CH-110 Advanced General Chemistry I

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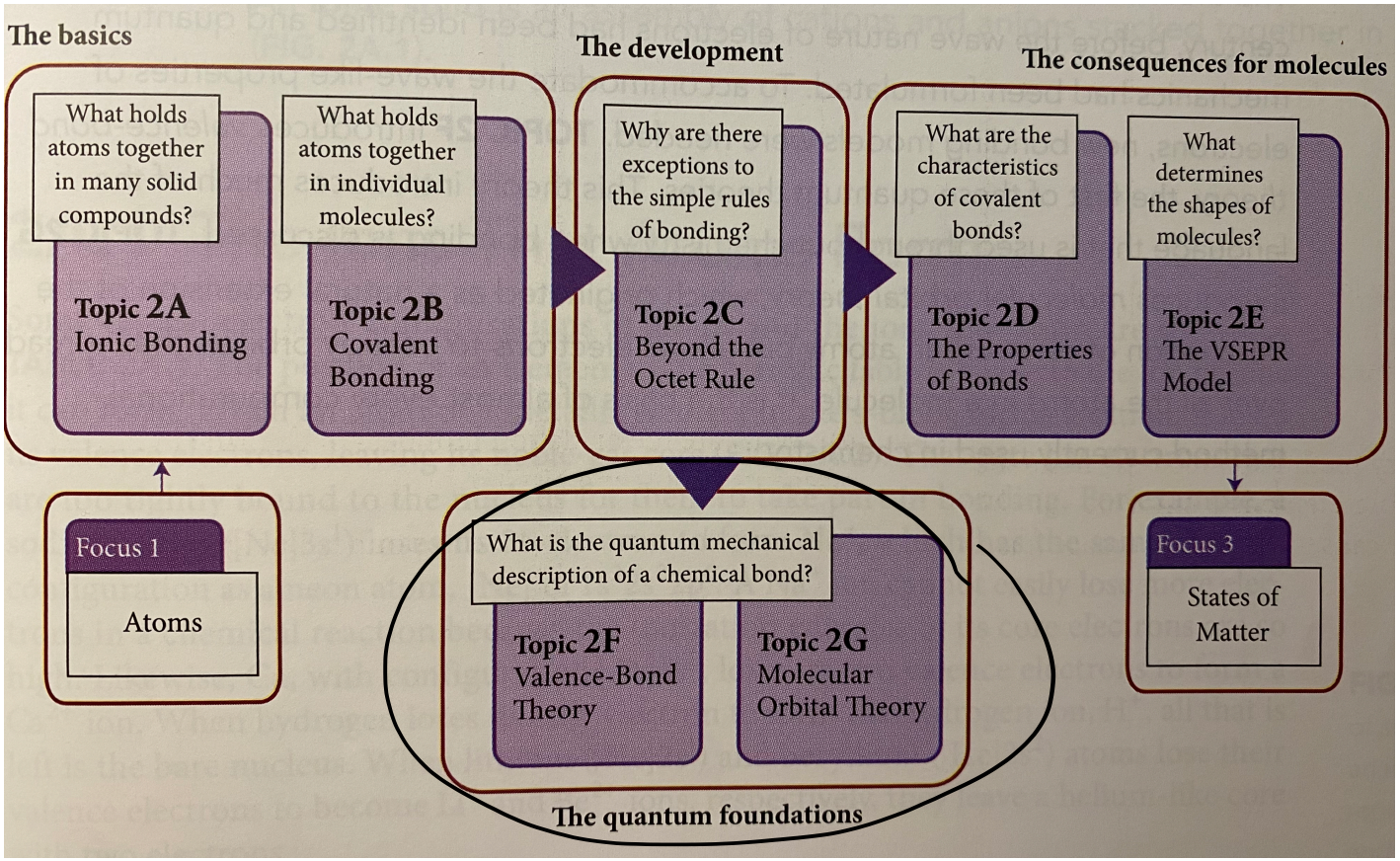
Housekeeping notes

- This is the last week of my class (Steinauer part)
- I will upload annotated study guide of chapter 2 at the end of the week.
- Last exercise session with TAs from this part of the class is this Friday.
- We have a lot of material to cover this week: please read the slides for Friday's lecture in advance. I will upload them tomorrow.

Overview Chapter 2 (Focus 2: Bonds Between Atoms)



Valence-Bond Theory

Topic 2F

Last time: Topic 2F.1 Sigma and pi bonds
Last time: 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?

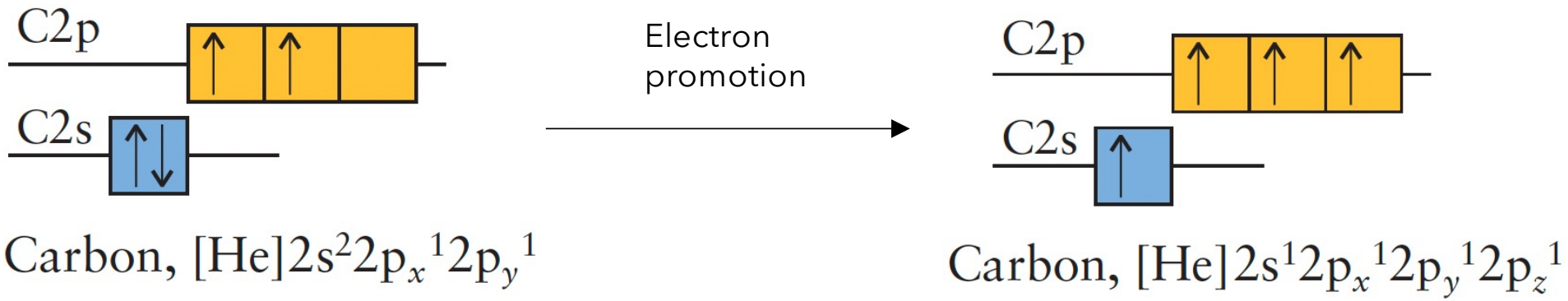
- Valence bond theory gives insight into the quantum mechanical nature of the covalent bond.
- Introduces language used throughout chemistry.

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.2 Electron promotion and the hybridization of orbitals

What happens to orbitals after electron promotion?



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

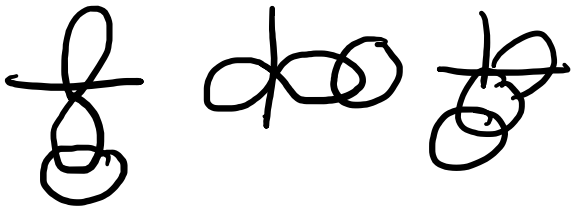
Carbon, $[He]2s^1 2p_x^1 2p_y^1 2p_z^1$

2F.2 Electron promotion and the hybridization of orbitals

What happens to orbitals after electron promotion?

CH_4: two different types of bonds:

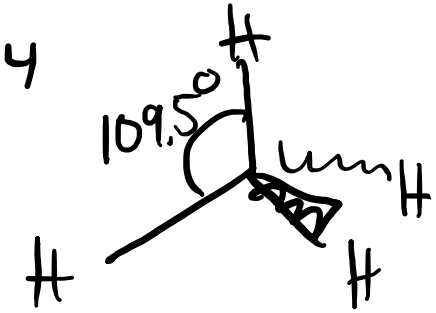
- C2s + H1s (1x)
- C2p + H1s (3x)



