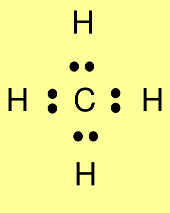
Shapes of Molecules

- In this section we will use Lewis structures as an introduction to the shapes of molecules.
- The key concepts are:
  - **Electron pairs repel each other.**
  - **Electron pairs assume orientations to minimize repulsion**
- This is the Valence Shell Electron Pair Repulsion Theory (VSEPR)

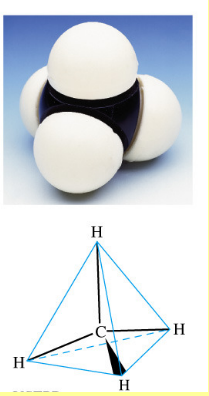
VSEPR

- Example: Methane CH_4



The 4 bond pairs must orient themselves to minimize their repulsion.

VSEPR Methane



The minimum interaction occurs when the electron pairs point towards the vertices of a tetrahedron.

The carbon is in the centre and the hydrogen are at the vertices. The molecule is tetrahedral.

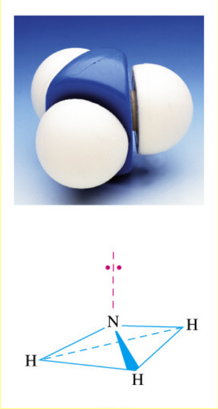
VSEPR Ammonia

- Example: Ammonia NH_3

$$\begin{array}{ccc} & \cdot\cdot & \\ H : & N & : H \\ & \cdot\cdot & \\ & H & \end{array}$$

The 4 electron pairs must still orient themselves to minimize their repulsion.

VSEPR Ammonia

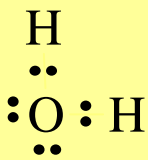


The minimum interaction still occurs when the electron pairs point towards the vertices of a tetrahedron.

The nitrogen is in the centre and the hydrogens are at three of the vertices. The lone pair points to the fourth. The molecule is trigonal pyramidal.

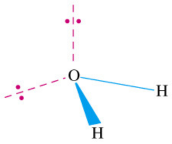
VSEPR Water

- Example: Water H_2O



The 4 electron pairs must orient themselves to minimize their repulsion.

VSEPR Water



The minimum interaction still occurs when the electron pairs point towards the vertices of a tetrahedron.

The oxygen is in the centre, the hydrogens are at two of the vertices. The lone pairs point to the other two. The molecule is bent.

Bond Angles

- This analysis suggests that all three molecules should have bond angles of $109.5^{o.}$
  - The methane bond angle is 109.5^{o} but for ammonia it is 107^{o} and in water it is 104.5^{o}
  - The lone pair electrons are not constrained as much as the bonding pairs. They spread out thus the repulsive forces are:

Lone pair-lone pair>Lone pair-bond pair>bond pair-bond pair

Molecular Geometry

- VSEPR theory can be used to describe the shapes of most molecules.
- Warnings
  - When you describe the shape, don’t include the lone pairs. (water is bent, not tetrahedral)
  - Molecules have three dimensions (methane is a tetrahedron not a square)
- Be familiar with table 10.1 pg 399-400

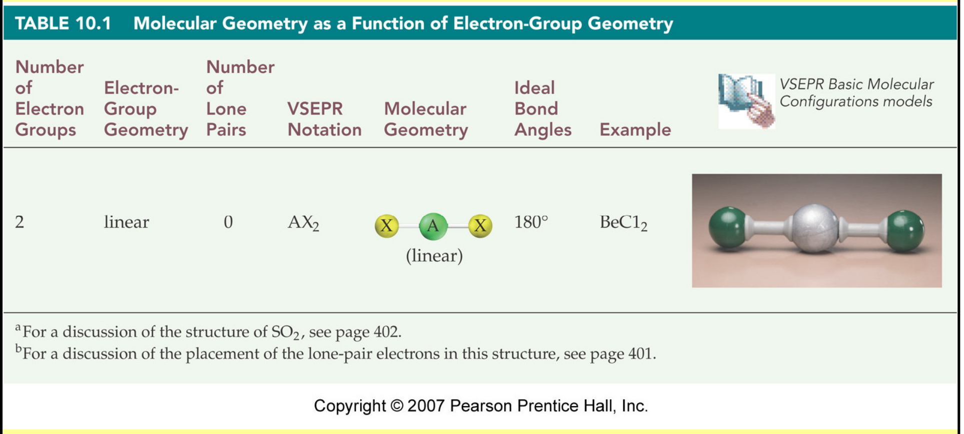
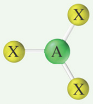
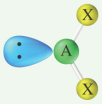


TABLE 10.1 Molecular Geometry as a Function of Electron-Group Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	*VSEPR Basic Molecular Configurations models*
2	linear	0	AX_2	X A X (linear)	180°	$BeC1_2$	

[a] For a discussion of the structure of SO_2, see page 402.
[b] For a discussion of the placement of the lone-pair electrons in this structure, see page 401.

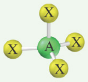
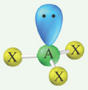
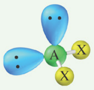
TABLE 10.1 (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
3	trigonal-planar	0	AX_3	 (trigonal planar)	120°	BF_3 
	trigonal-planar	1	AX_2E	 (bent)	120°	SO_2[a]

[a] For a discussion of the structure of SO_2, see page 402.

[b] For a discussion of the placement of the lone-pair electrons in this structure, see page 401.

