CH-110 Advanced General Chemistry I

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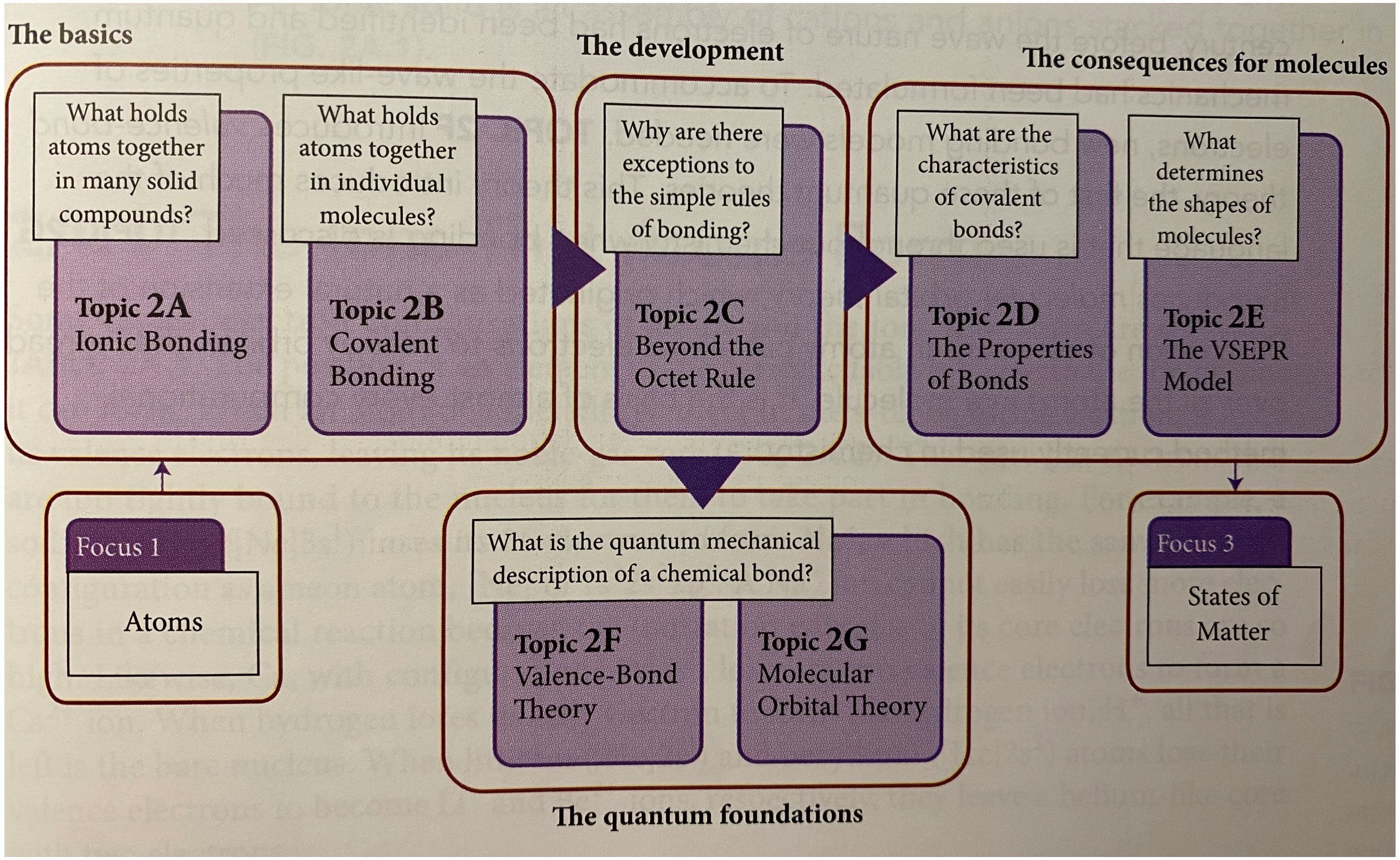
Overview Chapter 2 (Focus 2: Bonds Between Atoms)



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

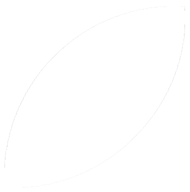
The quantum foundations

Focus 3

States of Matter

Valence-Bond Theory

Topic 2F



2F Valence-bond theory

Lead-in

- 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?

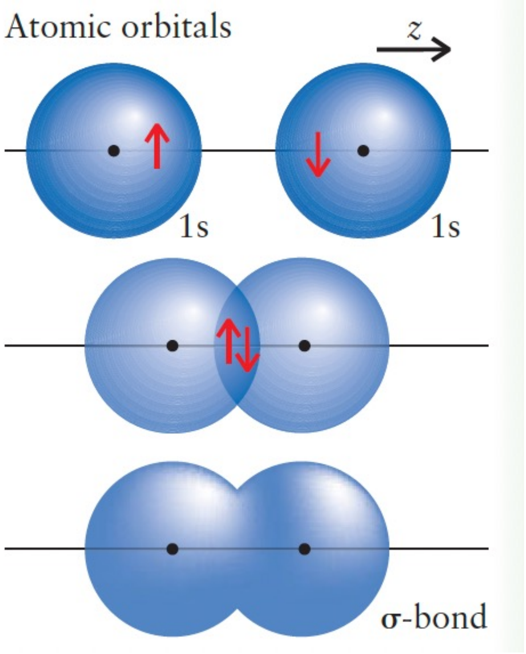
- Atomic structure in terms of occupation of orbitals (Topics 1D and 1E)
- The notion of a wavefunction (Topic 1C)
- Concept of electron spin (Topic 1D)

