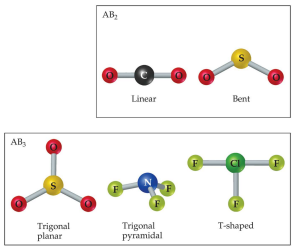
Molecular Geometry



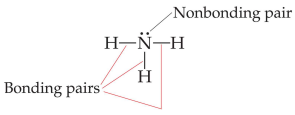
The shape of a molecule plays an important role in its reactivity.

By noting the number of bonding and nonbonding electron pairs we can easily predict the shape of the molecule.

What Determines Molecular Shape?

Electron pairs, (bonding or nonbonding), repel each other.

By assuming the electron pairs are placed as far as possible from each other, we can predict the shape of the molecule.



Electron Domains

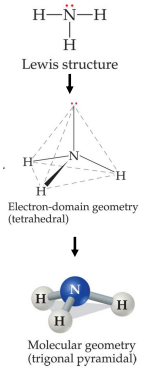
We can refer to the electron pairs around the central atom as electron domains.

In a double or triple bond, all electrons shared between those two atoms are on the same side of the central atom; therefore, they count as one electron domain.

•This molecule has four electron domains.

Electron Domain Geometries

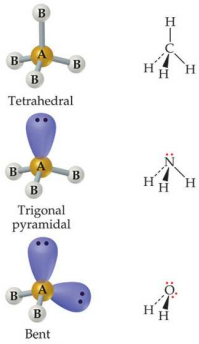
# e⁻ domains	Arrangement	e⁻ domain geometry
2		Linear
3		Trigonal Planar
4		Tetrahedral
5		Trigonal bipyramidal
6		Octahedral



Same number of e- domains – could be different shape

Within each electron domain, then, there might be more than one molecular geometry.

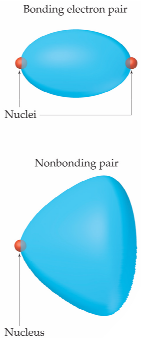
Depending on the number of nonbonding electron pairs

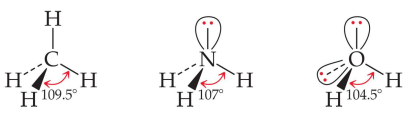


Nonbonding Pairs and Bond Angle

Nonbonding pairs are physically larger than bonding pairs.

Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.





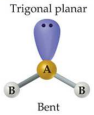
Linear Electron Domain

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	

2 e^- domains – molecule must be linear

Any diatomic molecule – must be linear

Trigonal Planar Electron Domain

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	

There are two molecular geometries:

- Trigonal planar, if all the electron domains are bonding
- Bent, if one of the domains is a nonbonding pair.

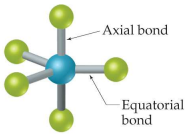
Tetrahedral Electron Domain

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

There are three molecular geometries:

- Tetrahedral, if all are bonding pairs
- Trigonal pyramidal if one is a nonbonding pair

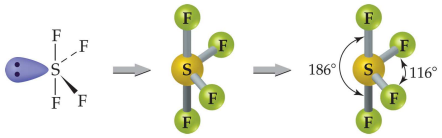
Trigonal Bipyramidal Electron Domain



There are two distinct positions in this geometry:

- Axial
- Equatorial

Lower-energy conformations result from having nonbonding electron pairs in equatorial, rather than axial, positions in this geometry.



Trigonal Bipyramidal Electron Domain

There are four distinct molecular geometries in this domain:

- Trigonal bipyramidal
- Seesaw
- T-shaped
- Linear

Total e- domains	Electron Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5		5	0		PCl_5
		4	1		SF_4
		3	2		ClF_3
		2	3		XeF_2

Octahedral Electron Domain

All positions are equivalent in the octahedral domain.

