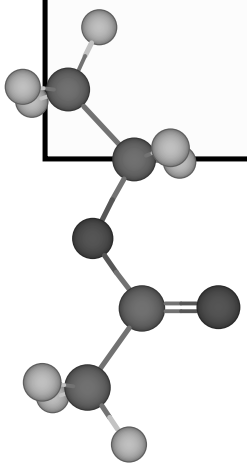
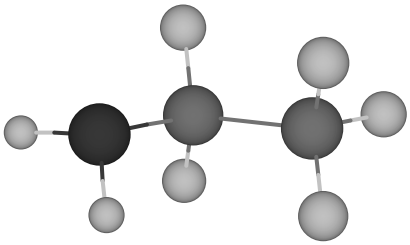
Covalent Bonds & Shapes of Molecules





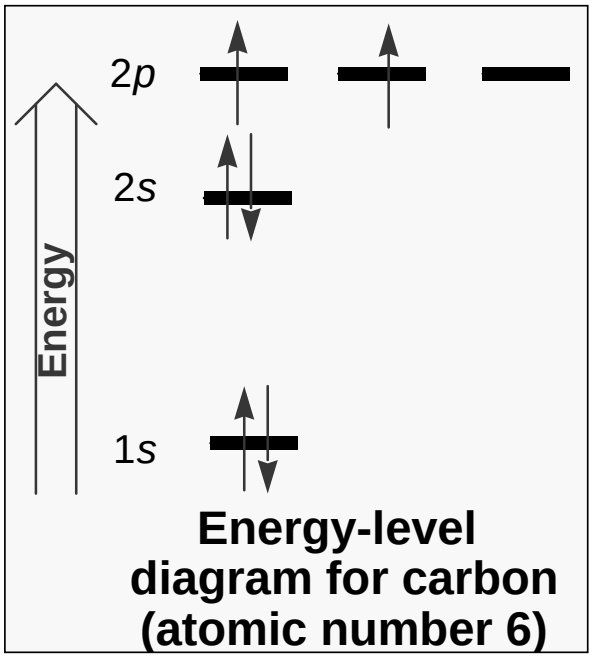
Chapter 1

Organic Chemistry

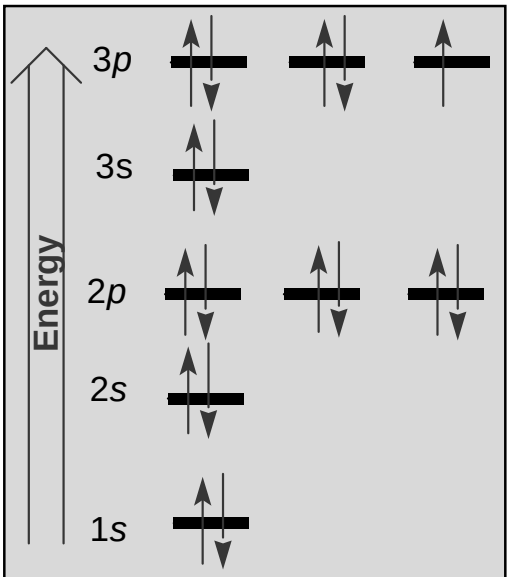
- The study of the compounds of carbon.
- Over 10 million compounds have been identified.
  - About 1000 new ones are identified each day!
- C is a small atom.
  - It forms single, double and triple bonds.
  - It is intermediate in electronegativity (2.5).
  - It forms strong bonds with C, H, O, N, and some metals.

Electron Configuration of Atoms

- Energy-level diagram; A pictorial designation of where electrons are placed in an electron configuration. For example, the energy-level diagram for the ground-state electron configuration of carbon is $1s^2\ 2s^2\ 2p^2$. For chlorine: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$.



Energy-level diagram for carbon (atomic number 6)



Energy-level diagram for chlorine (atomic number 17)

The Concept of Energy

- In the **ground state of carbon**, electrons are placed in accordance with the quantum chemistry principles (aufbau, Hund's rule, Pauli exclusion principle, etc.) that dictate the lowest energy form of carbon.
- If we place the electrons in a different manner (as for example with one electron in the 2*s* and three electrons in the 2*p*) we would have a higher energy level referred to as an **excited state.** When the electrons are rearranged back to the ground state, energy is released.

Lewis Dot Structures

Gilbert N. Lewis----

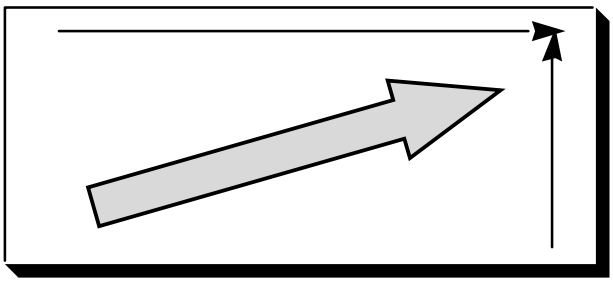
- **Valence shell:**
  - The outermost occupied electron shell of an atom.
- **Valence electrons:**
  - Electrons in the valence shell of an atom; these electrons are used to form chemical bonds and in chemical reactions.
- **Lewis dot structure:**
  - The symbol of an element represents the nucleus and all inner shell electrons.
  - Dots represent electrons in the valence shell of the atom.

