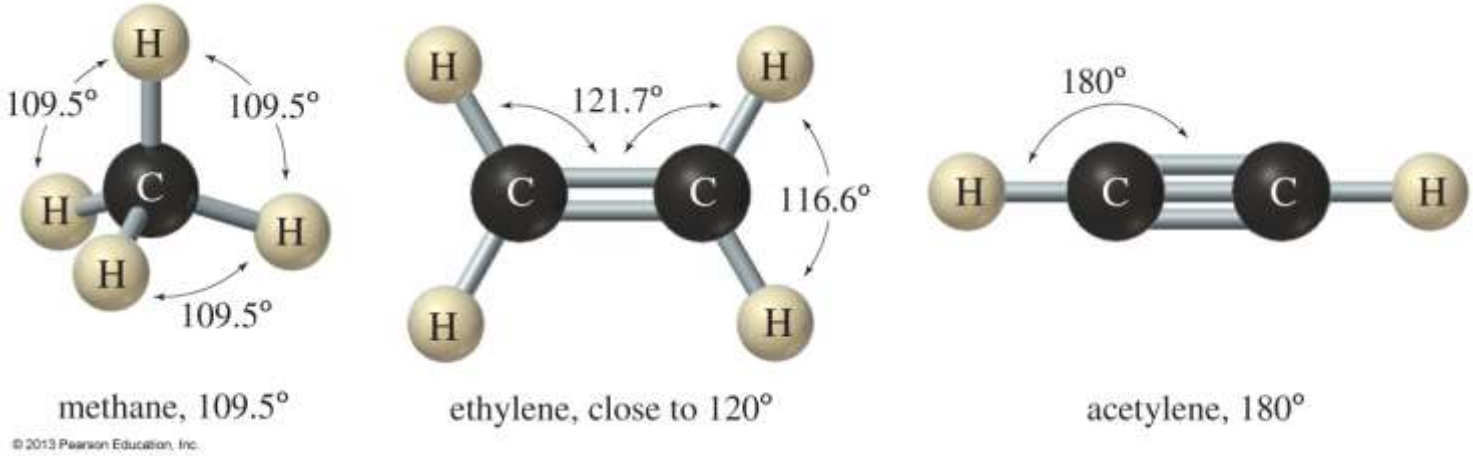
Lewis structure of ethylene

Hybrid orbitals

Hybrid atomic orbitals result from the mixing of atomic orbitals on the **same** atom.

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.



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).

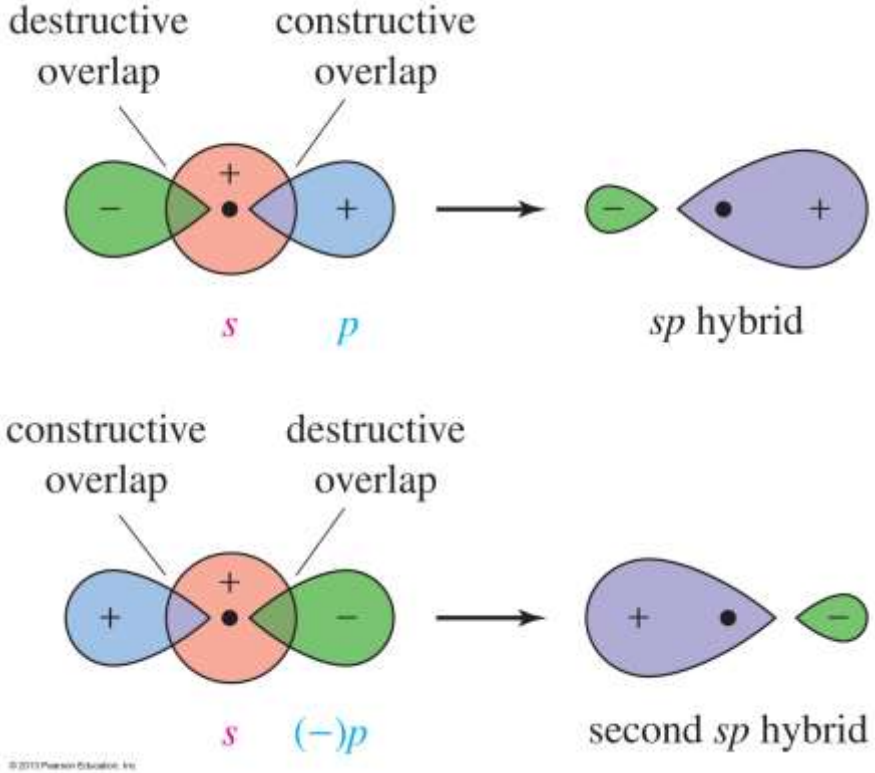
To separate 4 pairs, the best bond angle is 109.5^o.
To separate 3 pairs, the best bond angle is 120^o.
To separate 2 pairs, the best bond angle is 180^o.