TABLE 10.1 (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
4	tetrahedral	0	AX_4	 (tetrahedral)	109.5°	CH_4 
	tetrahedral	1	AX_3E	 (trigonal-pyramidal)	109.5°	NH_3
	tetrahedral	2	AX_2E_2	 (bent)	109.5°	OH_2

[a] For a discussion of the structure of SO_2, see page 402.

[b] For a discussion of the placement of the lone-pair electrons in this structure, see page 401.

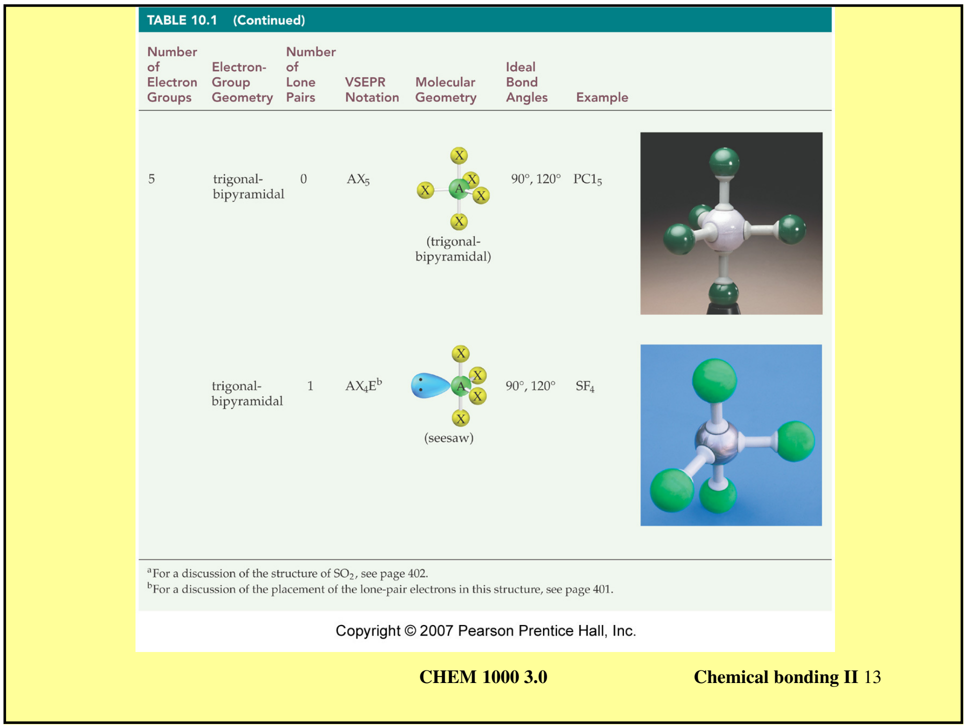


TABLE 10.1 (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
5	trigonal-bipyramidal	0	AX_5	(trigonal-bipyramidal)	90°, 120°	PCl_5
	trigonal-bipyramidal	1	AX_4E^b	(seesaw)	90°, 120°	SF_4

[a] For a discussion of the structure of SO_2, see page 402.
[b] For a discussion of the placement of the lone-pair electrons in this structure, see page 401.

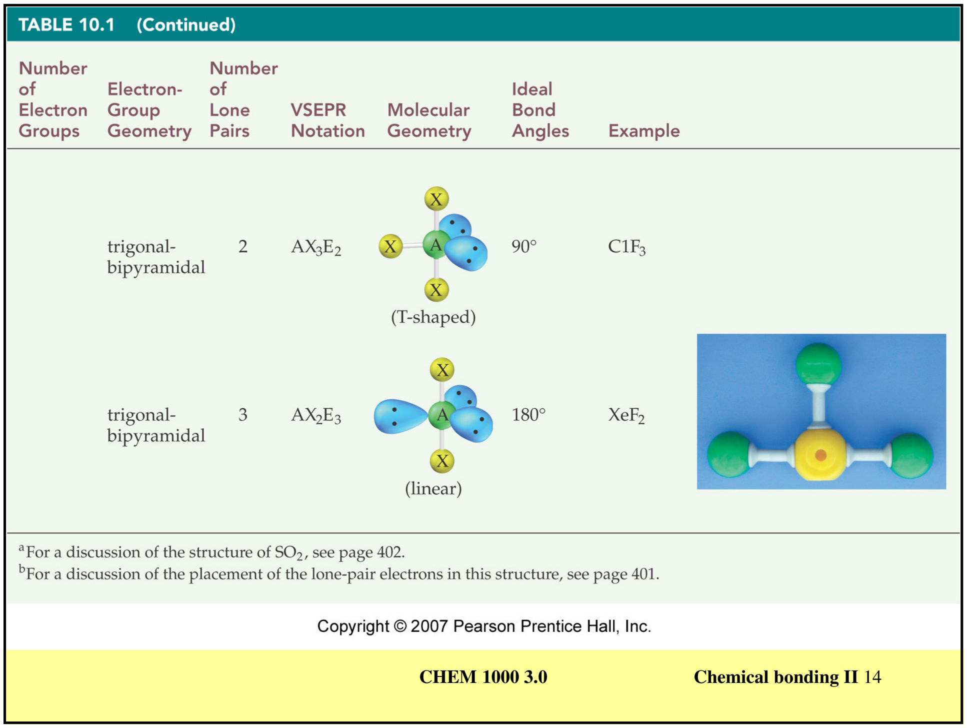


TABLE 10.1 (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
	trigonal-bipyramidal	2	AX_3E_2	(T-shaped)	90°	ClF_3
	trigonal-bipyramidal	3	AX_2E_3	(linear)	180°	XeF_2

[a] For a discussion of the structure of SO_2, see page 402.
[b] For a discussion of the placement of the lone-pair electrons in this structure, see page 401.