90° 3x

VSEPR: AX_4

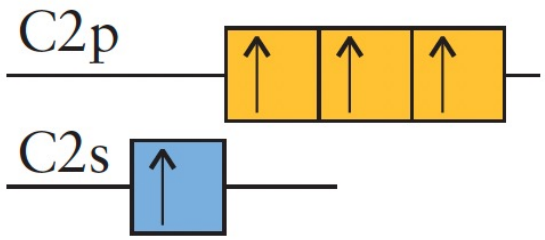
tetrahedral



four equal bonds

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

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

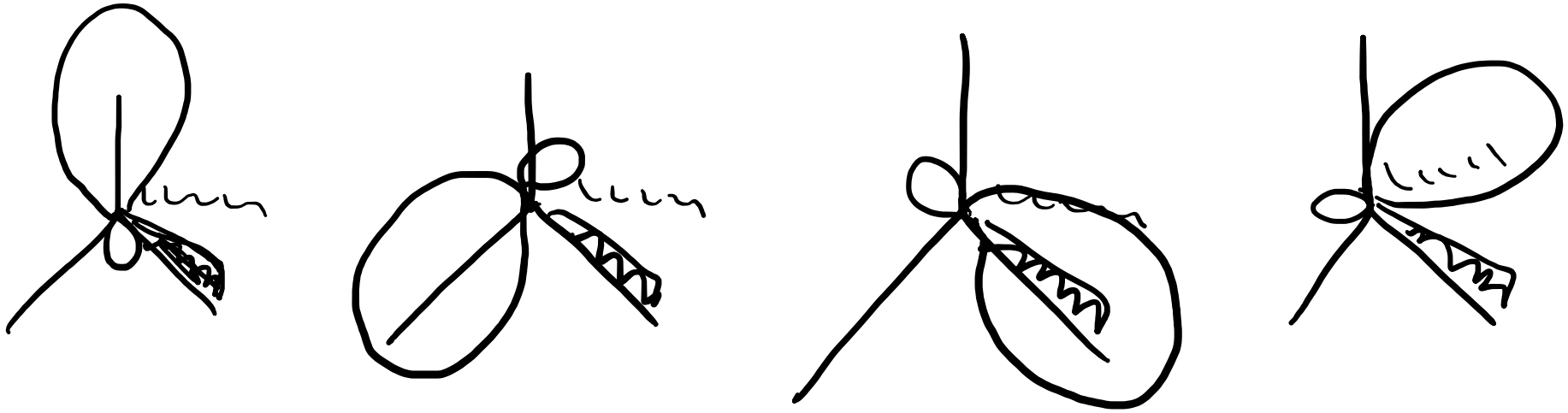
$$h_1 = s + p_x + p_y + p_z$$
$$h_2 = s - p_x - p_y + p_z$$
$$h_3 = s - p_x + p_y - p_z$$
$$h_4 = s + p_x - p_y - p_z$$

sp^3 hybridized carbon

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

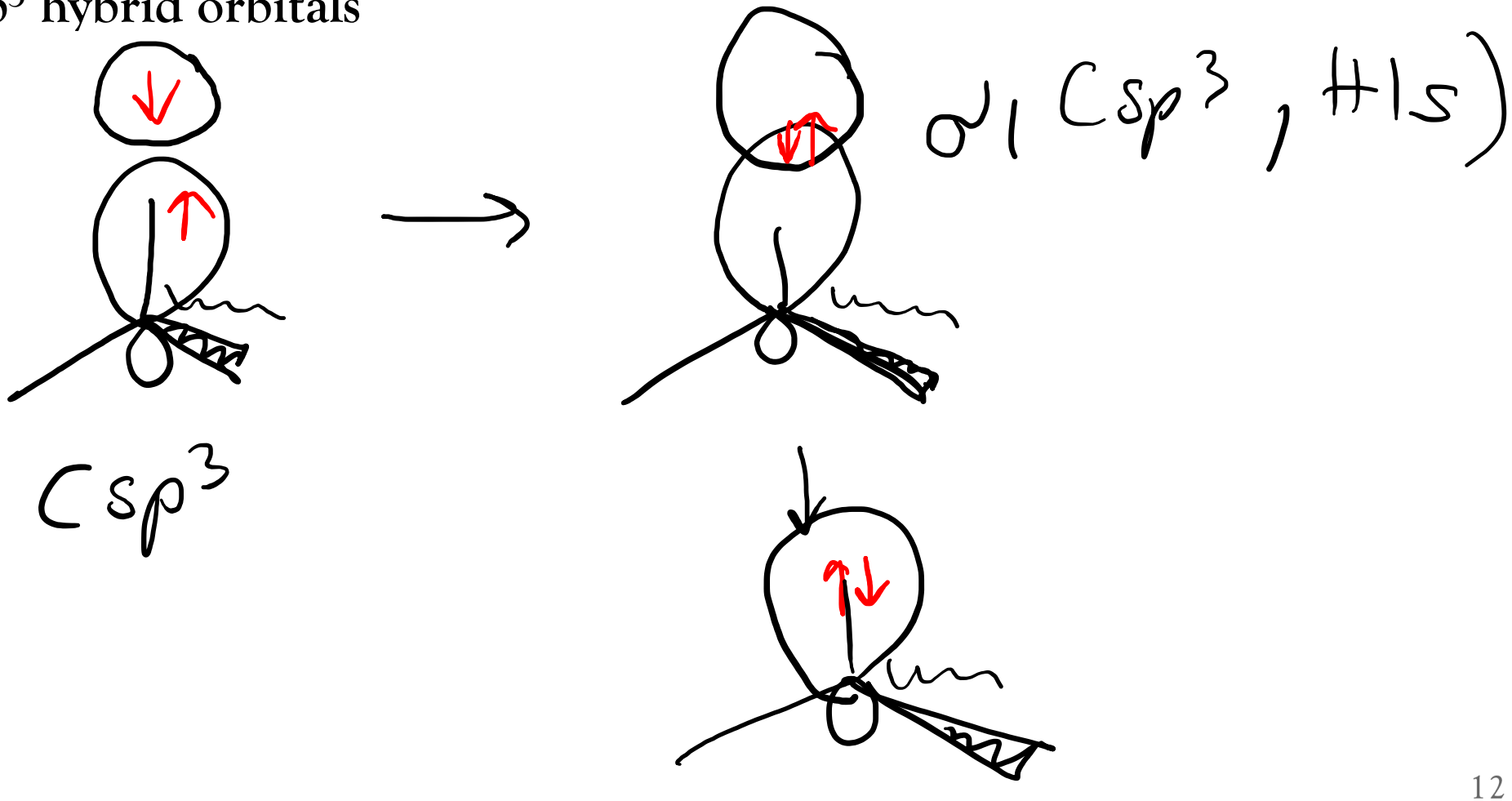
2F.2 Electron promotion and the hybridization of orbitals

sp^3 hybrid orbitals CH_4 sp^3 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

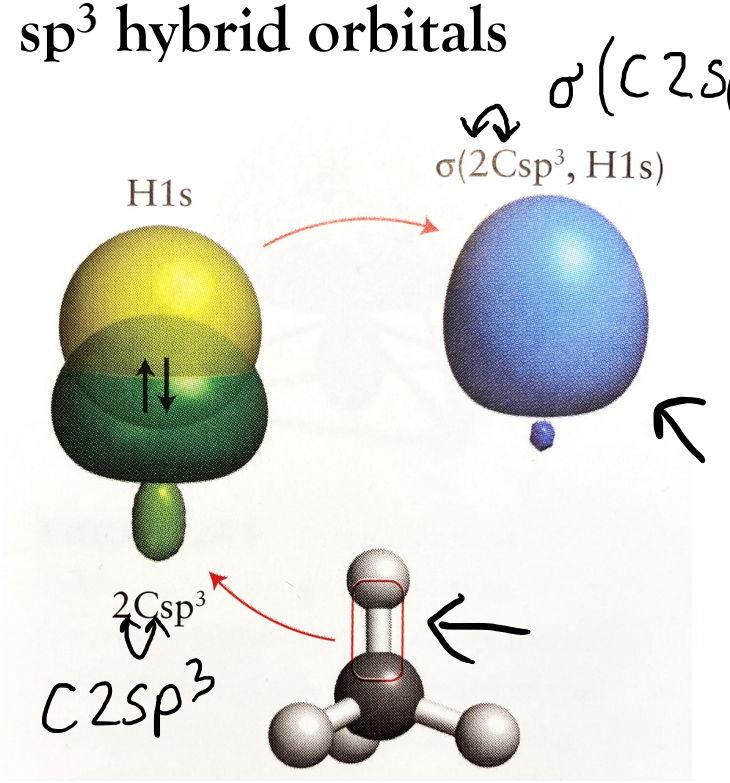
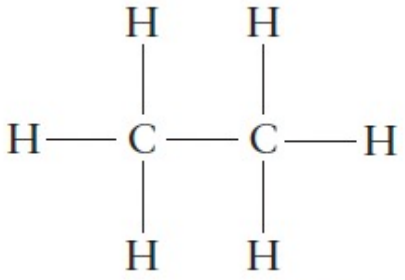


Figure 2F.7 (new book)

- 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.

