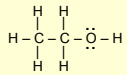
Chemistry: The Molecular Science

Moore, Stanitski and Jurs

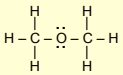
Chapter 9: Molecular Structures

Molecular Structures

Two C_2H_6O structural isomers:



ethanol



dimethyl ether

	ethanol	dimethyl ether
m.p./ °C	-114.1	-141.5
b.p./ °C	78.3	-24.8

Molecular shape is important!

Small structural changes cause large changes in physical (and chemical) properties.

Using Molecular Models

Physical models of 3D-structures:

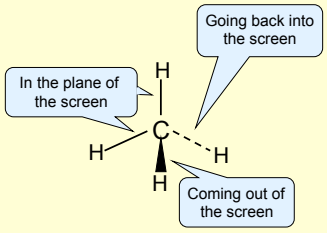
ball and stick

space filling

Computer versions:

Using Molecular Models

Hand-drawn molecules:



Predicting Molecular Shapes: VSEPR

The **Valence Shell Electron Pair Repulsion** model predicts shapes.

1. e^- pairs stay as far apart as possible to minimize repulsions.
2. The shape of a molecule is governed by the number of bonds and lone pairs present.
3. Treat a multiple bond like a single bond when determining a shape. Each is a single e-group.
4. Lone pairs occupy more volume than bonds.

Predicting Molecular Shapes: VSEPR

Linear

Triangular planar

Tetrahedral

Triangular bipyramidal

Octahedral

Predicting Molecular Shapes: VSEPR

Basic shapes that minimize repulsions:

linear | triangular planar | tetrahedral | triangular bipyramidal | octahedral

If the molecule contains:

- only bonding pairs – the angles shown are correct.
- lone pair/bond mixtures – the angles change a little.
  - lone pair/lone pair repulsions are largest.
  - lone pair/bond pair are intermediate in strength.
  - bond/bond interactions are the smallest.

Predicting Molecular Shapes: VSEPR

A molecule may be described by its:

- electron-pair (e-pair) geometry
- molecular geometry

These two geometries may be different.

- Atoms can be "seen", lone pairs are invisible.

Predicting Molecular Shapes: VSEPR

2 and 3 e-group central atoms

Linear e-pair geometry

Triangular planar e-pair geometry

2 e-groups

bond pairs	lone pairs	
2	0	linear
1	1	linear

molecular geometry

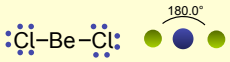
3 e-groups

bond pairs	lone pairs	
3	0	triangular planar
2	1	angular (bent)
1	2	linear

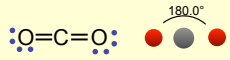
molecular geometry

Predicting Molecular Shapes: VSEPR

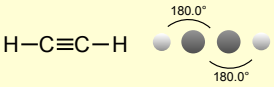
2 e-groups:



2 bonds, 0 lone pairs on Be.
Linear.



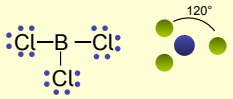
"2" bonds, 0 lone pairs on C.
(treat double bonds as 1 bond)
Linear.



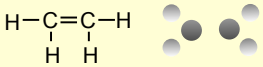
Each C has 2 e-groups.
Each H-C-C unit is linear.

Predicting Molecular Shapes: VSEPR

3 e-groups:



B has 3 bonds (0 lone pairs).
Triangular planar.



Each C has 3 e-groups.
Each C is triangular planar.

Predicting Molecular Shapes: VSEPR

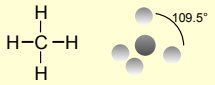
4 e-groups = tetrahedral e-pair geometry:

bond pairs	lone pairs	
4	0	tetrahedral
3	1	triangular pyramidal
2	2	angular

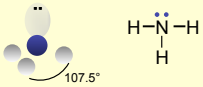
1 bond, 3 lone pairs?

All molecules with only 1 bond are linear!

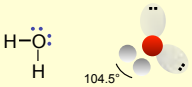
Predicting Molecular Shapes: VSEPR



4 bonds, 0 lone pairs.
All angles = tetrahedral angle



3 bonds, 1 lone pair.
Lone-pair/bond > bond/bond repulsion
H-N-H angle is reduced.

