

Chapter 1,2 – Continued

- 1. Orbitals and Hybridization**
- 2. Molecular Shape and Polarity**
- 3. Physical Properties**

◆ **Chemical Bonds: The Octet Rule**

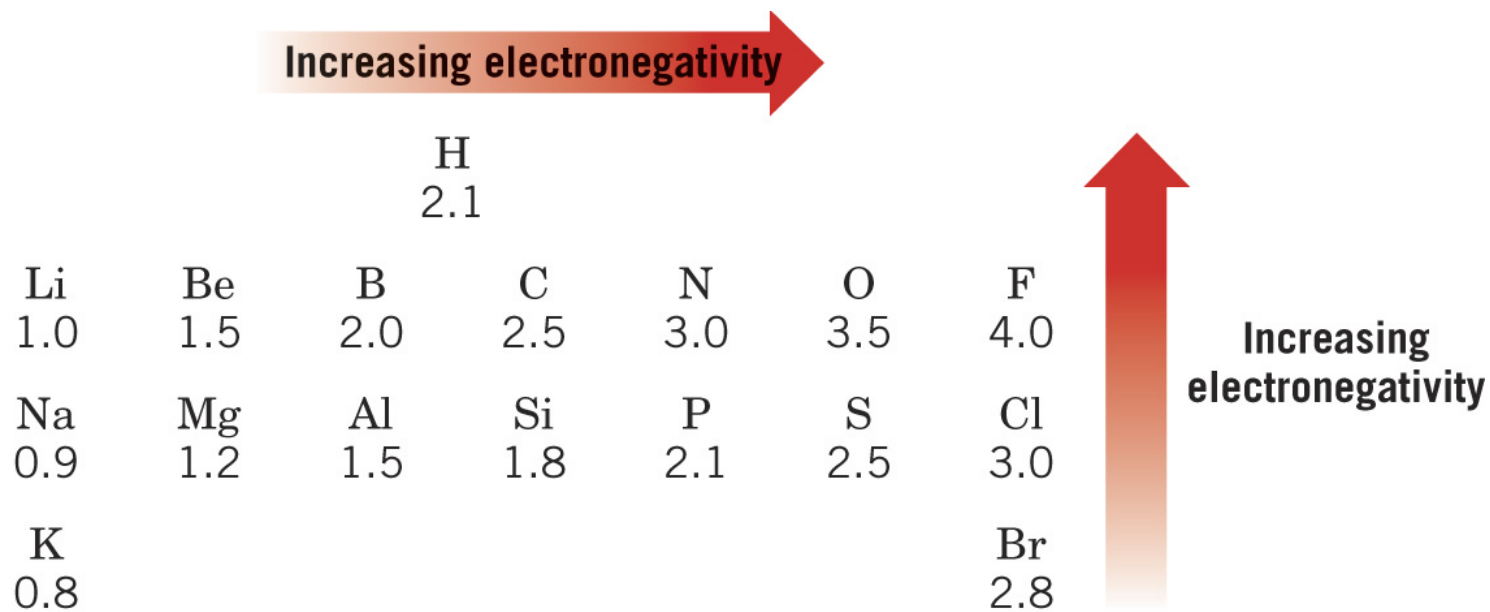
● **Octet Rule**

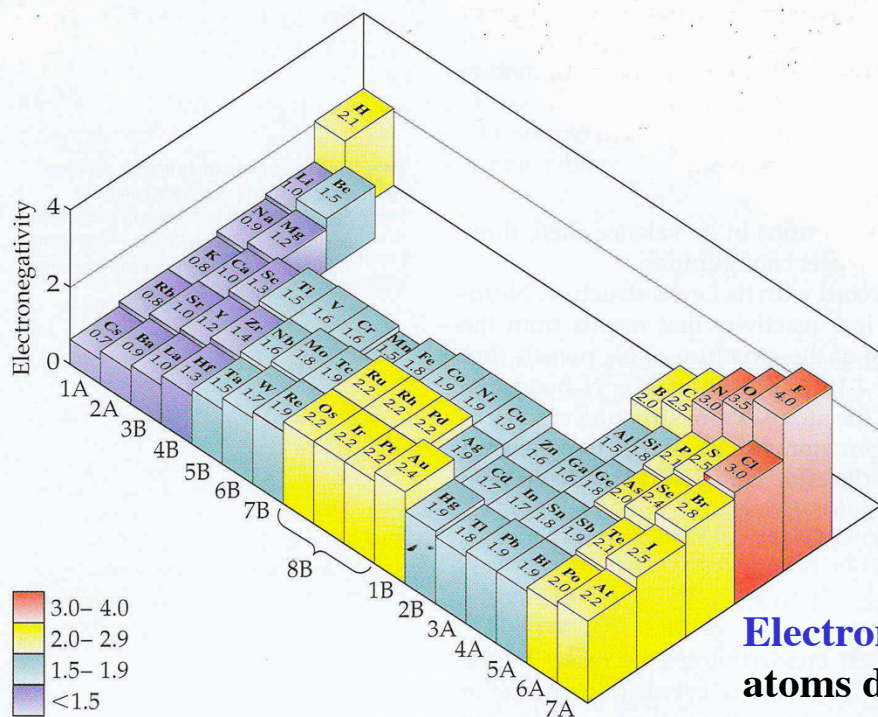
- ➔ **Atoms form bonds to produce the electron configuration of a noble gas (because the electronic configuration of noble gases is particularly stable)**
- ➔ **For most atoms of interest this means achieving a valence shell configuration of 8 electrons corresponding to that of the nearest noble gas**
- ➔ **Atoms close to helium achieve a valence shell configuration of 2 electrons**
- ➔ **Atoms can form either ionic or covalent bonds to satisfy the octet rule**

● Electronegativity

- ➔ Electronegativity is the ability of an atom to attract electrons
- ➔ It increases from left to right and from bottom to top in the periodic table (noble gases excluded)

★ Fluorine is the most electronegative atom and can stabilize excess electron density the best





Electronegativity difference between interacting atoms determines the type of bond that is formed.

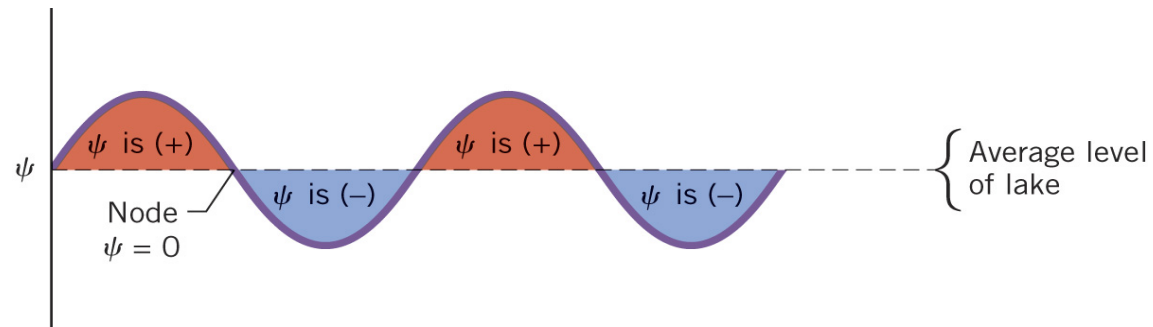
<i>compound</i>	F_2	HF	LiF
<i>electronegativity difference</i>	$4.0 - 4.0 = 0$	$4.0 - 2.1 = 1.9$	$4.0 - 1.0 = 3.0$
<i>type of bond</i>	nonpolar covalent	polar covalent	ionic

◆ Quantum Mechanics

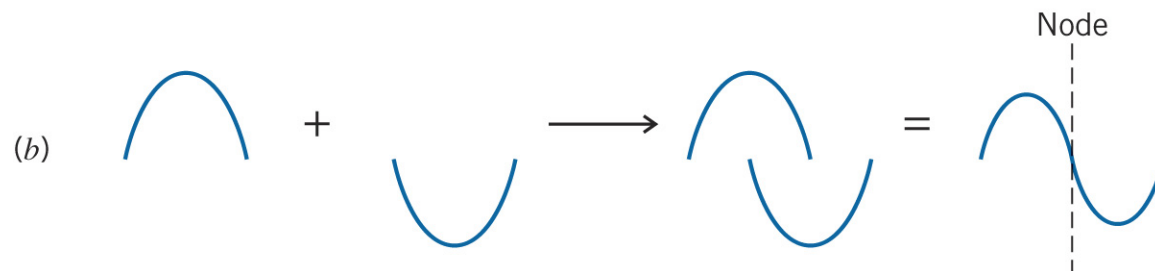
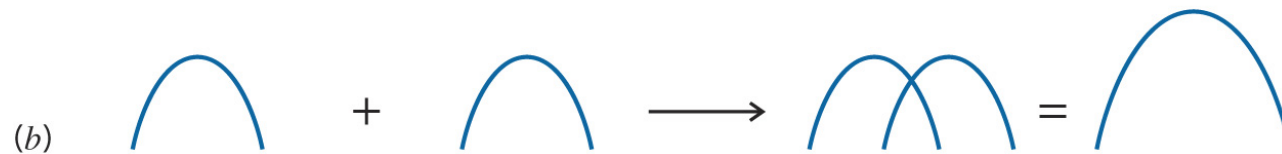
- ➡ A mathematical description of bonding that takes into account the wave nature of electrons
- ➡ A wave equation is solved to yield a series of wave functions for the atom
- ➡ The wave functions ψ (Ψ) describe a series of states with different energies for each electron
- ➡ Wave Equations are used to calculate:
 - ★ The energy associated with the state of the electron
 - ★ The probability of finding the electron in a particular state

➔ **Phase sign: Wave equations, when solved, may be positive, negative or zero**

- ★ In analogy to a wave in a lake, when the wave is above the average lake level, the sign is positive ($\psi = +$) ; when it is below the lake level it is negative ($\psi = -$)
- ★ When the wave is exactly at average lake level it has a sign of 0 and this is called a node ($\psi = 0$)

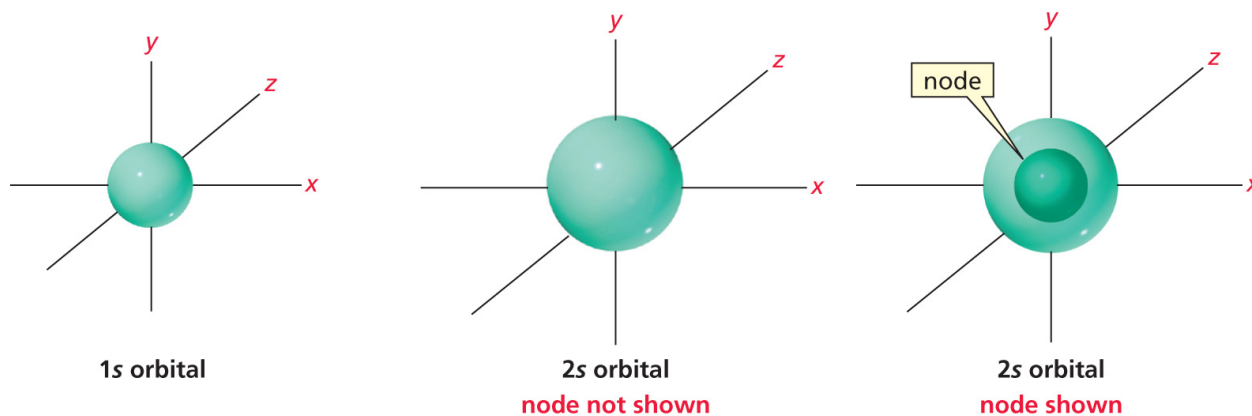


➔ **Wave equations can reinforce each other if they have the same sign or interfere with each other if they have different signs**

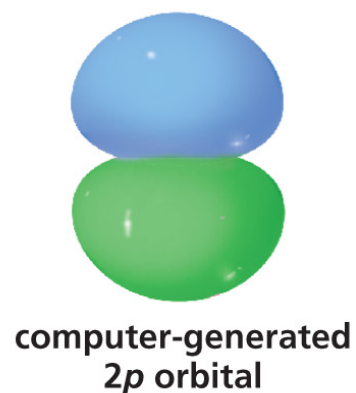
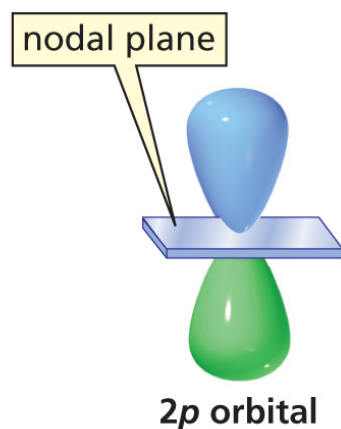


◆ Atomic Orbitals (AOs)

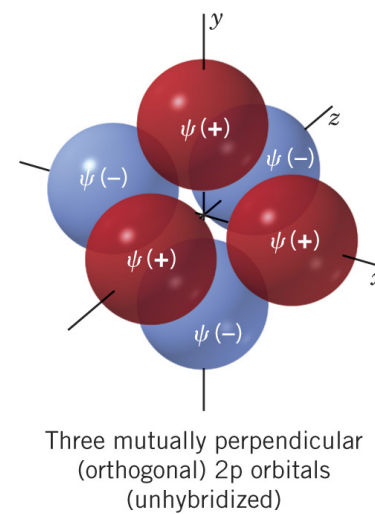
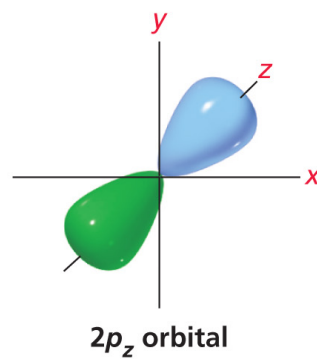
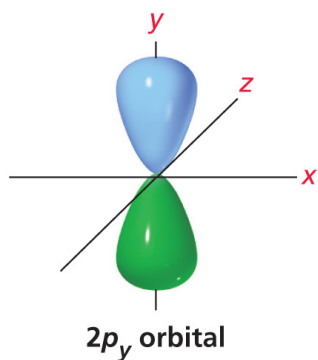
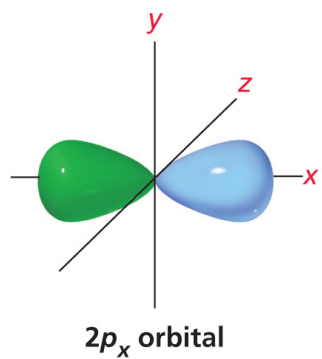
- ➔ The physical reality of Ψ is that when squared (Ψ^2) it gives the probability of finding an electron in a particular location in space
- ➔ Plots of Ψ^2 in three dimensions generate the shape of *s*, *p*, *d* and *f* orbitals
- ➔ Only *s* and *p* orbitals are very important in organic chemistry
- ➔ Orbital: a region in space where the probability of finding an electron is large
 - ★ The typical representation of orbitals are those volumes which contain the electron 90-95% of the time



- ➔ **1s and 2s orbitals are spheres centered around the nucleus**
 - ★ Each orbital can accommodate 2 electrons
 - ★ The 2s orbital is higher in energy and contains a nodal surface ($\Psi = 0$) in its center
- ➔ **Each 2p orbital has two nearly touching spheres (or lobes)**
 - ★ One sphere has a positive phase sign and the other a negative phase sign; a nodal plane separates the spheres
- ➔ **There are three 2p orbitals which are perpendicular (orthogonal) to each other**
 - ★ Each p orbital can accommodate 2 electrons for a total of 6 electrons
 - ★ All three p orbitals are degenerate (equal in energy)
- ➔ **The 2p orbitals are higher in energy than the 1s or 2s**



- ➔ The sign of the wave function *does not* indicate a greater or lesser probability of finding an electron in that location
- ➔ The greater the number of nodes in an orbital the higher its energy
 - ★ $2s$ and $2p$ orbitals each have one node and are higher in energy than the $1s$ orbital which has no nodes

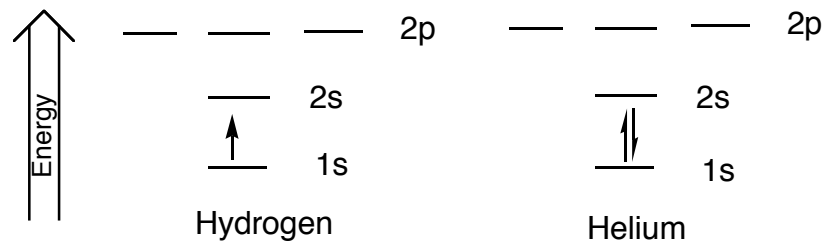


Structure and Bonding

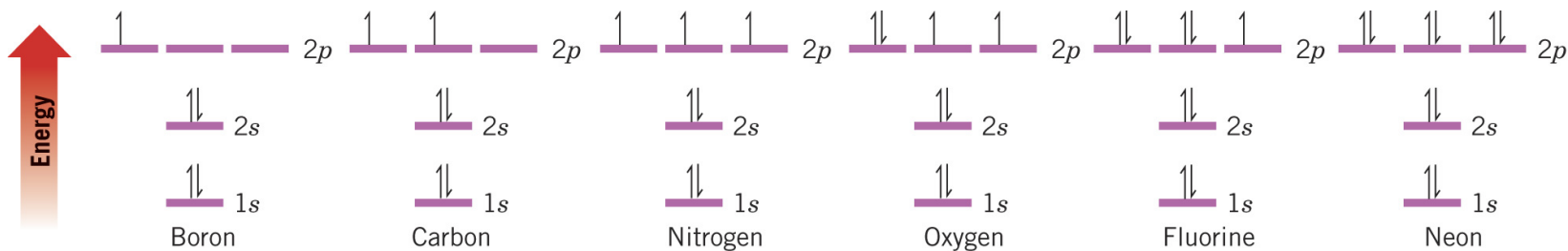
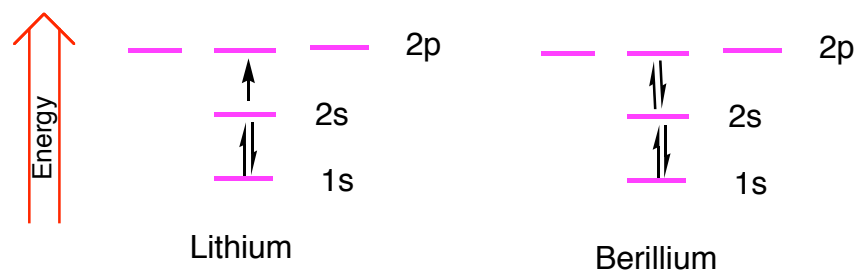
● **Atoms can be assigned electronic configuration using the following rules:**

- ➡ **Aufbau Principle:** The lowest energy orbitals are filled first
- ➡ **Pauli Exclusion Principle:** A maximum of two spin paired electrons may be placed in each orbital
- ➡ **Hund's Rule:** One electron is added to each degenerate (equal energy orbital) before a second electron is added

Since there is only one orbital in the first shell, and each shell can hold a maximum of two electrons, there are two possible elements in the first row, H and He.