Lewis Model of Bonding

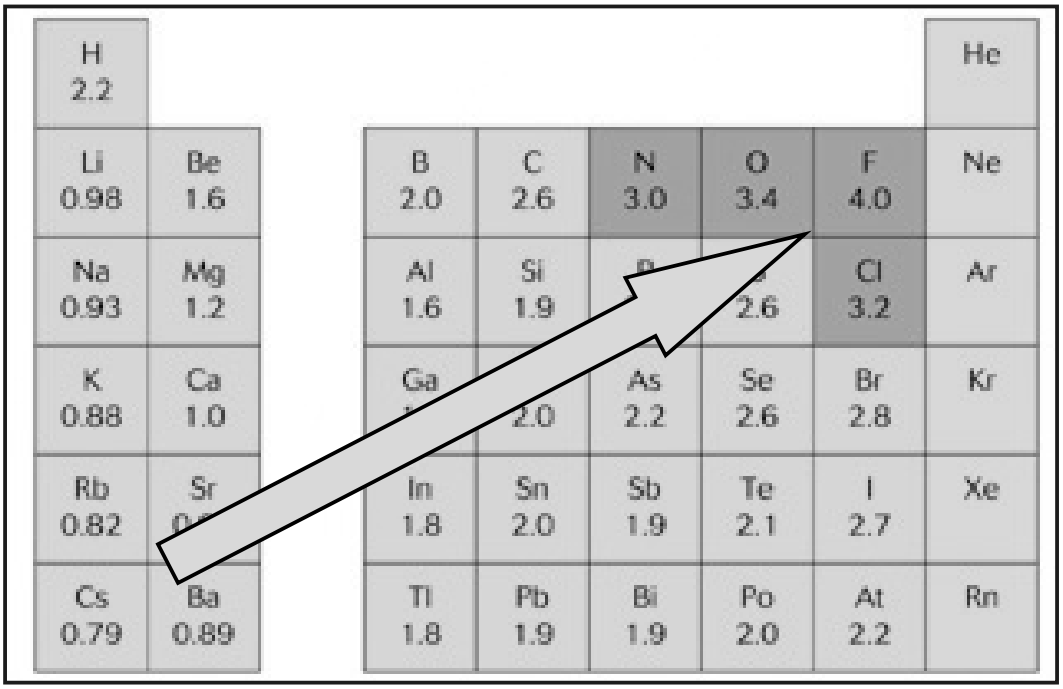
- Atoms interact in such a way that each participating atom acquires an electron configuration that is the same as that of the noble gas nearest it in atomic number.
  - An atom that gains electrons becomes an **anion**.
  - An atom that loses electrons becomes a **cation**.
  - The attraction of anions and cations leads to the formation of **ionic solids**. This ionic interaction is often referred to as an **ionic bond.**
  - An atom may share electrons with one or more atoms to complete its valence shell; a chemical bond formed by sharing electrons is called a **covalent bond**. Bonds may be partially ionic or partially covalent; these bonds are called **polar covalent bonds**

Electronegativity

- Electronegativity:
  - A measure of an atom's attraction for the electrons it shares with another atom in a chemical bond.
- Pauling scale
  - Generally increases left to right in a row.
  - Generally increases bottom to top in a column.



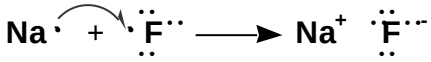
Electronegativity



H 2.2						He
Li 0.98	Be 1.6	B 2.0	C 2.6	N 3.0	O 3.4	F 4.0	Ne
Na 0.93	Mg 1.2	Al 1.6	Si 1.9	P	S 2.6	Cl 3.2	Ar
K 0.88	Ca 1.0	Ga	2.0	As 2.2	Se 2.6	Br 2.8	Kr
Rb 0.82	Sr	In 1.8	Sn 2.0	Sb 1.9	Te 2.1	I 2.7	Xe
Cs 0.79	Ba 0.89	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	Rn

Formation of Ions

- A rough guideline:
  - Ions will form if the difference in electronegativity between interacting atoms is 1.9 or greater.
  - Example: sodium (EN 0.9) and fluorine (EN 4.0)
  - We use a single-headed (barbed) curved arrow to show the transfer of one electron from Na to F.

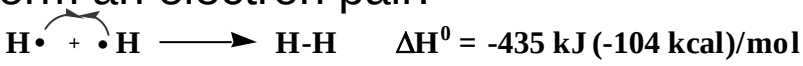


  - In forming Na^+F^-, the single 3*s* electron from Na is transferred to the partially filled valence shell of F.

$$Na(1s^2 2s^2 2p^6 3s^1) + F(1s^2 2s^2 2p^5) \longrightarrow Na^+(1s^2 2s^2 2p^6) + F^-(1s^2 2s^2 2p^6)$$

Covalent Bonds

- The simplest covalent bond is that in H_2
  - The single electrons from each atom combine to form an electron pair.



  - The shared pair functions in two ways simultaneously; it is shared by the two atoms and fills the valence shell of each atom.
- The number of shared pairs
  - One shared pair forms a single bond
  - Two shared pairs form a double bond
  - Three shared pairs form a triple bond

Polar and Nonpolar Covalent Bonds

- Although all covalent bonds involve sharing of electrons, they differ widely in the degree of sharing.
- Covalent bonds can be divided into:
  - nonpolar covalent bonds and
  - polar covalent bonds.