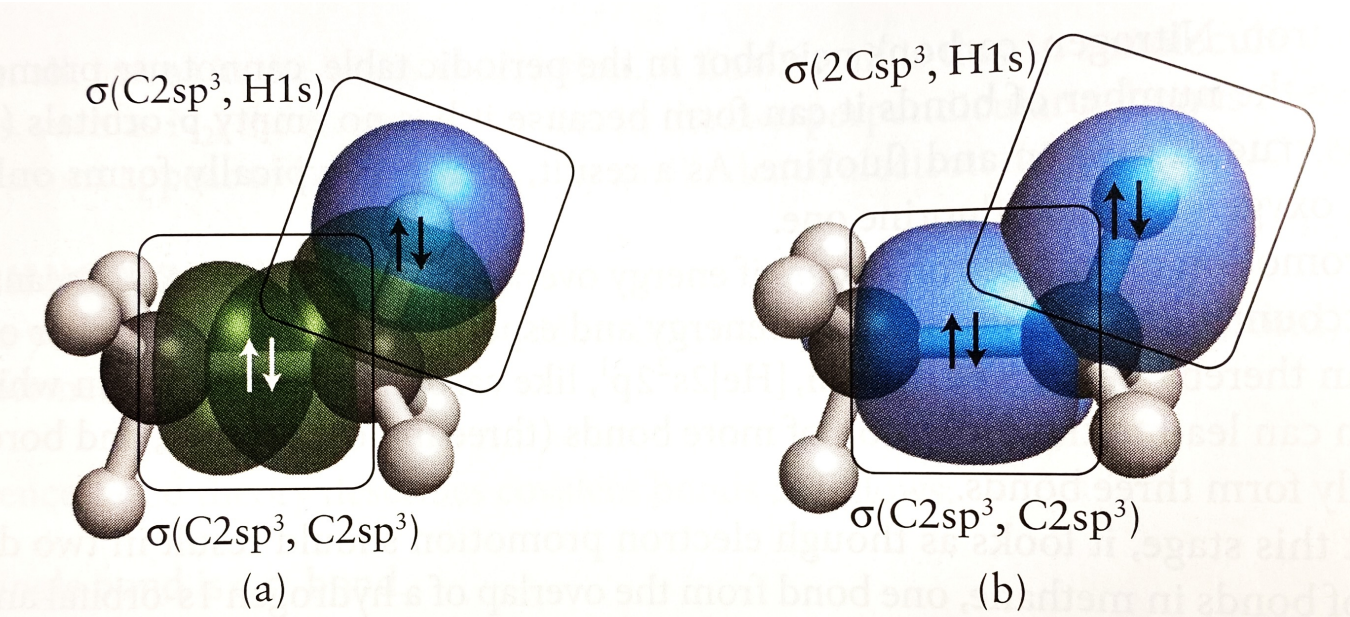
2F.2 Electron promotion and the hybridization of orbitals

Ethane



Ethane, CH_3CH_3

Figure 2F.8 (new book)

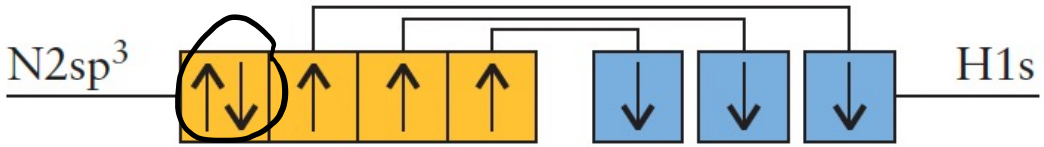


Boundary surfaces of two bonds are shown.

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

1s + 1p

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

$$h_1 = s + p$$

$$h_2 = s - p$$

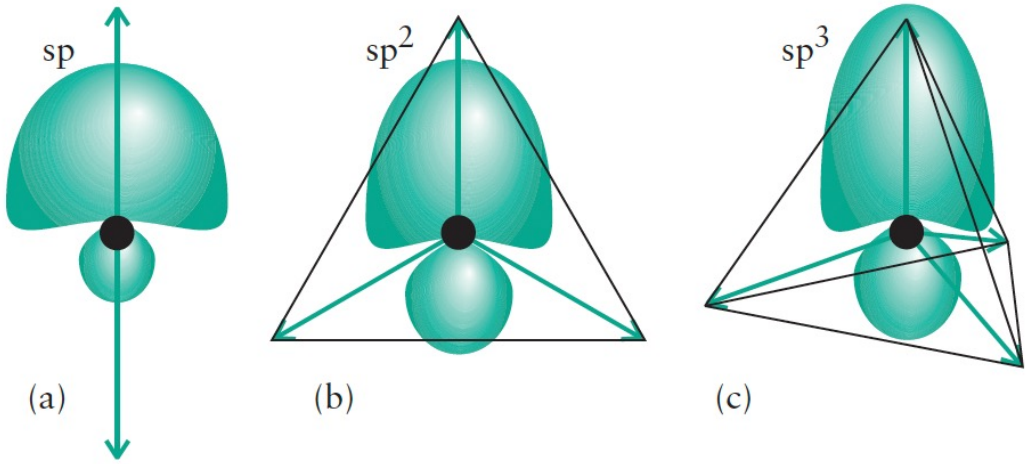
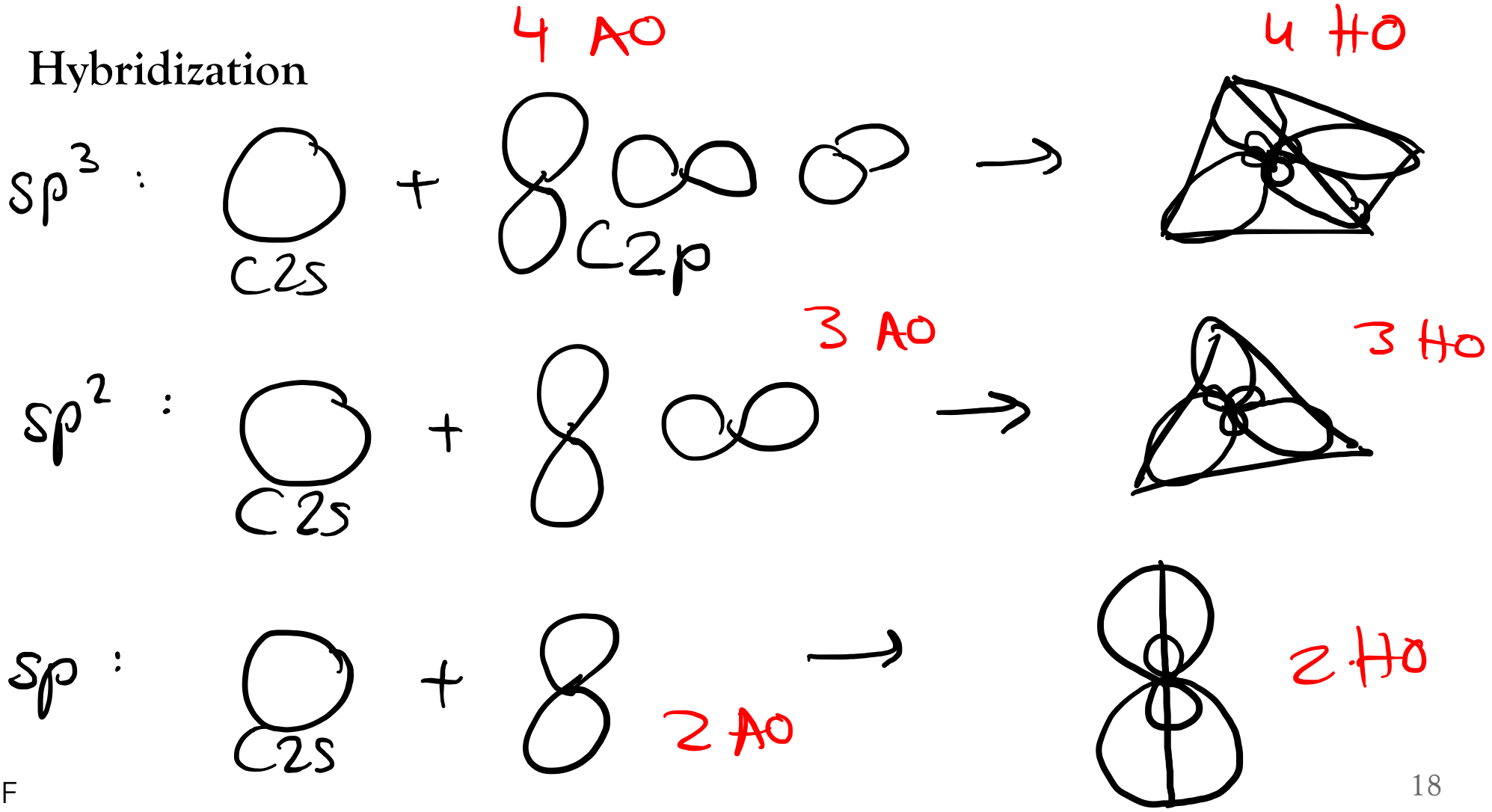