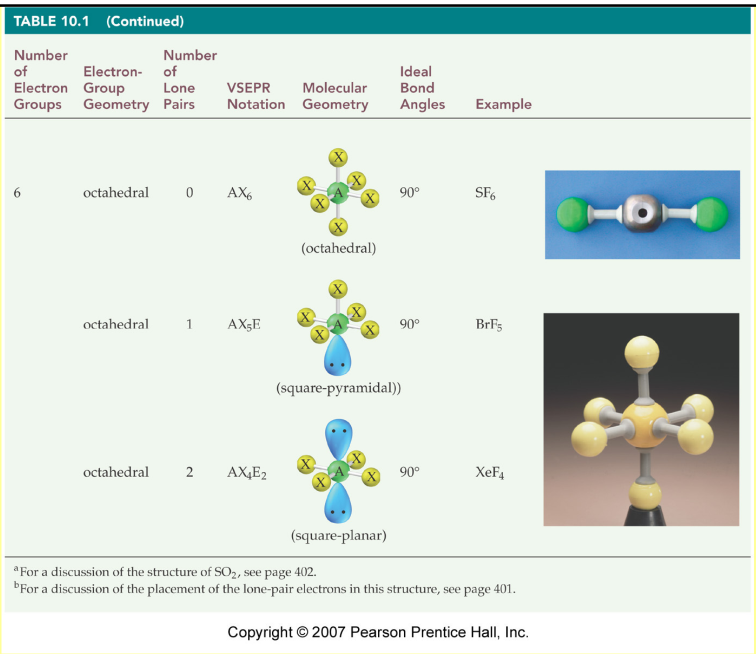


TABLE 10.1 (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
6	octahedral	0	AX_6	(octahedral)	90°	SF_6
	octahedral	1	AX_5E	(square-pyramidal))	90°	BrF_5
	octahedral	2	AX_4E_2	(square-planar)	90°	XeF_4

[a] For a discussion of the structure of SO_2, see page 402.

[b] For a discussion of the placement of the lone-pair electrons in this structure, see page 401.

Going Beyond Lewis Structures

- Lewis structures are very useful in explaining the bonding in simple molecules and in predicting molecular shapes.
- They do not explain why electrons in bond pairs bring nuclei together.
- They can not be used to estimate bond lengths or bond strengths.

Going Beyond Lewis Structures

- There are two currently used bonding theories, valence bond theory and molecular orbital theory.
- Valence bond theory envisions bonding as resulting from the overlap of atomic orbitals.
- Molecular orbital theory moves past atomic orbitals and derives orbitals that belong to the molecule as a whole.
- We will concentrate on valence bond theory as that is sufficient to rationalize the structures we see.

Valence Bond Method

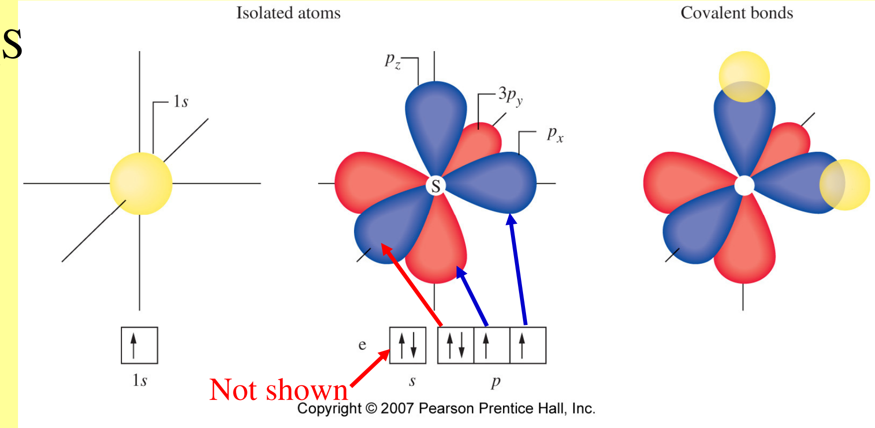
- This method considers what happens to the valence orbitals (the outer shell).
- If the atoms start a long way apart, there is no interaction.
- As the atoms move closer together the orbitals may overlap.
- If there is an electron in the orbital then there is a high probability of finding an electron between the nuclei.
- This is the region where there is a covalent bond.

Valence Bond Method

- We cannot ignore the previously developed rules, so there are only two electrons per bond
  - Overlap can only occur for 2 half filled orbitals or one empty and one filled orbital.

Valence Bond Method

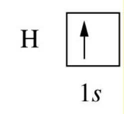
H_2S

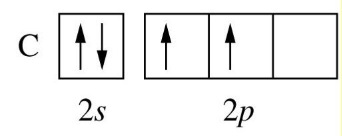


This suggests the bond angle should be 90^{o}.
It is 92^{o}.

Valence Bond method for methane

- Chemically methane is stable
- We know from VSEPR that methane is tetrahedral
- BUT



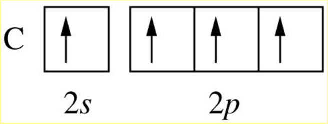


Valence Bond method for methane

- The valence bond theory (so far) would suggest that the 1s electrons from H will be donated to the p orbitals to “pair-up” the unpaired electrons.
- In this case we would have CH_2
- That’s not what is seen. We need CH_4.

