

# COMPOUNDS AND CHEMICAL BONDS

## 1.1 INTRODUCTION

1. Organic chemistry is the study of *the compounds of carbon*.
2. The compounds of carbon are the central substances of which all living things on this planet are made.
  - 1) DNA: the giant molecules that contain all the genetic information for a given species.
  - 2) proteins: blood, muscle, and skin.
  - 3) enzymes: catalyze the reactions that occur in our bodies.
  - 4) furnish the energy that sustains life.
3. Billion years ago most of the carbon atoms on the earth existed as  $\text{CH}_4$ :
  - 1)  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_2$  were the main components of the primordial atmosphere.
  - 2) Electrical discharges and other forms of highly energetic radiation caused these simple compounds to fragment into highly reactive pieces which combine into more complex compounds such as amino acids, formaldehyde, hydrogen cyanide, purines, and pyrimidines.
  - 3) Amino acids reacted with each other to form the first protein.
  - 4) Formaldehyde reacted with each other to become sugars, and some of these sugars, together with inorganic phosphates, combined with purines and pyrimidines to become simple molecules of ribonucleic acids (RNAs) and DNA.
4. We live in an *Age of Organic Chemistry*:
  - 1) clothing: natural or synthetic substance.
  - 2) household items:
  - 3) automobiles:
  - 4) medicines:
  - 5) pesticides:
5. Pollutions:
  - 1) insecticides: natural or synthetic substance.
  - 2) PCBs:

- 3) dioxins:
- 4) CFCs:

## 1.2 THE DEVELOPMENT OF ORGANIC CHEMISTRY AS A SCIENCE

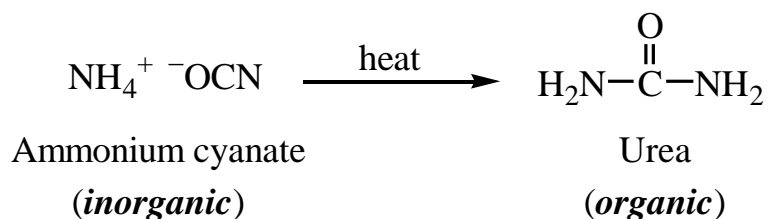
1. The ancient Egyptians used indigo (靛藍) and alizarin (茜素) to dye cloth.
2. The Phoenicians (腓尼基人) used the famous “royal purple (深藍紫色)”, obtained from mollusks (墨魚、章魚、貝殼等軟體動物), as a dyestuff.
3. As a science, organic chemistry is less than 200 years old.

### 1.2A Vitalism

“*Organic*” — derived from living *organism* (In 1770, Torbern Bergman, Swedish chemist)

- ⇒ the study of compounds extracted from living organisms
- ⇒ such compounds needed “**vital force**” to create them

1. In 1828, Friedrich Wöhler Discovered:



### 1.2B Empirical and Molecular Formulas

1. In 1784 Antoine Lavoisier (法國化學家拉瓦錫) first showed that organic compounds were composed primarily of carbon, hydrogen, and oxygen.
2. Between 1811 and 1831, *quantitative* methods for determining the composition of

organic compounds were developed by Justus Liebig (德國化學家), J. J. Berzelius, J. B. A. Dumas (法國化學家).

3. In 1860 Stanislao Cannizzaro (義大利化學家坎尼薩羅) showed that the earlier hypothesis of Amedeo Avogadro (1811, 義大利化學家及物理學家亞佛加厥) could be used to distinguish between **empirical** and **molecular formulas**.

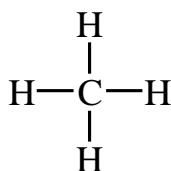
molecular formulas  $C_2H_4$  (ethylene),  $C_5H_{10}$  (cyclopentane), and  $C_6H_{12}$  (cyclohexane) all have the same empirical formula  $CH_2$ .

## 1.3 THE STRUCTURAL THEORY OF ORGANIC CHEMISTRY

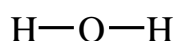
### 1.3A. The Structural Theory: (1858 ~ 1861)

August Kekulé (German), Archibald Scott Couper (Briton), and Alexander M. Butlerov

1. The atoms can form a fixed number of bonds (**valence**):



Carbon atoms  
are tetravalent



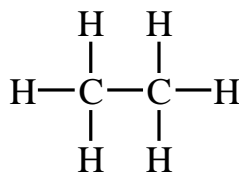
Oxygen atoms  
are divalent



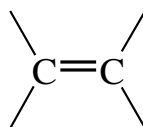
Hydrogen and halogen  
atoms are monovalent

2. A carbon atom can use one or more of its valence to form bonds to other atoms:

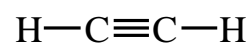
#### Carbon-carbon bonds



Single bond



Double bond



Triple bond

3. Organic chemistry: **A study of the compounds of carbon** (Kekulé, 1861).

### 1.3B. Isomers: The Importance of Structural Formulas

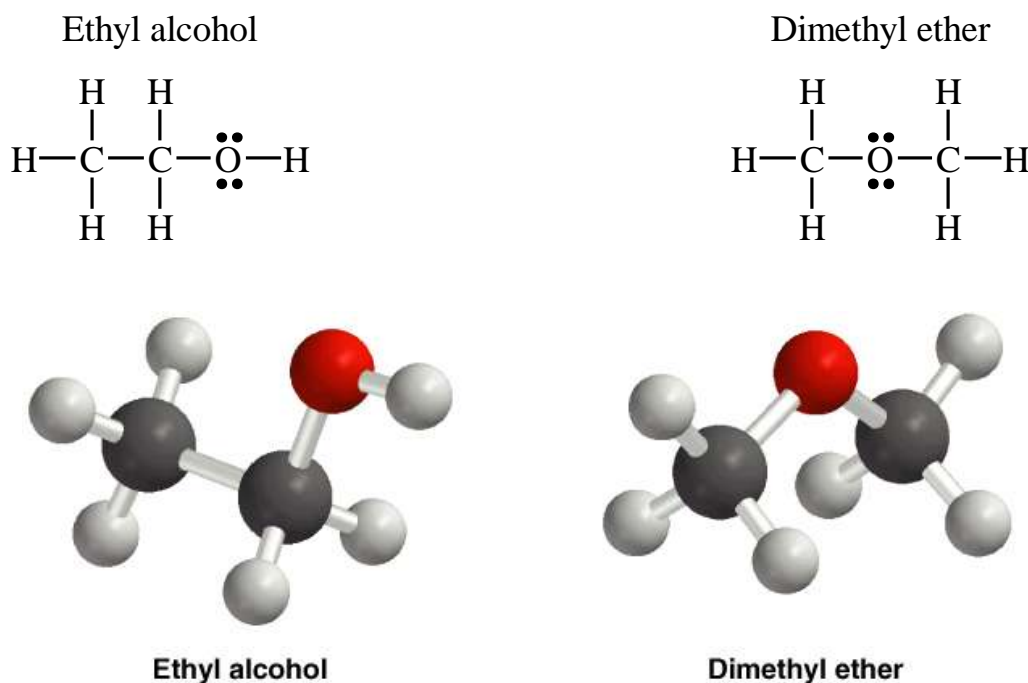
1. **Isomers: different compounds that have the same molecular formula**
2. There are two isomeric compounds with molecular formula  $C_2H_6O$ :
  - 1) dimethyl ether: a gas at room temperature, does not react with sodium.
  - 2) ethyl alcohol: a liquid at room temperature, does react with sodium.

