

Chemical Bonding: Putting it Together

1. chemical bond:

- ionic bond:

- covalent bond:

 - Electronegativity:

 - Polar Covalent:

2. octet rule:

EXCEPTIONS

3. Lewis dot structure

4. Formal Charge:

5. Resonance: Isomers:

4. Types of Bonds:

- Single vs. double
vs. triple bonds:

- Bond Strength:

- Bond Length:

5. VSEPR Model

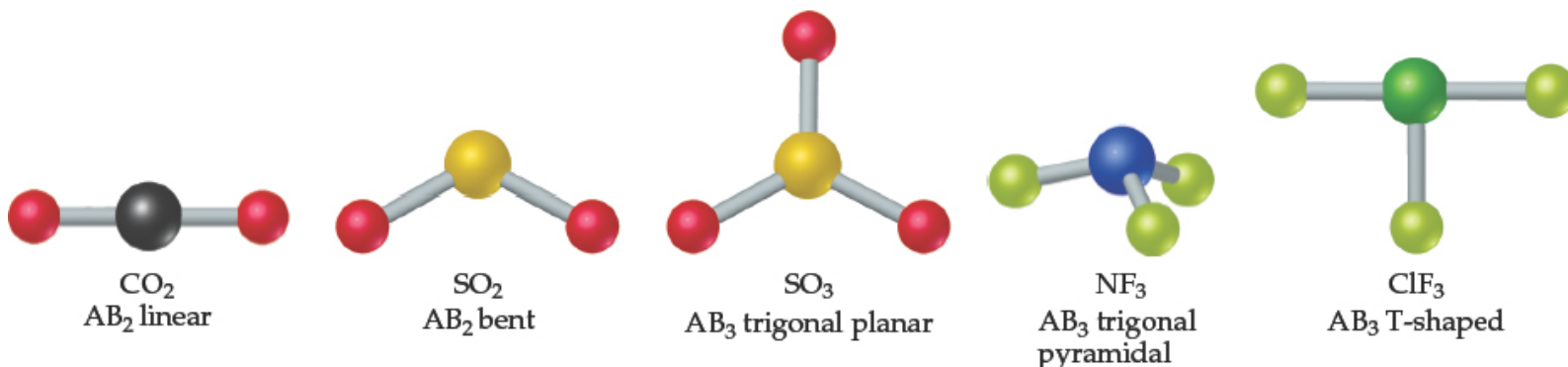
6. Polarity of Molecules

7. Valence Bond Theory

8. M.O. Theory

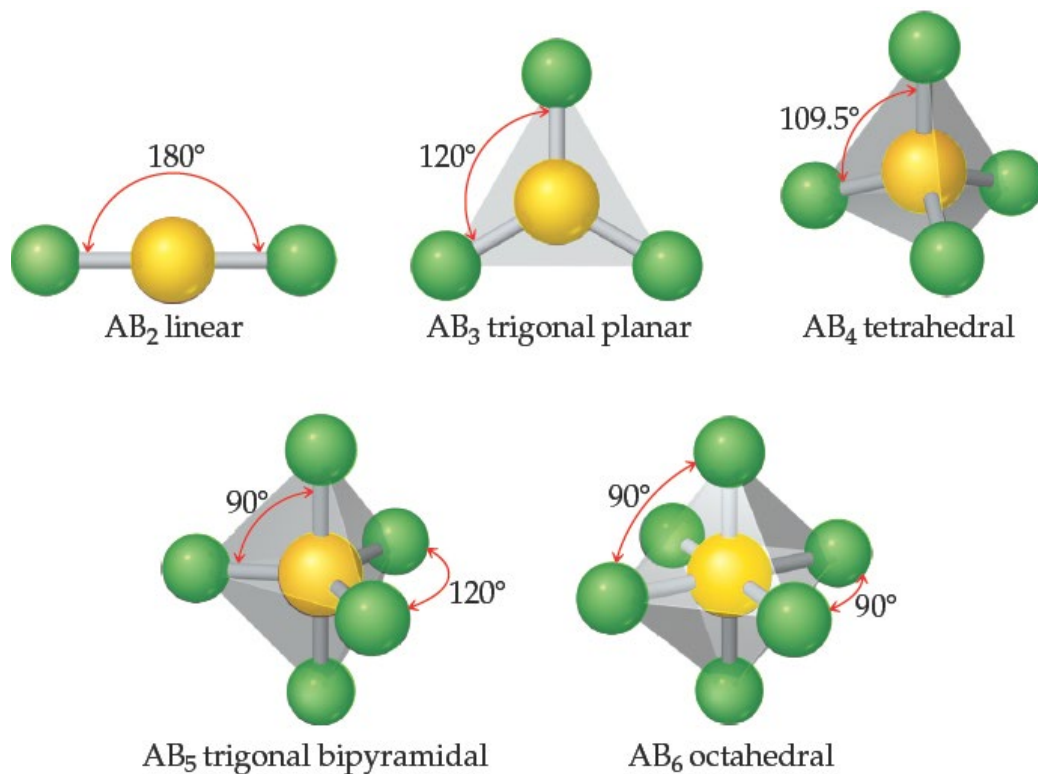
Molecular Shapes - Review

- Lewis structures show bonding and lone pairs but do **not** denote shape.
- However, we **use** Lewis structures to help us determine shapes.
- Here we see some common shapes for molecules with two or three atoms connected to a central atom.



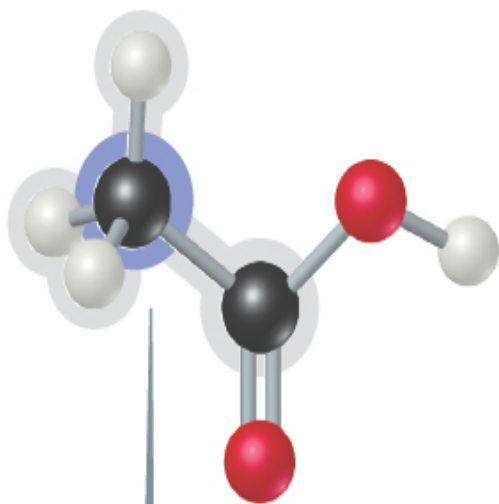
What Determines the Shape of a Molecule?

