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 (\(\sigma\)-bonding)
  - side-by-side overlap on each side of the internuclear axis (\(\pi\)-bonding)

Example: H\(_2\)
- The 1s orbitals of two H atoms contain unpaired electrons
- The orbitals overlap along the internuclear axis and form a \(\sigma\)-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 \(\sigma\)-bonds

Example: HF
- The 1s orbital of H and the 2p orbital of F contain unpaired electrons
- The orbitals overlap along the internuclear axis and form a \(\sigma\)-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 \(\sigma\)-bonds

Example: F\(_2\)
- The 2p\(_z\) orbitals of two F atoms overlap end-to-end along the internuclear axis and form a \(\sigma\)-bond
- The 2p\(_x\) and 2p\(_y\) orbitals are perpendicular to the 2p\(_z\) orbitals and overlap side-by-side to form a \(\pi\)-bond
- For the \(\pi\)-bonds the electron density increases in the regions of overlap on each side of the internuclear axis

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

- All single bonds are \(\sigma\)-bonds
- Double bonds contain one \(\sigma\)-bond and one \(\pi\)-bond
- Triple bonds contain one \(\sigma\)-bond and two \(\pi\)-bonds
9.10,11 Hybridization

- Without modifications the VB theory predicts bond angles of 90° at the central atom of polyatomic molecules such as H₂O, NH₃ and CH₄ which is inconsistent with the experiment.

Example: H₂O

- 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)

- sp³ hybridization – a combination of one s and three p orbitals
  - the resulting four sp³ hybrid orbitals are identical and point toward the corners of a tetrahedron (used to describe the tetrahedral e⁻ arrangement, bond angles 109.5°)

Example: CH₄ (tetrahedral electron arrangement)

- The s-orbitals of the four H atoms overlap with the four sp³ hybrids and form four σ-bonds with tetrahedral arrangement (bond angles of 109.5°)

- sp² hybridization – a combination of one s and two p orbitals
  - the resulting three sp² hybrid orbitals are identical and point toward the corners of an equilateral triangle (used to describe the trigonal planar electron arrangement, bond angles 120°)

- 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 180°)

- Hybrid orbitals are used to form σ-bonds or can be occupied by lone pairs
- For sp² 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: CH₂O (trigonal planar arrangement)

- the C atom is in sp² hybridization; two of the sp² hybrids are used to form σ-bonds with the Hs and one with the O
- the O atom is also in sp² hybridization; two of the sp² 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.