Valence Bond method for methane

- Somehow the carbon needs to have 4 unpaired electrons
- This gives 4 unpaired electrons



Valence Bond method for methane

- This costs energy, as it makes an excited state C atom.
- Also if we try to use these orbitals in bonding, the orientation is wrong.
  - If hydrogens attached to the “p” orbitals, they would be orthogonal.
  - Where would the overlap with the “s” be?
  - We know the molecule is tetrahedral.

Valence Bond Rethinking

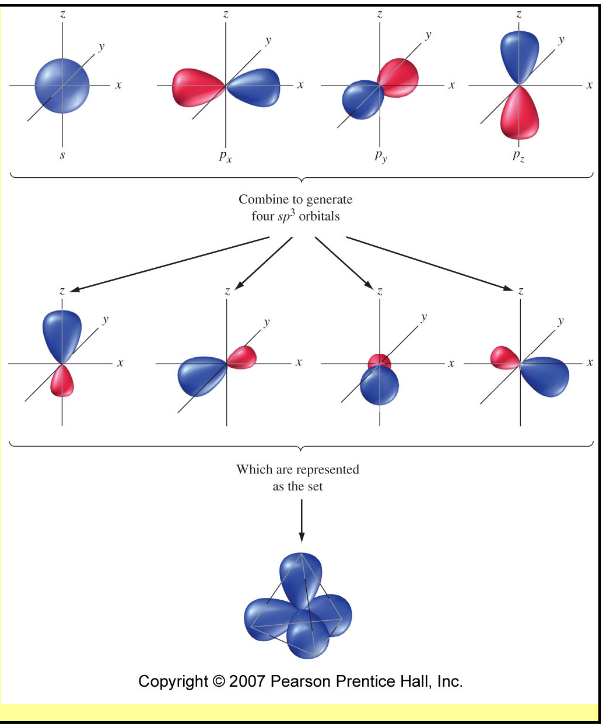
- We can no longer assume that the orbitals in a bonded atom are the same as those of an isolated atom.
- Remember that the atomic orbitals come from solving an equation assuming a single nucleus. In a molecule the electron has to respond to more nuclei.
- We should solve the “new” problem, but we usually say we can combine the atomic orbitals in some way.

Valence Bond method for methane

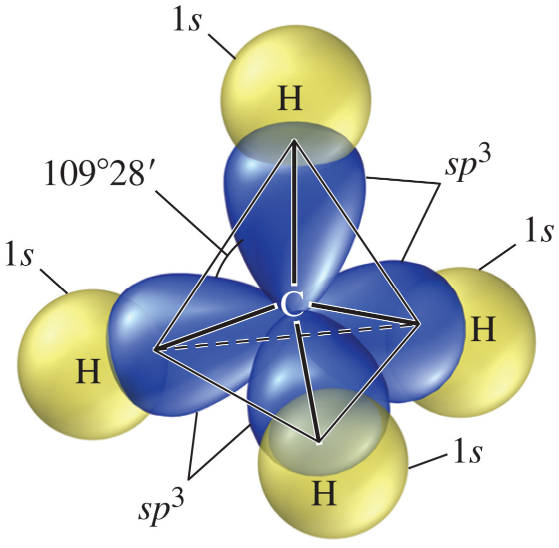
- Since the orbitals are wave functions, we can take the 2s and 2p wave functions and combine them to give 4 equivalent wave functions. These can be made to have the same shape and energy.
- This is called hybridization and the resulting orbitals are called hydrid orbitals.
- The combination of one “s” and three “p” orbitals gives four “sp^3” hybrid orbitals.

Generation of sp^3 hybrid orbitals

Same shape but different orientation to minimize interaction



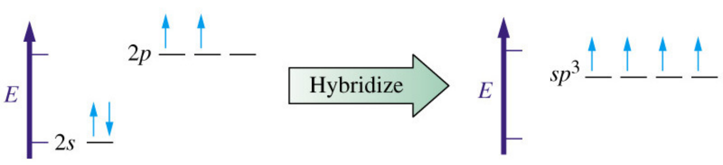
Methane



Energy and Hybrid Orbitals

- What about the energy?
- The energy of the orbitals is conserved because the sp^3 orbitals have an energy between the s and p orbitals.

C

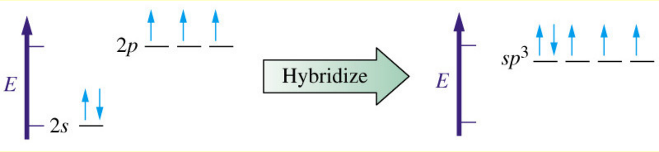


Energy and Hybrid Orbitals

- However there will be an energy cost in making the sp hybrids with one electron in each.
  - The orbitals are generated assuming only one electron
- So why would the molecule do something that will cost energy?
- Once the molecule is formed you release the bond energy. If this is greater than the “cost” then it is worthwhile.