- The **bond angles** and bond lengths determine the shape and size of molecules.
- Electron pairs repel each other.
- Electron pairs are as far apart as possible; this allows predicting the shape of the molecule.
- This is the valence-shell electron-pair repulsion (VSEPR) model.

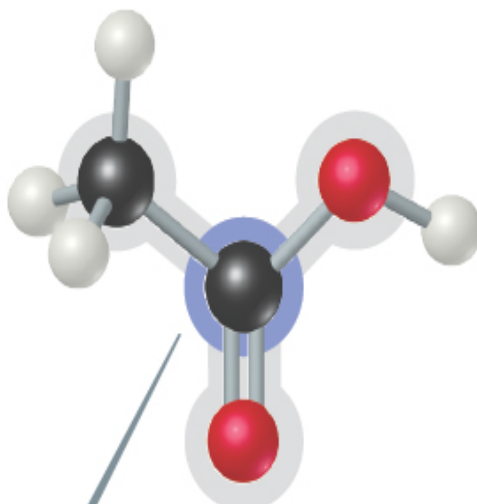


Shapes of Larger Molecules

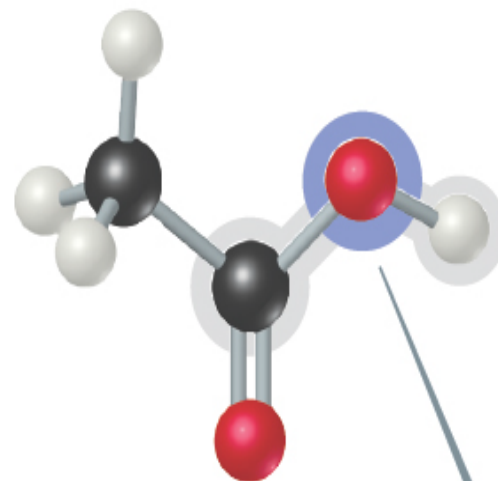
For larger molecules, look at the geometry about each atom rather than the molecule as a whole.



Electron-domain geometry tetrahedral,
molecular geometry tetrahedral



Electron-domain geometry trigonal planar,
molecular geometry trigonal planar



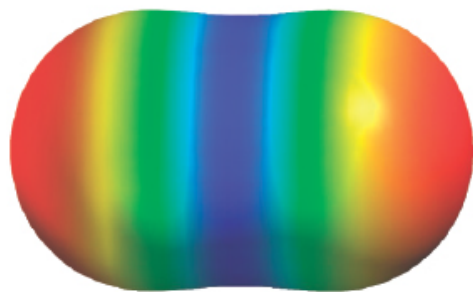
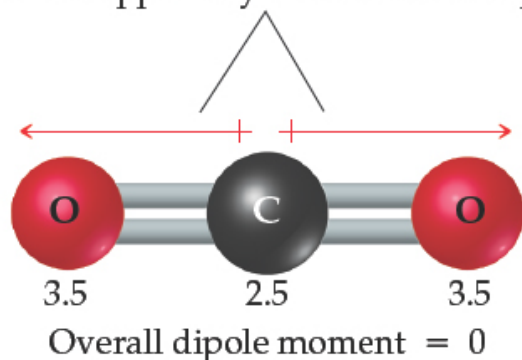
Electron-domain geometry tetrahedral,
molecular geometry bent

Comparison of the Polarity of Two Molecules

- A **nonpolar** molecule

CO2, nonpolar

Equal and oppositely directed bond dipoles

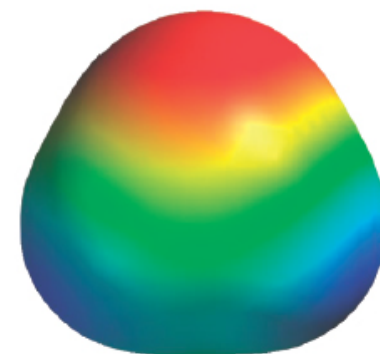
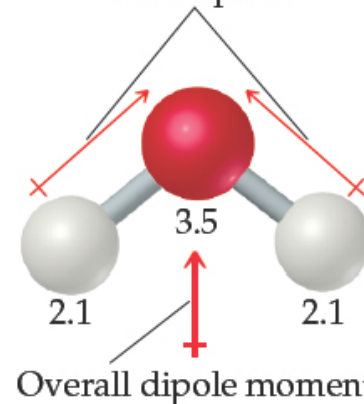


(a)

- A **polar** molecule

H2O, polar

Bond dipoles



(b)

Low electron density

High electron density



Valence Bond Theory

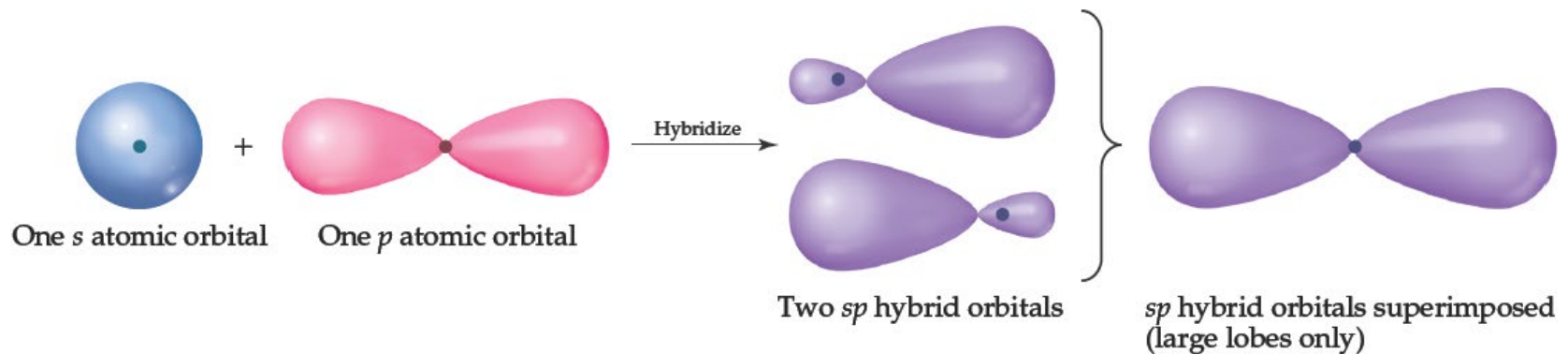
Based on Quantum Mechanics, it is an approximation theory that tries to explain the electron pair or covalent bond using quantum mechanics.

