CH-110 Advanced General Chemistry I

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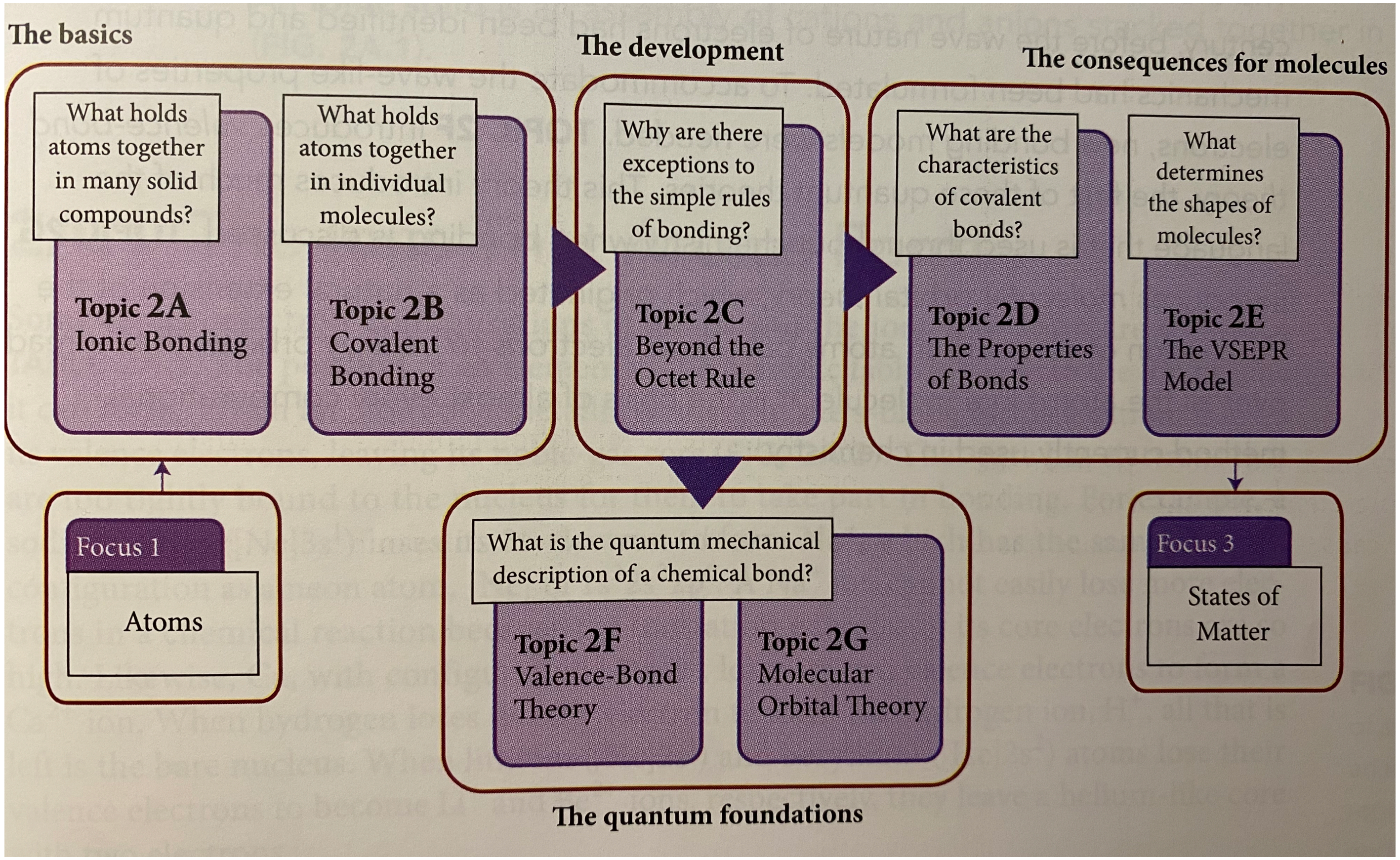
Housekeeping notes

- Updated syllabus: no “Topic 3D: Intermolecular Forces”
- Updated exercises 8 (Topic 2E: Valence Bond Theory) and 9 (Topic 2G: MO Theory)
- Practice exam on the last day (Friday, November 14)

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

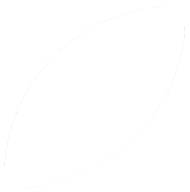
The quantum foundations

Focus 3

States of Matter

Valence-Bond Theory

Topic 2F



2F Valence-bond theory

Lead-in

2F Valence-bond theory

Lead-in

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)

Protocol for valence bond theory

1. Start from the Lewis structure: draw the molecule, identify bonding and lone pairs.
2. Determine geometry (VSEPR): count areas of high electron density around central atom.
3. Assign hybrid orbitals: mix s and p orbitals to match the geometry
4. Describe orbital overlap:
    - **σ-bonds: head-on overlap**
    - **π-bonds: side-on overlap** of **unhybridized** p orbitals
5. Relate to molecular properties: bond angles, bond strength/length, resonance

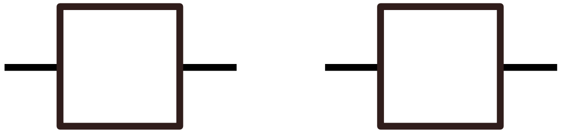
Sigma and Pi Bonds

Topic 2F.1

2F.1 Sigma and pi bonds

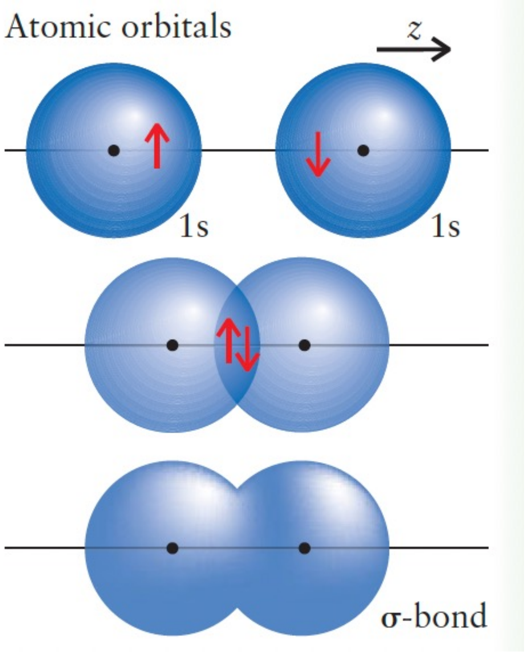
Sigma bonds

- A σ (sigma) bond is formed by **head-on overlap**.
- Simplest case: H_2



2F.1 Sigma and pi bonds

Sigma bonds



Older book version: Figure 3.8

Step 1: Start state

- Two H atoms, each with 1 electron in a 1s orbital

Step 2: Approach and overlap

- Atoms move closer: head-on overlap along internuclear axis

Step 3: Spin pairing

- The two electrons adopt opposite spins and pair in the overlap region

Step 4: The bond formed

- The resulting electron density is cylindrically symmetric ("sausage"): σ-bond

2F.1 Sigma and pi bonds

Sigma bonds

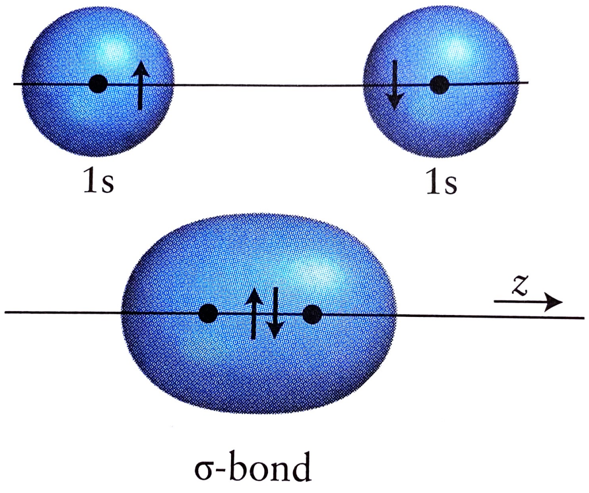


Figure 2F.1
(new book version)

A σ (sigma) bond is formed by **head-on overlap**.