Difference in Electronegativity Between Bonded Atoms	Type of Bond
Less than 0.5	Nonpolar covalent
0.5 to 1.9	Polar covalent
Greater than 1.9	Ions form

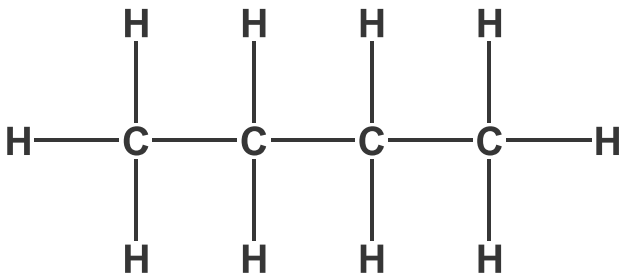
Polar and Nonpolar Covalent Bonds

- An example of a polar covalent bond is that of H-Cl.
- The difference in electronegativity between Cl and H is 3.0 - 2.1 = 0.9.
- We show polarity by using the symbols $\delta+$ and $\delta-$, or by using an arrow with the arrowhead pointing toward the negative end and a plus sign on the tail of the arrow at the positive end.

Drawing Molecular Formulas

C_4H_{10} Molecular Formula

$CH_3CH_2CH_2CH_3$ **Condensed Molecular Formula**



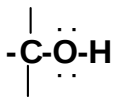
"Expanded" (Lewis) Formula

Functional Groups

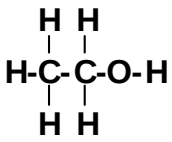
- Functional group: An atom or group of atoms within a molecule that shows a characteristic set of physical and chemical properties.
- Functional groups are important for three reason; they are:
  1. the units by which we divide organic compounds into classes.
  2. the sites of characteristic chemical reactions.
  3. the basis for naming organic compounds.

Alcohols

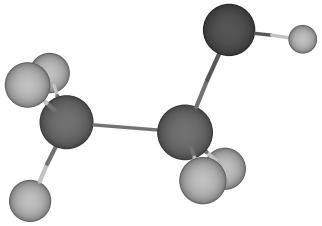
- Contain an -OH (hydroxyl) group bonded to a tetrahedral carbon atom.



Functional group



Ethanol (an alcohol)

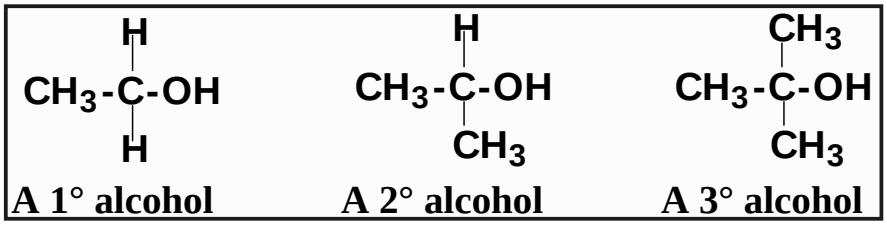


- Ethanol may also be written as a condensed structural formula.

$CH_3\text{-}CH_2\text{-}OH$ or CH_3CH_2OH

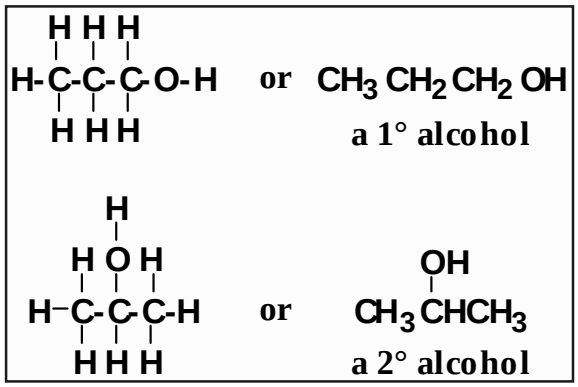
Alcohols

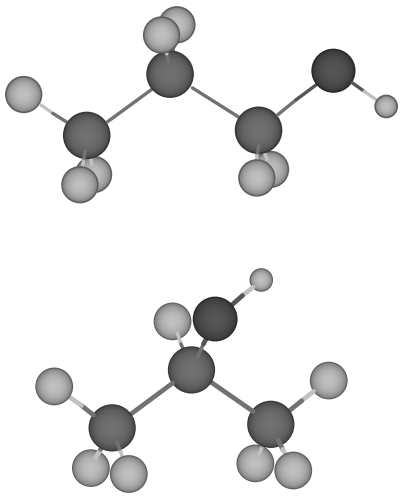
– Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°) depending on the number of carbon atoms bonded to the carbon bearing the -OH group.



Alcohols

– There are two alcohols with molecular formula C_3H_8O.

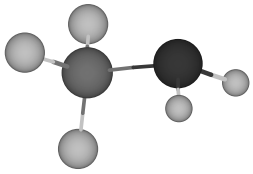
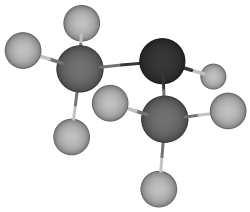
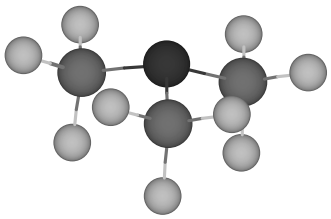




Amines

- Contain an amino group; an sp^3-hybridized nitrogen bonded to one, two, or three carbon atoms.
  - An amine may by 1°, 2°, or 3°.