**Table 1.1** Properties of ethyl alcohol and dimethyl ether

	Ethyl Alcohol $C_2H_6O$	Dimethyl Ether $C_2H_6O$
Boiling point, $^{\circ}C^a$	78.5	-24.9
Melting point, $^{\circ}C$	-117.3	-138
Reaction with sodium	Displaces hydrogen	No reaction

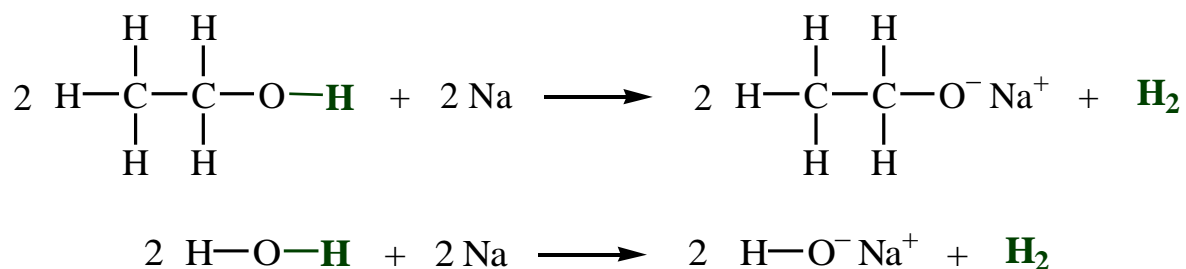
<sup>a</sup> Unless otherwise stated all temperatures in this text are given in degree Celsius.

3. The two compounds differ in their **connectivity**:  $C-O-C$  and  $C-C-O$



**Figure 1.1** Ball-and-stick models and structural formulas for ethyl alcohol and dimethyl ether

- 1) O–H: accounts for the fact that ethyl alcohol is a liquid at room temperature.



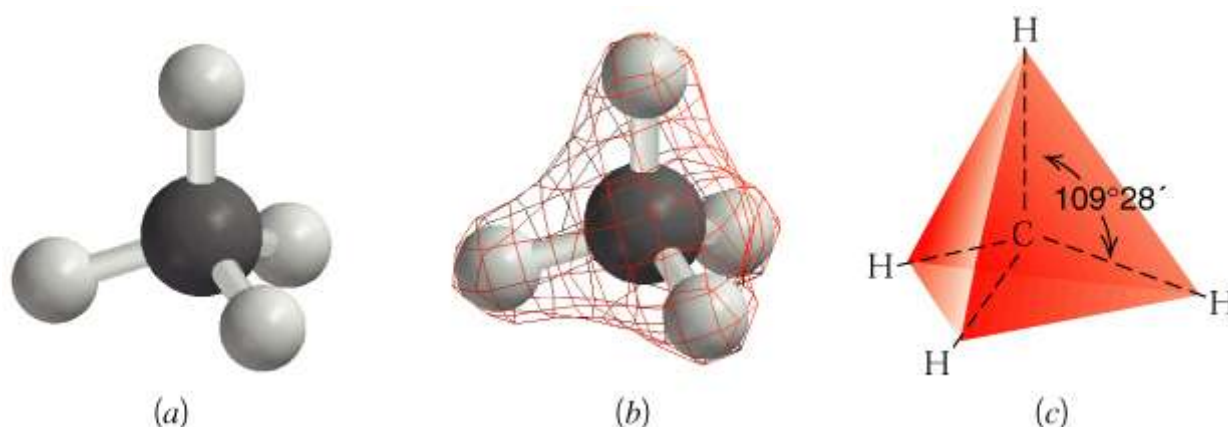
- 2) C–H: normally unreactive

4. **Constitutional isomers:**\* different compounds that have the same molecular formula, but differ in their connectivity (the sequence in which their atoms are bounded together).

\* An older term, **structural isomers**, is recommended by the International Union of Pure and Applied Chemistry (IUPAC) to be abandoned.

### 1.3C. THE TETRAHEDRAL SHAPE OF METHANE

1. In 1874, Jacobus H. van't Hoff (Netherlander) & Joseph A. Le Bel (French):  
The four bonds of the carbon atom in methane point toward the corners of a regular tetrahedron, the carbon atom being placed at its center.



**Figure 1.2** The tetrahedral structure of methane. Bonding electrons in methane principally occupy the space within the wire mesh.

## 1.4 CHEMICAL BONDS: THE OCTET RULE

Why do atoms bond together?                      more stable (has less energy)

How to describe bonding?

1. G. N. Lewis (of the University of California, Berkeley; 1875~1946) and Walter Kössel (of the University of Munich; 1888~1956) proposed in 1916:
  - 1) The **ionic** (or **electrovalent**) bond: formed by the transfer of one or more electrons from one atom to another to create ions.
  - 2) The **covalent** bond: results when atoms share electrons.
2. Atoms without the electronic configuration of a noble gas generally react to produce such a configuration.

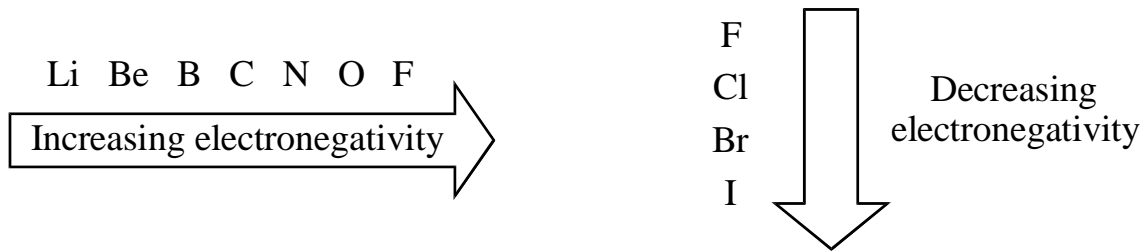
## 1.4A Ionic Bonds

1. **Electronegativity measures the ability of an atom to attract electrons.**

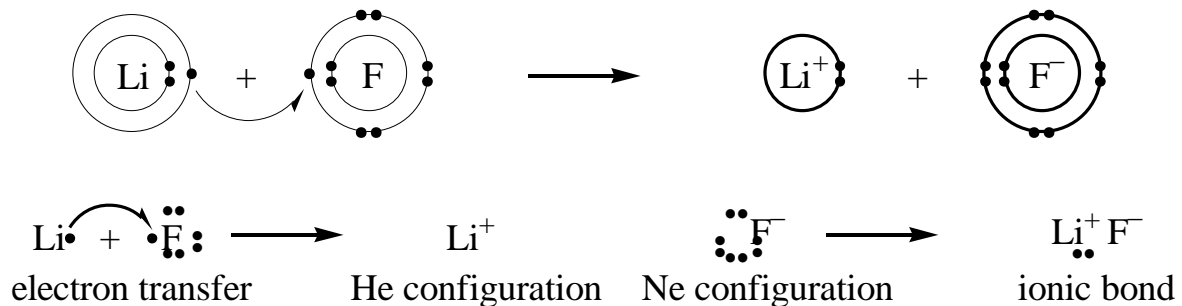
**Table 1.2** Electronegativities of Some of Elements

<b>H</b>							
2.1							
<b>Li</b>	<b>Be</b>		<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>
1.0	1.5		2.0	2.5	3.0	3.5	4.0
<b>Na</b>	<b>Mg</b>		<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>
0.9	1.2		1.5	1.8	2.1	2.5	3.0
<b>K</b>							<b>Br</b>
0.8							2.8

- 1) The electronegativity increases across a horizontal row of the periodic table from left to right:
- 2) The electronegativity decreases go down a vertical column:



3) 1916, Walter Kössel (of the University of Munich; 1888~1956)

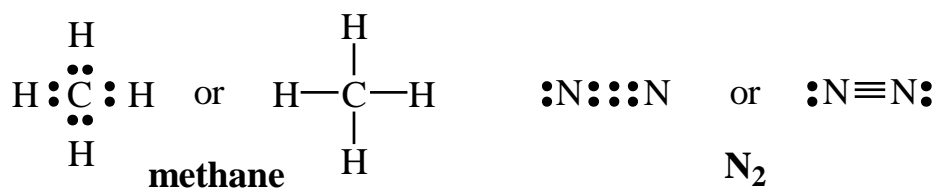
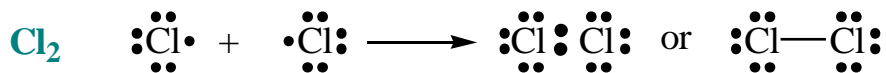
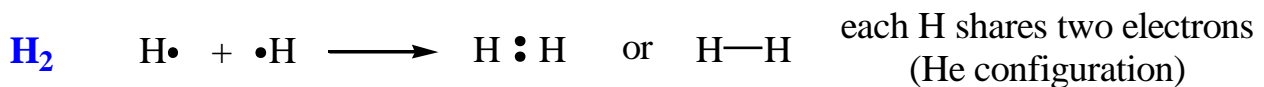


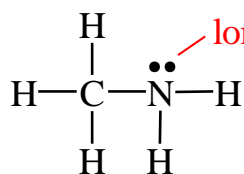
- 4) Ionic substances, because of their strong internal electrostatic forces, are usually very high melting solids, often having melting points above 1,000 °C.
- 5) In polar solvents, such as water, the ions are solvated, and such solutions usually conduct an electric current..

