CH-110 Advanced General Chemistry I

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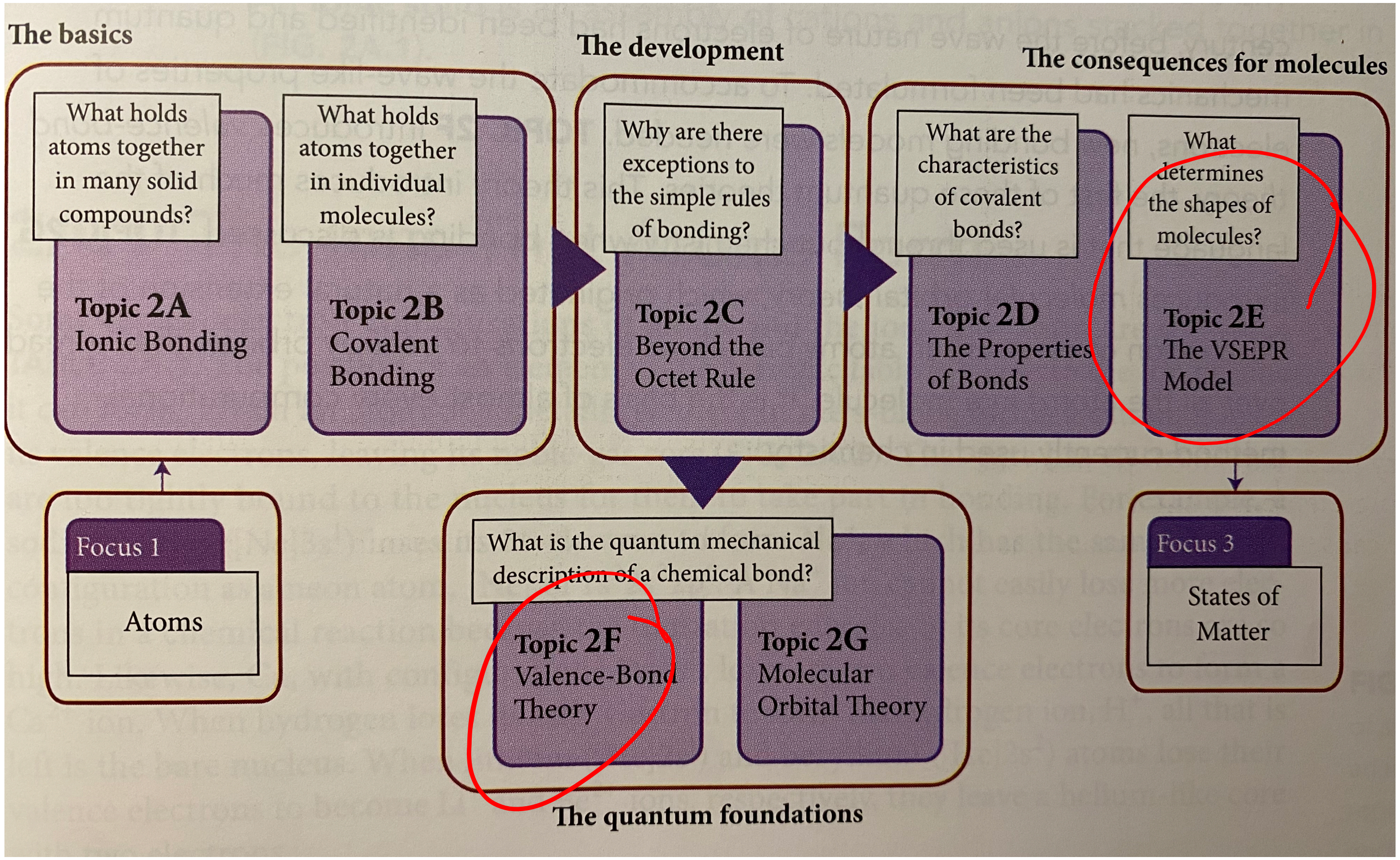
Overview Chapter 2 (Focus 2: Bonds Between Atoms)



The basics

What holds atoms together in many solid compounds?

Topic 2A Ionic Bonding

What holds atoms together in individual molecules?

Topic 2B Covalent Bonding

The development

Why are there exceptions to the simple rules of bonding?

Topic 2C Beyond the Octet Rule

The consequences for molecules

What are the characteristics of covalent bonds?

Topic 2D The Properties of Bonds

What determines the shapes of molecules?

Topic 2E The VSEPR Model

Focus 1

Atoms

What is the quantum mechanical description of a chemical bond?

Topic 2F Valence-Bond Theory

Topic 2G Molecular Orbital Theory

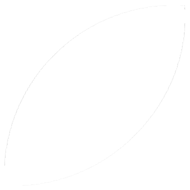
The quantum foundations

Focus 3

States of Matter

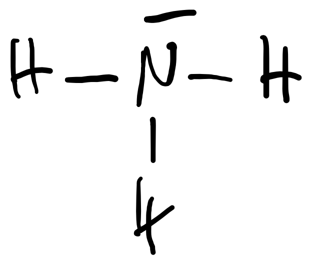
Valence-Bond Theory

Topic 2F

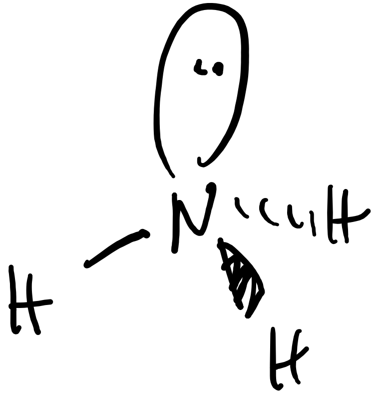


2F Valence-bond theory

Lead-in NH_3

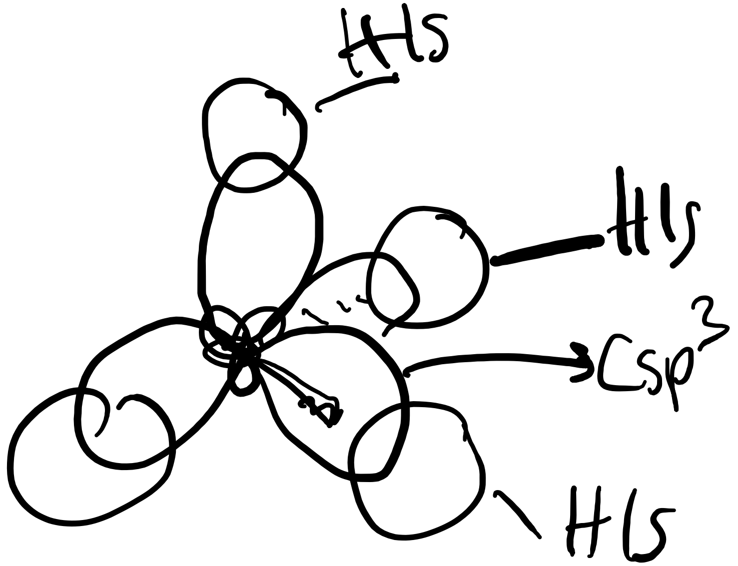


Lewis



VSEPR

shape: trigonal pyramidal



VB

Combinations of atomic orbitals

shape → bonds!

2F Valence-bond theory

Lead-in

Electrons behave like waves, they are *not* localized dot-like particles.

Valence-bond theory is a description of covalent bonding in terms of atomic orbitals.

It is a quantum mechanical description of the distribution of electrons in bonds that goes beyond Lewis's theory and the VSEPR model.

