CHEM 103
CHEMISTRY I

CHAPTER 9:
MOLECULAR GEOMETRY AND BONDING THEORIES

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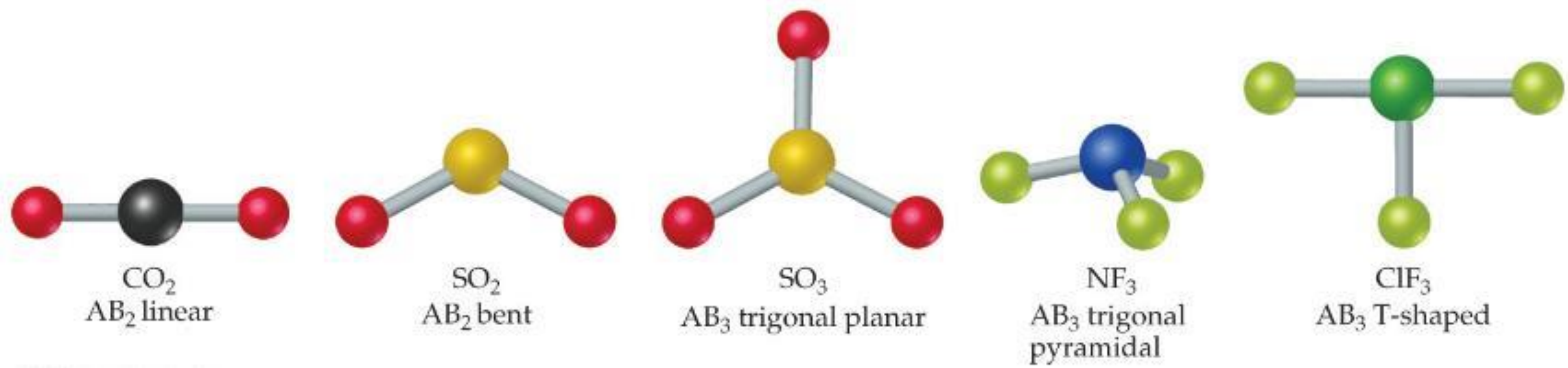
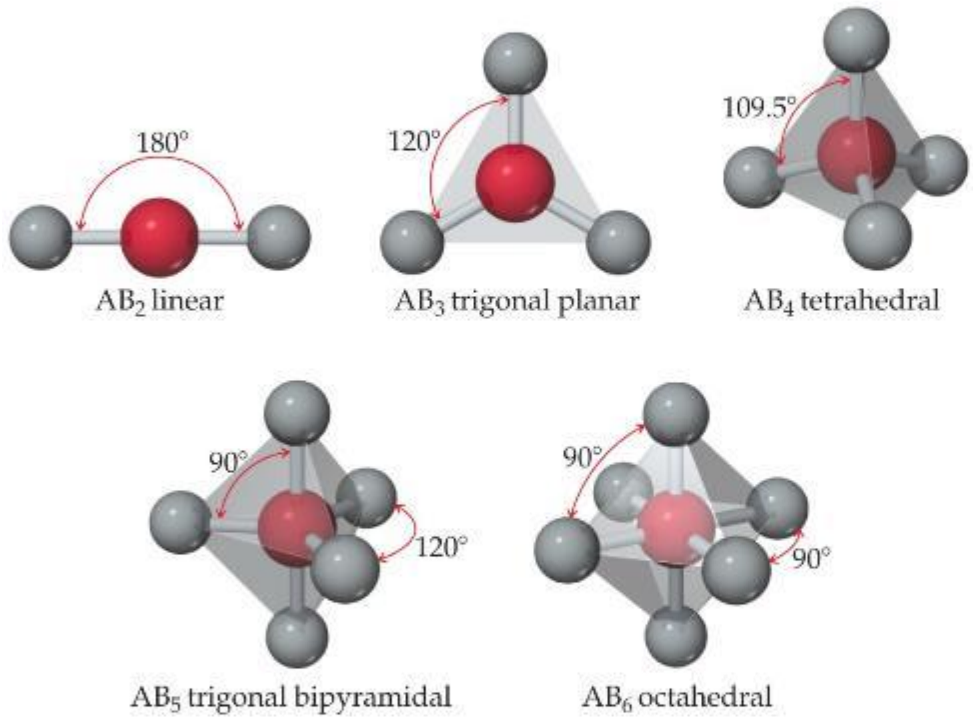
Molecular Shapes

- 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.



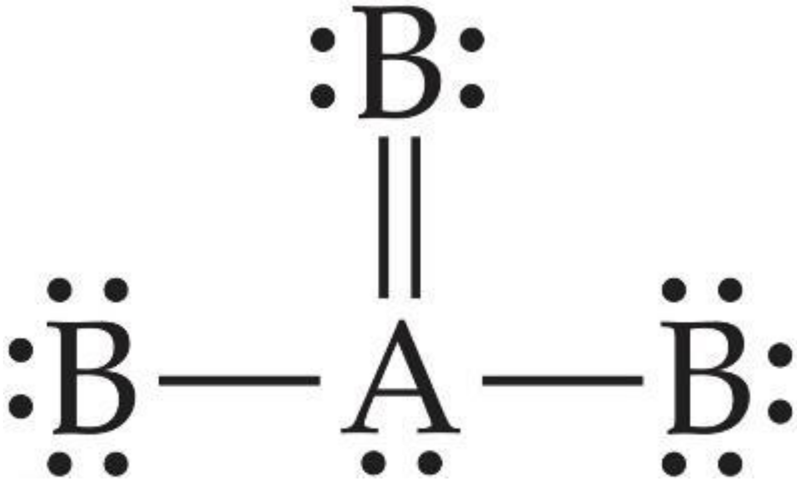
What Determines the Shape of a Molecule?

- Simply put, electron pairs, whether they be 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.



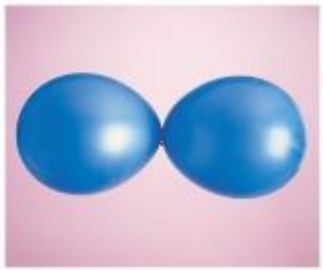
- This is the Valence-Shell Electron-Pair Repulsion (VSEPR) model.

Electron Domains



- We can refer to the directions to which electrons point as **electron domains**. This is true whether there is one or more electron pairs pointing in that direction.
- The central atom in this molecule, A, has four electron domains.