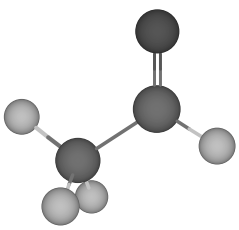
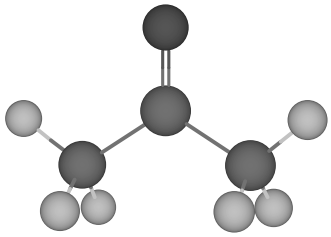
$CH_3-\ddot{N}(H)-H$	$CH_3-\ddot{N}(CH_3)-H$	$CH_3-\ddot{N}(CH_3)-CH_3$
Methylamine (a 1° amine)	**Dimethylamine (a 2° amine)**	**Trimethylamine (a 3° amine)**

Aldehydes and Ketones

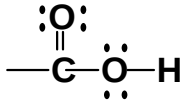
- Contain a carbonyl (C=O) group.

$\ddot{O}$ $\|\|$ $-C-H$	$CH_3-\overset{O}{\overset{\|\|}{C}}-H$	$\ddot{O}$ $\|\|$ $-C-$	$CH_3-\overset{O}{\overset{\|\|}{C}}-CH_3$
Functional group	**Acetaldehyde (an aldehyde)**	**Functional group**	**Acetone (a ketone)**

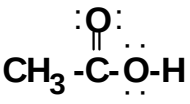



Carboxylic Acids

- Contain a carboxyl (-COOH) group.

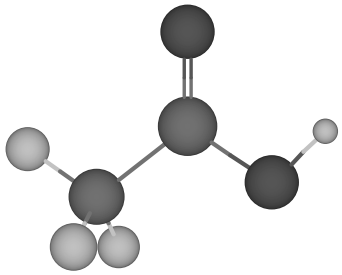


Functional group



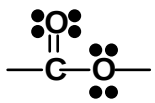
Acetic acid (a carboxylic acid)

CH_3COOH or CH_3CO_2H

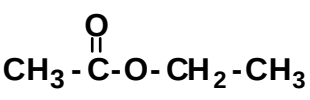


Carboxylic Esters

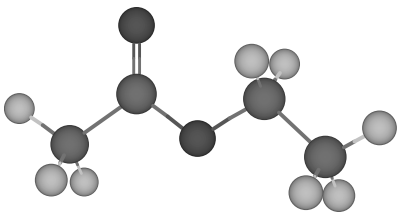
- Ester: A derivative of a carboxylic acid in which the carboxyl hydrogen is replaced by a carbon group.



Functional group

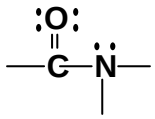


Ethyl acetate (an ester)

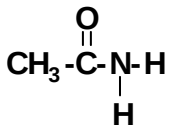


Carboxylic Amide

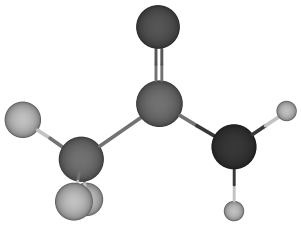
- Carboxylic amide, commonly referred to as an amide: A derivative of a carboxylic acid in which the -OH of the -COOH group is replaced by an amine.



Functional group



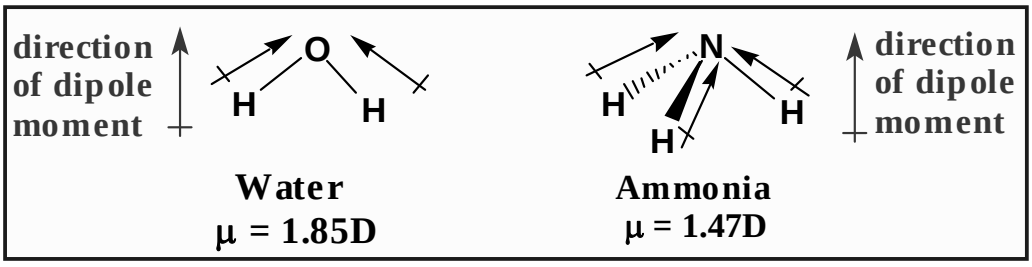
Acetamide (a 1° amide)

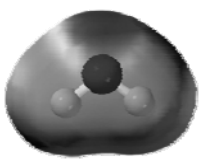


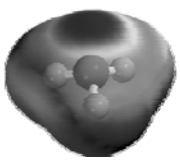
  - The six atoms of the amide functional group lie in a plane with bond angles of approximately 120°.

Polar and Nonpolar Molecules

- These molecules have polar bonds and are polar molecules.

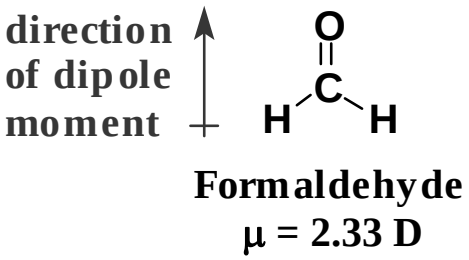




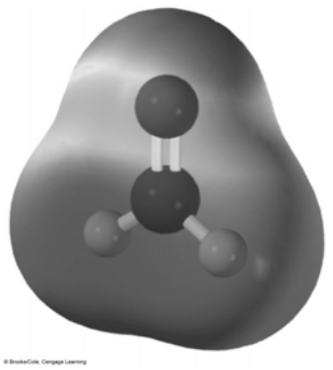


Polar and Nonpolar Molecules

– Formaldehyde has polar bonds and is a polar molecule.



