Overlap and Bonding

• We think of covalent bonds forming through the sharing of electrons by adjacent atoms.
• In such an approach this can only occur when orbitals on the two atoms overlap.

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.

Hybrid Orbitals

But it’s hard to imagine tetrahedral, trigonal bipyramidal, and other geometries arising from the atomic orbitals we recognize.
Hybrid Orbitals

• Consider beryllium:
  – In its ground electronic state, it would not be able to form bonds because it has no singly-occupied orbitals.

But if it absorbs the small amount of energy needed to promote an electron from the 2s to the 2p orbital, it can form two bonds.

Hybrid Orbitals

• Mixing the s and p orbitals yields two degenerate orbitals that are hybrids of the two orbitals.
  – These sp hybrid orbitals have two lobes like a p orbital.
  – One of the lobes is larger and more rounded as is the s orbital.
Hybrid Orbitals

• These two degenerate orbitals would align themselves 180° from each other.
• This is consistent with the observed geometry of beryllium compounds: linear.

Using a similar model for boron leads to…
Hybrid Orbitals

...three degenerate $sp^2$ orbitals.

Hybrid Orbitals

With carbon we get...

<table>
<thead>
<tr>
<th>2s</th>
<th>2p</th>
<th>$sp^2$</th>
<th>1s</th>
<th>2s</th>
<th>2p</th>
<th>$sp^3$</th>
</tr>
</thead>
</table>

Hybrid Orbitals

...four degenerate $sp^3$ orbitals.
Hybrid Orbitals

For geometries involving expanded octets on the central atom, we must use d orbitals in our hybrids.

This leads to five degenerate $sp^3d$ orbitals…

…or six degenerate $sp^3d^2$ orbitals.

Once you know the electron-domain geometry, you know the hybridization state of the atom.
Valence Bond Theory

- Hybridization is a major player in this approach to bonding.
- There are two ways orbitals can overlap to form bonds between atoms.

Sigma ($\sigma$) Bonds

- Sigma bonds are characterized by
  - Head-to-head overlap.
  - Cylindrical symmetry of electron density about the internuclear axis.

Pi ($\pi$) Bonds

- Pi bonds are characterized by
  - Side-to-side overlap.
  - Electron density above and below the internuclear axis.
Single Bonds

Single bonds are always $\sigma$ bonds, because $\sigma$ overlap is greater, resulting in a stronger bond and more energy lowering.

![Diagram of single bonds](image)

Multiple Bonds

In a multiple bond one of the bonds is a $\sigma$ bond and the rest are $\pi$ bonds.

![Diagram of multiple bonds](image)

- 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 $p$ orbitals overlap in $\pi$ fashion.
Multiple Bonds

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

Delocalized Electrons: Resonance

When writing Lewis structures for species like the nitrate ion, we draw resonance structures to more accurately reflect the structure of the molecule or ion.

Delocalized Electrons: Resonance

- In reality, each of the four atoms in the nitrate ion has a p orbital.
- The p orbitals on all three oxygens overlap with the p orbital on the central nitrogen.
Delocalized Electrons: Resonance

This means the $\pi$ electrons are not localized between the nitrogen and one of the oxygens, but rather are delocalized throughout the ion.

Resonance

The organic molecule benzene has six $\sigma$ bonds and a $p$ orbital on each carbon atom.

Resonance

- In reality the $\pi$ electrons in benzene are not localized, but delocalized.
- The even distribution of the $\pi$ electrons in benzene makes the molecule unusually stable.