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

Hybrid Orbitals

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

Hybrid Atomic Orbitals are produced when orbitals on the same atom interact.
Consider the interaction of an s and a p orbital on the same atom.

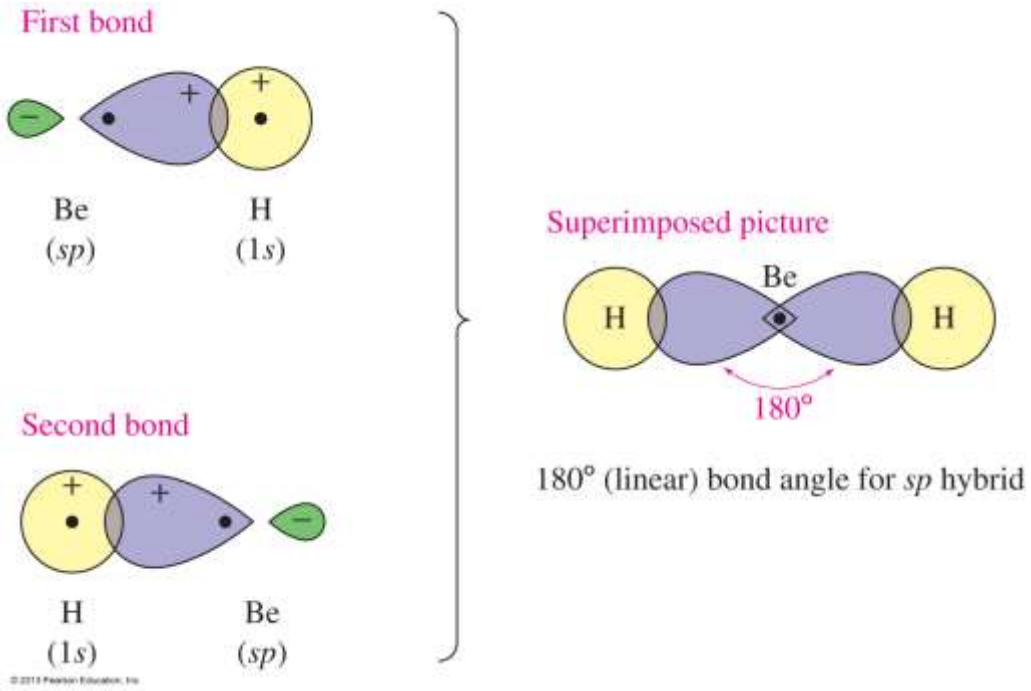


This results in two sp hybrid orbitals.

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

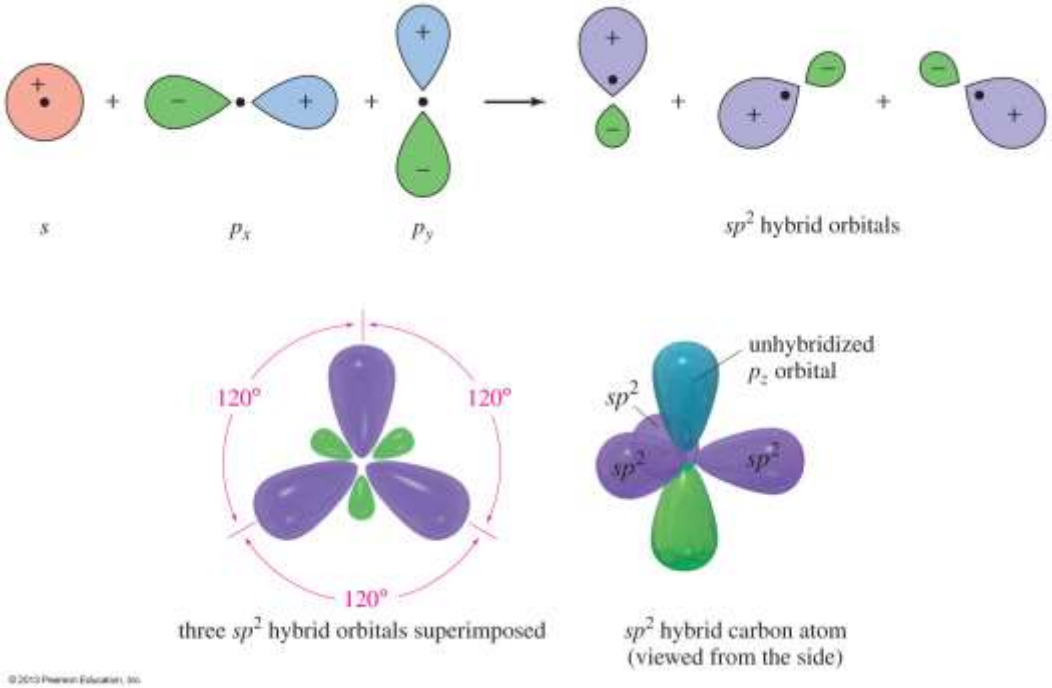
The hybrid orbitals have enhanced electron density oriented either to the left or right of the nucleus.