Formaldehyde
μ = 2.33 D

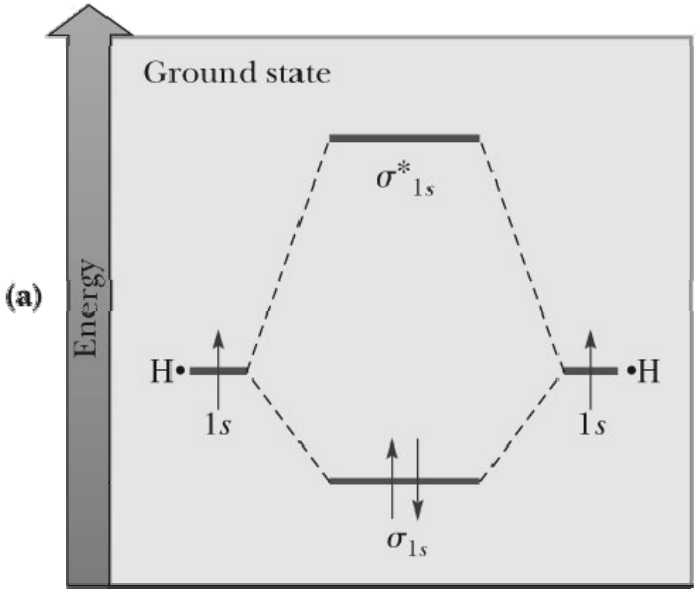


Covalent Bonding-Combined VB & MO

- Bonding molecular orbital: A MO in which electrons have a lower energy than they would have in isolated atomic orbitals.
- Sigma (σ) bonding molecular orbital: A MO in which electron density is concentrated between two nuclei along the axis joining them and is cylindrically symmetrical.

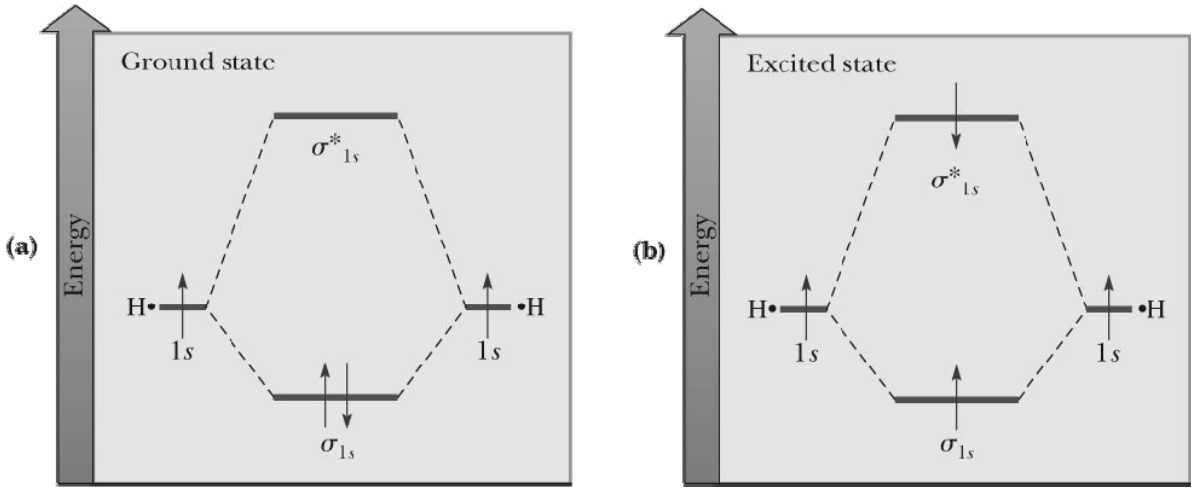
Covalent Bonding-Combined VB & MO

- Figure 1.11 A MO energy diagram for H_2. (a) Ground state



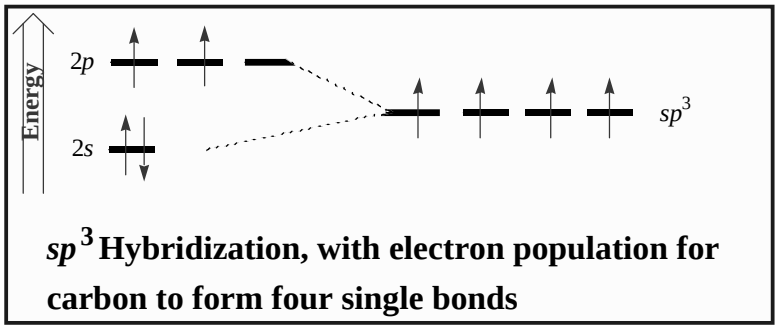
Covalent Bonding-Combined VB & MO

- Figure 1.11 A MO energy diagram for H_2. (a) Ground state and (b) lowest excited state.



