Valence-Bond (VB) Theory

– covalent bonds result from the overlap of valence atomic orbitals on neighboring atoms occupied by unpaired electrons and formation of electron pairs

9.9 Sigma- and Pi-Bonds

- The overlap (merging) of atomic orbitals can occur in two geometric configurations
  - – end-to-end overlap along the internuclear axis (**σ-bonding**)
  - – side-by-side overlap on each side of the internuclear axis (**π-bonding**)

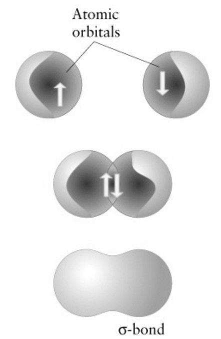


Fig. 9.25

Example: H_2

The **1s** orbitals of two **H** atoms contain unpaired electrons

The orbitals overlap along the internuclear axis and form a **σ-bond** (the two electrons are paired)

The electron density increases in the overlapped region between the nuclei

The overlap between two **s** orbitals always leads to **σ-bonds**

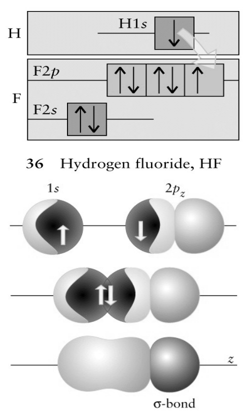


Fig. 9.26

Example: HF

The **1s** orbital of **H** and the **$2p_z$** orbital of **F** contain unpaired electrons

The orbitals overlap along the internuclear axis and form a **σ-bond** (the two electrons are paired)

The electron density increases in the overlapped region between the nuclei

The overlap between **s** and **p** orbitals always leads to **σ-bonds**

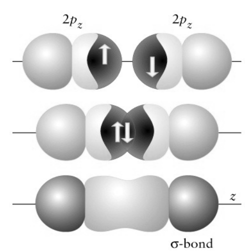
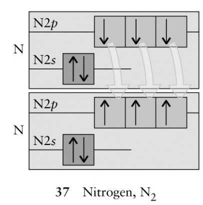


Fig. 9.27

Example: F_2

The **$2p_z$** orbitals of two **F** atoms overlap end-to-end along the internuclear axis and form a **σ-bond**



Example: N_2

The **2p** orbitals of **N** contain three unpaired electrons, 1 in each p-orbital

Three bonds can be formed by pairing the electrons of two **N** atoms

The **$2p_z$** orbitals overlap end-to-end along the internuclear axis and form a **σ-bond**

The **$2p_x$** orbitals are perpendicular to the **$2p_z$** orbitals and overlap side-by-side to form a **π-bond**

The **$2p_y$** orbitals are perpendicular to the **$2p_z$** and **$2p_x$** orbitals and also overlap side-by-side to for a **π-bond**

For the **π-bonds** the electron density increases in the regions of overlap on each side of the internuclear axis

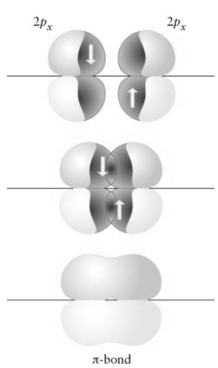


Fig. 9.28

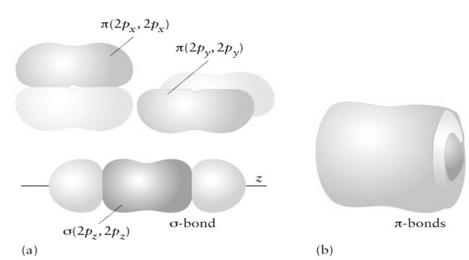


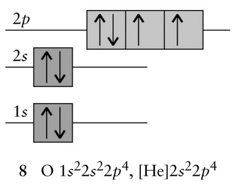
Fig. 9.29

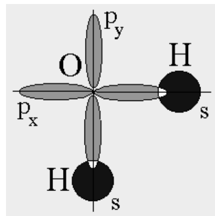
- All **single** bonds are **σ-bonds**
- **Double** bonds contain one **σ-bond** and one **π-bond**
- **Triple** bonds contain one **σ-bond** and two **π-bonds**