## 1.4B Covalent Bonds

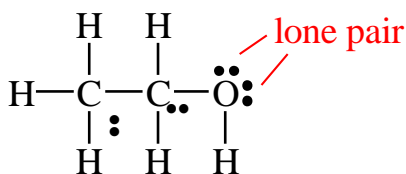
1. Atoms achieve noble gas configurations by sharing electrons.

1) Lewis structures:

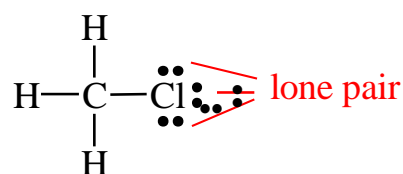




methyl amine

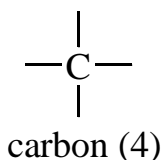


ethanol

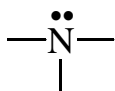


chloromethane

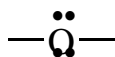
• nonbonding electrons  $\Rightarrow$  affect the reactivity of the compound



carbon (4)



nitrogen (3)



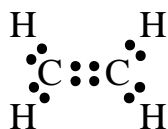
oxygen (2)



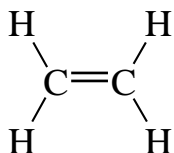
hydrogen



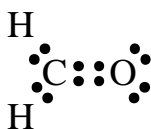
halogens (1)



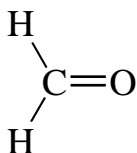
or



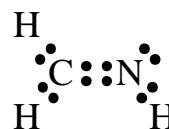
ethylene



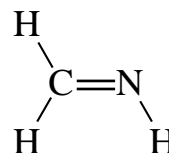
or



formaldehyde



or



formaldimine

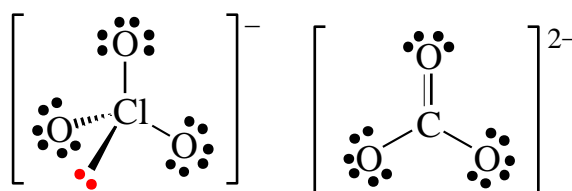
**double bond**

## 1.5 WRITING LEWIS STRUCTURES

### 1.5A. Lewis structure of $\text{CH}_3\text{F}$

1. The number of valence electrons of an atom is equal to the group number of the atom.
2. For an ion, add or subtract electrons to give it the proper charge.
3. Use multiple bonds to give atoms the noble gas configuration.

### 1.5B. Lewis structure of $\text{ClO}_3^-$ and $\text{CO}_3^{2-}$





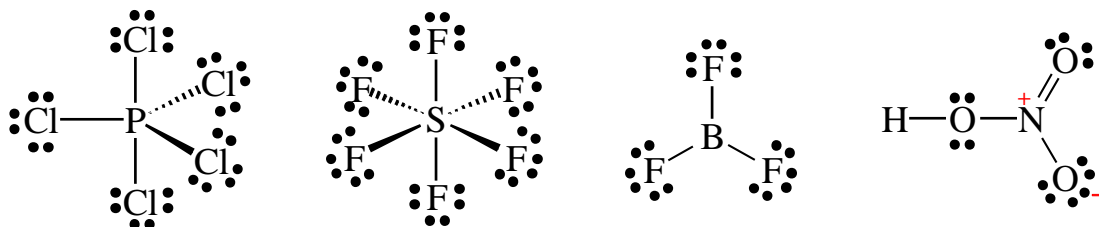
## 1.6 EXCEPTIONS TO THE OCTET RULE

### 1.6A. $\text{PCl}_5$

### 1.6B. $\text{SF}_6$

### 1.6C. $\text{BF}_3$

### 1.6D. $\text{HNO}_3$ ( $\text{HONO}_2$ )



## 1.7 FORMAL CHARGE

### 1.7A In normal covalent bond:

1. Bonding electrons are shared by both atoms. Each atom still “owns” one electron.
2. “**Formal charge**” is calculated by subtracting the number of valence electrons assigned to an atom in its bonded state from the number of valence electrons it has as a neutral free atom.

### 1.7B For methane:

1. Carbon atom has four valence electrons.
2. Carbon atom in methane still owns four electrons.
3. Carbon atom in methane is electrically neutral.

### 1.7C For ammonia:

1. Atomic nitrogen has five valence electrons.
2. Ammonia nitrogen still owns five electrons.
3. Nitrogen atom in ammonia is electrically neutral.

### 1.7D For nitromethane:

1. Nitrogen atom:
  - 1) Atomic nitrogen has five valence electrons.
  - 2) Nitromethane nitrogen has only *four* electrons.
  - 3) Nitrogen has lost an electron and must have a positive charge.
2. Singly bound oxygen atom:
  - 1) Atomic oxygen has six valence electrons.
  - 2) Singly bound oxygen has *seven* electrons.
  - 3) Singly bound oxygen has gained an  $e^-$  and must have a negative charge.