Each of the elements in the second row of the periodic table has four orbitals available to accept additional electrons: *one 2s orbital*, and *three 2p orbitals*.

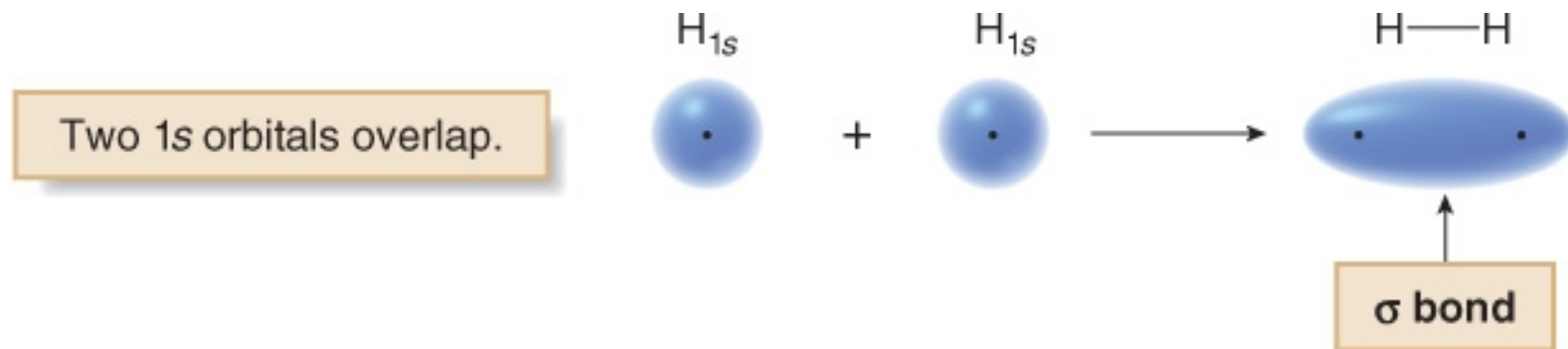


Structure and Bonding

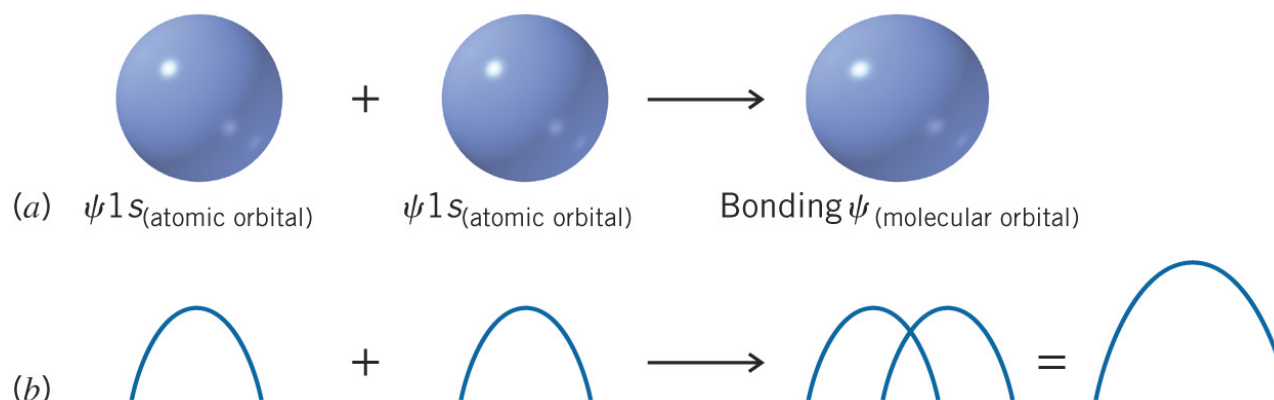
Molecular Orbitals : Hydrogen

When the 1s orbital of one H atom overlaps with the 1s orbital of another H atom, a sigma (σ) bond that concentrates electron density between the two nuclei is formed.

This bond is cylindrically symmetrical because the electrons forming the bond are distributed symmetrically about an imaginary line connecting the two nuclei.

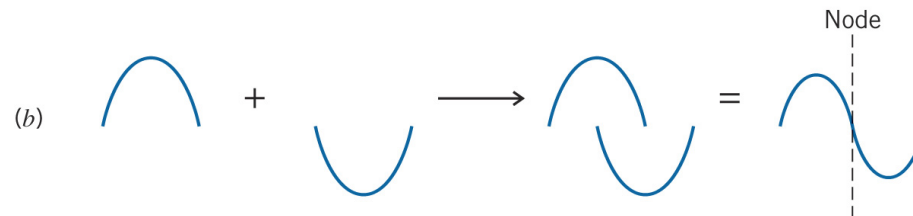
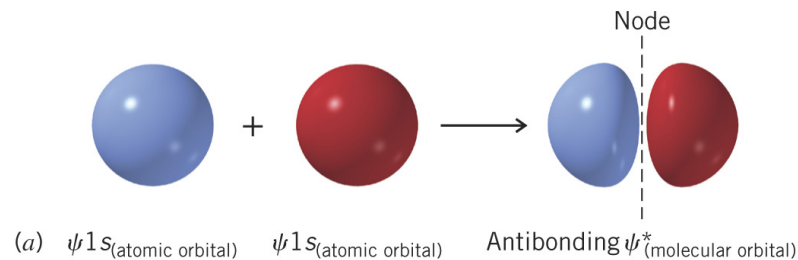


- **Bonding Molecular Orbitals (Ψ_{molec})**
 - ➔ AOs combine by addition (the AOs of the same phase sign overlap)
 - ➔ The wave functions reinforce
 - ➔ The value of Ψ increases between the two nuclei
 - ➔ The value of Ψ^2 (electron probability density) in the region between the two nuclei increases
 - ➔ The two electrons between the nuclei serve to attract the nuclei towards each other
 - ➔ This is the ground state (lowest energy state) of the MO

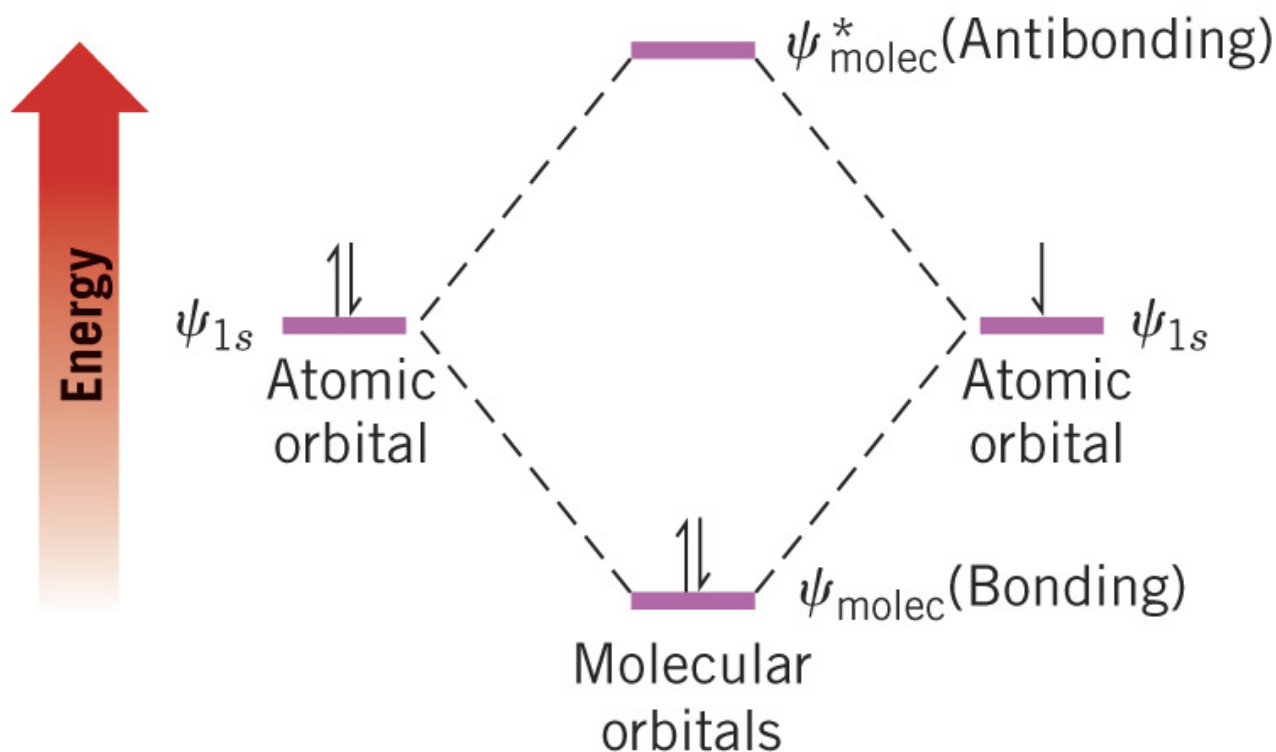


● **Antibonding molecular orbital (Ψ^*_{molec})**

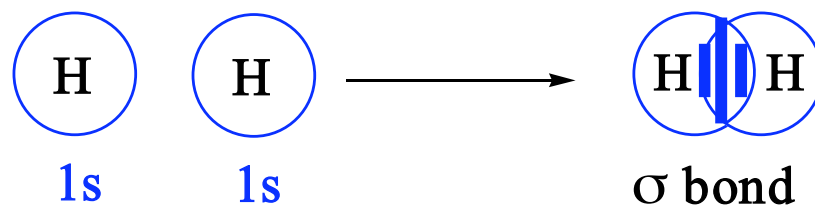
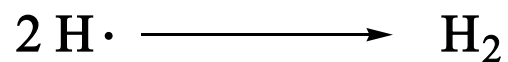
- ➔ **Formed by interaction of AOs with opposite phase signs**
- ➔ **Wave functions interfere and a node is produced ($\Psi = 0$)**
- ➔ **In the region between the two nuclei**
 - ★ A node is produced
 - ★ On either side of the node Ψ is small
 - ★ Ψ^2 (electron probability density) is small
- ➔ **Electrons in the antibonding orbital avoid the region between the two nuclei**
- ➔ **Repulsive forces between the nuclei predominate and electrons in antibonding orbitals make nuclei fly apart**



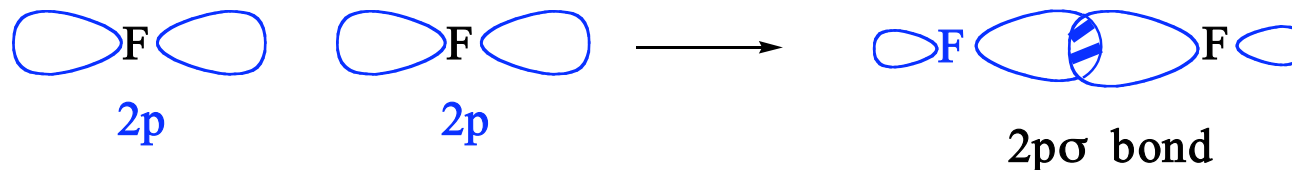
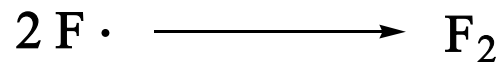
- ➡ The energy of electrons in the bonding orbitals is substantially less than the energy of electrons in the individual atoms
 - ★ The energy of electrons in the antibonding orbitals is substantially more
- ➡ In the ground state of the hydrogen molecule electrons occupy the lower energy bonding orbital only



Examples of Covalent Bonds



bond length 0.74 Å
BDE 435 kJ/mol



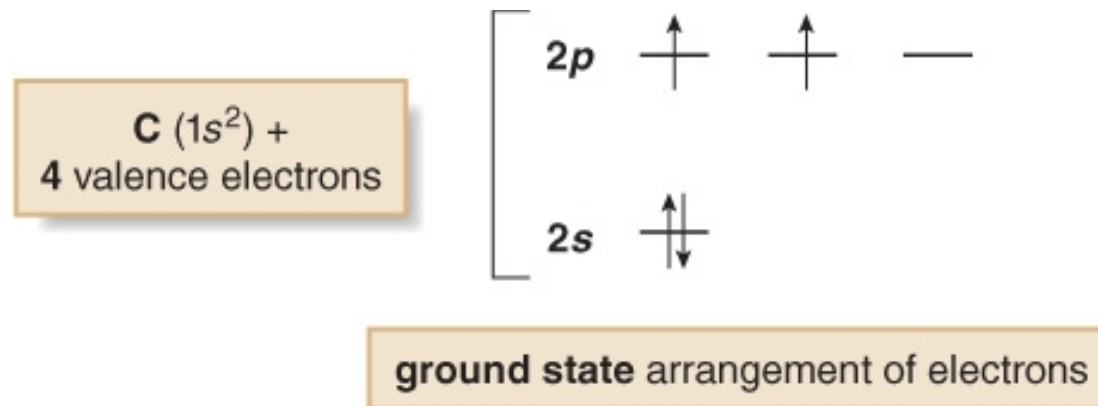
bond length 1.42 Å
BDE 159 kJ/mol

Structure and Bonding

Orbitals and Bonding: Methane

To account for the bonding patterns observed in more complex molecules, we must take a closer look at the $2s$ and $2p$ orbitals of atoms in the second row.

Carbon has two core electrons, plus four valence electrons. To fill atomic orbitals in the most stable arrangement, electrons are placed in the orbitals of lowest energy. For carbon, this places two in the $2s$ orbital and one each in $2p$ orbitals.



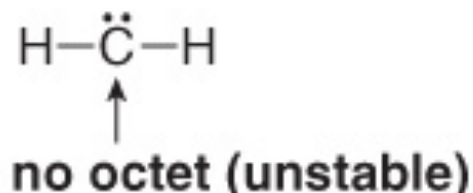
Note: the lowest energy arrangement of electrons for an atom is called its ground state.

Structure and Bonding

Orbitals and Bonding: Methane

In this description, carbon should form only two bonds because it has only two unpaired valence electrons, and CH_2 should be a stable molecule. However, CH_2 is a very unstable species that cannot be isolated under typical laboratory conditions. Note that in CH_2 , carbon would not have an octet of electrons.

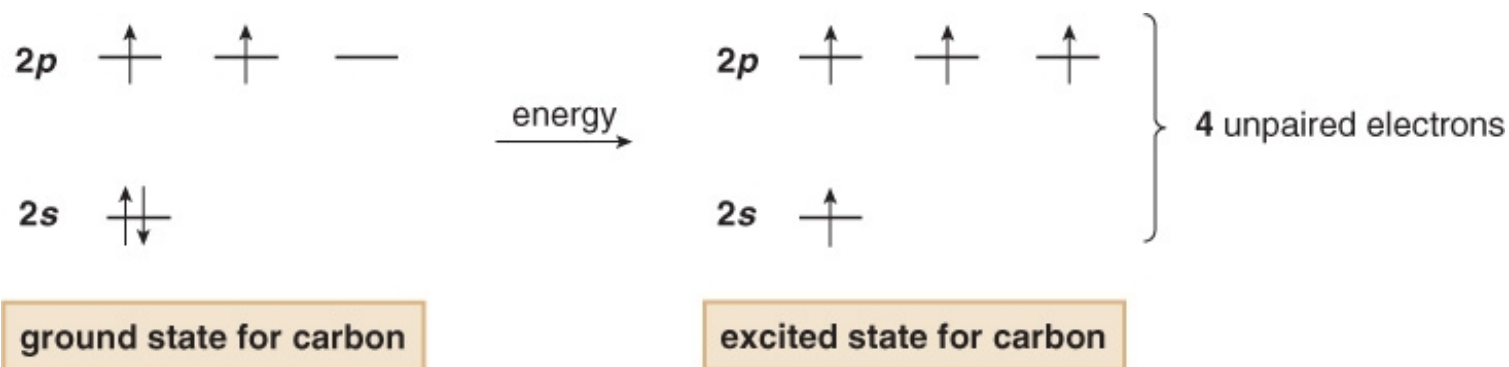
Two bonds from two unpaired electrons



Structure and Bonding

Orbitals and Bonding: Methane

There is a second possibility. Promotion of an electron from a $2s$ to a vacant $2p$ orbital would form four unpaired electrons for bonding. This process requires energy because it moves an electron to a higher energy orbital. This higher energy electron configuration is called an **electronically excited state**.