VB: Hybridization of Atomic Orbitals

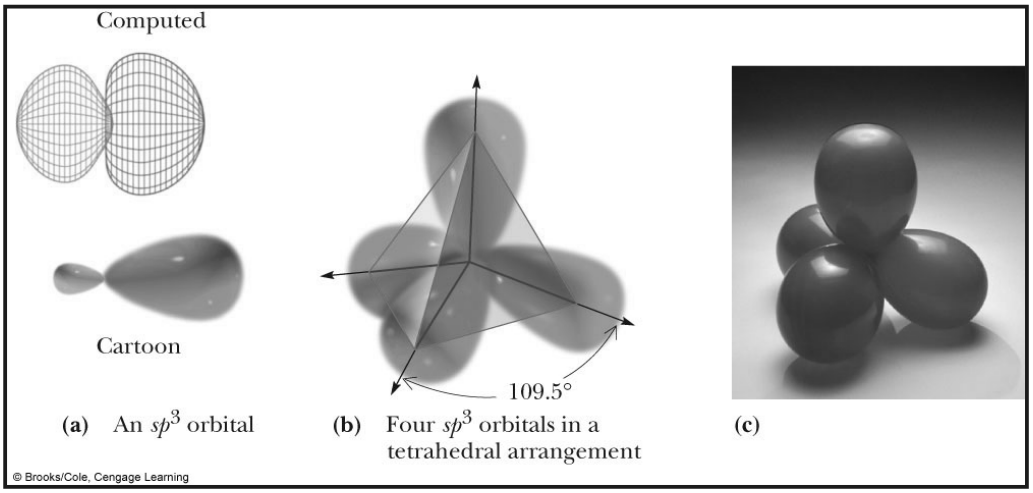
- The number of hybrid orbitals formed is equal to the number of atomic orbitals combined.
- Elements of the 2nd period form three types of hybrid orbitals, designated sp^3, sp^2, and sp.
- The mathematical combination of one 2*s* atomic orbital and three 2*p* atomic orbitals forms four equivalent sp^3 hybrid orbitals.



sp^3 Hybridization, with electron population for carbon to form four single bonds

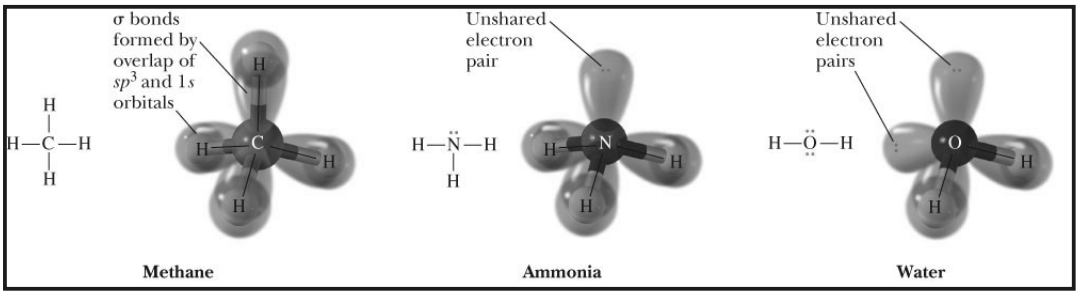
VB: Hybridization of Atomic Orbitals

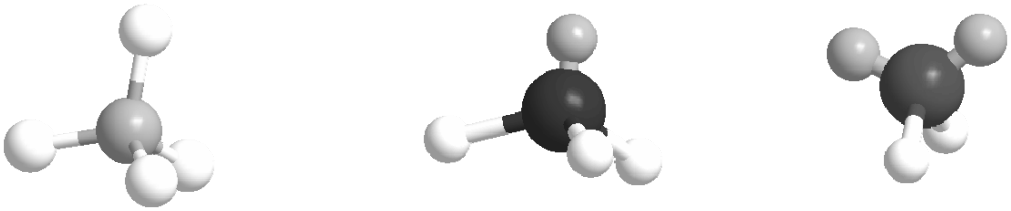
- Figure 1.12 sp^3 Hybrid orbitals. (a) Computed and (b) cartoon three-dimensional representations. (c) Four balloons of similar size and shape tied together, will assume a tetrahedral geometry.



VB: Hybridization of Atomic Orbitals

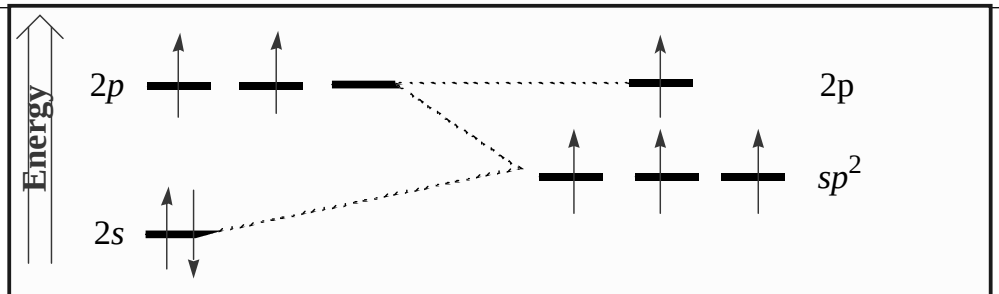
- Figure 1.13 Orbital overlap pictures of methane, ammonia, and water.





VB: Hybridization of Atomic Orbitals

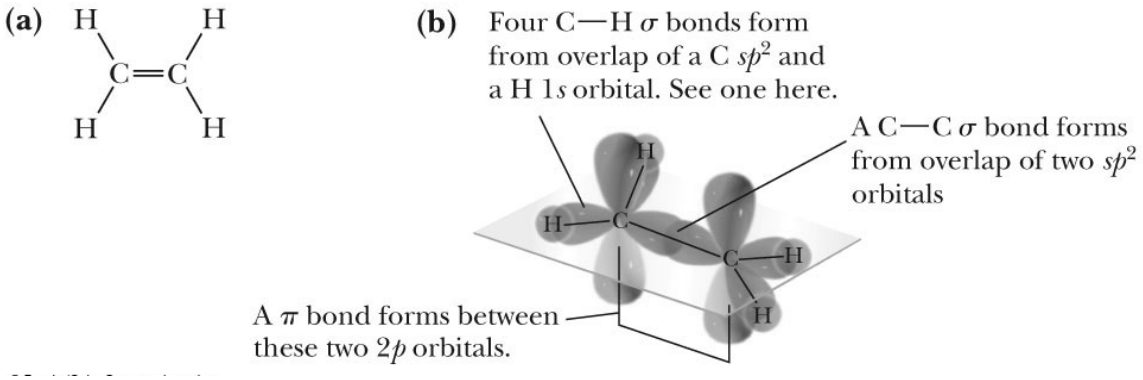
- The mathematical combination of one 2*s* atomic orbital wave function and two 2*p* atomic orbital wave functions forms three equivalent sp^2 hybrid orbitals.