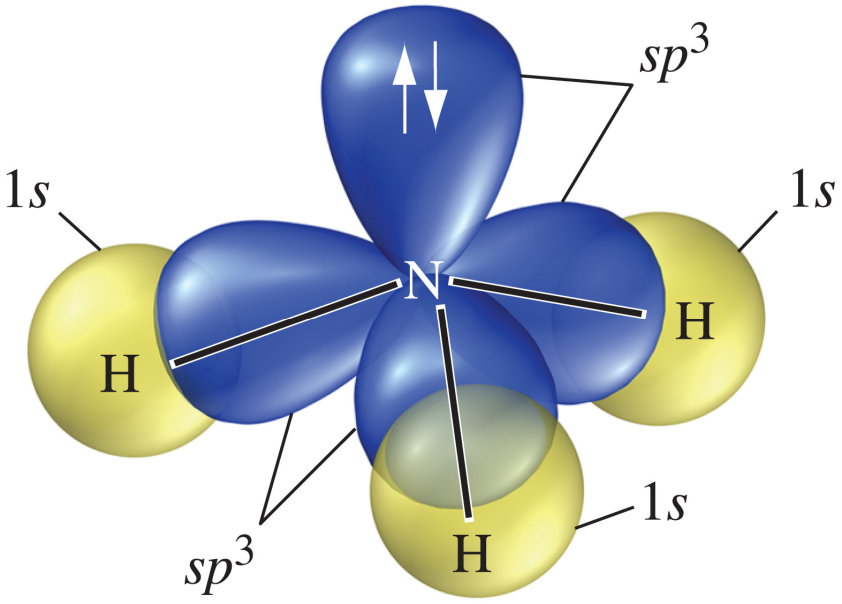
Ammonia

N



- Now we have a pair of electrons in one of the sp^3 hybrid orbitals, so it can’t bond with hydrogen.

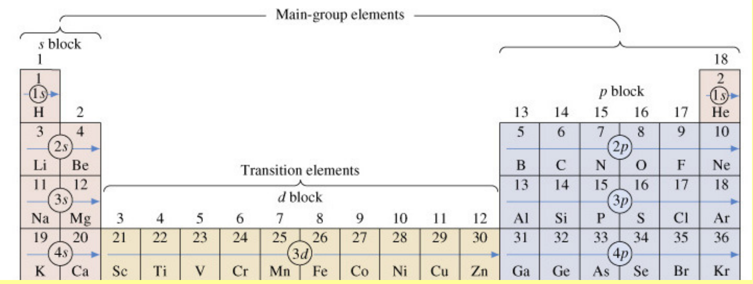
Ammonia



NH_3 versus PH_3

- NH_3 has sp^3 bonding and a bond angle of ~109.
- PH_3 does not hybridize.
- WHY NOT?
- The energy gain in forming the bonds is not enough to get back the energy to make the hybrids.
- This is because the energy separation between 3s and 3p is higher than 2s and 2p on a relative basis.
- Going down a main group in the periodic table, elements tend to make less use of valence s electrons and form weaker bonds with smaller angles.

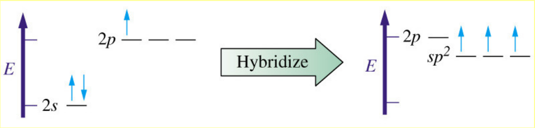
- The sp^3 hybrid orbitals don't explain the bonding for Boron (group 13) or for Beryllium (group 2)



- The problem appears to be that there are insufficient electrons to even half fill the 4 sp^3 orbitals.
- In these case we need to consider different hybridization schemes.
- We define hybrids such that the number of hybrids is the same as the number of valence electrons.

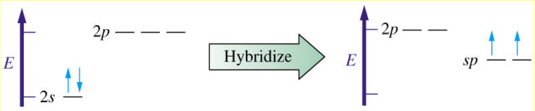
sp^2 and sp hybrid orbitals

Boron

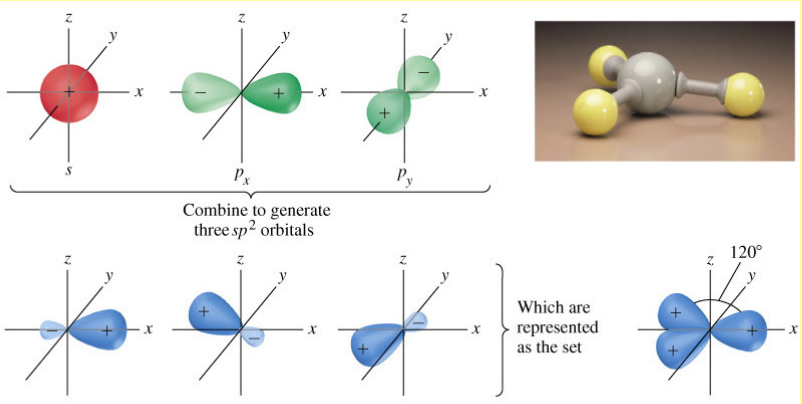


The number of orbitals is conserved.

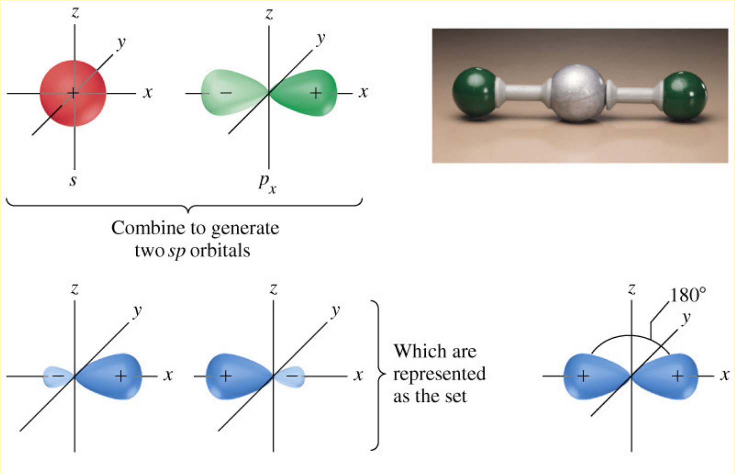
Beryllium



sp^2 hybrid orbitals (BCl$_3$)