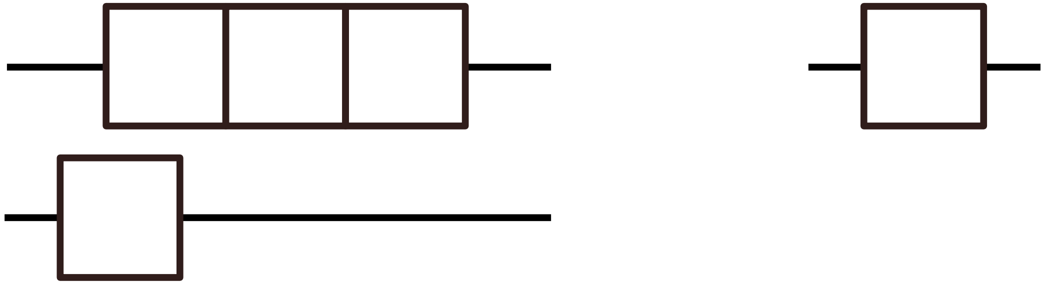
A σ-bond is **cylindrically symmetrical** (the same in all directions around the long axis of the bond), with **no nodal planes** containing the internuclear axis.

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

The greater the orbital overlap, the stronger the bond.

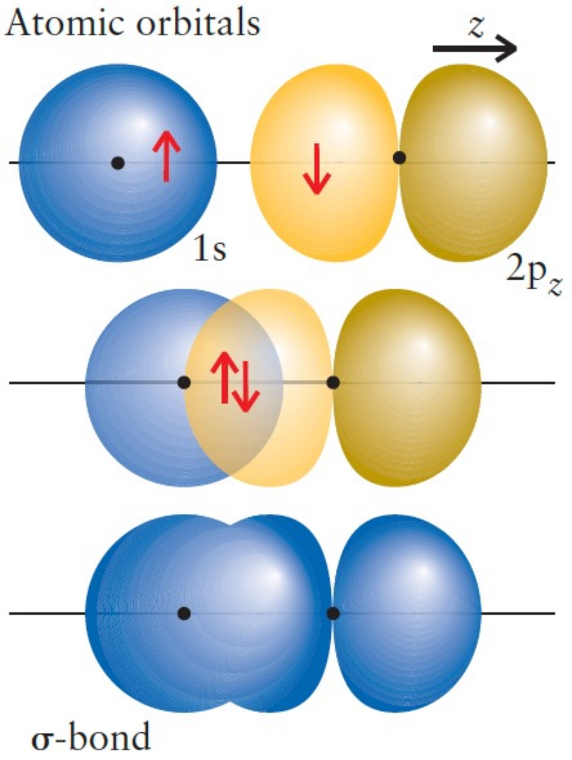
2F.1 Sigma and pi bonds

HF



2F.1 Sigma and pi bonds

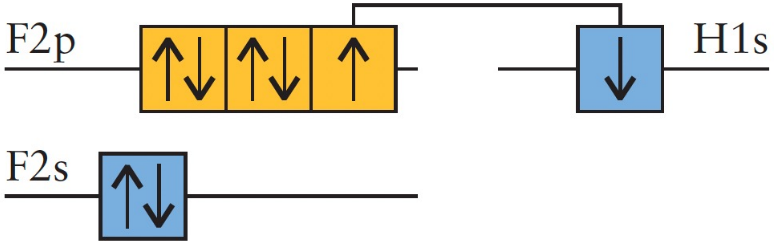
Sigma bonds: HF



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

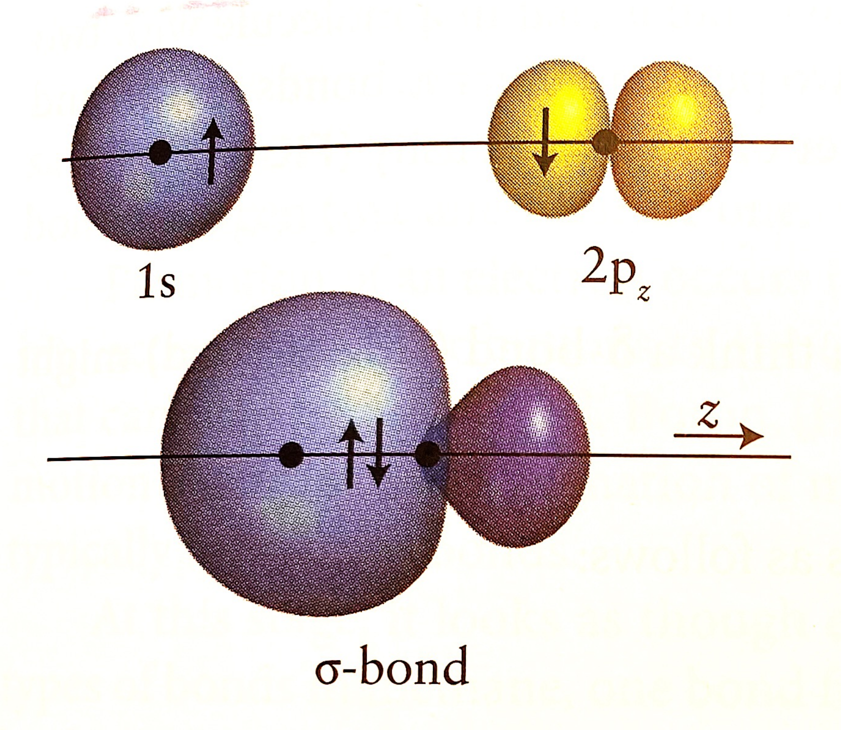
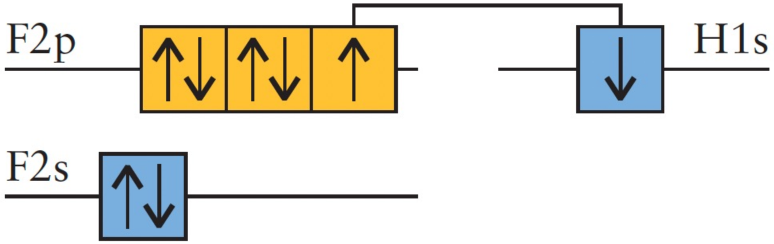


Figure 2F.2 (new book)