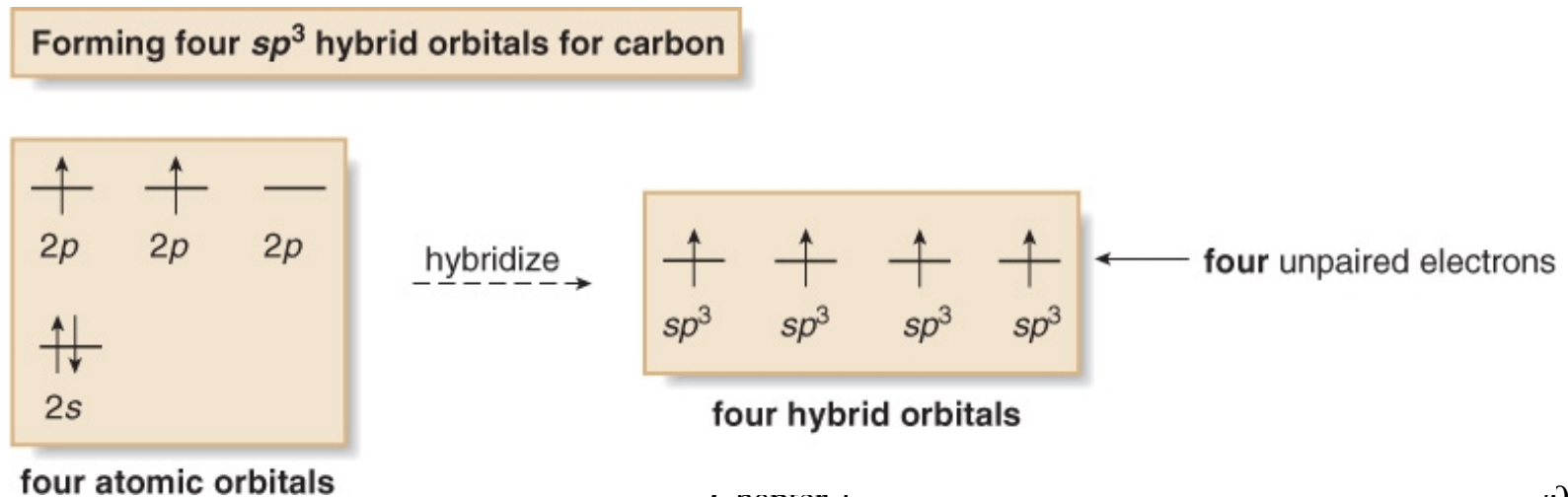
But this description is still not adequate. Carbon would form two different types of bonds: three with $2p$ orbitals and one with a $2s$ orbital. However, experimental evidence points to carbon forming four identical bonds in methane.

Structure and Bonding

Orbitals and Bonding: Methane

To solve this dilemma, chemists have proposed that atoms like carbon do not use pure s and pure p orbitals in forming bonds. Instead, atoms use a set of new orbitals called hybrid orbitals.

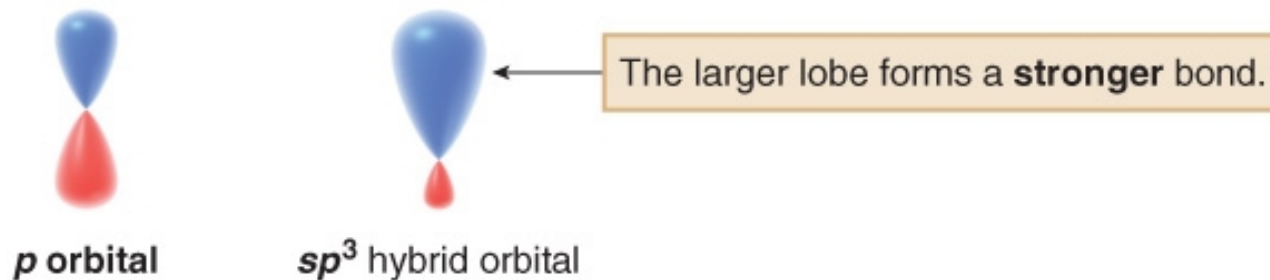
Hybridization is the combination of two or more atomic orbitals to form the same number of hybrid orbitals, each having the same shape and energy.



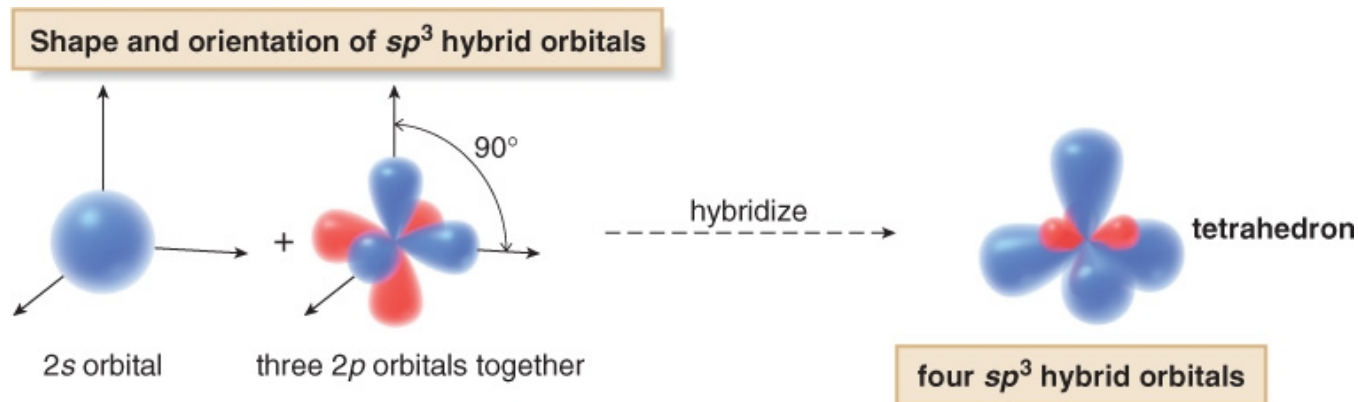
Structure and Bonding

Shape and Orientation of sp^3 Hybrid Orbitals

The mixing of a spherical $2s$ orbital and three dumbbell shaped $2p$ orbitals together produces four orbitals, each having one large lobe and one small lobe.

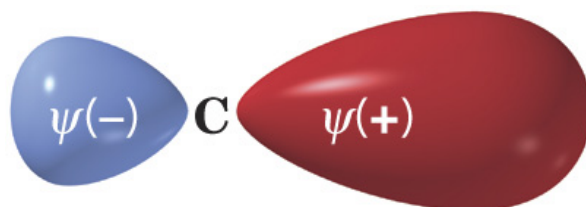


The four hybrid orbitals are oriented towards the corners of a tetrahedron, and form four equivalent bonds.

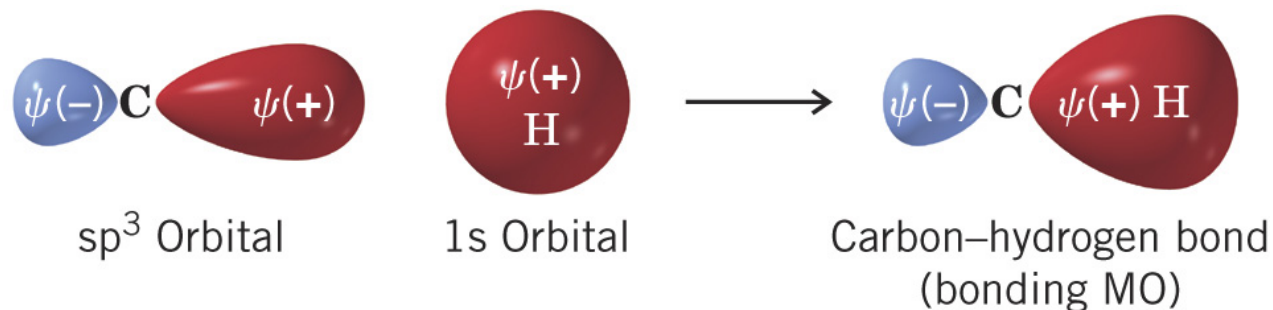


➡ An sp^3 orbital looks like a p orbital with one lobe greatly extended

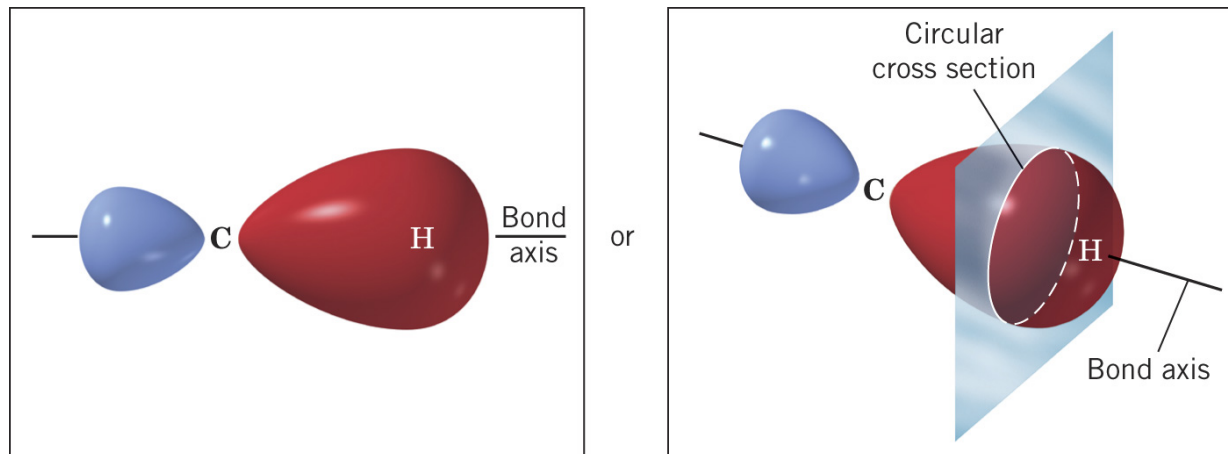
★ Often the small lobe is not drawn



➡ The extended sp^3 lobe can then overlap well with the hydrogen $1s$ to form a strong bond

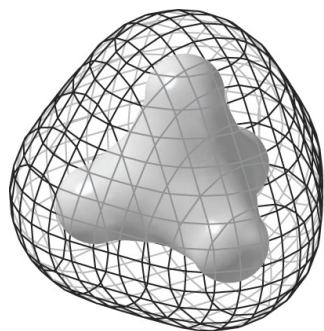


➡ The bond formed is called a sigma (σ) bond because it is circularly symmetrical in cross section when view along the bond axis

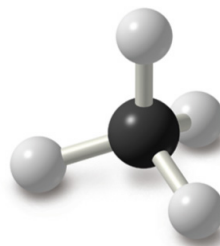


➔ **A variety of representations of methane show its tetrahedral nature and electron distribution**

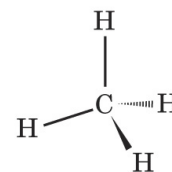
- ★ a. calculated electron density surface b. ball-and-stick model c. a typical 3-dimensional drawing



(a)



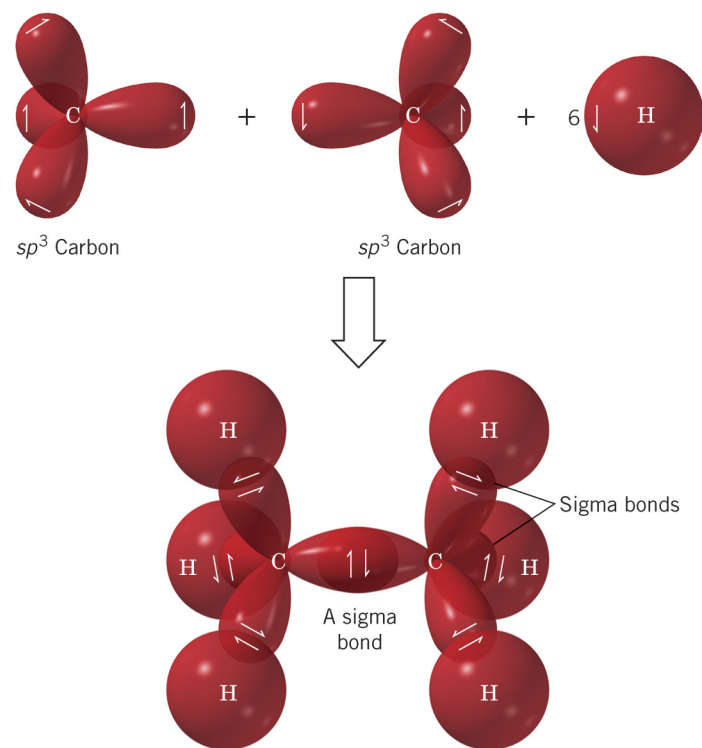
(b)



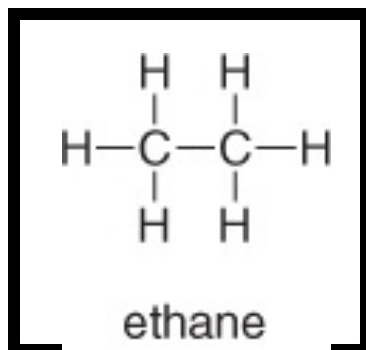
(c)

- Ethane (C_2H_6)

- ➔ The carbon-carbon bond is made from overlap of two sp^3 orbitals to form a σ bond
- ➔ The molecule is approximately tetrahedral around each carbon

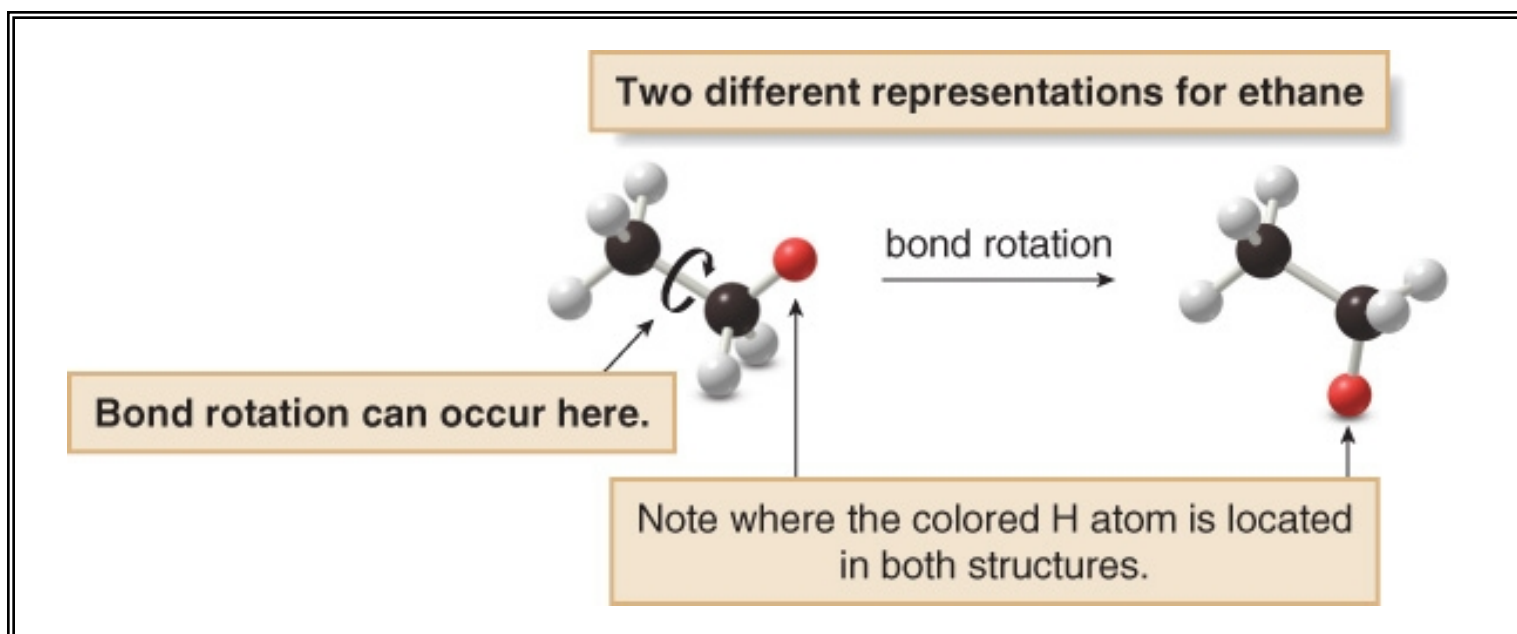


Structure and Bonding



Generally there is relatively free rotation about σ bonds

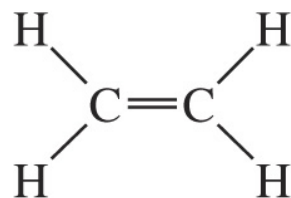
★Very little energy (13-26 kcal/mol) is required to rotate around the carbon-carbon bond of ethane