Figure 2F.9 (new book) / Figure 3.16 (old book)

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:

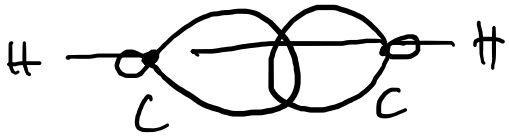
***N* atomic orbitals always produce *N* hybrid orbitals.**

TABLE 3.2 Hybridization and Molecular Shape*

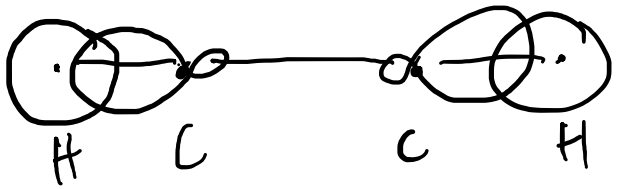
Electron arrangement		Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
linear	180°	2	sp	2
trigonal planar	120°	3	sp^2	3
tetrahedral	109.5°	4	sp^3	4

Self-test 2F.2B

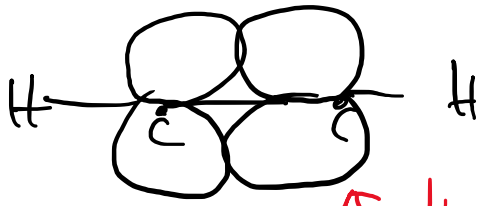
Suggest a structure in terms of hybrid orbitals for each carbon atom in ethyne, C_2H_2. Lewis structure: H–C≡C–H linear → sp hybridized



σ(C 2sp, C 2sp)



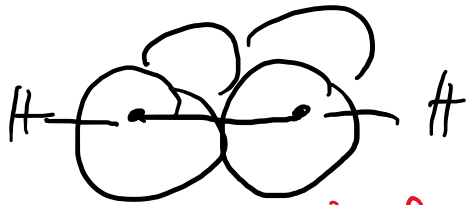
2 × σ(C 2sp, H 1s)



π(C 2p, C 2p) ↑ in plane of paper

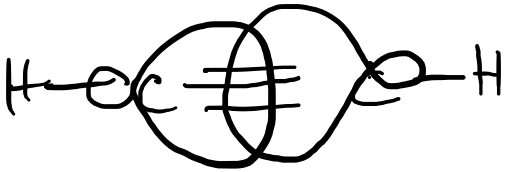
behind plane of paper ↓

π(C 2p, C 2p)

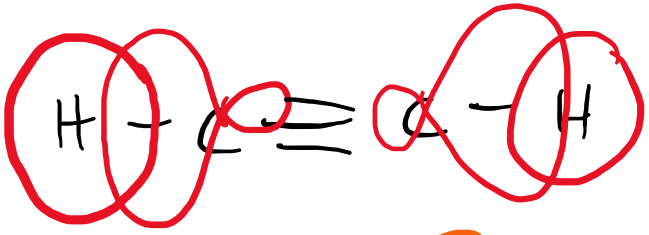


↑ in front of plane of paper

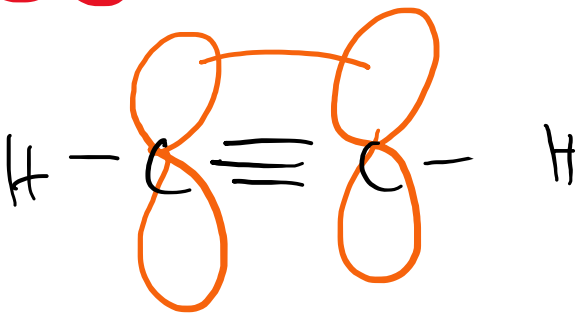
Bonds drawn separately:



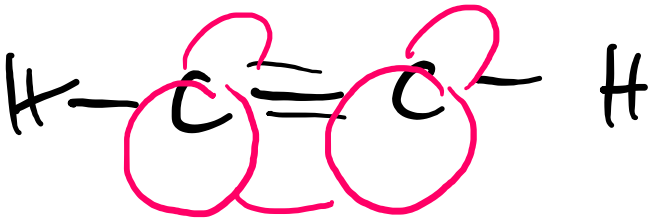
$\sigma(C2sp, C2sp)$



$2 \times \sigma(C2sp, H1s)$



$\pi(C2p, C2p)$



$\pi(C2p, C2p)$

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

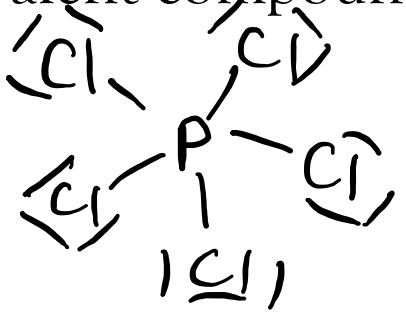
2F.3 Valence-bond theory and hypervalent compounds

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

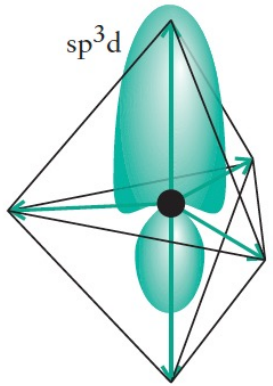
PCl_5 example of hypervalency



$5 + 5 \cdot 7 = 40$
$20\,e^-$

AX_5: trigonal bipyramidal

Figure 3.17 (old book)



- 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)

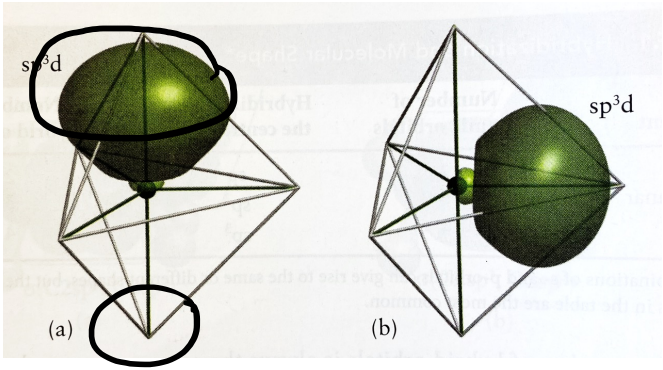


Figure 2F.10 (new book)

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)

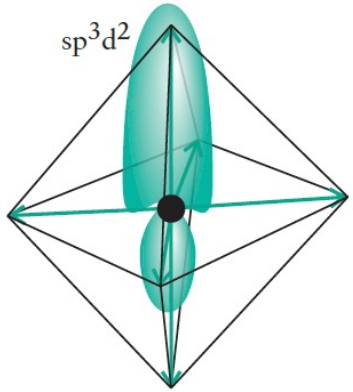


Figure 3.18 (old book)

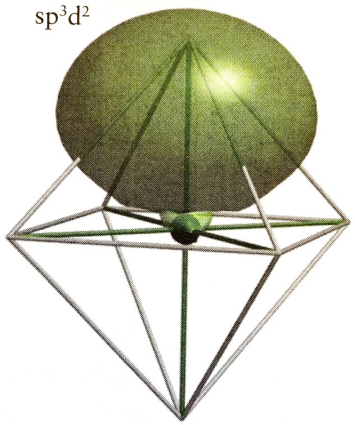


Figure 2F.11 (new book)

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).