2p$_z$-orbital of fluorine

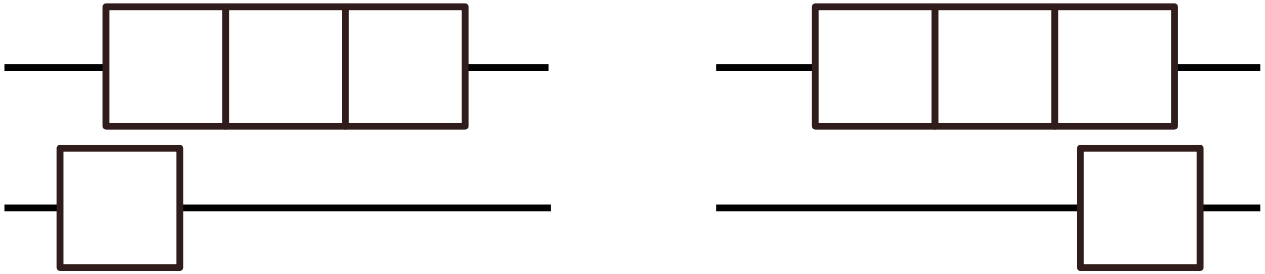
+ 1s-orbital of hydrogen



33 Hydrogen fluoride, HF

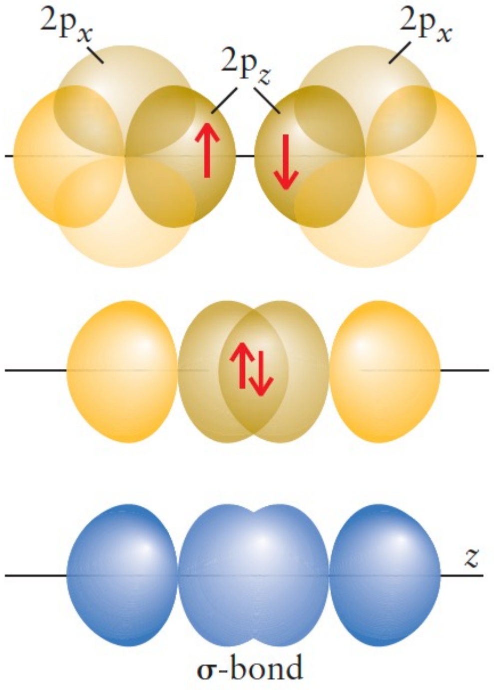
2F.1 Sigma and pi bonds

Sigma bond in N_2



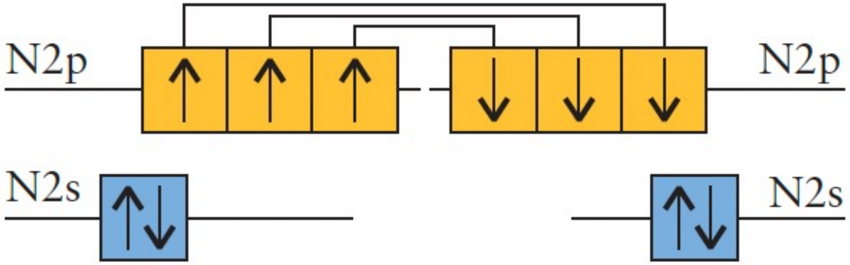
2F.1 Sigma and pi bonds

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

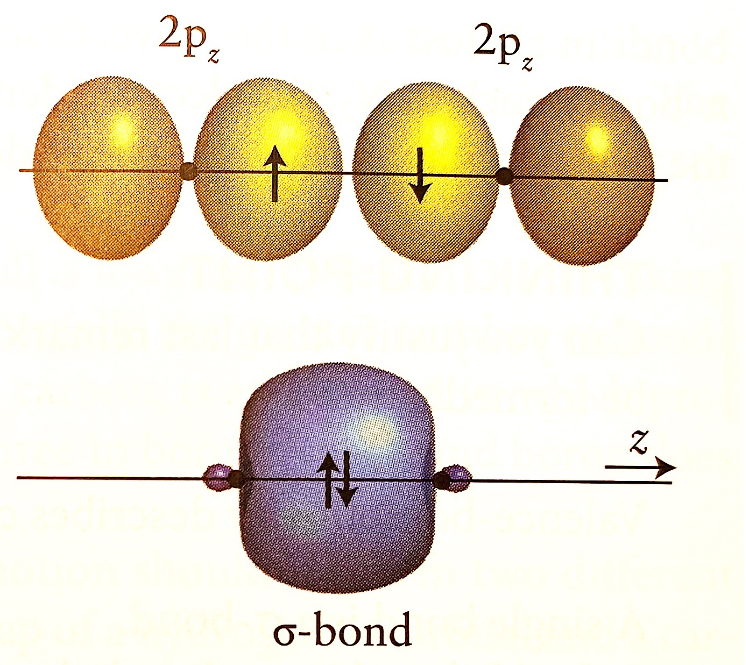
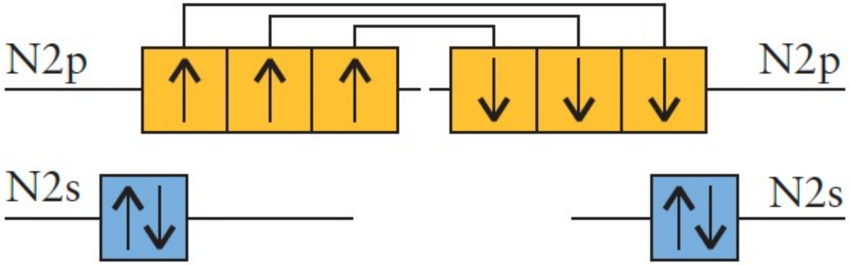


Figure 2F.3 (new book)

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



34 Nitrogen, N_2

2F.1 Sigma and pi bonds

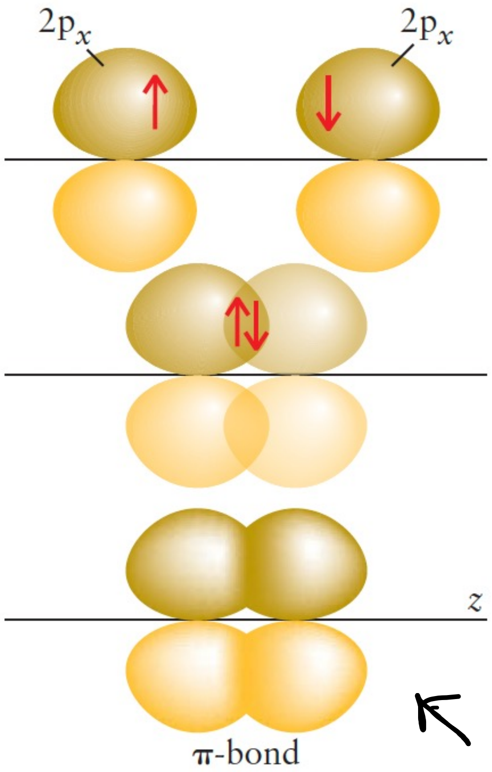
Pi bonds in N_2

2F.1 Sigma and pi bonds

Pi bonds in N_2

2F.1 Sigma and pi bonds

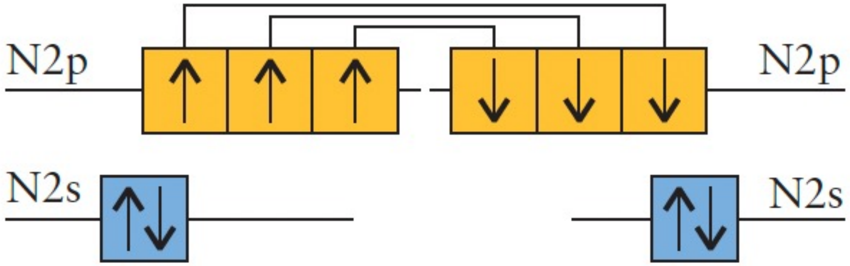
Pi bonds in N_2



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

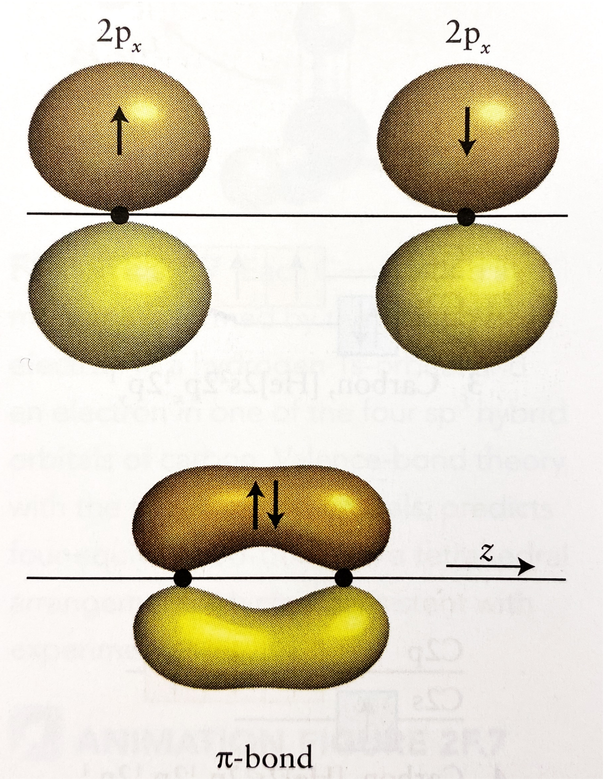
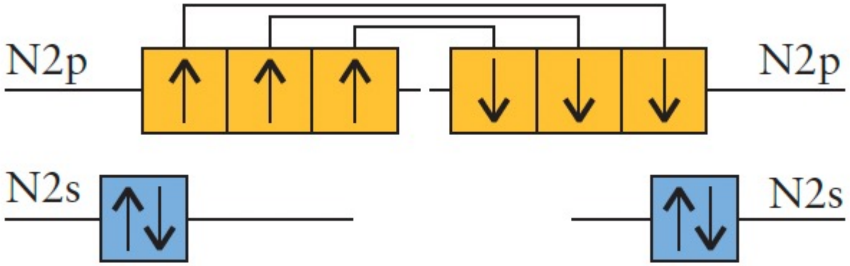


Figure 2F.4 (new book)