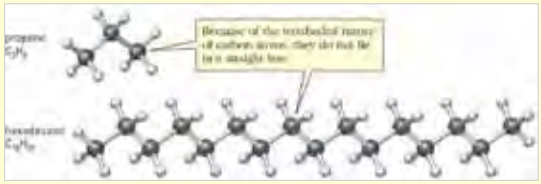


2 bonds, 2 lone pairs.
Two lone pairs
H-O-H angle even smaller.

Predicting Molecular Shapes: VSEPR

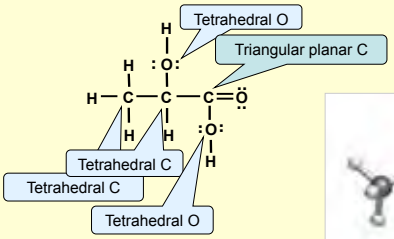
VSEPR applies to each atom in a molecule.

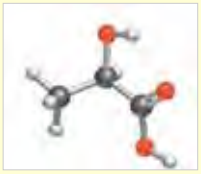
- Alkanes: each C is tetrahedral.



Predicting Molecular Shapes: VSEPR

Lactic acid:





Predicting Molecular Shapes: VSEPR

Expanded octet atoms:

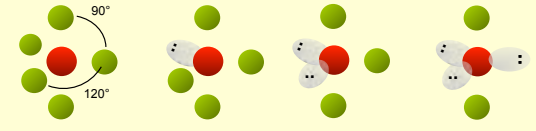
bond pairs	lone pairs	Shape
5	0	Triangular bipyramidal
4	1	Seesaw
3	2	T-shaped
2	3	Linear
6	0	Octahedral
5	1	Square pyramidal
4	2	Square planar
3	3	T-shaped

Remember

- lone pairs repel the most.
- they get as far apart as possible.

Predicting Molecular Shapes: VSEPR

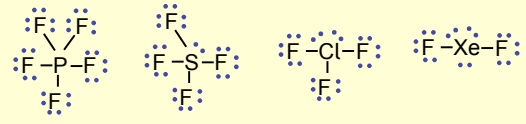
5 e-groups = Triangular bypyramidal e-pair geometry

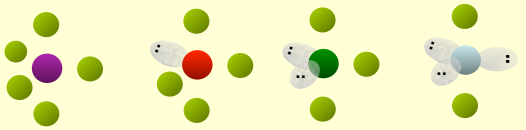


Triangular bipyramidal | Seesaw | T-shaped | Linear

The atoms are non-equivalent.
Green atoms are axial; blue atoms are equatorial.

Predicting Molecular Shapes: VSEPR

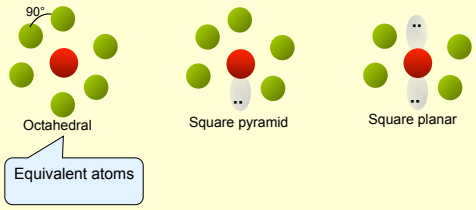




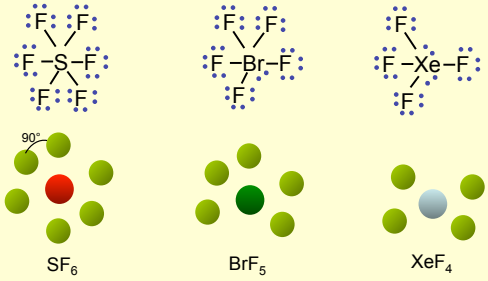
PF_5 | SF_4 | ClF_3 | XeF_2

Predicting Molecular Shapes: VSEPR

Six e-groups = octahedral e-pair geometry



Predicting Molecular Shapes: VSEPR



Orbitals Consistent with Molecular Shapes

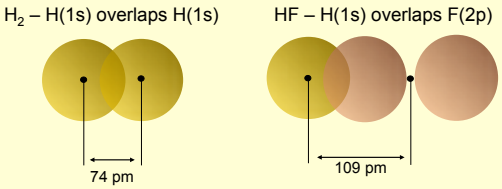
Lewis dot + VSEPR gives the correct shape for a molecule. **BUT**…

How do atomic orbitals (*s, p, d* …) produce these shapes?

Valence bond theory associates a bond with an overlap of atomic orbitals.

