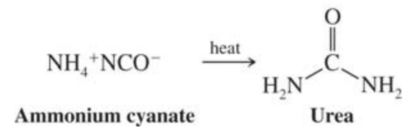
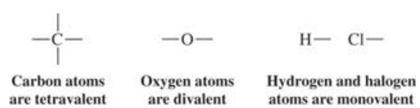
Chapter 1
Carbon Compounds and Chemical Bonds

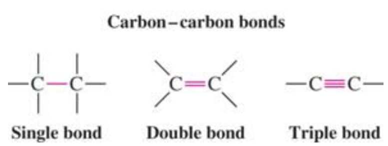
- ♦ **Introduction**
  - **Organic Chemistry**
    - ➔ The chemistry of the compounds of carbon
    - ➔ The human body is largely composed of organic compounds
    - ➔ Organic chemistry plays a central role in medicine, bioengineering etc.
  - **Vitalism**
    - ➔ It was originally thought organic compounds could be made only by living things by intervention of a "vital force"
    - ➔ Fredrich Wöhler disproved vitalism in 1828 by making the organic compound urea from the inorganic salt ammonium cyanate by evaporation:



- ♦ **Structural Theory**
  - **Central Premises**
    - ➔ Valency: atoms in organic compounds form a fixed number of bonds



    - ➔ Carbon can form one or more bonds to other carbons

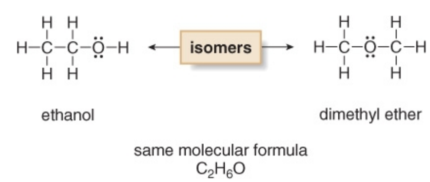


Structure and Bonding

Isomers

In drawing a Lewis structure for a molecule with several atoms, sometimes more than one arrangement of atoms is possible for a given molecular formula.

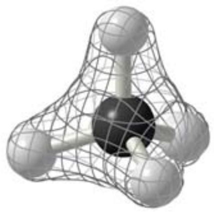
Example:

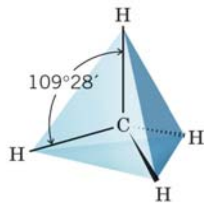


Both are valid Lewis structures and both molecules exist. These two compounds are called isomers.

Isomers are different molecules having the same molecular formula.

- **Three Dimensional Shape of Molecules**
  - ➔ Virtually all molecules possess a 3-dimensional shape which is often not accurately represented by drawings
  - ➔ It was proposed in 1874 by van't Hoff and le Bel that the four bonds around carbon where not all in a plane but rather in a tetrahedral arrangement *i.e.* the four C-H bonds point towards the corners of a regular tetrahedron



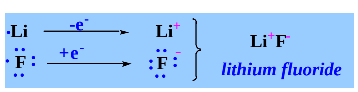


Structure and Bonding

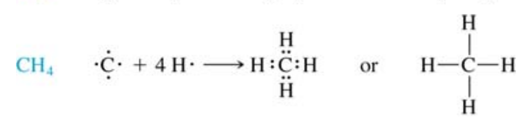
Review of Bonding

- Bonding is the joining of two atoms in a stable arrangement.
- Through bonding, atoms attain a complete outer shell of valence electrons.
- Through bonding, atoms attain a stable noble gas configuration.
- Ionic bonds result from the transfer of electrons from one element to another.
- Covalent bonds result from the sharing of electrons between two nuclei.

- **Ionic Bonds**
  - ➔ When ionic bonds are formed atoms gain or lose electrons to achieve the electronic configuration of the nearest noble gas
    - In the process the atoms become ionic
  - ➔ The resulting oppositely charged ions attract and form ionic bonds
  - ➔ This generally happens between atoms of widely different electronegativities
  - ➔ Example
    - Lithium loses an electron (to have the configuration of helium) and becomes positively charged
    - Fluoride gains an electron (to have the configuration of neon) and becomes negatively charged
    - The positively charged lithium and the negatively charged fluoride form a strong ionic bond (actually in a crystalline lattice)



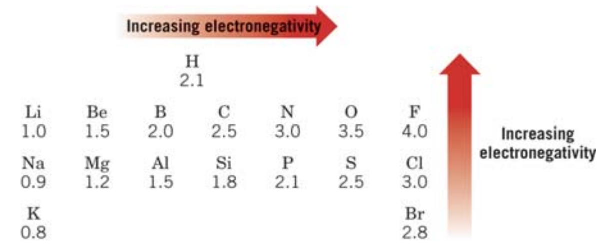
- **Covalent Bonds**
  - ➔ Covalent bonds occur between atoms of similar electronegativity (close to each other in the periodic table)
  - ➔ Atoms achieve octets by *sharing* of valence electrons
  - ➔ Molecules result from this covalent bonding
  - ➔ Valence electrons can be indicated by dots (electron-dot formula or Lewis structures) but this is time-consuming
  - ➔ The usual way to indicate the two electrons in a bond is to use a line (one line = two electrons)

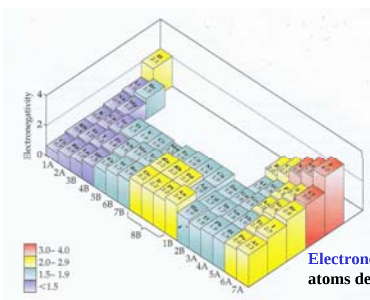


♦ Chemical Bonds: The Octet Rule

- **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**





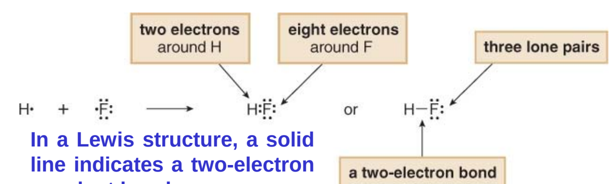
Electronegativity difference between interacting atoms determines the type of bond that is formed.

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

Writing Lewis Structures

Lewis structures are electron dot representations for molecules. There are five general rules for drawing Lewis structures:

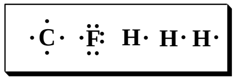
1. **Arrange atoms in correct position on the page.**
2. **Using only the valence electrons, connect each two adjacent atoms using a pair of electrons.**
3. **Make sure that every second-row element has an octet of electrons, if possible. Give each hydrogen atom two electrons.**
4. **Use double bonds or triple bonds, if necessary.**
5. **Indicate formal charges where appropriate.**



In a Lewis structure, a solid line indicates a two-electron covalent bond.

