



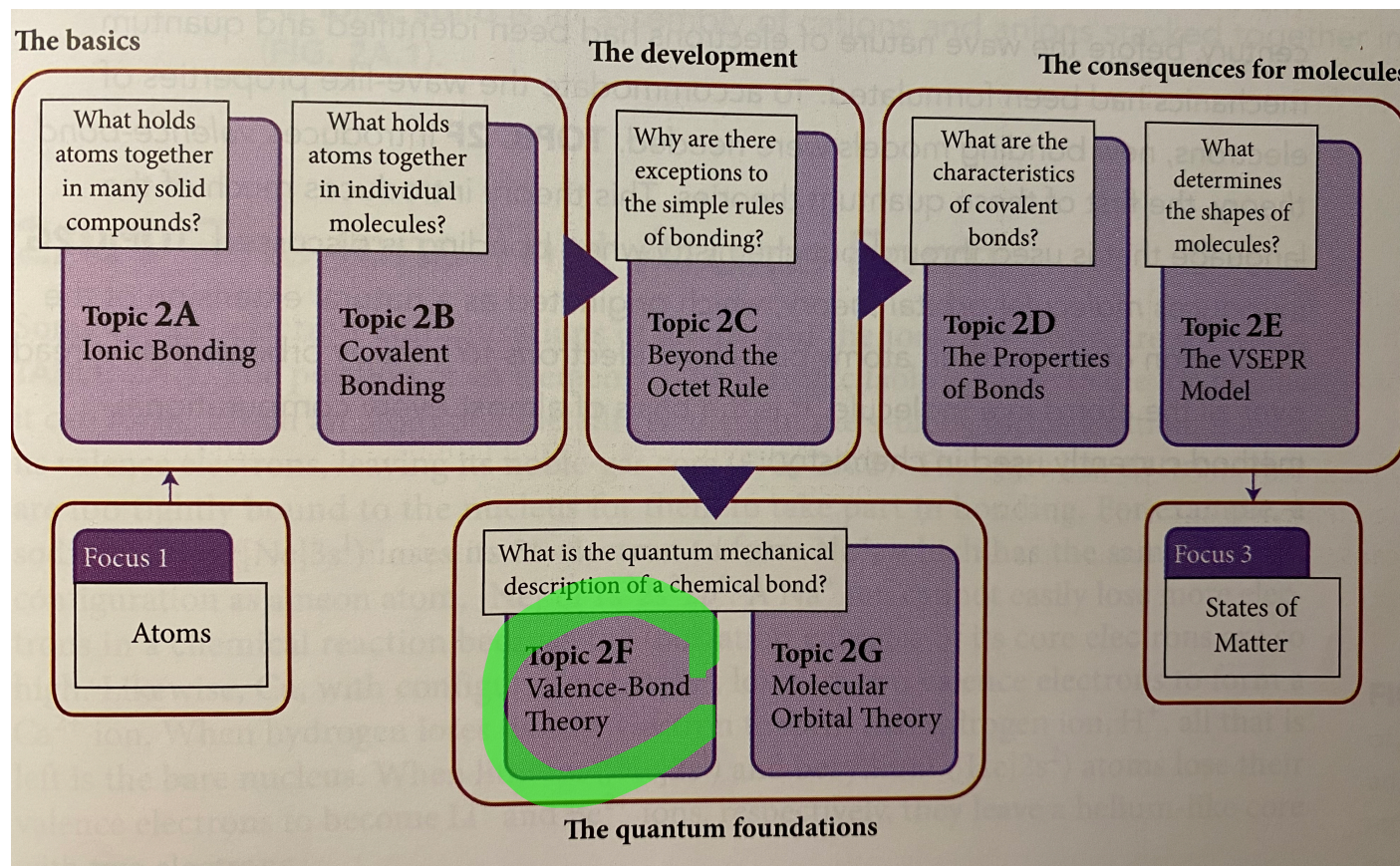
CH-110 Advanced General Chemistry I

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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)
- Take advantage of last two TA sessions!
- Practice exam on the last day (Friday, November 14), solutions will be uploaded on Moodle after the exam
- Review session will be scheduled for January (Class representative: please contact me sometime after class in the next two weeks)

Overview Chapter 2 (Focus 2: Bonds Between Atoms)



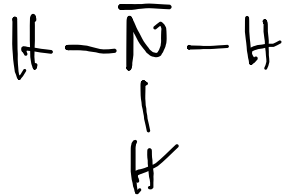
Valence-Bond Theory

Topic 2F

2F Valence-bond theory

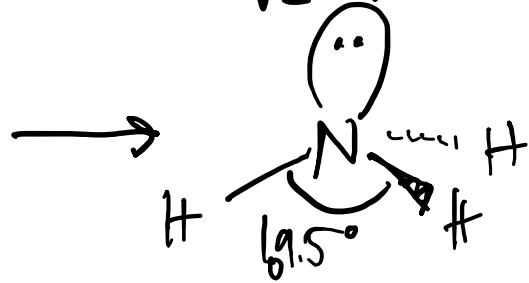
Lead-in

(Lewis) structure



- Atoms' connectivity
- Electron counting

VSEPR



- 3D geometry
- bond angles

What's missing?

- What's a bond, really?
- Why only certain angles (109.5° , 120° , 180°)?
- How does electron sharing arise from the atomic orbitals?

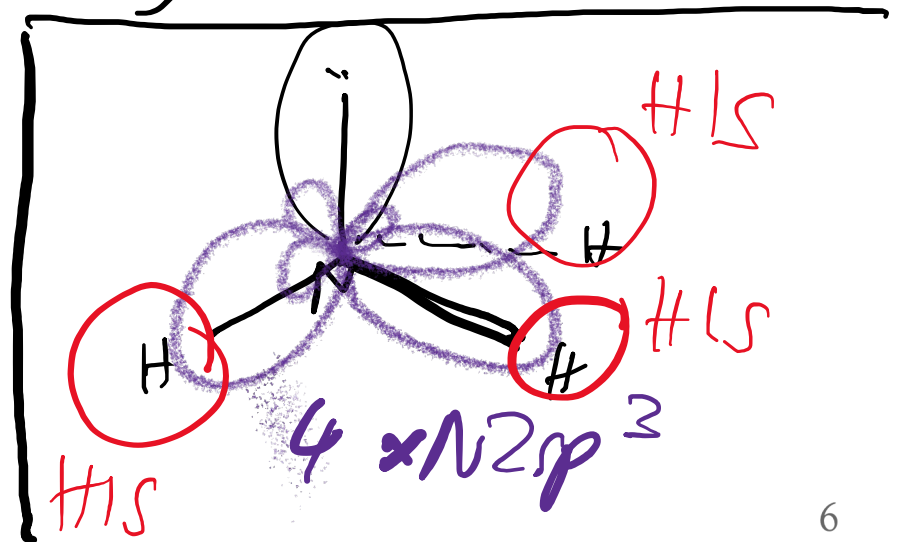
Valence bond theory

2F Valence-bond theory

Lead-in

- Bonds form when atomic orbitals overlap
- Two wavefunctions (= atomic orbitals) merge to create shared electron density between atoms
⇒ to make bonds

- Hybridization: atomic orbitals can mix to explain molecular geometry!



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)

2F Valence-bond theory

Protocol for valence bond theory

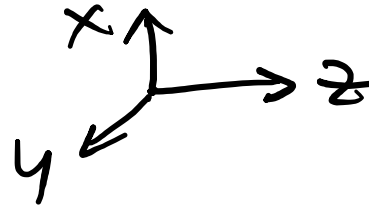
1. Start from the **Lewis structure**: draw the molecule, identify bonding and lone pairs.
2. Determine **geometry (VSEPR)**: count areas of high electron density around central atom.
3. Assign hybrid orbitals: **mix s and p orbitals** to match the geometry
4. Describe orbital overlap:
 - **σ -bonds: 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