Orbitals Consistent with Molecular Shapes

VB theory: bonds occur when atomic orbitals overlap.



Valence Bond Theory

This works for H_2 and HF, but…

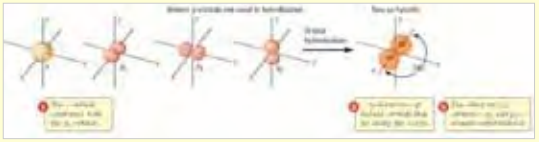
- Why does Be form compounds?
  - Be ($1s^2\,2s^2$)
  - No unpaired e^- to share.
  - *Experiments show:* linear BeH_2, $BeCl_2$, …
- Why does C form 4 bonds at tetrahedral angles?
  - C ($1s^2\,2s^2\,2p^2$)
  - $2p_x^1\ 2p_y^1$ Two bonds?
  - *p* orbitals are at 90° to each other
  - *Experiments show:* tetrahedral CH_4, CCl_4, …

Orbitals Consistent with Molecular Shapes

Atomic orbitals (AOs) can be **hybridized** (mixed).

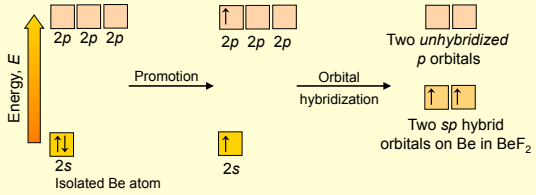
- Sets of identical **hybrid** orbitals form identical bonds
- Number of hybrids formed = number of AOs mixed.

One *s* orbital + one *p* orbital → two *sp* hybrids.



sp Hybrid Orbitals

Be compounds (BeH_2, BeF_2 …):

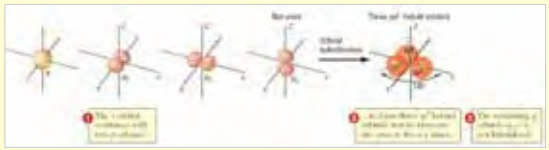


Each *sp* hybrid (180° apart) holds one e⁻.
Two equivalent covalent bonds form.

sp^2 Hybrid Orbitals

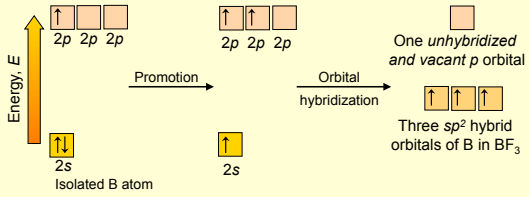
B forms three sp^2 hybrid orbitals:

- One *s* orbital mixes with two *p* orbitals.
- One p orbital is unmixed.



sp^2 Hybrid Orbitals

B compounds (BH_3, BF_3 …):

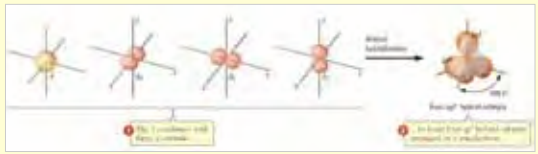


Each sp^2 hybrid (120° apart) holds one e⁻.
Three equivalent covalent bonds form.

sp^3 Hybrid Orbitals

C forms four sp^3 hybrid orbitals:

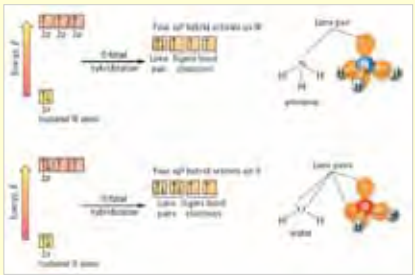
- One *s* orbital mixes with three *p* orbitals.
- All *p* orbitals are mixed.



In C, each sp^3 hybrid (109.5° apart) holds one e⁻.
Four equivalent covalent bonds form.

sp^3 Hybrid Orbitals

N and O compounds (NH_3, H_2O…) have more e⁻:



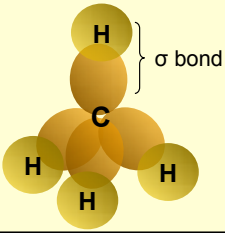
sp^3 Hybrid Orbitals

"Octet rule" molecules have tetrahedral e-pair shape.