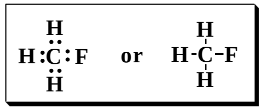
Example CH_3F *methyl fluoride*

The Lewis structures of the atoms are:

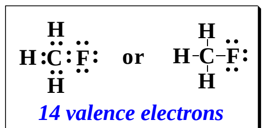


There are 4 + 7 + 3 = 14 valence electrons available for chemical bonding and as nonbonding electron pairs.

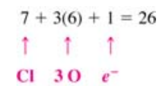
The four covalent bonds to the central carbon atom account for 8 of the valence electrons:



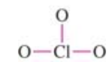
The remaining 6 valence electrons are nonbonding electrons around the fluorine atom. The octet rule applies to both the carbon and fluorine atoms.



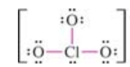
- **Example**
  - ➔ Write the Lewis structure for the chlorate ion (ClO_3^-)
    - The total number of valence electrons including the electron for the negative charge is calculated



    - Three pairs of electrons are used to bond the chlorine to the oxygens



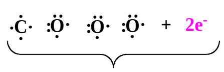
    - The remaining 20 electrons are added to give each atom an octet



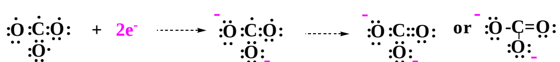
Lewis Structures of Ions

The Lewis structure of an ion is constructed from the atomic components, but with electrons added or subtracted to achieve the required charge.

Example CO_3^{2-} carbonate ion



Assemble in accord with the Octet Rule:

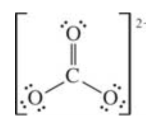


22 valence electrons

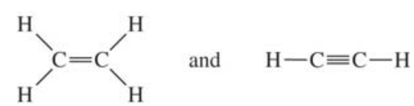
24 valence electrons but the octet rule is not satisfied at C and one O

OK

➔ The carbonate ion with 24 valence electrons and two negative charges must incorporate a double bond to satisfy the octet rule for every atom



➔ The organic molecules ethene (C_2H_4) and ethyne (C_2H_2) must also use multiple bonds to satisfy the octet rule for each atom

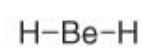


Structure and Bonding

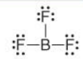
Exceptions to the Octet Rule

Elements in Groups 2A and 3A

Two second-row elements without an octet



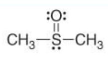
four electrons around Be



six electrons around B

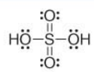
Elements in the Third Row

10 electrons around S



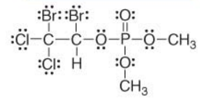
dimethyl sulfoxide
(abbreviated as DMSO)

12 electrons around S



sulfuric acid

10 electrons around P



1,2-dibromo-2,2-dichloroethyl dimethyl phosphate
(Naled)

Structure and Bonding

Formal Charge

- **Formal charge is the charge assigned to individual atoms in a Lewis structure.**
- **By calculating formal charge, we determine how the number of electrons around a particular atom compares to its number of valence electrons. Formal charge is calculated as follows:**

formal charge = number of valence electrons − number of electrons an atom "owns"

- **The number of electrons "owned" by an atom is determined by its number of bonds and lone pairs.**
- **An atom "owns" *all* of its unshared electrons and *half* of its shared electrons.**

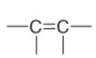
Structure and Bonding

The number of electrons "owned" by different atoms is indicated in the following examples:

Example 1

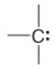
- C shares eight electrons.
- C "owns" **four** electrons.

Example 2



- Each C shares eight electrons.
- Each C "owns" **four** electrons.

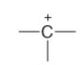
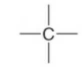
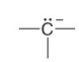
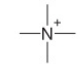
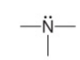
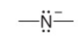
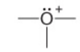
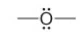
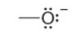
Example 3



- C shares six electrons.
- C has two unshared electrons.
- C "owns" **five** electrons.

Structure and Bonding

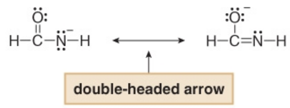
TABLE 1.1 Formal Charge Observed with Common Bonding Patterns for C, N, and O

		Formal charge		
Atom	**Number of valence electrons**	**+1**	**0**	**–1**
C	4			
N	5			
O	6			

Structure and Bonding

Resonance

Some molecules cannot be adequately represented by a single Lewis structure. For example, two valid Lewis structures can be drawn for the anion $(HCONH)^-$. One structure has a negatively charged N atom and a C-O double bond; the other has a negatively charged O atom and a C-N double bond.



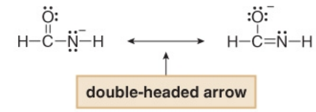
These structures are called resonance structures or resonance forms. A double headed arrow is used to separate the two resonance structures.

- *Resonance structures* are two Lewis structures having the *same* placement of atoms but a *different* arrangement of electrons.

Structure and Bonding

Introduction to Resonance Theory

Regarding the two resonance forms of $(HCONH)^-$ shown below, it should be noted that:



- **Neither resonance structure is an accurate representation for $(HCONH)^-$. The true structure is a composite of both resonance forms and is called a resonance hybrid.**
- **The hybrid shows characteristics of both structures.**
- **Resonance allows certain electron pairs to be delocalized over several atoms, and this delocalization adds stability.**
- **A molecule with two or more resonance forms is said to be resonance stabilized.**

Structure and Bonding

Introduction to Resonance.

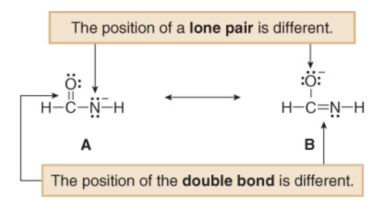
The following basic principles of resonance theory should be kept in mind:

1. **An individual resonance structure does not accurately represent the structure of a molecule or ion. Only the hybrid does.**
2. **Resonance structures are not in equilibrium with each other. There is no movement of electrons from one form to another.**
3. **Resonance structures are not isomers. Two isomers differ in the arrangement of both atoms and electrons, whereas resonance structures differ only in the arrangement of electrons.**

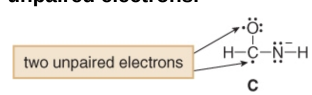
Structure and Bonding

Drawing Resonance Structures

Rule [1]: Two resonance structures differ in the position of multiple bonds and nonbonded electrons. The placement of atoms and single bonds always stays the same.



Rule [2]: Two resonance structures must have the same number of unpaired electrons.