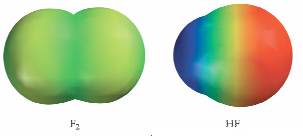
There are three molecular geometries:

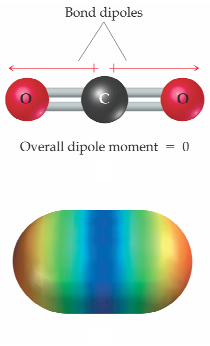
- Octahedral
- Square pyramidal
- Square planar

Total e- domains	Electron Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6		6	0		SF_6
		5	1		BrF_5
		4	2		XeF_4

Polar Molecules

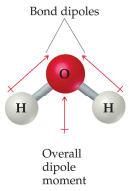
In Chapter 8 we discussed polar bonds.

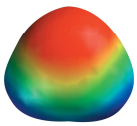




•But just because a molecule possesses polar bonds does not mean the molecule *as a whole* will be polar.

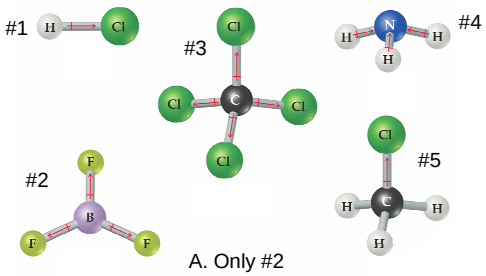
Polar Molecules





By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.

Which of the following molecules are polar?



A. Only #2
B. Only #5
C. #1, #4, and #5
D. #2 and #3

Molecular Geometry Summary

- Identify how many e- domains there are

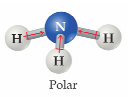
- Select the overall geometry (linear, trigonal planar, etc.)

- Use the number of nonbonding electrons to pick the actual molecular geometry

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	Linear	2	0	Linear	O=C=O
3	Trigonal planar	3	0	Trigonal planar	
		2	1	Bent	

Net dipole = sum of individual dipoles.

If net dipole = 0 then nonpolar otherwise, polar

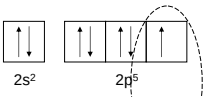


Polar

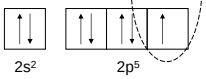
Valence Bond Theory

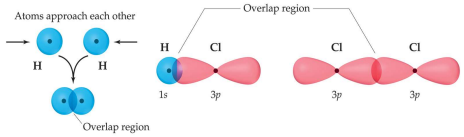
- Valence bond theory says that atoms are bonded together when their valence electrons overlap

Chlorine : [Ne] $2s^2\ 2p^5$ ·Cl:

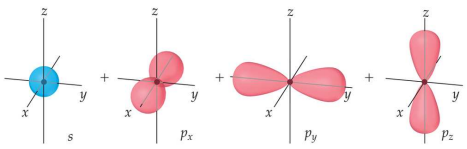


Chlorine : [Ne] $2s^2\ 2p^5$ ·Cl:





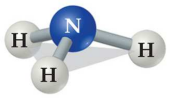
Valence Bond Theory and Molecular Geometry



How do shapes like trigonal pyramidal arise from these orbitals?

The orbitals above cannot explain all the shapes we observe

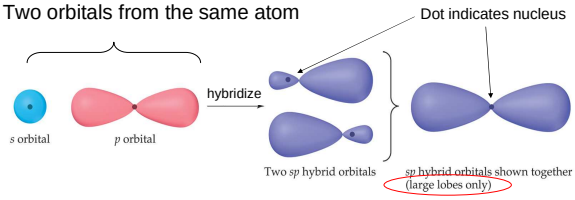
SOLUTION: Hybrid Orbitals



Molecular geometry (trigonal pyramidal)