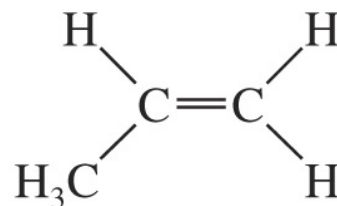
◆ The Structure of Ethene (Ethylene) : sp^2 Hybridization

➔ Ethene (C_2H_2) contains a carbon-carbon double bond and is in the class of organic compounds called *alkenes*

★ Another example of the alkenes is propene



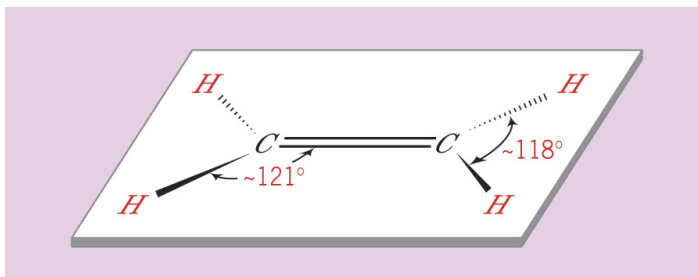
Ethene



Propene

➔ The geometry around each carbon is called *trigonal planar*

- ★ All atoms directly connected to each carbon are in a plane
- ★ The bonds point towards the corners of a regular triangle
- ★ The bond angle are approximately 120°

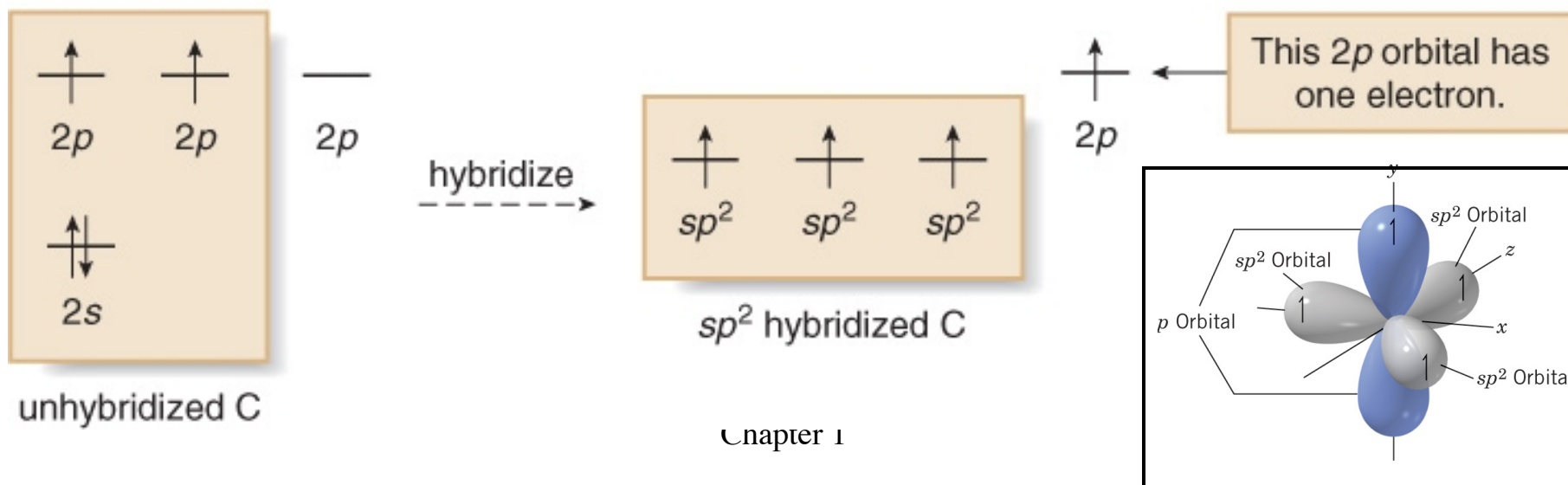


Structure and Bonding

Hybridization and Bonding in Organic Molecules

- ➡ There are three σ bonds around each carbon of ethene and these are formed by using sp^2 hybridized orbitals
- ➡ The three sp^2 hybridized orbitals come from mixing one s and two p orbitals
 - ★ One p orbital is left unhybridized
- ➡ The sp^2 orbitals are arranged in a trigonal planar arrangement
 - ★ The p orbital is perpendicular (orthogonal) to the plane

Forming an sp^2 hybridized carbon atom



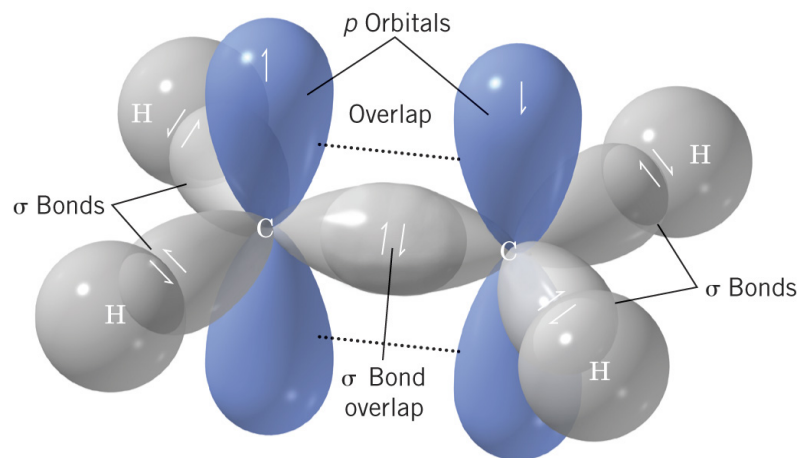
➡ **Overlap of sp^2 orbitals in ethylene results in formation of a σ framework**

- ★ One sp^2 orbital on each carbon overlaps to form a carbon-carbon σ bond; the remaining sp^2 orbitals form bonds to hydrogen

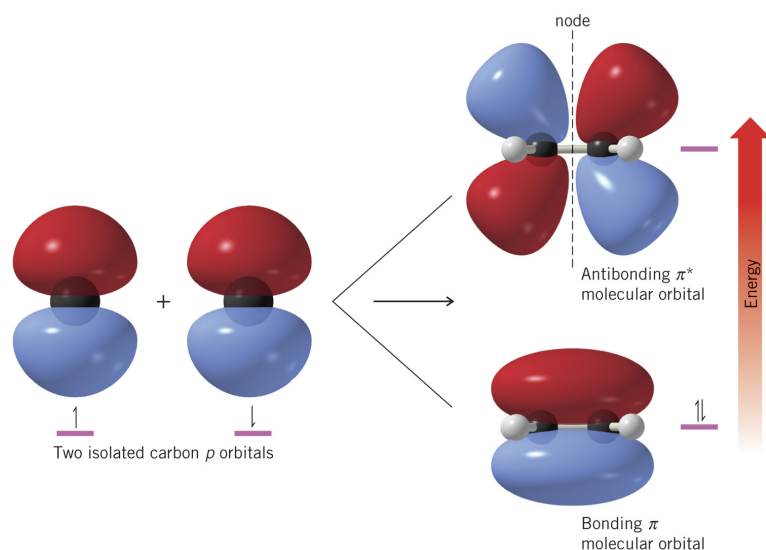
➡ **The leftover p orbitals on each carbon overlap to form a bonding π bond between the two carbons**

➡ **A π bond results from overlap of p orbitals above and below the plane of the σ bond**

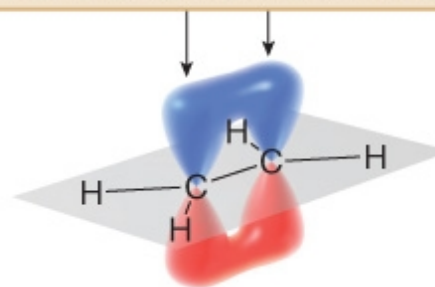
- ★ It has a nodal plane passing through the two bonded nuclei and between the two lobes of the π molecular orbital



- ➔ The bonding π orbital results from overlap of p orbital lobes of the same sign
- ➔ The antibonding π^* orbital results from overlap of p orbital lobes of opposite sign
 - ★ The antibonding orbital has one node connecting the two nuclei and another node between the two carbons
- ➔ The bonding π orbital is lower in energy than the antibonding orbital
 - ★ In the ground state two spin paired electrons are in the bonding orbital
 - ★ The antibonding π^* orbital can be occupied if an electron becomes promoted from a lower level (e.g. by absorption of light)

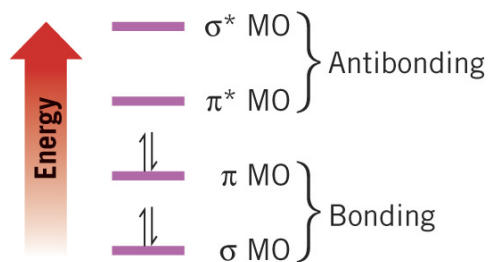


Overlap of the $2p$ orbitals forms the second C–C bond.



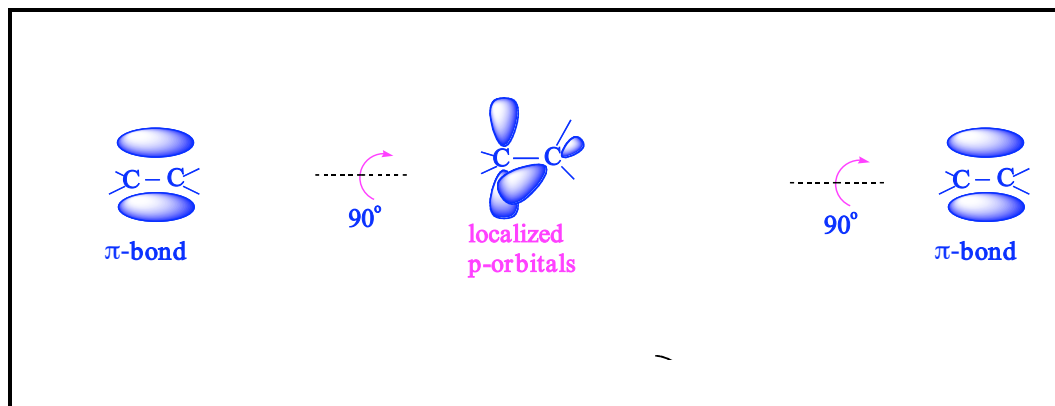
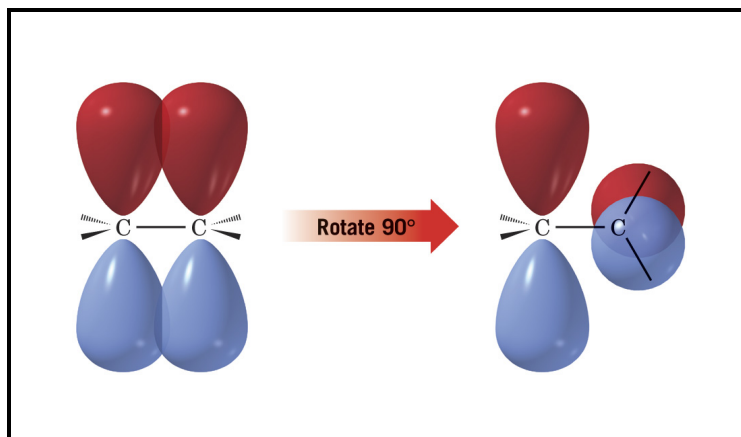
➔ **The σ orbital is lower in energy than the π orbital**

★ The ground state electronic configuration of ethene is shown



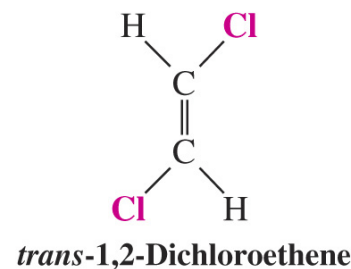
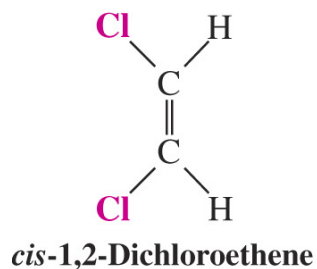
◆ Restricted Rotation and the Double Bond

- ➔ There is a large energy barrier to rotation (about 264 kJ/mol) around the double bond
 - ★ This corresponds to the strength of a π bond
 - ★ The rotational barrier of a carbon-carbon single bond is 13-26 kJ/mol
- ➔ This rotational barrier results because the p orbitals must be well aligned for maximum overlap and formation of the π bond
- ➔ Rotation of the p orbitals 90° totally breaks the π bond

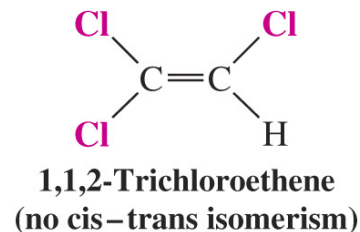
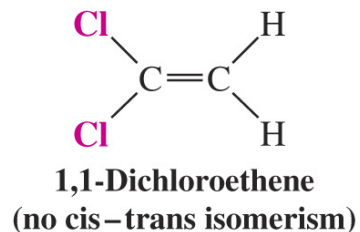


● Cis-trans isomers

- ➔ Cis-trans isomers are the result of restricted rotation about double bonds
- ➔ These isomers have the same connectivity of atoms and differ only in the arrangement of atoms in space
 - ★ This puts them in the broader class of stereoisomers
- ➔ The molecules below do not *superpose* on each other
- ➔ One molecule is designated cis (groups on same side) and the other is trans (groups on opposite side)

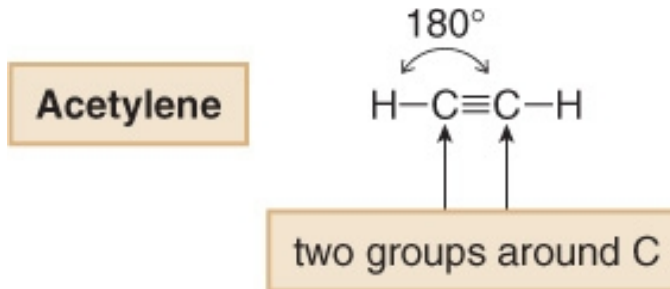


- ➔ Cis-trans isomerism is not possible if one carbon of the double bond has two identical groups

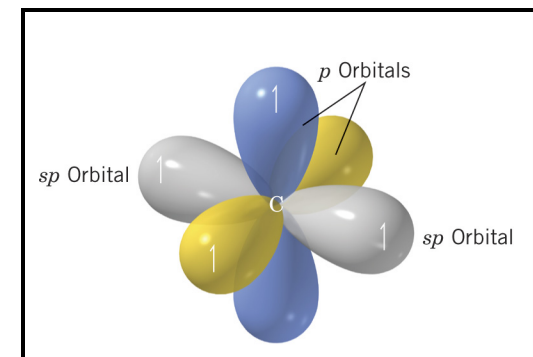
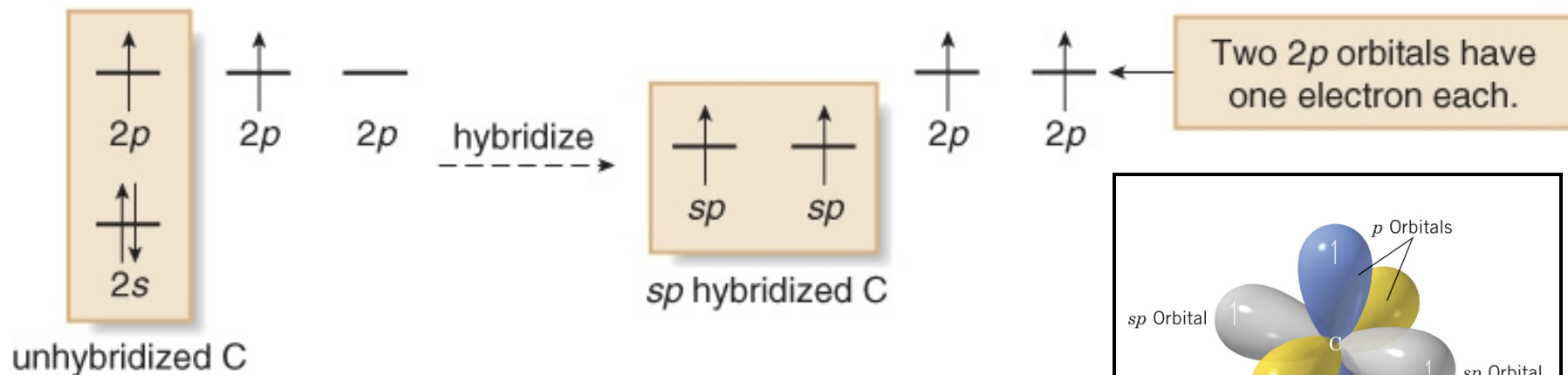