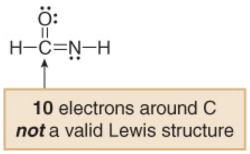


- **A** and **B** have no unpaired electrons.
- **C** is ***not*** a resonance structure of **A** and **B**.

Structure and Bonding

Drawing Resonance Structures (continued)

Rule [3]: Resonance structures must be valid Lewis structures. Hydrogen must have two electrons and no second-row element can have more than eight.



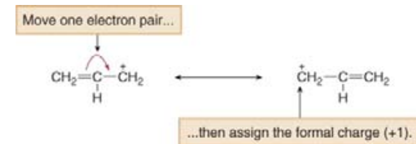
Structure and Bonding

Drawing Resonance Structures

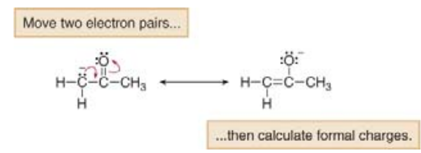
Curved arrow notation is a convention that is used to show how electron position differs between the two resonance forms.

Curved arrow notation shows the movement of an electron pair. The tail of the arrow always begins at the electron pair, either in a bond or lone pair. The head points to where the electron pair “moves.”

Example 1:



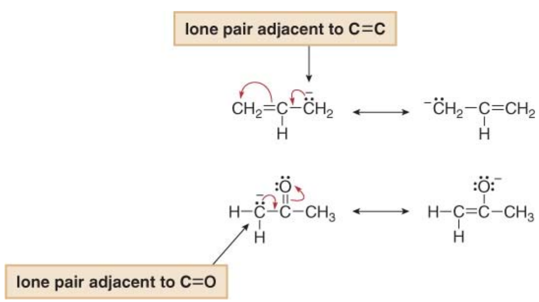
Example 2:



Structure and Bonding

Resonance Structure Examples

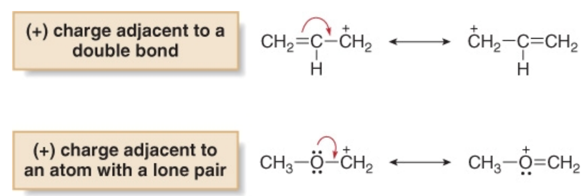
In this case, a lone pair is located on an atom directly bonded to a double bond:



Structure and Bonding

Resonance Structure Examples

In this case, an atom bearing a (+) charge is bonded either to a double bond or an atom with a lone pair:



Structure and Bonding

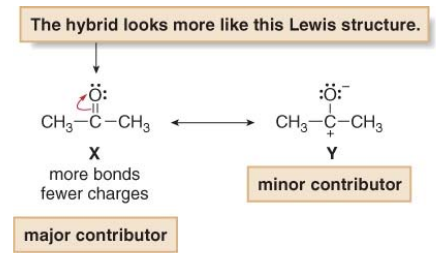
Resonance Hybrids

- **A resonance hybrid is a composite of all possible resonance structures. In the resonance hybrid, the electron pairs drawn in different locations in individual resonance forms are delocalized.**
- **When two resonance structures are different, the hybrid looks more like the “better” resonance structure. The “better resonance structure is called the major contributor to the hybrid, and all others are minor contributors.**
- **The hybrid is a weighted average of the contributing resonance structures.**

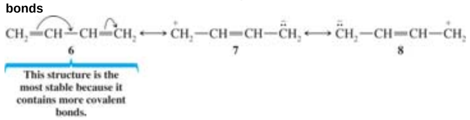
Structure and Bonding

Resonance Hybrids

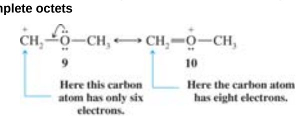
A “better” resonance structure is one that has more bonds and fewer charges.



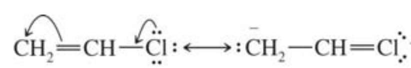
- **Rules to Assign Relative Importance of Resonance Forms**
  - ➔ **A resonance form with more covalent bonds is more important than one with less**
    - **Example: 6 is more stable and more important because it has more total covalent bonds**



  - ➔ **Resonance forms in which all atoms have a complete valence shell of electrons are more important**
    - **Example: 10 is more important because all atoms (except hydrogen) have complete octets**



➔ **Resonance forms with separation of charge are less important**
- **Separation of charge cost energy and results in a less stable resonance contributor**
- **Example: 12 is less important because it has charge separation**

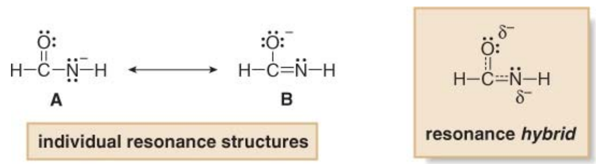


11 **12**

➔ **Forms with negative charge on highly electronegative atoms are more important**
- **Those with positive charge on less electronegative atoms are also more important**

Structure and Bonding

Drawing Resonance Hybrids

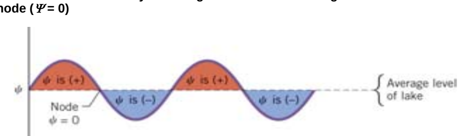


♦ Quantum Mechanics

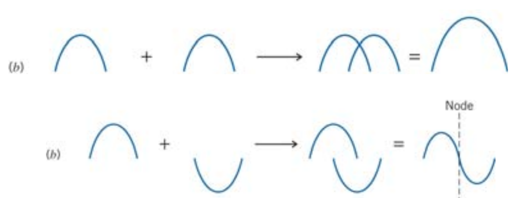
- ➔ A mathematical description of bonding that takes into account the wave nature of electrons
- ➔ A wave equation is solved to yield a series of wave functions for the atom
- ➔ The wave functions psi (Ψ) describe a series of states with different energies for each electron
- ➔ Wave Equations are used 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 (Ψ = +) ; when it is below the lake level it is negative (Ψ = -)
  - When the wave is exactly at average lake level it has a sign of 0 and this is called a node (Ψ = 0)

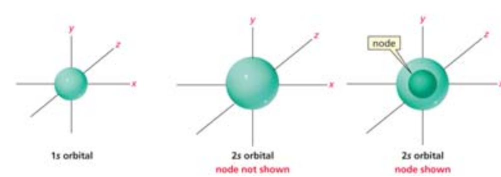


- ➔ Wave equations can reinforce each other if they have the same sign or interfere with each other if they have different signs