### 1.7E Summary of Formal Charges

See Table 1.3

## 1.8 RESONANCE

### 1.8A. General rules for drawing “realistic” resonance structures:

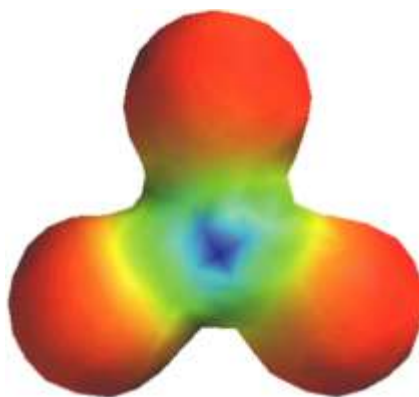
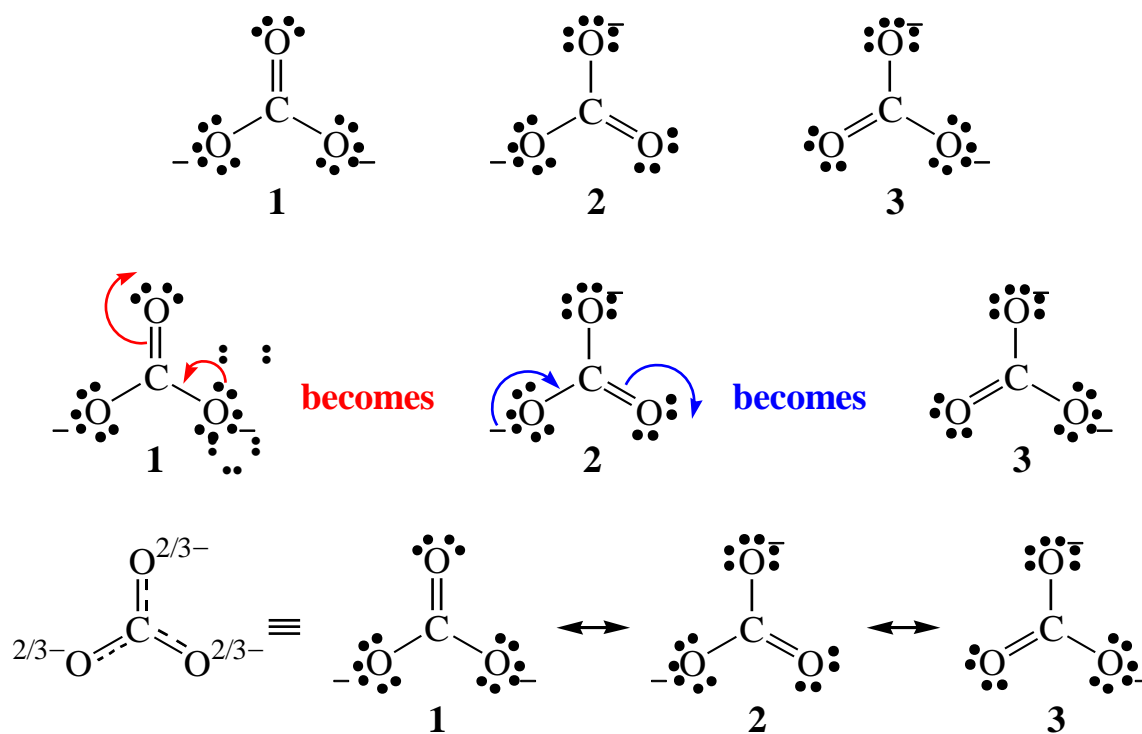
1. Must be valid Lewis structures.
2. Nuclei cannot be moved and bond angles must remain the same. Only electrons may be shifted.
3. The number of unpaired electrons must remain the same. All the electrons must remain paired in all the resonance structures.
4. Good contributor has all octets satisfied, as many bonds as possible, as little charge separation as possible. Negative charge on the more EN atoms.
5. Resonance stabilization is most important when it serves to delocalize a charge

over two or more atoms.

6. **Equilibrium:**  $\rightleftharpoons$

7. **Resonance:**  $\longleftrightarrow$

### 1.8B. $\text{CO}_3^{2-}$

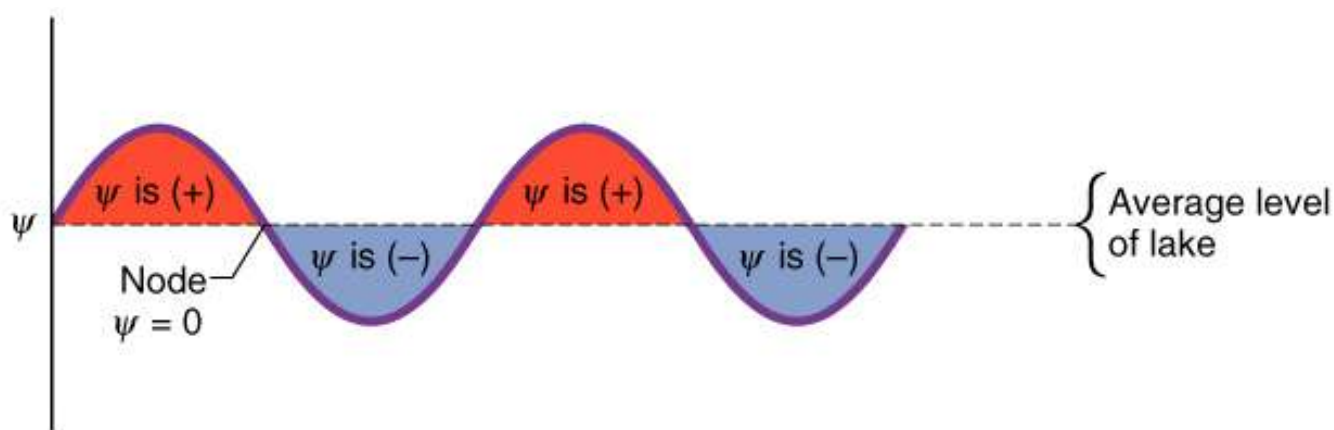


**Figure 1.3** A calculated electrostatic potential map for carbonate dianion, showing the equal charge distribution at the three oxygen atoms. In electrostatic potential maps like this one, colors trending toward red mean increasing concentration of negative charge, while those trending toward blue mean less negative (or more positive) charge.

## 1.9 QUANTUM MECHANICS

### 1.9A Erwin Schrödinger, Werner Heisenberg, and Paul Dirac (1926)

1. **Wave mechanics** (Schrödinger) or **quantum mechanics** (Heisenberg)
  - 1) Wave equation  $\Rightarrow$  wave function (solution of wave equation, denoted by Greek letter psi ( $\Psi$ ))
  - 2) Each wave function corresponds to a different state for the electron.
  - 3) Corresponds to each state, and calculable from the wave equation for the state, is a particular energy.
  - 4) The value of a wave function: **phase sign**
  - 5) **Reinforce:** a crest meets a crest (waves of the same phase sign meet each other)  $\Rightarrow$  add together  $\Rightarrow$  resulting wave is larger than either individual wave.
  - 6) **Interfere:** a crest meets a trough (waves of opposite phase sign meet each other)  $\Rightarrow$  subtract each other  $\Rightarrow$  resulting wave is smaller than either individual wave.
  - 7) **Node:** the value of wave function is zero  $\Rightarrow$  **the greater the number of nodes, the greater the energy.**

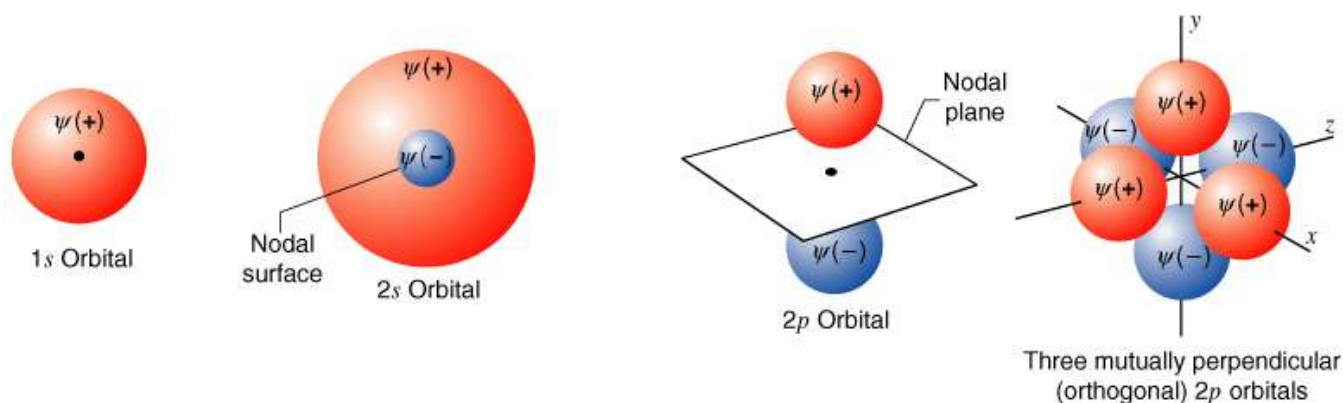


**Figure 1.4** A wave moving across a lake is viewed along a slice through the lake. For this wave the wave function,  $\Psi$ , is plus (+) in crests and minus (-) in troughs. At the average level of the lake it is zero; these places are called nodes.

## 1.10 ATOMIC ORBITALS

## 1.10A. ELECTRON PROBABILITY DENSITY:

1.  $\Psi^2$  for a particular location  $(x,y,z)$  expresses the **probability** of finding an electron at that particular location in space (Max Born).
  - 1)  $\Psi^2$  is large: large **electron probability density**.
  - 2) Plots of  $\Psi^2$  in three dimensions generate the shapes of the familiar *s*, *p*, and *d* atomic orbitals.
  - 3) An **orbital** is a region of space where the probability of finding an electron is large (the volumes would contain the electron 90-95% of the time).