Structure and Bonding

The Structure of Ethyne (Acetylene): sp Hybridization Hybridization and Bonding in Organic Molecules

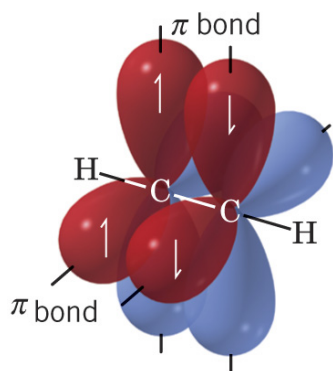


Forming an sp hybridized carbon atom

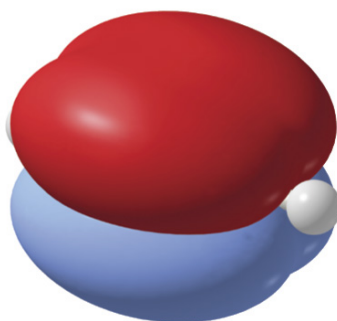


➔ **Depictions of ethyne show that the electron density around the carbon-carbon bond has circular symmetry**

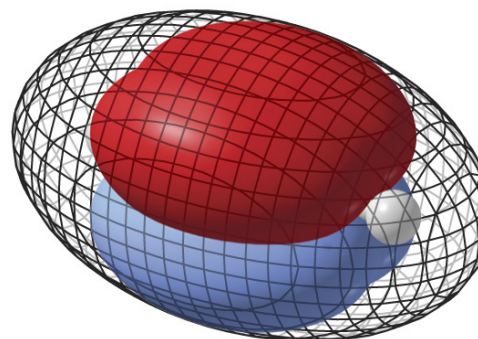
- ★ Even if rotation around the carbon-carbon bond occurred, a different compound would not result



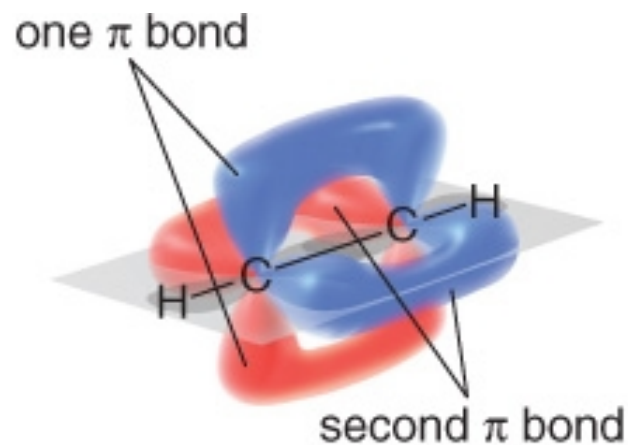
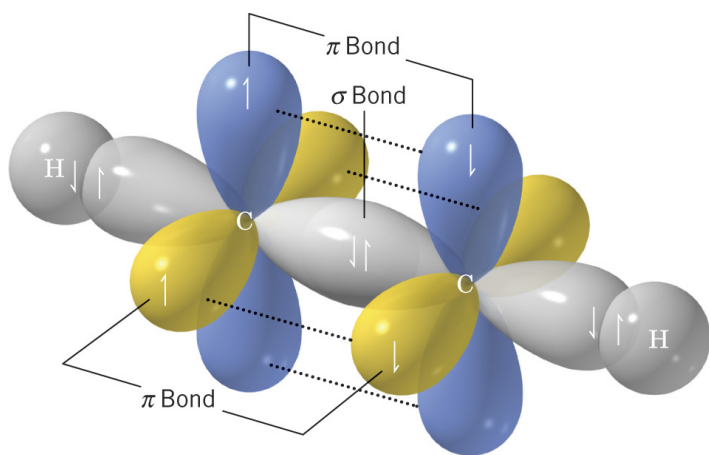
(a)



(b)

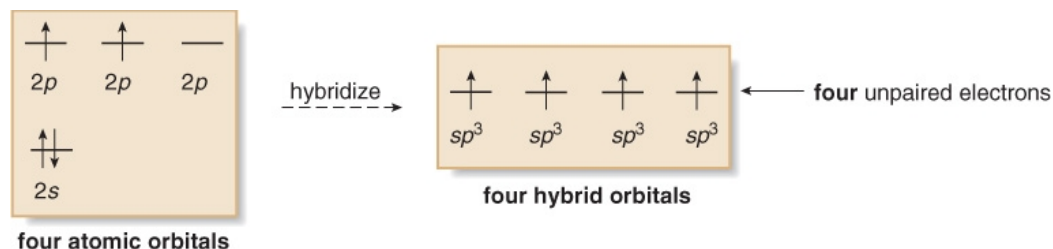


(c)

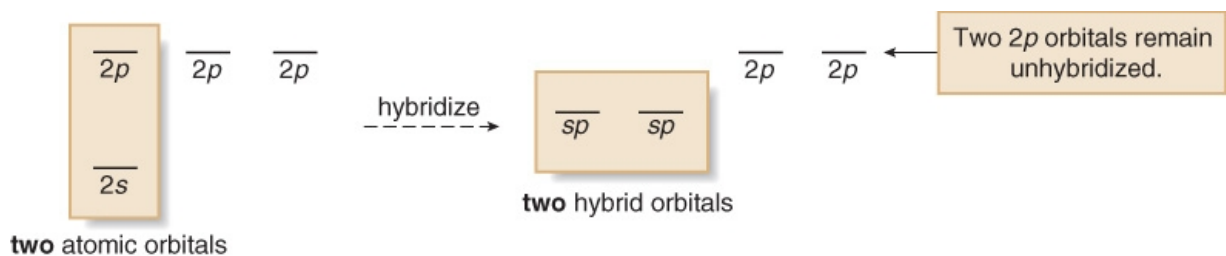


Summary of Hybridization

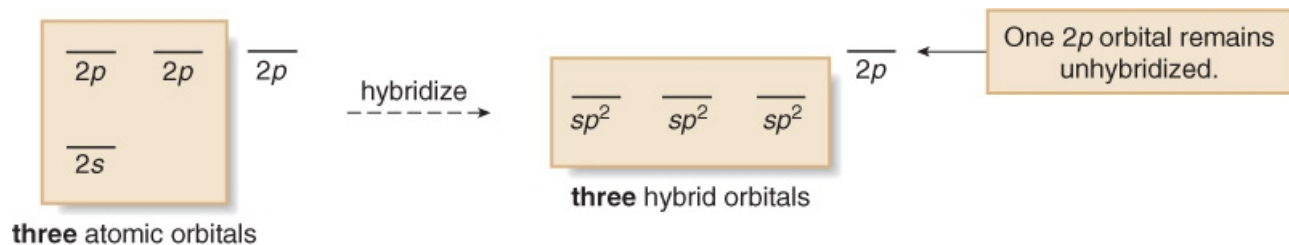
- **One 2s orbital and three 2p orbitals forming:**



Forming **four sp³ hybrid orbitals** using **one 2s** and **three 2p** orbitals.



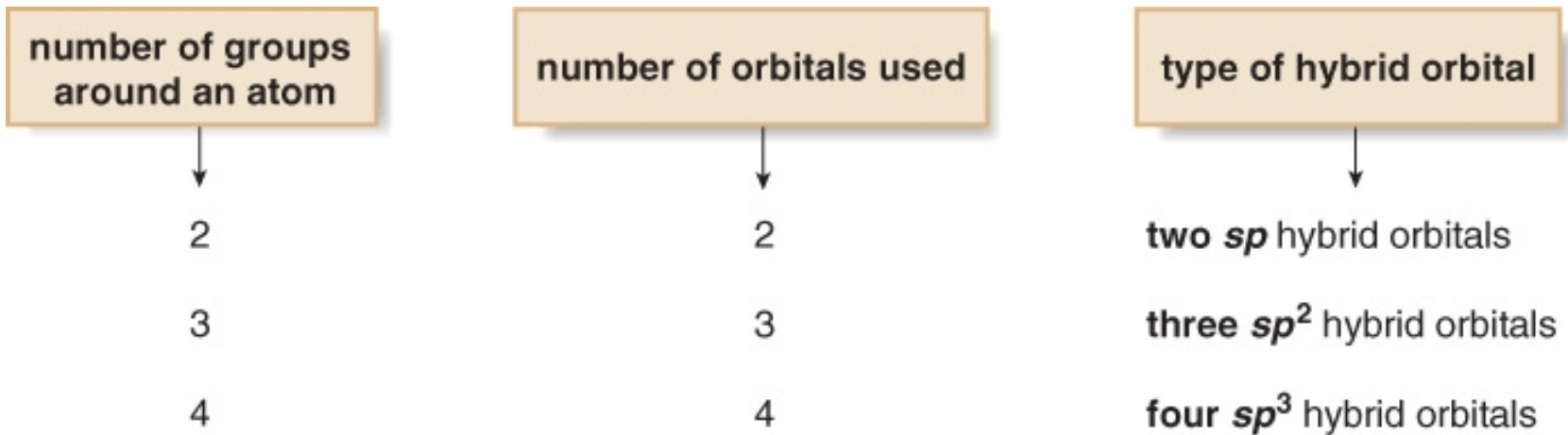
- Forming **two sp hybrid orbitals** uses **one 2s** and **one 2p** orbital, leaving **two 2p orbitals unhybridized**.



- Forming **three sp² hybrid orbitals** uses **one 2s** and **two 2p** orbitals, leaving **one 2p orbital unhybridized**.

Structure and Bonding

To determine the hybridization of an atom in a molecule, we count the number of groups around the atom. The number of groups (atoms and nonbonded electron pairs) corresponds to the number of atomic orbitals that must be hybridized to form the hybrid orbitals.



Structure and Bonding

Orbital Hybridization

Increased percent s-character \dashrightarrow Increased bond strength \dashrightarrow Decreased bond length

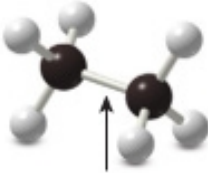
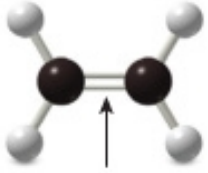
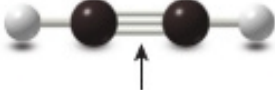
$$sp \text{ hybrid} \quad \frac{\text{one } 2s \text{ orbital}}{\text{two hybrid orbitals}} = \mathbf{50\% \text{ s-character}}$$

$$sp^2 \text{ hybrid} \quad \frac{\text{one } 2s \text{ orbital}}{\text{three hybrid orbitals}} = \mathbf{33\% \text{ s-character}}$$

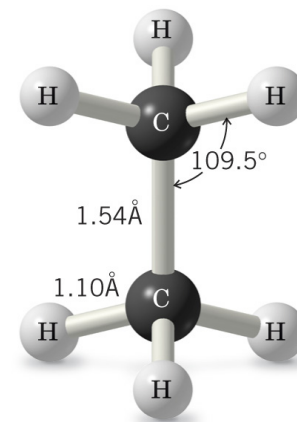
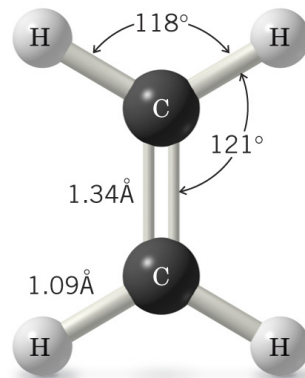
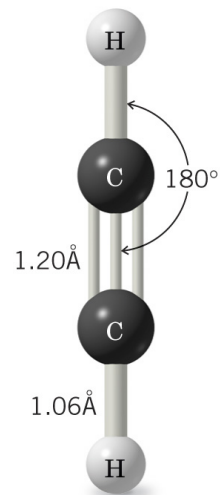
$$sp^3 \text{ hybrid} \quad \frac{\text{one } 2s \text{ orbital}}{\text{four hybrid orbitals}} = \mathbf{25\% \text{ s-character}}$$

Note: As the percent s-character increases, a hybrid orbital holds its electrons closer to the nucleus, and the bond becomes shorter and stronger.

Summary of Covalent Bonding Seen in Carbon Compounds

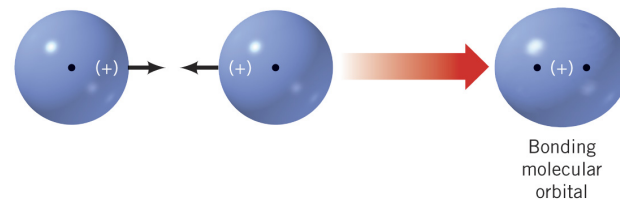
Number of groups bonded to C	Hybridization	Bond angle	Example	Observed bonding
4	sp^3	109.5°	CH_3CH_3 ethane	 <p>one σ bond</p> <p>$\text{C}_{sp^3}-\text{C}_{sp^3}$</p>
3	sp^2	120°	$\text{CH}_2=\text{CH}_2$ ethylene	 <p>one σ bond + one π bond</p> <p>$\text{C}_{sp^2}-\text{C}_{sp^2}$ $\text{C}_{2p}-\text{C}_{2p}$</p>
2	sp	180°	$\text{HC}\equiv\text{CH}$ acetylene	 <p>one σ bond + two π bonds</p> <p>$\text{C}_{sp}-\text{C}_{sp}$ $\text{C}_{2p}-\text{C}_{2p}$ $\text{C}_{2p}-\text{C}_{2p}$</p>

Ethyne, Ethene and Ethane

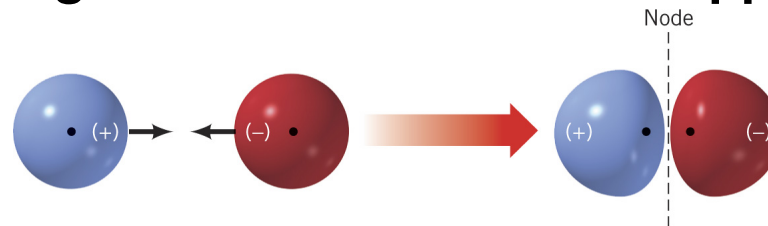


◆ Summary of Concepts from Quantum Mechanics

- **Atomic Orbital(AO):** region in space around a nucleus where there is a high probability of finding an electron
- **Molecular Orbital (MO):** results from overlap of atomic orbitals
- **Bonding Orbitals:** when AOs of same sign overlap



- **Antibonding Orbitals:** when AOs of opposite sign overlap



- **The energy of electrons in a bonding orbital is less than the energy of the individual atoms**

★ The energy of electrons in an antibonding orbitals is more

- **The number of molecular orbitals formed equals the number of the atomic orbitals used**
- **Hybridized orbitals are obtained by mixing the wave functions of different types of orbitals**
 - ➡ **Four sp^3 orbitals are obtained from mixing one s and three p orbitals**
 - ★ The geometry of the four orbitals is tetrahedral
 - ★ This is the hybridization used in the carbon of methane
 - ➡ **Three sp^2 orbitals are obtained from mixing one s and two p orbitals**
 - ★ The geometry of the three orbitals is trigonal planar
 - ★ The left over p orbital is used to make a π bond
 - ★ This is the hybridization used in the carbons of ethene
 - ➡ **Two sp orbitals are obtained from mixing one s and one p orbital**
 - ★ The geometry of the two orbitals is linear
 - ★ The two leftover p orbitals are used to make two π bonds
 - ★ This is the hybridization used in the carbons of ethyne
 - ➡ **Sigma (σ) bonds have circular symmetry when viewed along the bond axis**
 - ➡ **Pi (π) bonds result from sideways overlap of two p orbitals**

Structure and Bonding

Determining Molecular Shape

Bond angle determines the shape around any atom bonded to two other atoms.