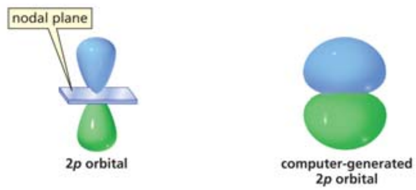


♦ Atomic Orbitals (AOs)

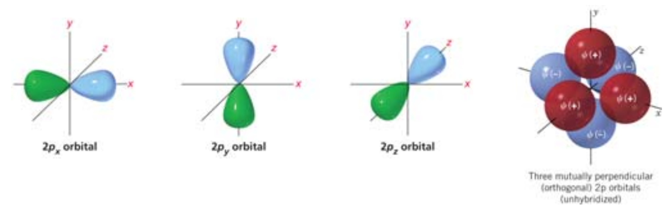
- ➔ The physical reality of Ψ is that when squared (Ψ^2) it gives the probability of finding an electron in a particular location in space
- ➔ Plots of Ψ^2 in three dimensions generate the shape of *s*, *p*, *d* and *f* orbitals
- ➔ Only *s* and *p* orbitals are very important in organic chemistry
- ➔ 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



- ➔1*s* and 2*s* orbitals are spheres centered around the nucleus
  - Each orbital can accommodate 2 electrons
  - The 2*s* orbital is higher in energy and contains a nodal surface ($\Psi = 0$) in its center
- ➔Each 2*p* 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 2*p* orbitals which are perpendicular (orthoganol) 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 2*p* orbitals are higher in energy than the 1*s* or 2*s*



- ➔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
  - 2*s* and 2*p* orbitals each have one node and are higher in energy than the 1*s* orbital which has no nodes

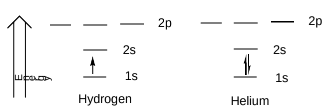


Structure and Bonding

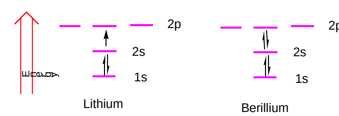
●**Atoms can be assigned electronic configuration using the following rules:**

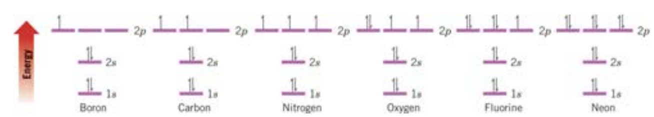
- ➔**Aufbau Principle: The lowest energy orbitals are filled first**
- ➔**Pauli Exclusion Principle: A maximum of two spin paired electrons may be placed in each orbital**
- ➔**Hund's Rule: One electron is added to each degenerate (equal energy orbital) before a second electron is added**

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*.



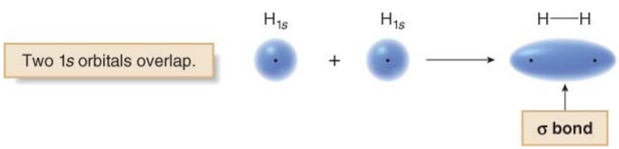


Structure and Bonding

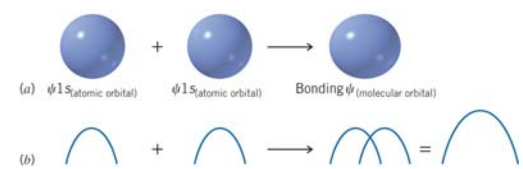
Molecular Orbitals : Hydrogen

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

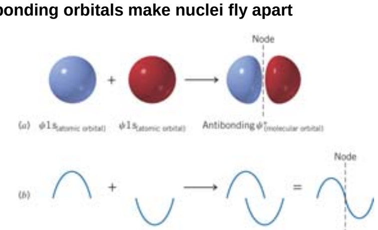
This bond is cylindrically symmetrical because the electrons forming the bond are distributed symmetrically about an imaginary line connecting the two nuclei.



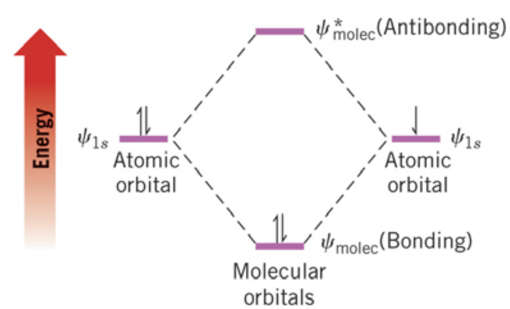
- **Bonding Molecular Orbitals (Ψ_{molec})**
  - ➔ AOs combine by addition (the AOs of the same phase sign overlap)
  - ➔ The wave functions reinforce
  - ➔ The value of Ψ increases between the two nuclei
  - ➔ The value of Ψ^2 (electron probability density) in the region between the two nuclei increases
  - ➔ 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

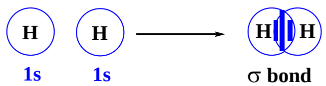


- ➔ The energy of electrons in the bonding orbitals is substantially less than the energy of electrons in the individual atoms
  - The energy of electrons in the antibonding orbitals is substantially more
- ➔ In the ground state of the hydrogen molecule electrons occupy the lower energy bonding orbital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



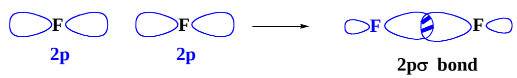
Examples of Covalent Bonds

$2\,H\cdot \longrightarrow H_2$



bond length 0.74
BDE 435 kJ/mol

$2\,F\cdot \longrightarrow F_2$



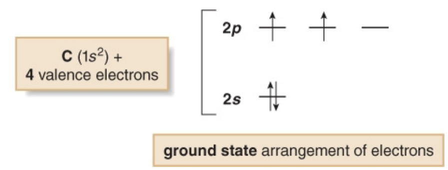
bond length 1.42
BDE 159 kJ/mol

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 2*s* and 2*p* 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 2*s* orbital and one each in 2*p* orbitals.

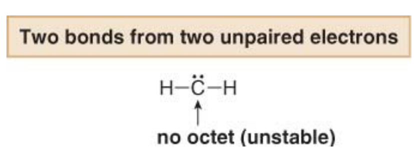


Note: the lowest energy arrangement of electrons for an atom is called its ground state.

Structure and Bonding

Orbitals and Bonding: Methane

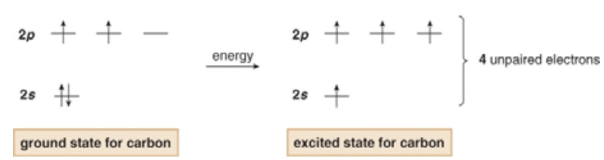
In this description, carbon should form only two bonds because it has only two unpaired valence electrons, and CH_2 should be a stable molecule. However, CH_2 is a very unstable species that cannot be isolated under typical laboratory conditions. Note that in CH_2, carbon would not have an octet of electrons.