- sp^3 hybridized (CH_4, NH_3, H_2O, H_2S, PH_3, …)

Head-to-head bond = a **sigma bond** (**σ bond**).
There are:

- 4 σ bonds in CH_4
- 3 σ bonds in NH_3
- 2 σ bonds in H_2O



Hybridization in Expanded Octets

Summary:

Mixed	Hybrids (#)	Remaining	Geometry
s+*p*	*sp* (2)	*p*+*p*	Linear
s+*p*+*p*	sp^2 (3)	*p*	Triangular planar
s+*p*+*p*+*p*	sp^3 (4)		Tetrahedral

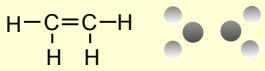
d orbitals can also form hybrids:

Mixed	Hybrids (#)	Remaining	Geometry
s+*p*+*p*+*p*+*d*	sp^3d (5)	*d*+*d*+*d*+*d*	Triangular bipyramid
s+*p*+*p*+*p*+*d*+*d*	sp^3d^2 (6)	*d*+*d*+*d*	Octahedral

Hybridization in Molecules with Multiple Bonds

A carbon atom can have a:

- tetrahedral center (CH_4, CHF_3 , C_2H_6…) = sp^3
- triangular-planar center (H_2CO, C_2H_4 …) = sp^2

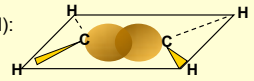


The double bond in ethene is composed of:

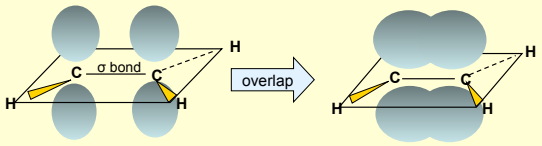
- a **σ bond** – head-to-head overlap of sp^2 on each C atom.
- a **π bond** – sideways overlap of *p* AOs on the C atoms.

Hybridization in Molecules with Multiple Bonds

C (sp^2) + C (sp^2) overlap (σ bond):



Unhybridized C *p* orbitals each contain one e⁻.

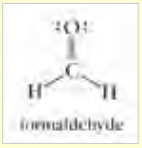


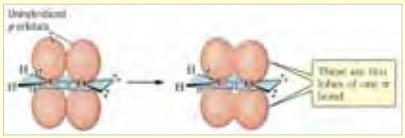
Sideways overlap forms ***one*** π bond

- the lobes above and below the plane *together* equal 1 bond

Hybridization in Molecules with Multiple Bonds

Formaldehyde is similar:

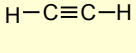




Hybridization in Molecules with Multiple Bonds

A third type of C center is seen:

- linear center (C_2H_2, acetylene) = *sp* hybridized

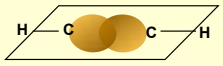


The triple bond is:

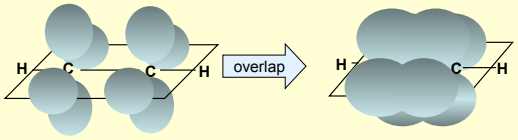
- one **σ bond**
- two **π bonds**
  - *sp* hybridization leaves ***two*** unmixed *p* orbitals on each C.

Hybridization in Molecules with Multiple Bonds

σ bond: C (*sp*) + C (*sp*) overlap:



Two *p* orbitals on **each** C contain a single e⁻.



Two π bonds

- ***above and below*** overlaps are 1 bond.
- ***front and back*** overlaps are a second bond.

Hybridization in Molecules with Multiple Bonds

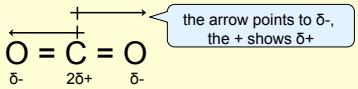
π bonds prevent bond rotation:

Molecule	C-C bonding	C-C rotation
ethane (CH_3–CH_3)	σ	yes
ethene (CH_2=CH_2)	σ + π	no
ethyne (HC≡CH)	σ + π + π	no

Non-rotating double bonds allow *cis-trans* isomerism to occur.

Molecular Polarity

- Most *bonds* are polar (e.g. C-O)
  - O is δ-, C is δ+ (EN_O = 3.5, EN_C = 2.5)
- But many ***molecules*** are nonpolar (e.g. CO_2).