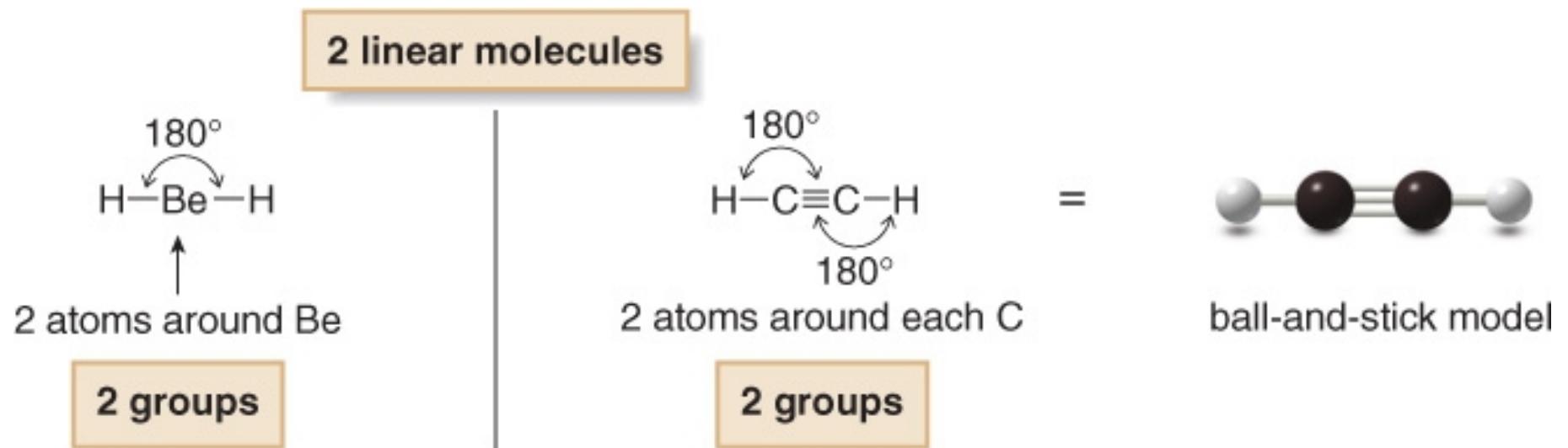
- The number of groups surrounding a particular atom determines its geometry. **A group is either an atom or a lone pair of electrons.**
- The most stable arrangement keeps these groups as far away from each other as possible. This is exemplified by **Valence Shell Electron Pair Repulsion (VSEPR) theory.**

Number of groups	Geometry	Bond angle
• two groups	linear	180°
• three groups	trigonal planar	120°
• four groups	tetrahedral	109.5°

Structure and Bonding

Determining Molecular Shape

Two groups around an atom—

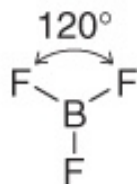


Structure and Bonding

Determining Molecular Shape

Three groups around an atom—

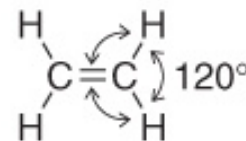
Two trigonal planar molecules



three atoms around B

three groups

All three B–F bonds lie in one plane.

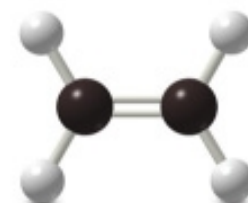


three atoms around each C

three groups

All six atoms lie in one plane.

=



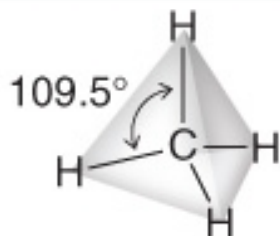
ethylene

Structure and Bonding

Determining Molecular Shape

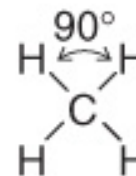
Four groups around an atom—

Tetrahedral arrangement



preferred geometry
larger H-C-H bond angle

Square planar arrangement

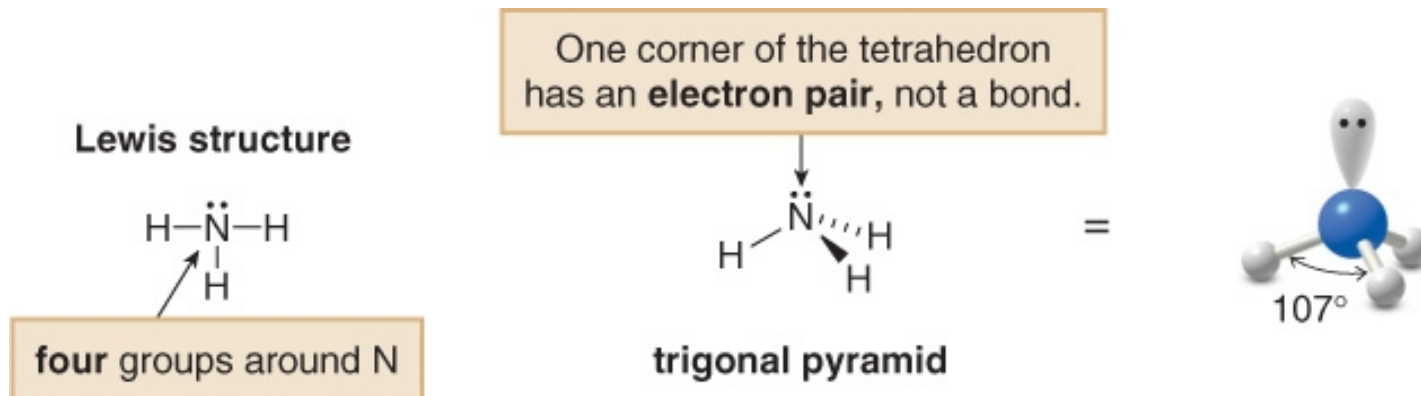


This geometry does *not* occur.

Structure and Bonding

A Nonbonded Pair of Electrons is Counted as a “Group”

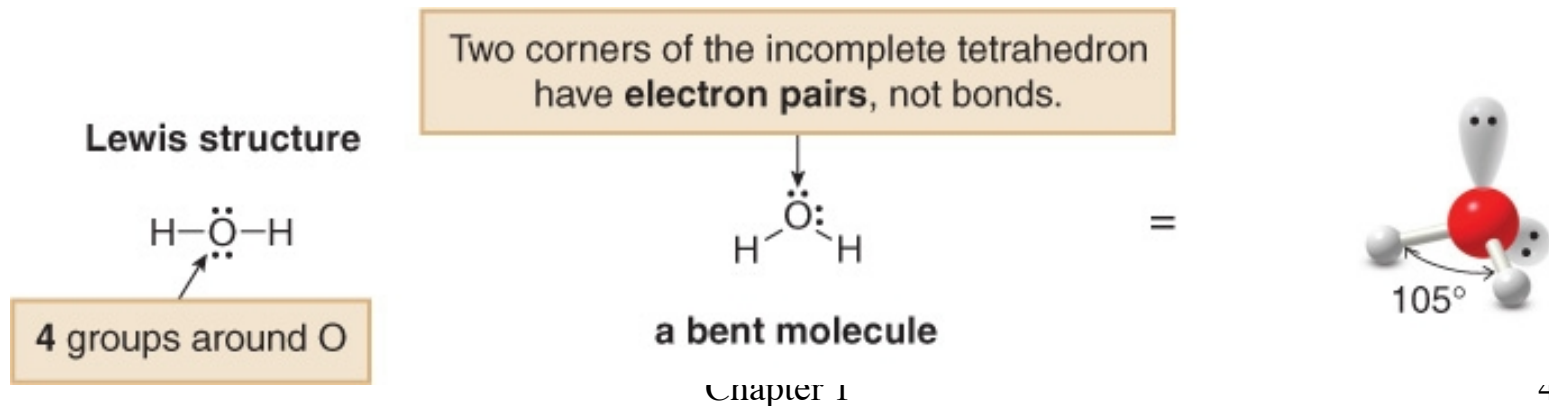
In ammonia (NH_3), one of the four groups attached to the central N atom is a lone pair. The three H atoms and the lone pair point to the corners of a tetrahedron. The H-N-H bond angle of 107° is close to the theoretical tetrahedral bond angle of 109.5° . This shape is referred to as a **trigonal pyramid**.

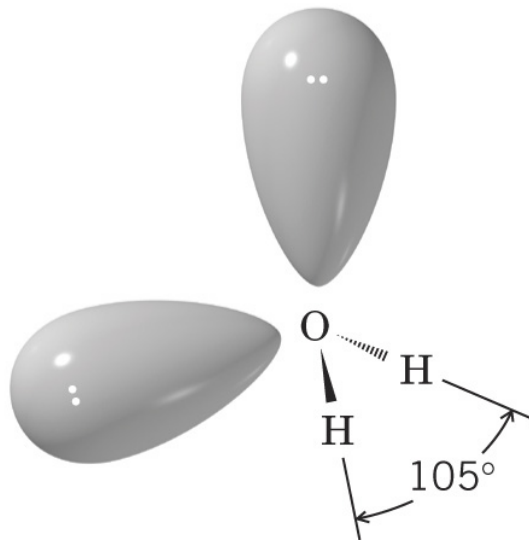


Structure and Bonding

A Nonbonded Pair of Electrons is Counted as a “Group”

In water (H_2O), two of the four groups attached to the central O atom are lone pairs. The two H atoms and two lone pairs around O point to the corners of a tetrahedron. The H-O-H bond angle of 105° is close to the theoretical tetrahedral bond angle of 109.5° . Water has a bent shape, because the two groups around oxygen are lone pairs of electrons.





Water

Bent Shape

A Summary of VSEPR Theory

TABLE 1.4 Shapes of Molecules and Ions from VSEPR Theory

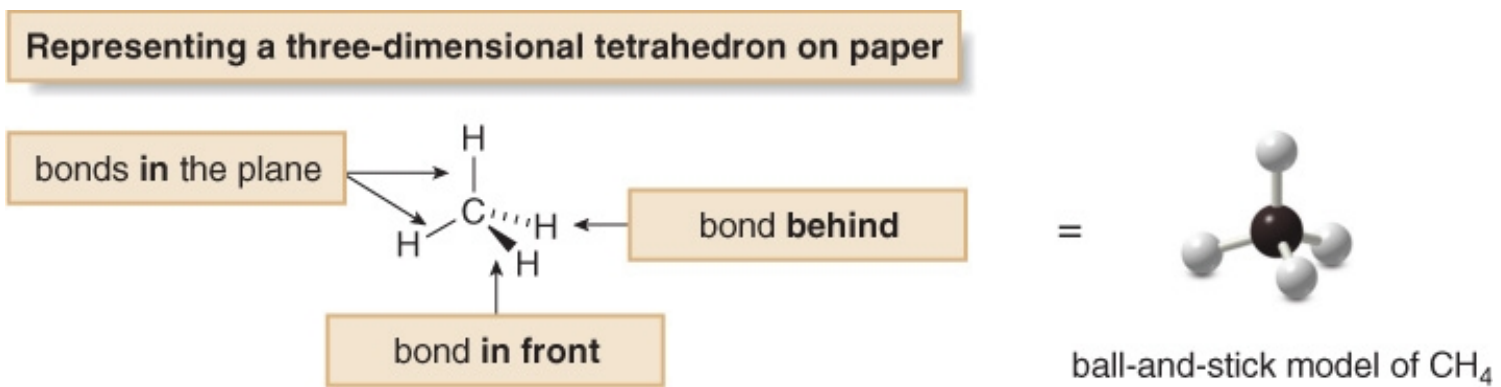
Number of Electron Pairs at Central Atom			Hybridization State of Central Atom	Shape of Molecule or Ion ^a	Examples
Bonding	Nonbonding	Total			
2	0	2	sp	Linear	BeH ₂
3	0	3	sp^2	Trigonal planar	BF ₃ , CH ₃ ⁺
4	0	4	sp^3	Tetrahedral	CH ₄ , NH ₄ ⁺
3	1	4	$\sim sp^3$	Trigonal pyramidal	NH ₃ , CH ₃ ⁻
2	2	4	$\sim sp^3$	Angular	H ₂ O

^aReferring to positions of atoms and excluding nonbonding pairs.

Structure and Bonding

Drawing Three Dimensional Structures

- A solid line is used for a bond in the plane of the paper.
- A wedge is used for a bond in front of the plane.
- A dashed line is used for a bond behind the plane.

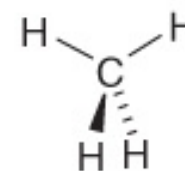
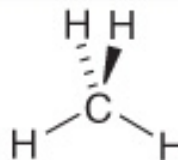
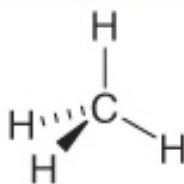
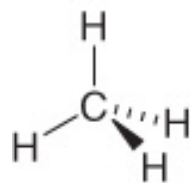


Structure and Bonding

Drawing Three Dimensional Structures

The molecule can be turned in many different ways, generating many equivalent representations. All of the following are acceptable drawings for CH_4 .

Four equivalent drawings of CH_4

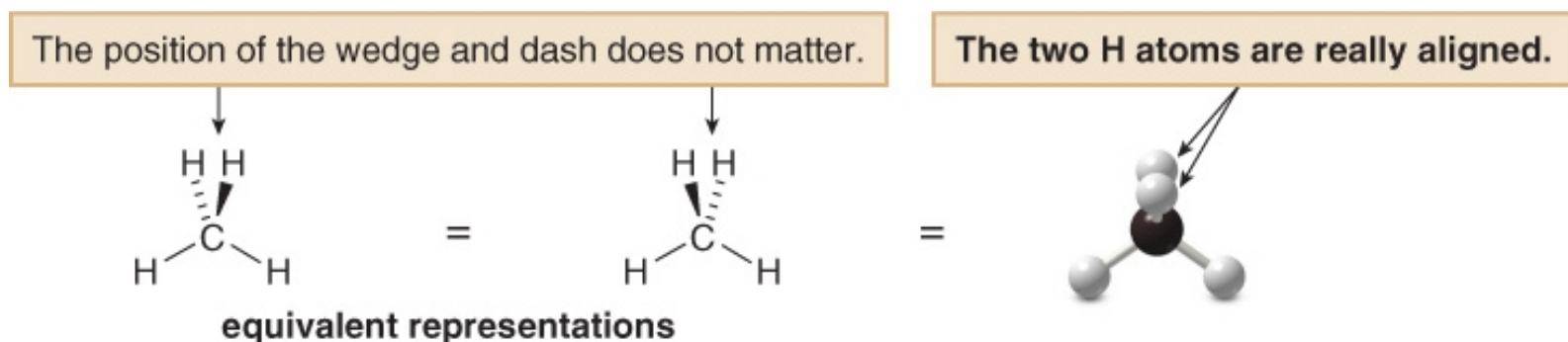


Each drawing has two solid lines, one wedge, and one dashed line.

Structure and Bonding

Drawing Three Dimensional Structures

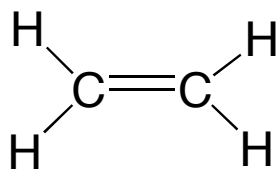
Note that wedges and dashes are used for groups that are really aligned one behind another. It does not matter in the following two drawings whether the wedge or dash is skewed to the left or right, because the two H atoms are really aligned.



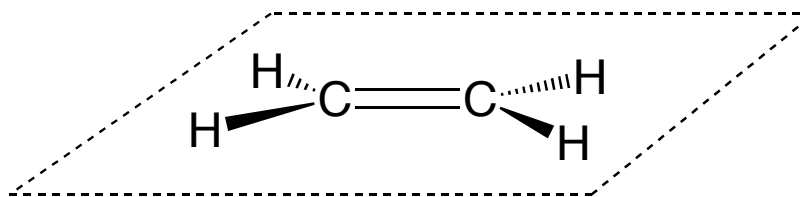
- ➔ **Trigonal planar arrangements of atoms can be drawn in 3-dimensions in the plane of the paper (top view)**

★ Bond angles should be approximately 120°

- ➔ **These can also be drawn side-on with the central bond in the plane of the paper, one bond forward and one bond back**

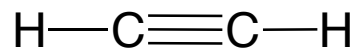


Top View (most common)

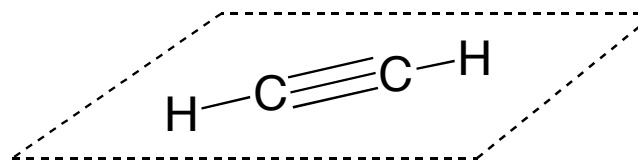


Side (Perspective) View

- ➔ **Linear arrangements of atoms are best drawn in the plane of the paper, but they can also be drawn at an angle to show perspective.**



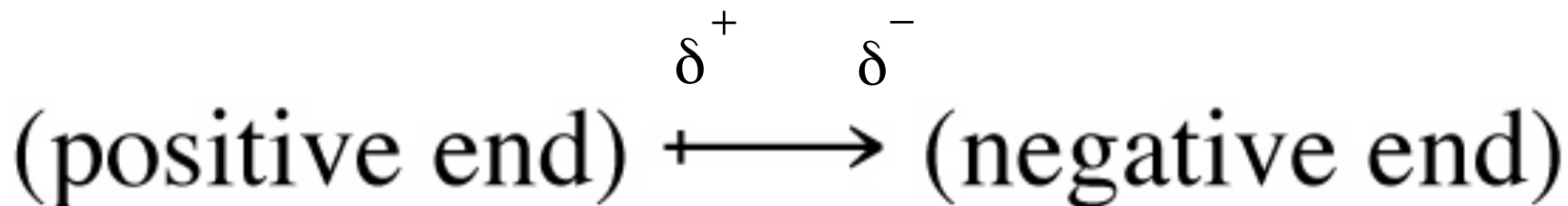
Top View (most common)



Side (Perspective) View

Polar Covalent Bonds

- ◆ **When a covalent bond is formed between two atoms of differing electronegativities, the bond will be polar.**
 - **The more electronegative atom draws electron density closer to itself**
 - **The more electronegative atom develops a partial negative charge (δ^-) and the less electronegative atom develops a partial positive charge (δ^+)**
 - **A bond which is polarized is a dipole and has a dipole moment**
 - **The direction of the dipole can be indicated by a dipole arrow**



Example: the molecule HCl

The more electronegative chlorine draws electron density away from the hydrogen

- Chlorine develops a partial negative charge



The dipole moment of a molecule can be measured

- It is the product of the magnitude of the charges (in electrostatic units: esu) and the distance between the charges (in cm)
- The actual unit of measurement is the Debye (D) which is equivalent to 1×10^{-18} esu cm