Valence-Shell Electron-Pair Repulsion (VSEPR) Model



Two balloons
linear orientation

Three balloons
trigonal-planar orientation

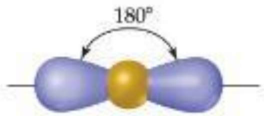
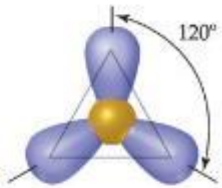
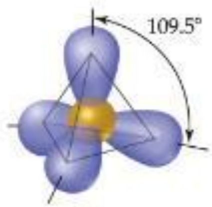
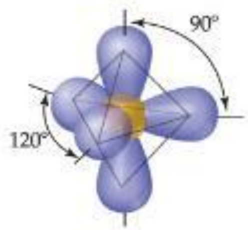
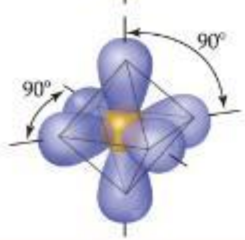
Four balloons
tetrahedral orientation

"The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them."

(The balloon analogy in the figure to the left demonstrates the maximum distances, which minimize repulsions.)

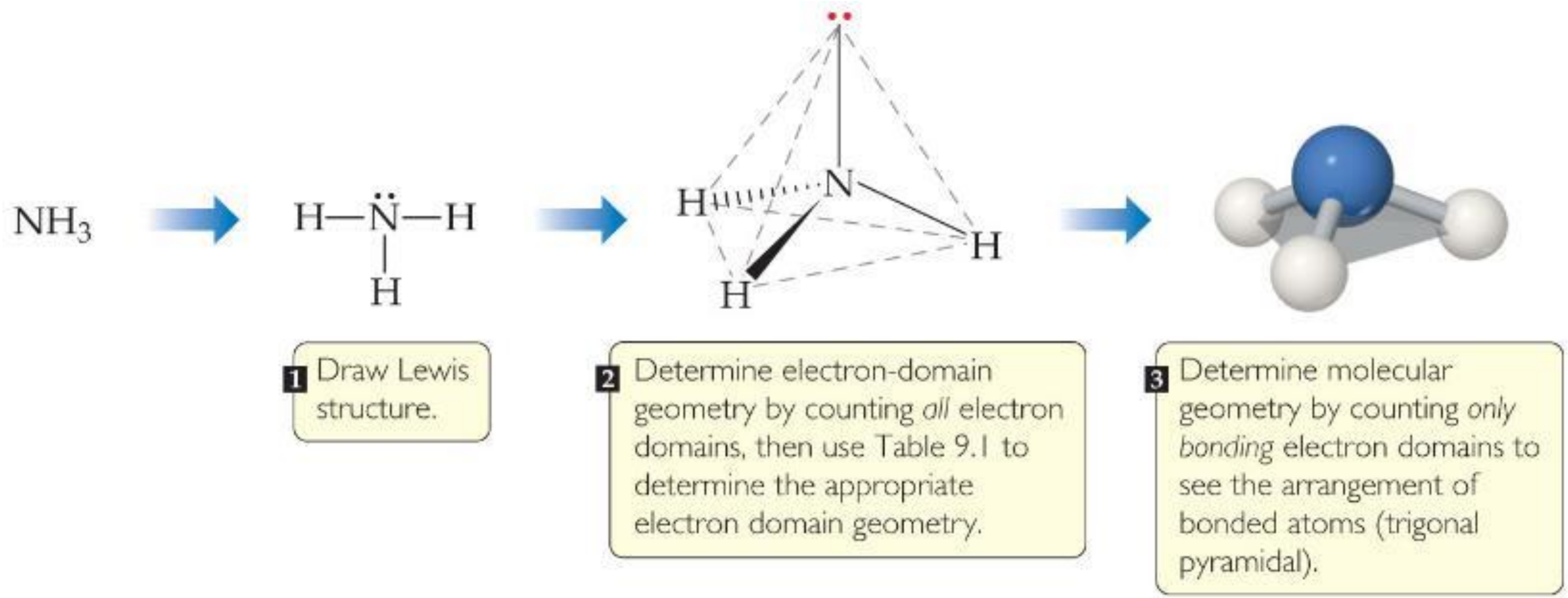
Electron-Domain Geometries

Table 9.1 Electron-Domain Geometries as a Function of Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

- The Table shows the electron-domain geometries for two through six electron domains around a central atom.
- To determine the electron-domain geometry, count the total number of lone pairs, single, double, and triple bonds on the central atom.

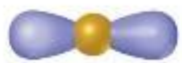
Molecular Geometries



- Once you have determined the electron-domain geometry, use the arrangement of the bonded atoms to determine the **molecular geometry**.
- Tables 9.2 and 9.3 show the potential molecular geometries. We will look at each electron domain to see what molecular geometries are possible.

Linear Electron Domain

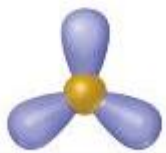
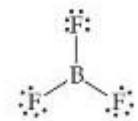
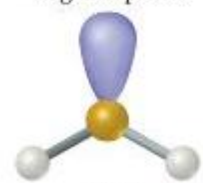
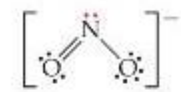
Table 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\underset{..}{O}}=C=\ddot{\underset{..}{O}}$

- In the linear domain, there is only one molecular geometry: linear.
- NOTE: If there are only two atoms in the molecule, the molecule will be linear no matter what the electron domain is.

Trigonal Planar Electron Domain

Table 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

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 electron domains are bonding, and
  - – bent, if one of the domains is a nonbonding pair.