These sp hybrids provide bond angles of 180°.

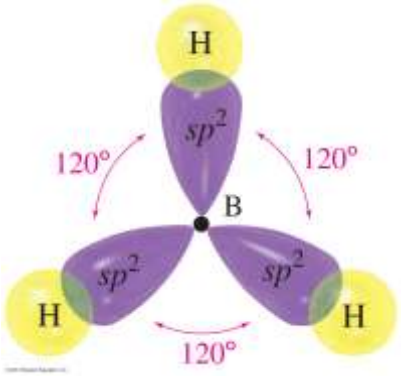


sp^2 Hybrid Orbitals

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

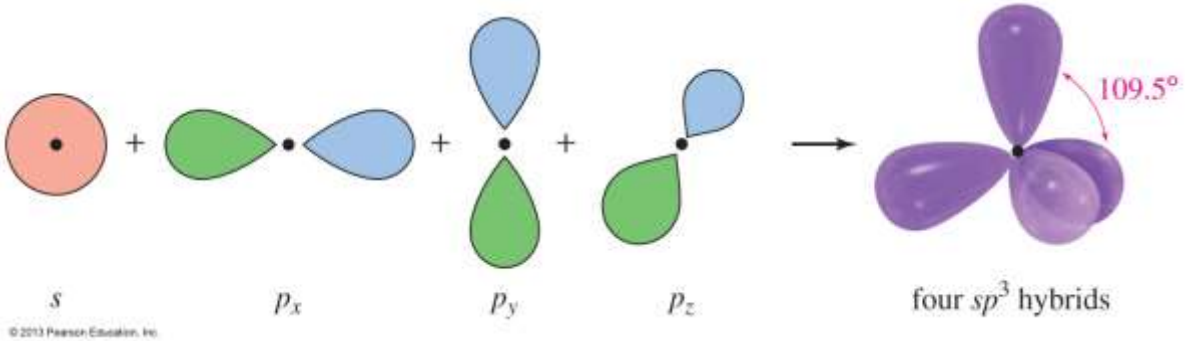


The sp^2 orbitals give rise to the necessary 120° bond angles required to most efficiently orient 3 bond pairs in space.



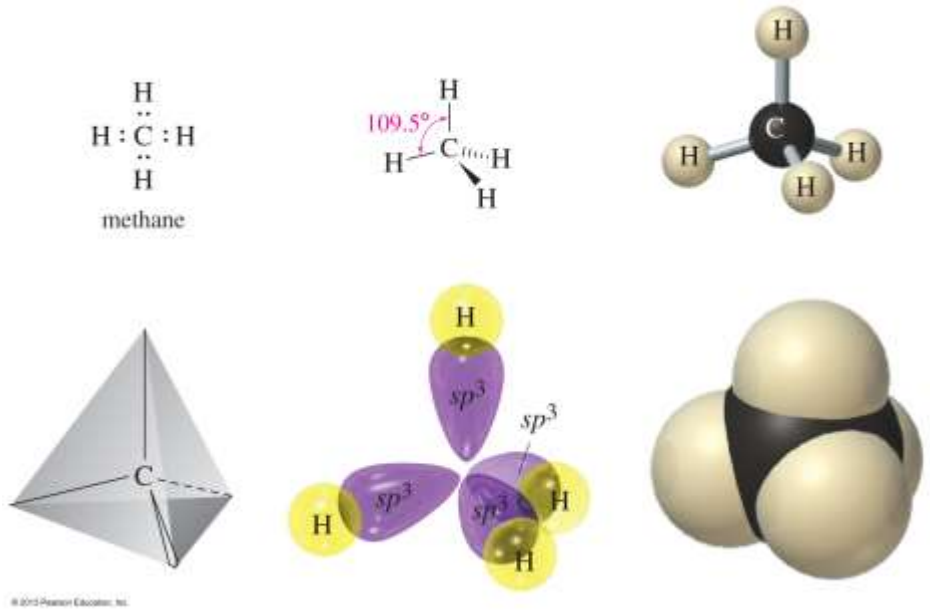
sp^3 Hybrid orbitals

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.