Sigma and Pi Bonds

Topic 2F.1

2F.1 Sigma and pi bonds

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

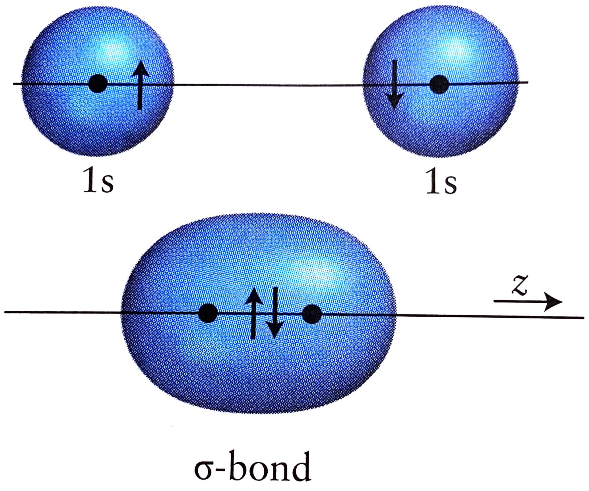


Figure 2F.1 (new book version)

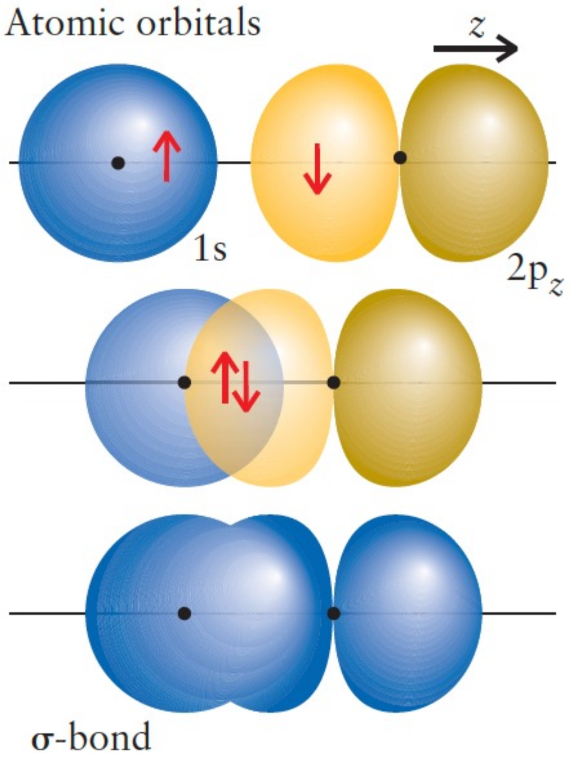
A σ-bond is **cylindrically symmetrical** (the same in all directions around the long axis of the bond), with **no nodal planes** containing the internuclear axis.

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

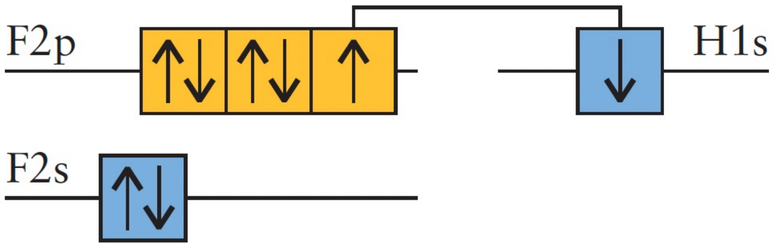
Sigma bonds: HF



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

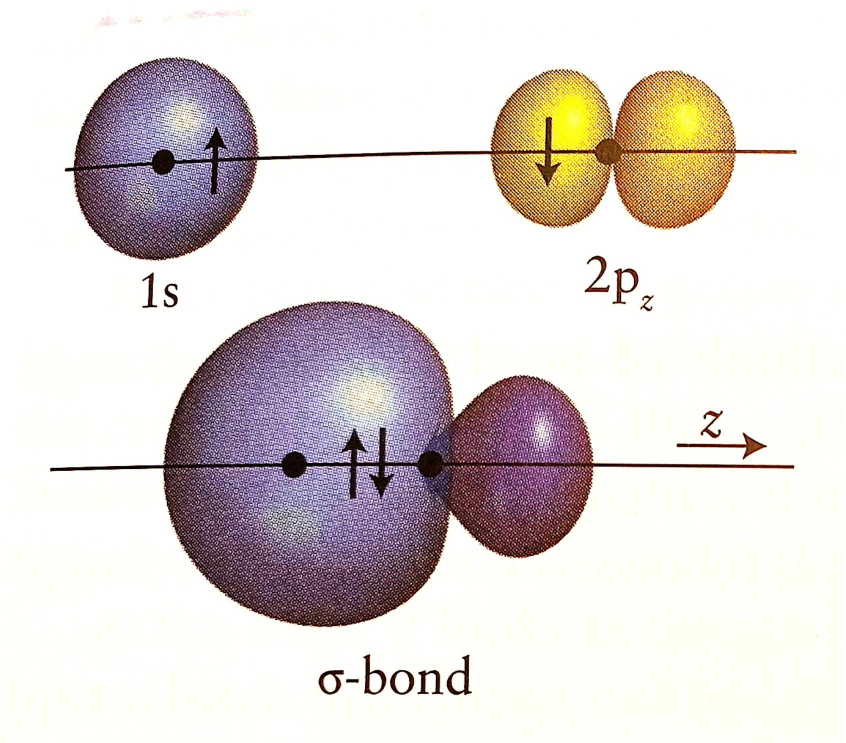
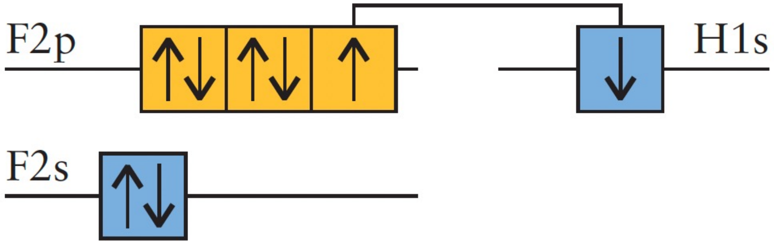