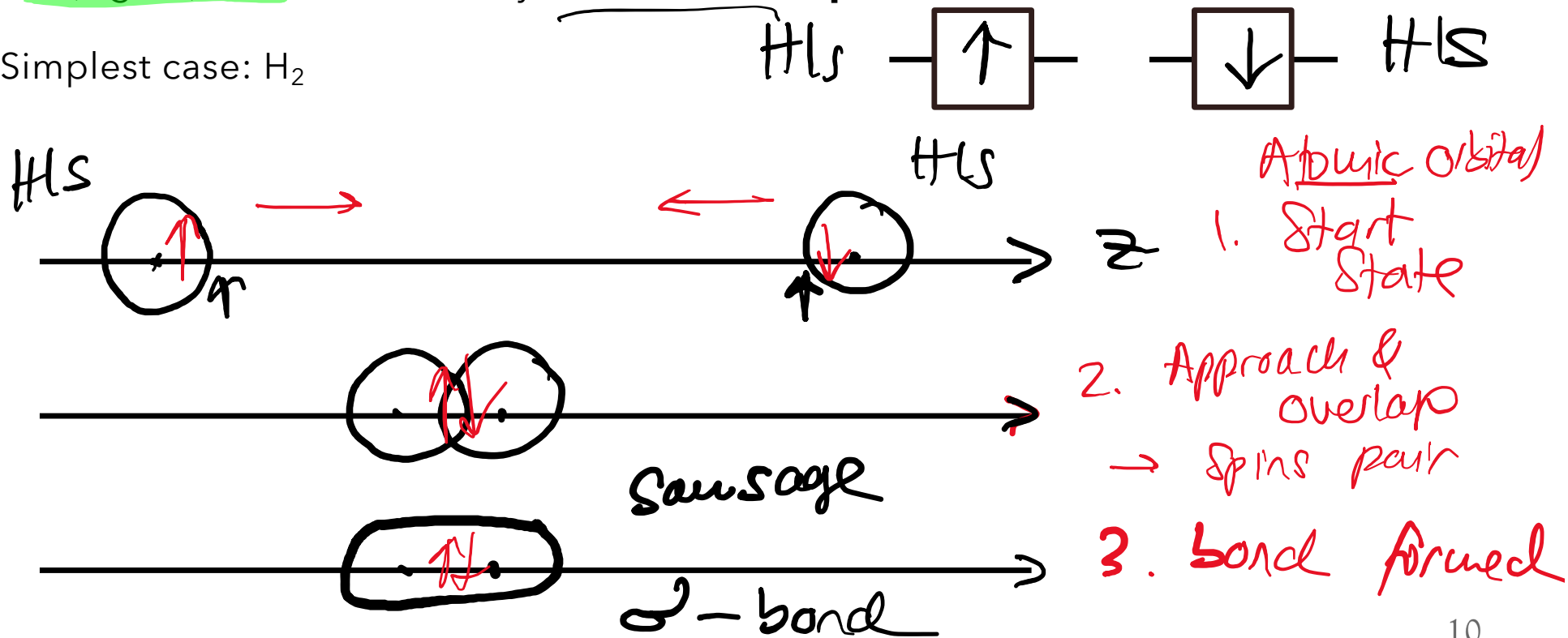
Topic 2F.1

2F.1 Sigma and pi bonds

Sigma bonds $H - H$

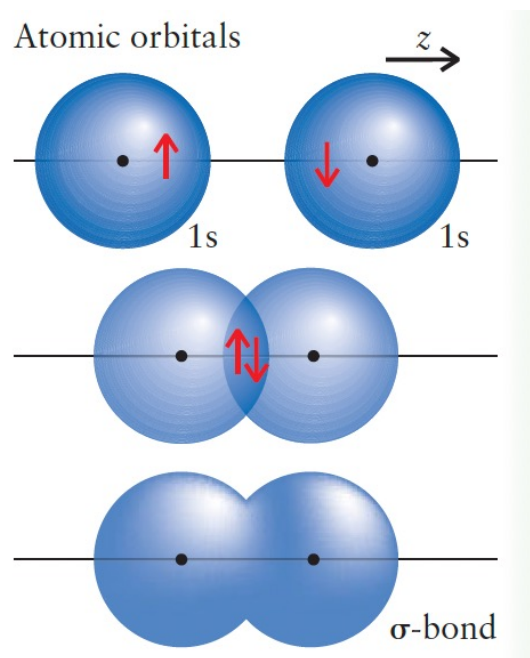


- A σ (sigma) bond is formed by **head-on overlap**.
- Simplest case: H_2



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

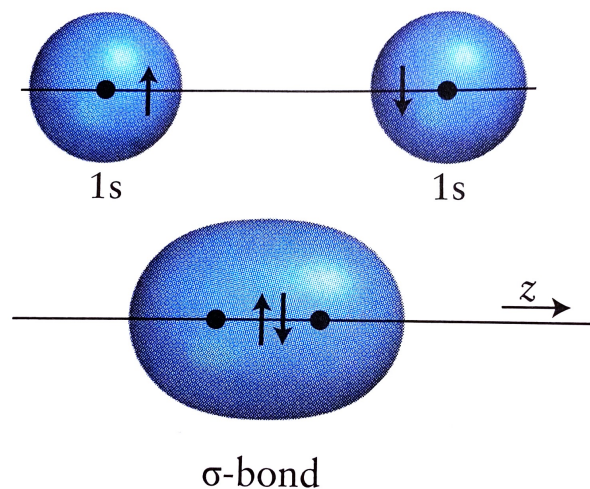


Figure 2F.1
(new book version)

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

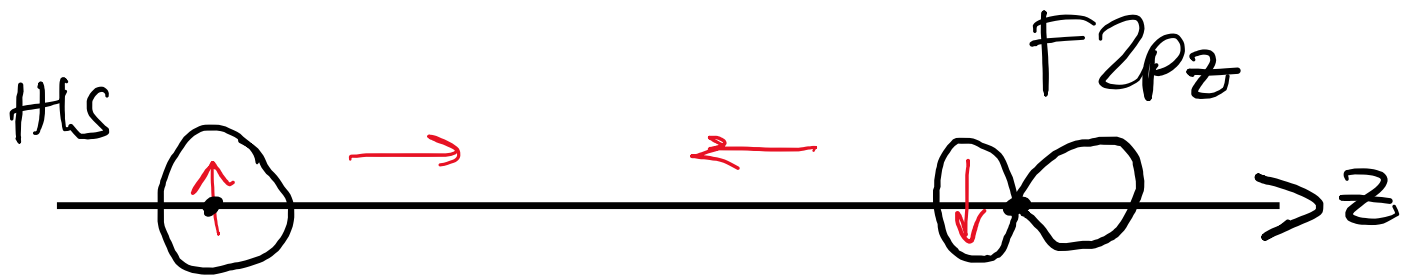
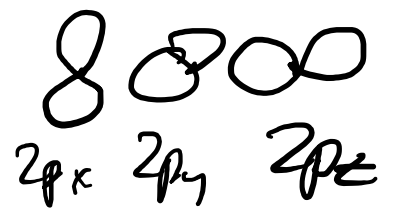
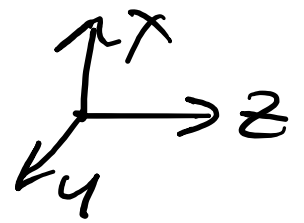
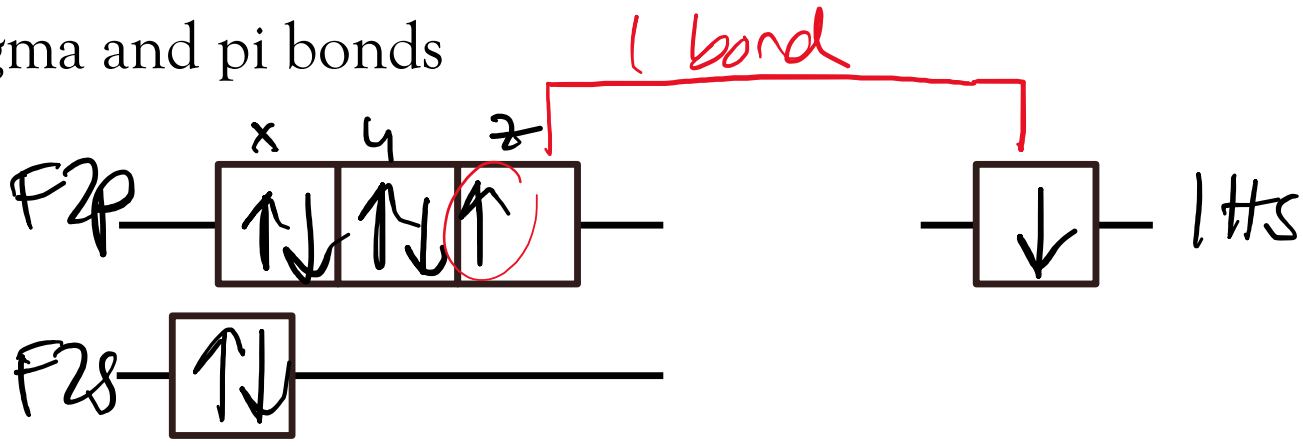
A σ -bond is **cylindrically symmetrical** (the same in all directions around the long axis of the bond), with **no nodal planes** containing the internuclear axis.

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

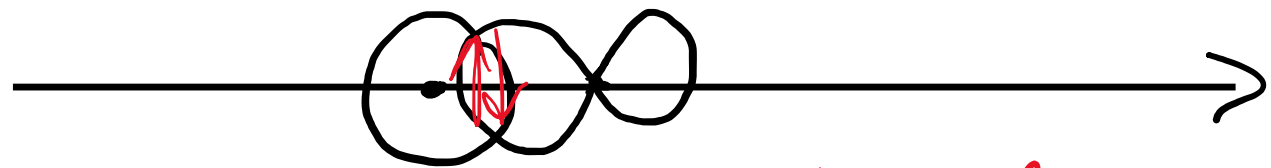
The greater the orbital overlap, the stronger the bond.

2F.1 Sigma and pi bonds

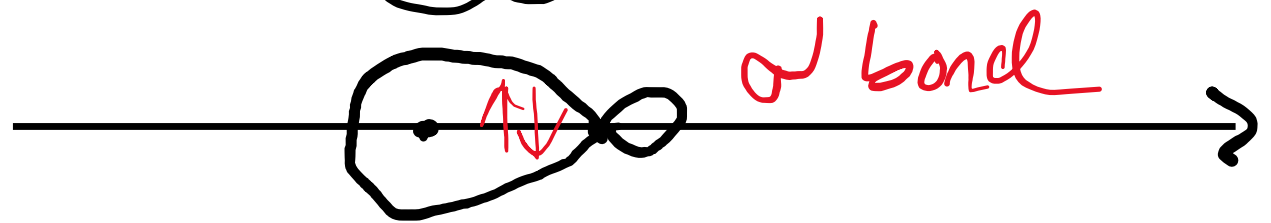
HF



Start state



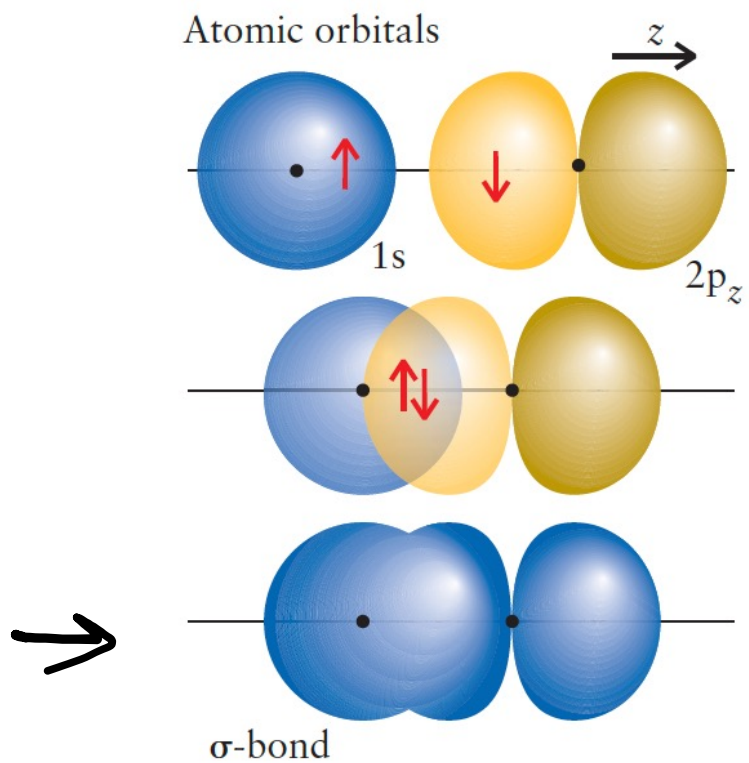
approach & overlap



bond formed

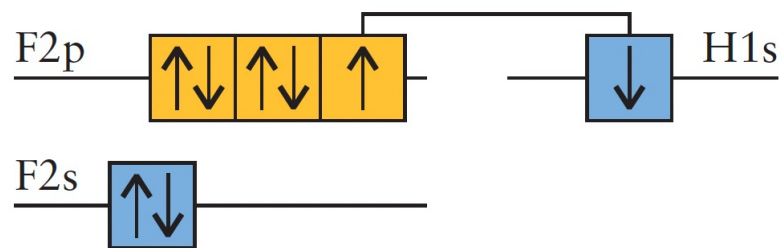
2F.1 Sigma and pi bonds

Sigma bonds: HF



Older book version: Figure 3.9

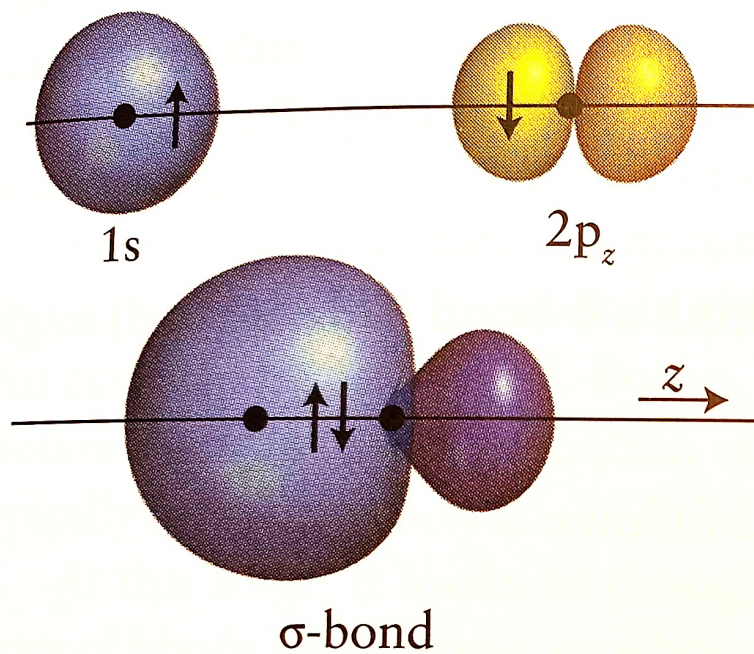
$2p_z$ -orbital of fluorine
+ $1s$ -orbital of hydrogen