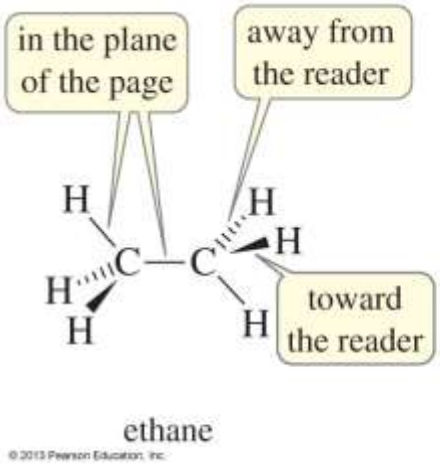
The bond angles are 109.5^o. This tetrahedral arrangement of sp^3 orbitals is especially important for Carbon, and is thus fundamental to organic chemistry.

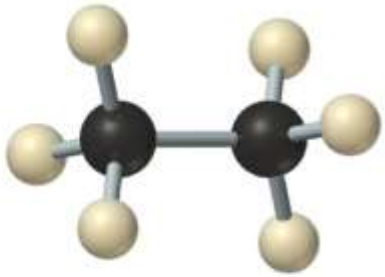


Three Dimensional Structures

Organic molecules are 3 dimensional objects.

Shorthand notation for drawing 3D pictures:





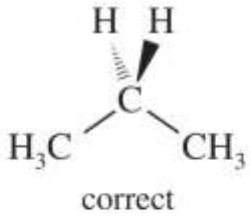
ethane

Straight lines are in the plane of the paper

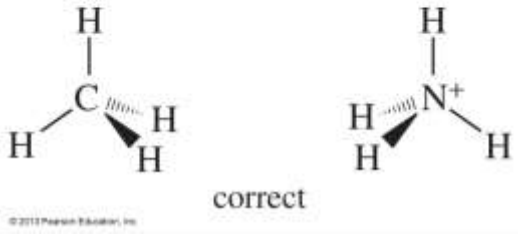
Bold wedges are coming out of the plane

Dashed wedges are going into the plane.

incorrect



correct



correct

HYBRIDIZATION

Atoms adopt hybridizations to achieve the lowest energy situation.

In the absence of other complicating factors (see later e.g. conjugation and aromaticity), the driving force is to separate σ bonds and lone pairs as far apart as possible.

Rules for hybridization of Atoms

From a correct lewis structure, determine for each atom…

(# of σ bonds) + (# of lone pairs) = *a number between 2 and 4*

True for for C/N/O and 2nd row elements, can be higher for 3rd row elements.
(Notice it says SIGMA bonds, and lone PAIRS)

(# of σ bonds) + ***(# of lone pairs)***

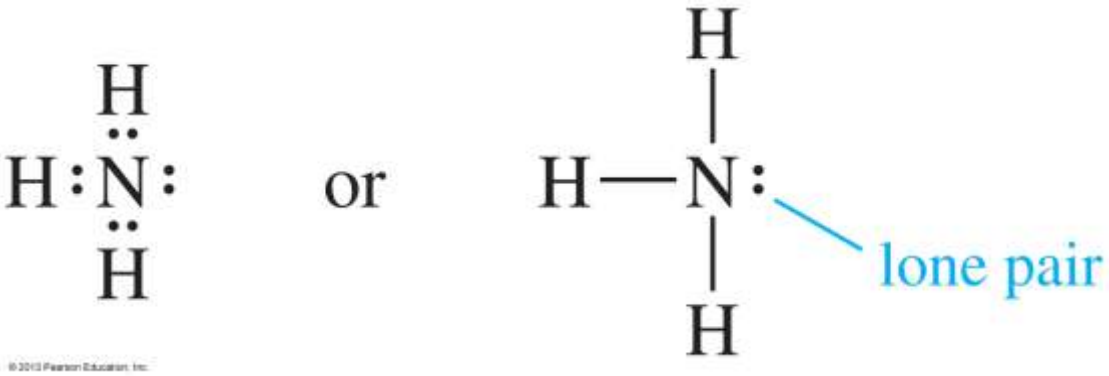
= **4** → ***sp³*** *hybridization = 4x sp^3 hybrid orbitals, tetrahedron, 109.5° bond angles*

= **3** → ***sp²*** *hybridization = 3x sp^2 hybrid orbitals and 1x p orbital, trigonal planar, 120° bond angles*
(p orbital is perpendicular to the bonding plane).