Valence-bond theory helps to explain why an electron pair is so fundamental to the formation of bonds and provides a way of calculating the numerical values of bond strengths, lengths, and angles.

Quantitative applications of VB theory are beyond the scope of this text, but the concepts and the language the theory introduces are used throughout chemistry, especially in organic chemistry.

2F Valence-bond theory

Lead-in

- Lewis model assumes: each bonding electron pair is located between two bonded atoms: a localized electron model.
- However, from Topic 1C, we know that the location of an electron in an atom cannot be described in terms of a precise location and only in terms of its wavefunction.
- The wavefunction is interpreted in terms of the probability of finding the electron somewhere in a region of space defined by its orbital.
- **Valence-bond theory takes this wave nature of electrons into account.**

→ Topic 2F.1 Sigma and pi bonds
→ Topic 2F.2 Electron promotion and the hybridization of orbitals
Topic 2F.3 Valence-bond theory and hypervalent compounds
Topic 2F.4 Characteristics of multiple bonds

WHY DO YOU NEED TO KNOW THIS MATERIAL?

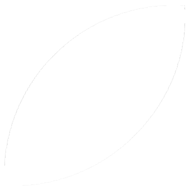
- Valence bond theory gives insight into the quantum mechanical nature of the covalent bond.
- Introduces language used throughout chemistry.

WHAT DO YOU NEED TO KNOW ALREADY?

- Atomic structure in terms of occupation of orbitals (Topics 1D and 1E)
- The notion of a wavefunction (Topic 1C)
- Concept of electron spin (Topic 1D)

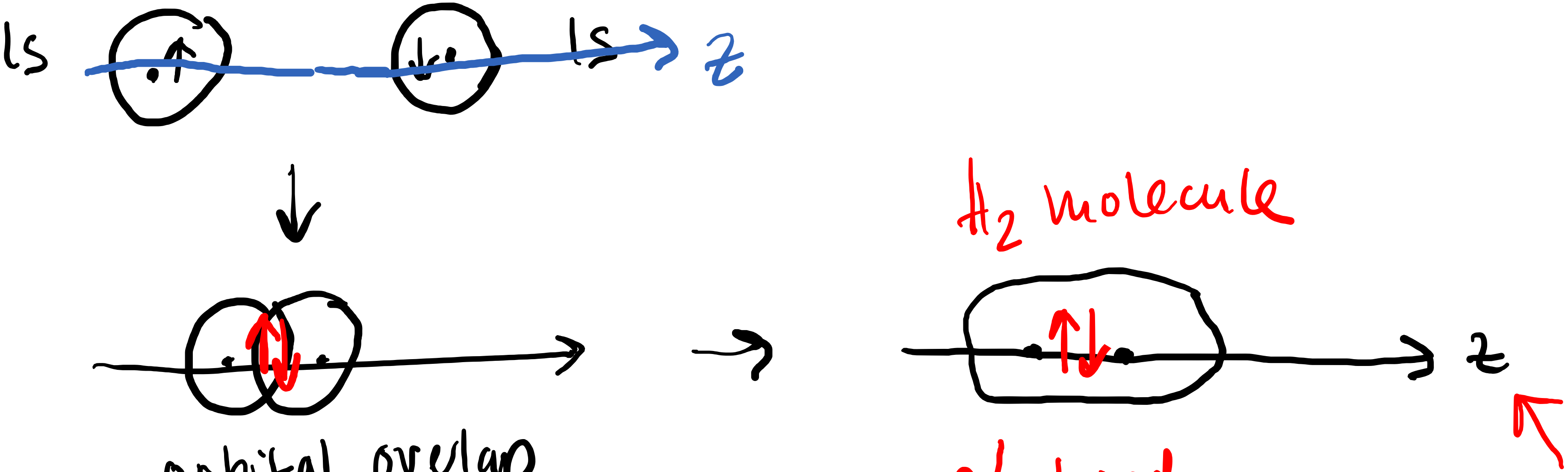
Sigma and Pi Bonds

Topic 2F.1



2F.1 Sigma and pi bonds

Simplest case: H_2



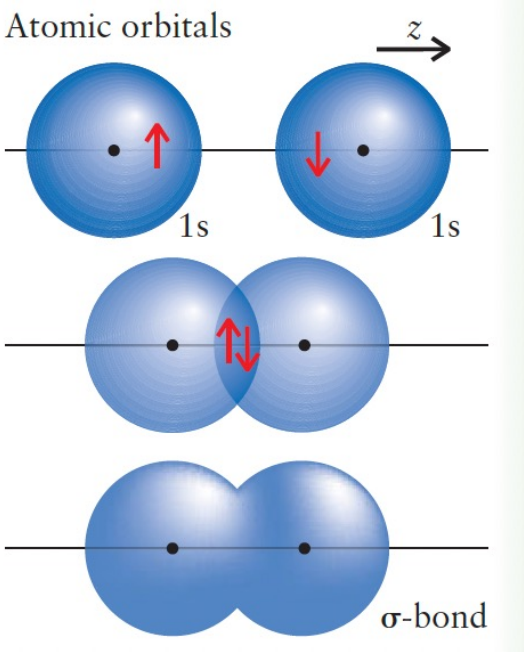
orbital overlap
spins are paired

σ-bond

- cylindrically symmetric
- no nodal planes along z

2F.1 Sigma and pi bonds

Sigma bonds



Older book version: Figure 3.8

Consider the formation of H_2:

- Each H atom in its ground state has one electron in a 1s-orbital.
- Valence-bond theory: as the two atoms come together, the spins of their 1s-electron pairs (denoted ↑↓) and the two atomic orbitals merge
- The resulting sausage-shaped distribution of electrons is called a "σ-bond" (a sigma bond).
- The letter σ (sigma) is equivalent to "s", for s-orbital.

2F.1 Sigma and pi bonds

Sigma bonds

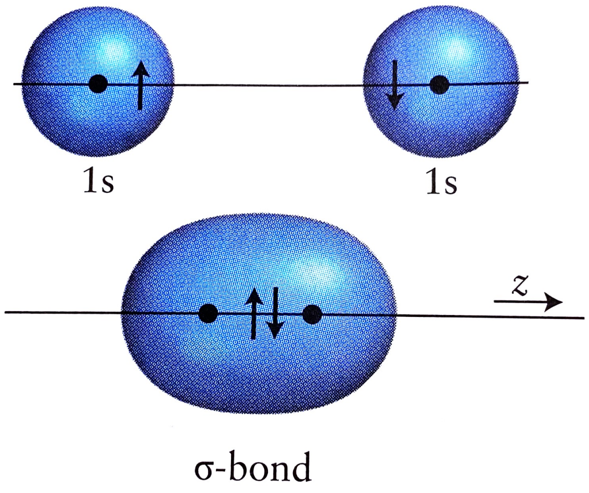


Figure 2F.1 (new book version)