Tetrahedral Electron Domain

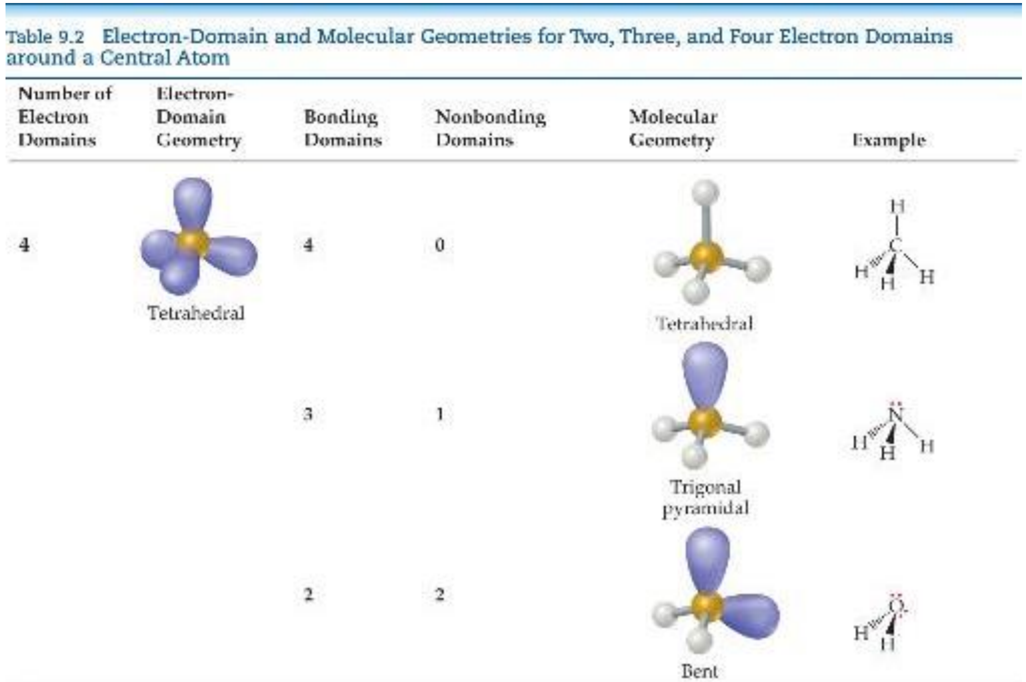


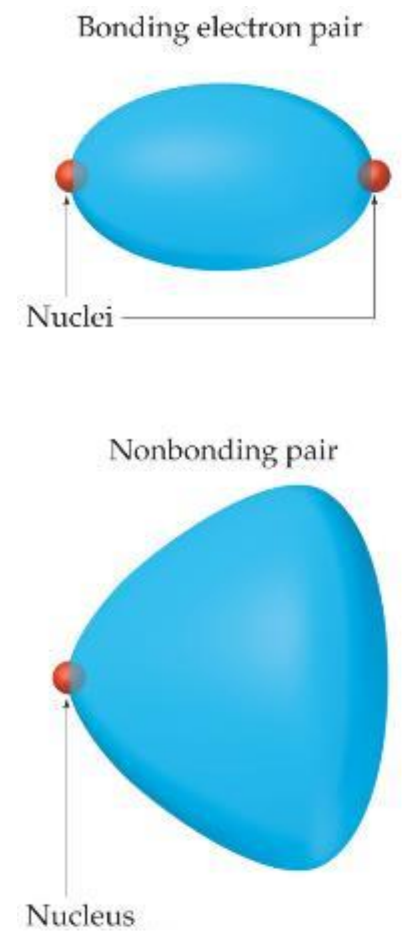
Table 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

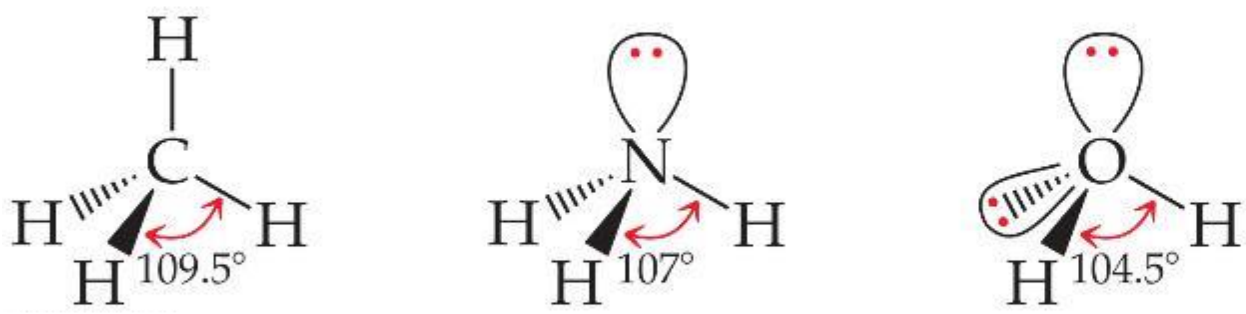
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4	Tetrahedral	4	0	Tetrahedral	CH_4
		3	1	Trigonal pyramidal	NH_3
		2	2	Bent	H_2O

- There are three molecular geometries:
  - tetrahedral, if all are bonding pairs,
  - trigonal pyramidal, if one is a nonbonding pair, and
  - bent, if there are two nonbonding pairs.

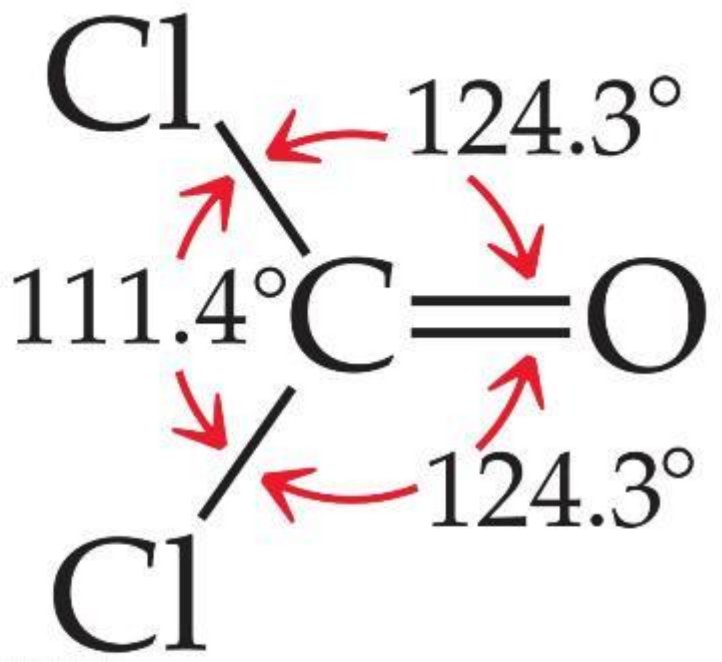
Nonbonding Pairs and Bond Angle

- Nonbonding pairs are physically larger than bonding pairs.
- Therefore, their repulsions are greater; this tends to compress bond angles.