A bond will form if:

- (1) an orbital on one atom comes to occupy a portion of the same region of space as an orbital on the other atom. **“orbitals overlap”**
- (2) the total number of electrons in both orbitals is no more than 2.
- (3) the strength of a bond depends on the amount of overlap.
“the greater the overlap=the greater the strength”
- (4) the electrons are attracted to both nuclei thus pulling the atoms together.

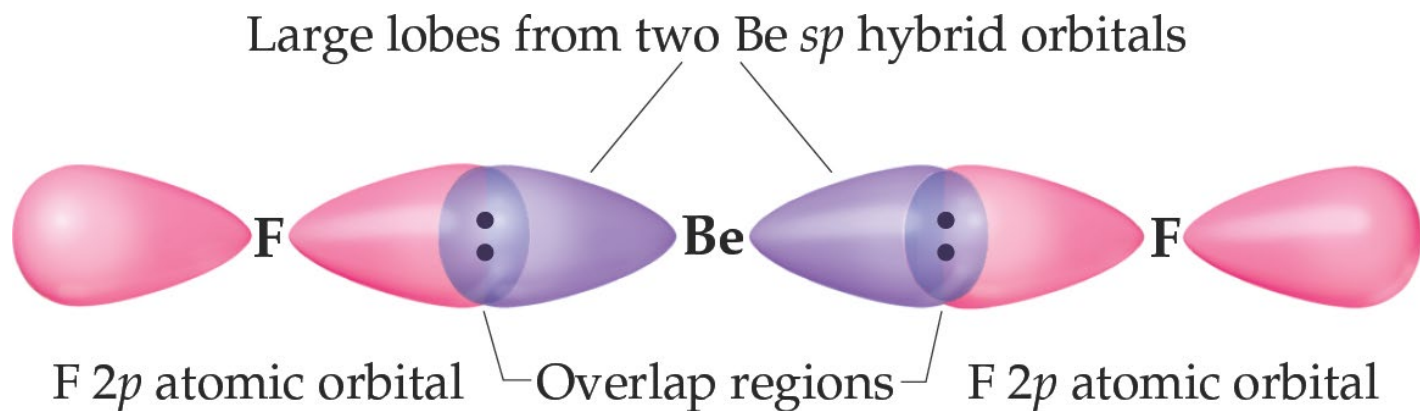
sp Orbitals

- Mixing the s and p orbitals yields two degenerate orbitals that are hybrids of the two orbitals.
 - The sp hybrid orbitals each have two lobes like a p orbital.
 - One of the lobes is larger and more rounded, as is the s orbital.