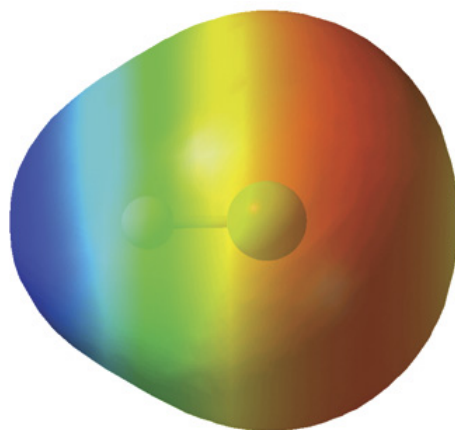
Dipole moment = charge (in esu) \times distance (in cm)

$$\mu = e \times d$$

Visualization of charge distribution

Computer-generated map of electrostatic potential (MEP)

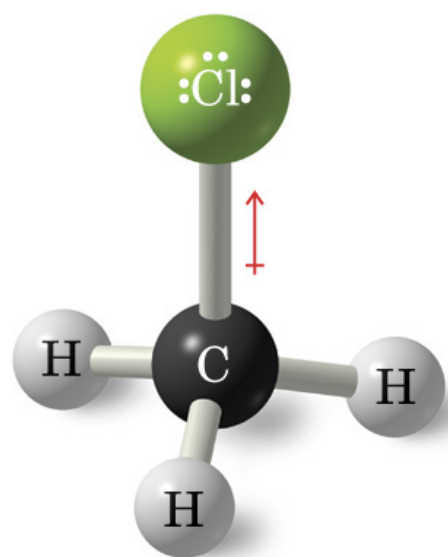
- ◆ **Red = regions of highest electron density**
- ◆ **Blue = regions of lowest electron density**
- ◆ **The MEP is plotted at the van Der Waals surface of a molecule**
 - This is the farthest extent of a molecule's electron cloud
- ◆ **The MEP of hydrogen chlorine shows the negative charge is concentrated near the chlorine**
 - The overall shape of the molecule is also represented



Example: Chloromethane CH_3Cl

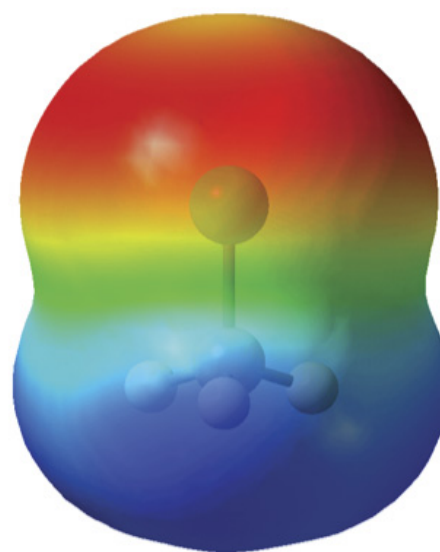
In larger complicated molecules the molecular dipole is the vector sum of the individual bond dipoles.

In chloromethane the C-H bonds have only small dipoles but the C-Cl bond has a large dipole, making molecule quite polar



$$\mu = 1.87 \text{ D}$$

(a)

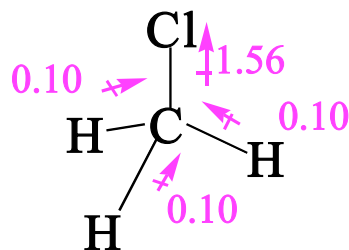


Chloromethane

(b)

Chloromethane – a closer look

The analysis assumes a tetrahedral geometry.



The net dipole moment in the +Z direction is

$$\begin{array}{r} \uparrow 1.56 \quad (\text{C-Cl}) \\ \uparrow 0.10 \quad 3 \times (\text{C-H}) \\ \hline 1.66 \text{ D} \end{array}$$

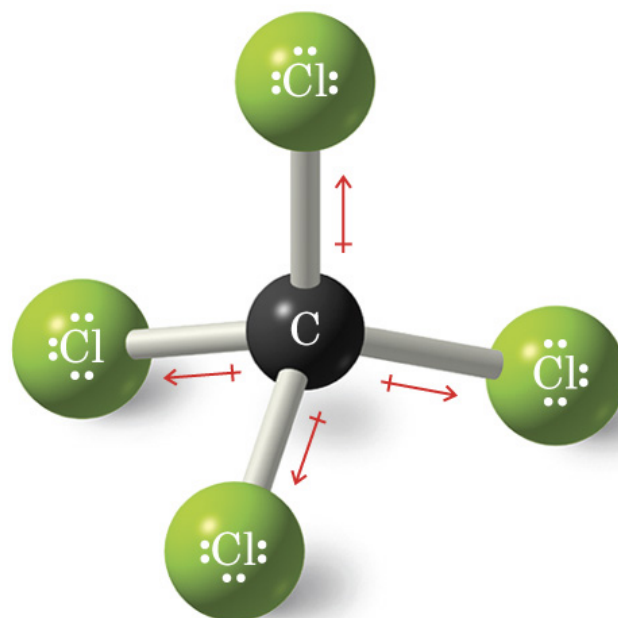
Note: The **direction** of the C-H bond moment is determined from this and similar analyses to be H-C.



Example: Carbon tetrachloride

Some molecules with polar bonds will have no net molecular dipole because **the bond dipoles cancel out**.

In carbon tetrachloride the bond dipoles cancel and the overall molecular dipole is 0 Debye.

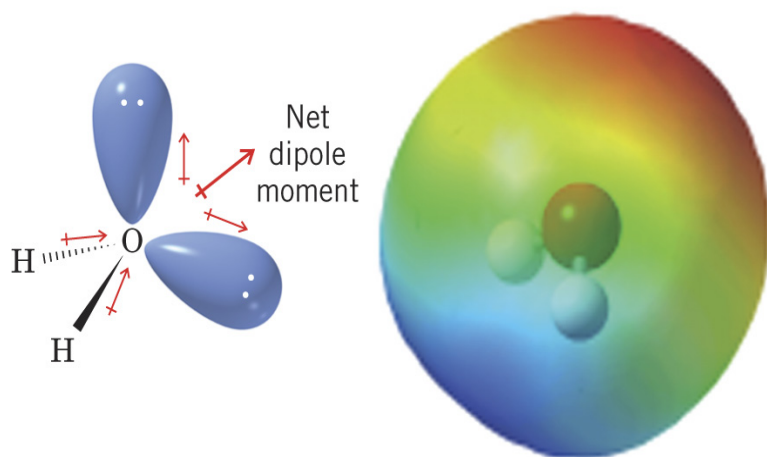


$$\mu = 0 \text{ D}$$

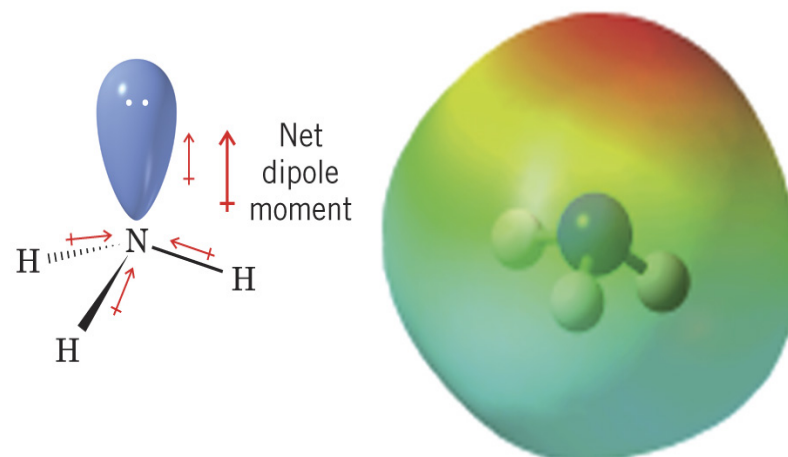
Lone pairs can contribute to dipoles

An unshared pair of electrons on atoms such as oxygen and nitrogen contribute a great deal to a dipole

Water and ammonia have very large net dipoles



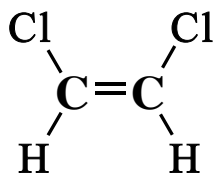
Water



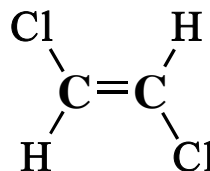
Ammonia

Geometric isomers may be identified by dipole moments

- In **trans 1,2-dichloroethene** the two carbon-chlorine dipoles cancel out and the molecular dipole is 0 Debye
- In the **cis isomer** the carbon-chlorine dipoles reinforce and there is a large molecular dipole



cis-1,2-dichloroethene



trans-1,2-dichloroethene

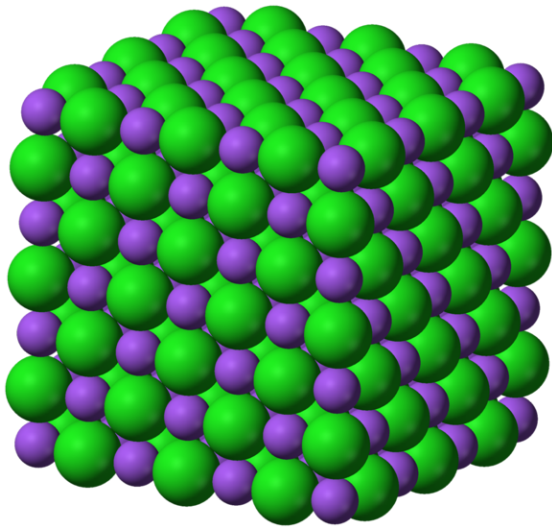
Compound	Melting Point (°C)	Boiling Point (°C)	Dipole Moment (D)
cis-1,2-Dichloroethene	- 80	60	1.90
trans-1,2-Dichloroethene	- 50	48	0
cis-1,2-Dibromoethene	- 53	112.5	1.35
trans-1,2-Dibromoethene	- 6	108	0

Structure and Physical Properties

- ◆ What makes atoms and molecules stick to one another?
- ◆ **Intermolecular Attractive Forces**
- ◆ If there were no intermolecular attractive forces, everything would be a gas!
 - Helium - exists as a gas down to 4° K
- ◆ In order to exist as solids or liquids, molecules must have some attractive forces, which are overcome in melting, boiling, and solubility
- ◆ Higher melting points and boiling points will be a measure of the strength of the intermolecular attractive forces
- ◆ Intermolecular attractive forces are based on electrostatic attractions, either permanent or temporarily-induced

Greatest intermolecular forces are between ions

- ◆ Ions of opposite charge attract each other strongly
- ◆ They form a solid consisting of ions held together in a crystalline lattice
- ◆ Ionically bonded compounds are usually well ordered crystals with high melting points



mp 801°C

NaCl

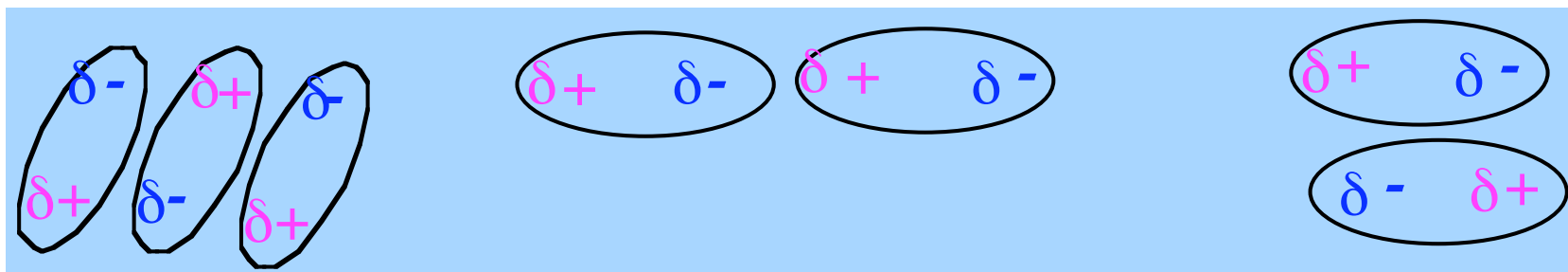


Dipole-Dipole Forces

(a second type of Intermolecular Attractive Force)

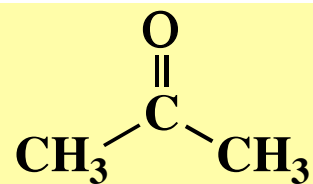
Forces are between molecules with permanent dipoles

- There is an attraction between $\delta+$ and $\delta-$ areas in each molecule
- Much weaker than ion-ion forces
- Molecules align to maximize attraction of $\delta+$ and $\delta-$ parts of molecules

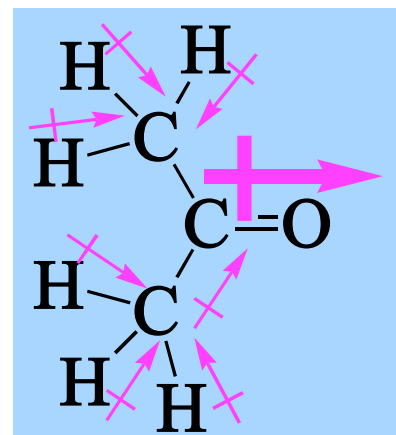


These interactions are felt in the close distances of condensed phases
(liquids and solids)

An Example of a Polar Molecule: Acetone

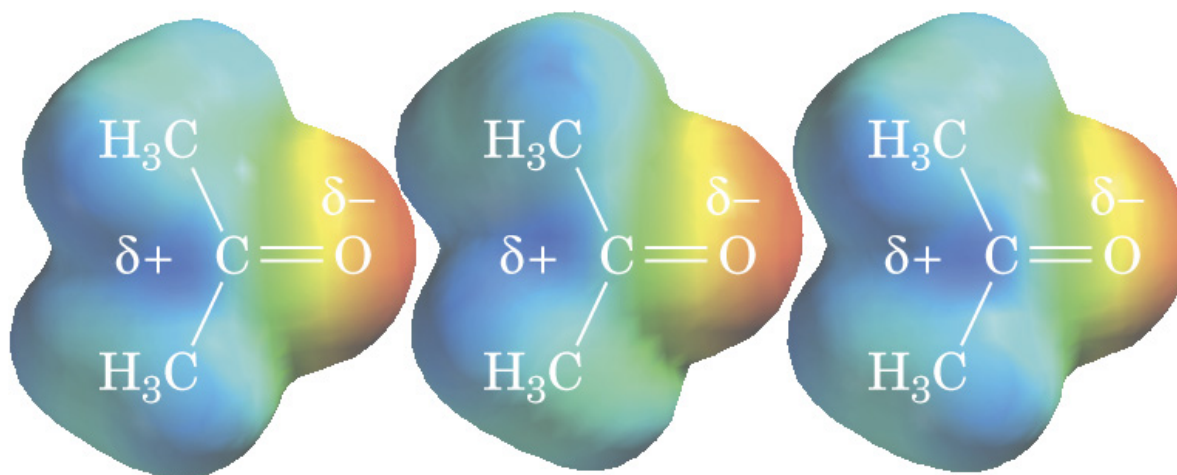


The **carbonyl** is a highly polarized bond because of the electronegative oxygen atom and the highly polarizable π electrons.