Figure 2F.2 (new book)

$2p_z$-orbital of fluorine

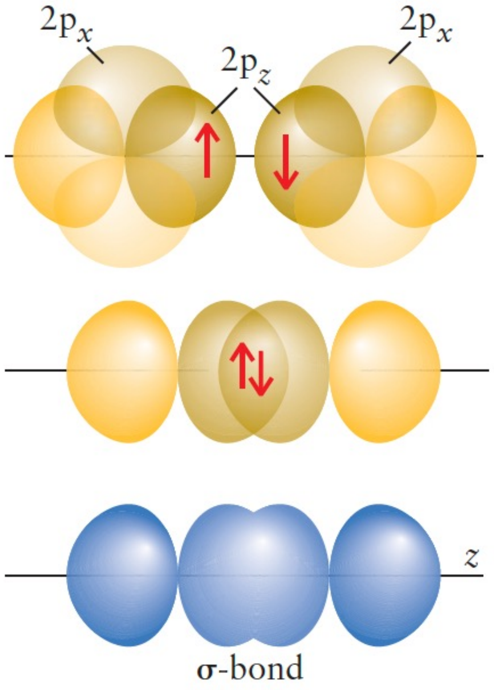
+ 1s-orbital of hydrogen



33 Hydrogen fluoride, HF

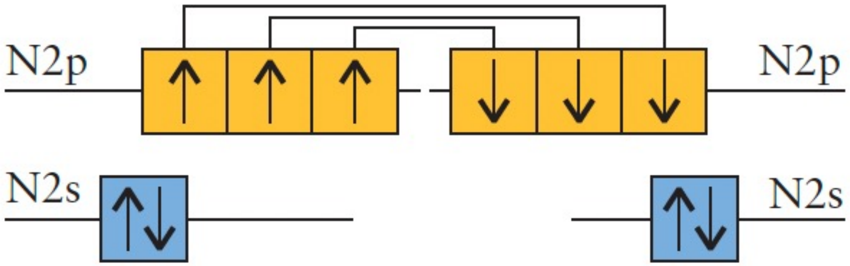
2F.1 Sigma and pi bonds

Sigma bond in N_2



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

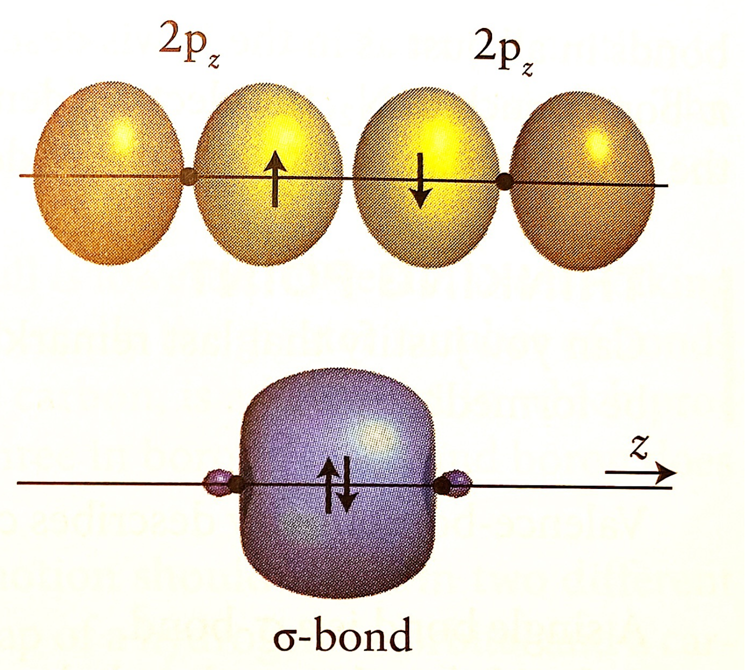
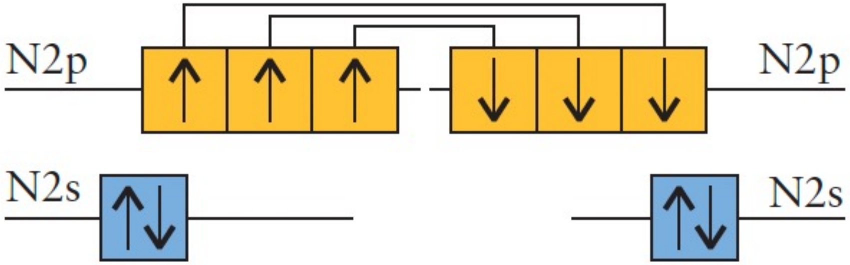