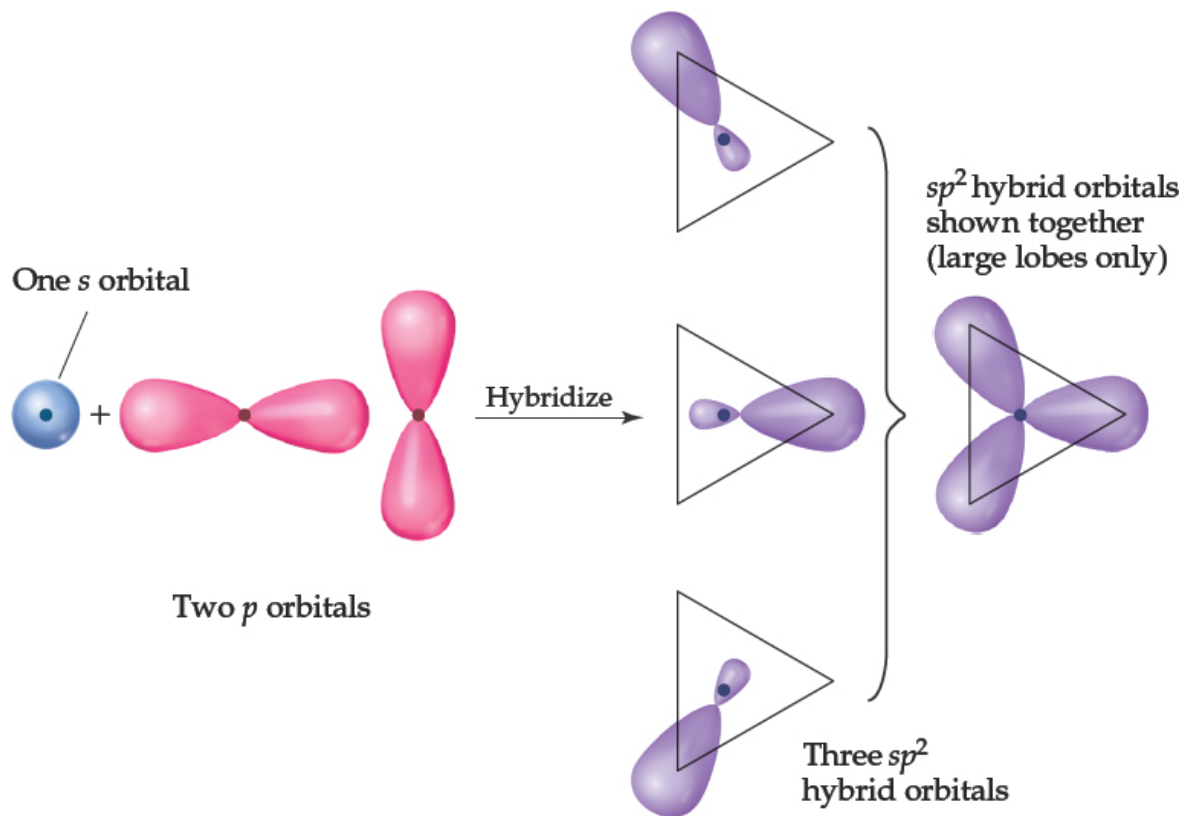
Position of sp Orbitals

- These two degenerate orbitals would align themselves 180° from each other.
- This is consistent with the observed geometry of Be compounds (like BeF_2) and VSEPR: linear.



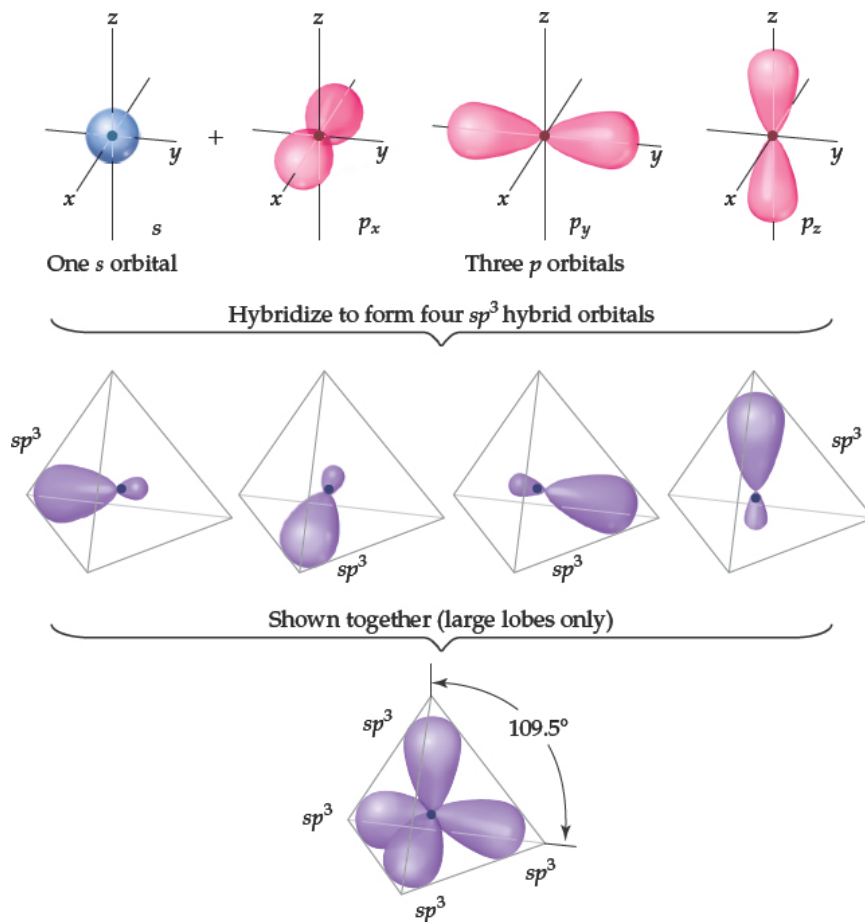
Boron—Three Electron Domains Gives sp^2 Hybridization

Using a similar model for boron leads to three degenerate sp^2 orbitals.



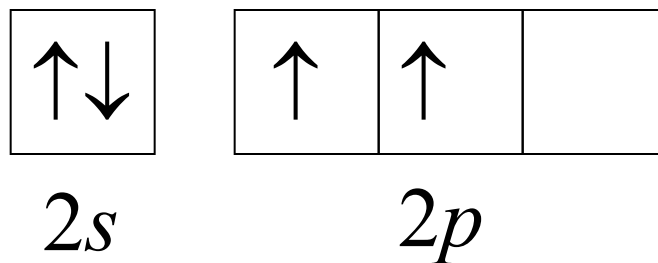
Carbon: sp^3 Hybridization

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

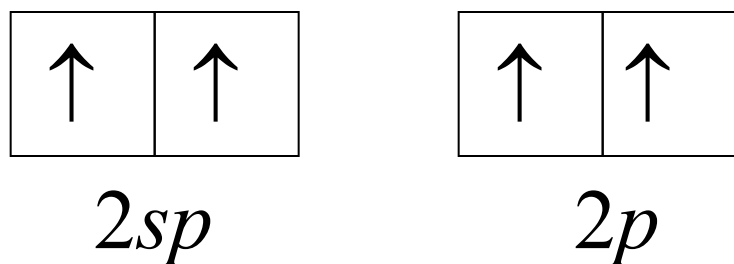


Carbon Hybridizations

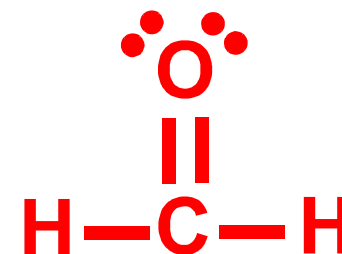
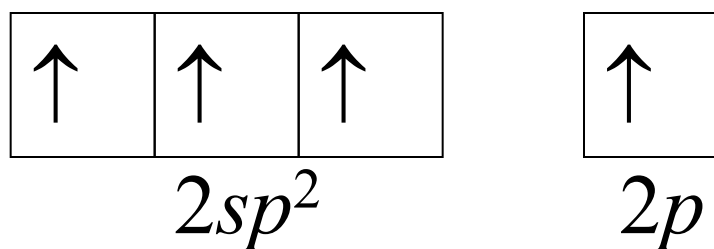
Unhybridized