33 Hydrogen fluoride, HF

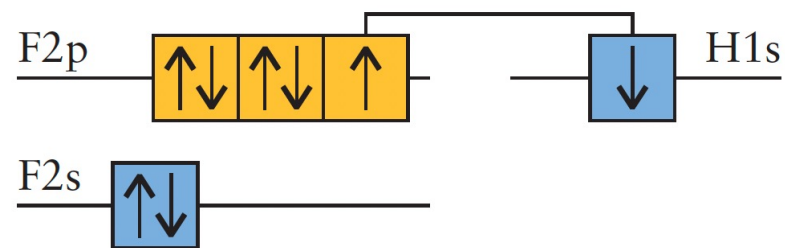
2F.1 Sigma and pi bonds

Sigma bond in HF



$2p_z$ -orbital of fluorine

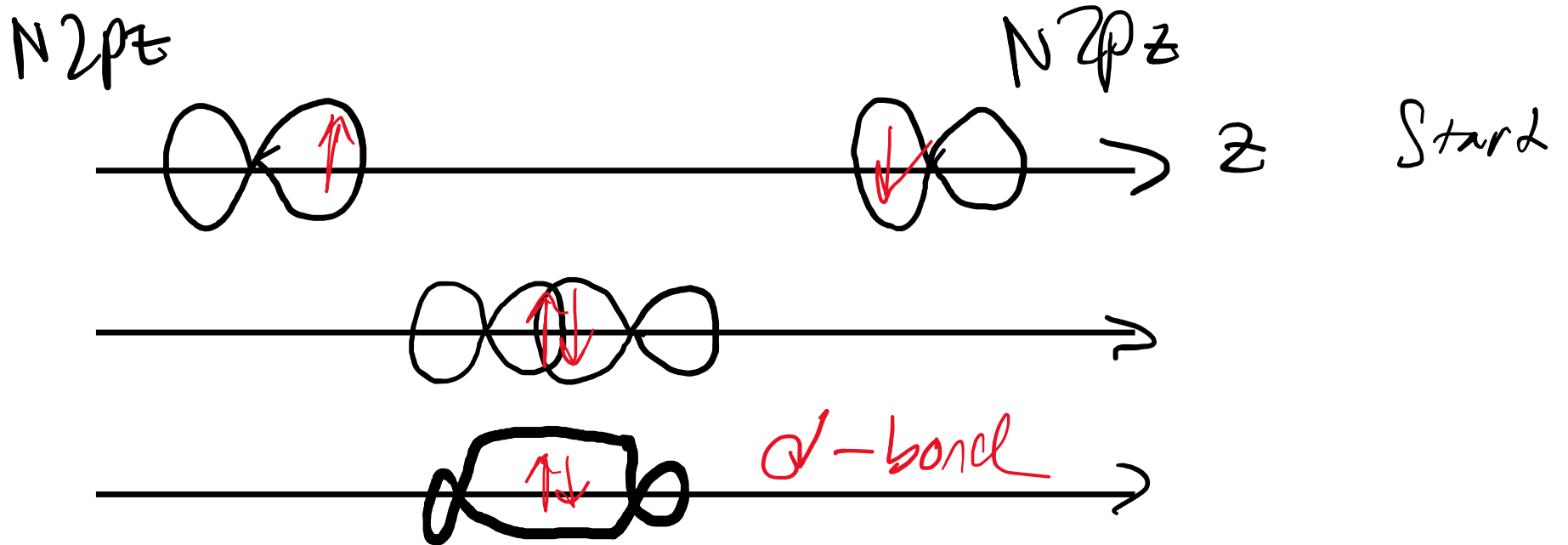
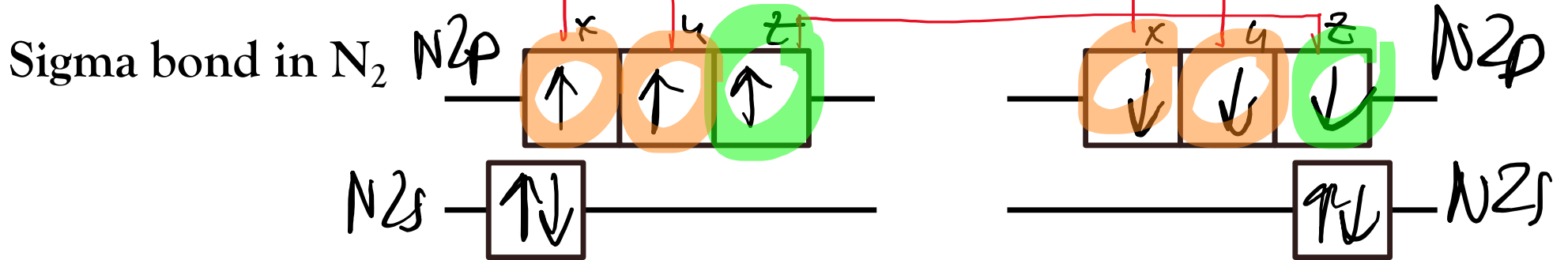
+ 1s-orbital of hydrogen



33 Hydrogen fluoride, HF

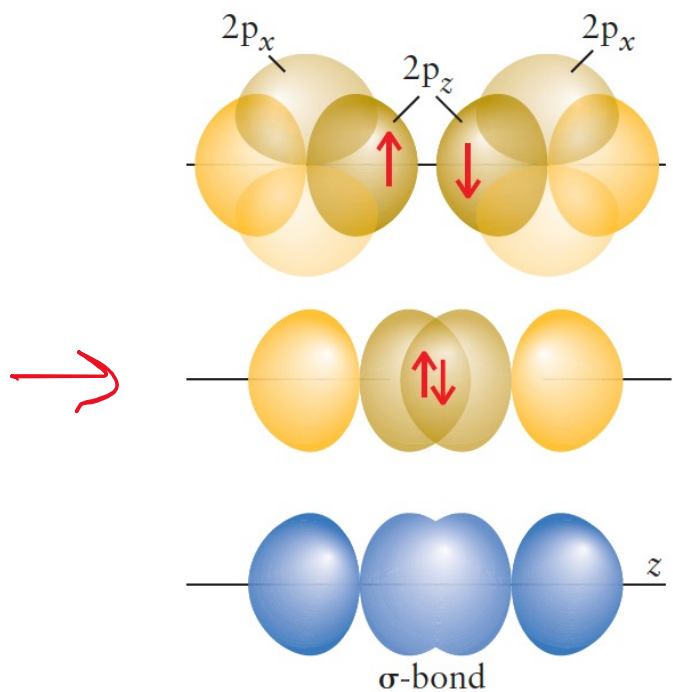
Figure 2F.2 (new book)

2F.1 Sigma and pi bonds



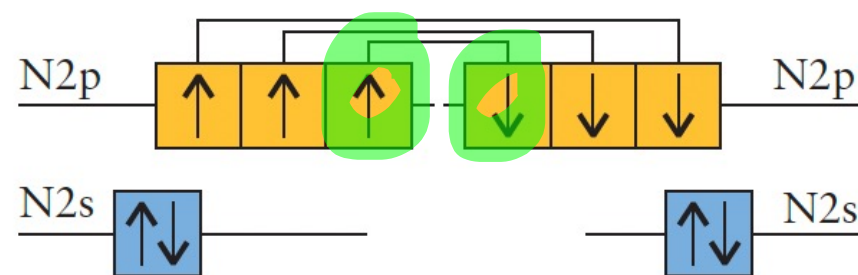
2F.1 Sigma and pi bonds

Sigma bond in N₂



Older book version: Figure 3.10

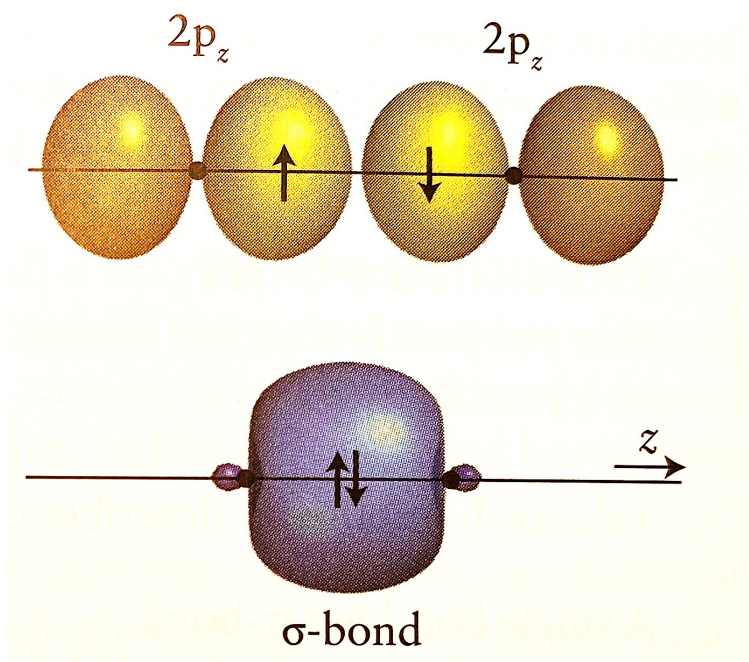
The 2p_z-orbitals of nitrogen overlap to form a sigma bond