Structure and Bonding

Orbitals and Bonding: Methane

There is a second possibility. Promotion of an electron from a 2*s* to a vacant 2*p* 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.



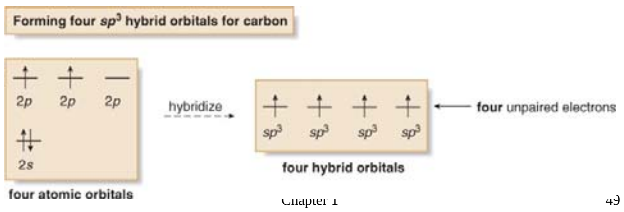
But this description is still not adequate. Carbon would form two different types of bonds: three with 2*p* orbitals and one with a 2*s* orbital. However, experimental evidence points to carbon forming four identical bonds in methane.

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.

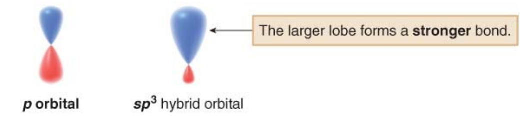
***Hybridization* is the combination of two or more atomic orbitals to form the same number of hybrid orbitals, each having the same shape and energy.**



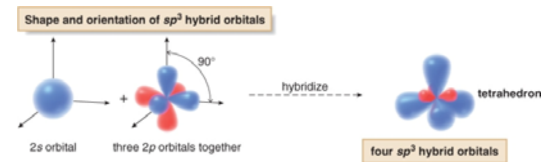
Structure and Bonding

Shape and Orientation of sp^3 Hybrid Orbitals

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

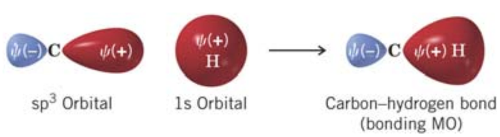


The four hybrid orbitals are oriented towards the corners of a tetrahedron, and form four equivalent bonds.

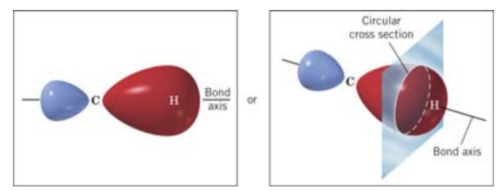


➔ **An sp^3 orbital looks like a *p* orbital with one lobe greatly extended**
- **Often the small lobe is not drawn**

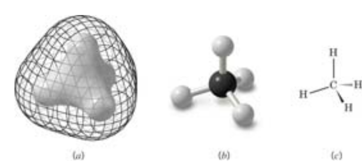
➔ **The extended sp^3 lobe can then overlap well with the hydrogen 1*s* to form a strong bond**



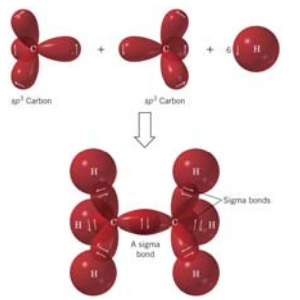
➔ **The bond formed is called a sigma (σ) bond because it is circularly symmetrical in cross section when view along the bond axis**



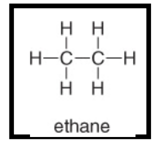
➔ **A variety of representations of methane show its tetrahedral nature and electron distribution**
- **a. calculated electron density surface b. ball-and-stick model c. a typical 3-dimensional drawing**



- Ethane (C_2H_6)
  - ➔The carbon-carbon bond is made from overlap of two *sp³* orbitals to form a σ bond
  - ➔The molecule is approximately tetrahedral around each carbon

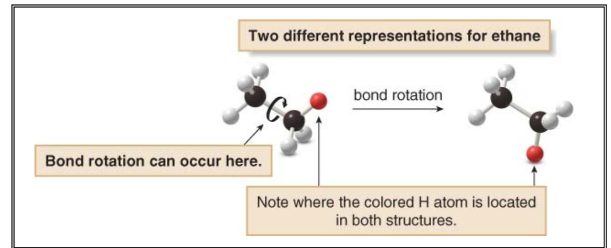


Structure and Bonding

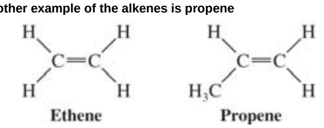


Generally there is relatively free rotation about σ bonds

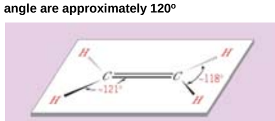
- Very little energy (13-26 kcal/mol) is required to rotate around the carbon-carbon bond of ethane



- ♦ **The Structure of Ethene (Ethylene) : *sp²* Hybridization**
  - ➔Ethene (C_2H_4) contains a carbon-carbon double bond and is in the class of organic compounds called *alkenes*
    - Another example of the alkenes is propene



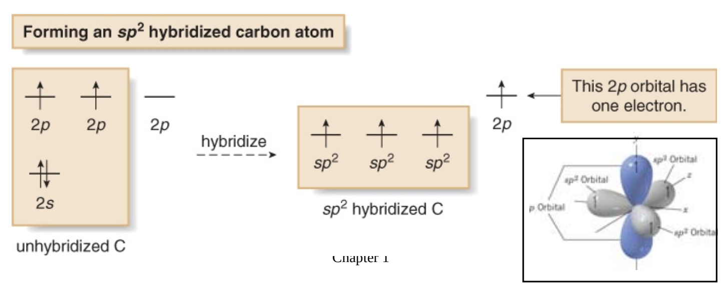
  - ➔The geometry around each carbon is called *trigonal planar*
    - All atoms directly connected to each carbon are in a plane
    - The bonds point towards the corners of a regular triangle
    - The bond angle are approximately 120º



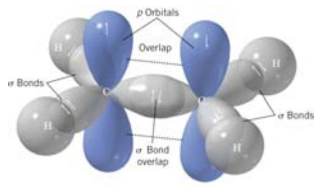
Structure and Bonding

Hybridization and Bonding in Organic Molecules

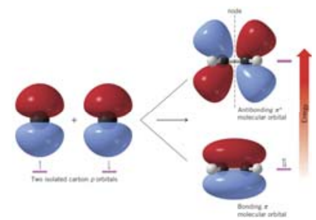
- ➔There are three σ bonds around each carbon of ethene and these are formed by using *sp²* hybridized orbitals
- ➔The three *sp²* hybridized orbitals come from mixing one *s* and two *p* orbitals
  - One *p* orbital is left unhybridized
- ➔The *sp²* orbitals are arranged in a trigonal planar arrangement
  - The *p* orbital is perpendicular (orthoganol) to the plane