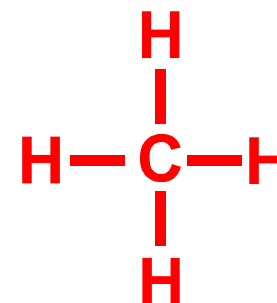
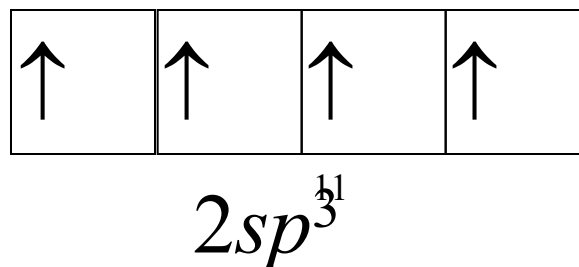
sp hybridized



sp^2 hybridized



sp^3 hybridized

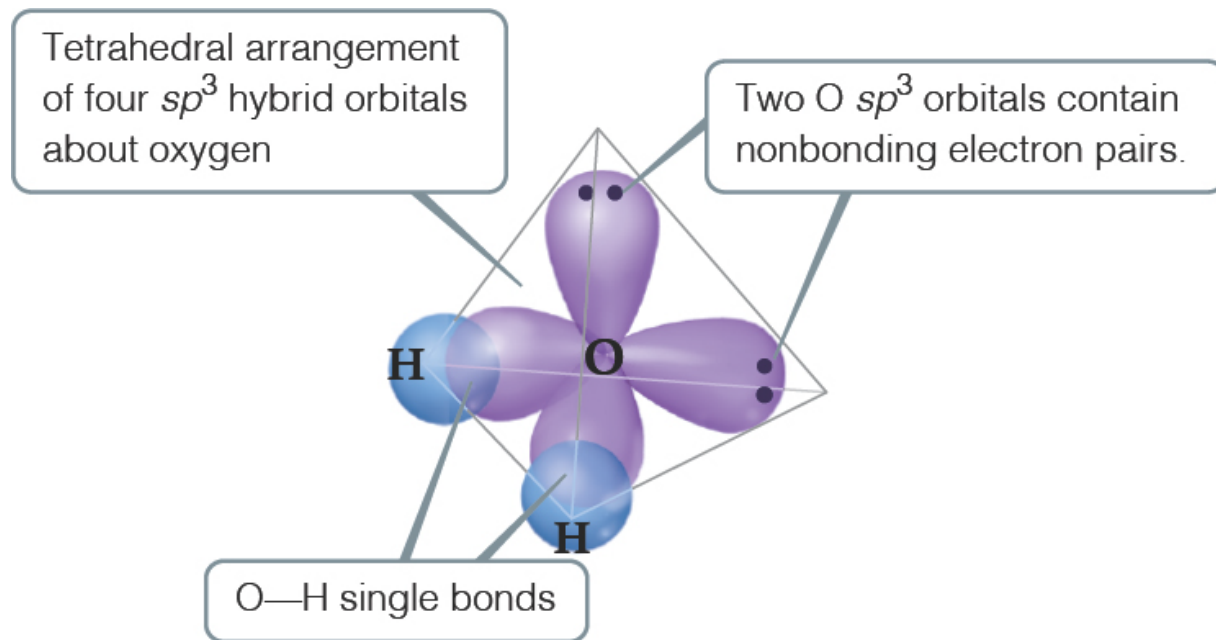


What Happens with Water?

- We started this discussion with H_2O and the angle question: Why is it 104.5 degrees instead of 90 degrees?
- Oxygen has two bonds and two lone pairs—four electron domains.

• The result is

sp^3 hybridization!



Hybrid Orbitals

1. Draw the Lewis structure
2. Use VSEPR for molecular geometry
3. From the geometry, deduce the type of hybrid orbital on the central atom.
4. Assign electrons to hybrid orbitals of the central atom, one at a time, pairing only if necessary.
5. Form bonds to the central atom by overlapping singularly occupied orbitals of outer atoms to the central atom.

Hypervalent Molecules

- The elements that have **more** than an octet
- Valence-bond model would use *d* orbitals to make more than four bonds.
- This view works for period 3 and below.
- Theoretical studies suggest that the energy needed would be too great for this.
- A more detailed bonding view is needed than we will use in this course.

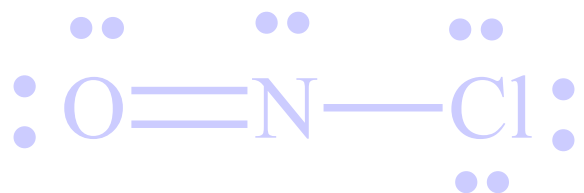
While VSEPR provides a simple means for predicting shapes of molecules, it does not explain why bonds exist between atoms. Instead, let's turn to Valence Bond Theory, relying on hybridization to further describe the overlap of atomic orbitals that form molecular orbitals:

Cheat table

<u>Atomic Orbital Set</u>	<u>Hybrid Orbital Set</u>	<u>Electronic Geometry</u>
s, p	Two sp	Linear
s, p, p	Three sp^2	Trigonal Planar
s, p, p, p	Four sp^3	Tetrahedral
s, p, p, p, d	Five sp^3d	Trigonal Bipyramidal
s, p, p, p, d, d	Six sp^3d^2	Octahedral

Each single bond in a molecule represents a **σ bond**; each subsequent bond within each single (σ) bond represents a **π bond**. Once the framework of a molecule is set up using the appropriate hybrid orbitals for σ bonds, the remaining orbitals may mix together to form π bonds.

