Module 3, Lecture 3

Structure and Reactions of Organic Molecules

Part 3 - Valence bond theory for organic molecules

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References to Brown *et al* text shown in BLUE

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Learning Objectives:

to understand hybridisation in multiple bonded molecules

to understand the formation of σ bonding frameworks

to understand the formation of π bonding frameworks

Textbook: **Chapter 9, sections 9.1-9.6; Chapter 26, section 26.1, Brown**

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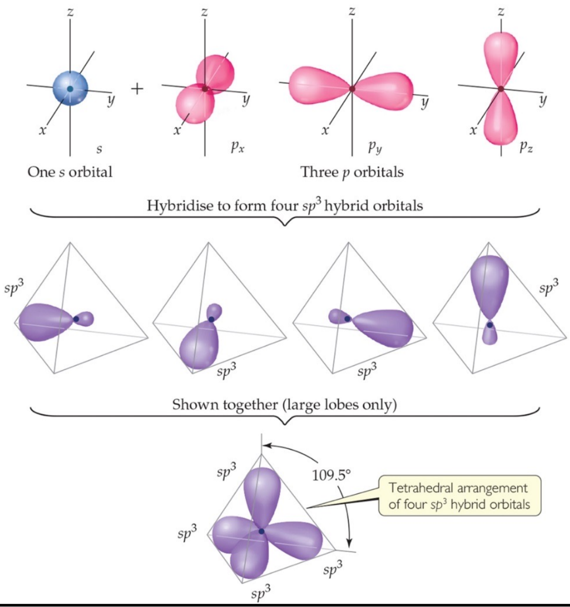
Recap: methane sp^3 hybrids – Tetrahedral Molecules



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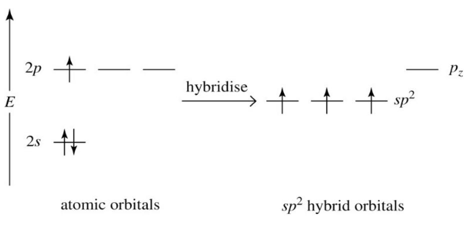
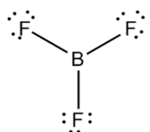
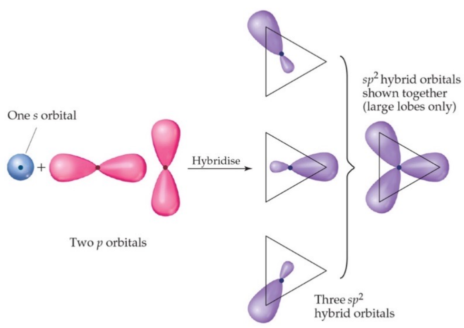
Boron trifluoride BF_3 -Trigonal planar sp^2







four atomic orbitals

three hybrid + one p orbitals

one s orbital

two p orbitals

sp^2

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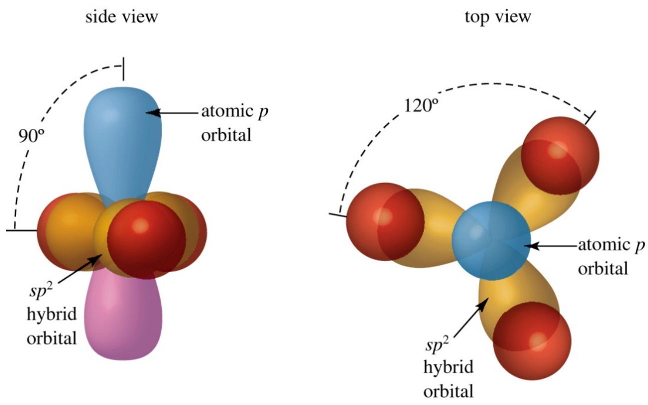
Boron trifluoride BF_3 -Trigonal planar sp^2



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Practice Exercise

Try NH_3 or H_2O or $BeCl_2$ as an exercise

- Nature of hybrids sp^2 or sp^3
- any lone pairs?

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Multiple Bonding

Situations occur where there are more than two electrons involved in bonding two atoms

Called multiple bonds

Common in organic chemistry between C atoms

4 bonding electrons $\longrightarrow$ double bond

6 bonding electrons $\longrightarrow$ triple bond

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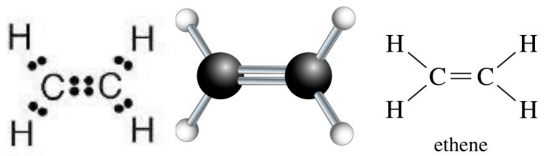
Ethene CH_2=CH_2

This molecule has a carbon-carbon double bond



Each carbon has three sets of electrons around it, meaning that the angles are about 120°.