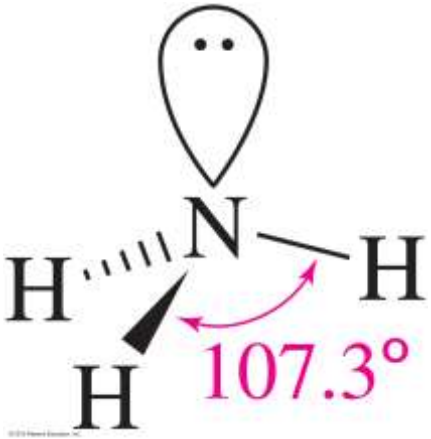
= **2** → ***sp*** *hybridization = 2x sp hybrid orbitals and 2x p orbitals, linear, 180° bond angles*
(p orbitals perpendicular to bonding region and each other).

Consider ammonia, NH_3.

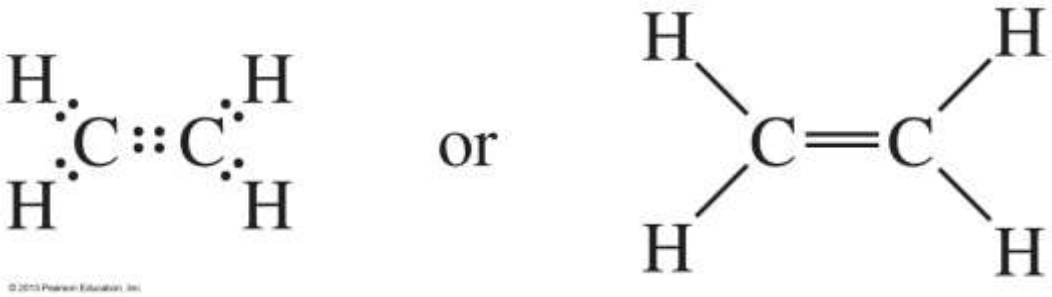
3 sigma bonds and 1 lone pair = 4 hybrid orbitals => sp^3



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).

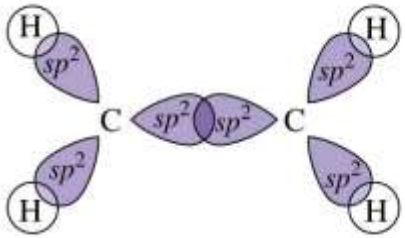


Ethylene C_2H_4

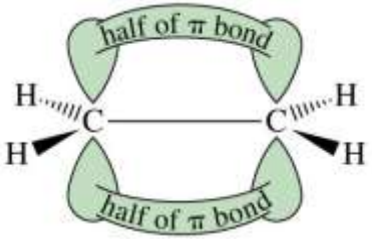


Each carbon is bound to 2 hydrogens, and a double bond to carbon
Each carbon has 3 sigma bonds, no lone pairs => sp^2.

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)

