

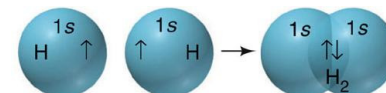
Theories of Covalent Bonding

- Explain the observed shapes, polarities, magnetic and spectroscopic properties of molecules by using quantum mechanics – atomic and molecular orbitals
- The application of quantum mechanics to chemical bonding has led to two bonding theories

11.1 Valence Bond (VB) Theory

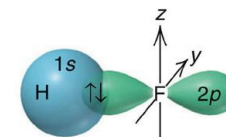
- A covalent bond results from the **overlap of valence atomic orbitals** on neighboring atoms occupied by unpaired electrons and the formation of an electron pair which has highest probability to be between the nuclei

- The two electrons in the pair must have **opposite spins** – Pauli exclusion principle



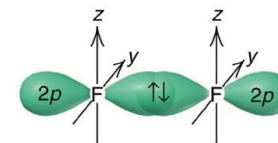
A Hydrogen, H₂

- The overlapping orbitals are oriented in a way that provides **maximum overlap** between them



B Hydrogen fluoride, HF

- *s-s* orbital overlap is independent of orientation (H₂)
- *s* and *p* orbitals overlap along the axis of the *p* orbital (HF)

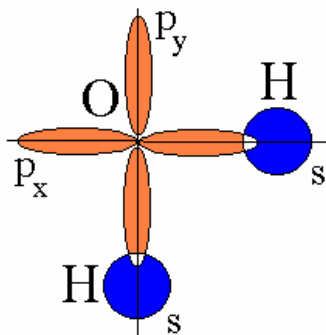
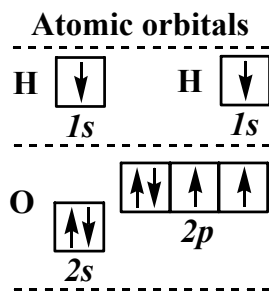


C Fluorine, F₂

• Hybridization of atomic orbitals

- 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

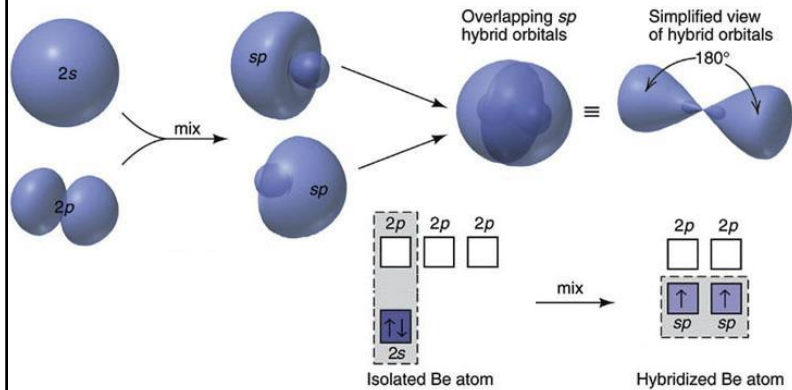
Example: H₂O



- 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)

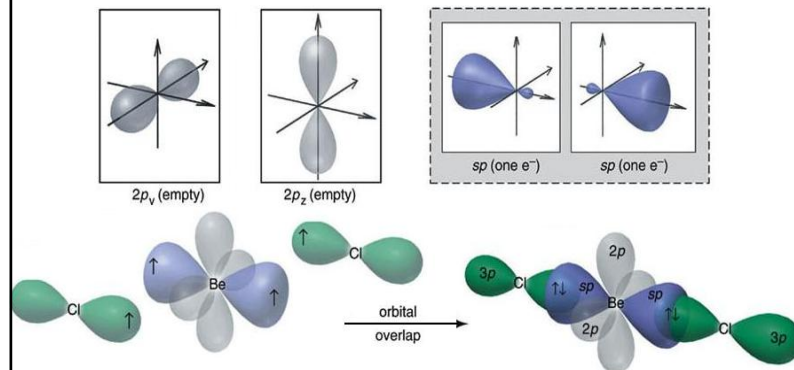
• **sp Hybridization** – a combination of one s and one p orbital

- The resulting two **sp hybrid** orbitals are identical and have linear orientation (used to describe the **linear electron group arrangement, bond angles 180°**)