This means that sp^3 hybrid orbitals will not work.

Need to form three orbitals (which will lie at 120° apart)

So, hybridise the 2s orbital and only two of the 2p orbitals, to get three **sp^2 hybrid orbitals**.

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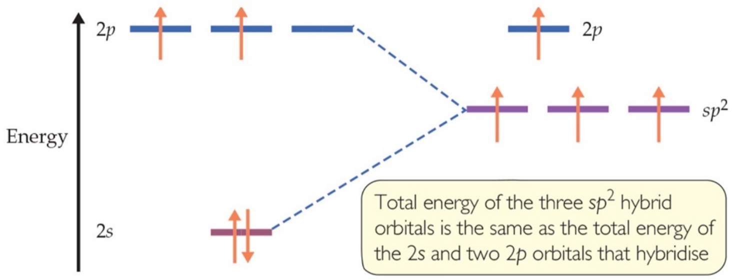
Ethene $CH_2{=}CH_2$



one p orbital untouched

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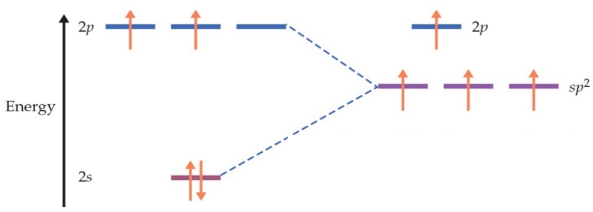
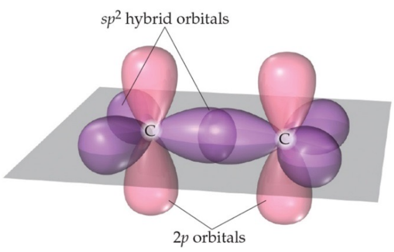
σ-bonding framework

The sp^2 hybrid orbitals overlap with the hydrogen1s orbitals make our sigma (σ) bonds –the ***sigma bonding framework***





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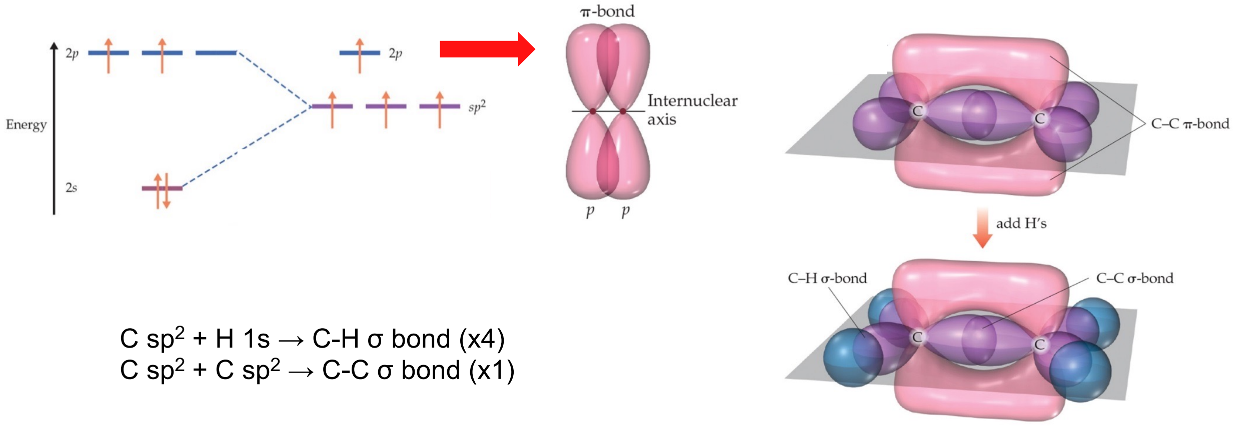
π-bonding framework

The unused 2p orbitals on the carbons overlap with each other to make a new type of bond – a **pi (π) bond**.