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

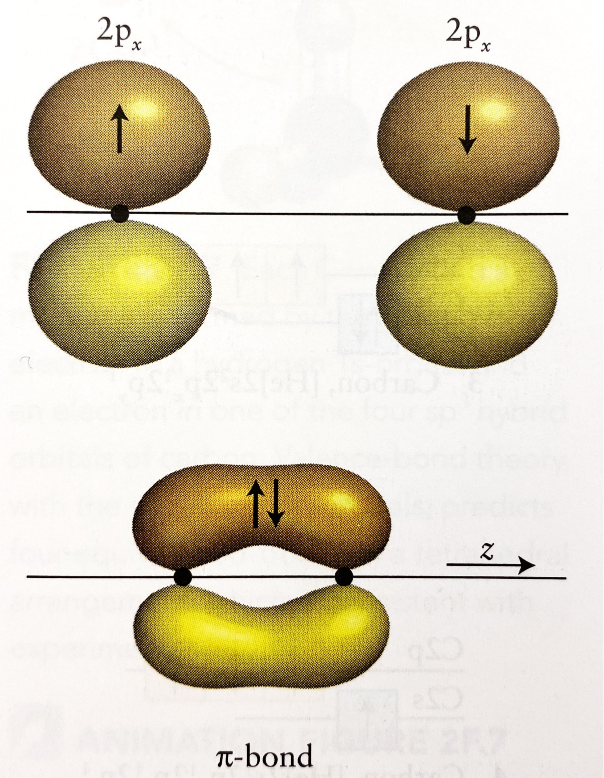


Figure 2F.4 (new book)

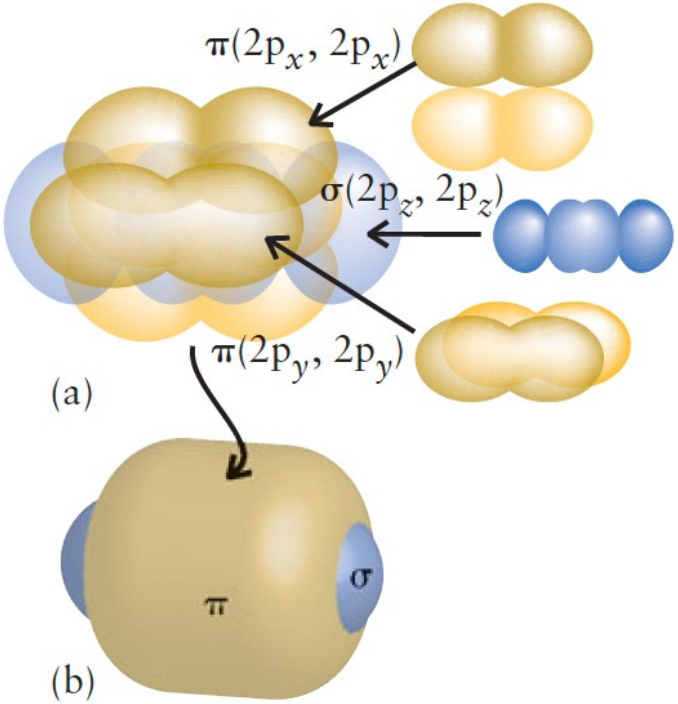
A π-bond has a single nodal plane containing the internuclear axis.

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

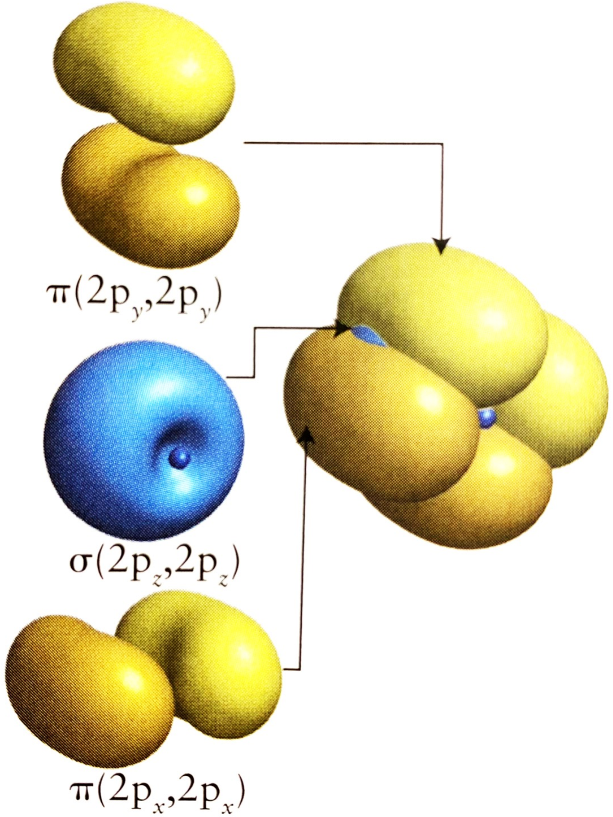


Figure 2F.5 (new book)

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?

2F.1 Sigma and pi bonds

Self-test 2F.1B

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

(b) HCN?

2F.1 Sigma and pi bonds

Summary

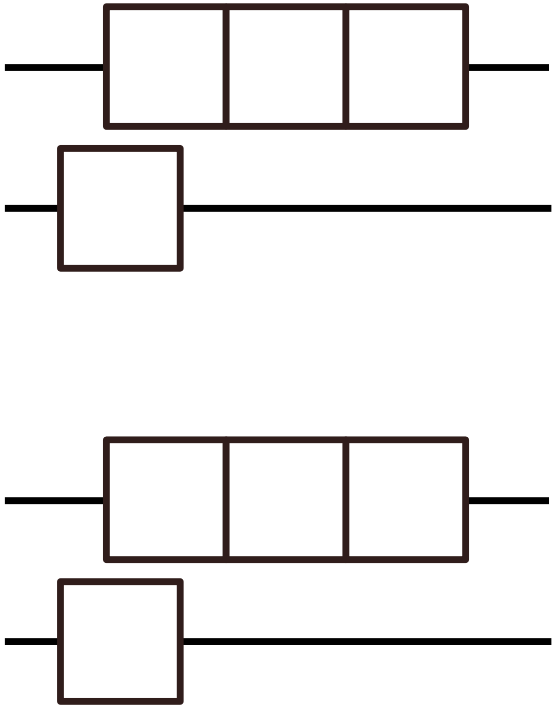
According to valence-bond theory, bonds form when individual valence electrons on neighbouring atoms pair with each other; the atomic orbitals overlap **end to end to form σ-bonds** or **side by side to form π-bonds**.

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



2F.2 Electron promotion and the hybridization of orbitals

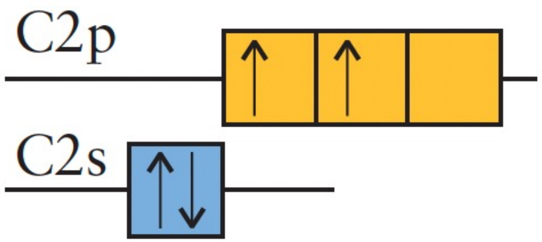
Valence-bond theory refinement: Carbon in CH_4

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.

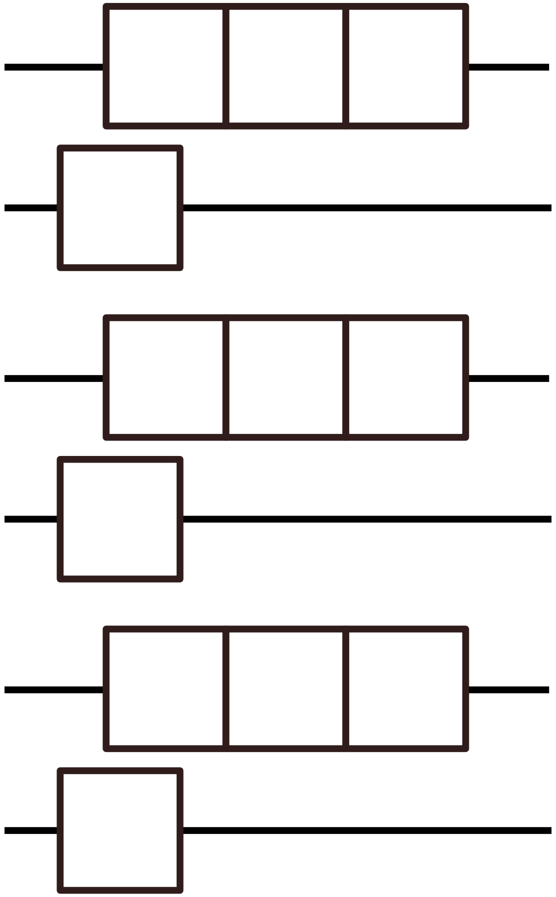
But: it has a **valence of four** and is **tetrahedral**.