sp^2 Hybridization, with electron population for carbon to form double bonds

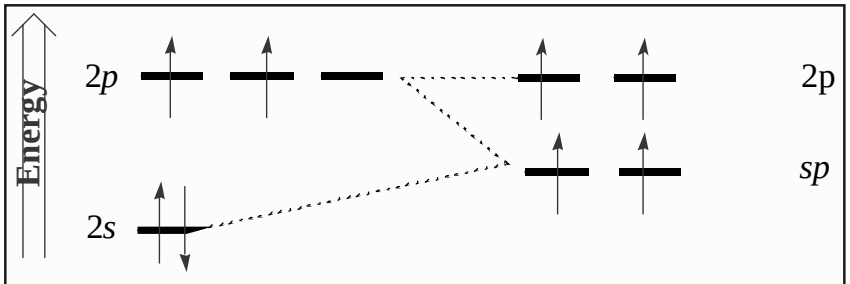
Combining VB & MO Theories

- A double bond uses sp^2 hybridization.
- Consider ethylene, C_2H_4. Carbon and other second-period elements use a combination of sp^2 hybrid orbitals and the unhybridized 2*p* orbital to form double bonds.



VB: Hybridization of Atomic Orbitals

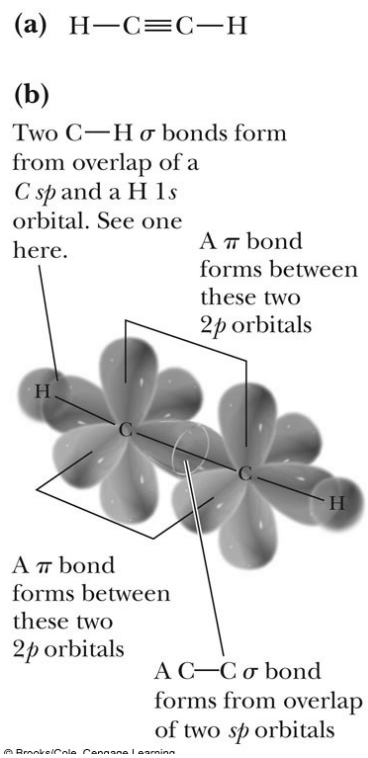
- The mathematical combination of one 2*s* atomic orbital and one 2*p* atomic orbital gives two equivalent *sp* hybrid orbitals.



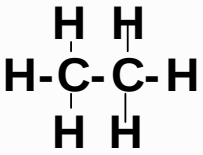
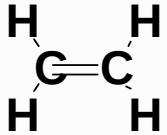
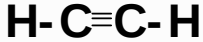
***sp* Hybridization, with electron population for carbon to form triple bonds**

Combining VB & MO Theories

- A carbon-carbon triple bond consists of one σ bond formed by overlap of sp hybrid orbitals and two π bonds formed by the overlap of parallel 2*p* atomic orbitals.

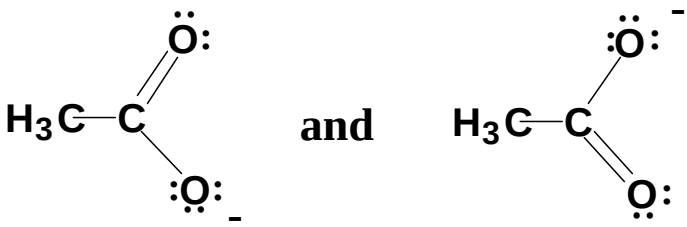


Covalent Bonding of Carbon

Groups Bonded to Carbon	Orbital Hybrid-ization	Predicted Bond Angles	Types of Bonds to Each Carbon	Example	Name
4	***sp*³**	**109.5°**	four σ bonds		**Ethane**
3	***sp*²**	**120°**	three σ bonds and one π bond		**Ethene**
2	***sp***	**180°**	two σ bonds and two π bonds		**Ethyne**

Resonance

- For many molecules and ions, no single Lewis structure provides a truly accurate representation.



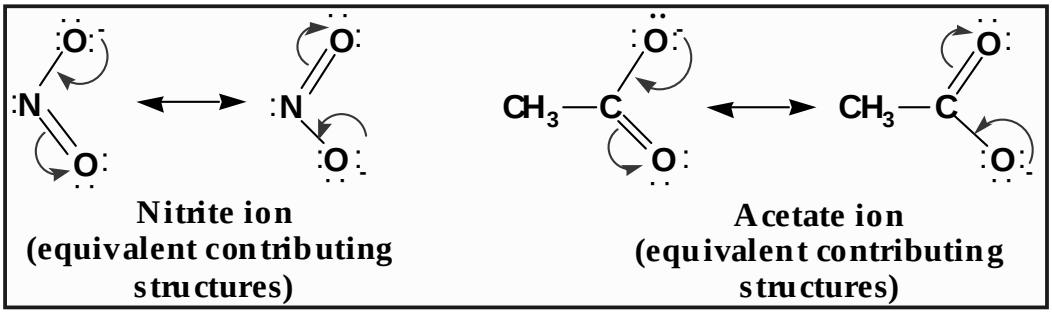
Ethanoate ion
(acetate ion)

Resonance

- Linus Pauling - 1930s
  - Many molecules and ions are best described by writing two or more Lewis structures.
  - Individual Lewis structures are called contributing structures.
  - Connect individual contributing structures by double-headed (resonance) arrows.
  - The molecule or ion is a hybrid of the various contributing structures.