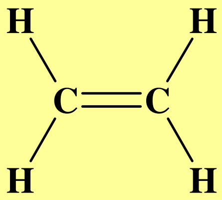


sp hybrid orbitals (BeCl$_2$)



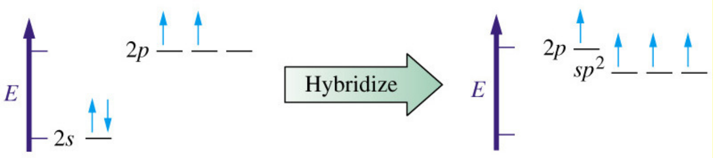
Multiple bonds

- How do we deal with the Lewis structures that have multiple bonds?
- Consider ethylene C_2H_4



Multiple bonds: ethylene (C_2H_4)

- The geometry suggests sp^2 hybrid orbitals are involved.

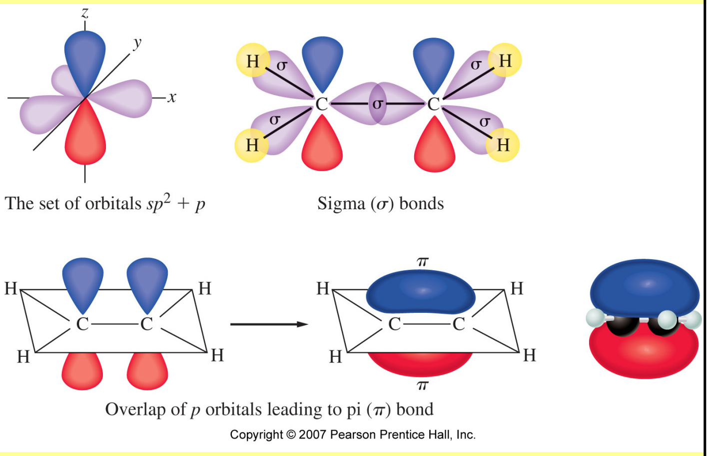


There is still an electron in the remaining 2p orbital.

Multiple bonds: ethylene (C_2H_4)

The sp^2 hybrid orbitals are in purple.

The “p” orbital is blue



The set of orbitals $sp^2 + p$

Sigma (σ) bonds

Overlap of *p* orbitals leading to pi (π) bond

Multiple bonds: ethylene (C_2H_4)

The orbitals that overlap along the axis of the nuclei are called sigma bonds - σ bonds.

Those where the overlap is side-to-side are pi bonds - π bonds.

Multiple bonds: ethylene

The σ bonds determine the shape of the molecule, the π bonds restrict the rotation about the C-C axis.

The orbital overlap is more extensive for the σ bonds so the π bond is weaker than the σ bond.

Bond strengths

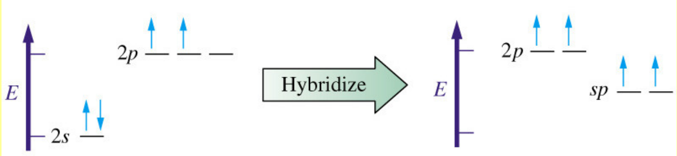
C-C 347 kJ mol^{-1} C=C 611 kJ mol^{-1}

difference = 264 kJ mol^{-1}

Multiple bonds: acetylene (ethyne)

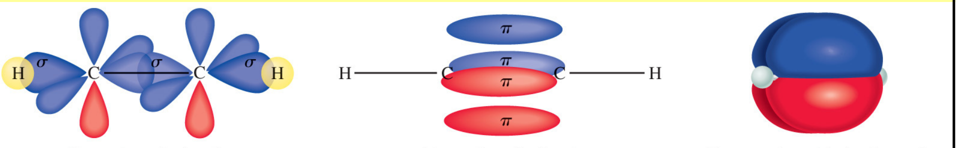
H—C≡C—H

- The geometry suggests sp hybrid orbitals are involved.



There is still an electron in each of the remaining 2p orbitals.

Multiple bonds: acetylene (ethyne)

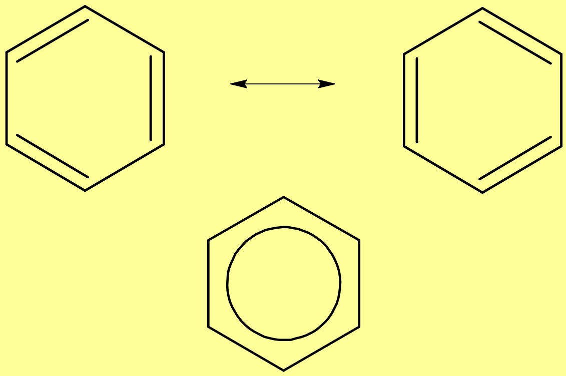


Formation of σ bonds

Formation of π bonds

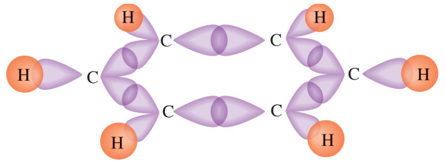
Computed π orbitals of acetylene

Multiple Bonds: Benzene

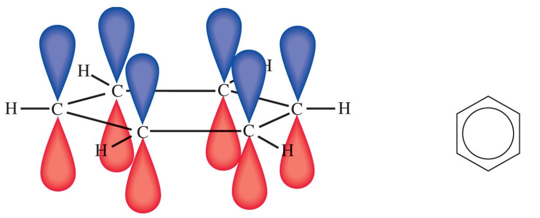


This structure is planar and suggests sp^2.