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



2F.2 Electron promotion and the hybridization of orbitals

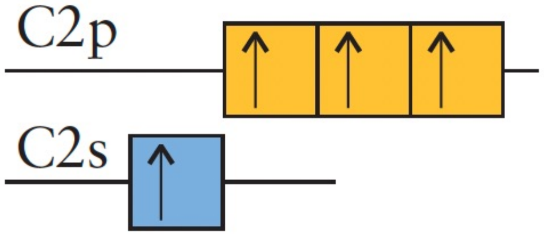
Valence-bond theory refinement: Carbon in CH_4

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

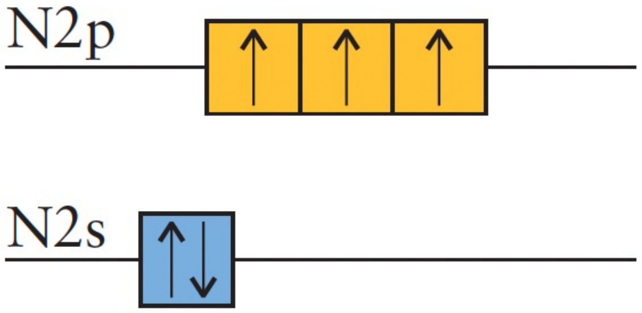
Valence-bond theory refinement: Carbon in CH_4

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

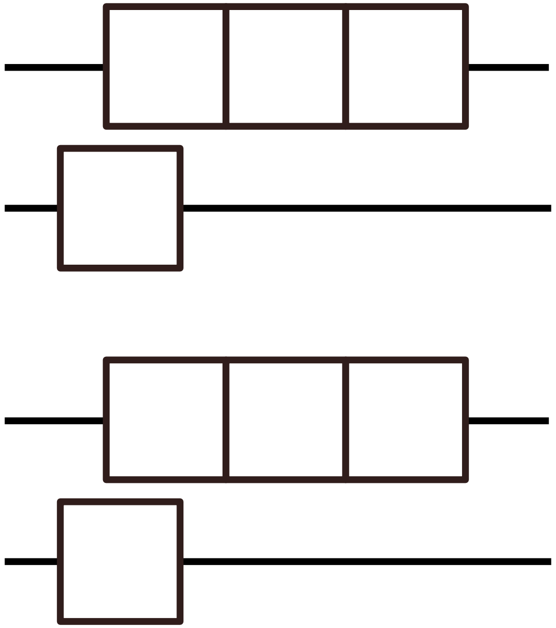
2F.2 Electron promotion and the hybridization of orbitals

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?

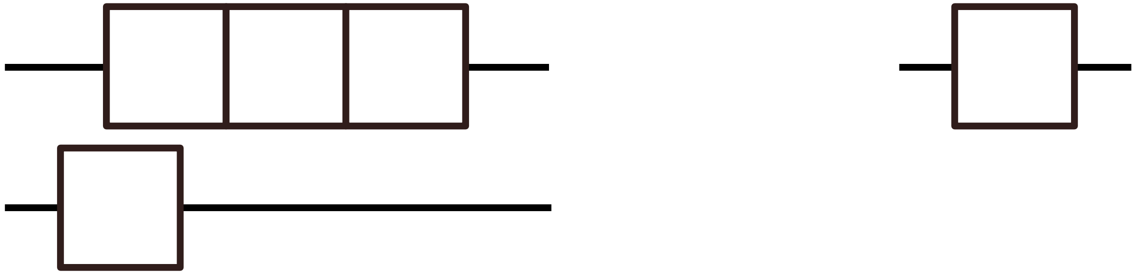
Electron
promotion

Carbon, $[\mathrm{He}]2s^2 2p_x^{\,1} 2p_y^{\,1}$

Carbon, $[\mathrm{He}]2s^1 2p_x^{\,1} 2p_y^{\,1} 2p_z^{\,1}$

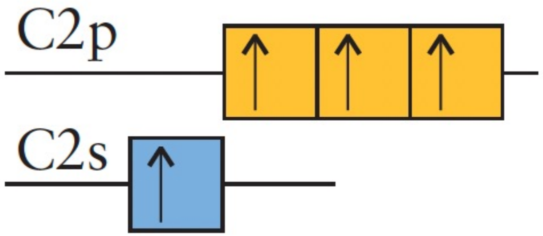
2F.2 Electron promotion and the hybridization of orbitals

What happens to orbitals after electron promotion?



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 would 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

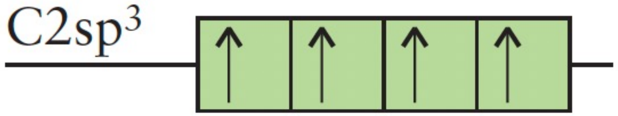
Hybrid orbitals are formed by **mixing (adding and subtracting)** atomic orbitals on the *same atom*. This process is called a **linear combination**, we mathematically *combine wavefunctions.*

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

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

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

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



sp^3 hybridized carbon

- Four sp^3 hybrid orbitals are formed from one s- and three p-orbitals.
- Four sp^3 orbitals of **equal shape** and **equal energy**, just oriented differently.

Rule: If *N* atomic orbitals mix, they always form *N* new hybrid orbitals.

2F.2 Electron promotion and the hybridization of orbitals

sp^3 hybrid orbitals

2F.2 Electron promotion and the hybridization of orbitals

sp^3 hybrid orbitals

2F.2 Electron promotion and the hybridization of orbitals

sp^3 hybrid orbitals

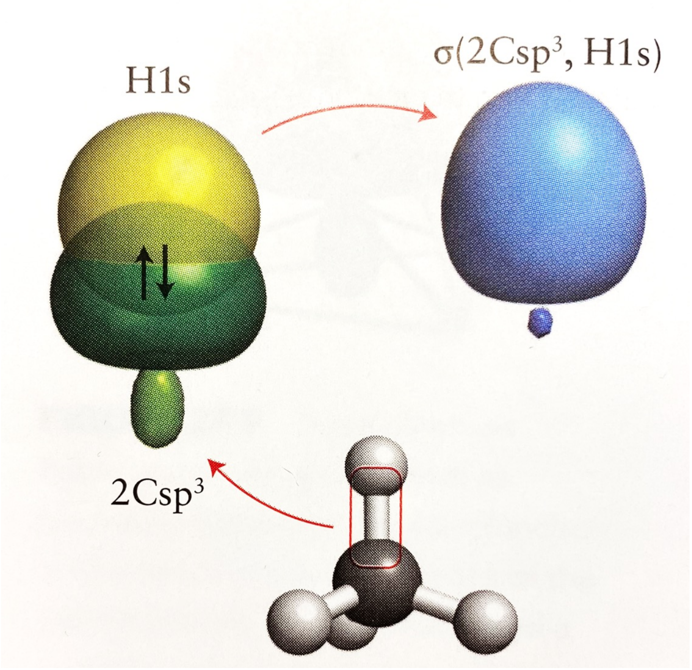
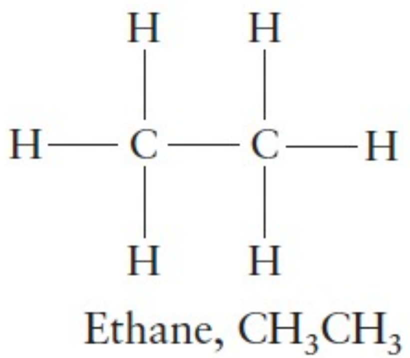


Figure 2F.7 (new book)

- 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.