**Figure 1.5** The shapes of some *s* and *p* orbitals. Pure, unhybridized *p* orbitals are almost-touching spheres. The *p* orbitals in hybridized atoms are lobe-shaped (Section 1.14).

## 1.10B. Electron configuration:

1. The **aufbau principle** (German for “building up”):
2. The **Pauli exclusion principle**:
3. **Hund’s rule**:
  - 1) Orbitals of equal energy are said to **degenerate orbitals**.

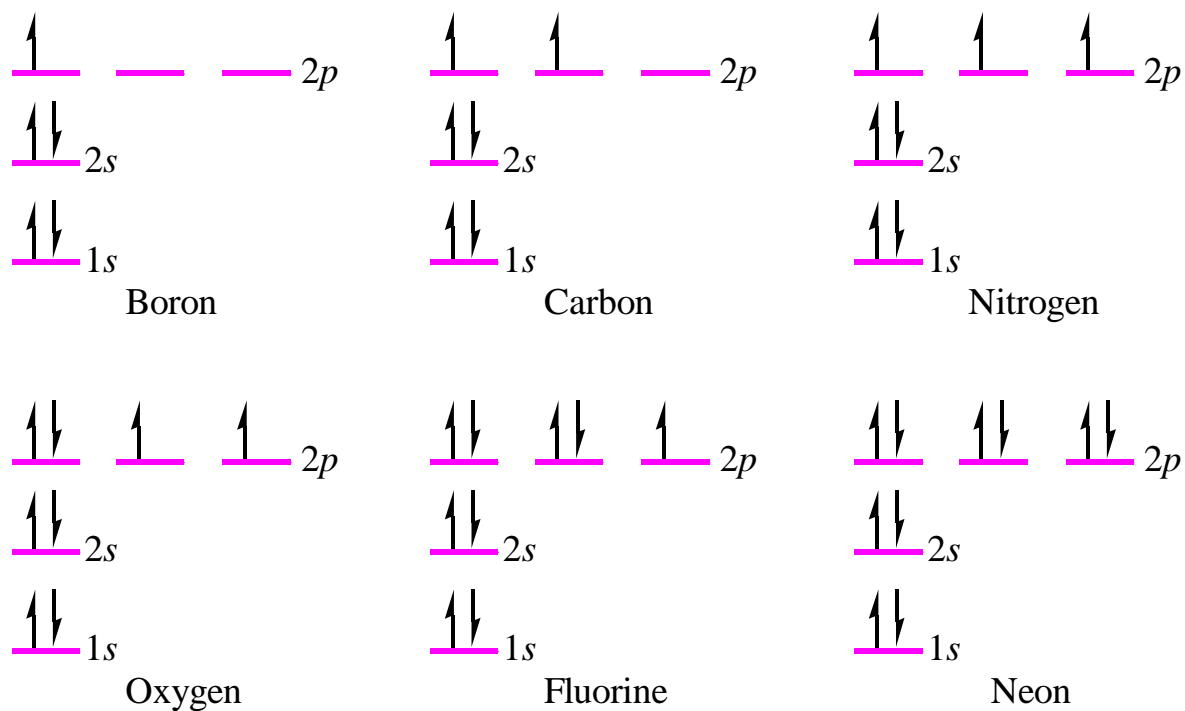


Figure 1.6 The electron configurations of some second-row elements.

## 1.11 MOLECULAR ORBITALS

### 1.11A. Potential energy:

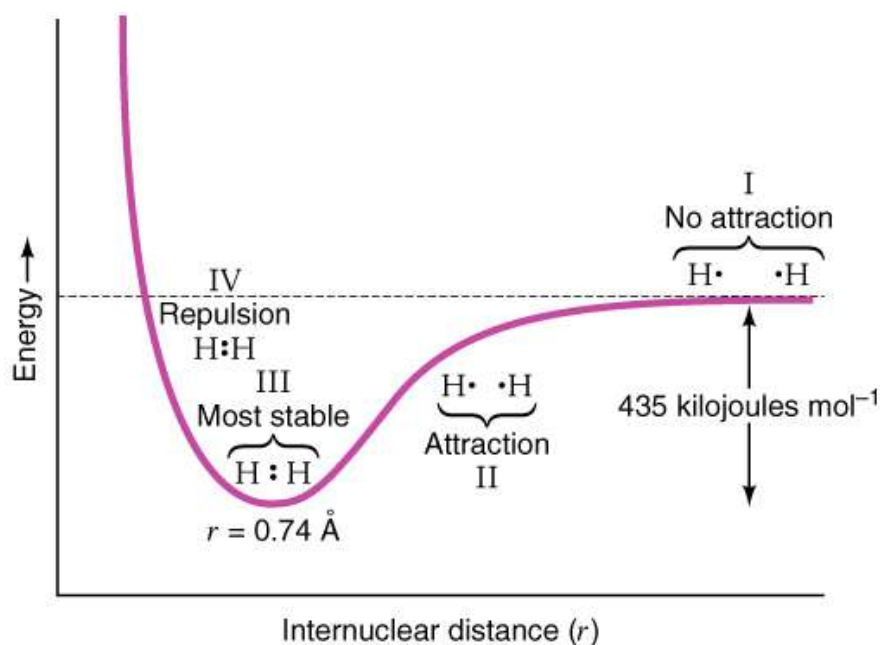


Figure 1.7 The potential energy of the hydrogen molecule as a function of internuclear distance.

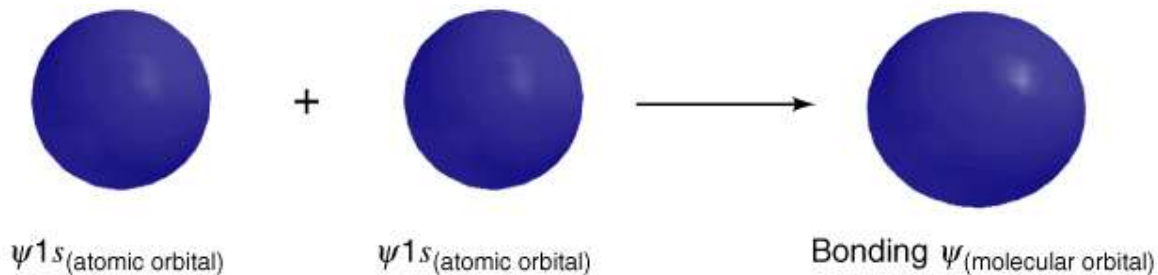
1. Region **I**: the atoms are far apart  $\Rightarrow$  **No attraction**
2. Region **II**: each nucleus increasingly attracts the other's electron  $\Rightarrow$  the attraction more than compensates for the repulsive force between the two nuclei (or the two electrons)  $\Rightarrow$  **the attraction lowers the energy of the total system**
3. Region **III**: the two nuclei are  $0.74 \text{ \AA}$  apart  $\Rightarrow$  **bond length**  $\Rightarrow$  **the most stable (lowest energy) state is obtained**
4. Region **IV**: the repulsion of the two nuclei predominates  $\Rightarrow$  **the energy of the system rises**

### 1.11B. Heisenberg Uncertainty Principle

1. We can not know simultaneously the position and momentum of an electron.
2. We describe the electron in terms of probabilities ( $\Psi^2$ ) of finding it at particular place.
  - 1) *electron probability density*  $\Rightarrow$  **atomic orbitals (AOs)**