Figure 2F.3 (new book)

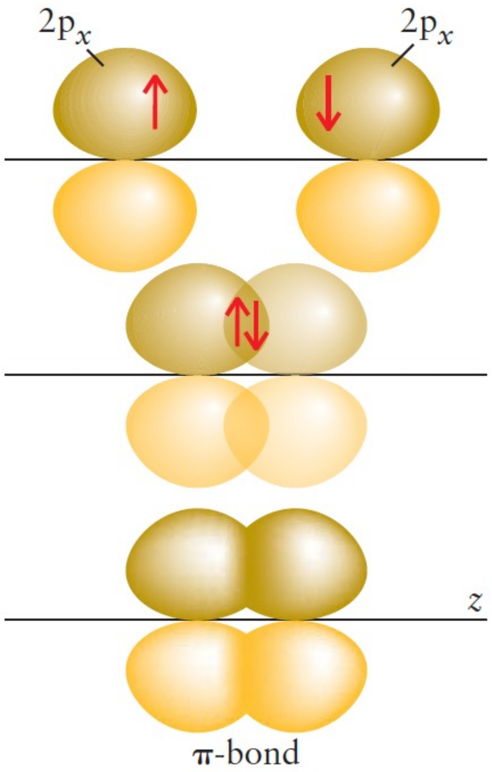
The $2p_z$-orbitals of nitrogen overlap to form a sigma bond



34 Nitrogen, N_2

2F.1 Sigma and pi bonds

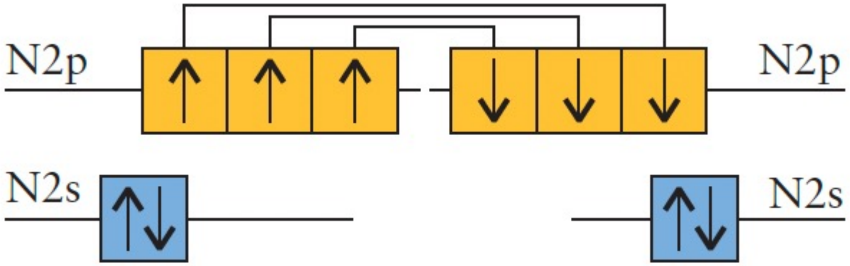
Pi bonds in N_2



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

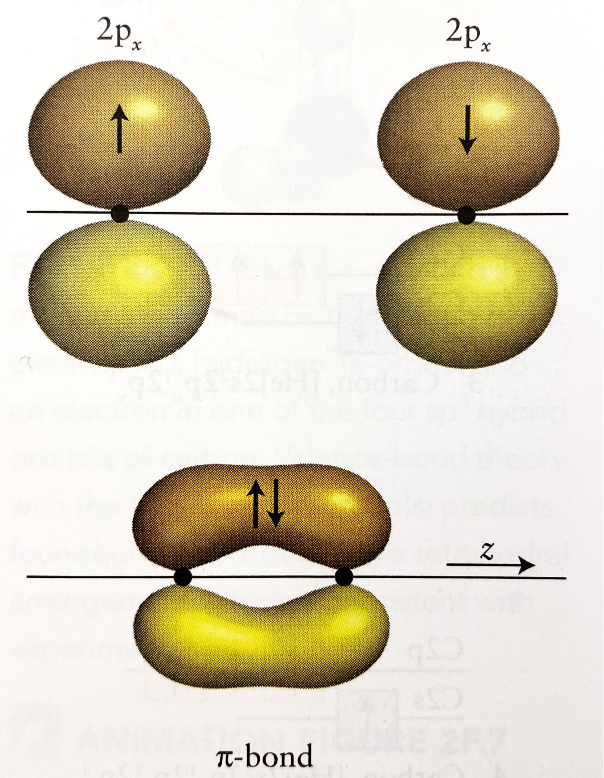
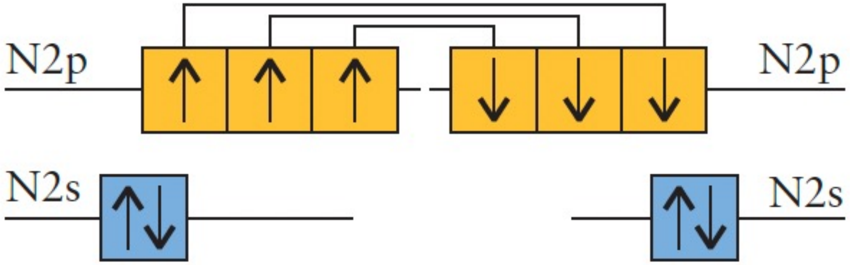


Figure 2F.4 (new book)