Multiple Bonds: Benzene



(a) σ bond framework



(b) Carbon 2p orbitals to be used in π bonding

(c) Symbolic representation

Multiple Bonds: Benzene

- The overlap of the "p" orbitals can be thought of as giving the three double bonds, but in reality the π orbital system is delocalized around the whole ring. This eliminates the need to discuss resonance.

Other kinds of "bonds"

- In the section on gases we said there were forces between the molecules. Now we know more about bonding and electronic structure we can revisit the question.
- What kinds of forces exist between molecules?

Van der Waal Forces

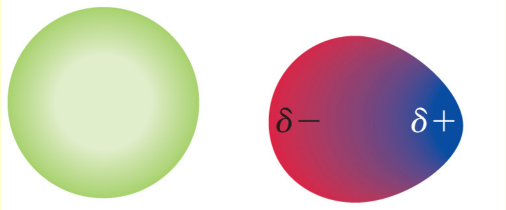
- Van der Waal forces are those attractive forces between molecules that are responsible for:
  - Real gas behaviour (Van der Waal "a")
  - Condensation
- There are a number of such forces resulting in different types of interactions between molecules.

Van der Waal Forces
London or Dispersion Force

- The quantum concept of electronic structure talks about the probability of an electron being in a certain region at a certain time.
- Even for an atom or a perfectly symmetrical molecule there is a finite chance that the electronic charges are not uniformly distributed.
- This produces an instantaneous dipole.

Van der Waal Forces
London or Dispersion Force

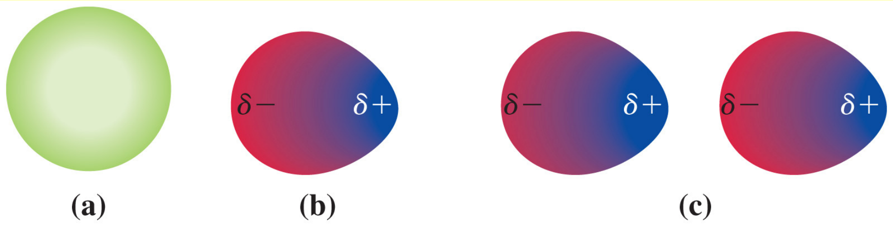
Molecule on average



Instantaneous dipole

- The instantaneous dipole can then influence neighbouring molecules and induce a dipole in them. (an induced dipole)
- This gives two dipoles that can attract. This is usually called a dispersion force or a London force.

Van der Waal Forces
London or Dispersion Force



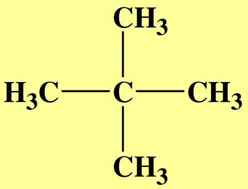
a. Normal
b. Instantaneous dipole
c. Instantaneous dipole (left) induced dipole (right)

Van der Waal Forces
London or Dispersion Force

- This force is going to be strongest in a molecule with a large number of electrons or for an elongated molecule.
- The ability or tendency of a molecule to have charge separation occur is called polarizability.
- The effect of London forces can often be seen in the boiling points of similar compounds.

Effect of London Forces

- Bpt(He) = 4K
- Bpt(Rn) = 211K   Rn is larger



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

Bpt 9.5°C

n-pentane is more elongated

CH_3-CH_2-CH_2-CH_2-CH_3

Bpt 36.1°C

Van der Waal Forces
Dipole-Dipole interactions

- Bonds where the elements have different electronegativity have a permanent charge separation.

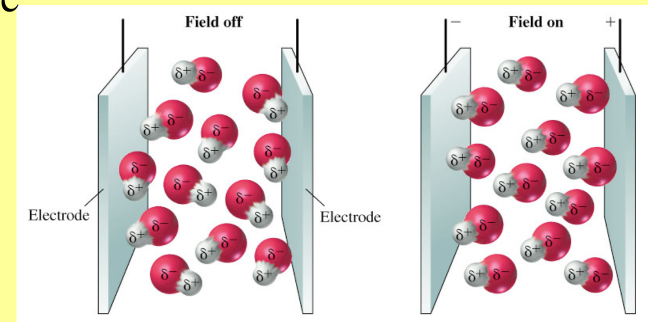
E.g. HCl

- $\mathrm{H}\mapsto\mathrm{Cl}$
- If this shows up in the molecule we say the molecule has a permanent dipole.

Van der Waal Forces
Dipole-Dipole interactions

- How do we tell if a molecule has a dipole?

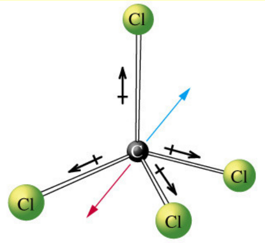
We can put the molecules in an electric field and see the effects of them “lining up”.



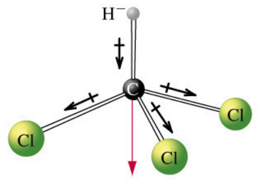
Van der Waal Forces
Dipole-Dipole interactions

- Not all molecules with polar bonds have a dipole.
- This is because the dipoles can cancel each other out.