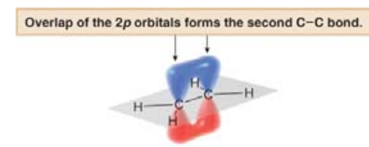


- ➔Overlap of sp^2 orbitals in ethylene results in formation of a σ framework
  - One sp^2 orbital on each carbon overlaps to form a carbon-carbon σ bond; the remaining sp^2 orbitals form bonds to hydrogen
- ➔The leftover *p* orbitals on each carbon overlap to form a bonding π bond between the two carbons
- ➔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

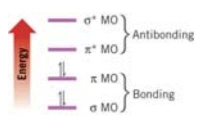


- ➔The bonding π orbital results from overlap of *p* orbital lobes of the same sign
- ➔The antibonding π* orbital results from overlap of *p* orbital lobes of opposite sign
  - The antibonding orbital has one node connecting the two nuclei and another node between the two carbons
- ➔The bonding π orbital 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)



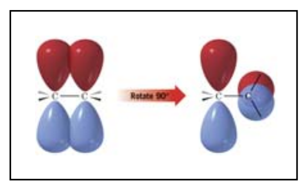


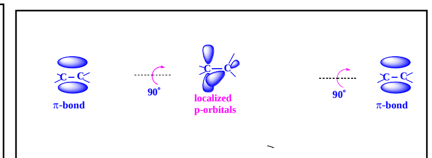
- ➔The σ orbital is lower in energy than the π orbital
  - The ground state electronic configuration of ethene is shown



♦ 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 90º 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)**

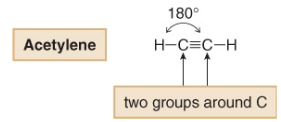
cis-1,2-Dichloroethene   *trans*-1,2-Dichloroethene

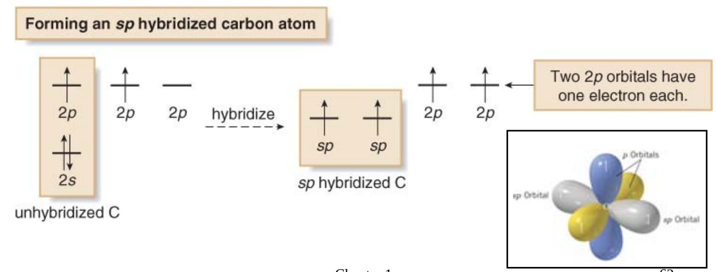
  - ➔**Cis-trans isomerism is not possible if one carbon of the double bond has two identical groups**

1,1-Dichloroethene (no cis–trans isomerism)   1,1,2-Trichloroethene (no cis–trans isomerism)

Structure and Bonding

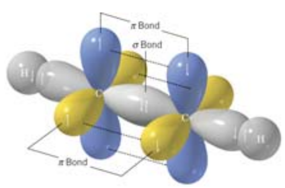
The Structure of Ethyne (Acetylene): *sp* Hybridization Hybridization and Bonding in Organic Molecules

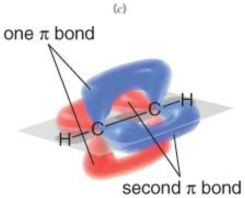




- ➔**Depictions of ethyne show that the electron density around the carbon-carbon bond has circular symmetry**
  - **Even if rotation around the carbon-carbon bond occurred, a different compound would not result**

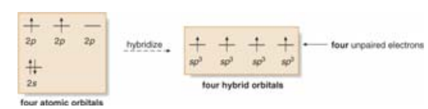
(*a*)   (*b*)   (*c*)



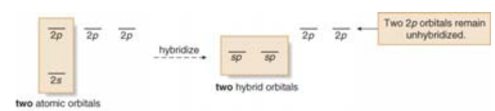


Summary of Hybridizaton

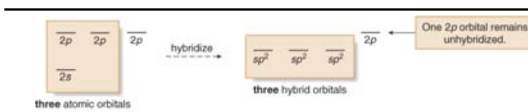
- **One 2*s* orbital and three 2*p* orbitals forming:**



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.

number of groups around an atom	number of orbitals used	type of hybrid orbital
2	2	**two *sp*** hybrid orbitals
3	3	**three sp^2** hybrid orbitals
4	4	**four sp^3** hybrid orbitals

Structure and Bonding

Orbital Hybridization

Increased percent *s*-character → Increased bond strength → Decreased bond length

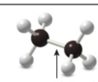
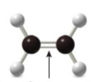
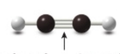
$$sp \text{ hybrid} \quad \frac{\text{one } 2s \text{ orbital}}{\text{two hybrid orbitals}} = \mathbf{50\%\ s\text{-character}}$$

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

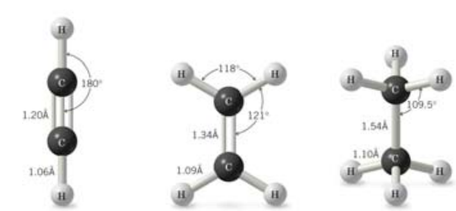
$$sp^3 \text{ hybrid} \quad \frac{\text{one } 2s \text{ orbital}}{\text{four hybrid orbitals}} = \mathbf{25\%\ s\text{-character}}$$

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

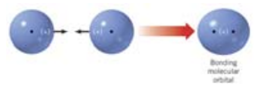
Number of groups bonded to C	Hybridization	Bond angle	Example	Observed bonding
4	sp^3	109.5°	CH_3CH_3 ethane	 one σ bond $C_{sp^3}-C_{sp^3}$
3	sp^2	120°	$CH_2{=}CH_2$ ethylene	 one σ bond + one π bond $C_{sp^2}-C_{sp^2}$ $C_{2p}-C_{2p}$
2	sp	180°	HC≡CH acetylene	 one σ bond + two π bonds $C_{sp}-C_{sp}$ $C_{2p}-C_{2p}$ $C_{2p}-C_{2p}$

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.