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

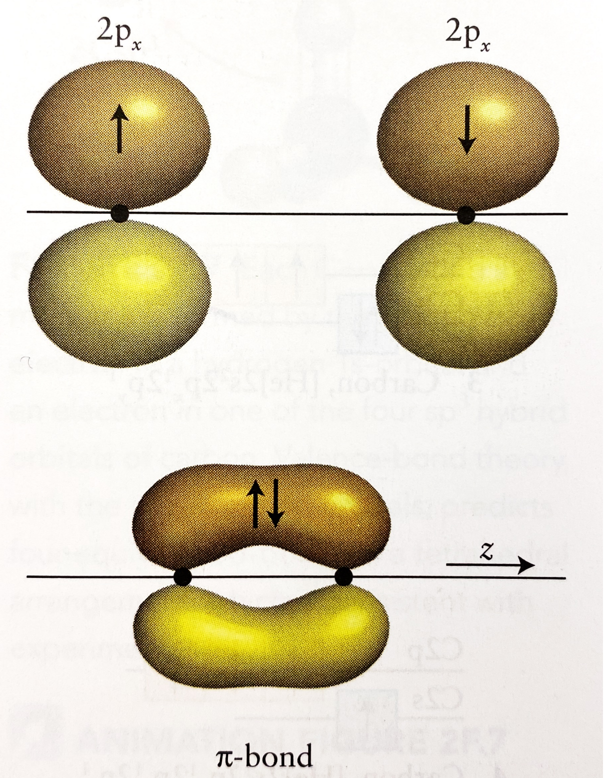


Figure 2F.4 (new book)

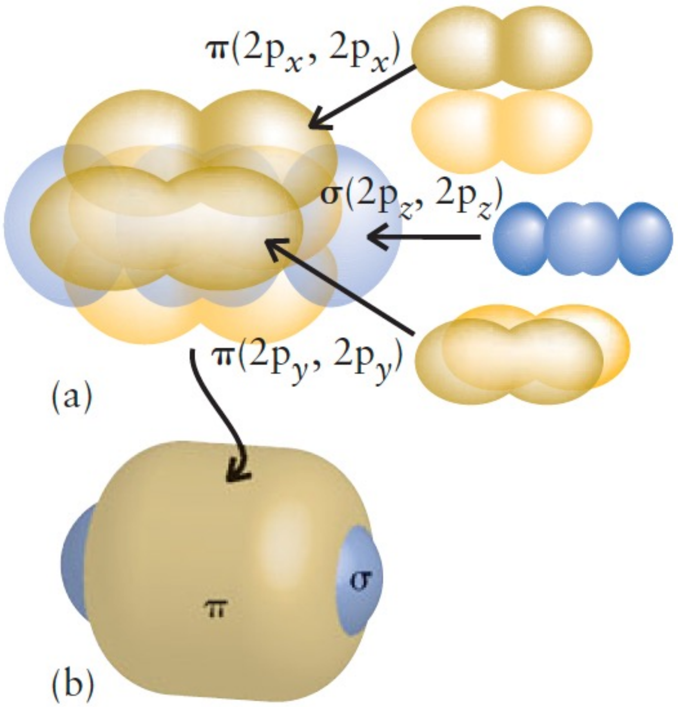
A π-bond has a single nodal plane containing the internuclear axis.

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

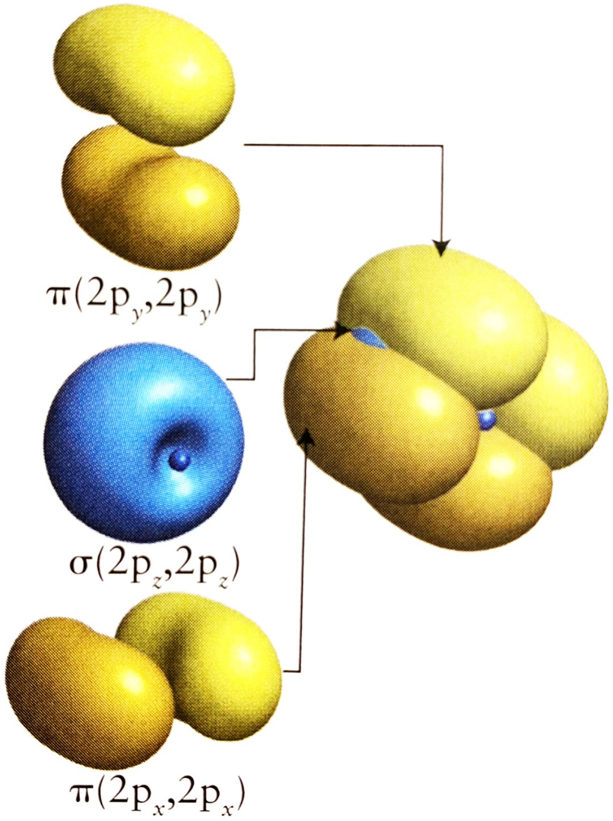


Figure 2F.5 (new book)

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 and in (b) HCN?