sp – hybrid orbital

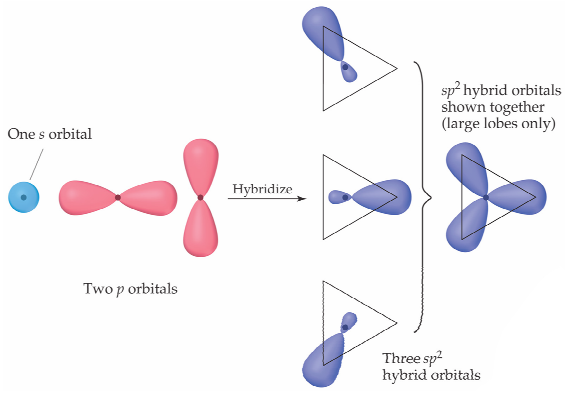
Two orbitals from the same atom



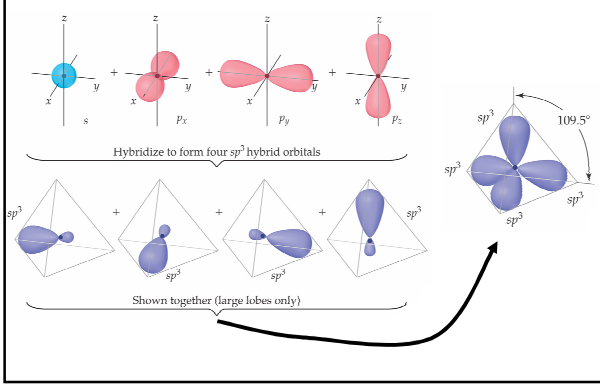
Two hybrid oribtals

Number of initial orbitals = number of hybrid orbitals

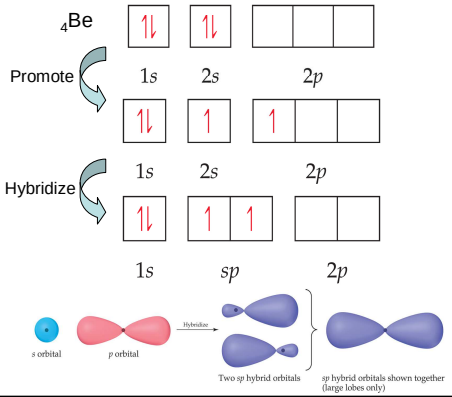
sp^2 – hybrid orbital



sp^3 – hybrid orbital

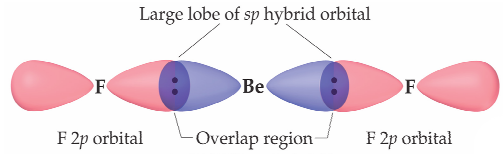


How do Hybrid Orbitals Form?



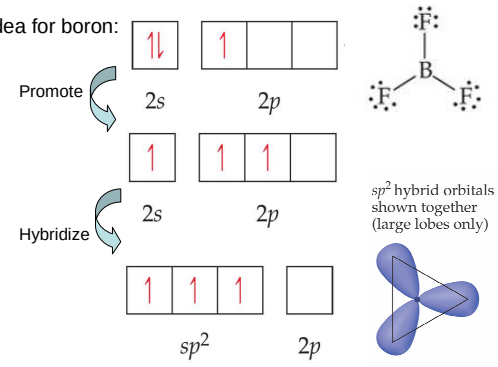
sp – Hybrid Orbitals

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



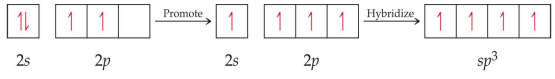
sp^2 - Hybrid Orbitals

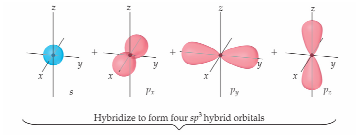
Same idea for boron:

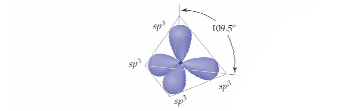


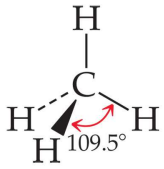
sp^3 - Hybrid Orbitals

Carbon electronic configuration



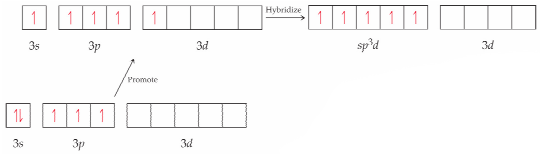




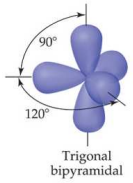


Hybrid Orbitals

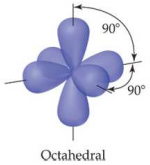
For geometries involving expanded octets on the central atom, we must use *d* orbitals in our hybrids.