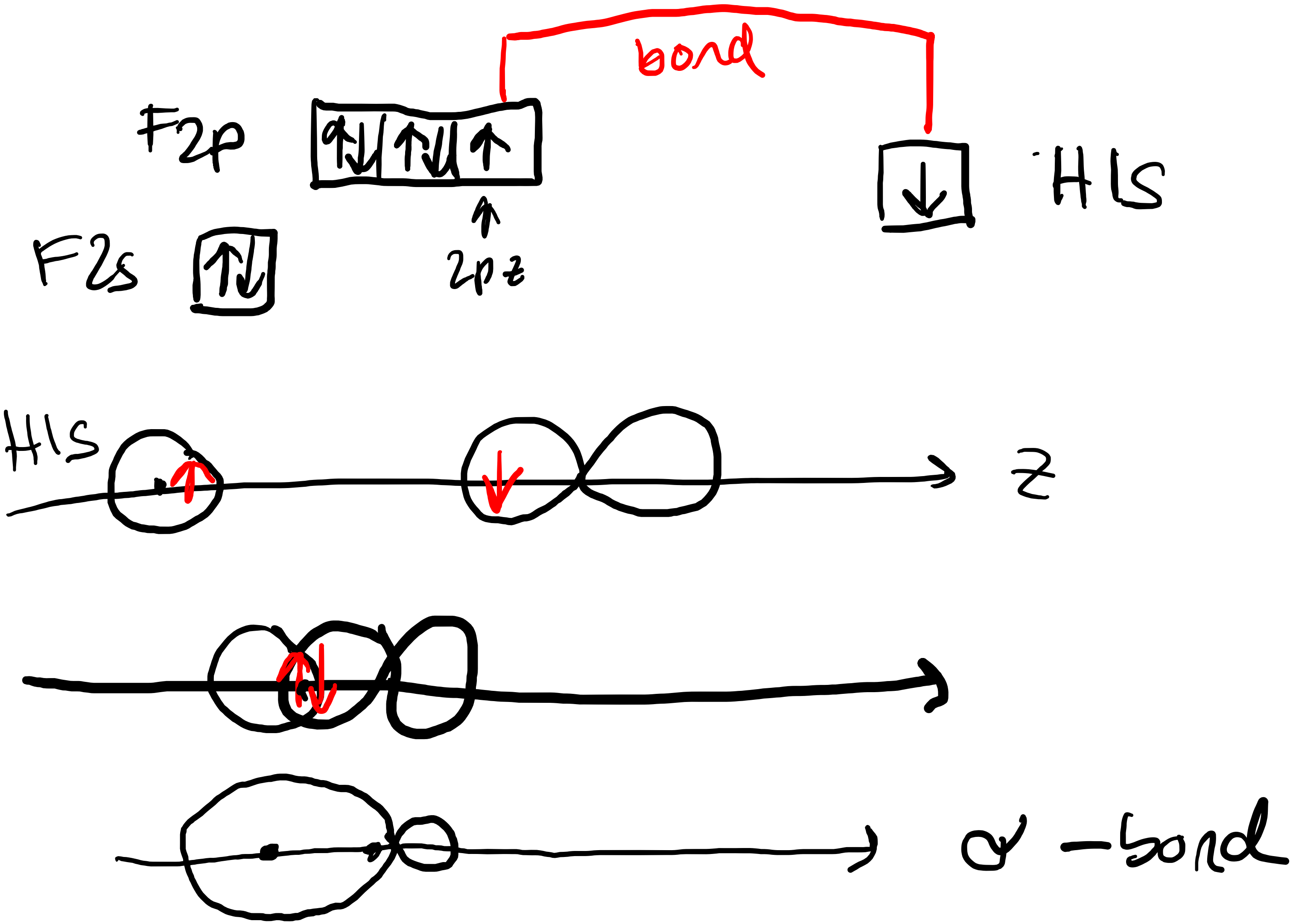
A σ-bond is **cylindrically symmetrical** (the same in all directions around the long axis of the bond), with **no nodal planes** containing the internuclear axis.

The merging of the two atomic orbitals is called the **overlap of orbitals**.

The greater the orbital overlap, the stronger the bond.

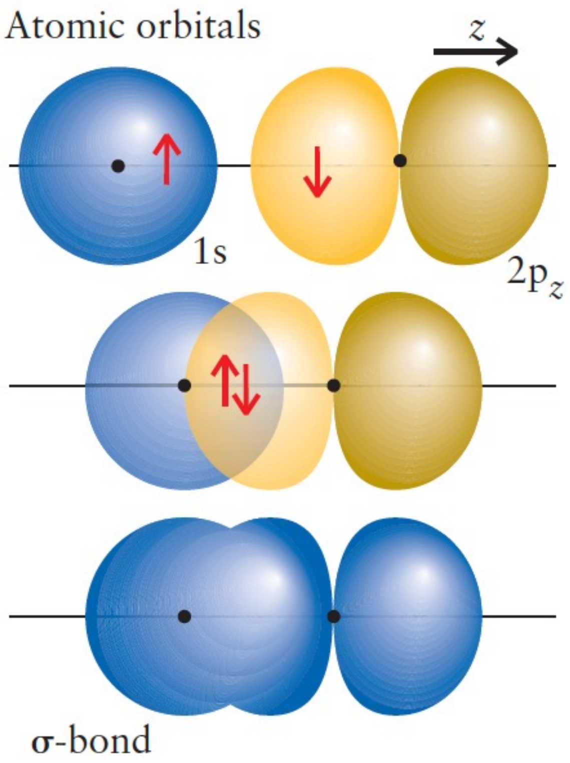
2F.1 Sigma and pi bonds

HF



2F.1 Sigma and pi bonds

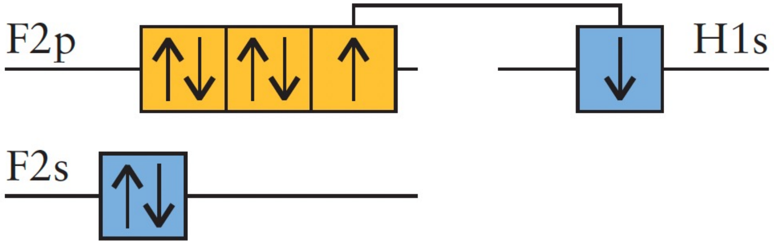
Sigma bonds: HF



Older book version: Figure 3.9

$2p_z$-orbital of fluorine

+ 1s-orbital of hydrogen



33 Hydrogen fluoride, HF

2F.1 Sigma and pi bonds

Sigma bond in HF

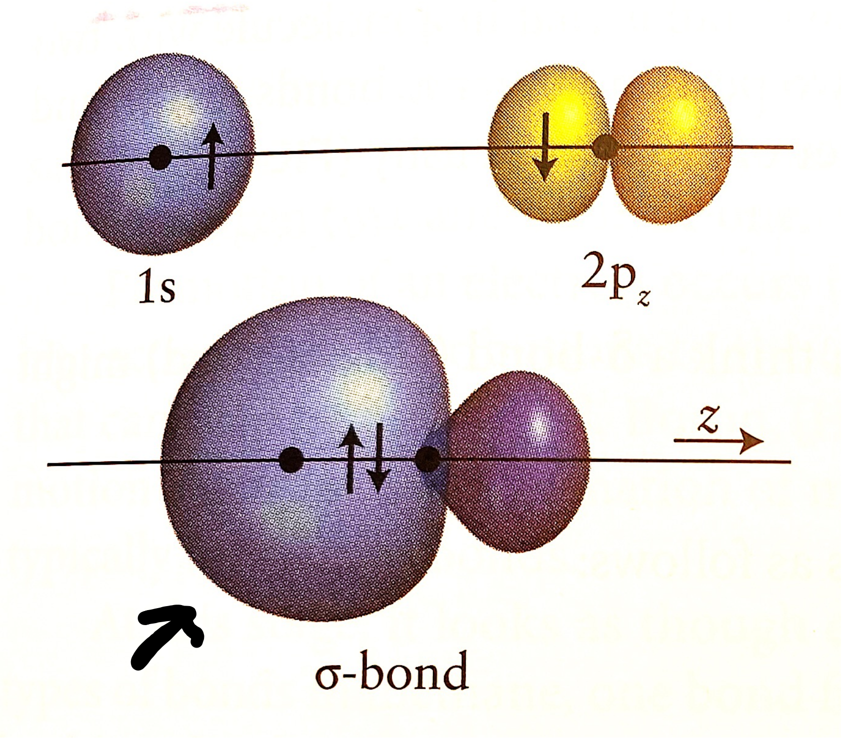
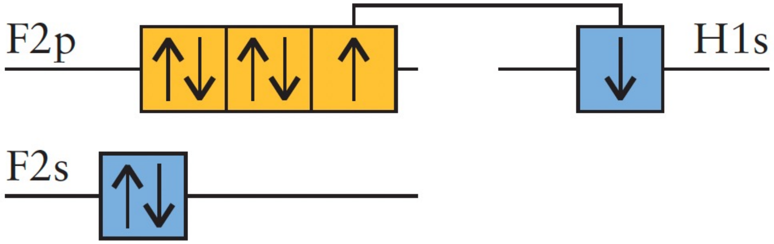