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

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

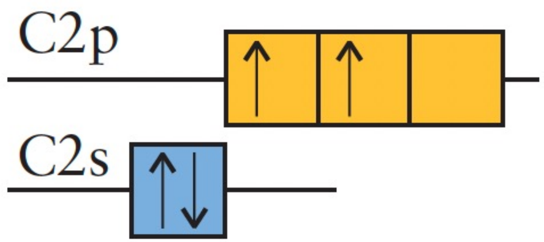
Valence-bond theory refinement: Carbon in CH_4

Configuration in carbon atom: $[He]2s^22p_x^12p_y^1$ 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, $[He]2s^22p_x^12p_y^1$

2F.2 Electron promotion and the hybridization of orbitals

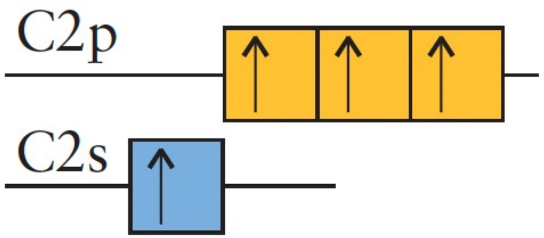
Valence-bond theory refinement: Carbon in CH_4

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

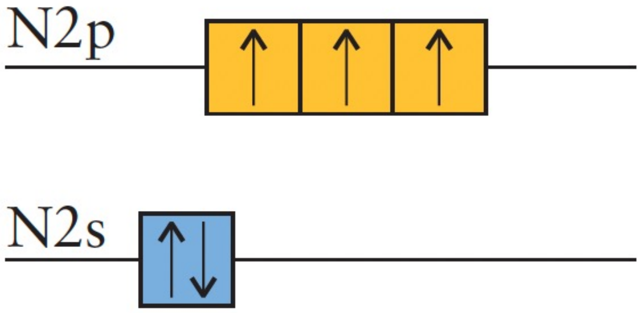
Valence-bond theory refinement: Carbon in CH_4

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

2F.2 Electron promotion and the hybridization of orbitals

Self-test

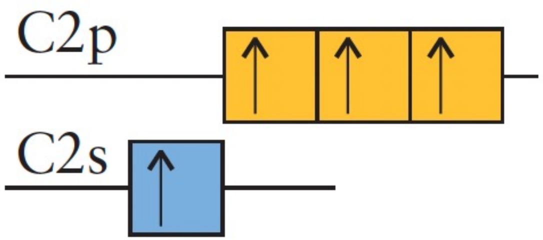
How many bonds does boron make?

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

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

2F.2 Electron promotion and the hybridization of orbitals

What happens to orbitals after electron promotion?



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

According to this image, we will form two types of bonds:

C2s-H1s (1x) and C2p-H1s (3x)

The three C2p-H1s bonds at 90° from one another

What we find:

There are **four equal bonds** in CH_4

Tetrahedral geometry.

2F.2 Electron promotion and the hybridization of orbitals

Another refinement of the VB model: Hybridization

- s- and p-orbitals can be thought as WAVES of electron density
- The four waves (s- and p-orbitals) will interfere with one another, like waves in water
- **Interference between orbitals of the same atom = hybridization**
- **Result: hybrid orbitals**

2F.2 Electron promotion and the hybridization of orbitals

sp^3 hybrid orbitals

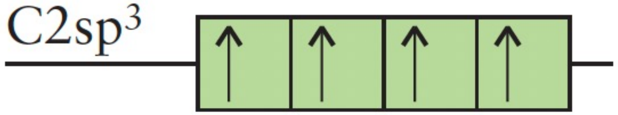
Each of the four hybrid orbitals, h_i, is formed from a linear combination of the four atomic orbitals:

$$h_1 = s + p_x + p_y + p_z$$

$$h_2 = s - p_x - p_y + p_z$$

$$h_3 = s - p_x + p_y - p_z$$

$$h_4 = s + p_x - p_y - p_z$$



sp^3 hybridized carbon

- Sp^3 hybrid orbitals are formed from one s- and three p-orbitals.
- Four sp^3 orbitals of **equal energy.**

2F.2 Electron promotion and the hybridization of orbitals

sp^3 hybrid orbitals

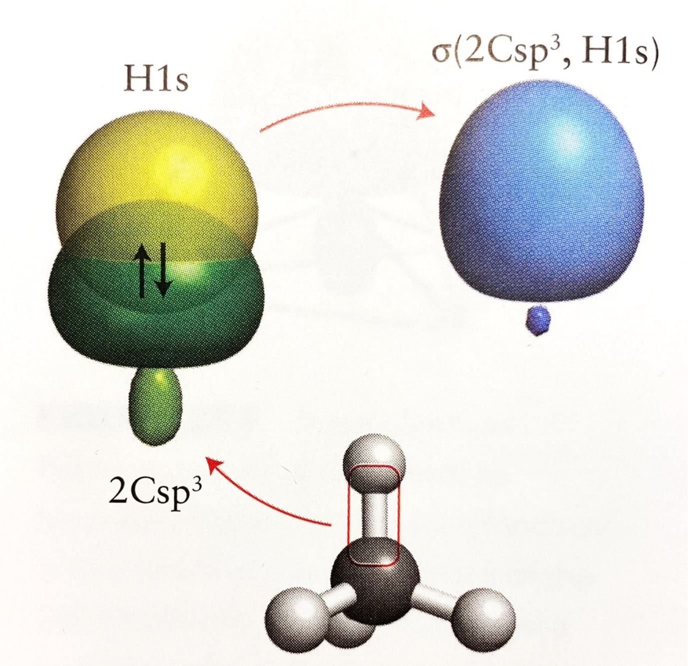
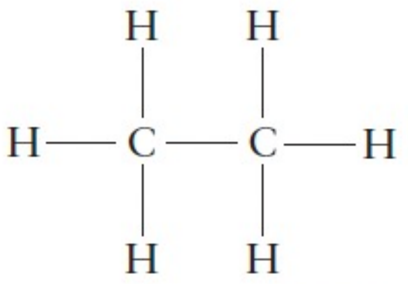