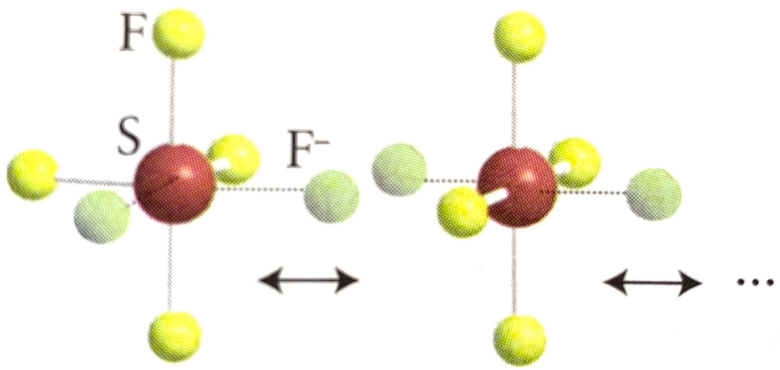


Figure 2F.12 (new book)

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

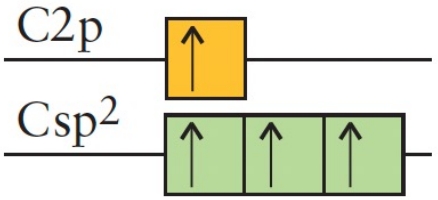
Summary

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

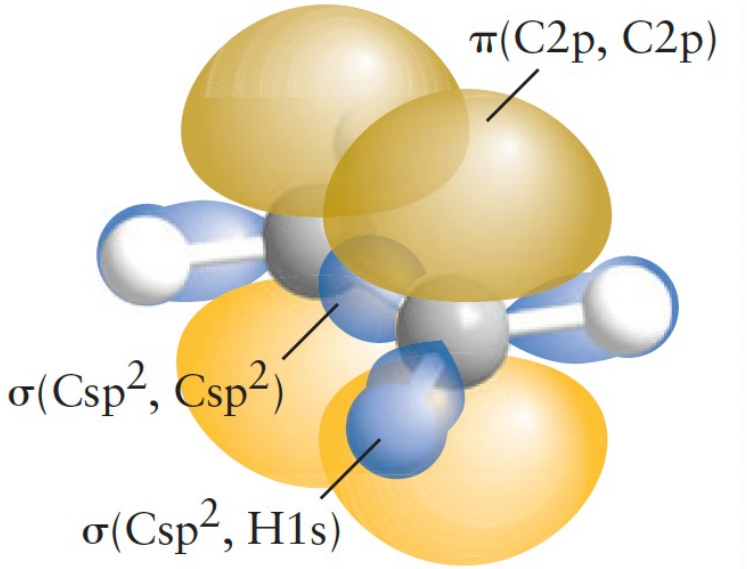


Figure 3.19 (old book)

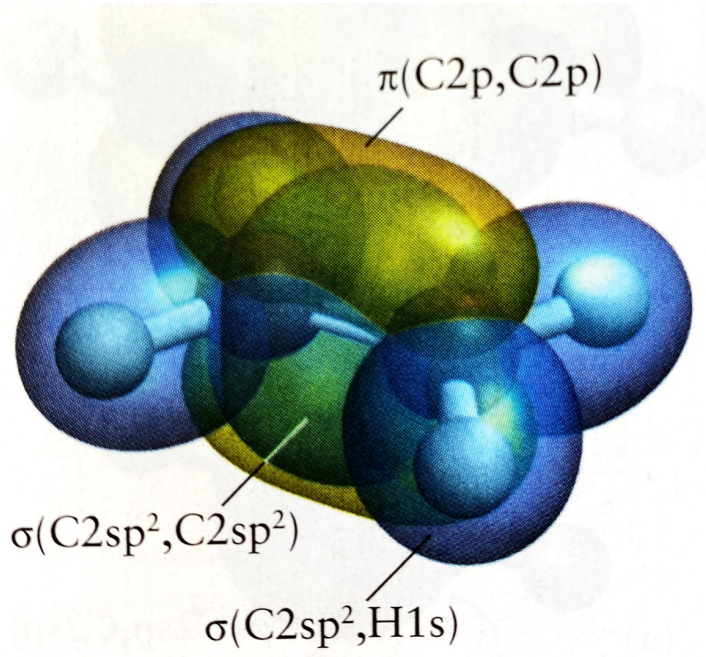
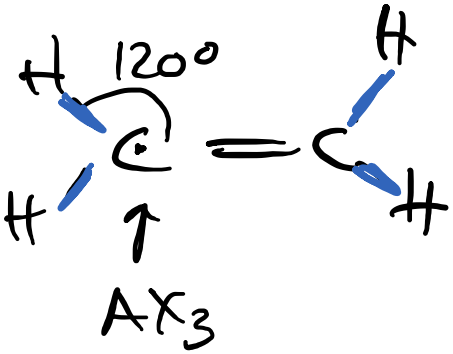


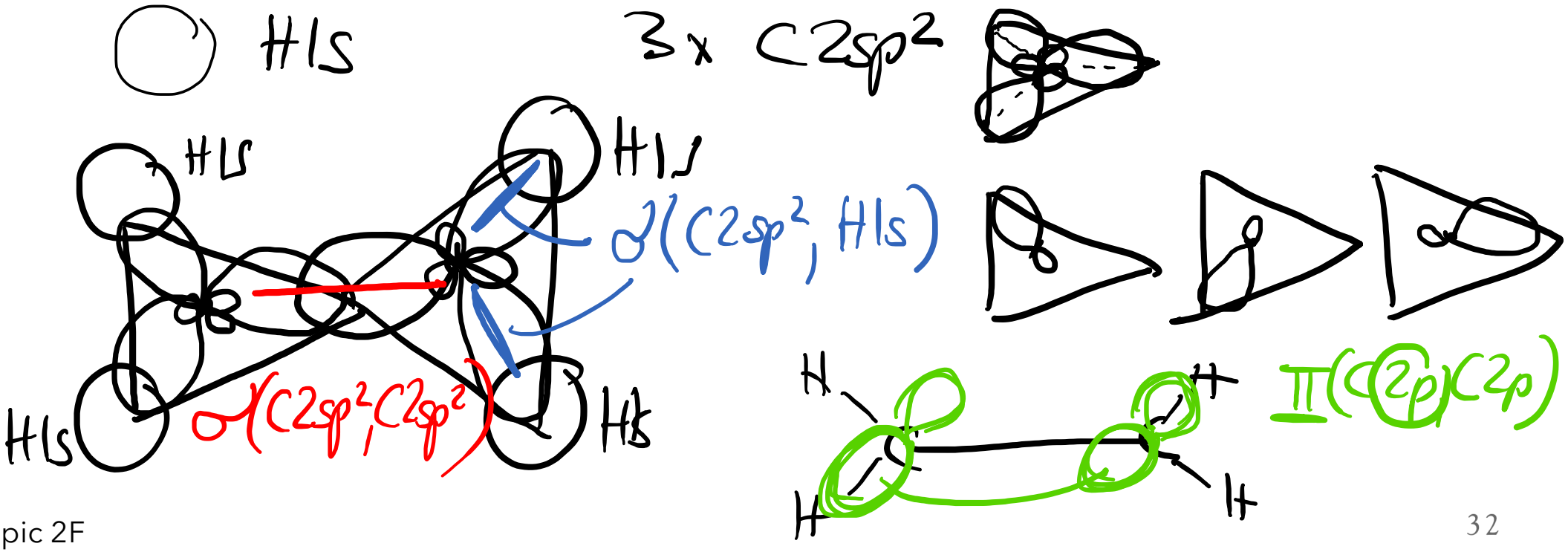
Figure 2F.13 (new book)