Figure 2F.2 (new book)

$2p_z$-orbital of fluorine

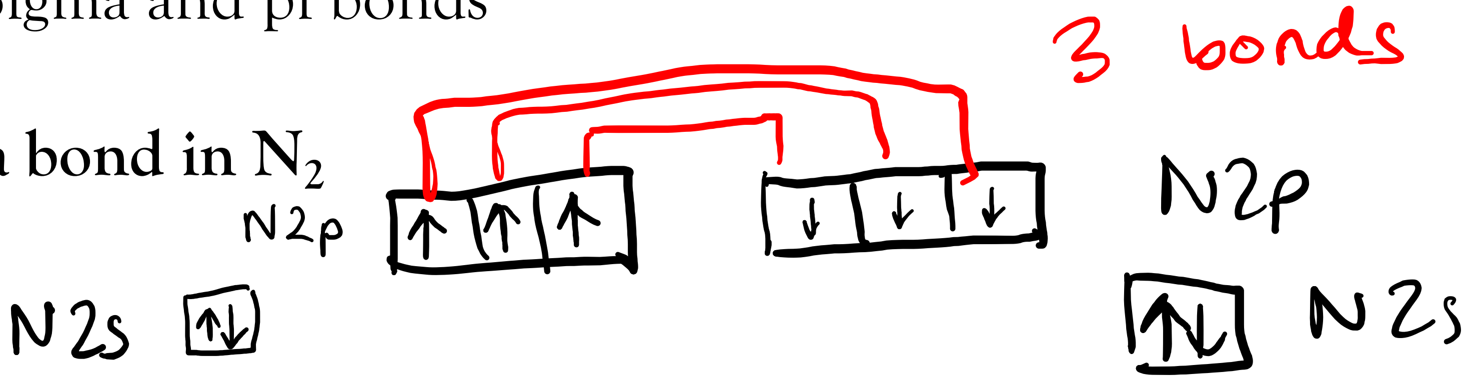
+ 1s-orbital of hydrogen

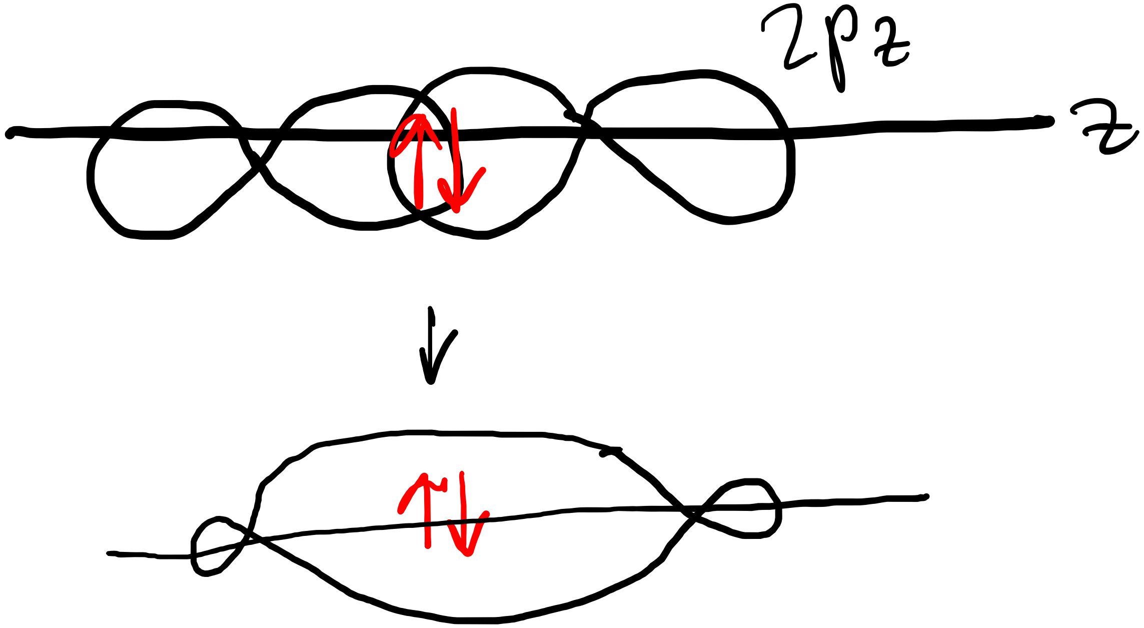


33 Hydrogen fluoride, HF

2F.1 Sigma and pi bonds

Sigma bond in N_2



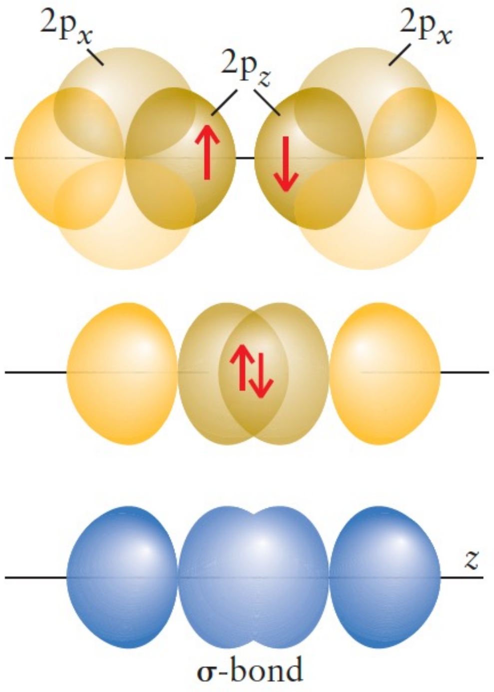


σ-bonds

end-to-end orbital overlap

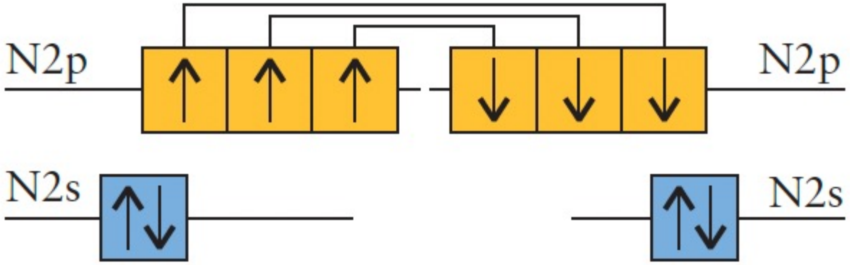
2F.1 Sigma and pi bonds