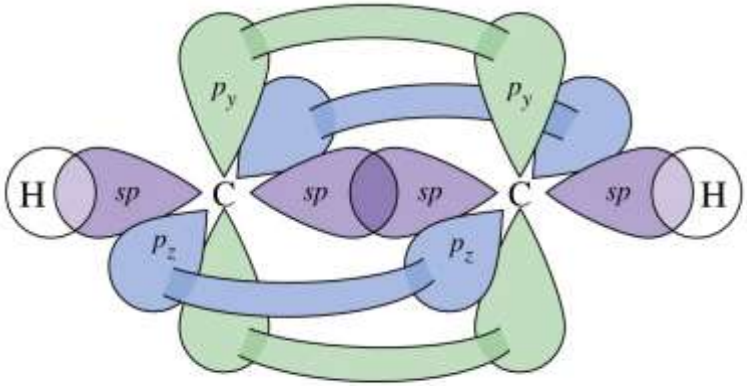
ethylene

Acetylene C_2H_2

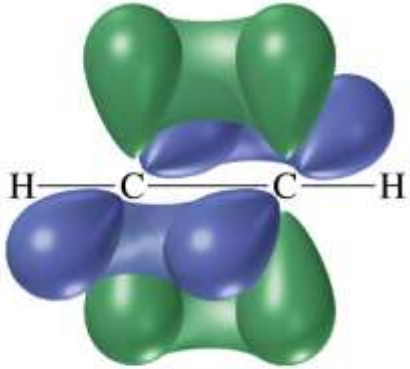
$$H-C\equiv C-H$$

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

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



acetylene



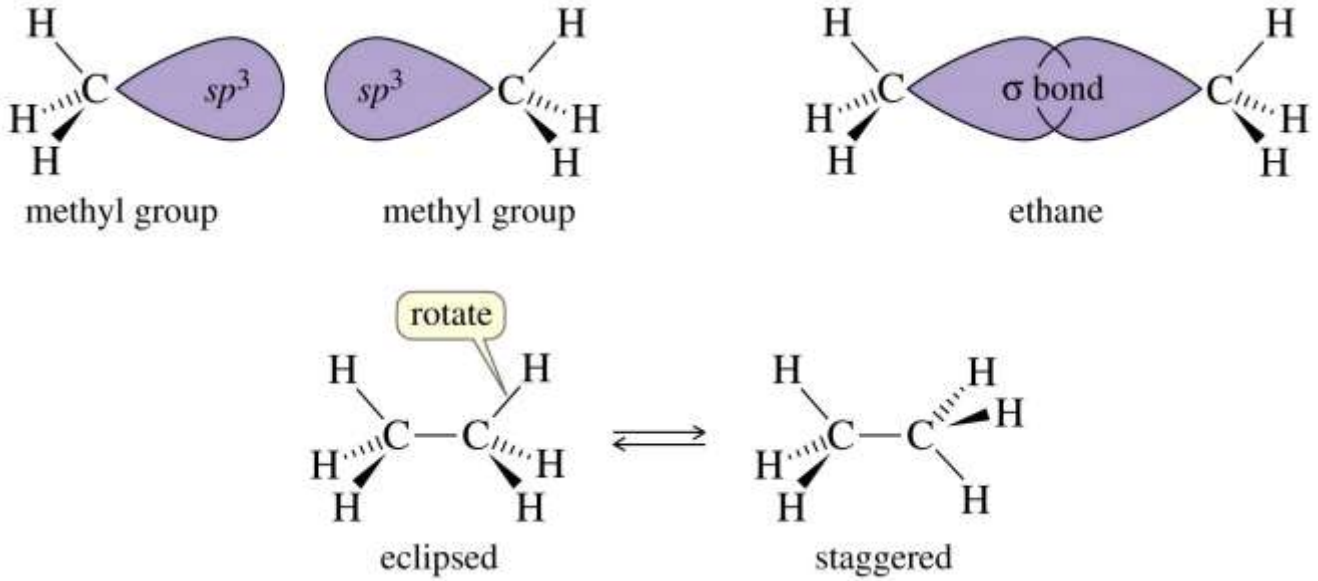
acetylene

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.

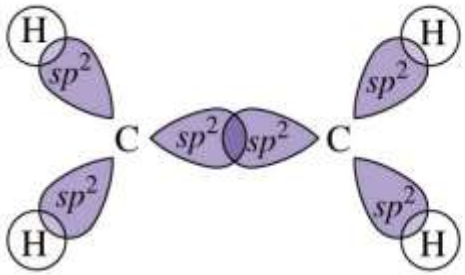
The sp^3 orbitals which overlap to form the C-C bond are shaped such that rotation about the bond axis does not interfere with their overlap.

This bond can freely rotate.

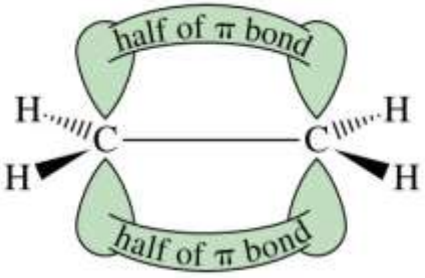
Rigidity of Double Bonds

Not all bonds can freely rotate.

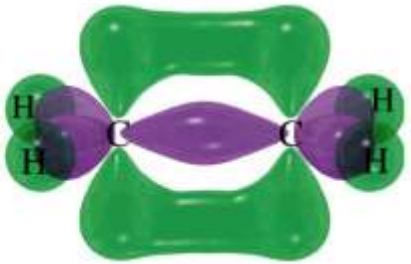
Consider the bonding in ethylene: a sigma and a pi bond.



σ bond framework
(viewed from above the plane)



π bond
(viewed from alongside the plane)