Multiple Bonds and Bond Angles

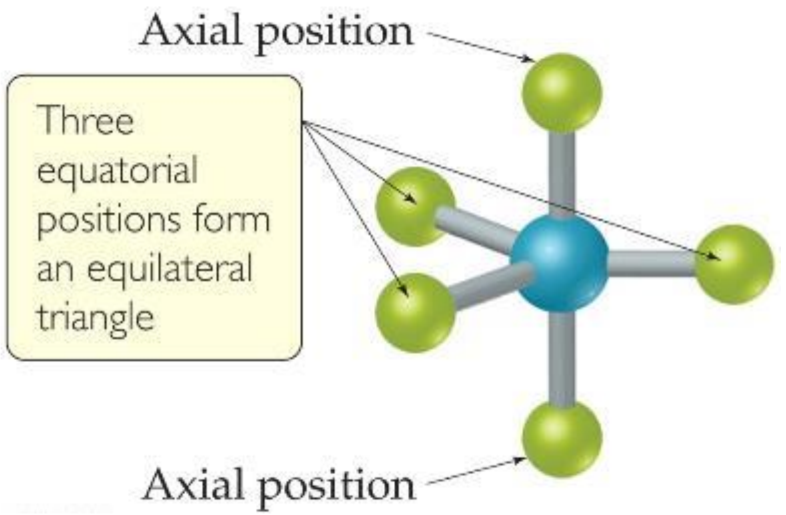


- Double and triple bonds have larger electron domains than single bonds.
- They exert a greater repulsive force than single bonds, making their bond angles greater.

Expanding beyond the Octet Rule

- Remember that some elements can break the octet rule and make *more* than four bonds (or have more than four electron domains).
- The result is two more possible electron domains: five = trigonal bipyramidal; six = octahedral (as was seen in the slide on electron-domain geometries).

Trigonal Bipyramidal Electron Domain



- There are two distinct positions in this geometry:
  - Axial
  - Equatorial
- Lone pairs occupy equatorial positions.

Trigonal Bipyramidal Electron Domain

- There are four distinct molecular geometries in this domain:
  - Trigonal bipyramidal
  - Seesaw
  - T-shaped
  - Linear

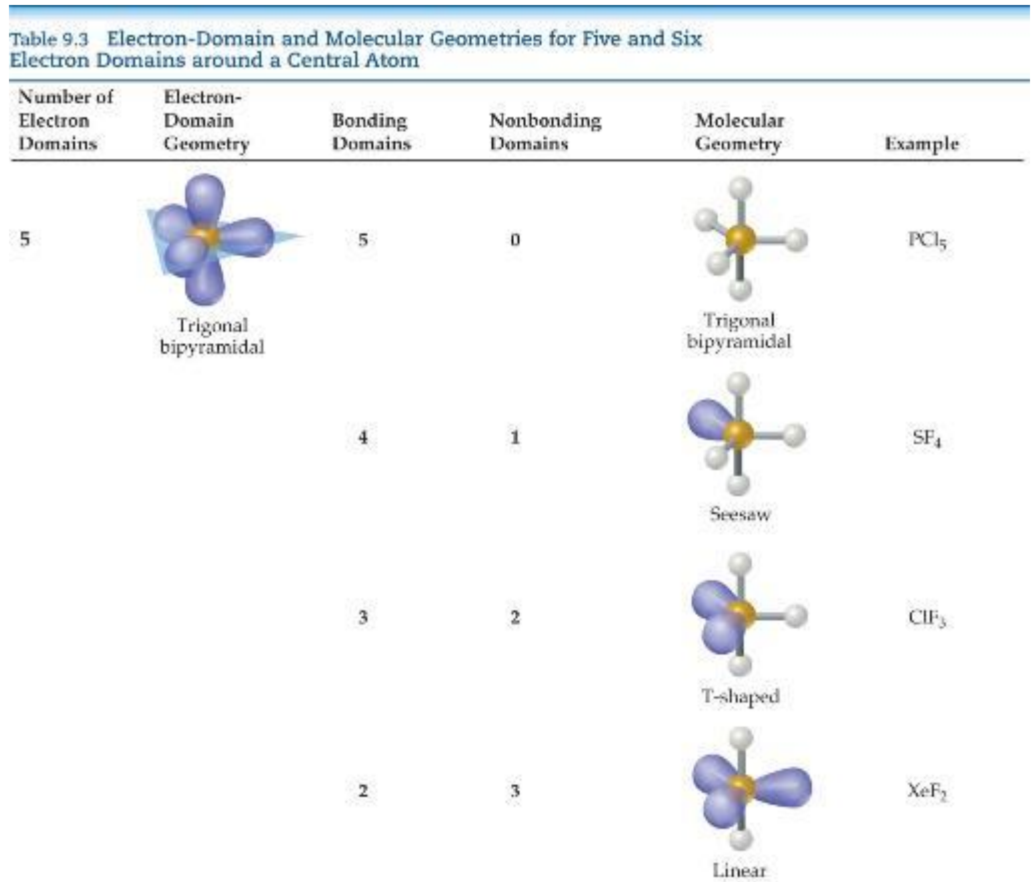
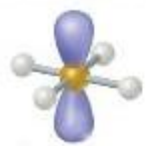


Table 9.3 Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
		4	1	Seesaw	SF_4
		3	2	T-shaped	ClF_3
		2	3	Linear	XeF_2

Octahedral Electron Domain

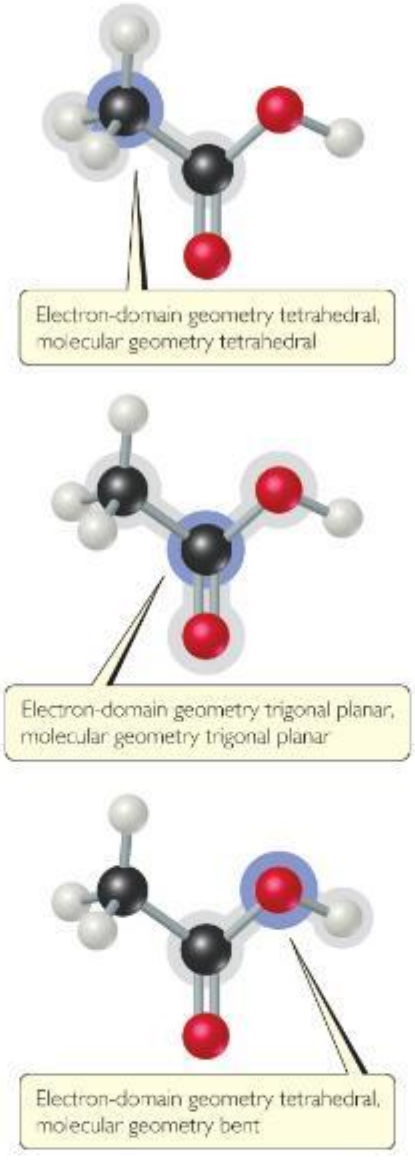
Table 9.3 Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

- All positions are equivalent in the octahedral domain.
- There are three molecular geometries:
  - Octahedral
  - Square pyramidal
  - Square planar

Shapes of Larger Molecules

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



Polarity of Molecules

Ask yourself:

COVALENT or IONIC? If COVALENT:

Are the BONDS polar?