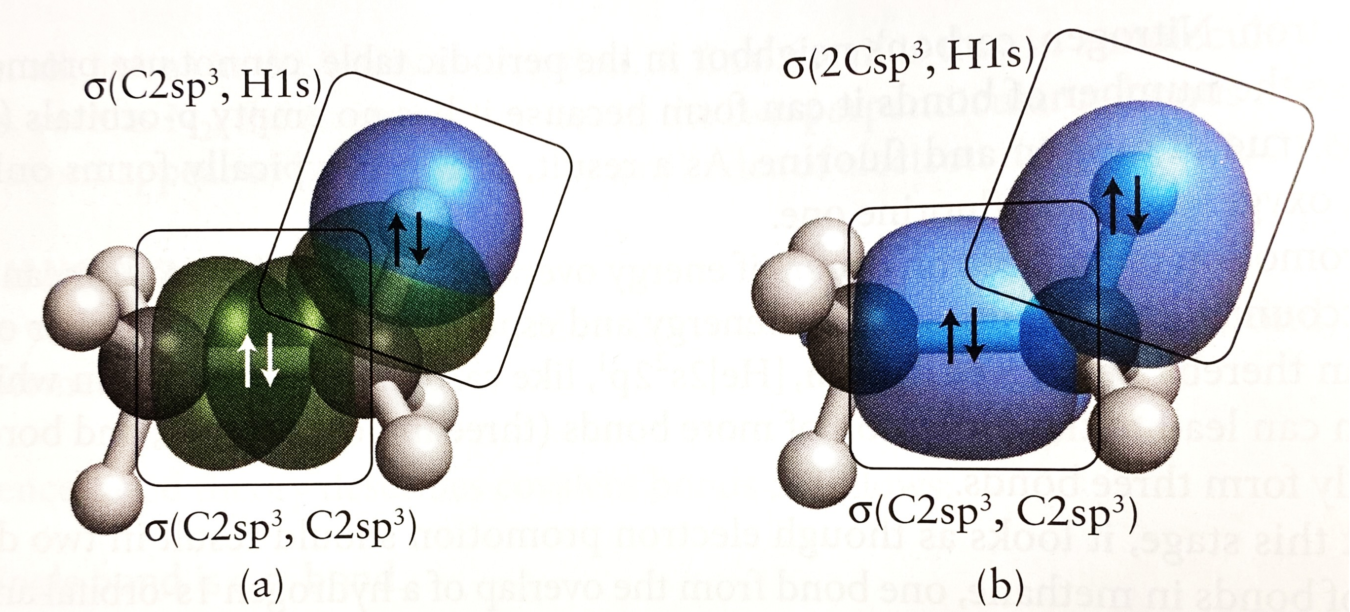
2F.2 Electron promotion and the hybridization of orbitals

Ethane



Ethane, CH_3CH_3

Figure 2F.8 (new book)

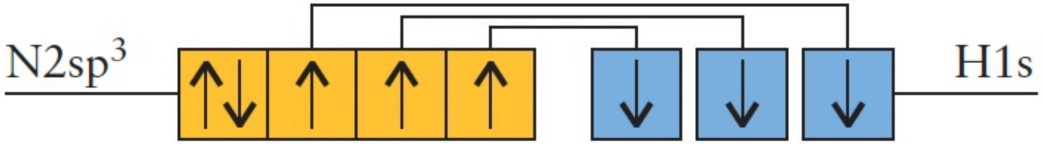


Boundary surfaces of two bonds are shown.

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 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.

Note: The terms in front of the p_x and p_y orbitals in the hybrid orbitals h_1, h_2, and h_3 come from the mathematical requirements for orthogonality and normalization (linear algebra: beyond this class).

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):

$$h_1 = s + p$$

$$h_2 = s - p$$

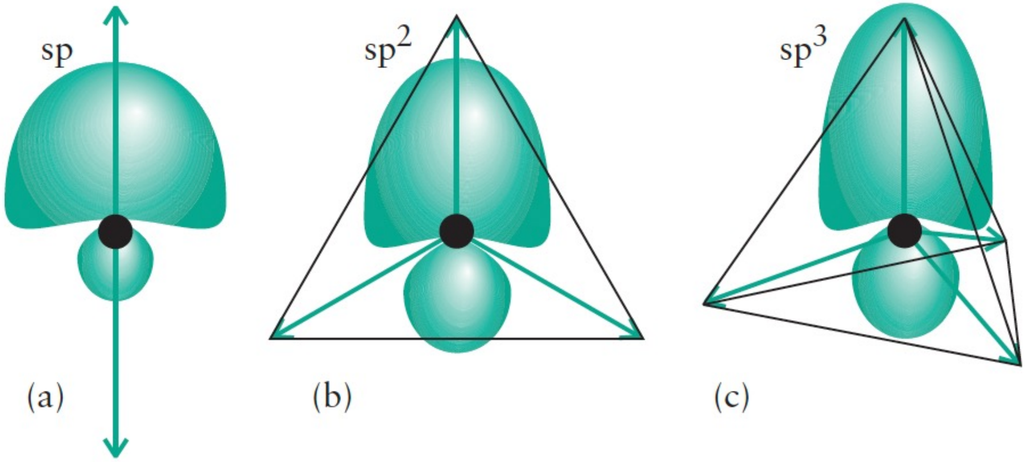


Figure 2F.9 (new book) / Figure 3.16 (old book)

2F.2 Electron promotion and the hybridization of orbitals

Hybridization

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.**

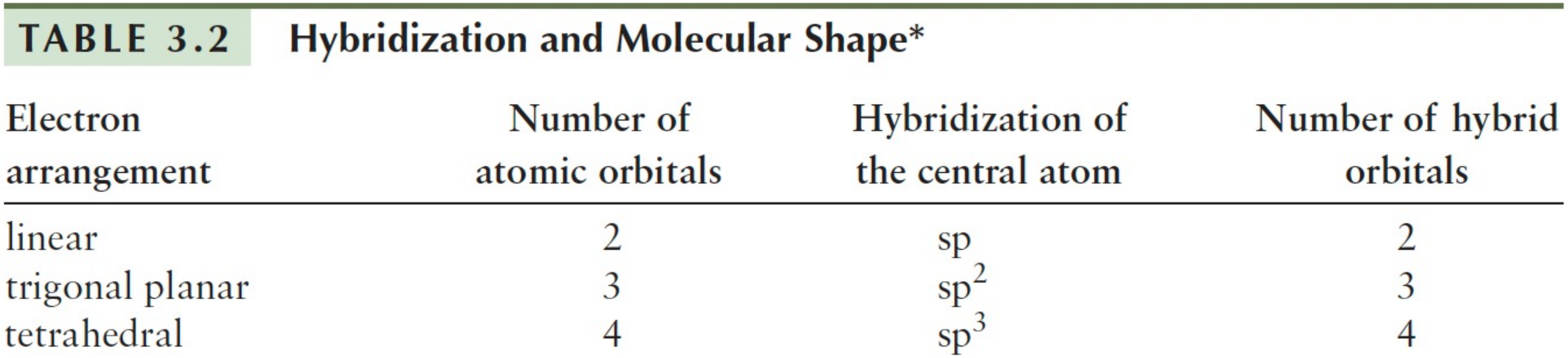


TABLE 3.2 **Hybridization and Molecular Shape***

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

Self-test 2F.2B

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

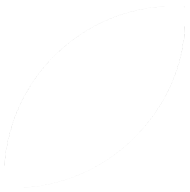
2F.2 Electron promotion and the hybridization of orbitals

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.

Valence-Bond Theory and Hypervalent Compounds

Topic 2F.3



2F.3 Valence-bond theory and hypervalent compounds

Hypervalency

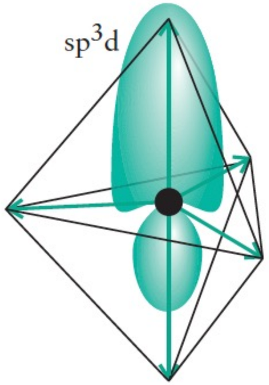
- Concepts of promotion and hybridization work well to describe the tetravalence of carbon.
- What about hypervalent molecules?
- Two approaches to describe hypervalent compounds with VB theory

2F.3 Valence-bond theory and hypervalent compounds

PCl_5 example of hypervalency

- Consider PCl_5:
  - Five Cl atoms attached to central P atom, five equal bonds
  - Five atomic orbitals → five hybrid orbitals
  - 1 s-orbital + 3 p-orbitals. **What is the fifth orbital?**
  - d-orbitals are close in energy: electron can be promoted to a d-orbital
  - Results: **sp^3d orbitals** (trigonal bipyramidal)
    - Two axial orbitals (Figure a)
    - Two equatorial orbitals (Figure b)

Figure 3.17 (old book)



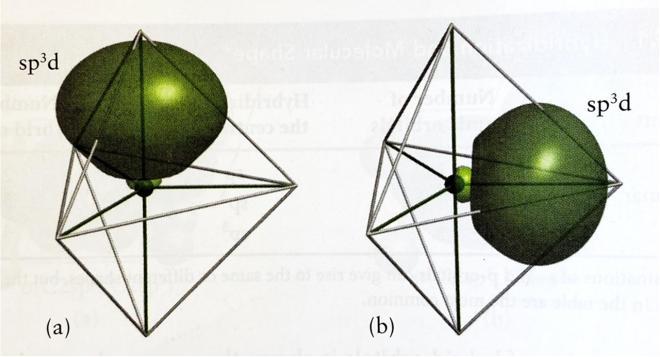


Figure 2F.10 (new book)