C sp^2 + H 1s → C-H σ bond (x4)
C sp^2 + C sp^2 → C-C σ bond (x1)

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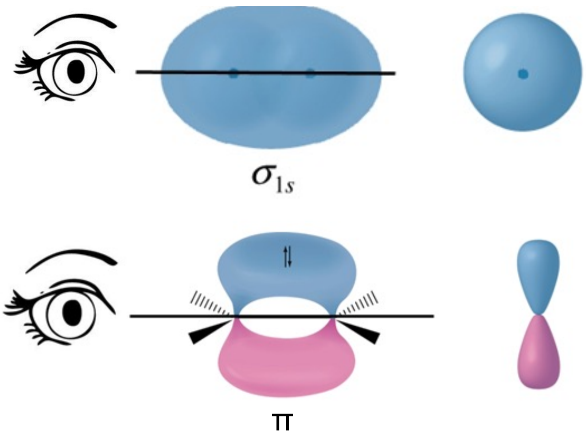
σ and π molecular orbitals

Consider looking along the internuclear axis



End on view similar to s and p atomic orbitals

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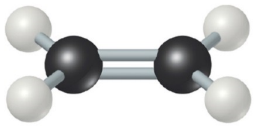
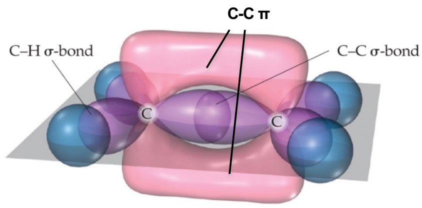
Ethene $CH_2{=}CH_2$

Combination of one σ and one π bond gives a C=C double bond.

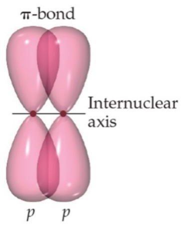




Note the different ways that the orbitals overlap.

The π bond (side ways overlap) is weaker than the σ bond (front on overlap), and will more readily break in chemical reactions

- more of this later.



Must first have a σ bond before can form π bonds

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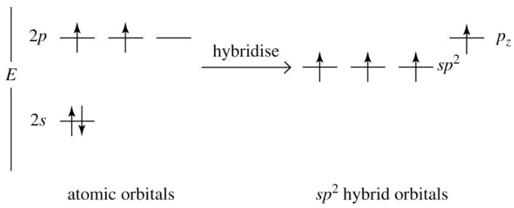
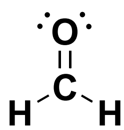
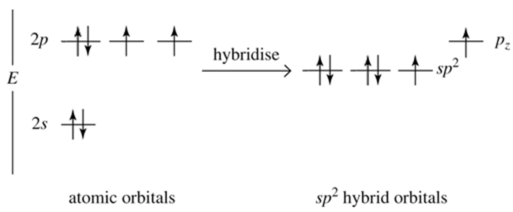
Methanal $H_2C{=}O$

Form sp^2 hybrid orbitals on the carbon and the oxygen to form the sigma bonds and accommodate lone pairs
– the remaining p orbitals are used to make the π bond.

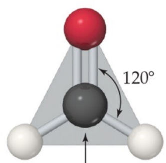


C forms 4 bonds
3 σ bonds and 1 π bond





O forms 2 bonds
1 σ bond and 1 π bond
2 lone pairs occupy remaining sp^2 hybrid orbitals



Trigonal planar
2 single bonds
1 double bond
sp^2 hybridisation

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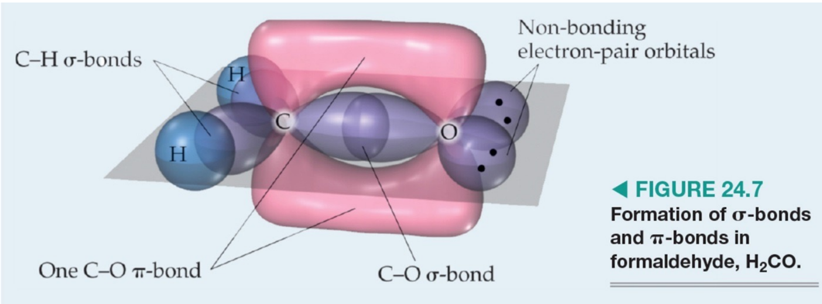
Methanal $H_2C=O$

We form sp^2 hybrid orbitals on the carbon and the oxygen to form the sigma bonds and to take the lone pairs
– the remaining p orbitals are used to make the pi bond.