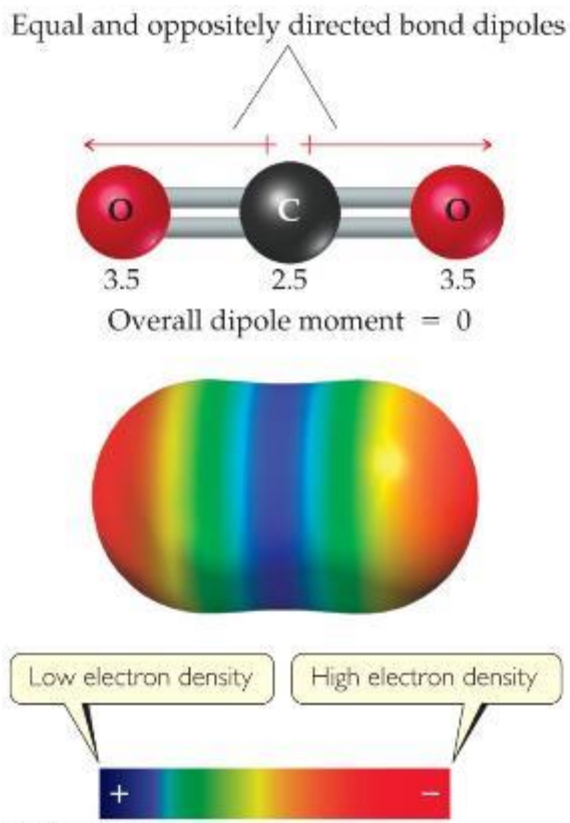
a. NO: The molecule is NONPOLAR!
b. YES: Continue—Do the AVERAGE position of δ+ and δ– coincide?

1) YES: The molecule is NONPOLAR.
2) NO: The molecule is POLAR.

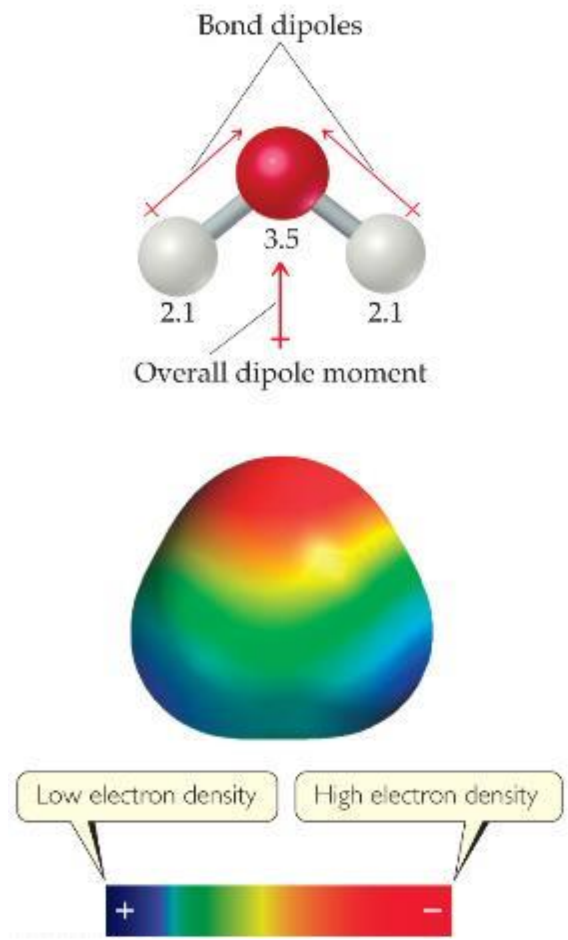
NOTE: Different atoms attached to the central atom have different polarity of bonds.