Resonance

- Examples: equivalent contributing structures.



Resonance

- Curved arrow: A symbol used to show the redistribution of valence electrons.
- In using curved arrows, there are only two allowed types of electron redistribution:
  - from a bond to an adjacent atom.
  - from a lone pair on an atom to an adjacent bond.
- Electron pushing is a survival skill in organic chemistry.
  - learn it well!

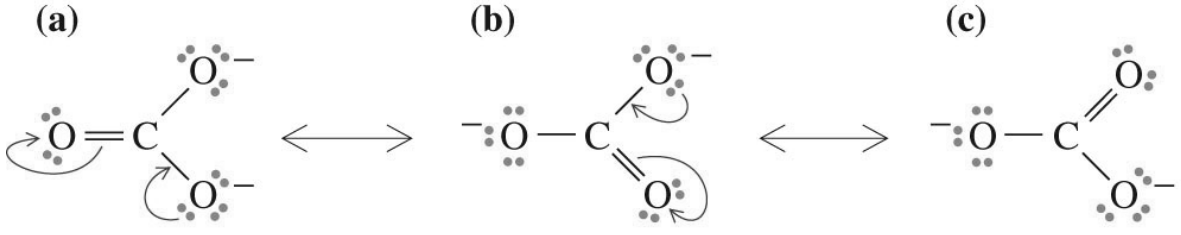
Resonance

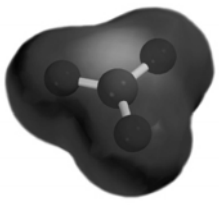
- All contributing structures must

1. have the same number of valence electrons.
2. obey the rules of covalent bonding:
   - no more than 2 electrons in the valence shell of H.
   - no more than 8 electrons in the valence shell of a 2nd period element.
3. differ only in distribution of valence electrons; the position of all nuclei must be the same.
4. have the same number of paired and unpaired electrons.

Resonance

- The carbonate ion
  - Is a hybrid of three equivalent contributing structures.
  - The negative charge is distributed equally among the three oxygens as shown in the elpot.

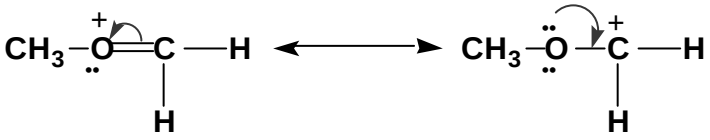




Resonance

Preference 1: filled valence shells

Structures in which all atoms have filled valence shells contribute more than those with one or more unfilled valence shells.



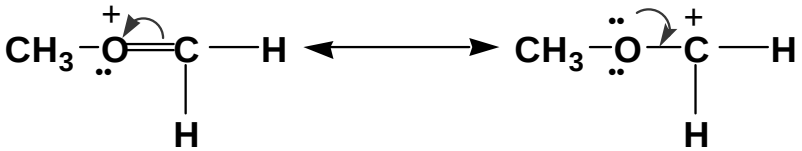
Greater contribution; both carbon and oxygen have complete valence shells

Lesser contribution; carbon has only 6 electrons in its valence shell

Resonance

Preference 2: maximum number of covalent bonds

Structures with a greater number of covalent bonds contribute more than those with fewer covalent bonds.



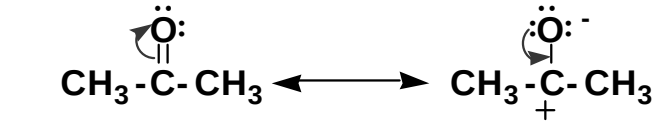
Greater contribution (8 covalent bonds)

Lesser contribution (7 covalent bonds)

Resonance

Preference 3: least separation of unlike charge

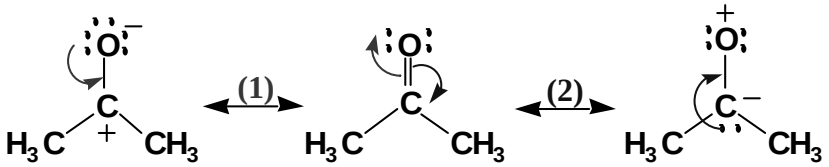
Structures with separation of unlike charges contribute less than those with no charge separation.



Greater contribution (no separation of unlike charges) ⟷ **Lesser contribution (separation of unlike charges)**

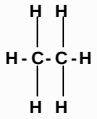
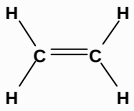
Resonance

- Preference 4: negative charge on the more electronegative atom.
  - Structures that carry a negative charge on the more electronegative atom contribute more than those with the negative charge on a less electronegative atom.



(a) Lesser contribution ⟷ **(b) Greater contribution** ⟷ **(c) Should not be drawn**

Bond Lengths and Bond Strengths

Name	Formula	Bond	Orbital Overlap	Bond Length (pm)
Ethane		C-C	sp^3-sp^3	153.2
		C-H	sp^3-1s	111.4
Ethene		C-C	sp^2-sp^2, 2p-2p	133.9
		C-H	sp^2-1s	110.0
Ethyne		C-C	sp -sp , two 2 p-2p	121.2
		C-H	sp -1s	109.0