### 1.11C. Molecular Orbitals

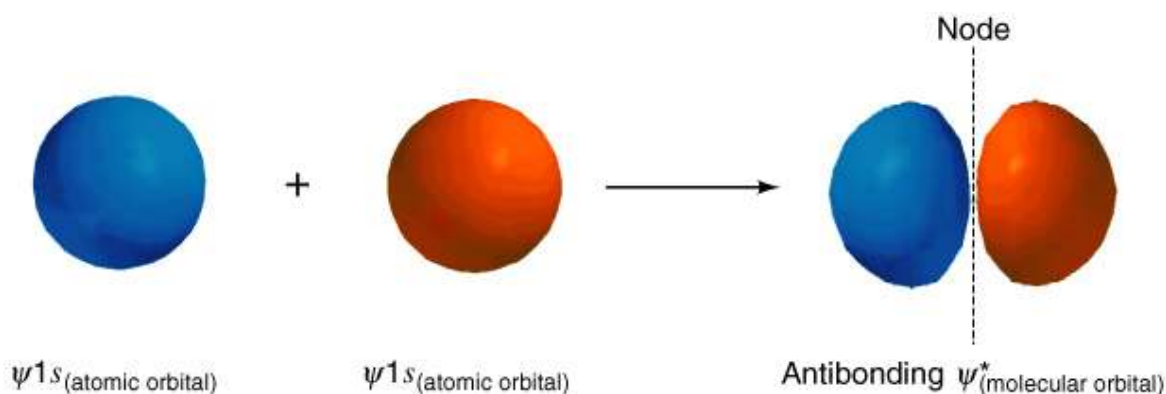
1. AOs combine (overlap) to become **molecular orbitals (MOs)**.
  - 1) The MOs that are formed encompass both nuclei, and, in them, the electrons can move about both nuclei.
  - 2) The MOs *may contain a maximum of two spin-paired electrons*.
  - 3) The number of MOs *that result always equals the number of AOs that combine*.
2. **Bonding molecular orbital ( $\Psi_{\text{molec}}$ ):**
  - 1) *AOs of the same phase sign overlap*  $\Rightarrow$  leads to *reinforcement* of the wave function  $\Rightarrow$  **the value of is larger between the two nuclei**  $\Rightarrow$  **contains both electrons in the lowest energy state, ground state**



**Figure 1.8** The overlapping of two hydrogen 1s atomic orbitals with the same phase sign (indicated by their identical color) to form a bonding molecular orbital.

3. **Antibonding molecular orbital ( $\psi_{\text{molec}}^*$ ):**

- 1) **AOs of opposite phase sign overlap  $\Rightarrow$  leads to interference of the wave function in the region between the two nuclei  $\Rightarrow$  a node is produced  $\Rightarrow$  the value of is smaller between the two nuclei  $\Rightarrow$  the highest energy state, excited state  $\Rightarrow$  contains no electrons**



**Figure 1.9** The overlapping of two hydrogen 1s atomic orbitals with opposite phase signs (indicated by their different colors) to form an antibonding molecular orbital.

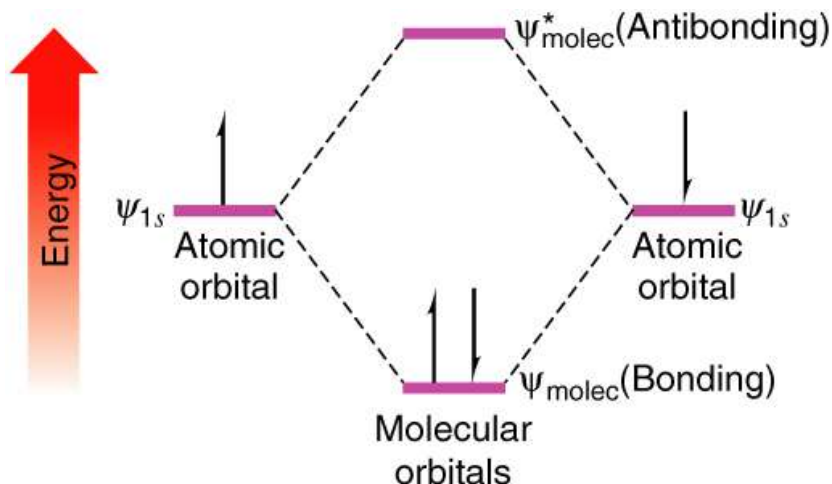
4. **LCAO (linear combination of atomic orbitals):**

5. **MO:**

- 1) Relative energy of an electron in the bonding MO of the hydrogen molecule is substantially less than its energy in a  $\psi_{1s}$  AO.
- 2) Relative energy of an electron in the antibonding MO of the hydrogen molecule is substantially greater than its energy in a  $\psi_{1s}$  AO.



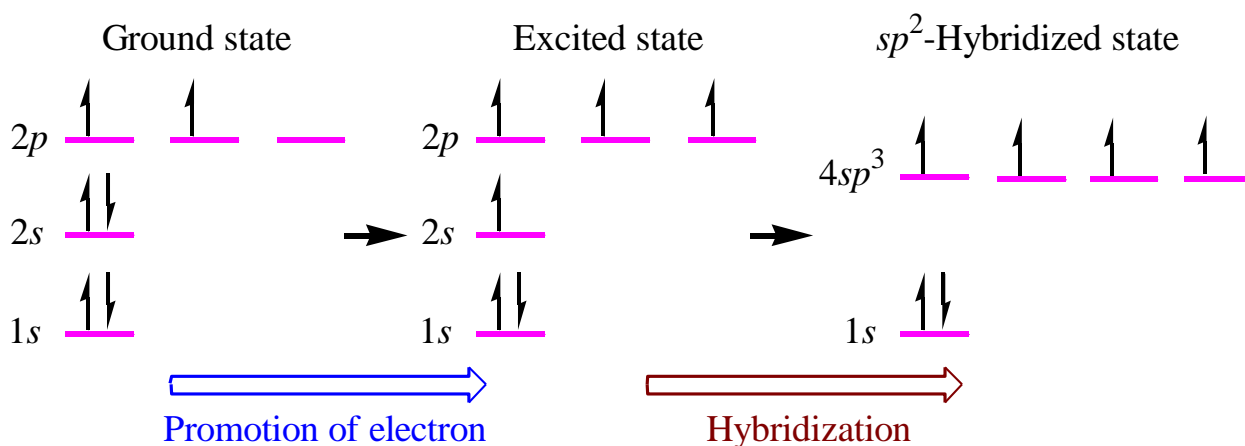
## 1.11D. Energy Diagram for the Hydrogen Molecule



**Figure 1.10** Energy diagram for the hydrogen molecule. Combination of two atomic orbitals,  $\psi_{1s}$ , gives two molecular orbitals,  $\psi_{\text{molec}}$  and  $\psi_{\text{molec}}^*$ . The energy of  $\psi_{\text{molec}}$  is lower than that of the separate atomic orbitals, and in the lowest electronic state of molecular hydrogen it contains both electrons.