2F.4 Characteristics of multiple bonds

Alkenes: Ethene (ethylene) C_2H_4

- Same plane





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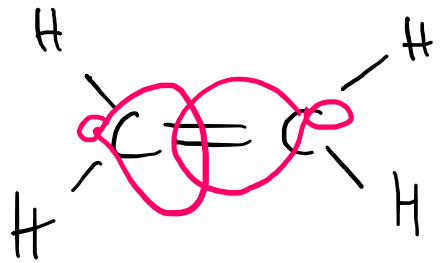
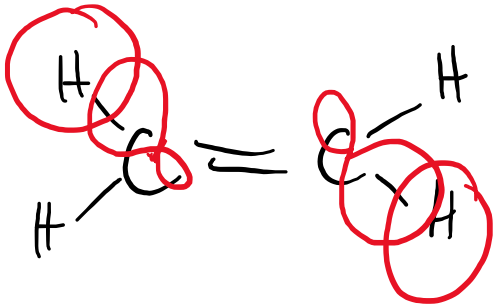
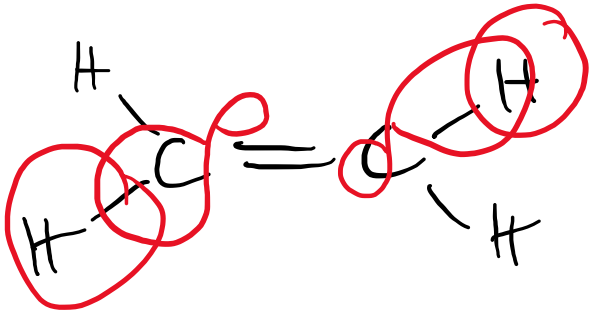


$\sigma(C2sp^2, C2sp^2)$

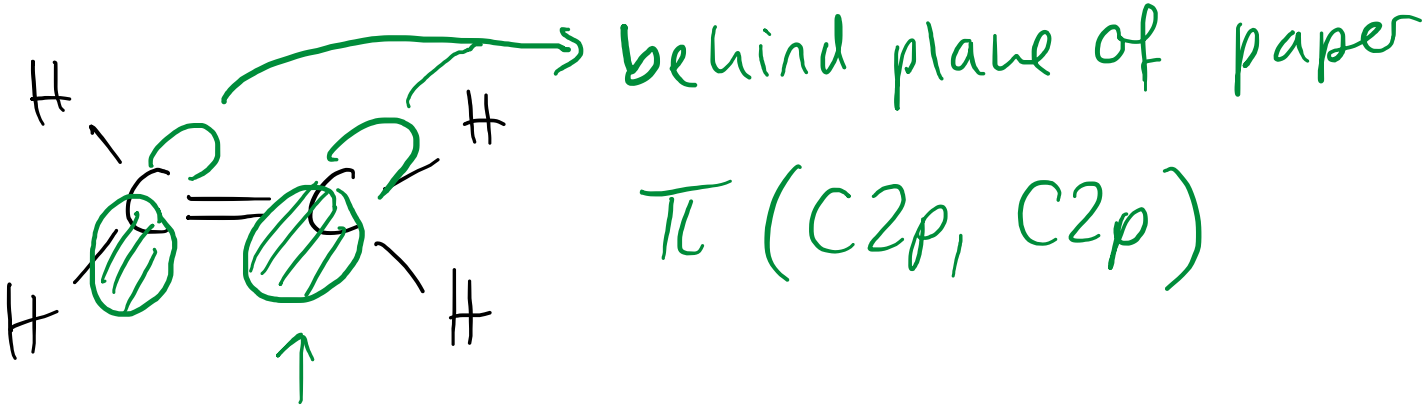


$2 \times \sigma(C2sp^2, H1s)$



$2 \times \sigma(C2sp^2, H1s)$

} Four identical bonds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π (C2p, C2p)
In front of plane of paper

2F.4 Characteristics of multiple bonds

Benzene

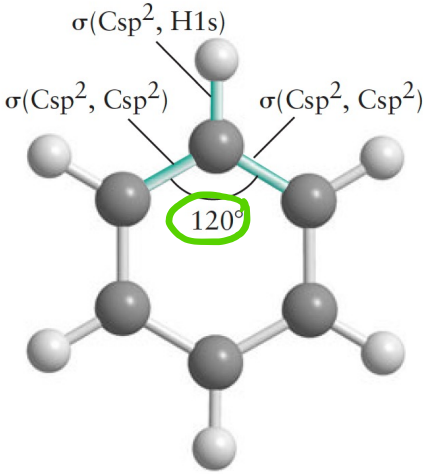


Figure 2F.14 (new book):

The framework of sigma-bonds in benzene.

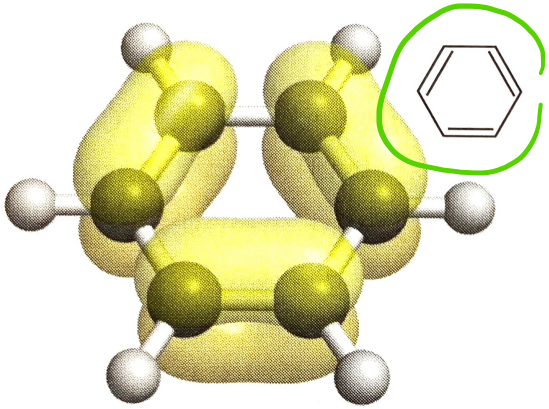


Figure 2F.15 (new book):

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

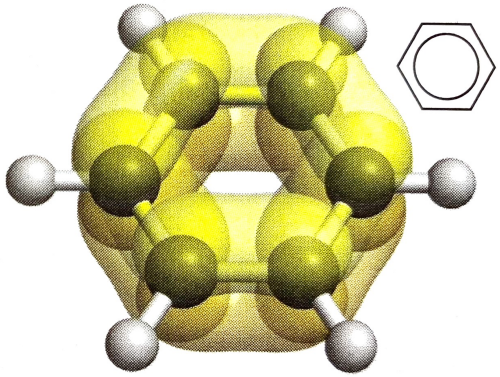


Figure 2F.16 (new book):

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
-

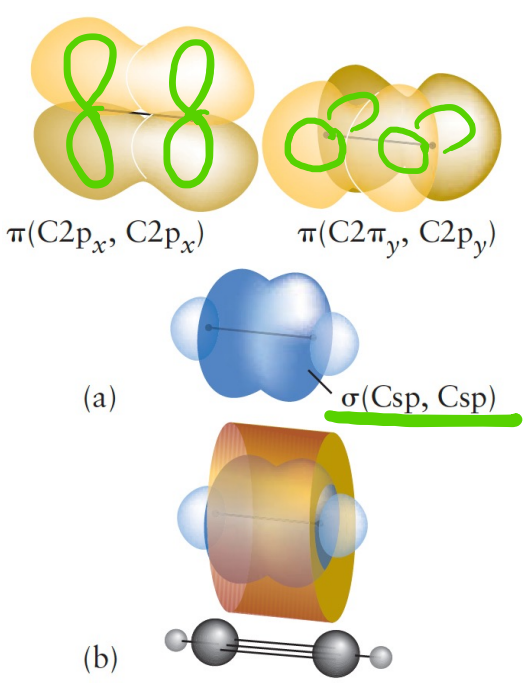


Figure 3.23 (old book)