34 Nitrogen, N₂

2F.1 Sigma and pi bonds

Sigma bonds in N₂



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

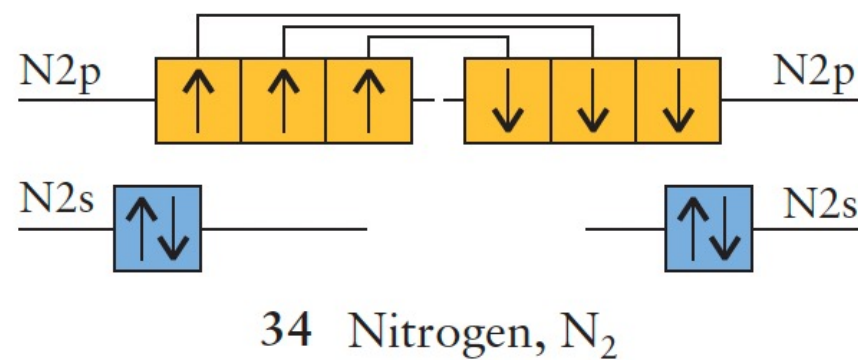
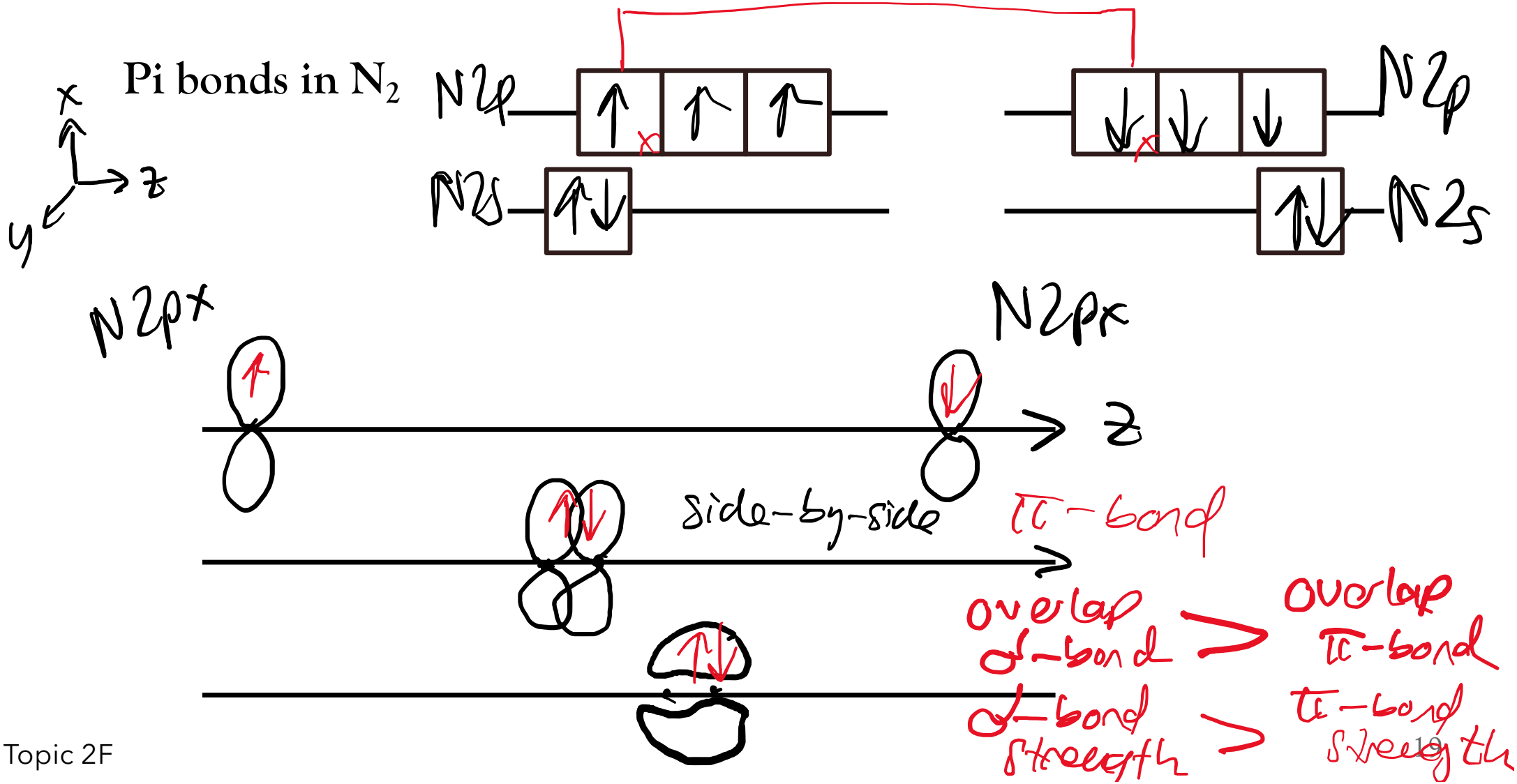
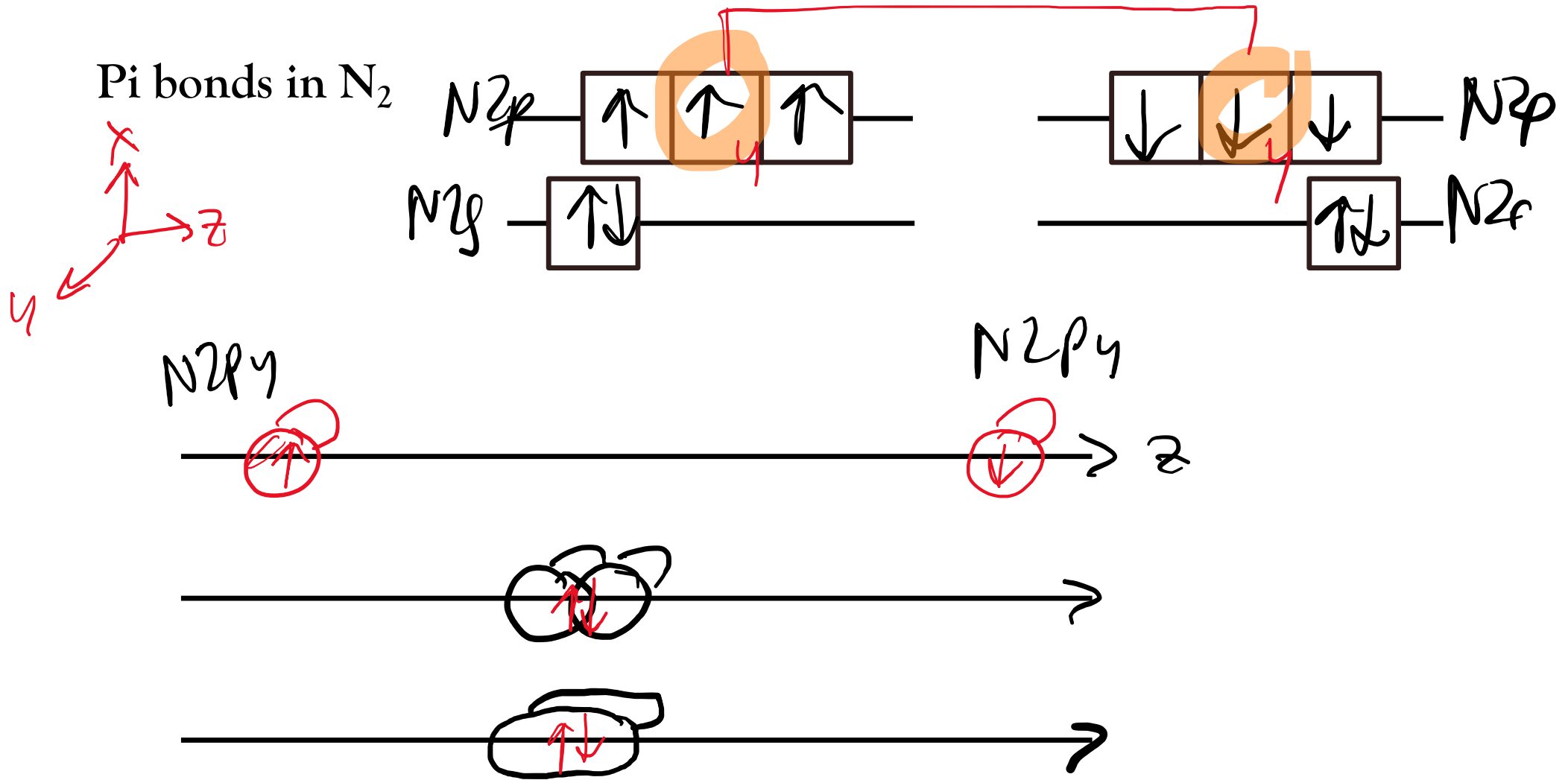


Figure 2F.3 (new book)

2F.1 Sigma and pi bonds

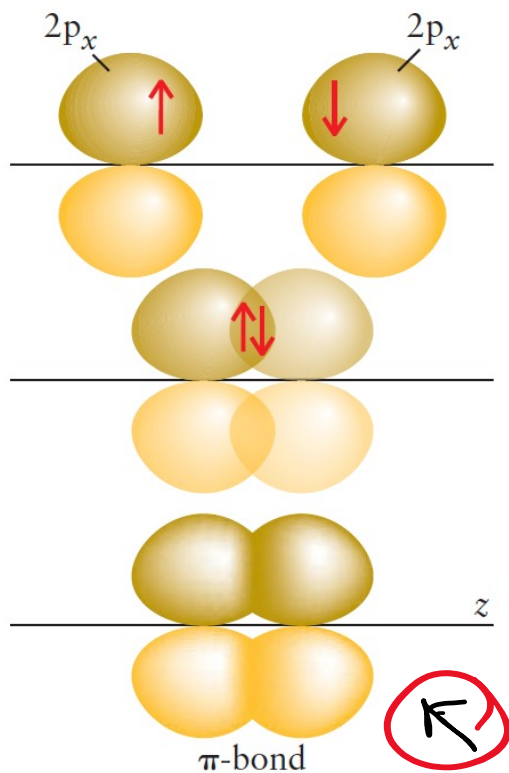


2F.1 Sigma and pi bonds



2F.1 Sigma and pi bonds

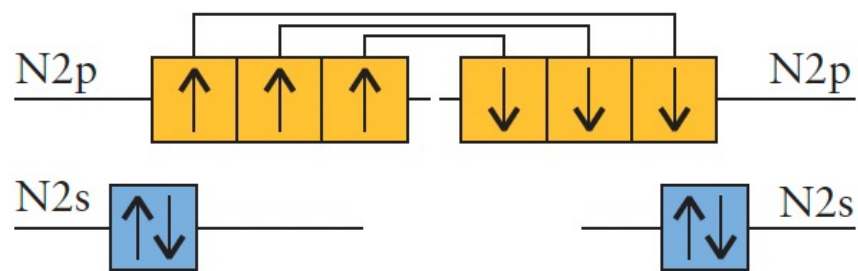
Pi bonds in N₂



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, N₂

2F.1 Sigma and pi bonds

Pi bonds in N_2

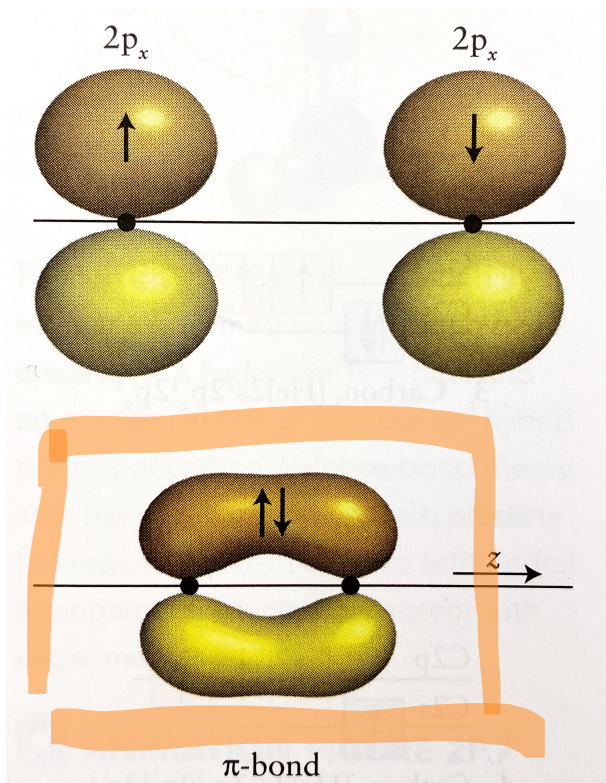
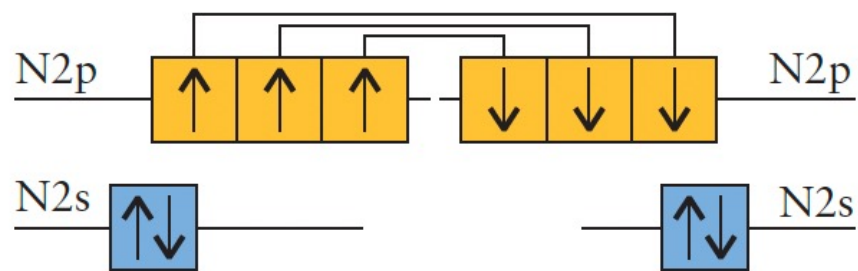