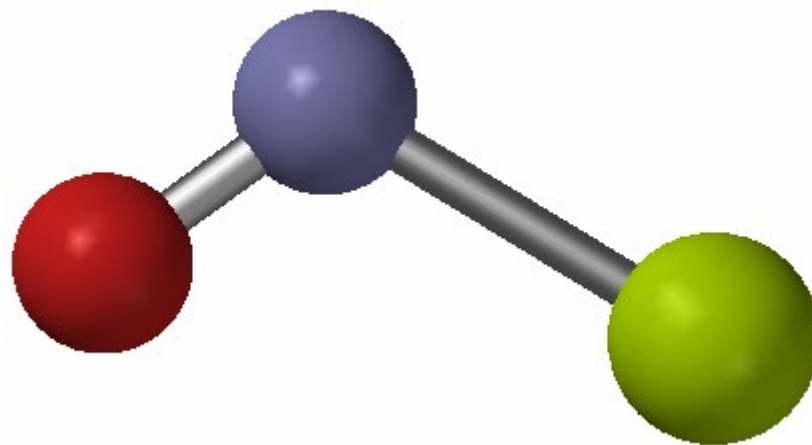
Practice - Predict the Hybridization and Bonding Scheme of All the Atoms in NClO



N = 3 electron groups = sp^2

O = 3 electron groups = sp^2

Cl = 4 electron groups = sp^3



Lecture examples

Determine the hybridization of the following



MULTIPLE BONDS

One hybrid orbital is needed for each bond whether single or multiple and for each lone pair.

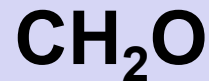
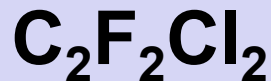
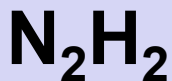
σ (sigma) bond:

Cylindrical shape about the bond axis. It is either composed of 2 "s" orbitals overlapping or directional orbitals overlapping along the axis.

π (pi) bonds:

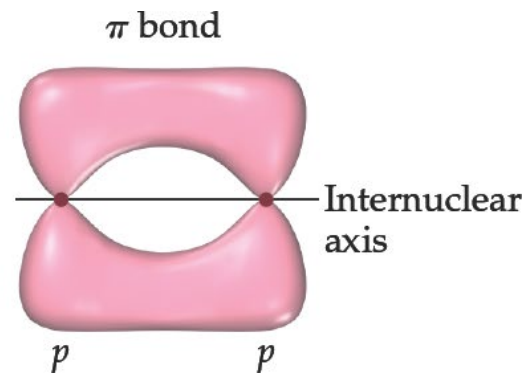
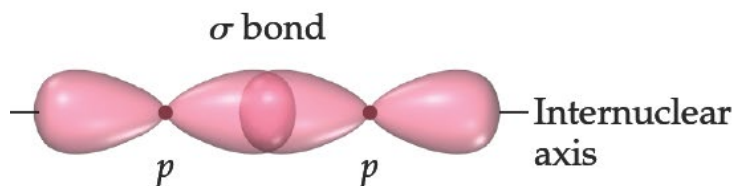
The electron distribution is above & below the bond axis and forms a sideways overlap of two parallel "p" orbitals.

Draw the valence bond sketch and give the hybridization for the following:



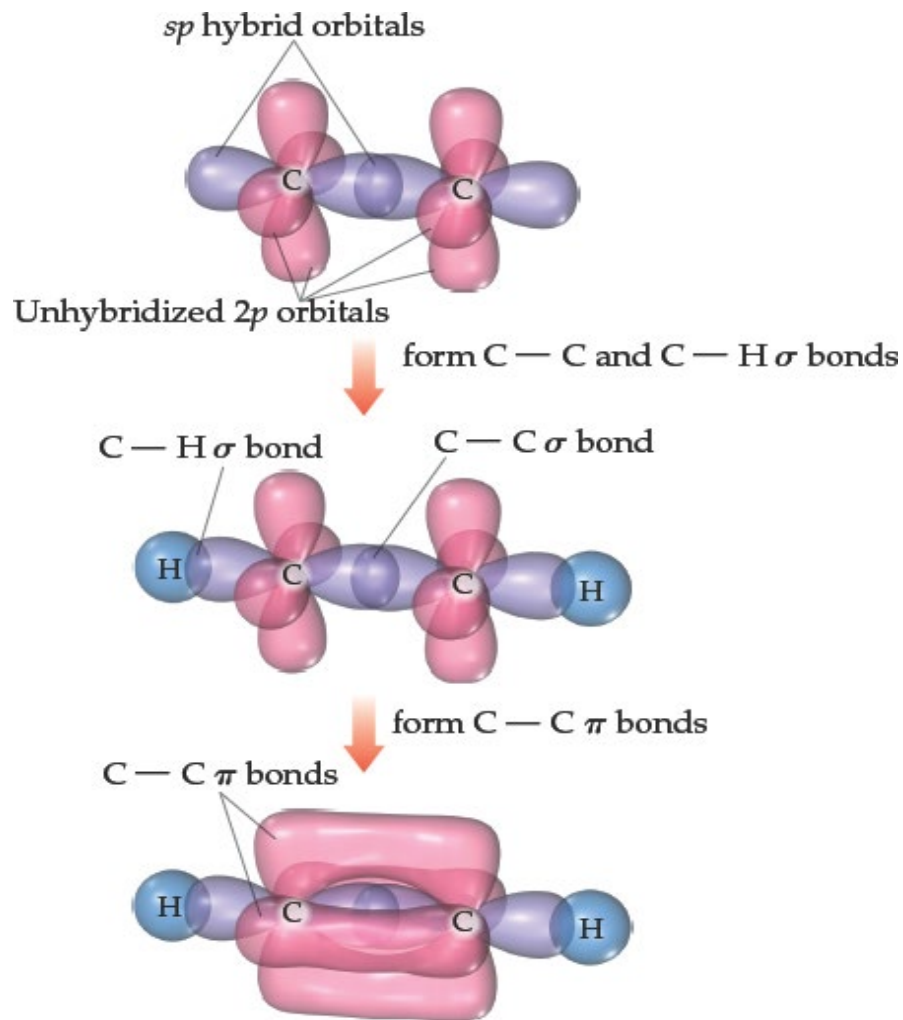
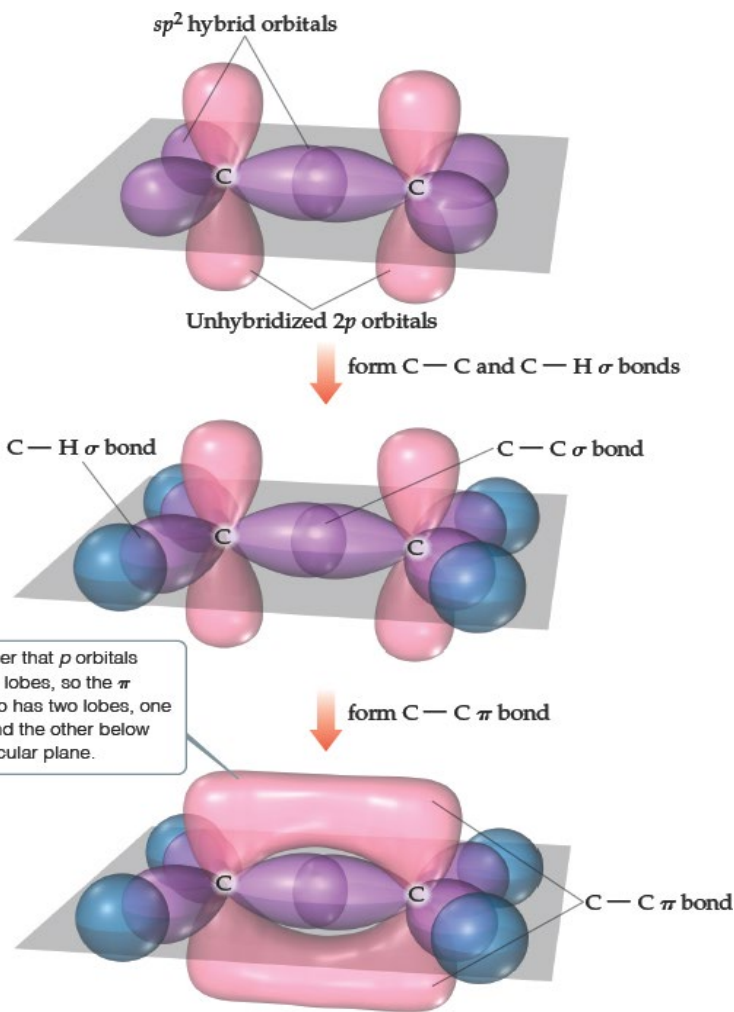
Sigma (σ) and Pi (π) Bonds