Sigma bond in N_2



Older book version: Figure 3.10

The $2p_z$-orbitals of nitrogen overlap to form a sigma bond



34 Nitrogen, N_2

2F.1 Sigma and pi bonds

Sigma bonds in N_2

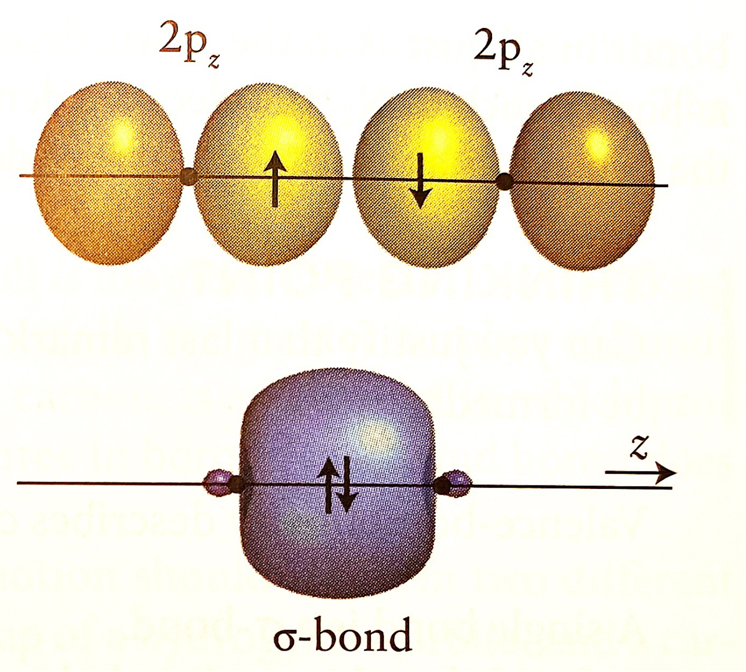
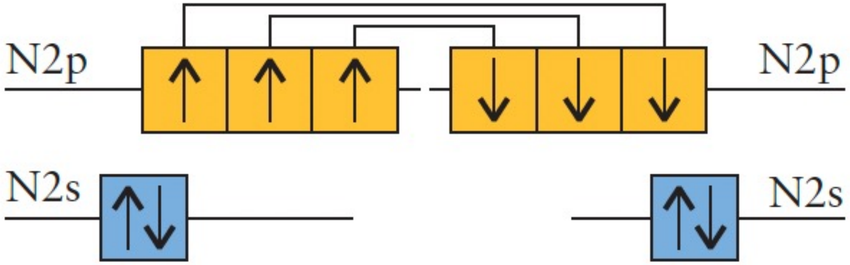


Figure 2F.3 (new book)

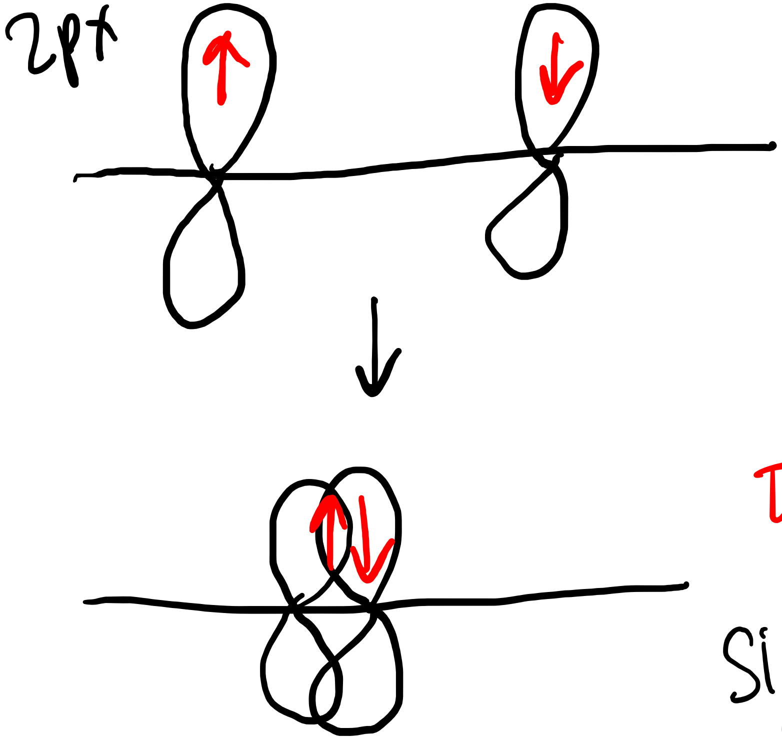
The $2p_z$-orbitals of nitrogen overlap to form a sigma bond