Figure 2F.7 (new book)

- Each C–H bond in methane is formed by the pairing of an electron in a hydrogen 1s-orbital (H1s) and an electron in one of the four sp^3 hybrid orbitals of carbon (Csp^3).
- VB theory predicts **four equivalent sigma-bonds in a tetrahedral arrangement**, which is consistent with experimental results.
- An sp^3 orbital has two lobes: one reaching farther than the contributing p-orbital, the other shortened.
- Hybrid orbitals have amplitudes concentrated on one side of the nucleus to allow to optimize orbital overlap.

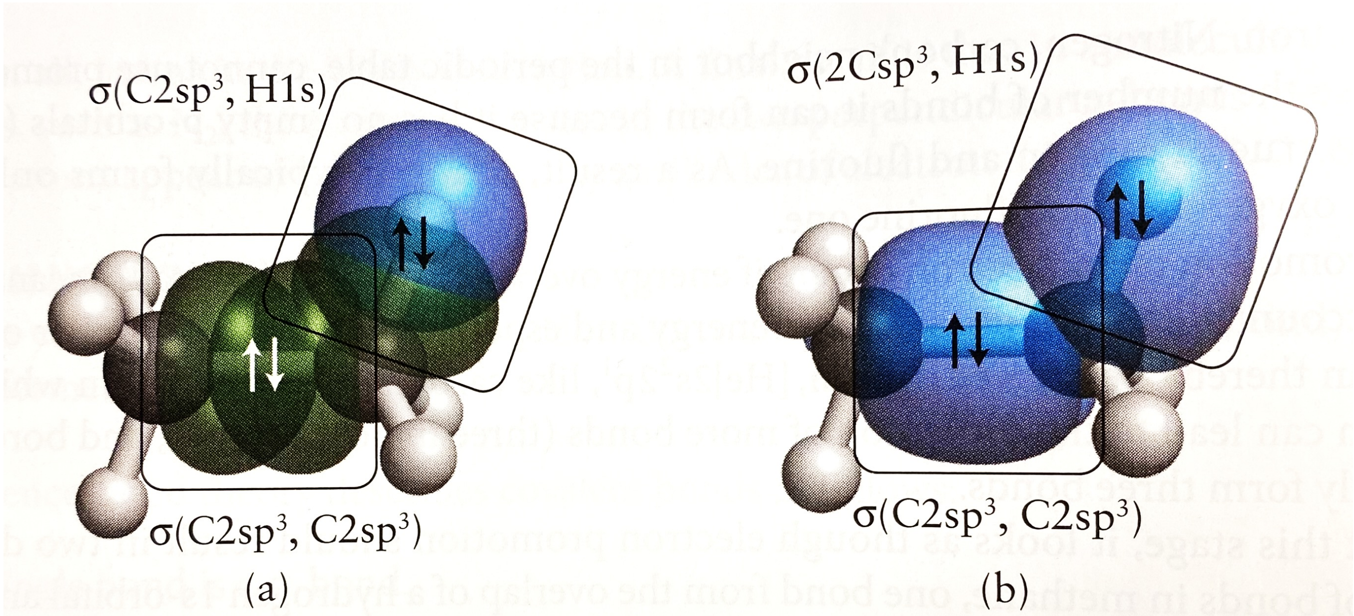
2F.2 Electron promotion and the hybridization of orbitals

Ethane



Ethane, CH_3CH_3

Figure 2F.8 (new book)



(a)

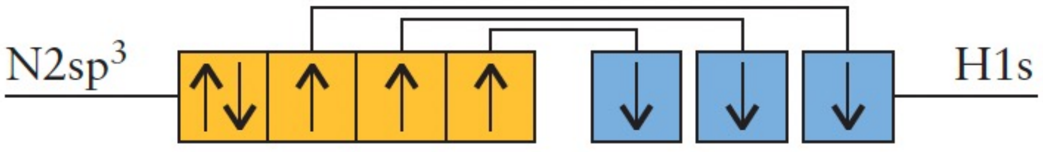
(b)

Boundary surfaces of two bonds are shown.

Bond angles are close to 109.5°.

2F.2 Electron promotion and the hybridization of orbitals

Ammonia



Ammonia, NH_3

- VSEPR: Ammonia has tetrahedral electron arrangement and trigonal pyramidal shape
- Nitrogen atom forms four sp^3 hybrid orbitals, one of which is already doubly occupied
- The three remaining sp^3 hybrid orbitals pair with the 1s orbitals of three H atoms
- N–H sigma-bonds
- Whenever an atom of a nonmetallic element in a molecule has a tetrahedral electron arrangement, it is considered to be sp^3 hybridized.