Figure 2F.4 (new book)

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

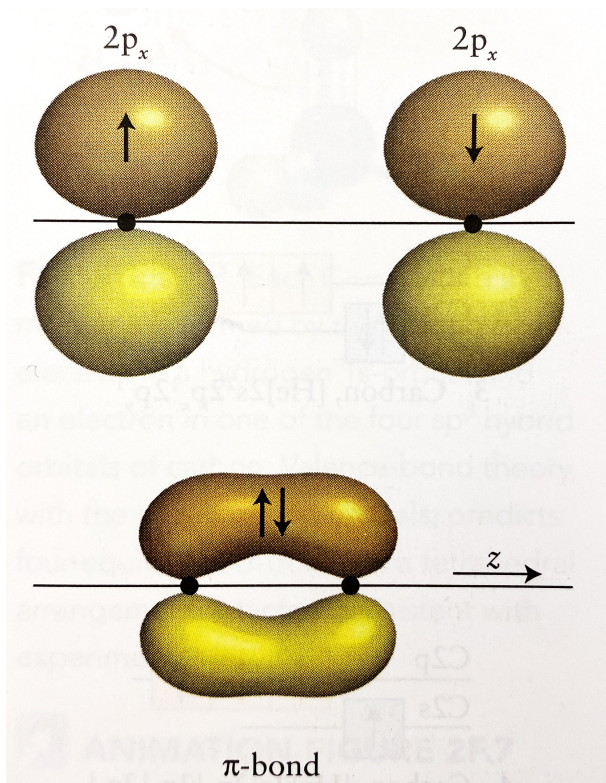


Figure 2F.4 (new book)

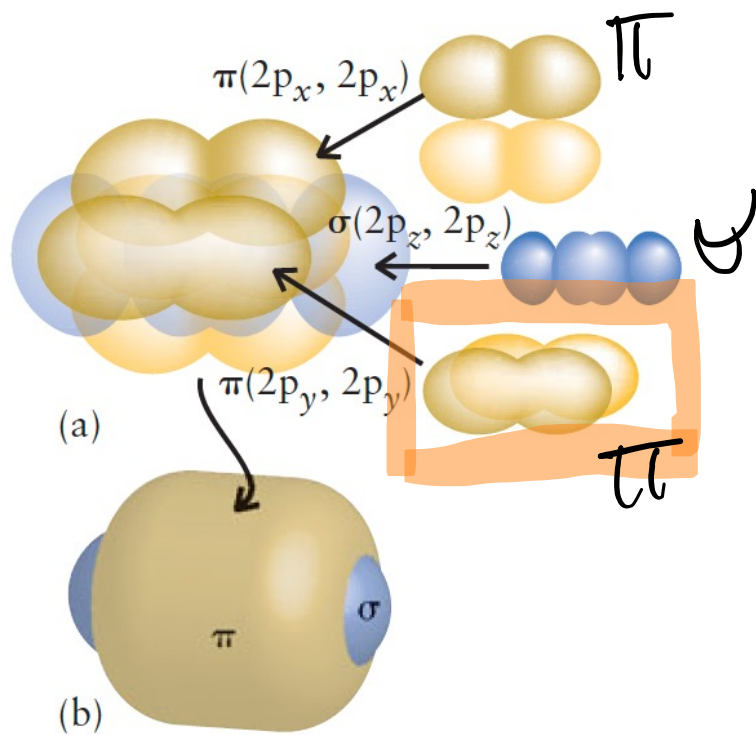
A π -bond has a single nodal plane containing the internuclear axis.

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

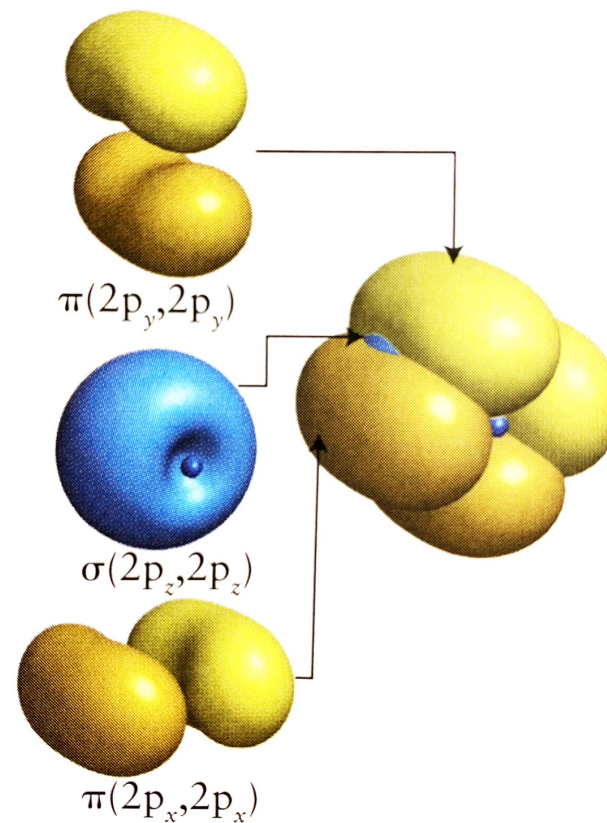


Figure 2F.5 (new book)

2F.1 Sigma and pi bonds

Valence-bond theory describes covalent bonds as follows:

A single bond is a 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 ?



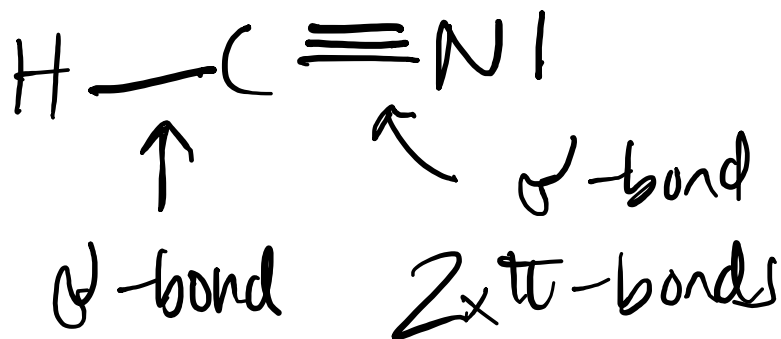
3 σ bonds

2F.1 Sigma and pi bonds

Self-test 2F.1B

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

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



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.**

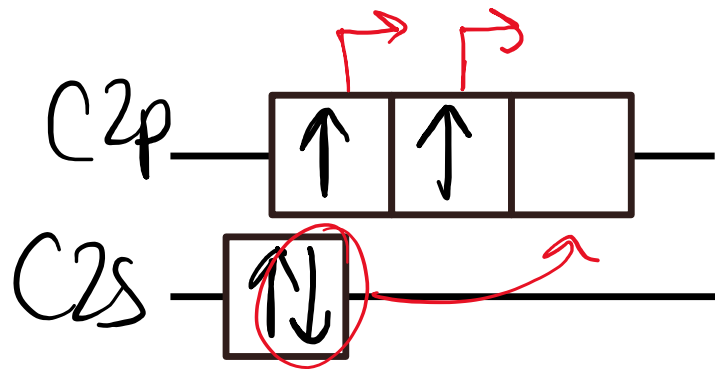
Electron Promotion and the Hybridization of Orbitals

Topic 2F.2



2F.2 Electron promotion and the hybridization of orbitals

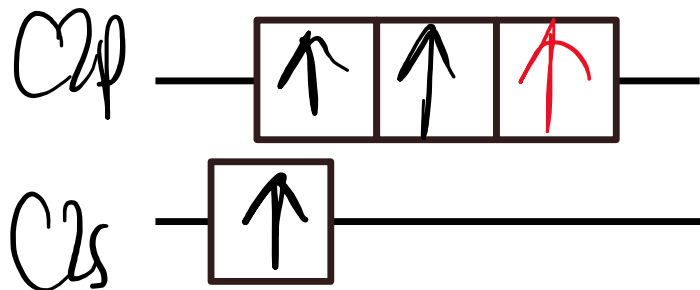
Valence-bond theory refinement: Carbon in CH_4



2 bonds ?

No! Carbon is tetravalent!

Four bonds \Rightarrow Need four unpaired electrons !



Electron promotion: \ominus is moved to a higher energy orbital

$$\Delta E(C2s \rightarrow C2p) < \Delta E \left(\begin{array}{l} \text{stabilization} \\ \text{from two} \\ \text{extra bonds} \end{array} \right)$$

2F.2 Electron promotion and the hybridization of orbitals

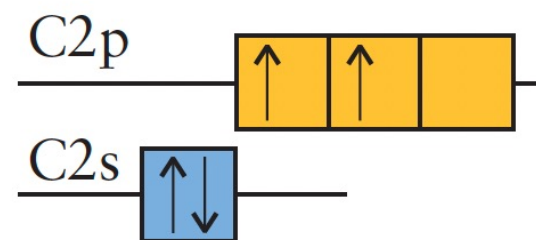
Valence-bond theory refinement: Carbon in CH₄

Configuration in carbon atom: [He]2s²2p_x¹2p_y¹ 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 bonds.