34 Nitrogen, N_2

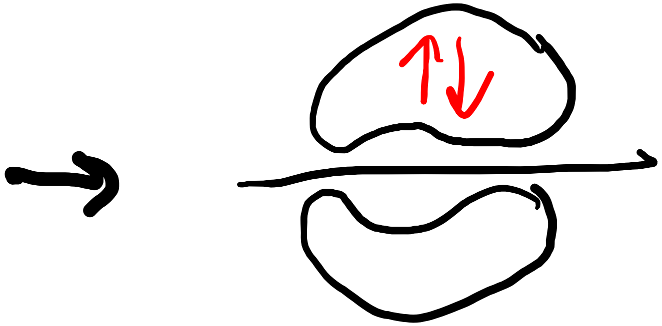
2F.1 Sigma and pi bonds

Pi bonds in N_2



π-bond

Side-by-side overlap

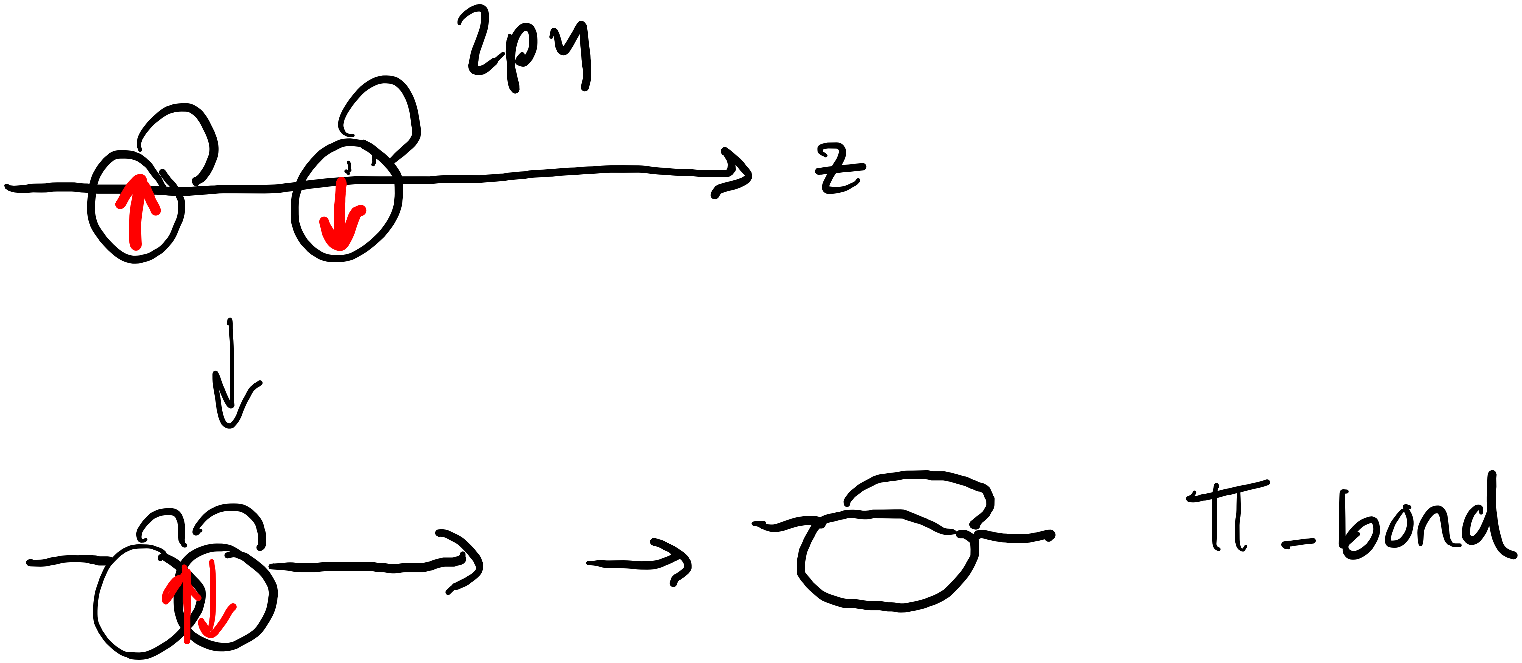


overlap σ-bonds > overlap of π-bonds

strength σ-bonds > strength π-bond

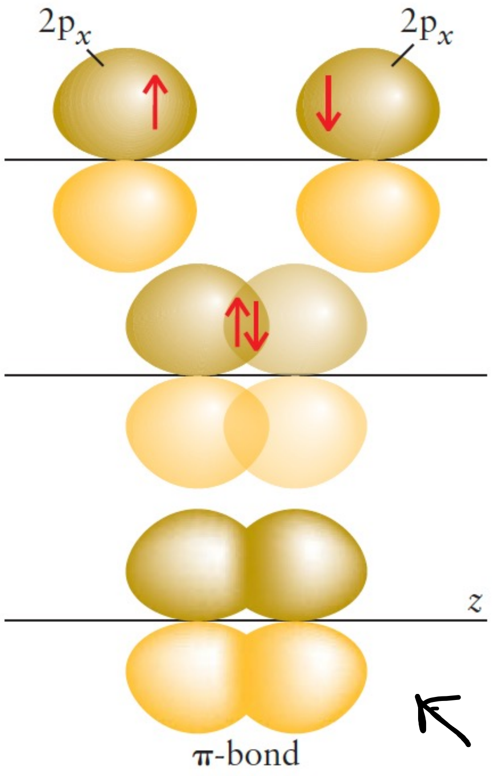
2F.1 Sigma and pi bonds

Pi bonds in N_2



2F.1 Sigma and pi bonds

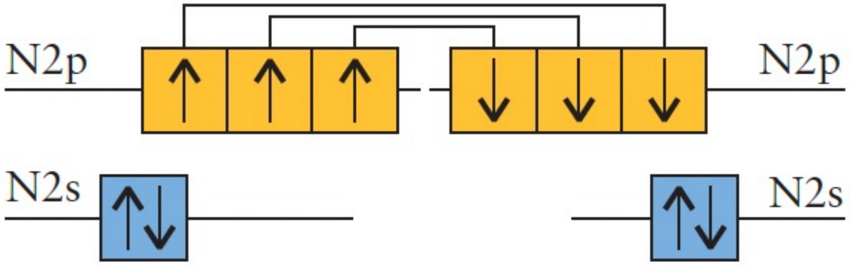
Pi bonds in N_2



Older book version: Figure 3.11

The $2p_x$-orbitals of nitrogen overlap **side-by-side** to form a first pi bond

The two $2p_y$-orbitals of nitrogen overlap to form a second pi bond (not shown)



34 Nitrogen, N_2

2F.1 Sigma and pi bonds

Pi bonds in N_2

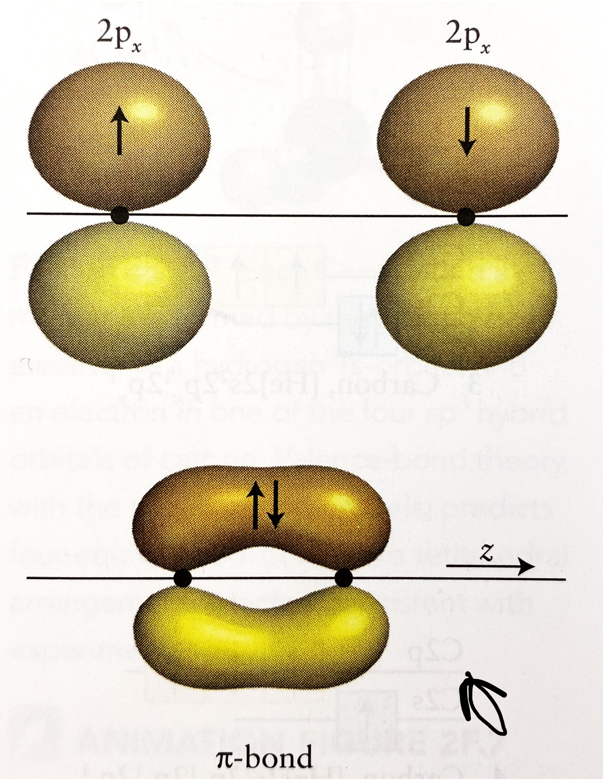
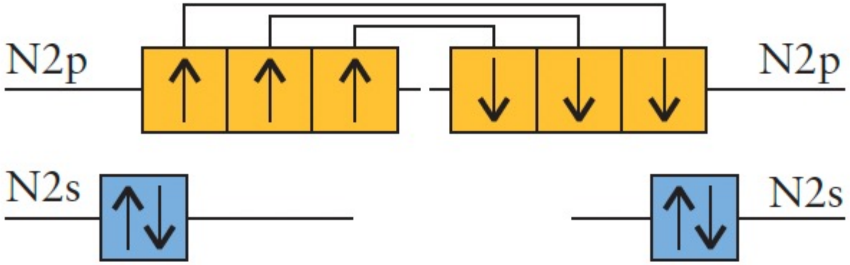


Figure 2F.4 (new book)

The $2p_x$-orbitals of nitrogen overlap **side-by-side** to form a first pi bond

The two $2p_y$-orbitals of nitrogen overlap to form a second pi bond (not shown)



34 Nitrogen, N_2

2F.1 Sigma and pi bonds

Pi bonds in N_2

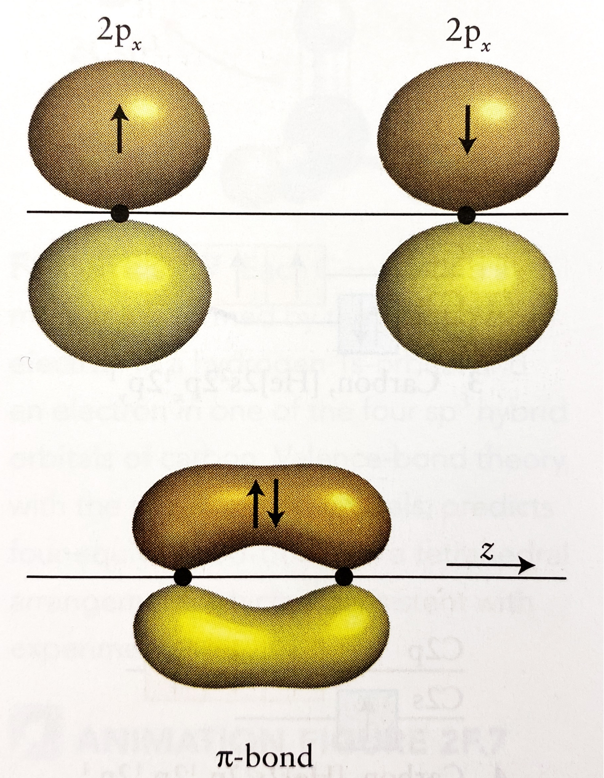


Figure 2F.4 (new book)