Hybrid Orbitals

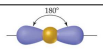


This leads to five degenerate sp^3d orbitals…



…or six degenerate sp^3d^2 orbitals.

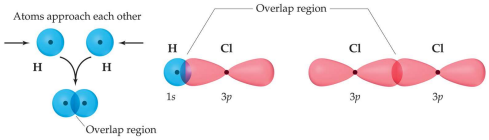
Hybrid Orbitals & Geometric Configuration

# e⁻ domains	Arrangement	e⁻ domain geometry	Hybrid Orbitals
2		Linear	sp
3		Trigonal Planar	sp^2
4		Tetrahedral	sp^3
5		Trigonal bipyramidal	sp^3d
6		Octahedral	sp^3d^2

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.

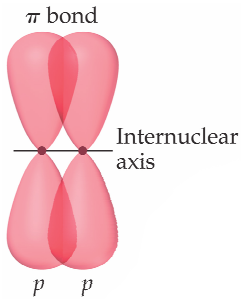
Sigma (σ) Bonds



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

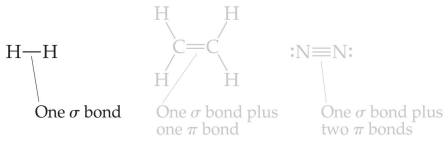
Pi (π) Bonds

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



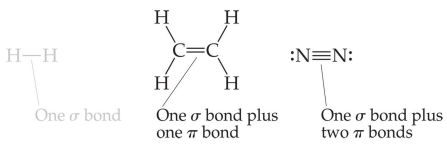
Single Bonds

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

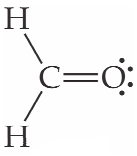


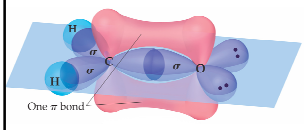
Multiple Bonds

In a multiple bond one of the bonds is a σ bond and the rest are π bonds.



Multiple Bonds

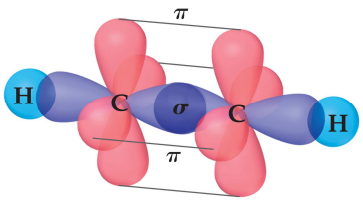




- In a molecule like formaldehyde (shown at left) an sp^2 orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.
- The unhybridized *p* orbitals overlap in π fashion.

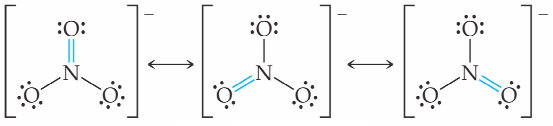
Multiple Bonds

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.

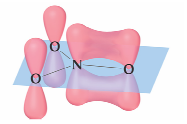


Delocalized Electrons: Resonance

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.

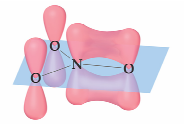


Delocalized Electrons: Resonance

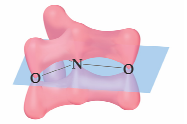


- In reality, each of the four atoms in the nitrate ion has a *p* orbital.
- The *p* orbitals on all three oxygens overlap with the *p* orbital on the central nitrogen.

Delocalized Electrons: Resonance

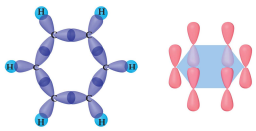


This means the π electrons are not localized between the nitrogen and one of the oxygens, but rather are delocalized throughout the ion.



Resonance

The organic molecule benzene has six σ bonds and a *p* orbital on each carbon atom.



Resonance

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