Van der Waal Forces
Dipole-Dipole interactions



(a) CCl_4: a nonpolar molecule



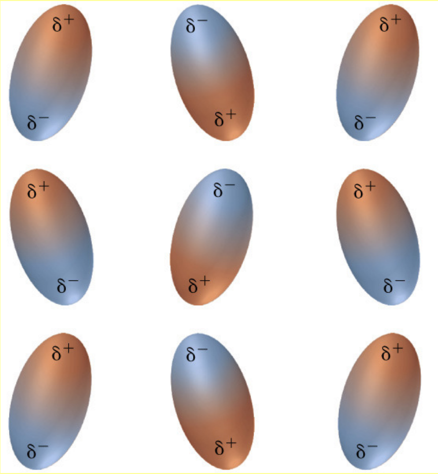
(b) $CHCl_3$: a polar molecule

Van der Waal Forces
Dipole-Dipole interactions

- For molecules with permanent dipoles, Dipole-Dipole interactions can occur.

Van der Waal Forces
Dipole-Dipole interactions

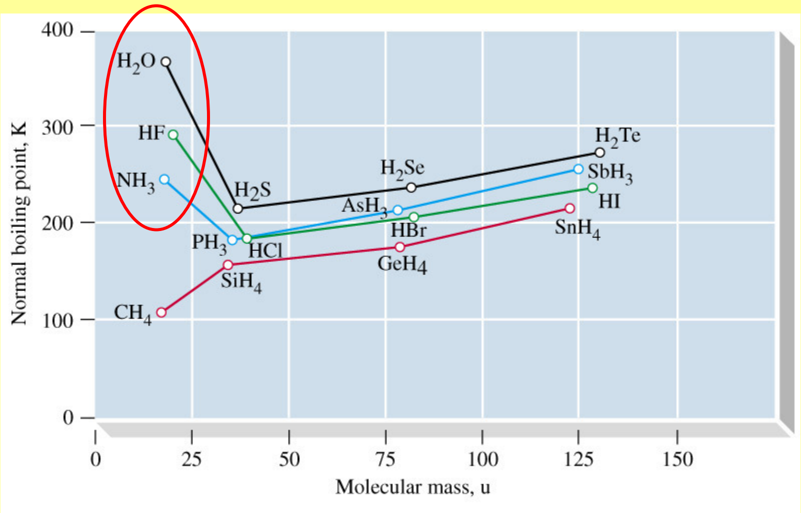
- Dipole-dipole interactions are in addition to the London forces.
- The overall interaction between polar molecules is higher than for non-polar molecules.



Hydrogen Bonding

- This is an extreme case.
- Hydrogen atoms bonded to very highly electronegative atoms can form weak bonds with the atom in an adjacent molecule.
- This only occurs for hydrogen bonded to F, O, and N.
- The bond energy is 15 - 40 kJ mol^{-1}, high compared to London forces but low compared to covalent bonds (>150 kJ mol^{-1})

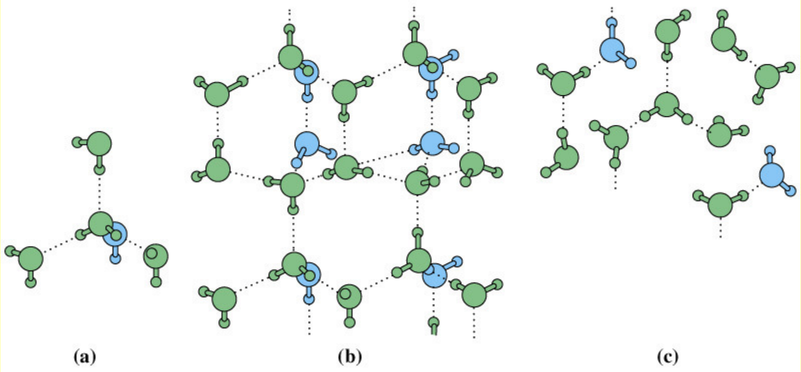
Effect of Hydrogen Bonding



Hydrogen Bonding in Water

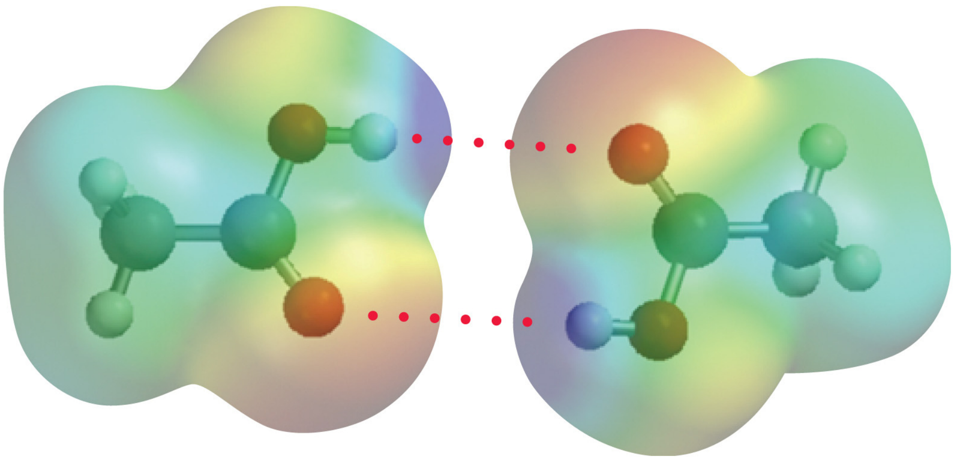
a) 4 hydrogen bonds per molecule

b) solid c) gas



Hydrogen Bonding (ctd)

Intermolecular - formation of a dimer of acetic acid



Hydrogen Bonding (ctd)

Intramolecular

- forces within a molecule of salicylic acid