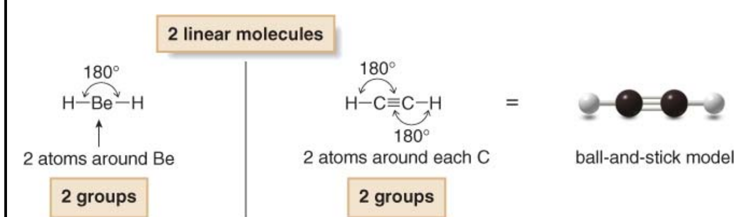
- **The number of groups surrounding a particular atom determines its geometry. A group is either an atom or a lone pair of electrons.**
- **The most stable arrangement keeps these groups as far away from each other as possible. This is exemplified by Valence Shell Electron Pair Repulsion (VSEPR) theory.**

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

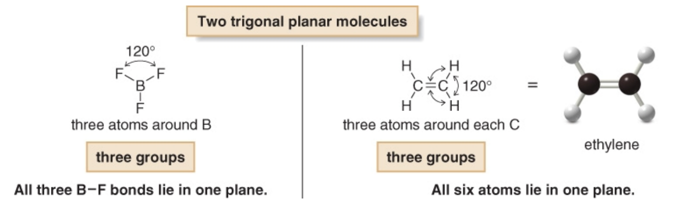
Two groups around an atom—



Structure and Bonding

Determining Molecular Shape

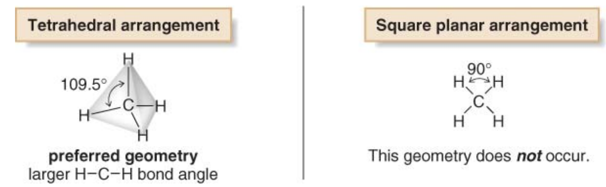
Three groups around an atom—



Structure and Bonding

Determining Molecular Shape

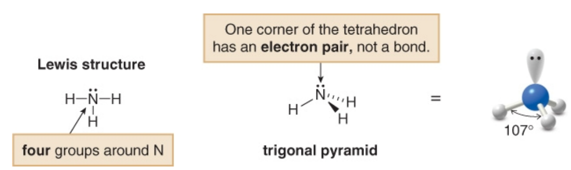
Four groups around an atom—



Structure and Bonding

A Nonbonded Pair of Electrons is Counted as a "Group"

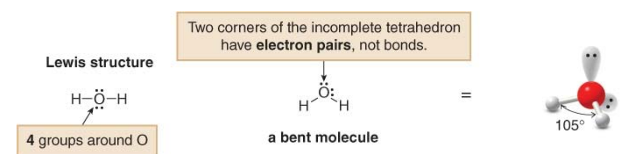
In ammonia (NH_3), one of the four groups attached to the central N atom is a lone pair. The three H atoms and the lone pair point to the corners of a tetrahedron. The H-N-H bond angle of 107^0 is close to the theoretical tetrahedral bond angle of 109.5^0. This shape is referred to as a trigonal pyramid.

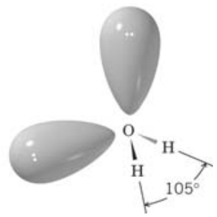


Structure and Bonding

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 105^0 is close to the theoretical tetrahedral bond angle of 109.5^0. Water has a bent shape, because the two groups around oxygen are lone pairs of electrons.





Water

Bent Shape

A Summary of VSEPR Theory

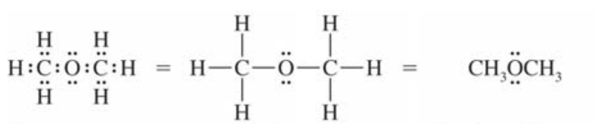
TABLE 1.4 Shapes of Molecules and Ions from VSEPR Theory

Number of Electron Pairs at Central Atom: Bonding	Nonbonding	Total	Hybridization State of Central Atom	Shape of Molecule or Ion[a]	Examples
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_2O

[a]Referring to positions of atoms and excluding nonbonding pairs.

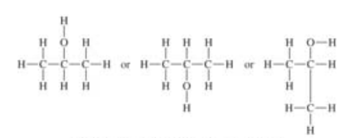
♦ Representations of Structural Formulas

- ➔ **Dot formulas are more cumbersome to draw than dash formulas and condensed formulas**
- ➔ **Lone-pair electrons are often (but not always) drawn in, especially when they are crucial to the chemistry being discussed**



Dot structure **Dash formula** **Condensed formula**

- **Dash formulas**
  - ➔ **Each dash represents a pair of electrons**
  - ➔ **This type of representation is meant to emphasize connectivity and does not represent the 3-dimensional nature of the molecule**
    - **The dash formulas of propyl alcohol appear to have 90º angles for carbons which actually have tetrahedral bond angles (109.5º)**



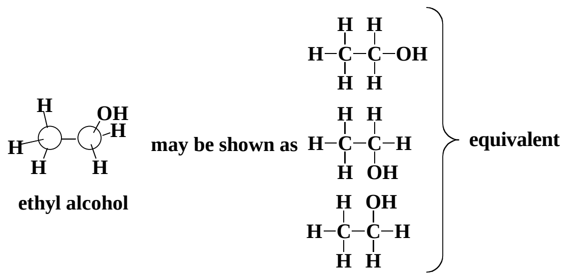
Equivalent dash formulas for isopropyl alcohol

- ➔ **Constitutional isomers**
  - **Constitutional isomers have the same molecular formula but different connectivity**
  - **Propyl alcohol (above) is a constitutional isomer of isopropyl alcohol (below)**

Equivalency of Dash Structural Formulas

Dash structural formulas may, to the inexperienced eye, appear to be nonequivalent, when, in fact, they represent the same compound.

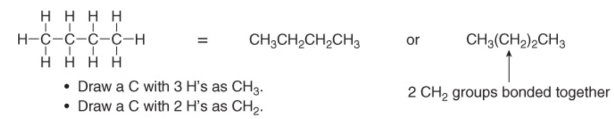
Because of rotation around single bonds, it is possible to have several perspectives of a structure that are drawn in different dash formulas . They all represent the same structure.