- Sigma bonds are characterized by
 - head-to-head overlap.
 - cylindrical symmetry of electron density about the internuclear axis.
- Pi bonds are characterized by
 - sideways overlap.
 - electron density above and below the internuclear axis.



Bonding in Molecules

- Single bonds are always σ -bonds.
- Multiple bonds have one σ -bond; all other bonds are π -bonds.

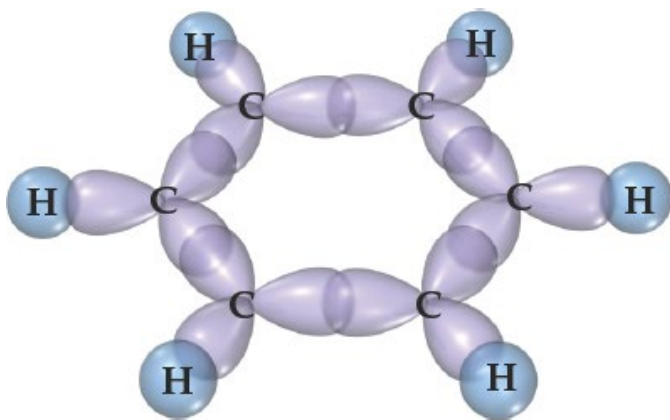


Localized or Delocalized Electrons

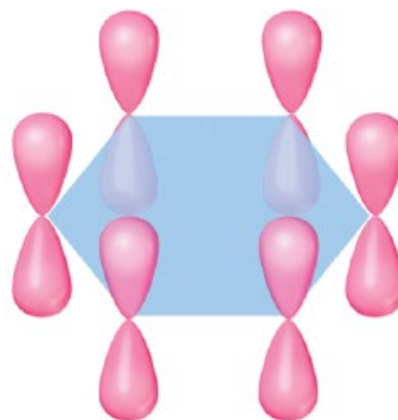
- Bonding electrons (σ or π) that are specifically shared between two atoms are called **localized** electrons.
- In many molecules, we can't describe all electrons that way (resonance); the other electrons (shared by multiple atoms) are called **delocalized** electrons.

Benzene

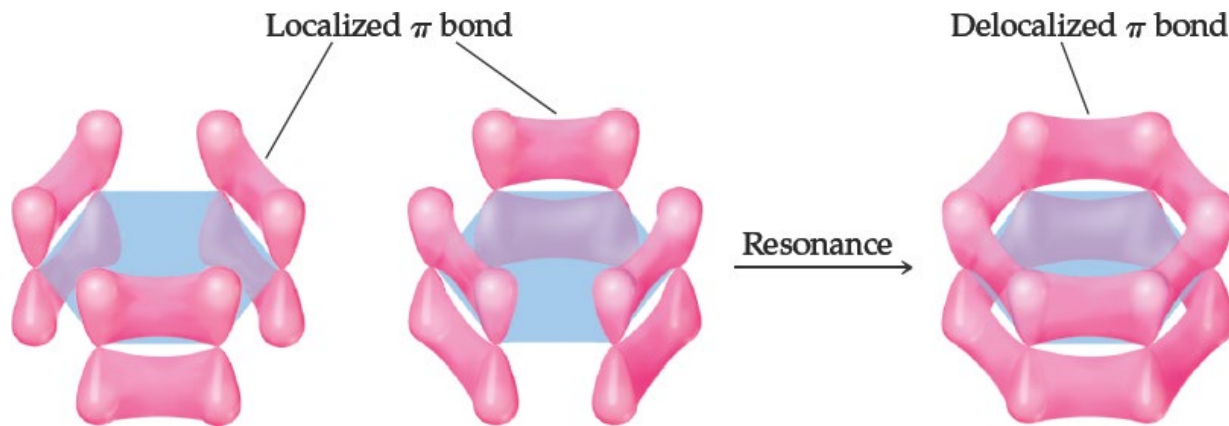
The organic molecule benzene (C_6H_6) has six σ -bonds and a p orbital on each C atom, which form delocalized bonds using one electron from each p orbital.