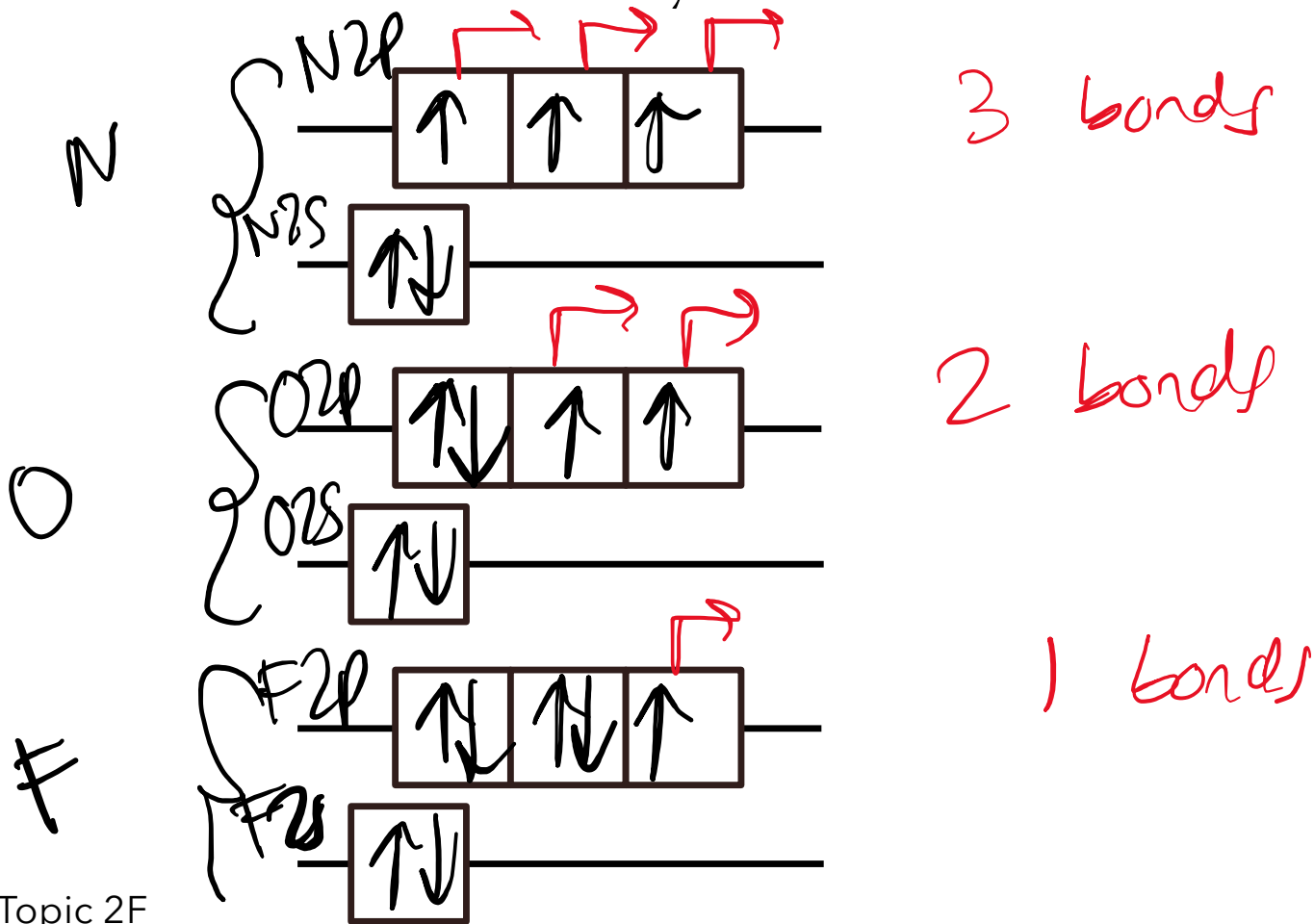
But: it has a **valence of four** and is **tetrahedral**.



Carbon, [He]2s²2p_x¹2p_y¹

2F.2 Electron promotion and the hybridization of orbitals

Valence-bond theory refinement: Carbon in CH₄



2F.2 Electron promotion and the hybridization of orbitals

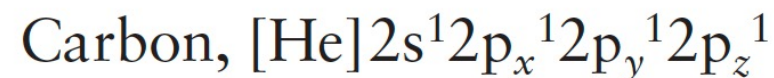
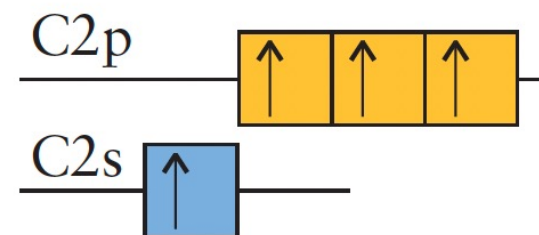
Valence-bond theory refinement: Carbon in CH₄

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]2s¹2p_x¹2p_y¹2p_z¹



2F.2 Electron promotion and the hybridization of orbitals

Valence-bond theory refinement: Carbon in CH₄

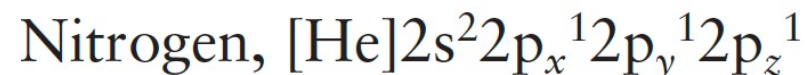
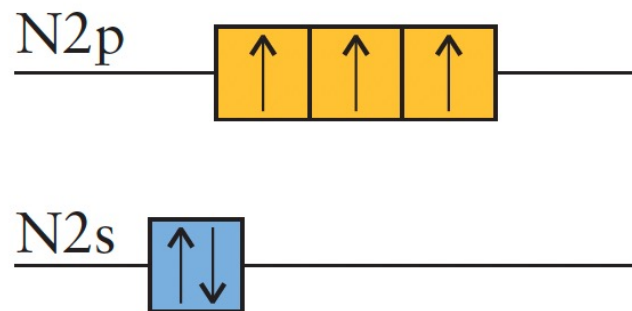
Where does the energy for this transition come from?

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.

for studying



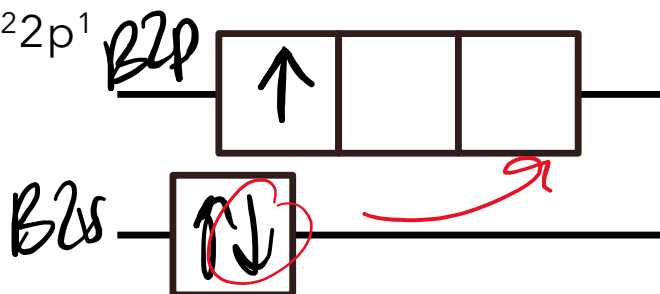
2F.2 Electron promotion and the hybridization of orbitals

Self-test

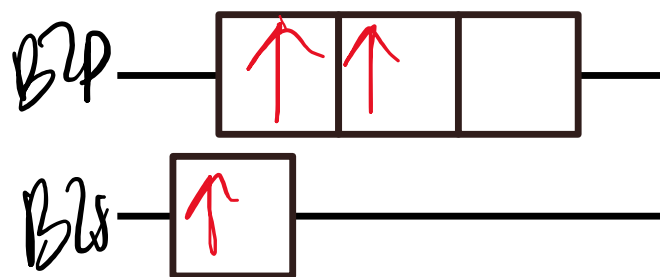
How many bonds does boron make?

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

$[\text{He}]2s^2 2p^1$



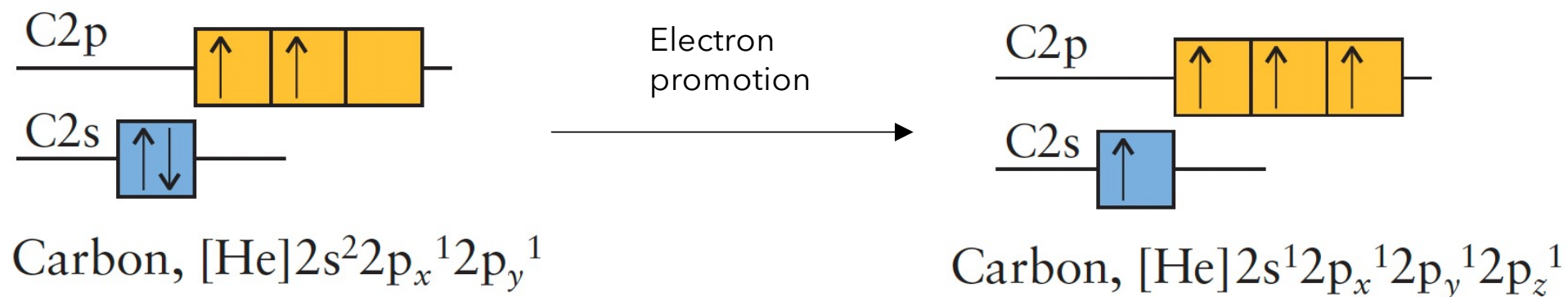
electron promotion



3 bonds!

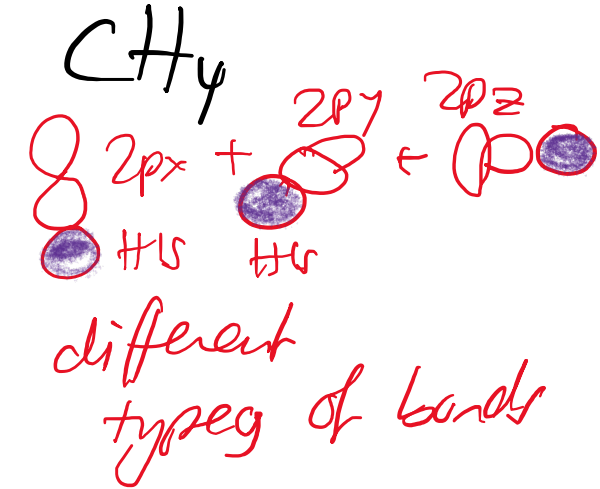
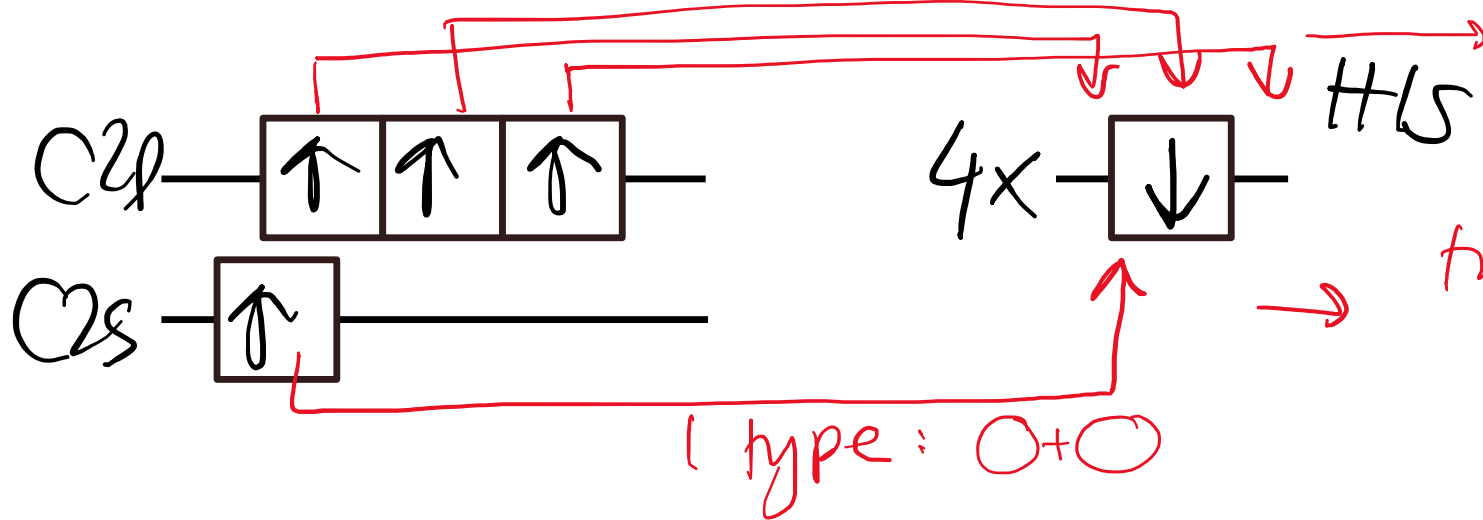
2F.2 Electron promotion and the hybridization of orbitals

What happens to orbitals after electron promotion?

