9.12 Hybrids Including d-Orbitals

- **d**-orbitals can be involved in the hybridization at central atoms from the third or later periods of the table which form expanded octets
- **sp^{3}d-hybridization** – a combination of one **s**, three **p** and one **d** orbitals (used to describe the **trigonal bipyramidal e$^-$ arrangement**)
- **sp^{3}d^2-hybridization** – a combination of one **s**, three **p** and two **d** orbitals (used to describe the **octahedral e$^-$ arrangement**)

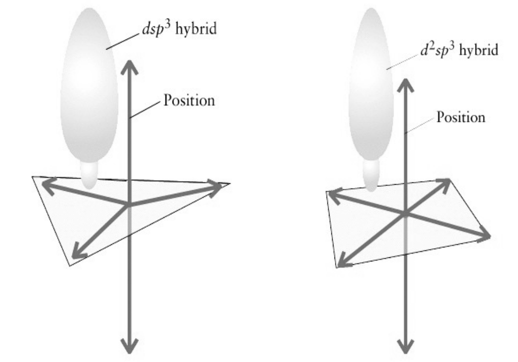


Fig. 9.37, 9.38

- Identification of the hybridization scheme
  - draw the Lewis structure and identify the electron arrangement
  - use the following correspondence

*Table 9.5 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
trigonal bipyramidal	5	*sp*^{3}*d*	5
octahedral	6	*sp*^{3}*d*^{2}	6

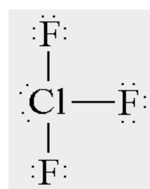
*Other combinations of *s*-, *p*-, and *d*-orbitals can give rise to the same or different shapes, but these combinations are the most common.

Example: What is the hybridization at the Cl atom in **ClF_3**.

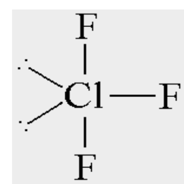
1. Lewis structure: **n_{tot}=28, n_{rem}=22, n_{need}=20**

n_{need}<n_{rem} ⇒ 2 extra e$^-$ (place at the central atom)

2. **2** lone pairs + **3** bonded atoms = **5**



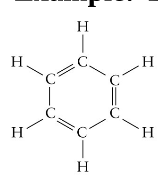
⇒ trigonal bipyramidal **e$^-$** arrangement
⇒ **sp^{3}d - hybridization**



9.13 Multiple Carbon-Carbon Bonds

- In molecules with more than one central atom, the hybridization is determined individually for each central atom

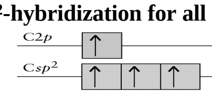
Example: Benzene, **C_6H_6**



16 Kekulé structure

Each **C** atom in benzene has a **trigonal planar** electron arrangement (**0** lone pairs + **3** bonded atoms = **3**)

⇒ **sp^2-hybridization for all Cs**



45 *sp*^{2} hybridized carbon

The **σ-skeleton** is formed by the **sp^2 hybrids** of the **C**s and the **s-orbitals** of the **H**s

Three **π-bonds** are formed from the sideways overlap of the unhybridized **p-orbitals** of the **C**s

The **resonance** spreads the **π-bonds** over the entire ring

The **molecule is flat**, because such geometry provides for the best overlap between the **p-orbitals**

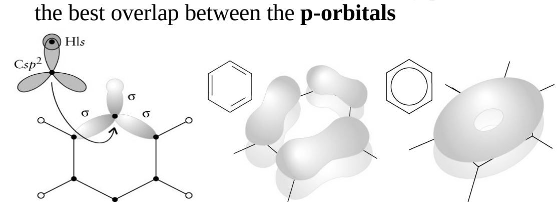
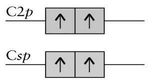


Fig. 9.44, 9.45, 9.46

Example: Acetylene, C_2H_2

H–C≡C–H (linear e^- arrangement for both **C**s)

⇒ **sp-hybridization** for both **C**s



46 *sp* hybridized carbon

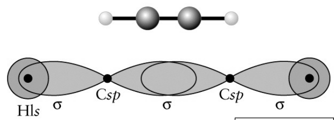
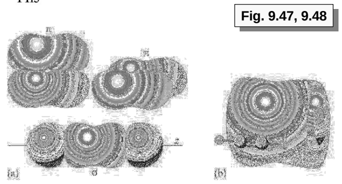


Fig. 9.47, 9.48

σ-skeleton – formed by the **sp hybrids** of **C** and the **s-orbitals** of **H**

Two **π-bonds** at 90º to each other – formed by the sideways overlap of the unhybridized **p-orbitals** of the **C**s



- Internal rotation in molecules
  - **allowed** around **single bonds** (the overlap between the orbitals is preserved during rotation)
  - **not allowed** around **double bonds** (rotation disturbs the parallel alignment of the p-orbitals and reduces their overlap, the **π-bond** breaks)

Example:

C_2H_6 - rot. is allowed

C_2H_4 - rot. is not allowed

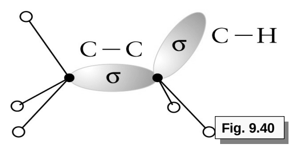


Fig. 9.40

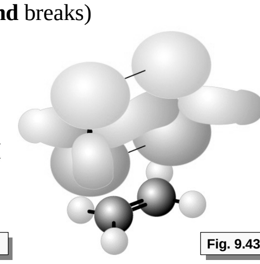


Fig. 9.43

Molecular Orbital Theory

9.14 The Limitations of Lewis's Theory

- Lewis's theory fails in describing:
  - **electron-deficient compounds** – have too few electrons (**B_2H_6**, Diborane – must have at least **7** bonds (**14 e^-**) to bond the 8 atoms, but has only 12 valence **e^-**)
  - **radicals** – odd electron species (**NO**, 11 **e^-**s)
  - **paramagnetism** – attraction to magnetic fields characteristic for substances with unpaired **e^-**s (**O_2**, is paramagnetic, but has no unpaired **e^-**s in its Lewis structure)

- The molecular orbital theory resolves these problems by introducing **molecular orbitals**
  - similar to the atomic orbitals, but spread throughout the whole molecule
  - can be occupied by no more than 2 electrons with opposite spins – Pauli exclusion principle (explains the significance of **e^-** pairs)
  - can be occupied by single electrons (provides explanations of odd-electron species and paramagnetic properties)