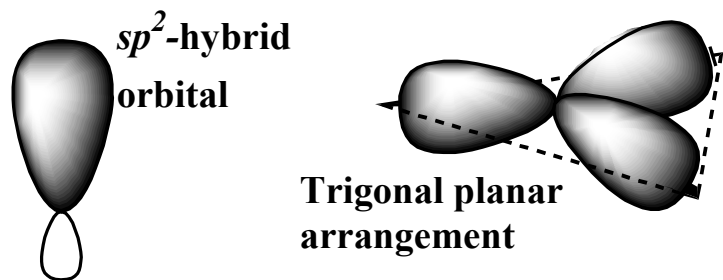
Example: BeCl_2 (linear e-group arrangement)

The **$3p$ -orbitals** of two **Cl** atoms overlap with the two **sp -hybrids** of **Be** and form two bonds with linear arrangement (bond angle of 180°); The two unhybridized **$2p$ -orbitals** of **Be** remain empty



• **sp^2 Hybridization** – a combination of one s and two p orbitals

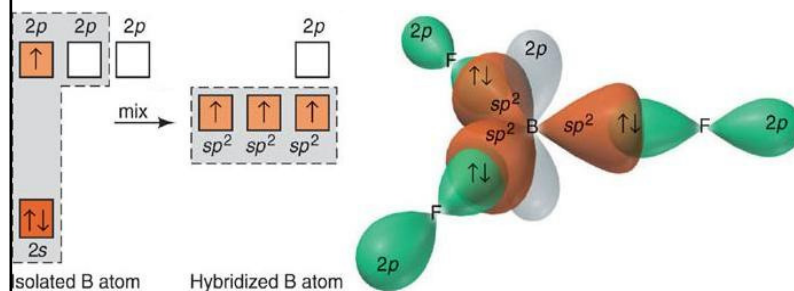
- The resulting three **sp^2 hybrid** orbitals are identical and point toward the corners of an equilateral triangle (used to describe the **trigonal planar e-group arrangement, bond angles 120°**)



Example:

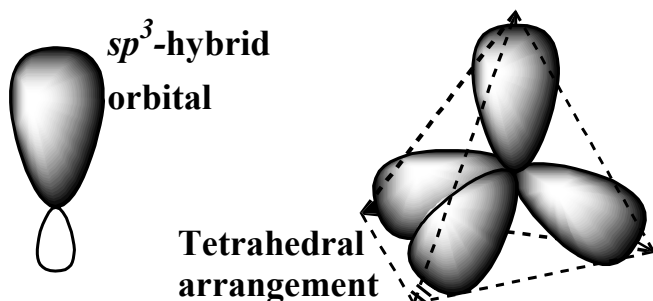
BF_3 (trigonal planar e-group arrangement)

The **$2p$ -orbitals** of three **F** atoms overlap with the three **sp^2 -hybrids** of **B** and form three bonds with trigonal planar arrangement (bond angle of 120°); The unhybridized **$2p$ -orbital** of **B** remains empty



• **sp^3 Hybridization** – a combination of **one s** and **three p** orbitals

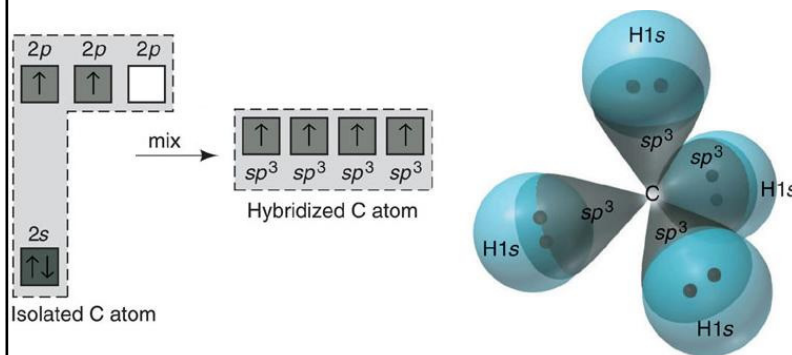
- The resulting four **sp^3 hybrid** orbitals are identical and point toward the corners of a tetrahedron (used to describe the **tetrahedral e-group arrangement, bond angles 109.5°**)