Comparison of the Polarity of Two Molecules

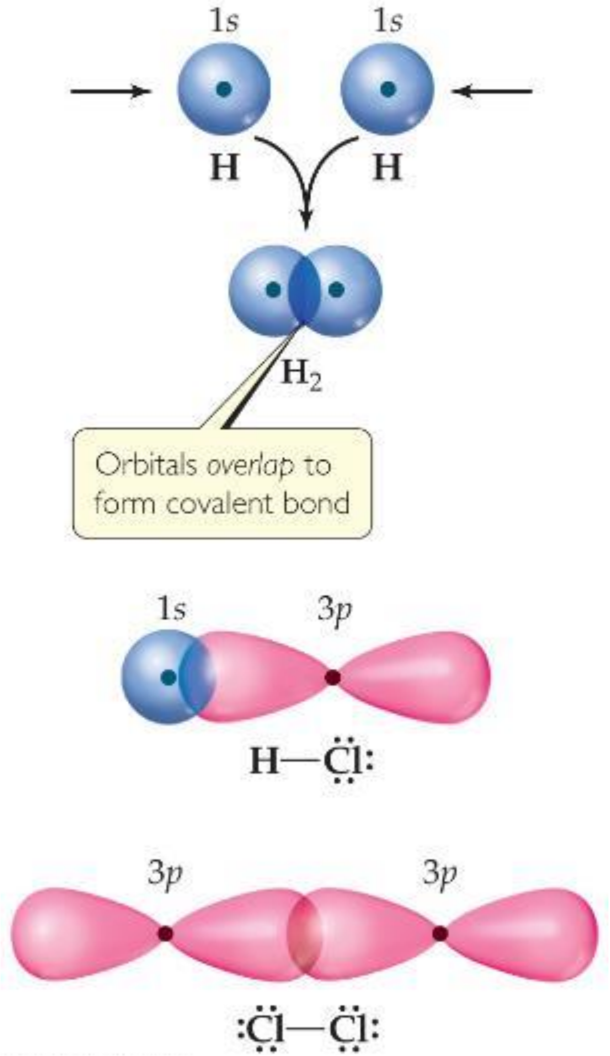
A NONPOLAR molecule



A POLAR molecule



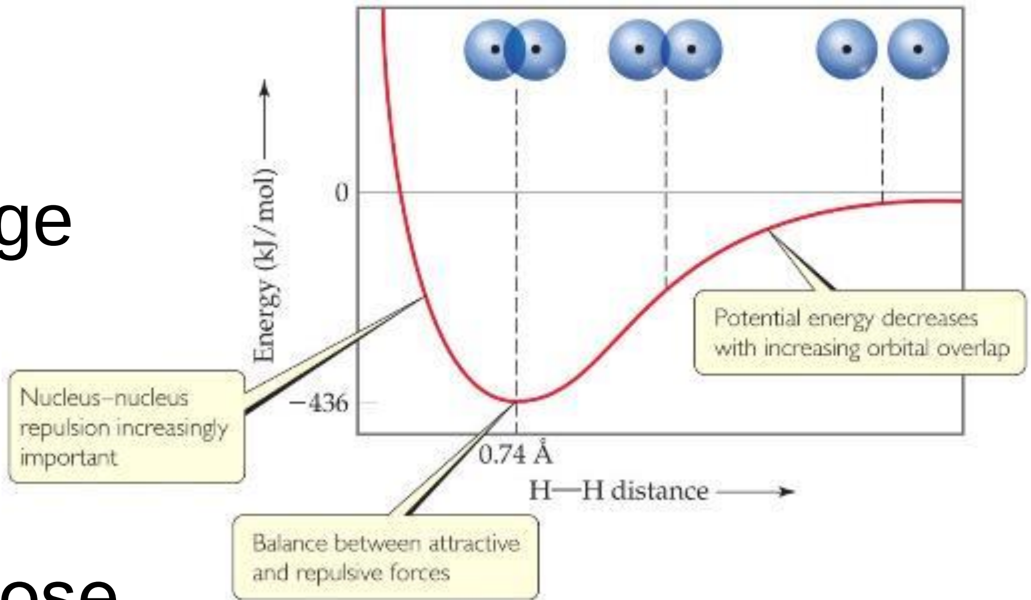
Valence-Bond Theory



- In Valence-Bond Theory, electrons of two atoms begin to occupy the same space.
- This is called “overlap” of orbitals.
- The sharing of space between two electrons of opposite spin results in a covalent bond.

Overlap and Bonding

- Increased overlap brings the electrons and nuclei closer together until a balance is reached between the like charge repulsions and the electron-nucleus attraction.
- Atoms can't get too close because the internuclear repulsions get too great.



VSEPR and Hybrid Orbitals

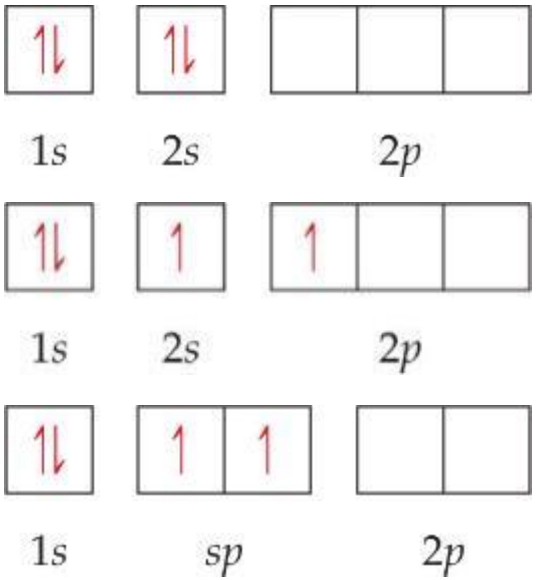
- VSEPR predicts shapes of molecules very well.
- How does that fit with orbitals?
- Let's use H_2O as an example:
- If we draw the best Lewis structure to assign VSEPR, it becomes bent.
- If we look at oxygen, its electron configuration is $1s^2 2s^2 2p^4$. If it shares two electrons to fill its valence shell, they should be in $2p$.
- Wouldn't that make the angle 90° ?
- Why is it 104.5° ?

Hybrid Orbitals

- **Hybrid orbitals** form by “mixing” of atomic orbitals to create new orbitals of equal energy, called degenerate orbitals.
- When two orbitals “mix” they create two orbitals; when three orbitals mix, they create three orbitals; etc.

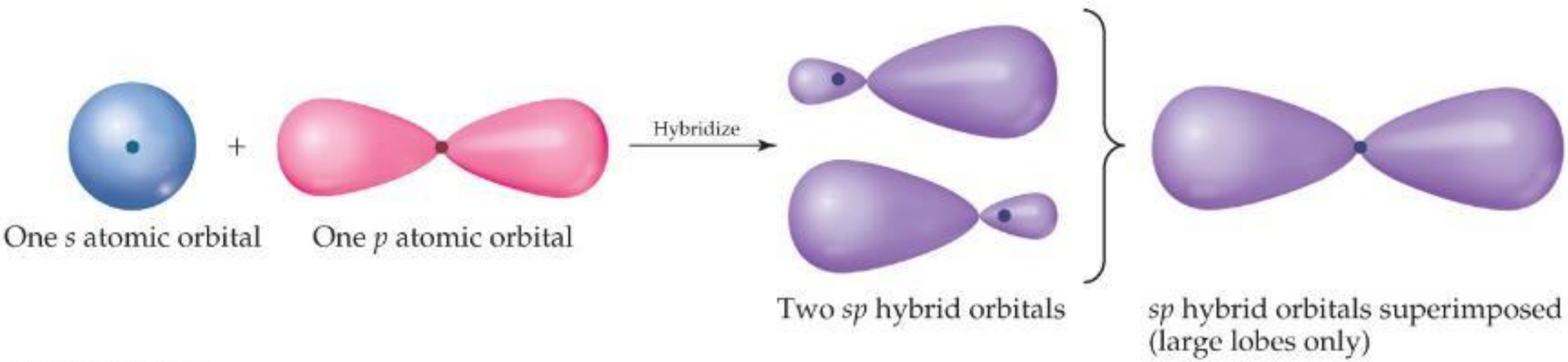
Be—*sp* hybridization

- When we look at the orbital diagram for beryllium (Be), we see that there are only paired electrons in full sub-levels.
- Be makes electron deficient compounds with two bonds for Be. Why? *sp* hybridization (mixing of one *s* orbital and one *p* orbital)