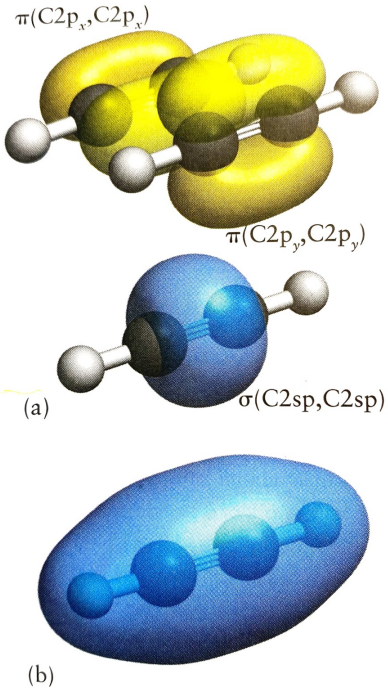
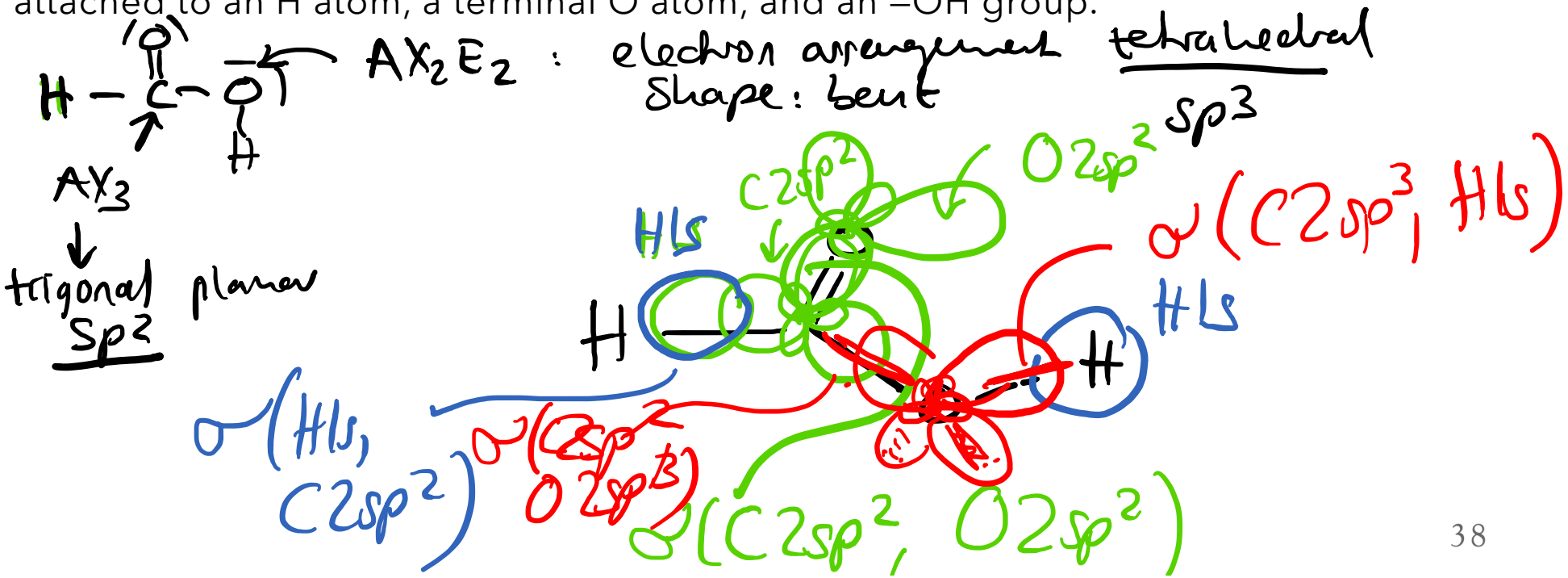


Figure 2F.17 (new book)

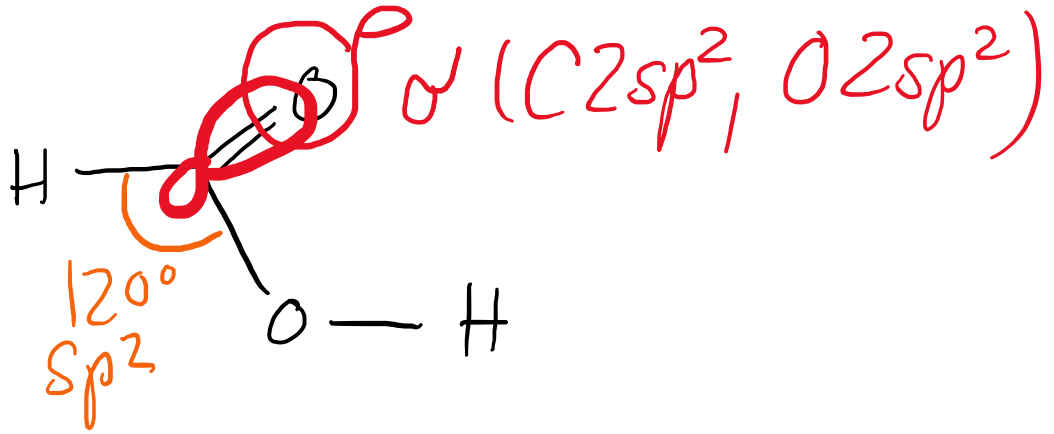
2F.4 Characteristics of multiple bonds

If time: **Example 2F.1 Accounting for the structure of a molecule with multiple bonds**

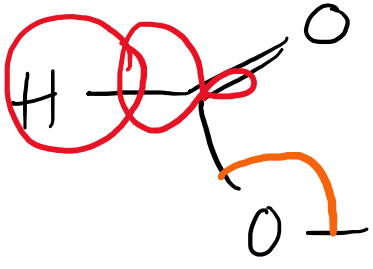
- Account for the structure of a formic acid molecule (methanoic acid, HCOOH) in terms of hybrid orbitals, bond angles, and σ- and π-bonds. The C atom is attached to an H atom, a terminal O atom, and an –OH group.



Drawn separately:

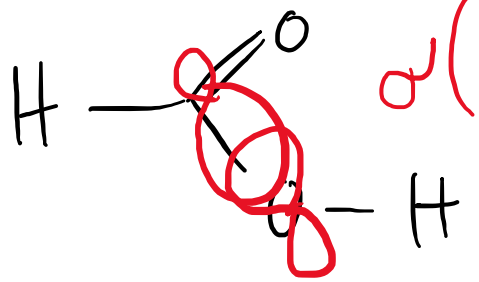


$\sigma(C2sp^2, O2sp^2)$

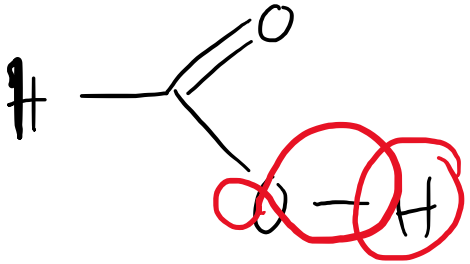


$\sigma(C2sp^2, H1s)$

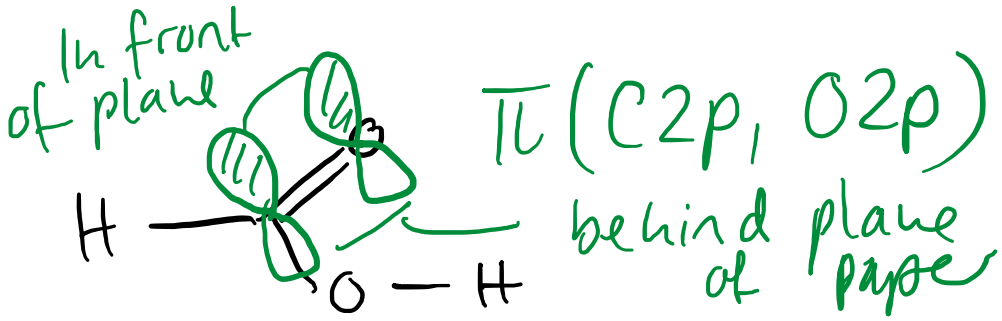
109.5° (sp^3)



$\sigma(C2sp^2, O2sp^3)$



$\sigma(O2sp^3, H1s)$



$\pi(C2p, O2p)$

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.