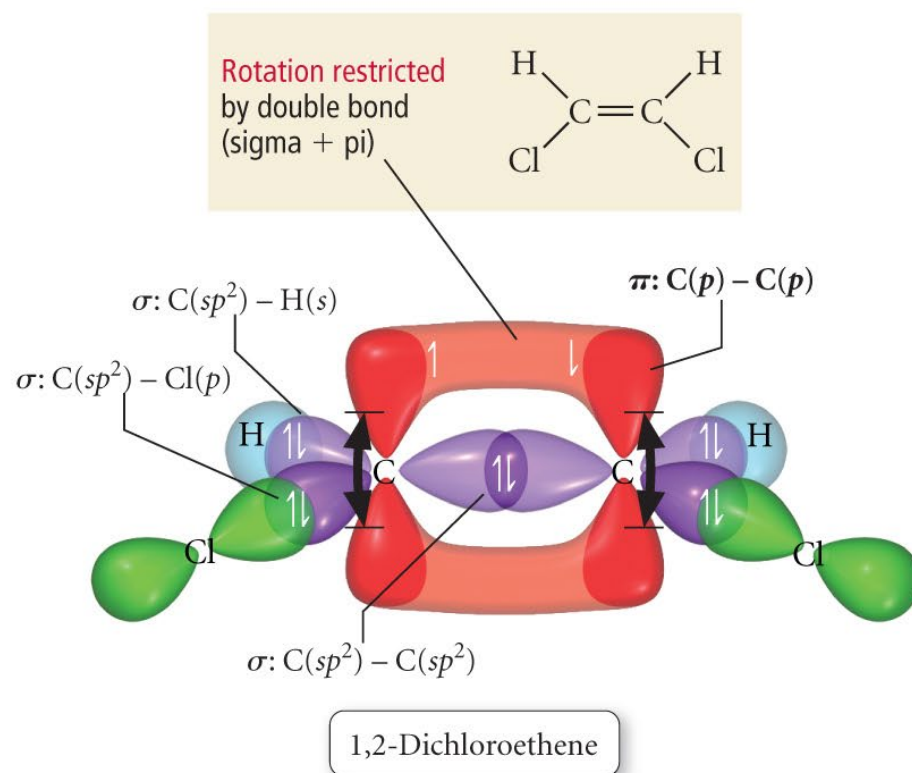
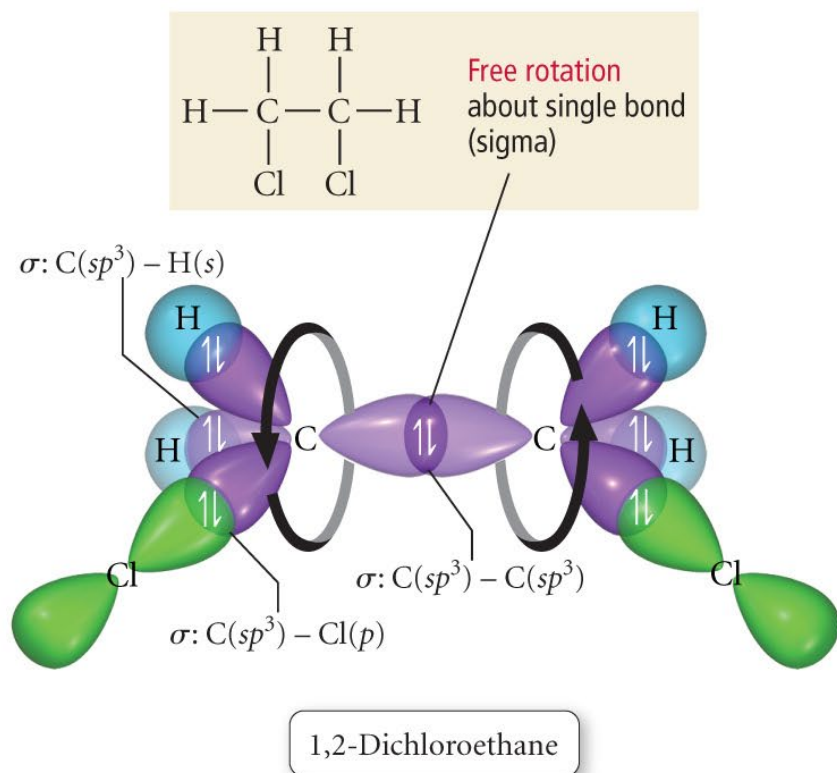
(a) σ bonds



(b) p orbitals



Visual interpretation of bonding orbitals



Lecture example

PRACTICE on hybridization

Determine the hybridization of the central atom. How many sigma (σ) and pi (π) bonds are contained within each compound?



Failures of Valence Bond Theory

- (1) Assumed the electrons were localized; did not account for resonance.**
- (2) Assumed radicals do not exist; all electrons were paired.**
- (3) Gave no information on bond energies; did not explain the following general trends:**
 - (i) An increase in bond energy corresponded to an increase in bond order**
 - (ii) A decrease in bond length corresponds to an increase in bond order.**