◀ **FIGURE 24.7** **Formation of σ-bonds and π-bonds in formaldehyde, H_2CO.**

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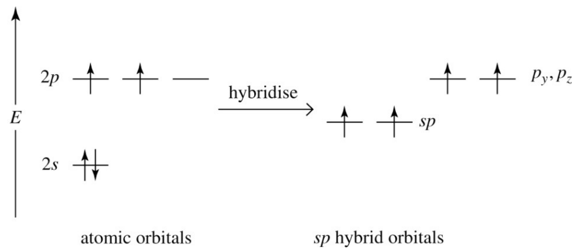
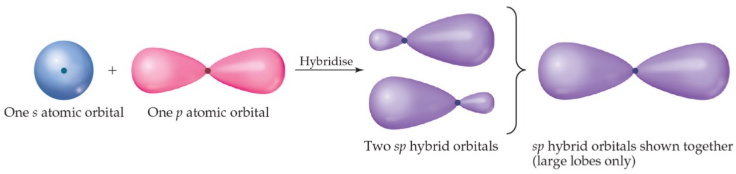
Ethyne $HC\equiv CH$

Each carbon has only two sets of electrons around it. Expect the molecule to be linear.
Neither sp^3 or sp^2 hybrid orbitals will work here – this time we use **sp hybrid orbitals**, made from the 2s and only one of the 2p orbitals





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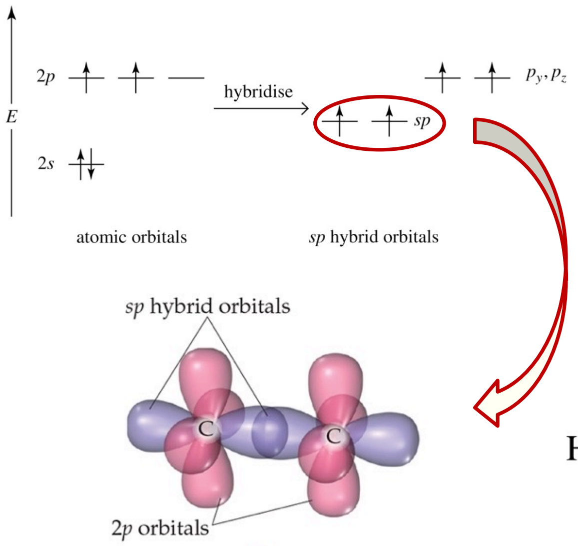
σ-bonding framework



H—C—C—H

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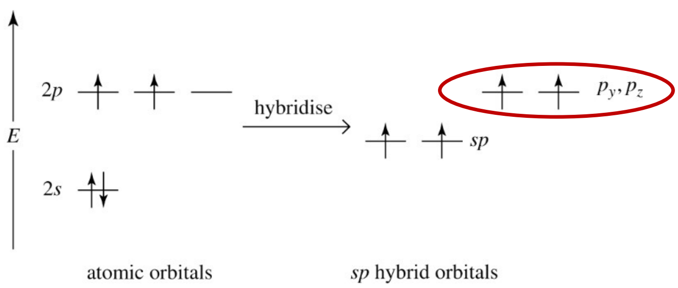
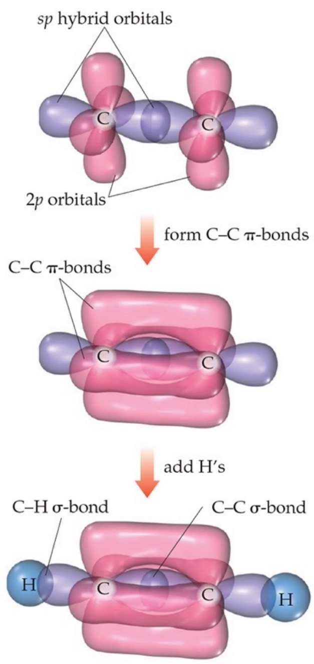
π-bonding framework





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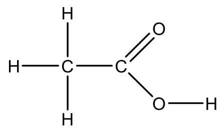
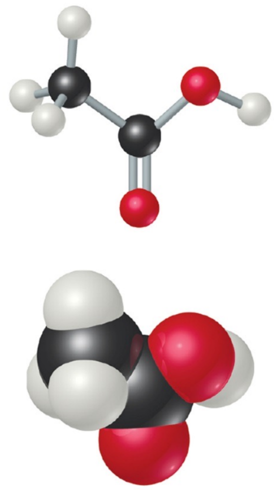
Practice Exercise

Try CO_2 or N_2 or O_2 as an exercise

- Nature of hybrids sp^2 or sp^3
- Consider multiple bonds
- any lone pairs?





▲ **FIGURE 9.10** Ball-and-stick (top) and space-filling (bottom) representations of acetic acid, CH_3COOH.

✱ Homework ✱

Chemistry – the central science 15th Ed

Brown et al.

Problems 26.44

Answers on Blackboard