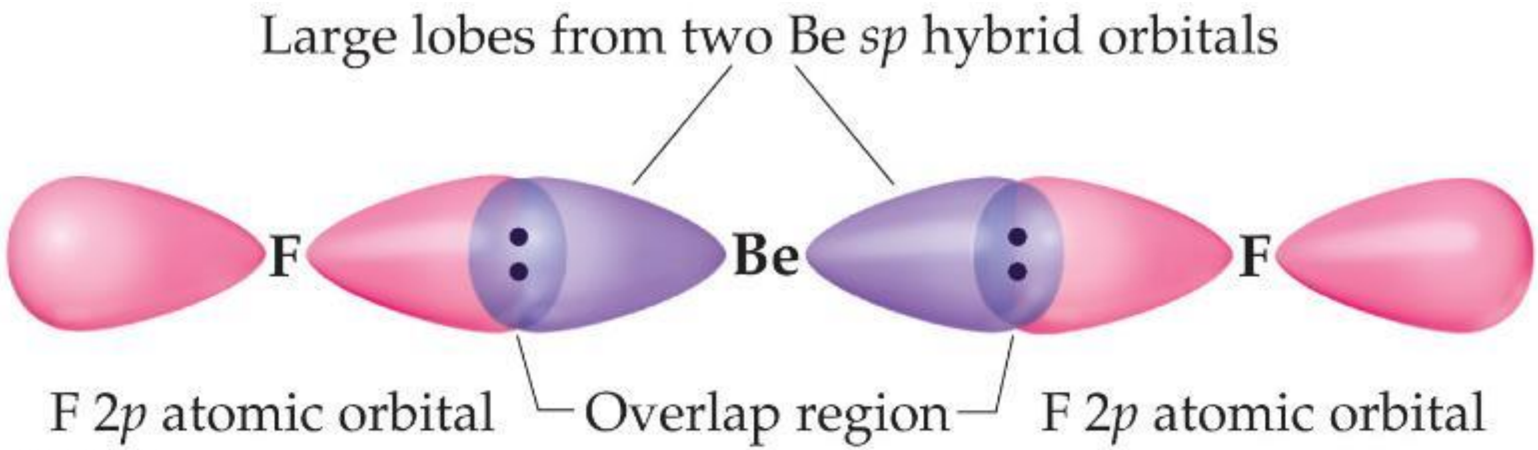
sp Orbitals

- 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.



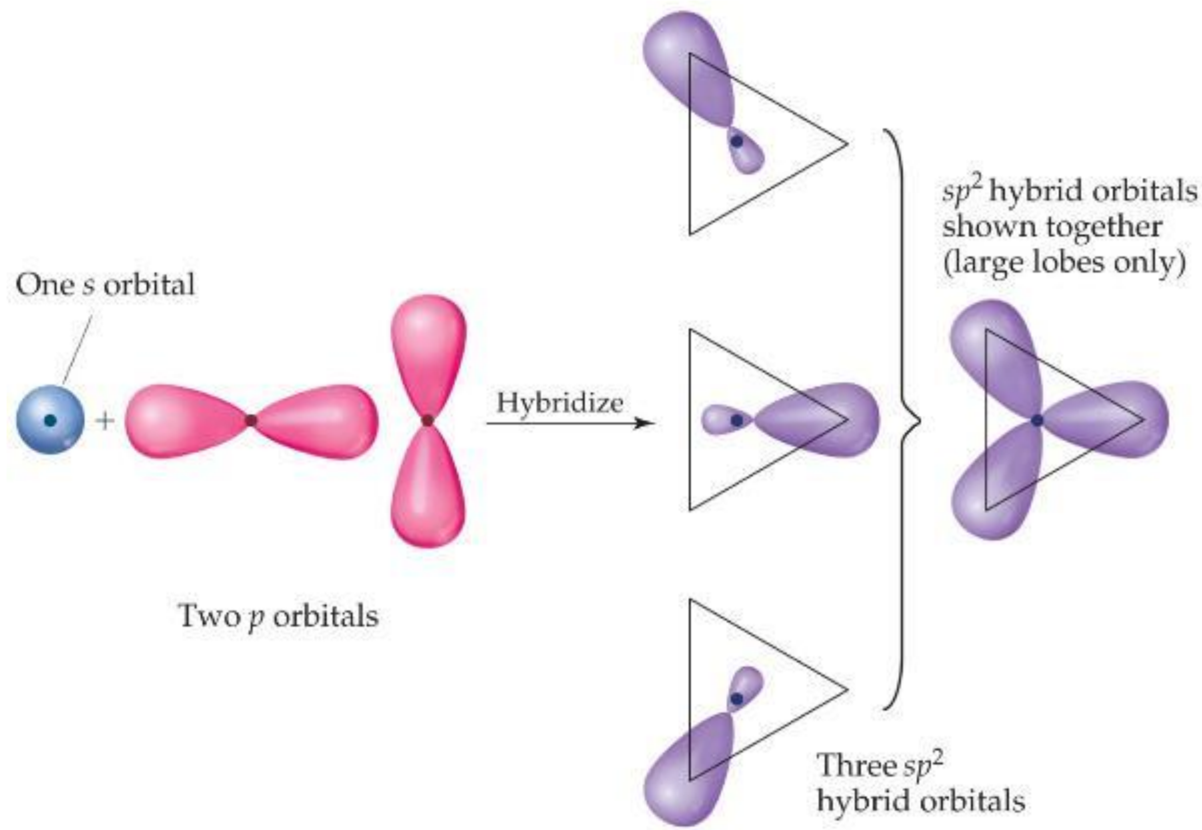
Position of *sp* Orbitals

- 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.



