

Models for Covalent Bonding

There are two popular and successful models for describing covalent bonding. In the localized electron (LE) model (Chapter 13.9) a molecule is considered to be a collection of atoms which have localized electron pairs. Bonding is achieved whenever two atoms share the same electron pair. If a localized electron pair is not being shared it remains a lone pair on the atom. The other model takes an opposite point of view by considering a molecule to be a collection of atoms whose electrons are delocalized over the entire molecule. Bonding is achieved whenever the probability for the delocalized electron is concentrated between two atoms. In quantum mechanical formulations the LE model yields **valence bond theory** while the delocalized model yields **molecular orbital theory**. While the two models may appear to be diametrically opposed, in a quantum mechanical framework when an approximate treatment of both models is refined to become more "exact", the two models merge to give the same result.

The localized electron model is relatively easy to use and intuitive - it accords with our perception of what a bond should be. It underlies many useful concepts that you have already learned:

1. **Lewis structures** - In 1902 G. N. Lewis (of Lewis acid/base fame) conceived of the octet rule (while lecturing to general chemistry students). He was the first to establish the concept of an electron pair bond. The localized picture is evident in
 - a) octet rule
 - b) bonding pairs
 - c) lone pairs
 - d) formal charges
 - e) resonance structures
2. **Valence Shell Electron Pair Repulsion Theory** - VSEPR was originally proposed in 1940 by Sidgwick and Powell. In 1957 it was further developed by Nyholm and especially Gillespie.
 - a) Thesis - a molecule adapts a shape which maximizes the distance between pairs of electrons in its valence shell. This minimizes the electron pair repulsion whose order is $BP/BP < BP/LP < LP/LP$.
 - b) Uses
 - 1) number of electron pairs (steric number, SN) -> **electronic geometry**
 - 2) **molecular geometry** -> bond angles and their distortions
 - 3) qualitative prediction of dipole moment and polarity
3. **Hybridization** - In the 1920's Linus Pauling (Nobel Laureate in both chemistry and peace) showed exactly how one could take an *s* and the three *p* orbitals of carbon and obtain four new orbitals directed to the corners of a tetrahedron which explained the bonding in CH_4 . In 1931 he similarly explained the bonding in octahedral complexes by taking an *s*, the three *p*'s and two of the five *d* orbitals to form six new orbitals directed to the six corners of an octahedron.

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| <p>SN=2 linear</p> | <p>HCN NO₂⁺</p> | <p>N₃⁻ CO₂</p> | <p>BeH₂ H-C≡C-H</p> |
| <p>SN=3 trigonal planar</p> | <p>SO₂ O₃ CH₂=CH₂ Sn(OH)₃⁻</p> | <p>SbCl₂⁺ BF₃ H₂C=O NO₃⁻</p> | <p>NO₂⁻ SO₃ benzene</p> |
| <p>SN=4 tetrahedral</p> | <p>H₂O H₃O⁺ SiCl₄ POCl₃ BF₄⁻ AsCl₃ ClO₃F</p> | <p>H₂S NH₃ CH₄ SnCl₄ AlH₄⁻ AsCl₄⁺ OF₂</p> | <p>SF₂ SnCl₃⁻ NH₄⁺ GeH₄ GaBr₄⁻ PCl₄⁺ BrO₃⁻</p> |
| <p>SN=5 trigonal bipyramidal</p> | <p>RnCl₂ BrF₃ PBr₅ I₃</p> | <p>BrCl₂⁻ SF₄ SnCl₅⁻ F₄SO</p> | <p>XeF₃⁺ IF₄⁺ SeF₅⁺</p> |
| <p>SN=6 octahedral</p> | <p>XeF₄ XeOF₄ PCl₆⁻ [GeF₆]²⁻ [BiCl₆]⁻</p> | <p>IF₄⁻ SF₆ AsF₆⁻ [SnBr₆]²⁻</p> | <p>ClF₅ BrF₆⁺ SbCl₅²⁻</p> |