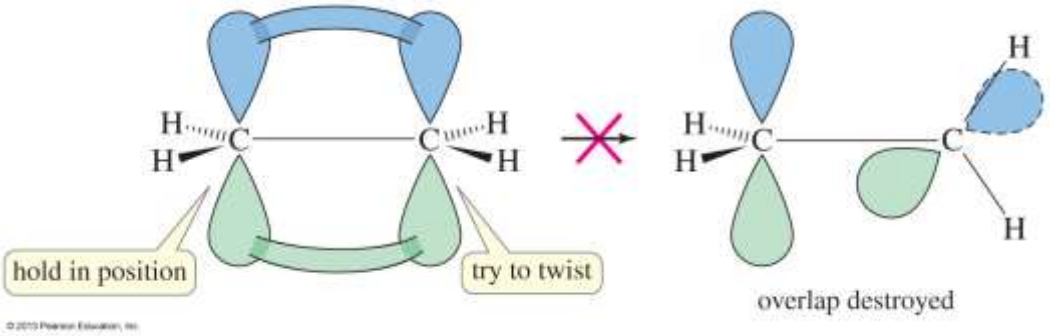


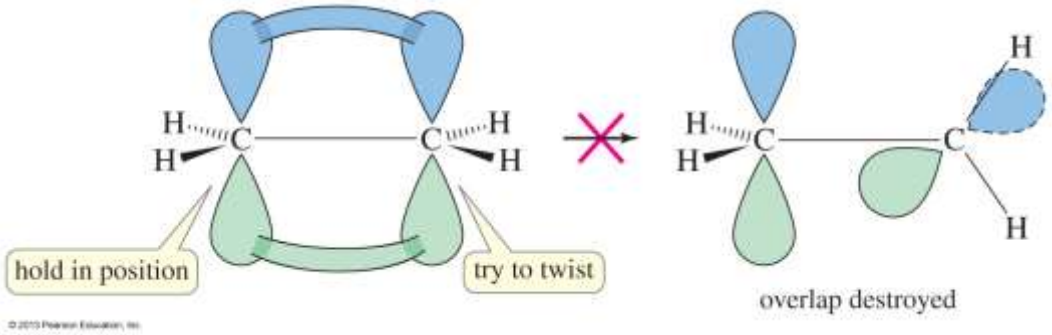
ethylene

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.

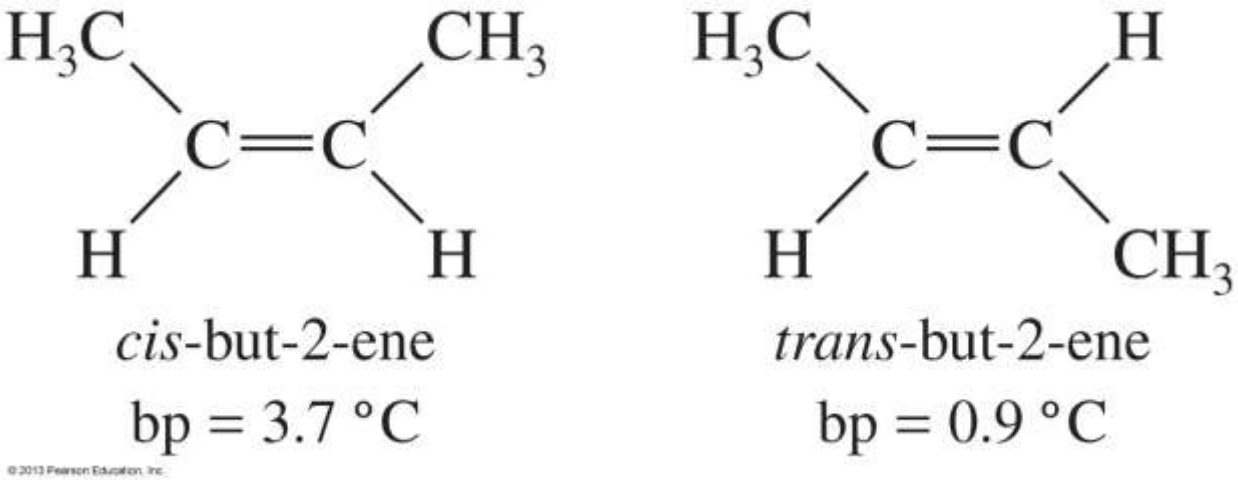
In general: Single bonds can rotate
Multiple bonds cannot.

Isomers

An **isomer** is a compound that has the same molecular formula as another, but is *different*.

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 but-2-enes:



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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 but-2-ene.

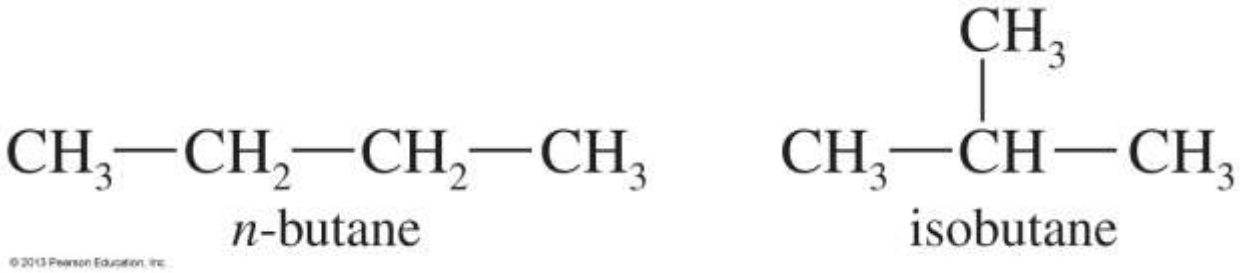
When isomers differ only in their arrangement in space, and not in the order they are bonded, they are called **Stereoisomers**.