9.10,11 Hybridization

- Without modifications the **VB** theory predicts bond angles of 90º at the central atom of polyatomic molecules such as H_2O, NH_3 and CH_4 which is inconsistent with the experiment

Example: H_2O





- The valence orbitals of the central atom must be modified in order to reproduce the experimentally observed bond angles
- **Hybridization** - mathematical mixing of two or more valence orbitals on the same atom
  - result → **hybrid orbitals**
  - the hybrid orbitals have shapes and orientations different than the original orbitals being mixed
  - the number of hybrid orbitals equals the number of original orbitals
  - the hybrid orbitals have equal energies (average of the energies of the original orbitals)

- **sp^3 hybridization** – a combination of one **s** and three **p** orbitals
  - the resulting four **sp^3 hybrid** orbitals are identical and point toward the corners of a tetrahedron (used to describe the **tetrahedral e^- arrangement, bond angles 109.5º**)

Example: CH_4 (tetrahedral electron arrangement)

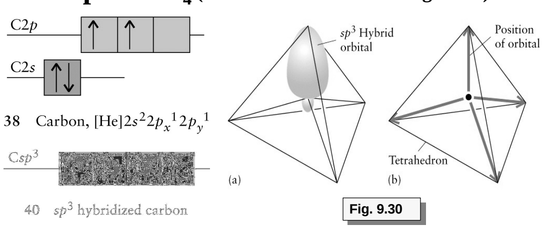


Fig. 9.30

The **s**-orbitals of the four **H** atoms overlap with the four **sp^3** hybrids and form four **σ-bonds** with tetrahedral arrangement (bond angles of **109.5º**)

- **sp^2** hybridization – a combination of one **s** and two **p** orbitals
  - the resulting three **sp^2 hybrid** orbitals are identical and point toward the corners of an equilateral triangle (used to describe the **trigonal planar electron arrangement, bond angles 120º**)
- **sp** hybridization – a combination of one **s** and one **p** orbitals
  - the resulting two **sp hybrid** orbitals are identical and have linear orientation (used to describe the **linear electron arrangement, bond angles 180º**)

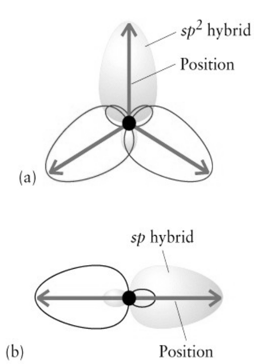


Fig. 9.32

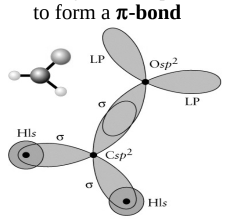
- **Hybrid orbitals** are used to form **σ-bonds** or can be occupied by **lone pairs**
- For **sp^2** and **sp** types of hybridization, the remaining unhybridized **p-orbitals** at the central atom are used to form **π-bonds** or can remain empty

Example: CH_2O (trigonal planar arrangement)

the **C** atom is in **sp^2** hybridization; two of the **sp^2** hybrids are used to form **σ-bonds** with the **H**s and one with the **O**

the **O** atom is also in **sp^2** hybridization; two of the **sp^2** hybrids are used to hold the **lone pairs** and one to form a **σ-bond** with **C**

the unhybridized p-orbitals of **C** and **O** overlap side-by-side to form a **π-bond**



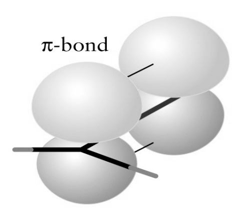


Fig. 9.33, 34