2F.3 Valence-bond theory and hypervalent compounds

SF_6 example of hypervalency

- Consider SF_6:
  - Six equivalent S–F bonds, octahedral
  - Six AOs → Six MOs
  - Two sulfur d-orbitals: **sp^3d^2 orbitals**
  - **Six identical orbitals** (no axial and equatorial distinction)

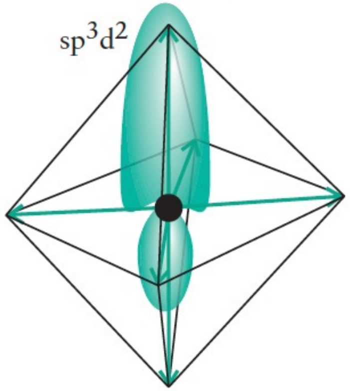


Figure 3.18 (old book)

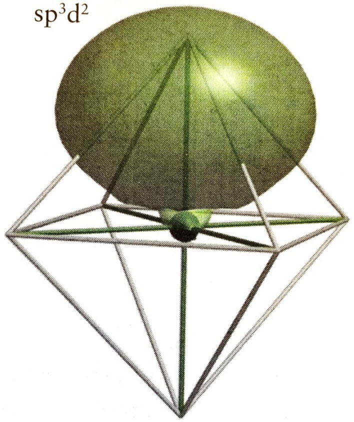


Figure 2F.11 (new book)

2F.3 Valence-bond theory and hypervalent compounds

Table 2F.2

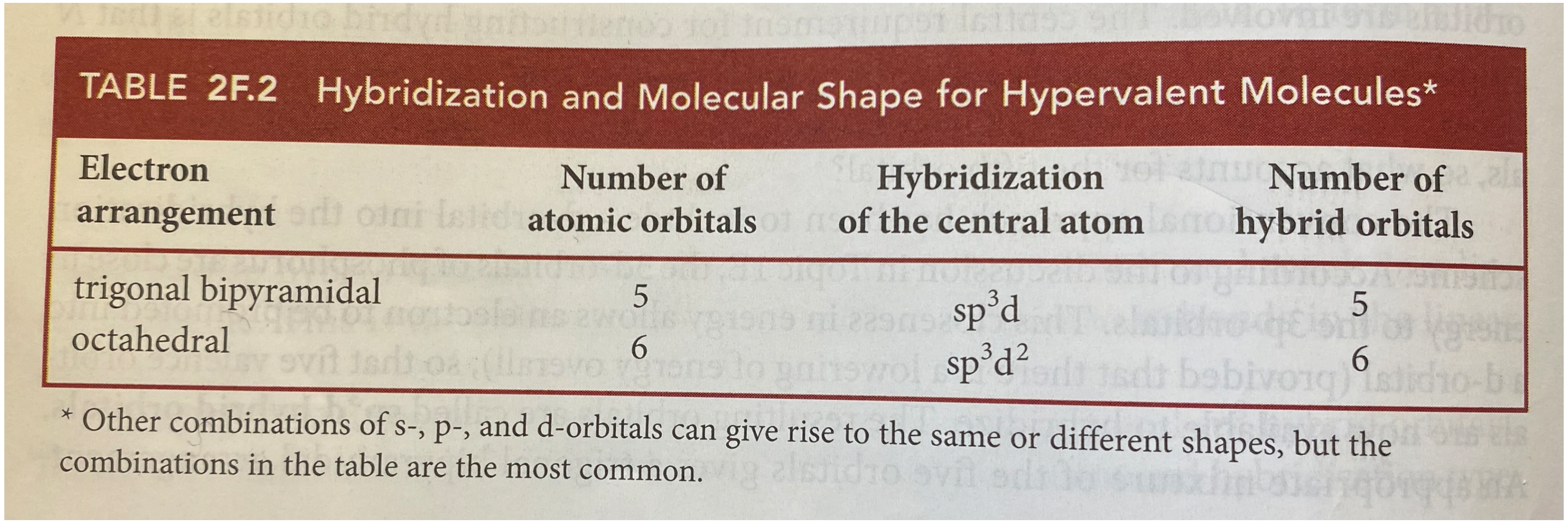


TABLE 2F.2 Hybridization and Molecular Shape for Hypervalent Molecules*

Electron arrangement	Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
trigonal bipyramidal	5	sp^3d	5
octahedral	6	sp^3d^2	6

* Other combinations of s-, p-, and d-orbitals can give rise to the same or different shapes, but the combinations in the table are the most common.

- **This type of hybridization only occurs in Period 3 and later**

2F.3 Valence-bond theory and hypervalent compounds

Alternative approach to hypervalency

- Approach 1 includes d-orbitals
- An alternative is to view compounds as extremes of ionic-covalent character (see Topic 2C).

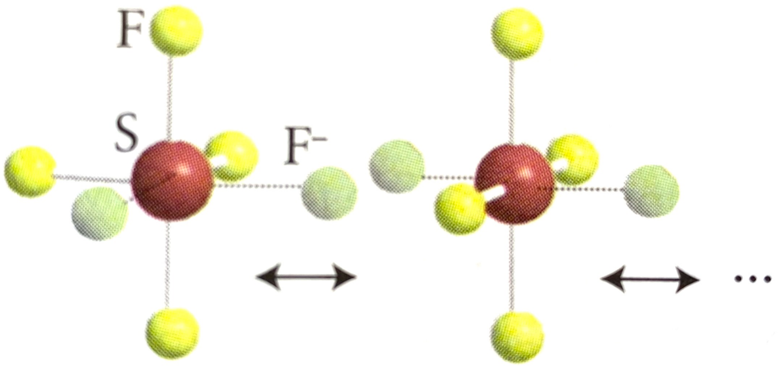


Figure 2F.12 (new book)

The structure of SF_6 can be accounted for by allowing for resonance between 15 structures of the form $(SF_4^{2+})(F^-)_2$, two of which are shown here.

Twelve of these structures have the F^- ions in the *cis* positions; the remaining three have the F^- ions in the *trans* positions.

Which model is more accurate? Would need to run calculations!

2F.3 Valence-bond theory and hypervalent compounds

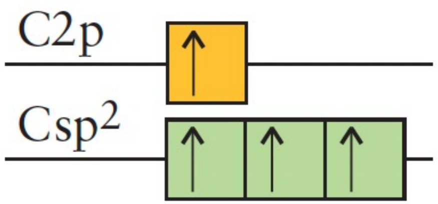
Summary

The bonding in hypervalent compounds can be described in two ways: hybridization schemes that incorporate d-orbitals and the use of ionic-covalent resonance.

Characteristics of Multiple Bonds

Topic 2F.4

2F.4 Characteristics of multiple bonds



Alkenes: Ethene (ethylene)

- Each carbon makes three sp^2 sigma-bonds and one pi-bond.
- 120 ° angles

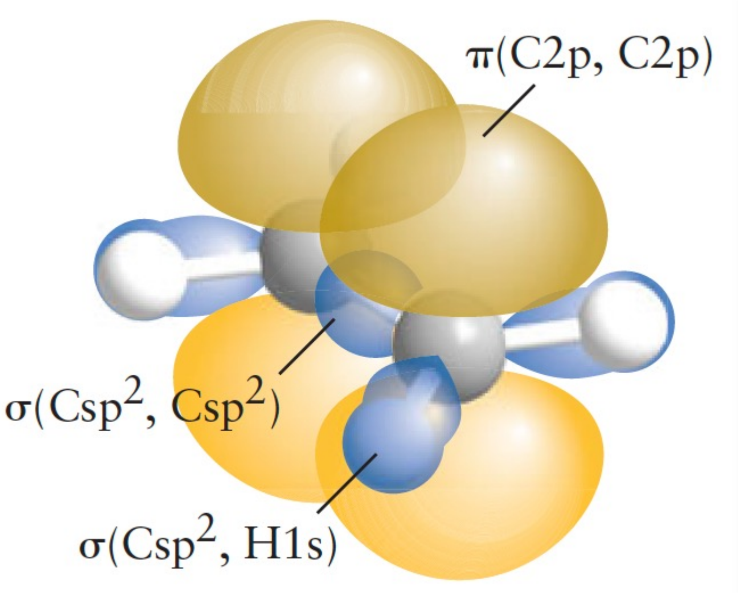


Figure 3.19 (old book)