2F.2 Electron promotion and the hybridization of orbitals

Other hybridization schemes: sp^2

- Sp^3 works well for tetrahedral electron arrangements
- For trigonal planar (e.g. BF_3), one s-orbital and two p-orbitals blend (sp^2)

$$h_1 = s + 2^{\frac{1}{2}} p_y$$

$$h_2 = s + \left(\frac{3}{2}\right)^{\frac{1}{2}} p_x - \left(\frac{1}{2}\right)^{\frac{1}{2}} p_y$$

$$h_3 = s - \left(\frac{3}{2}\right)^{\frac{1}{2}} p_x - \left(\frac{1}{2}\right)^{\frac{1}{2}} p_y$$

- These three orbitals are identical apart from their orientation in space. They lie in the same plane and point toward the corners of an equilateral triangle.

2F.2 Electron promotion and the hybridization of orbitals

Other hybridization schemes: sp

- For linear arrangements, one s-orbital is mixed with one p-orbital (sp):

$$h_1 = s + p$$

$$h_2 = s - p$$

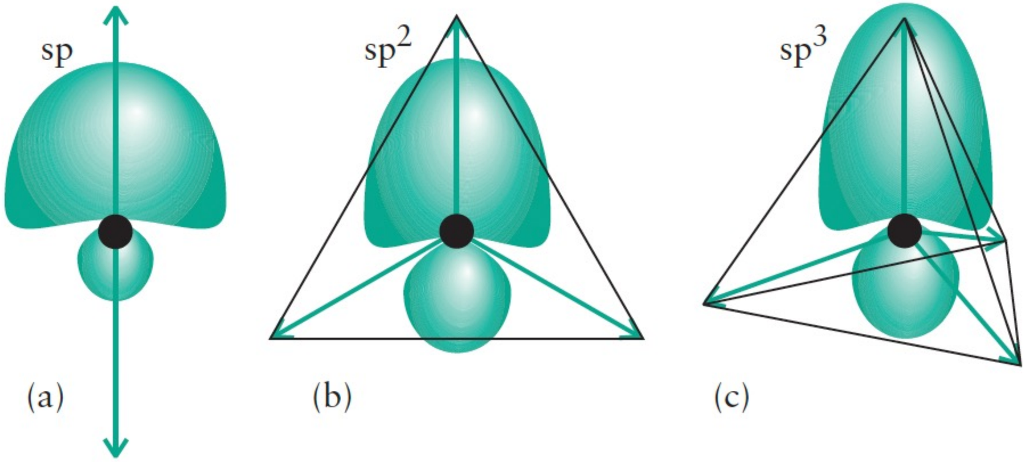


Figure 2F.9 (new book) / Figure 3.16 (old book)

2F.2 Electron promotion and the hybridization of orbitals

Hybridization and molecular shape

- Note: the number of hybrid orbitals is always the same as the number of atomic orbitals used in their construction:

  N atomic orbitals always produce *N* hybrid orbitals.

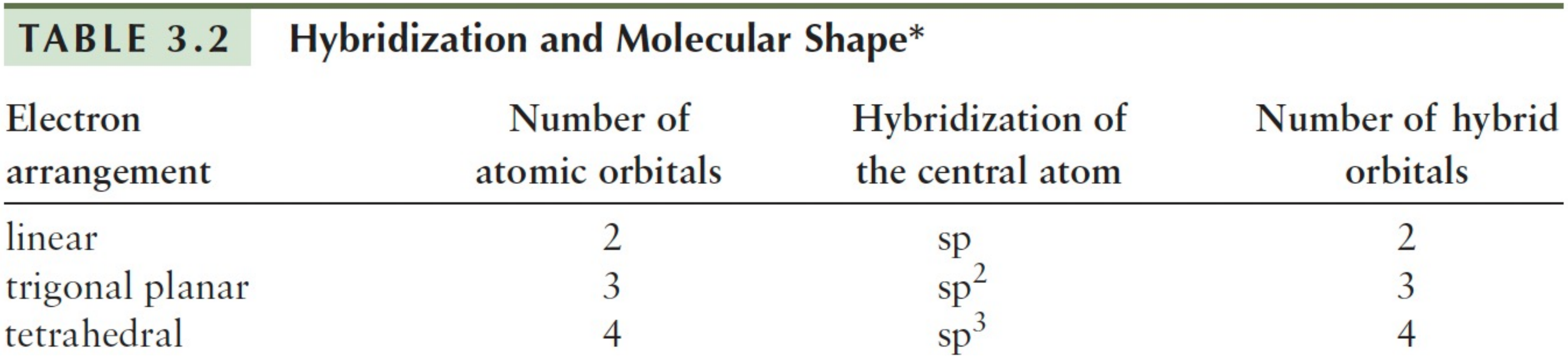


TABLE 3.2 Hybridization and Molecular Shape*

Electron arrangement	Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
linear	2	sp	2
trigonal planar	3	sp^2	3
tetrahedral	4	sp^3	4

2F.2 Electron promotion and the hybridization of orbitals

Self-test 2F.2B

Suggest a structure in terms of hybrid orbitals for each carbon atom in ethyne, $C_2H_{2.}$

2F.2 Electron promotion and the hybridization of orbitals

Summary

The promotion of electrons and formation of hybrid orbitals occurs if, overall, it leads to a lowering of energy by permitting the formation of more bonds. A hybridization scheme is adopted to match the electron arrangement of the central atom.