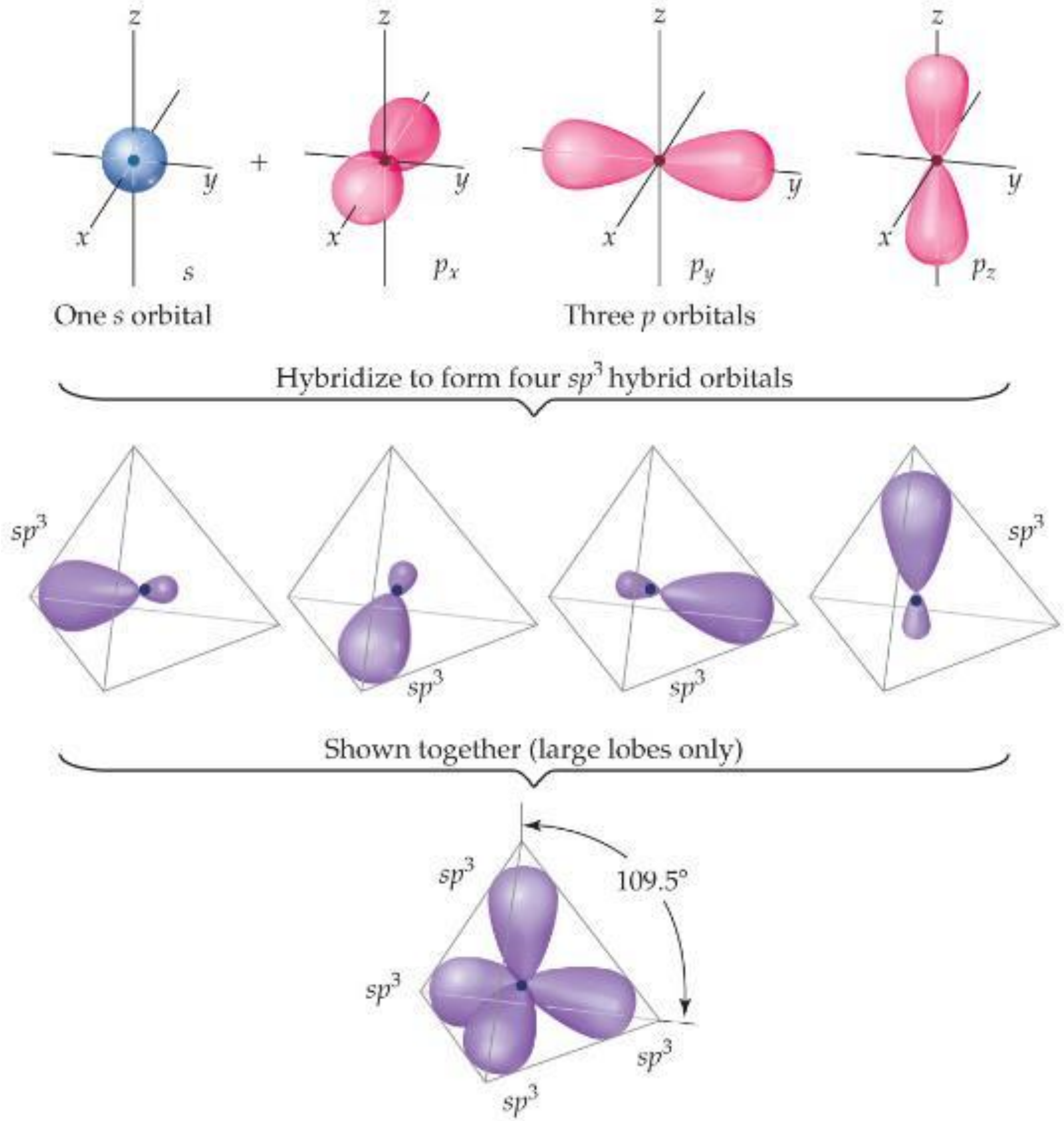
Boron—Three Electron Domains Gives *sp*^{2} Hybridization

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.

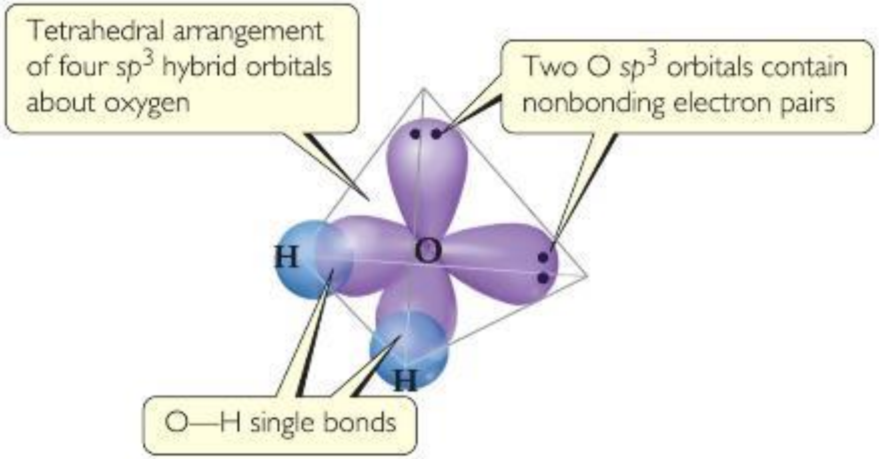


Hypervalent Molecules

- The elements which 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.

What Happens with Water?

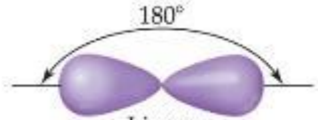
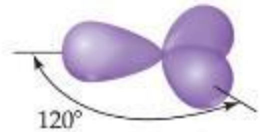
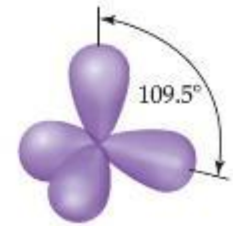
- We started this discussion with H_2O and the angle question: Why is it 104.5° instead of 90° ?
- Oxygen has two bonds and two lone pairs—four electron domains.
- The result is sp^3 hybridization!



Hybrid Orbital Summary

1) Draw the Lewis structure.
2) Use VSEPR to determine the electron-domain geometry.
3) Specify the hybrid orbitals needed to accommodate these electron pairs.

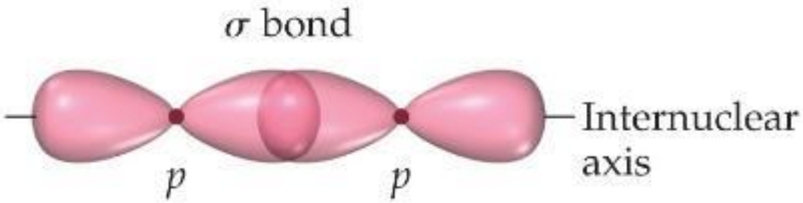
Table 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets

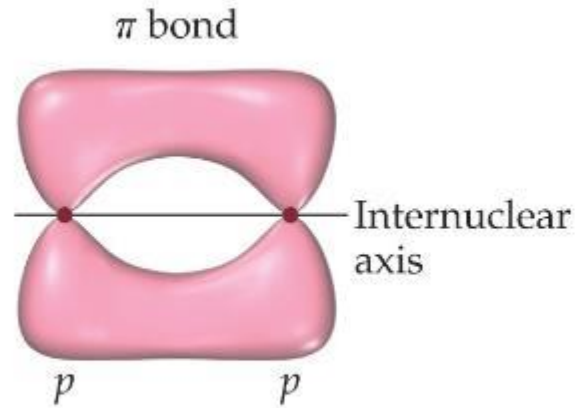
Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

Types of Bonds

- How does a double or triple bond form?
- It *can't*, if we only use hybridized orbitals.
- *However*, if we use the orbitals which are *not* hybridized, we can have a "side-ways" overlap.
- Two types of bonds:
- Sigma (σ) bond
- Pi (π) bond

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
  - side-to-side overlap.
  - electron density above and below the internuclear axis.