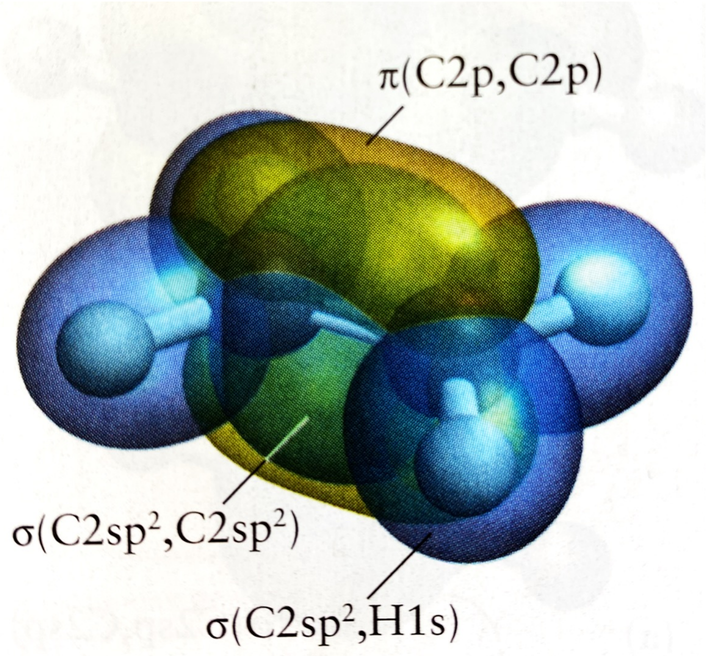


Figure 2F.13 (new book)

2F.4 Characteristics of multiple bonds

Alkenes: Ethene (ethylene)

2F.4 Characteristics of multiple bonds

Alkenes: Ethene (ethylene)

2F.4 Characteristics of multiple bonds

Benzene

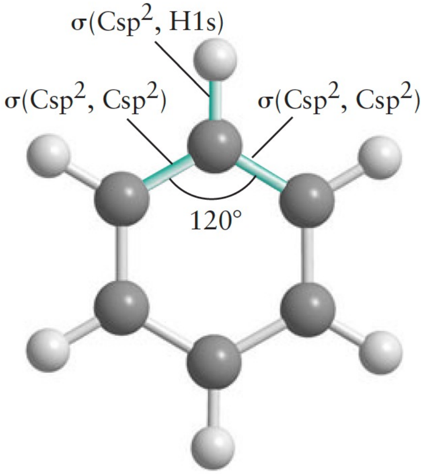


Figure 2F.14 (new book):

The framework of sigma-bonds in benzene.

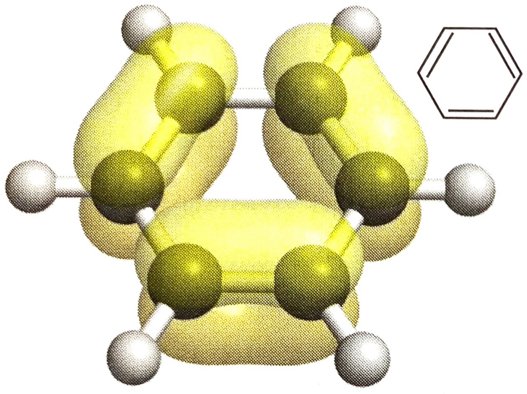


Figure 2F.15 (new book):

Unhybridized 2p-orbitals can form a pi-bond with either of their immediate neighbours. Two arrangements possible, one shown here.

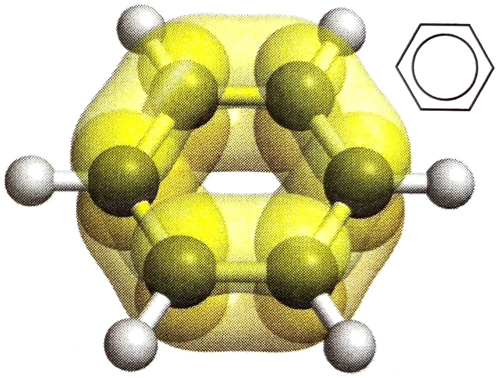


Figure 2F.16 (new book):

Resonance between two structures (one shown in Figure 2F.15) results in double doughnut-shaped cloud above and below the plane of the ring.

2F.4 Characteristics of multiple bonds

Rotation around double bonds

- Double bonds prevent one part of a molecule from rotating relative to another part.
- Double bond hold molecules flat.
- 2p-orbital overlap in ethene is best if all six atoms are in the same plane. In order for the molecule to rotate about the double bond, the π-bond would need to break and re-form.

2F.4 Characteristics of multiple bonds

Alkynes

- Each carbon makes two sp sigma-bonds and two pi-bonds.
- 180 ° angles
-

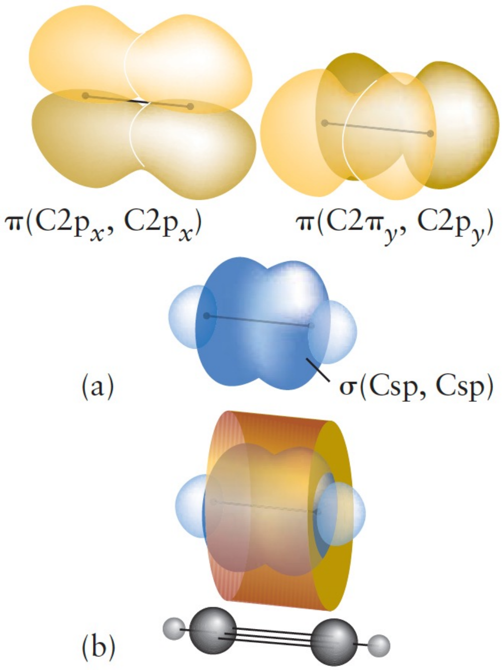


Figure 3.23 (old book)

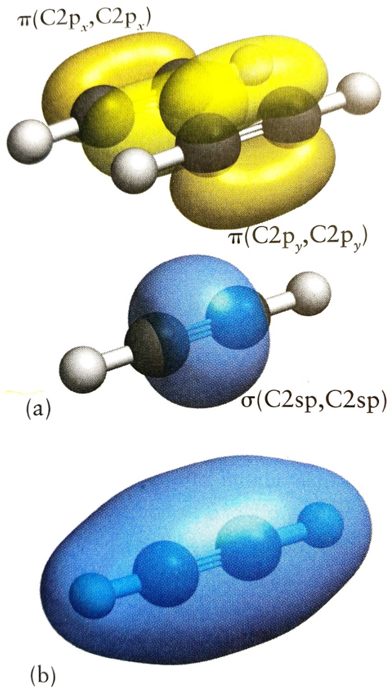


Figure 2F.17 (new book)

2F.4 Characteristics of multiple bonds

Example 2F.1 Accounting for the structure of a molecule with multiple bonds

- Account for the structure of a formic acid molecule (methanoic acid, HCOOH) in terms of hybrid orbitals, bond angles, and σ- and π-bonds. The C atom is attached to an H atom, a terminal O atom, and an –OH group.

2F.4 Characteristics of multiple bonds

Example 2F.1 Accounting for the structure of a molecule with multiple bonds

2F.4 Characteristics of multiple bonds

Summary

Multiple bonds are formed when an atom forms a σ-bond by using an sp or sp^2 hybrid orbital and one or more π-bonds by using unhybridized p-orbitals. The side-by-side overlap that forms a π-bond makes a molecule resistant to twisting, results in bonds that are weaker than σ-bonds, and prevents atoms with large radii from forming multiple bonds.

The skills you have mastered are the ability to

- Describe the difference between σ- and π-bonds and identify the composition of single, double, and triple bonds.
- Account for the occurrence and significance of promotion.
- Describe the formation of hybrid orbitals from the mixing of atomic orbitals.
- Account for the structure of a molecule in terms of hybrid orbitals and σ- and π-bonds.
- Account for hypervalent compounds by using the d-orbital hybridization and ionic-covalent resonance models.
- Explain the torsional rigidity of double bonds between atoms.

Summary: You have learned that according to valence-bond theory, a covalent bond forms when electrons in atomic orbitals pair their spins and the orbitals overlap. You have learned that there are two main types of covalent bonds (σ and π) and that electron promotion occurs if the increased number of bonds that can form repays the energy investment. Finally, You have encountered the concepts of hybridization, which enables the description of bond formation to be matched to the observed molecular shape, and the two alternative approaches to the desription of bonding in hypervalent molecules.