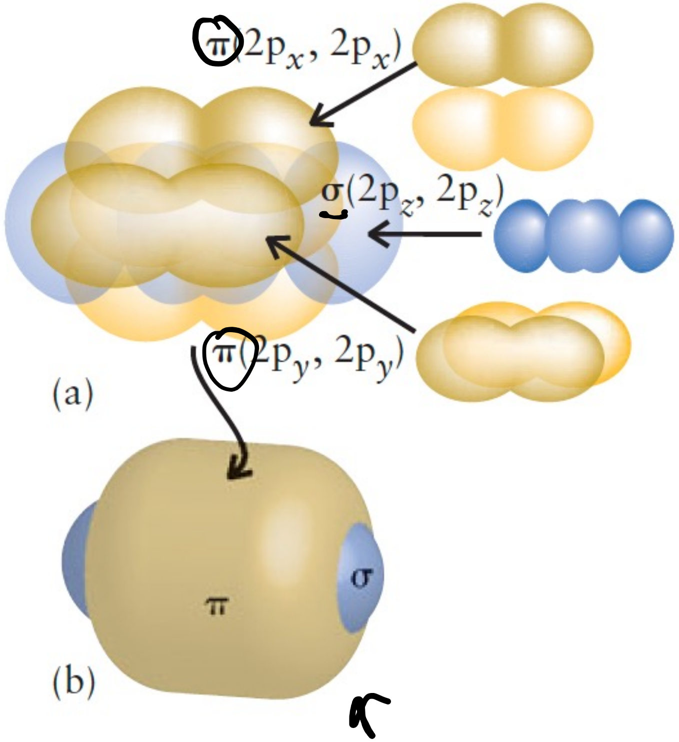
A π-bond has a single nodal plane containing the internuclear axis.

For a **π-bond,** electron density of the merged orbitals increases, but not as much as in the sigma bond.

→ A π-bond is weaker than a σ-bond.

2F.1 Sigma and pi bonds

All bonds in N_2



Older book version: Figure 3.12

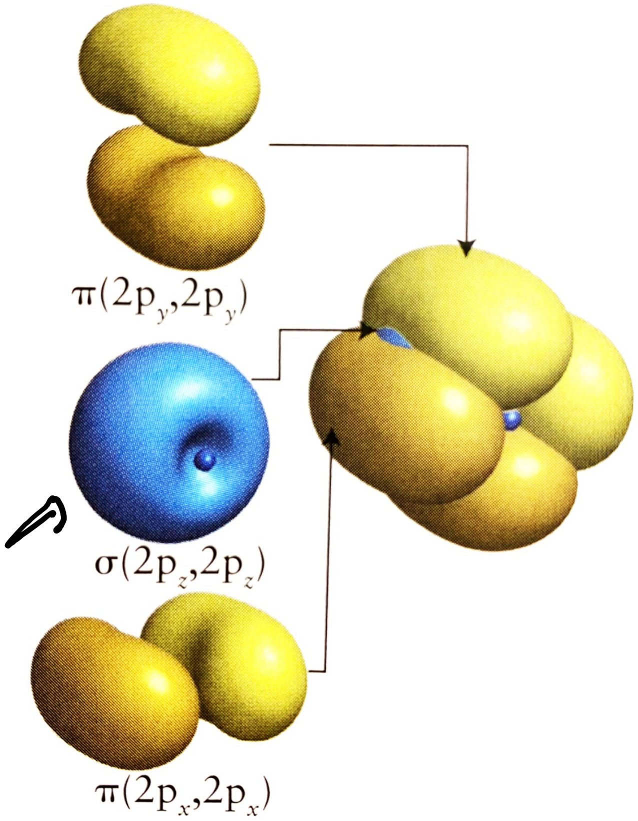


Figure 2F.5 (new book)

2F.1 Sigma and pi bonds

Valence-bond theory describes covalent bonds as follows:

A single bond is σ-bond (sigma bond).

A double bond is a σ-bond plus one π-bond (pi bond).

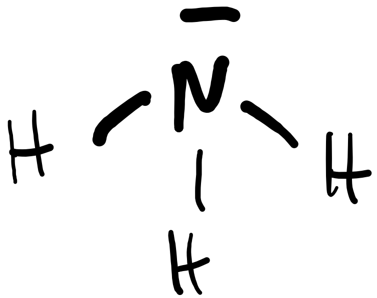
A triple bond is a σ-bond plus two π-bonds.

2F.1 Sigma and pi bonds

Self-test 2F.1B

How many σ-bonds and how many π-bonds are there in

(a) NH_3?



→ 3 σ-bonds

2F.1 Sigma and pi bonds

Self-test 2F.1B

How many σ-bonds and how many π-bonds are there in

(b) HCN? $1+4+5 = 10\ e^{\ominus}\ /\ 5\ e^{\ominus}p$

$H - C \equiv N|$

$\uparrow$ σ-bond

$\uparrow$ σ-bond + 2 π-bonds

2F.1 Sigma and pi bonds

Summary

According to valence-bond theory, bonds form when individual valence electrons on neighbouring atoms pair with each other; the atomic orbitals overlap **end to end to form σ-bonds** or **side by side to form π-bonds**.

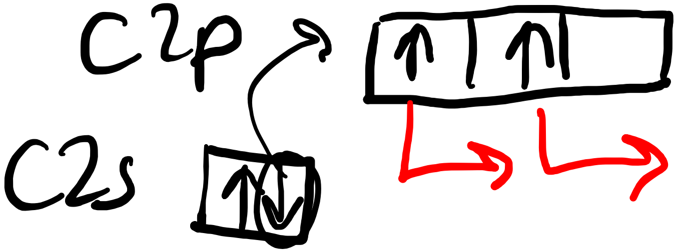
Electron Promotion and the Hybridization of Orbitals

Topic 2F.2

2F.2 Electron promotion and the hybridization of orbitals

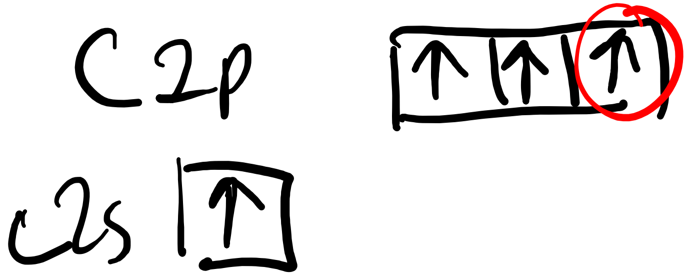
Valence-bond theory refinement: Carbon in CH_4

$[He]2s^2 2p_x^1 2p_y^1$



2 bonds? But! Carbon is tetra-valent.

Four bonds → four unpaired electrons?!



Electron promotion: to a higher energy orbital

$\Delta E(C2s \to C2p) < \Delta E$(stabilization from two extra bonds)

2F.2 Electron promotion and the hybridization of orbitals

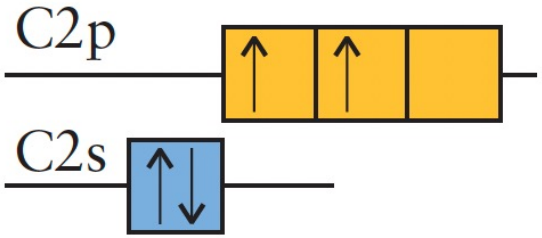
Valence-bond theory refinement: Carbon in CH_4

Configuration in carbon atom: [He]$2s^2 2p_x^1 2p_y^1$ with four valence electrons.