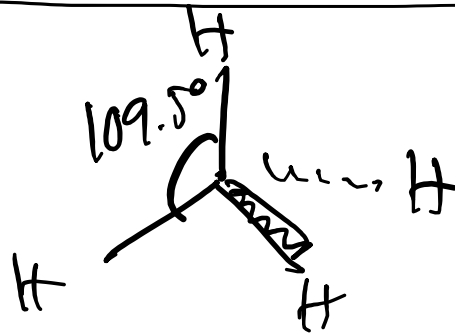


2F.2 Electron promotion and the hybridization of orbitals

What happens to orbitals after electron promotion?

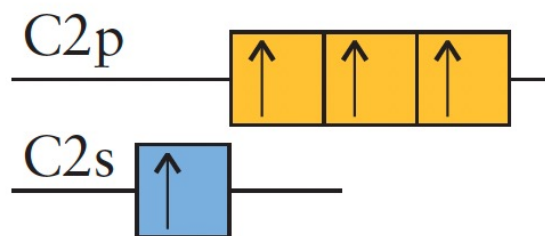


No! VSEPR, AX_4



2F.2 Electron promotion and the hybridization of orbitals

What happens to orbitals after electron promotion?



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

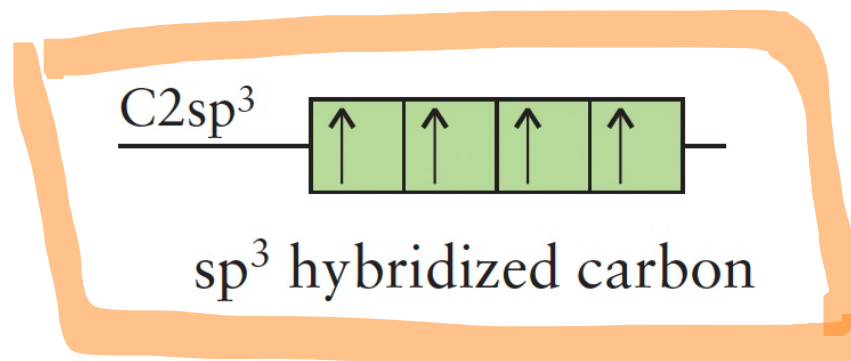
Hybrid orbitals are formed by **mixing (adding and subtracting)** atomic orbitals on the *same atom*. This process is called a **linear combination**, we mathematically *combine wavefunctions*.

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

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

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

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



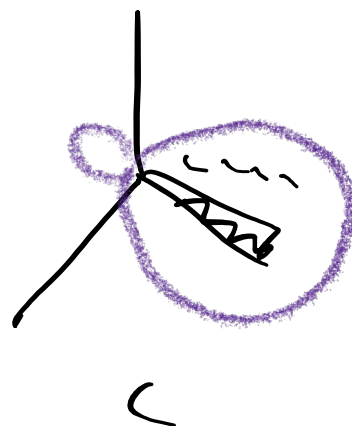
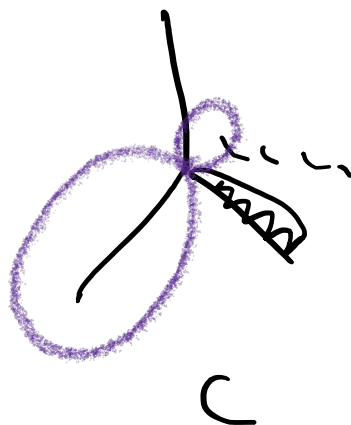
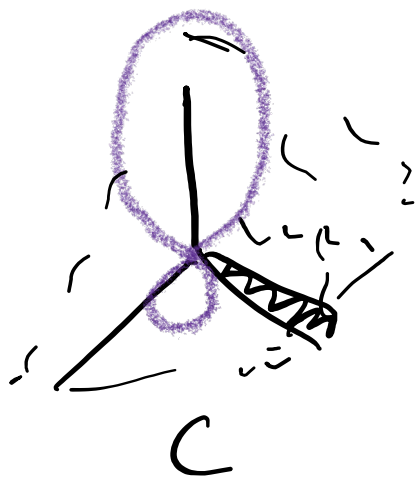
- Four sp^3 hybrid orbitals are formed from one s- and three p-orbitals.
- Four sp^3 orbitals of **equal shape** and **equal energy**, just oriented differently.

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



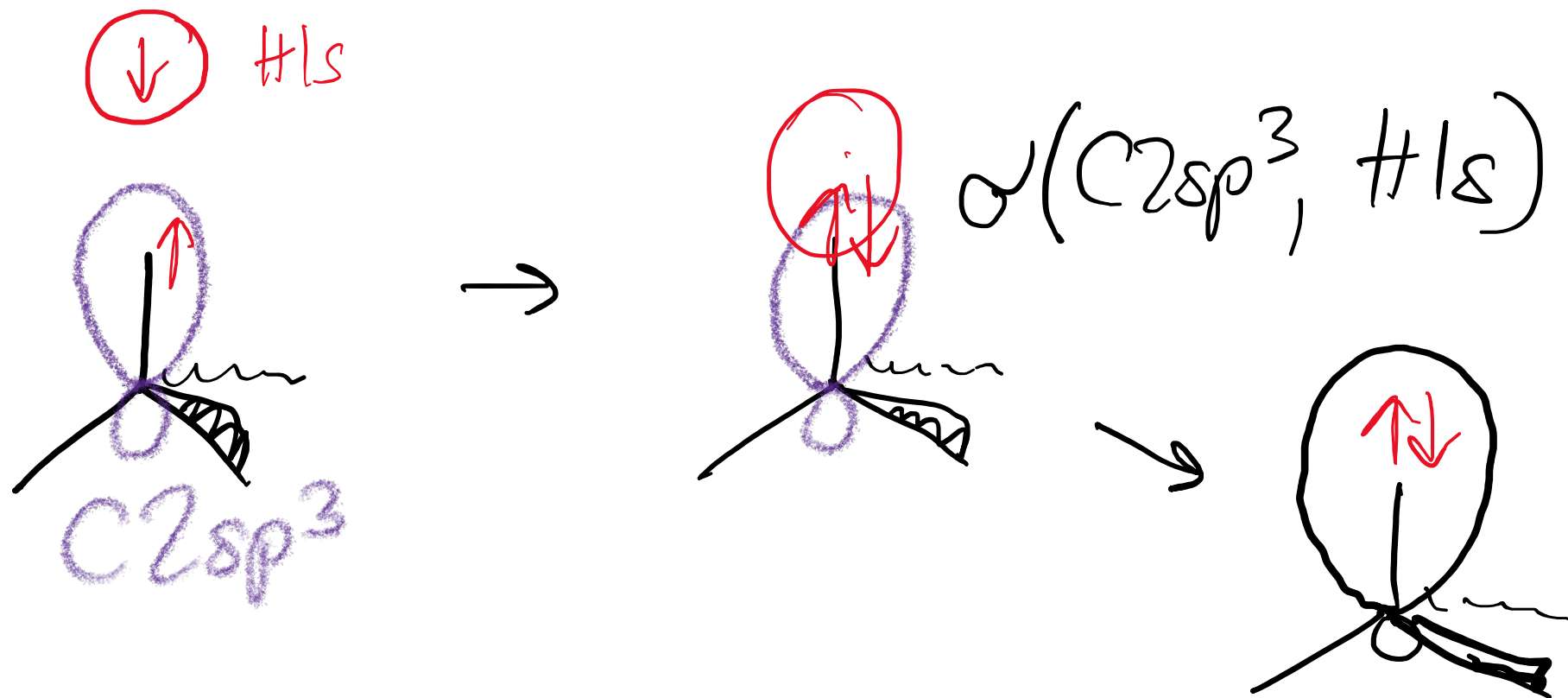
2F.2 Electron promotion and the hybridization of orbitals

sp^3 hybrid orbitals $CH_4 \rightarrow sp^3$



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

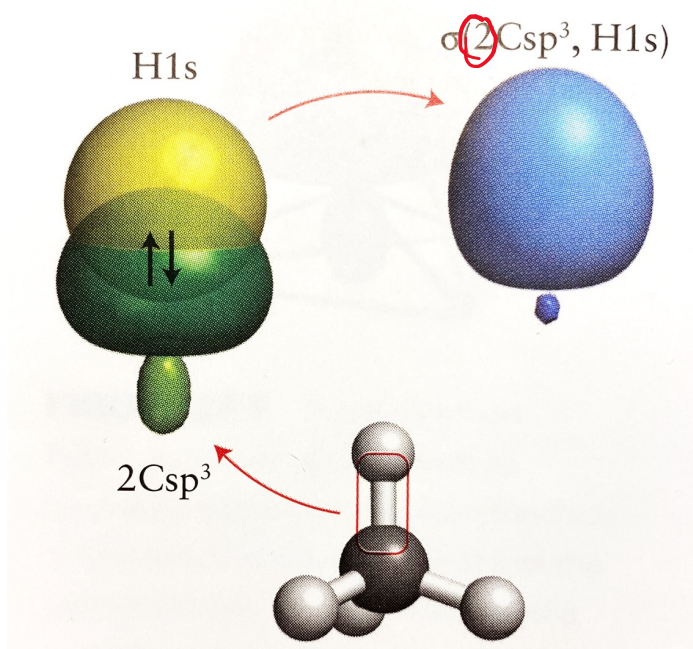


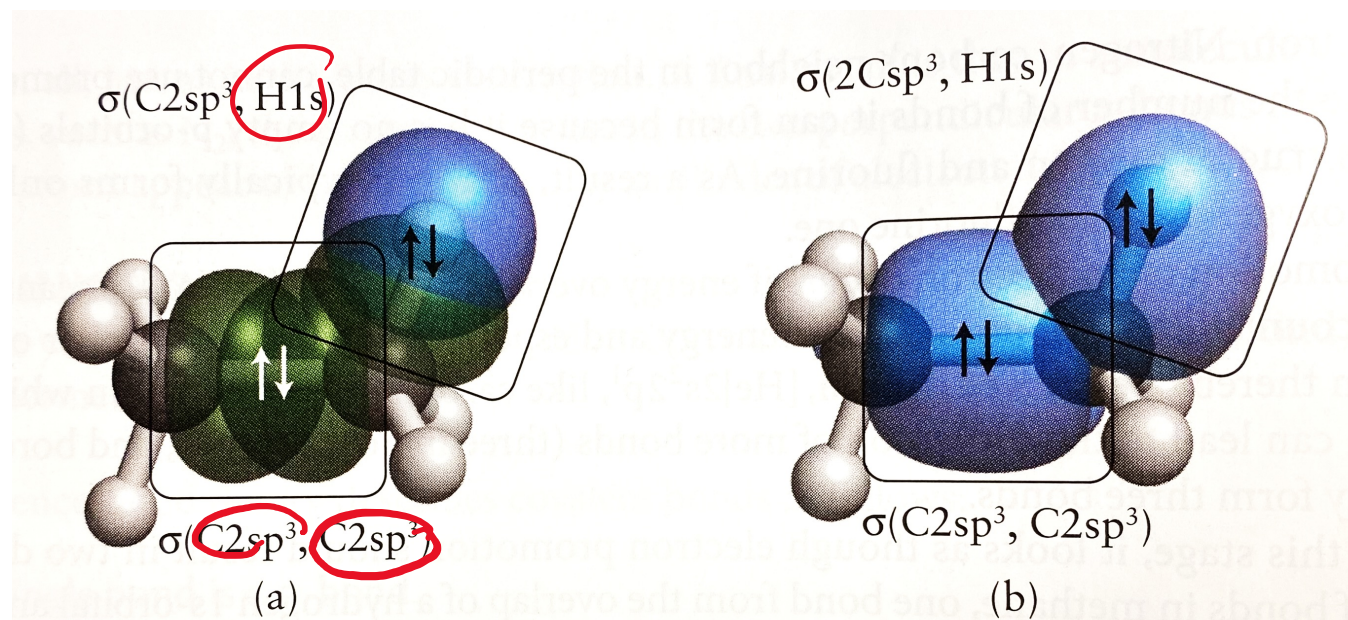
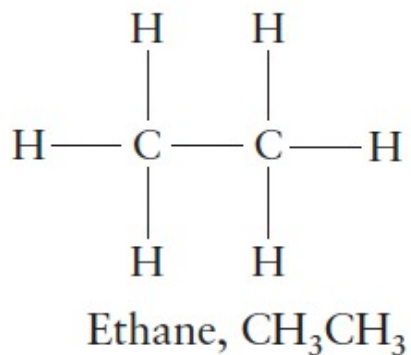
Figure 2F.7 (new book)