Molecular Orbital Theory

Topic 2E

Topic 2G.1 Molecular orbitals
Topic 2G.2 Electron configurations of diatomic molecules
Topic 2G.3 Bonding in heteronuclear diatomic molecules
Topic 2G.4 Orbitals in polyatomic molecules
Topic 2G.5 A comparison of bonding models

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- MO theory is the most common quantum mechanical approach used to describe electronic structure of molecules.
- Essential for understanding the properties of individual molecules and modern materials.

WHAT DO YOU NEED TO KNOW ALREADY?

- Atomic orbitals (Topic 1D)
- Born interpretation of wavefunction (Topic 1C)
- Building-up principle (Topic 1E)
- Electronegativity (Topics 1F and 2D)

2G.1 Molecular orbitals

Valence bond theory deficiencies

- **VB theory**: electrons are localized on atoms or between pairs of atoms
- **Molecular orbital (MO) theory**: electrons are described by wavefunctions called molecular orbitals, spread through entire molecule. All valence electrons are delocalized over the entire molecule, not confined to individual bonds or atoms.
- MOs in principle very complicated mathematical functions, we **approximate**: their form can be expressed in terms of **valence shell electrons only**.

For example, the molecular orbital for H_2 is approximated by the sum:

$$\Psi = \Psi_{\mathrm{A1s}} + \Psi_{B1s}$$

Where Ψ_{A1s} is a 1s orbital centered on one atom (A) and Ψ_{B1s} is a 1s orbital centered on the other atom B.

Linear combinations of atomic orbitals

- The technical term for adding together wavefunctions is «forming a linear combination».

$$\Psi = \Psi_{\mathrm{A1s}} + \Psi_{B1s}$$

- This equation represents a **linear combination of atomic orbitals (LCAO).**
- A molecular orbital formed from a linear combination of atomic orbitals on different atoms is called an **LCAO-MO**.

2G.1 Molecular orbitals

Linear combinations of atomic orbitals

- MOs are well-defined mathematical functions that can be evaluated at each point in space and pictured in three dimensions.
- The square of the wavefunction is the **probability density** for an electron that occupies it. Where Ψ^2 is large, the probability density is high.
- The precise form of the MO depends on the **internuclear separation**, which can be changed in the calculation to explore how its shape ad the corresponding energy vary with bond length.

Bonding orbitals

A combination of atomic orbitals that results in an overall lowering of energy, like that in Eq.1, is called a **bonding orbital**, **denoted σ** (here σ_{1s}).

The combination of *N* atomic orbitals results in the formation of *N* molecular orbitals.

Hydrogen example: LCAO-MOs are built from two atomic orbitals, *two* molecular orbitals are formed.

Bonding orbital: $\Psi = \Psi_{A1s} + \Psi_{B1s}$

Antibonding orbital: $\Psi = \Psi_{A1s} - \Psi_{B1s}$

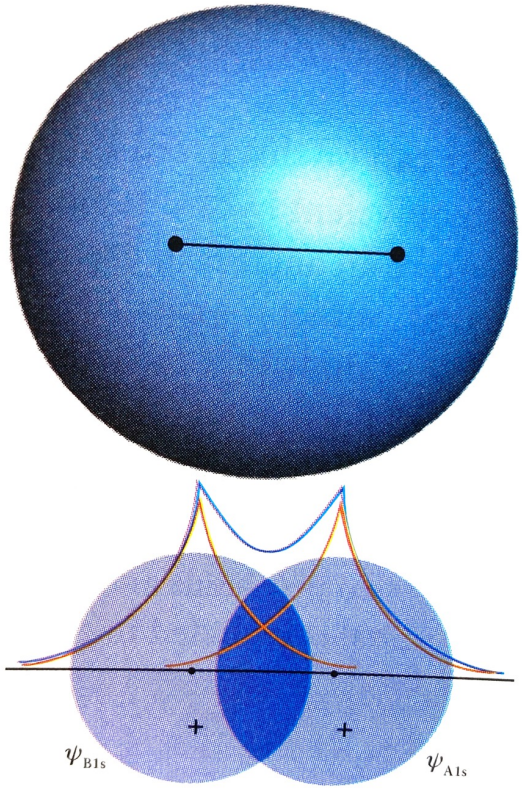


Figure 2G.1 (new book)

Antibonding orbitals

Bonding orbital: $\Psi = \Psi_{A1s} + \Psi_{B1s}$

Antibonding orbital: $\boldsymbol{\Psi = \Psi_{A1s} - \Psi_{B1s}}$

A negative sign indicates that the amplitude of Ψ_{B1s} **subtracts** from the amplitude of Ψ_{A1s} where they overlap. Subtraction leads to locations where the **AOs cancel completely**. A «nodal surface» is formed, a plane that lies halfway between two nuclei.

An electron that occupies that orbital is largely excluded from the internuclear space and has a **higher energy** when it occupies one of the atomic orbitals alone.

A combination of atomic orbitals that results in a higher energy than that of the original atomic orbitals is called an antibonding orbital, **denoted σ^*** (here: σ^*_{1s}).

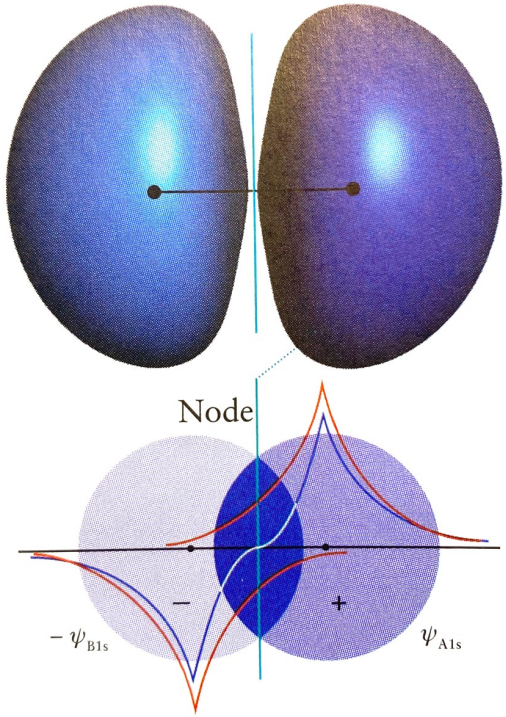


Figure 2G.2 (new book)

2G.1 Molecular orbitals

MO diagrams

The relative energies of the original atomic orbitals and the bonding and antibonding molecular orbitals are shown in a molecular orbital energy-level diagram (**Fig 2G.3**)

- Diagram shows **relative energies** of AOs and MOs.

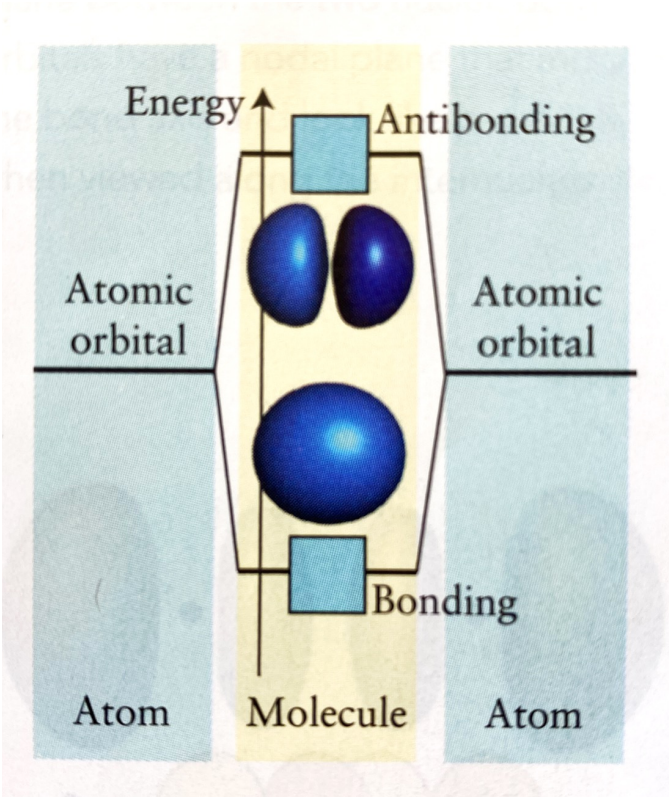


Figure 2G.3 (new book)