Example:

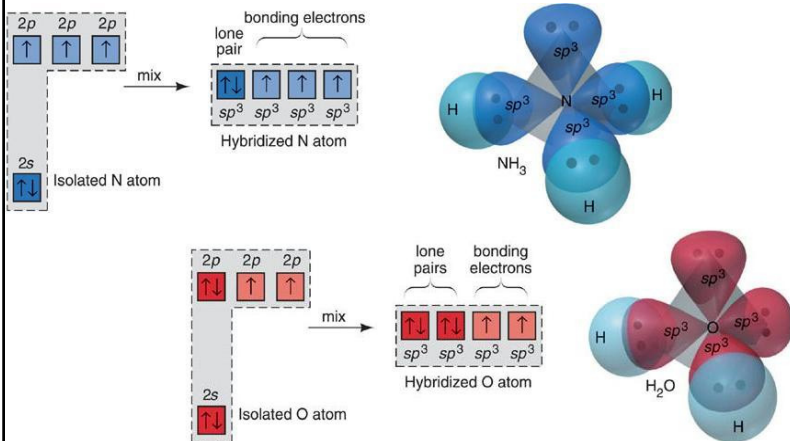
CH_4 (tetrahedral e-group arrangement)

The **1s**-orbitals of four **H** atoms overlap with the four **sp^3** -hybrids of **C** and form four bonds with tetrahedral arrangement (bond angles of 109.5°)



• Hybrid orbitals can be used for bonding as well as for holding the lone pairs of the central atom

Examples:
 NH_3 and H_2O (tetrahedral e-group arrangement)



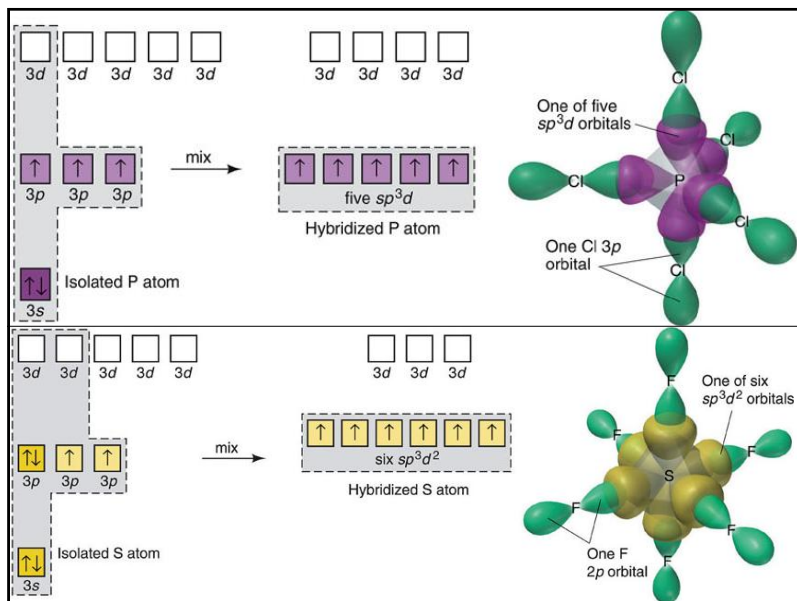
• **Hybrids involving d-Orbitals**

- **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^3d Hybridization** – a combination of one s, three p and one d orbitals (used to describe the **trigonal bipyramidal e-group arrangement**)
- **sp^3d^2 Hybridization** – a combination of one s, three p and two d orbitals (used to describe the **octahedral e-group arrangement**)

Examples:

PCl_5 (trigonal bipyramidal e-group arrangement)

SF_6 (octahedral e-group arrangement)



- Identification of the hybridization scheme
 - Draw the Lewis structure and identify the e-group arrangement
 - Use the following correspondence

Table 11.1 Composition and Orientation of Hybrid Orbitals

	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one s one p	one s two p	one s three p	one s three p one d	one s three p two d
Hybrid orbitals formed	two sp	three sp^2	four sp^3	five sp^3d	six sp^3d^2
Unhybridized orbitals remaining	two p	one p	none	four d	three d
Orientation					

Example:

What is the hybridization at the Cl atom in ClF_3 ?

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

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

2. 2 lone pairs + 3 bonded atoms = 5