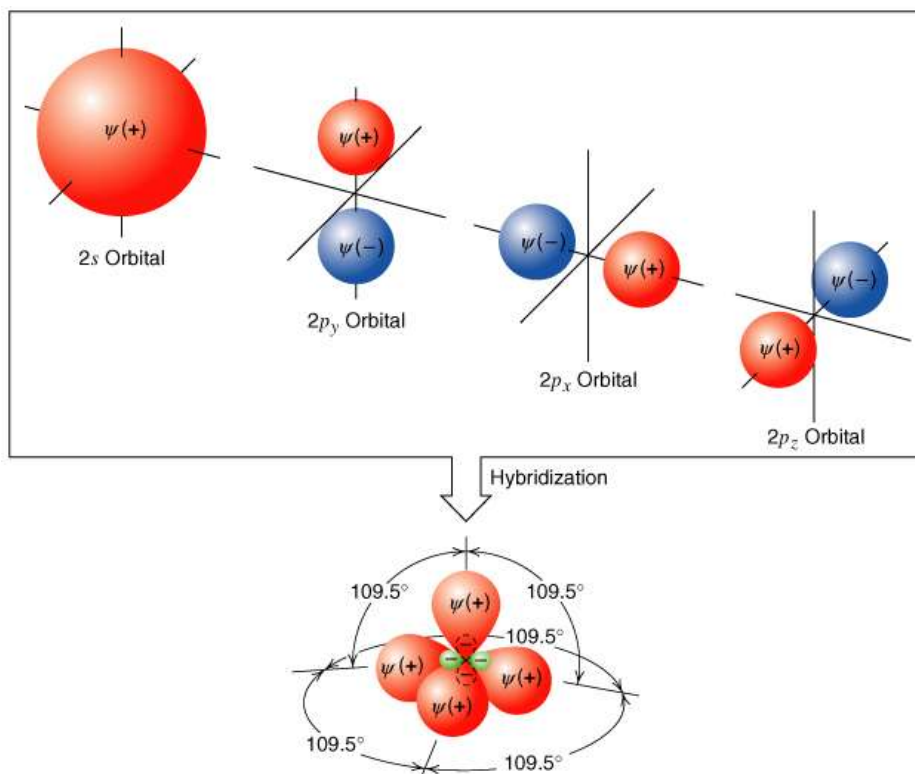
## 1.12 THE STRUCTURE OF METHANE AND ETHANE: $sp^3$ HYBRIDIZATION

- Orbital hybridization:** A mathematical approach that involves the combining of individual wave functions for s and p orbitals to obtain wave functions for new orbitals  $\Rightarrow$  **hybrid atomic orbitals**



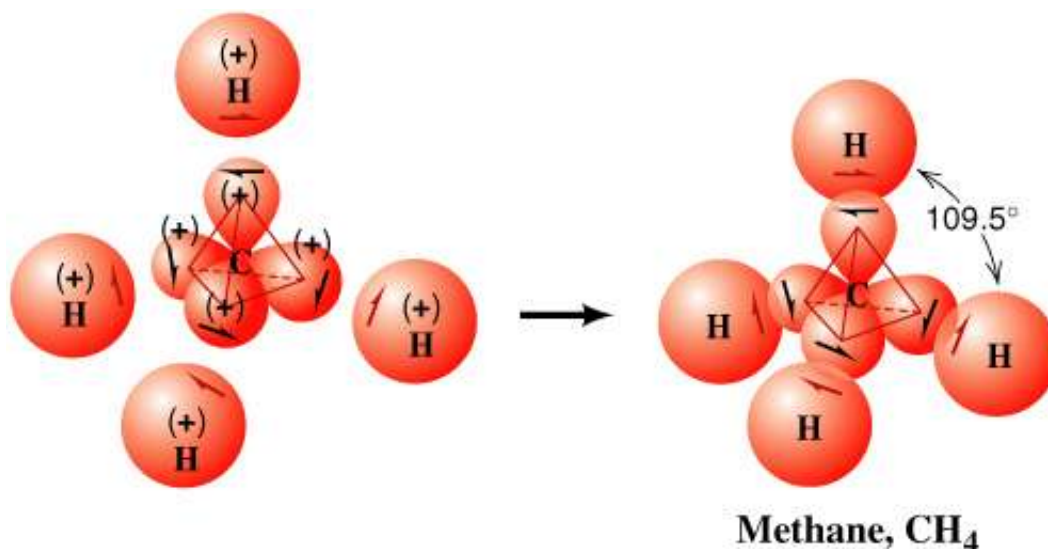
### 1.12A. The Structure of Methane

- Hybridization of AOs of a carbon atom:**



**Figure 1.11** Hybridization of pure atomic orbitals of a carbon atom to produce  $sp^3$  hybrid orbitals.

2. The four  $sp^3$  orbitals should be oriented at angles of  $109.5^\circ$  with respect to each other  $\Rightarrow$  **an  $sp^3$ -hybridized carbon gives a tetrahedral structure for methane.**



**Figure 1.12** The hypothetical formation of methane from an  $sp^3$ -hybridized carbon atom. In orbital hybridization we combine orbitals, *not* electrons. The electrons can then be placed in the hybrid orbitals as necessary for bond formation, but always in accordance with the Pauli principle of no more than two electrons (with opposite

spin) in each orbital. In this illustration we have placed one electron in each of the hybrid carbon orbitals. In addition, we have shown only the bonding molecular orbital of each C–H bond because these are the orbitals that contain the electrons in the lowest energy state of the molecule.

### 3. Overlap of hybridized orbitals:

- 1) The positive lobe of the  $sp^3$  orbital is large and is extended quite far into space.

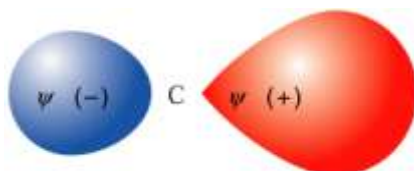


Figure 1.13 The shape of an  $sp^3$  orbital.

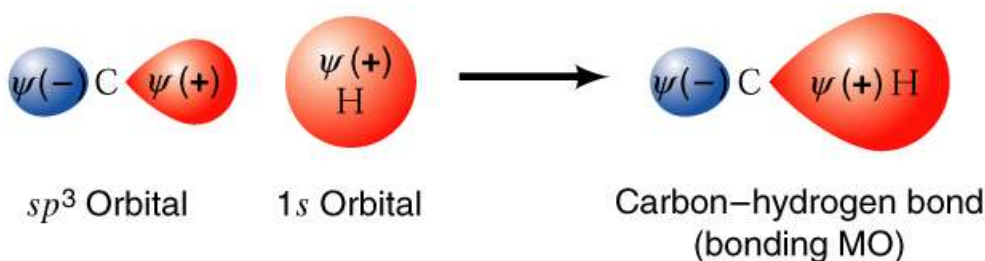


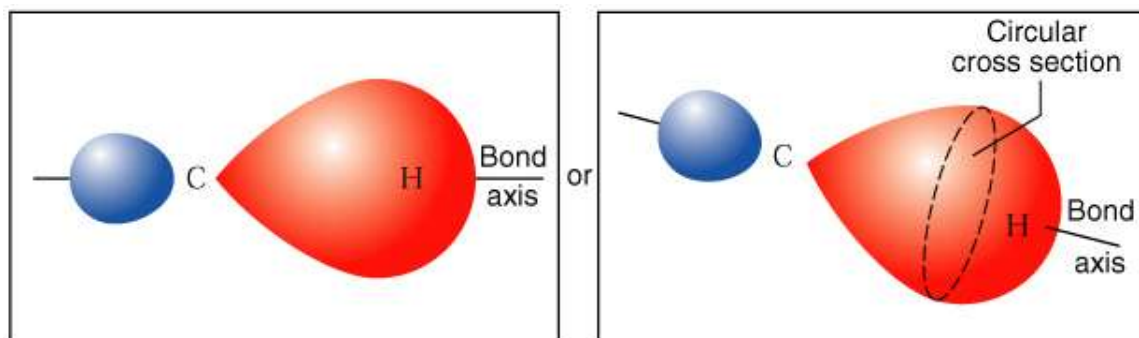
Figure 1.14 Formation of a C–H bond.