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

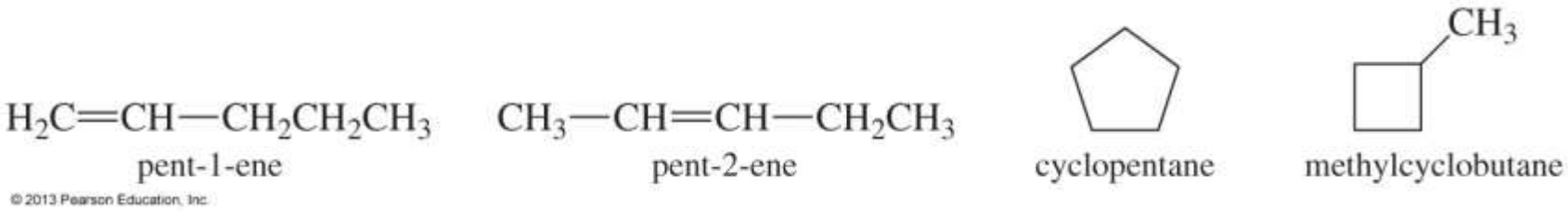
These are isomers that differ in their *bonding sequence*. They have different *bond connectivity*.



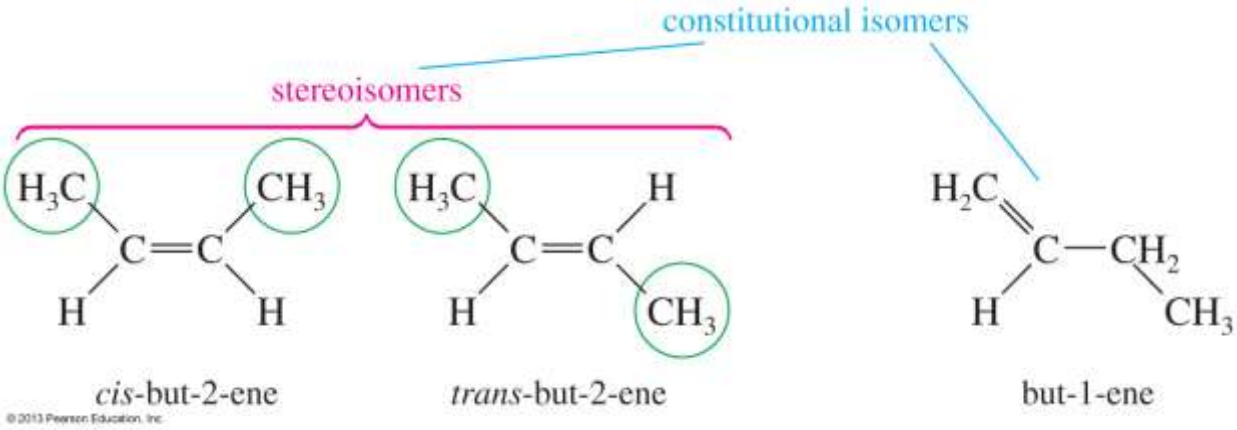
For example, the above compounds have the same structural formula of C_4H_{10}, but are different compounds.

They are **structural isomers** (or **constitutional isomers**).

Also e.g. C_5H_{10}



Stereoisomers and Structural (Constitutional) Isomers



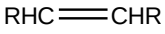
The previous work was mainly organic chemistry background knowledge.

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).

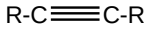
These are some of the most common functional groups:

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

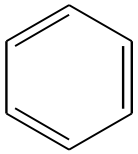
alkane

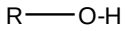


alkene

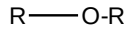


alkyne

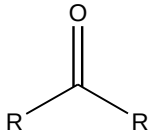

aromatic



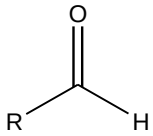
alcohol



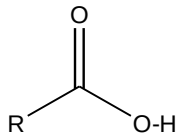
ether



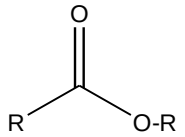
ketone



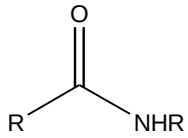
aldehyde



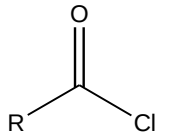
carboxylic acid



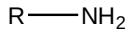
ester



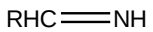
amide



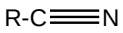
acid chloride



amine



imine



nitrile