But: two valence electrons are paired, not available for bonding.

It looks like carbon should have a valence of two and make two perpendicular bons.

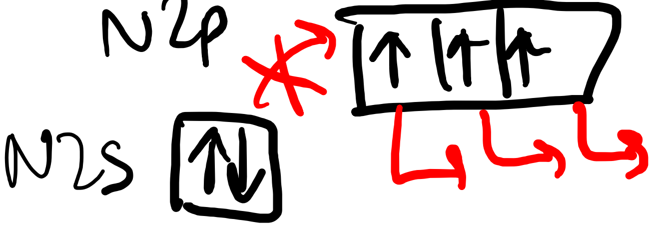
But: it has a **valence of four** and is **tetrahedral**.



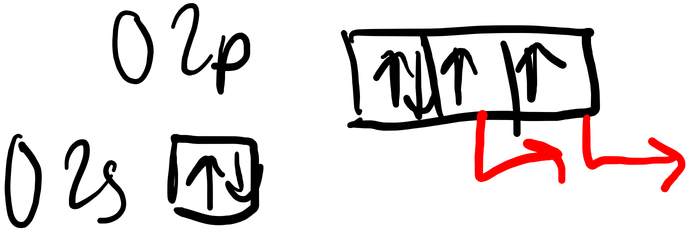
Carbon, [He]$2s^2 2p_x^1 2p_y^1$

2F.2 Electron promotion and the hybridization of orbitals

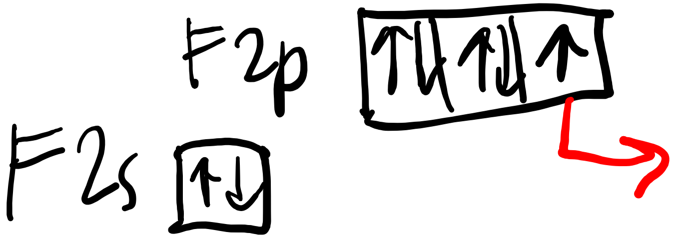
Valence-bond theory refinement: Carbon in CH_4



3 bonds (N)



2 bonds



1 bond

2F.2 Electron promotion and the hybridization of orbitals

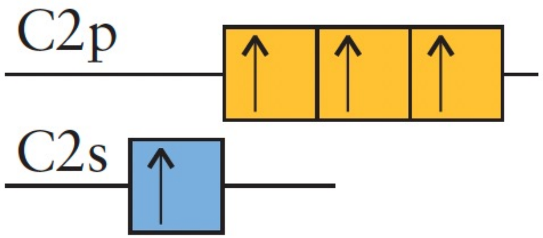
Valence-bond theory refinement: Carbon in CH_4

According to VB theory, a carbon atom can form four bonds only if it has **four unpaired electrons**.

How is this possible for carbon?

Carbon can have four unpaired electrons if one of its electrons is **promoted** – relocated to a higher-energy orbital.

In this case: $[He]2s^1 2p_x^1 2p_y^1 2p_z^1$



Carbon, $[He]2s^1 2p_x^1 2p_y^1 2p_z^1$

2F.2 Electron promotion and the hybridization of orbitals

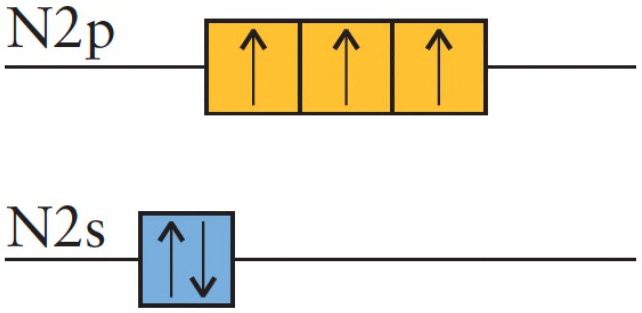
Valence-bond theory refinement: Carbon in CH_4

Where does the energy for this transition come from?

The energy gain from being able to make two additional bonds is higher compared to the investment of energy to promote an electron.

For the promotion of an electron from a 2s to a 2p orbital, a relatively small energy investment is required. Why? Less repulsion of electrons in doubly occupied orbitals. 2s and 2p orbitals are close in energy.

Nitrogen cannot use promotion to increase the number of bonds: no empty 2p orbitals. → Nitrogen only forms three bonds. → Oxygen only two → Fluorine only one.



Nitrogen, $[He]2s^22p_x^{\ 1}2p_y^{\ 1}2p_z^{\ 1}$

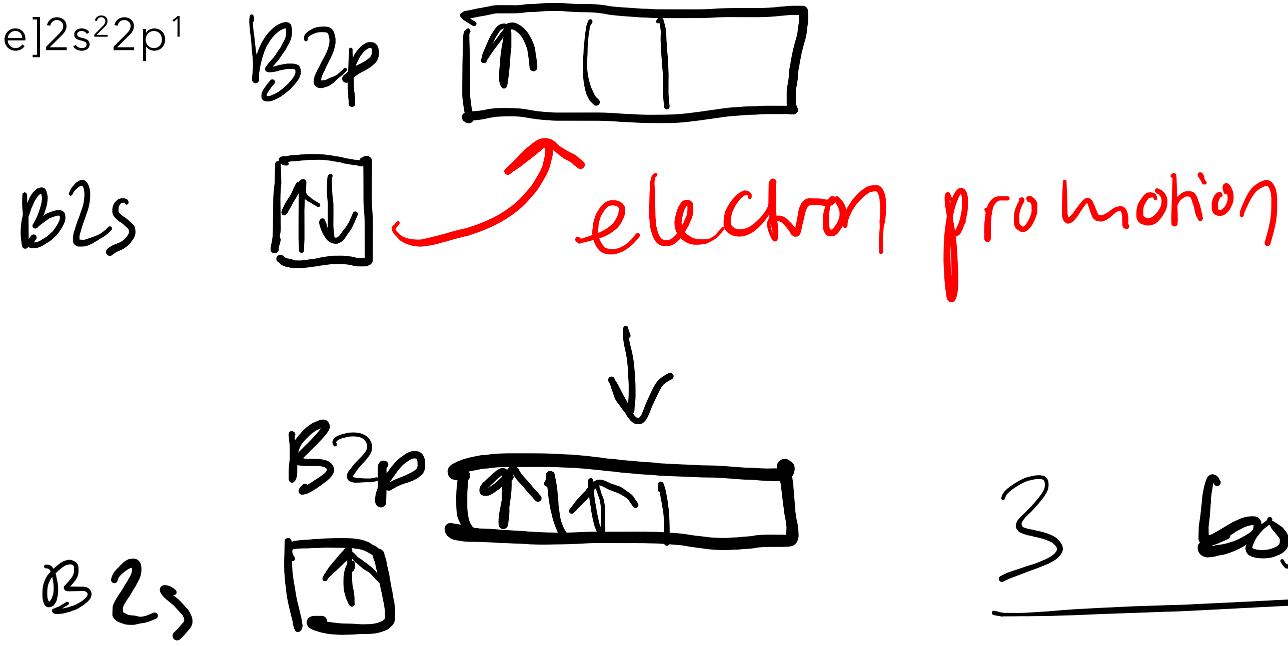
2F.2 Electron promotion and the hybridization of orbitals

Self-test

How many bonds does boron make?

Use the same logic we just saw for the case of carbon.

[He]$2s^22p^1$



3 bonds