- 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

Figure 2F.8 (new book)

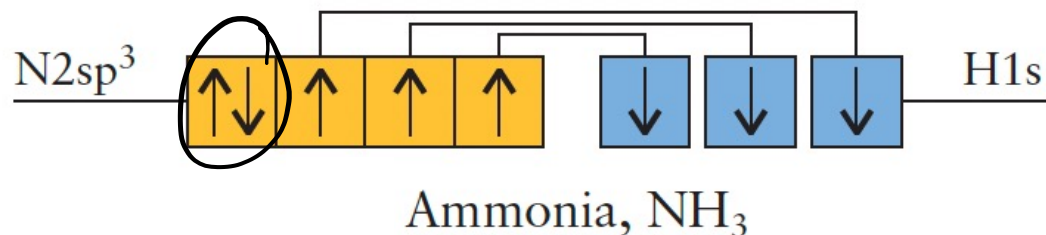


Boundary surfaces of two bonds are shown.

Bond angles are close to 109.5° .

2F.2 Electron promotion and the hybridization of orbitals

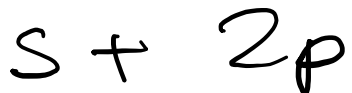
Ammonia



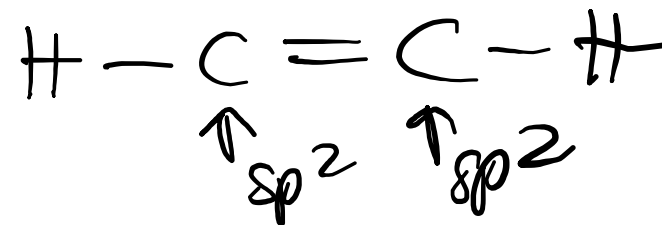
- VSEPR: Ammonia has tetrahedral electron arrangement and trigonal pyramidal shape
- Nitrogen atom forms four **sp³ hybrid orbitals**, one of which is already doubly occupied
- The three remaining sp³ hybrid orbitals pair with the 1s orbitals of three H atoms
- N-H sigma-bonds

Whenever an atom of a nonmetallic element in a molecule has a tetrahedral electron arrangement, it is **sp³ 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)**

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

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

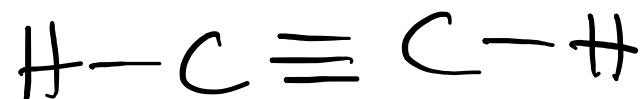
$$h_3 = s - \left(\frac{3}{2}\right)^{\frac{1}{2}} p_x - \left(\frac{1}{2}\right)^{\frac{1}{2}} p_y$$

- 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):

$$s + p \rightarrow 2h \begin{cases} h_1 = s + p \\ h_2 = s - p \end{cases}$$

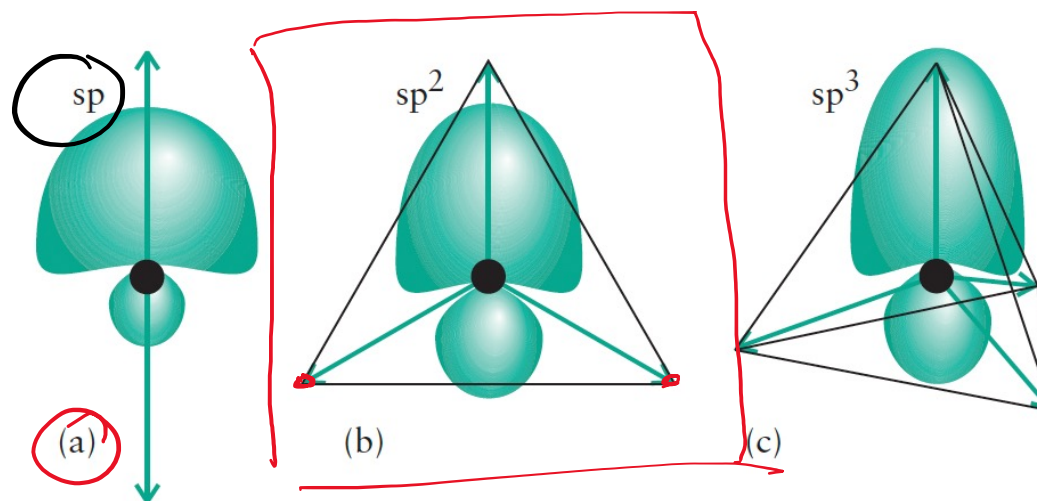
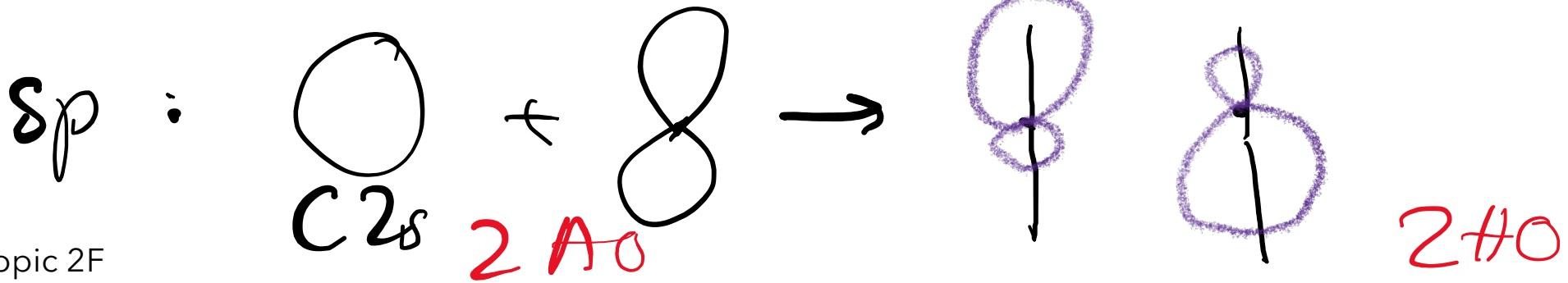
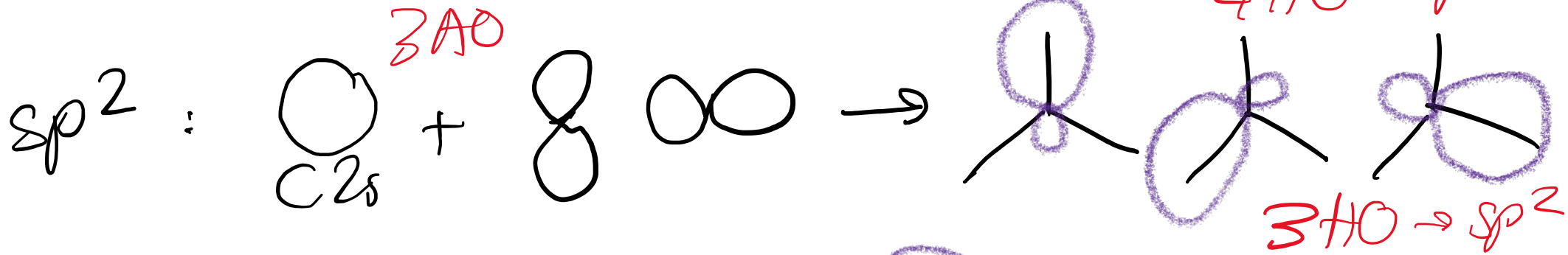
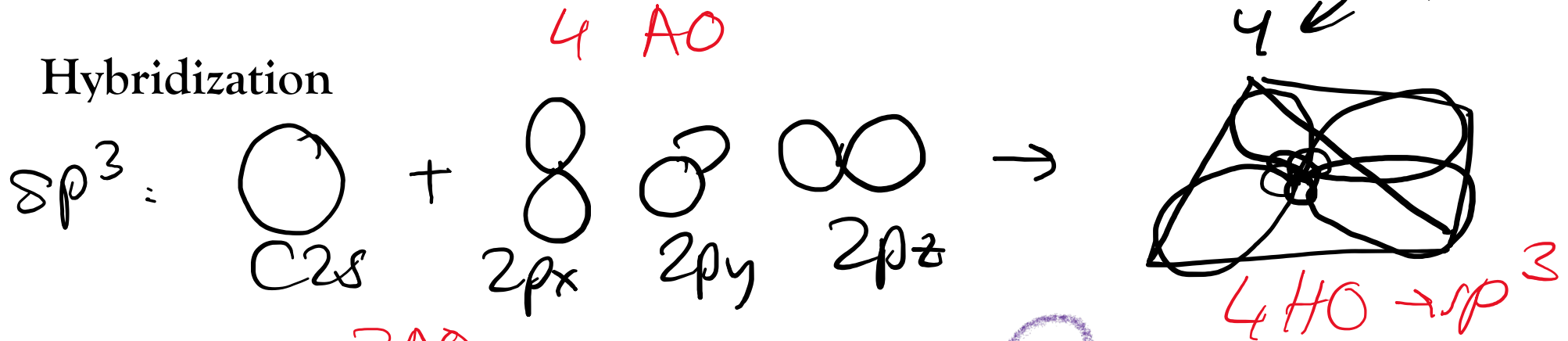


Figure 2F.9 (new book) / Figure 3.16 (old book)

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.

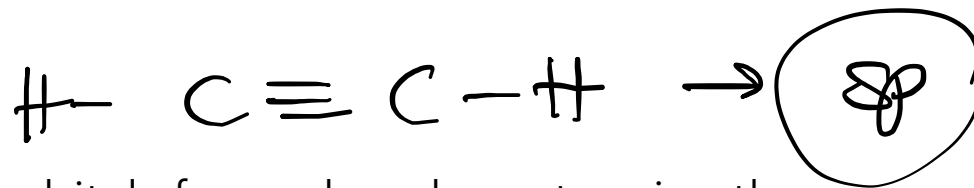
TABLE 3.2 Hybridization and Molecular Shape*

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

Handwritten notes in red:
AX₂ next to linear
AX₃ next to trigonal planar
AX₄ next to tetrahedral
The hybridization terms (sp, sp², sp³) are circled in red.

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 .