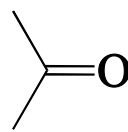
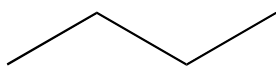


Net dipole moment = 2.72

D



Comparing Acetone and Butane

		
MW	58	58
MP	-95 °C	-138 °C
BP	56 °C	-0.5 °C
solubility in water	miscible	insoluble

More thermal energy (higher temp) is need to overcome intermolecular forces in more polar molecules. Therefore, higher melting point and boiling point

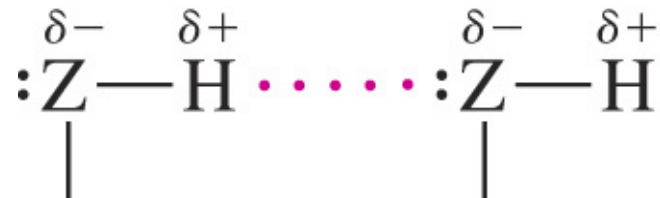
**Also, solubility reflects interaction of dipole with water molecules
(we' ll discuss this later)**

Hydrogen bonding

(a third type of Intermolecular Attractive Force)

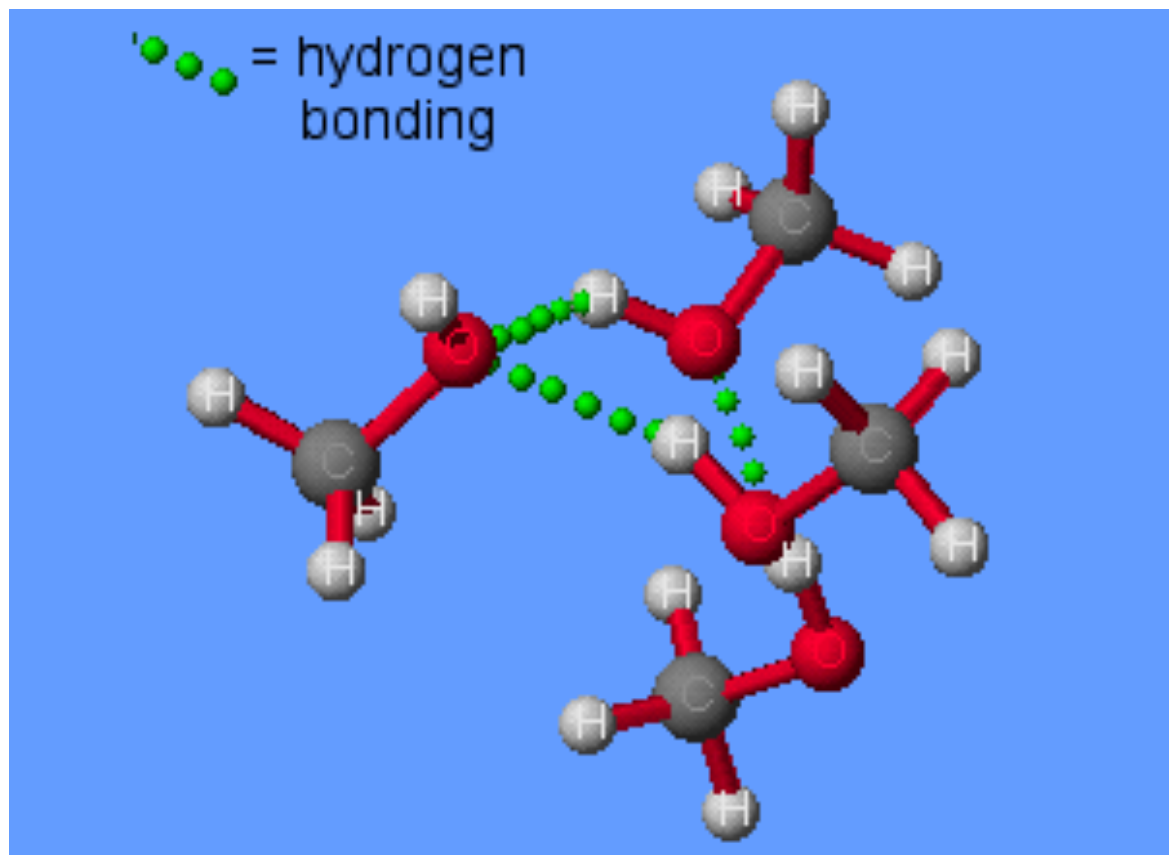
- **Hydrogen Bonds**

- ➔ There is an interaction between hydrogens bonded to strongly electronegative atoms (O, N or F) and nonbonding electron pairs on other strongly electronegative atoms (O, N or F)



Hydrogen bonding

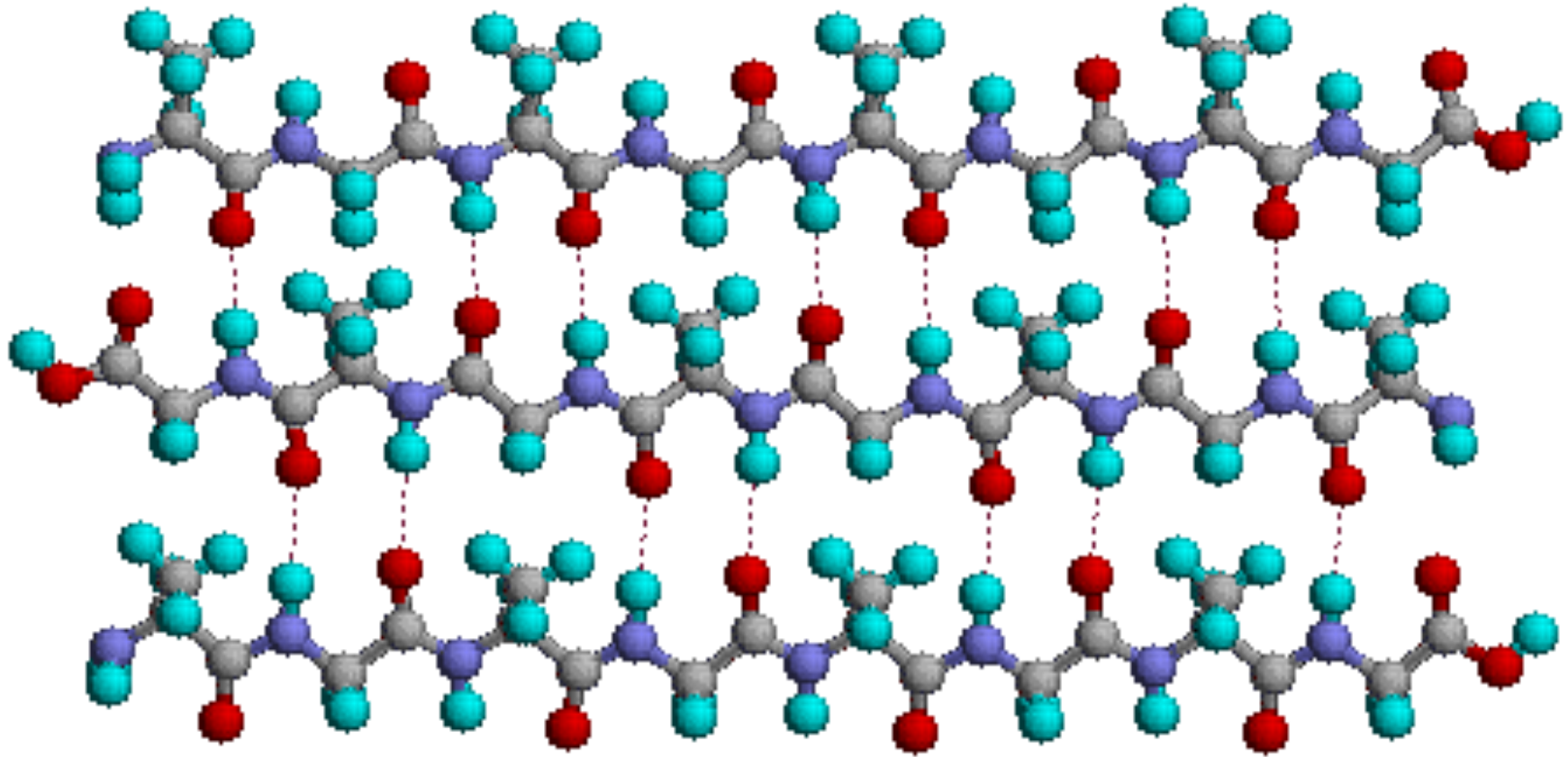
- ◆ H is electron-deficient in these bonds with small electronegative elements (O, N, and F)
- ◆ Links to the lone pairs on the X atom
- ◆ About 10% the strength of a covalent bond



**H-bonding in
Methyl alcohol
CH₃OH**

HYDROGEN BONDING IN PROTEINS

Model of H-bonding in a β -sheet protein

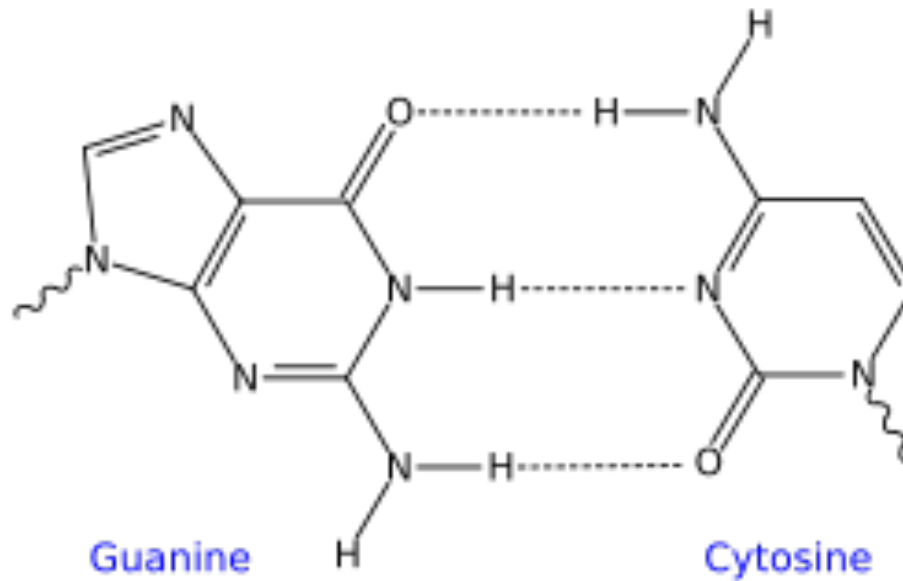


red=oxygen

purple=nitrogen

H-bonding in DNA bases

- ◆ The replication mechanism in DNA and RNA is dependent on the “perfect fit” between specific bases



Van der Waals Forces

(the fourth Intermolecular Attractive Force)

- ◆ Why does Methane (m.p. -182°C , b.p. -162°C) condense at all
- ◆ These are the weakest of the Intermolecular Attractive Forces
- ◆ Caused by **Induced dipoles**
 - At one instant, electrons may be more on one side than another
 - Electrons on adjacent molecule tend to align with that temporary dipole
 - These temporary opposite dipoles cause a weak attraction between the two molecules
- ◆ Also known as London Forces or London dispersion forces

Consider an oval molecule like ethane or N₂



Spontaneous dipole

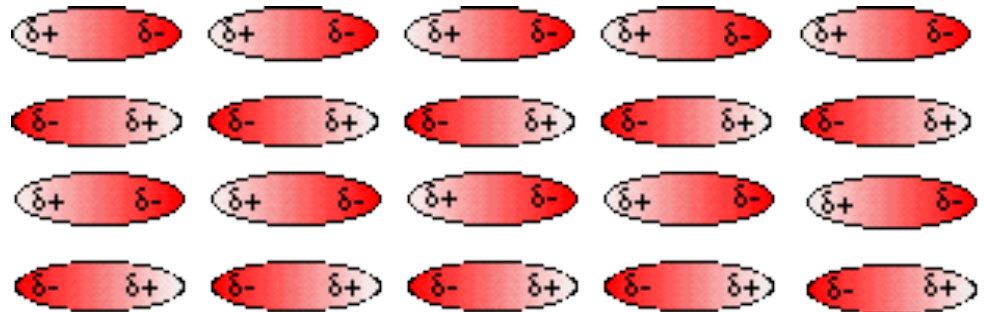


original temporary dipole

induced dipole



Fluctuates in sync



Into 3 dimensions

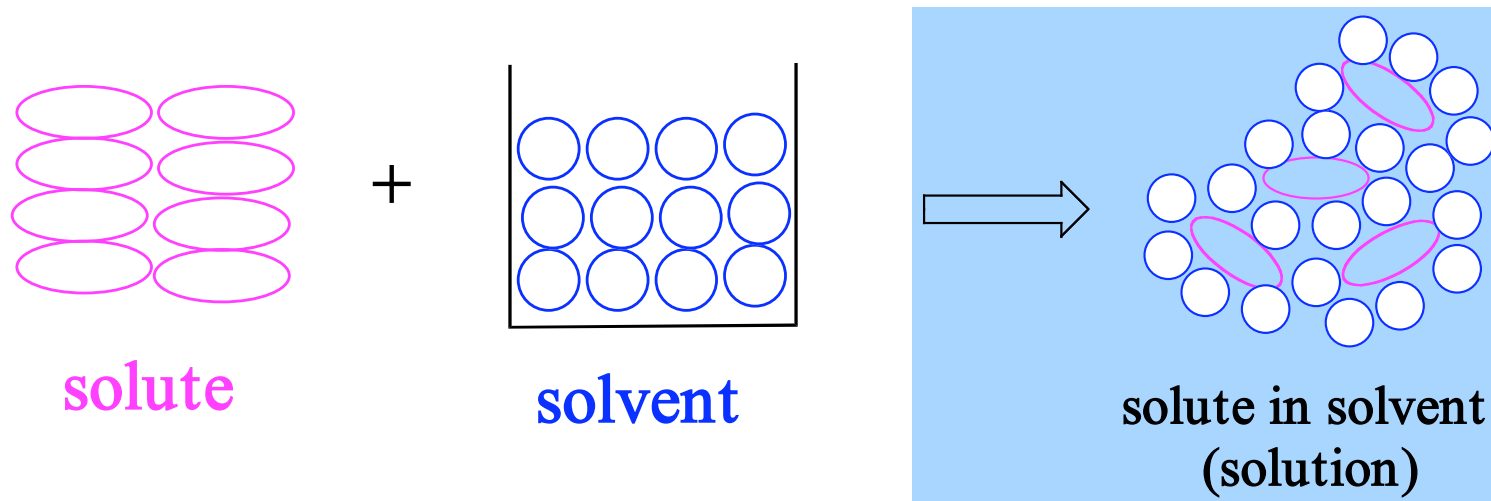
van der Waals Forces are small, but...

- Molecules which rely only on van der Waals forces generally have low melting points and boiling points

**A Gecko can hang
from 1 pad, with
no known stickum**

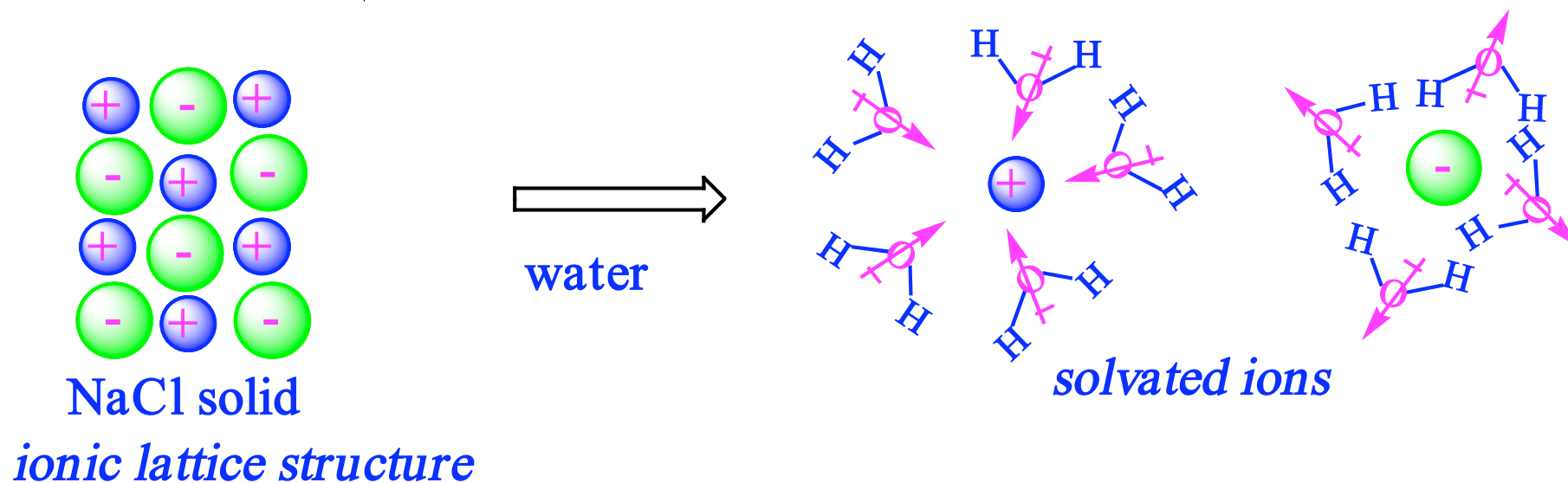


Solubilities are a Result of Intermolecular Attractive Forces



Solution occurs because IAF' s between solvent and solute molecules are stronger than between solute molecules with one another.

Why ionic compounds tend to dissolve in water



Ion-dipole interactions are strong

The solvation energy of the solvated ions is greater than the lattice energy of the ionic solid

“Like Dissolves Like”

- ◆ **Polar compounds tend to dissolve in polar solvents**
 - **Polar liquids are miscible with other polar liquids**
- ◆ **Hydrogen-bonding of oxygen or nitrogen facilitates solubility in protic solvents such as water or alcohol**
- ◆ **Non-polar compounds are more soluble in non-polar solvents**
 - **Non-polar liquids and polar liquids are usually immiscible**

➡ Generally the presence of one hydrophilic group (*e.g.*, hydroxyl) can make a compound with 3 carbons completely soluble in water.

★ One hydrophilic group can make a 5 carbon compound at least partially soluble in water.

★ A compound is said to be “water soluble” if at least 3g of it will dissolve in 100 mL of water

➡ A large alkyl group can overwhelm the ability of a polar group which is also in a molecule to solubilize that molecule in water.

For example

- ★ Decyl alcohol is only slightly soluble in water
- ★ The large alkyl portion is hydrophobic (“water hating”) and overwhelms the capacity of the hydrophilic (“water loving”) hydroxyl



Summary of attractive forces

Electric Force	Relative Strength	Type	Example
Cation–anion (in a crystal)	Very strong		Sodium chloride crystal lattice
Covalent bonds	Strong ($140\text{--}523\text{ kJ mol}^{-1}$)	Shared electron pairs	H—H (436 kJ mol^{-1}) CH ₃ —CH ₃ (378 kJ mol^{-1}) I—I (151 kJ mol^{-1})
Ion–dipole	Moderate		Na ⁺ in water (see Fig. 2.9)
Hydrogen bonds	Moderate to weak ($4\text{--}38\text{ kJ mol}^{-1}$)	$\delta^- \cdots \delta^+$	
Dipole–dipole	Weak	$\delta^+ \cdots \delta^-$	
van der Waals	Variable	Transient dipole	Interactions between methane molecules