- The dipoles cancel because of CO_2's shape.
  - the bond dipoles have equal size ***but*** point in opposite directions.

Molecular Polarity

Molecular Polarity

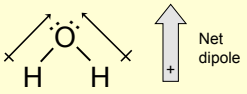
Dipole moment (μ) is a measure of the polarity of a molecule:

- large μ = highly polar molecule
- small μ = weakly polar molecule
- If μ = 0 the molecule is non-polar
- units: coulomb meter (Cm) or Debye (D)

Molecule	μ (D)
H_2	0
HF	1.78
HCl	1.07
HBr	0.79
HI	0.38
H_2O	1.85
H_2S	0.95
CO_2	0
CH_4	0
CH_3Cl	1.92
CH_2Cl_2	1.60
$CHCl_3$	1.04
CCl_4	0

Molecular Polarity

- Polar molecules: bond dipoles do not cancel
- Water is polar:



Observed dipole, μ = 1.85 D

Molecular Polarity

A molecule is **nonpolar** if:

- it has a basic VSEPR shape
  - linear, triangular planar, tetrahedral, triangular bipyramidal, octahedral
- ***and*** all the atoms are the same.

CO_2, linear CH_4, tetrahedral CCl_4, tetrahedral
PF_5, triangular bipyramidal

A molecule is **nonpolar** if:

- it can be "divided" into nonpolar VSEPR shapes

PCl_3F_2 = triangular planar (PCl_3) + linear (PF_2)
XeF_4 = linear (XeF_2) + linear (XeF_2)

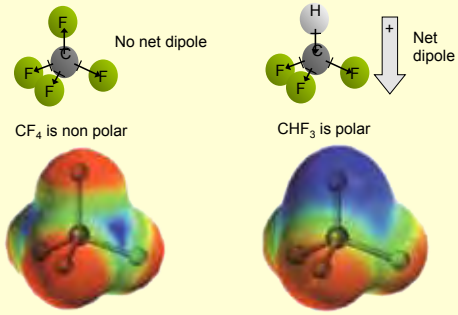
Molecular Polarity

A molecule is **polar** if:

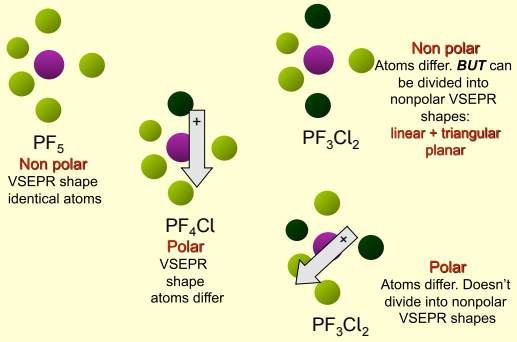
- it isn't a basic VSEPR shape
  H_2O bent **(polar)** NH_3 pyramidal **(polar)**
- the terminal atoms/groups in a basic VSEPR shape differ.
  CH_2Cl_2, tetrahedral **(polar)**
  (basic VSEPR shape, but non identical groups).
  PF_4Cl, triangular bipyramidal **(polar)**
  (basic VSEPR shape, but non identical groups).

How polar? It depends on the number, type, and geometry of the polar bonds.

Molecular Polarity



Molecular Polarity



Noncovalent Interactions

Molecules are sticky and attract each other.

Intermolecular forces:

- are small (compared to bonding forces).
- are called **noncovalent** interactions.
- do ***not*** include ionic-bonding or metallic-bonding forces.

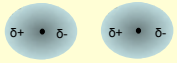
Three types:

- London forces
- dipole-dipole attraction
- hydrogen bonding

London Forces

Also called **dispersion** forces.

- Random e^- motion can produce a ***temporary*** dipole in a molecule. This can ***induce*** a dipole in another.



- Strength (0.05 ↔ 40 kJ/mol):
  Small molecule = few e^- = weak attraction.
  Large molecule = many e^- = stronger attraction.
- The ***only*** force between nonpolar molecules.