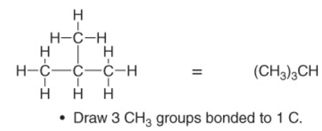


Structure and Bonding

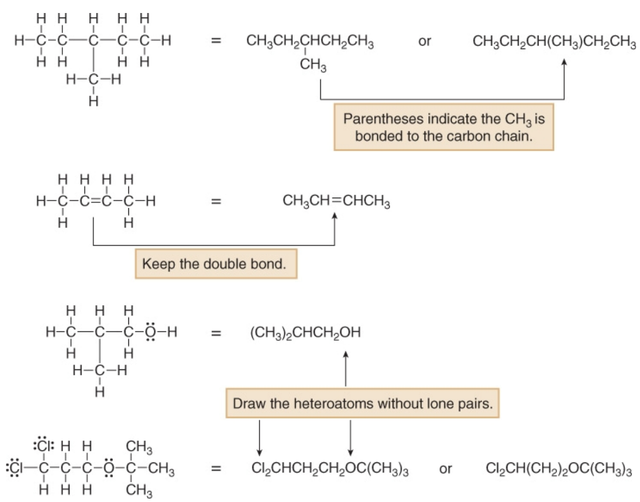
Condensed Structures

- All atoms are drawn in, but the two-electron bond lines are generally omitted.
- Atoms are usually drawn next to the atoms to which they are bonded.
- Parentheses are used around similar groups bonded to the same atom.
- Lone pairs are omitted.

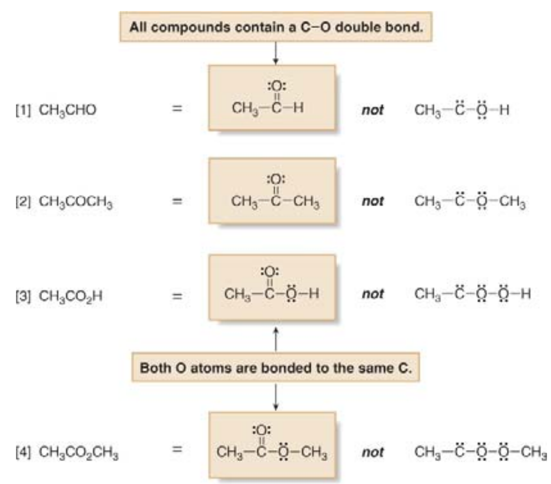




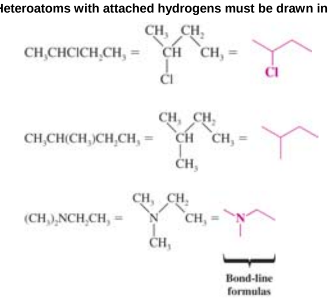
Examples of Condensed Structures



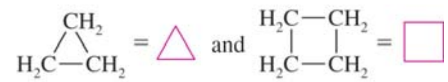
Examples of Condensed Structures Containing a C-O Double Bond



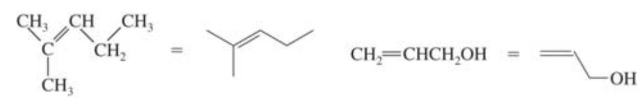
- **Bond-Line Formulas**
  - ➔ A further simplification of drawing organic molecules is to completely omit all carbons and hydrogens and only show heteroatoms (*e.g.* O, Cl, N) explicitly
  - ➔ Each intersection or end of line in a zig-zag represents a carbon with the appropriate amount of hydrogens
    - Heteroatoms with attached hydrogens must be drawn in explicitly



➔ Cyclic compounds are condensed using a drawing of the corresponding polygon

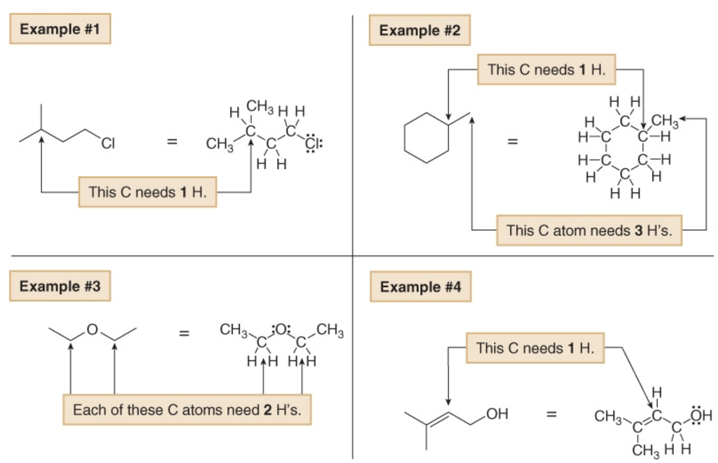


➔ Multiple bonds are indicated by using the appropriate number of lines connecting the atoms



Structure and Bonding

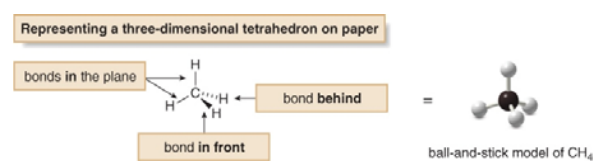
Examples of Bond-Line Structures



Structure and Bonding

Drawing Three Dimensional Structures

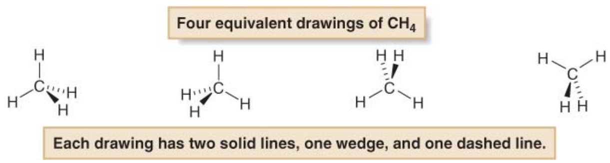
- **A solid line is used for a bond in the plane of the paper.**
- **A wedge is used for a bond in front of the plane.**
- **A dashed line is used for a bond behind the plane.**



Structure and Bonding

Drawing Three Dimensional Structures

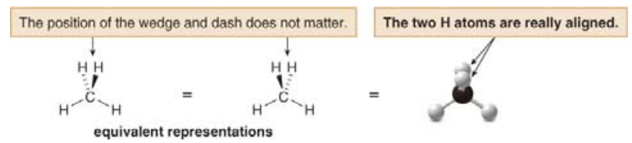
The molecule can be turned in many different ways, generating many equivalent representations. All of the following are acceptable drawings for CH_4.



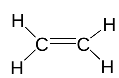
Structure and Bonding

Drawing Three Dimensional Structures

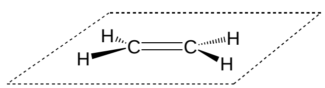
Note that wedges and dashes are used for groups that are really aligned one behind another. It does not matter in the following two drawings whether the wedge or dash is skewed to the left or right, because the two H atoms are really aligned.



- **Trigonal planar arrangements of atoms can be drawn in 3-dimensions in the plane of the paper (top view)**
  - **Bond angles should be approximately 120º**
- **These can also be drawn side-on with the central bond in the plane of the paper, one bond forward and one bond back**



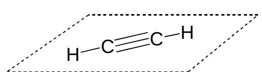
Top View (most common)



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