Localized Electron Model
Models for Chemical Bonding

Localized electron model

(Valence bond model)

Molecular orbital model
Localized Electron Model

Useful for explaining the structure of molecules especially nonmetals bonded to nonmetals
Localized electron model

Electron pair can be shared when half-filled orbital of one atom overlaps with half-filled orbital of another.

δ Bond: orbitals overlap along the internuclear axis

π Bond: side by side overlap of orbitals parallel to the internuclear axis
Overlap and Bonding

• Increased overlap brings the electrons and nuclei closer together while simultaneously decreasing electron–electron repulsion.

• However, if atoms get too close, the internuclear repulsion greatly raises the energy.
Overlap and Bonding

\[ s, s \delta \text{ bond} \]

\[ s, p \delta \text{ bond} \]

\[ p, p \delta \text{ bond} \]
Structure of Methane (CH₄)

structure of methane seems inconsistent with electron configuration of carbon
Carbon should form $\delta$-bonds with only two Hydrogen atoms?
Hybridization of Atomic Orbitals
Hybrid orbitals

atomic orbitals obtained when two or nonequivalent orbitals of the same atom combine in preparation for covalent bond formation
$sp^3$ Hybridization
$sp^3$ Hybridization

Promote an electron from the 2s to the 2p orbital

2p  ↑  ↑  ↑  2p  ↑  ↑  ↑  ↑  ↑  ↑  ↑

2s  ↓  ↓  2s  ↑
Mix together (hybridize) the 2s orbital and the three 2p orbitals

$sp^3$ Hybridization
Mix together (hybridize) the 2s orbital and the three 2p orbitals
Mix together (hybridize) the 2s orbital and the three 2p orbitals

$sp^3$ Hybridization
With carbon, we get four degenerate $sp^3$ orbitals.

Hybrid Orbitals

One s orbital + Three p orbitals

Hybridize to form four $sp^3$ hybrid orbitals

Shown together (large lobes only)

109.5°
δ Bond in CH₄

δ C — H

s

sp³
Justification for Orbital Hybridization

The model is consistent with structure of methane.

Allows for the formation of more bonds (4 rather than 2).

Bonds involving sp$^3$ orbitals are stronger than s-s overlap or p-p overlap.
Remember

Four electron pairs

\[ = \text{tetrahedral arrangement of those electron pairs} \]

\[ = \text{sp}^3 \text{ hybridization} \]
Four electron pairs

tetrahedral arrangement of electron pairs
$\text{NH}_3$

$N$

2 $sp^3$

$\uparrow \downarrow \uparrow \uparrow \uparrow$
$sp$ Hybridization
Beryllium chloride (BeCl$_2$)

Promote an electron from the 2s to the 2p orbital.
Beryllium chloride (BeCl$_2$)

Mix together (hybridize) the 2s orbital and one 2p orbitals
Beryllium chloride (BeCl$_2$)

Mix together (hybridize) the 2s orbital and one 2p orbitals
The $\text{Be} \rightarrow \text{Cl} \quad \delta$ Bond in $\text{BeCl}$
The Be—Cl $\delta$ Bond in BeCl
Hybrid Orbitals

- These two degenerate orbitals would align themselves $180^\circ$ from each other.
- This is consistent with the observed geometry of beryllium compounds: linear.

![Diagram of BeF$_2$ showing overlap of $sp$ hybrid orbitals](image-url)
$sp^2$ Hybridization
Boron trifloride

Promote an electron from the 2s to the 2p orbital

\[ \text{2s up down up down}\]

\[ \text{2p up up up up}\]
Boron trifluoride

Mix together (hybridize) the 2s orbital and two 2p orbitals

\[2p \uparrow \quad \uparrow \quad \uparrow\]

\[2s \uparrow\]
Mix together (hybridize) the 2s orbital and two 2p orbitals

2p

2 sp^2
Hybrid Orbitals

Using a similar model for boron leads to three degenerate $sp^2$ orbitals.
Boron trifluoride
Boron trifluoride
hybrid orbitals are used only for atoms in a molecule, not for isolated atoms.

hybrid orbitals are different in shape from the atomic orbitals from which we derive them.

number of hybrid orbitals equals number of atomic orbitals from which they were generated.

hybridization permits more bonds and stronger bonds.

covalent bond results from overlap of half-filled orbitals.
Procedure For Hybridizing Atomic Orbitals

draw the Lewis structure of the molecule

predict the overall arrangement of the electron pairs using the VSEPR model

deduce the hybridization of the central atom
$\text{SF}_6$  $\text{PF}_5$
Hybridization of s, p, and d Orbitals

Beginning with the third period of the periodic table

1 3s orbital + 3 3p orbital + 1 3d orbital

gives $sp^3d$

Permits five electron pairs (trigonal bipyramidal)

1 3s orbital + 3 3p orbital + 2 3d orbital

gives $sp^3d^2$

Permits six electron pairs (octahedral)
$\pi$-Bonds
Review: Valence bond model

Electron pair can be shared when the half-filled orbital of one atom overlaps with half-filled orbital of another.

Δ Bond: orbitals overlap along the internuclear axis

π Bond: side by side overlap of orbitals
Pi ($\pi$) Bonds

- Pi bonds are characterized by
  - Side-to-side overlap.
  - Electron density above and below the internuclear axis.
Structure of Ethylene

C₂H₄

CH₂ ≡ CH₂

planar

Bond angle 120°

Requires hybridization different from sp³
Orbital Hybridization

Promote an electron from the 2s to the 2p orbital
Orbital Hybridization

Mix together (hybridize) the 2s orbital and the two 2p orbitals
Orbital Hybridization

Mix together (hybridize) the 2s orbital and the two 2p orbitals
The carbon-carbon double bond of ethylene is a combination of a δ Bond and π Bond.
$\pi$ - Bonding in Ethylene

$2 \text{ sp}^2$
$\pi$ − Bonding in Ethylene

- $sp^2$
- $2p$

Diagram showing the bonding in ethylene with $sp^2$ hybridization and $2p$ orbitals.
$\pi$ – Bonding in Ethylene
$\pi$ - Bonding in Ethylene
Multiple Bonds

In a molecule like formaldehyde (shown at left), an $sp^2$ orbital on carbon overlaps in $\sigma$ fashion with the corresponding orbital on the oxygen.

- The unhybridized $\rho$ orbitals overlap in $\pi$ fashion.
Multiple Bonds

In triple bonds, as in acetylene, two $sp$ orbitals form a $\sigma$ bond between the carbons, and two pairs of $p$ orbitals overlap in $\pi$ fashion to form the two $\pi$ bonds.