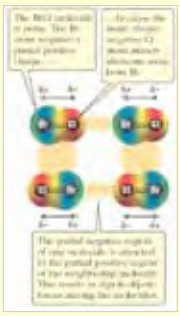
London Forces

Atom	Molecule	# of e^-	bp (°C)
He		2	−269
Ne		10	−246
Ar		18	−186
Kr		36	−152
	F_2	18	−188
	Cl_2	34	−34
	Br_2	70	+59
	I_2	106	+184
	CH_4	10	−161
	C_2H_6	18	−88
	C_3H_8	26	−42
	C_4H_{10}	34	0

More e^-
= larger attraction
= greater stickiness
= higher b.p.

Dipole-Dipole Attractions

Polar molecules attract each other.



Strength = 5 ↔ 25 kJ/mol.

Dipole-Dipole Attractions

nonpolar	# of e⁻	bp (°C)	polar	# of e-	bp (°C)
SiH_4	18	−112	PH_3	18	−88
GeH_4	36	−90	AsH_3	36	−62
Br_2	70	+59	ICl	70	+97

With equal number of e⁻ (and same shape):
dipole/dipole > London

BUT London can dominate with large numbers of e⁻

HI = small dipole + large London (54 e⁻) bp = −36°C
HCl = big dipole + small London (18 e⁻) bp = −85°C

Hydrogen Bonds

An especially large dipole-dipole attraction.

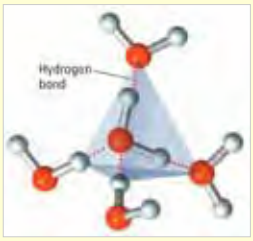
- 10 ↔ 40 kJ/mol
- Occurs when H bonds ***directly*** to F, O or N

F, O & N are small with large electronegativities.

- results in large δ+ and δ- values.

H-bonds are usually drawn as dotted lines.

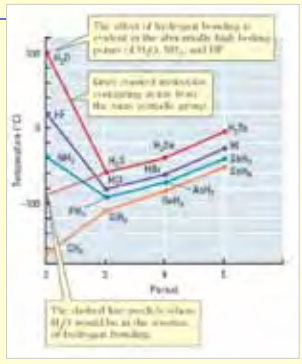
Hydrogen Bonds



H on one molecule interacts with O on another molecule.

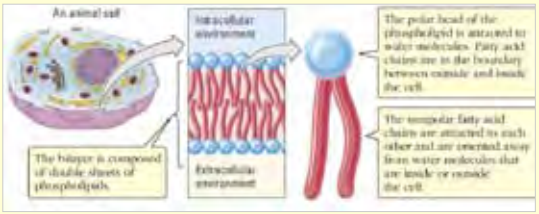
Hydrogen Bonds

Water is a liquid at room *T* (not a gas).



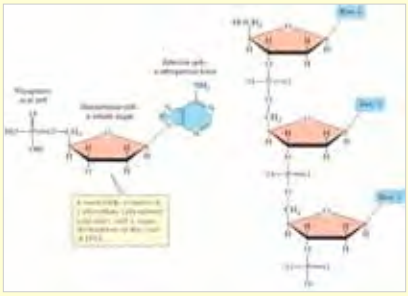
Noncovalent Forces in Living Cells

Phospholipids form lipid bilayers:



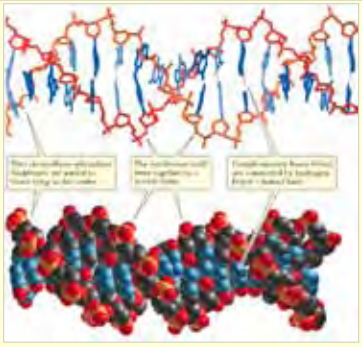
Polar end = hydrophilic (water loving).
Nonpolar end = hydrophobic (water hating).

Biomolecules: DNA and Molecular Structure



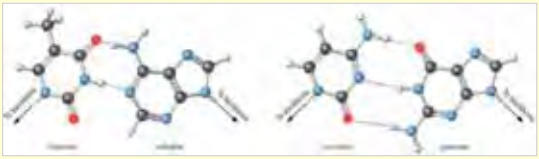
In DNA there are 4 possible bases—*adenine (A), thymine (T), guanine (G),* or *cytosine (C)*

Biomolecules: DNA and Molecular Structure



Biomolecules: DNA and Molecular Structure

Complementary base pairs:



Biomolecules: DNA and Molecular Structure