- 2) **Overlap integral:** a measure of the extent of overlap of orbitals on neighboring atoms.
- 3) **The greater the overlap achieved (the larger integral), the stronger the bond formed.**
- 4) **The relative overlapping powers of atomic orbitals have been calculated as follows:**

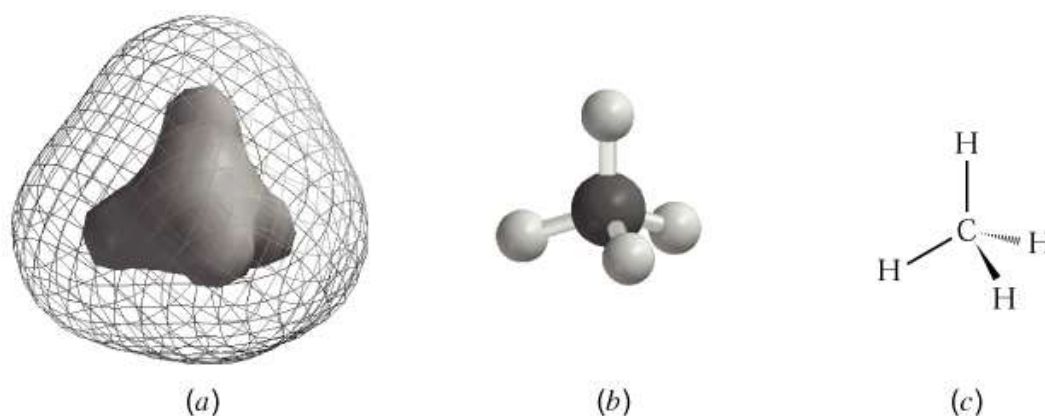
$$s: 1.00; \quad p: 1.72; \quad sp: 1.93; \quad sp^2: 1.99; \quad sp^3: 2.00$$

### 4. Sigma ( $\sigma$ ) bond:

- 1) A bond that is *circularly symmetrical in cross section when viewed along the bond axis*.
- 2) *All purely single bonds are sigma bonds.*

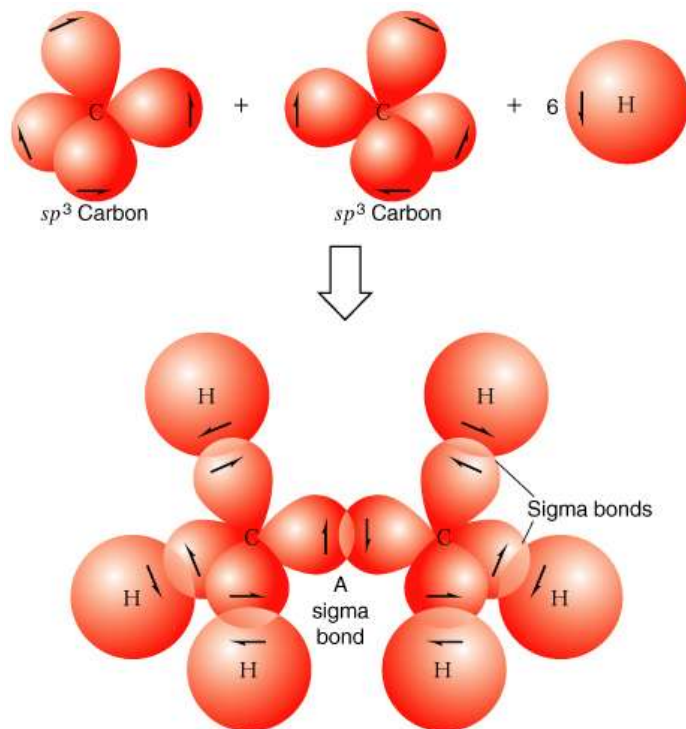


**Figure 1.15** A  $\sigma$  (sigma) bond.



**Figure 1.16** (a) In this structure of methane, based on quantum mechanical calculations, the inner solid surface represents a region of high electron density. High electron density is found in each bonding region. The outer mesh surface represents approximately the furthest extent of overall electron density for the molecule. (b) This ball-and-stick model of methane is like the kind you might build with a molecular model kit. (c) This structure is how you would draw methane. Ordinary lines are used to show the two bonds that are in the plane of the paper, a solid wedge is used to show the bond that is in front of the paper, and a dashed wedge is used to show the bond that is behind the plane of the paper.

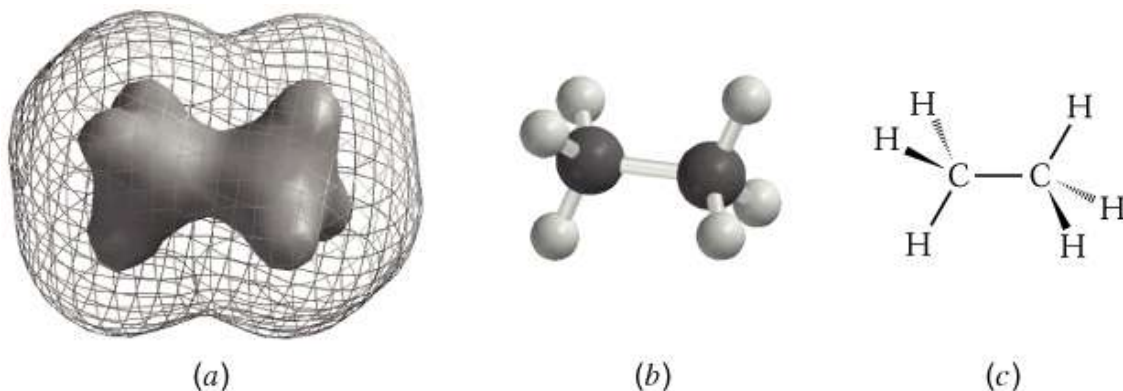
## 1.12B. The Structure of Ethane



**Figure 1.17** The hypothetical formation of the bonding molecular orbitals of ethane from two  $sp^3$ -hybridized carbon atoms and six hydrogen atoms. All of the bonds are sigma bonds. (Antibonding sigma molecular orbitals — are called  $\sigma^*$  orbitals — are formed in each instance as well, but for simplicity these are not shown.)

### 1. Free rotation about C–C:

- 1) A sigma bond has cylindrical symmetry along the bond axis  $\Rightarrow$  **rotation of groups joined by a single bond does not usually require a large amount of energy  $\Rightarrow$  free rotation.**

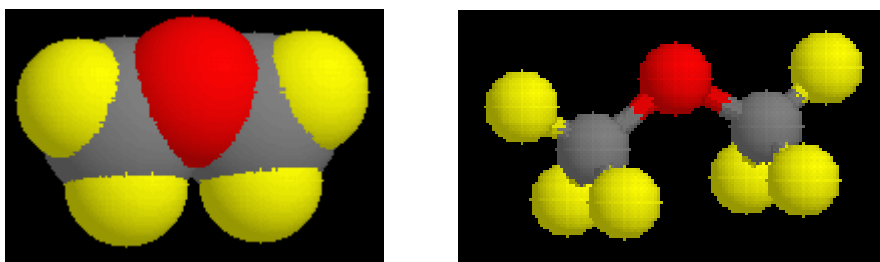


**Figure 1.18** (a) In this structure of ethane, based on quantum mechanical calculations, the inner solid surface represents a region of high electron density. High electron density is found in each bonding region. The outer mesh surface represents approximately the furthest extent of overall electron density for the molecule. (b) A ball-and-stick model of ethane, like the kind you might build with a

molecular model kit. (c) A structural formula for ethane as you would draw it using lines, wedges, and dashed wedges to show in three dimensions its tetrahedral geometry at each carbon.

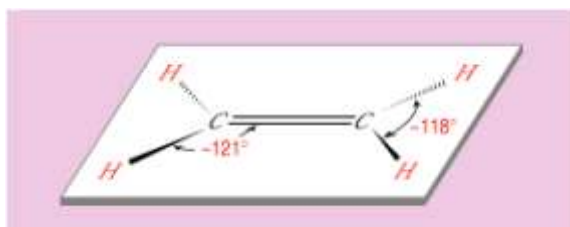
## 2. Electron density surface:

- 1) An electron density surface shows points in space that happen to have the same electron density.
- 2) A “**high**” electron density surface (also called a “bond” electron density surface) shows the *core* of electron density around each atomic nucleus and regions where neighboring atoms share electrons (covalent bonding regions).
- 3) A “**low**” electron density surface roughly shows the *outline* of a molecule’s electron cloud. This surface gives information about molecular shape and volume, and usually looks the same as a van der Waals or space-filling model of the molecule.



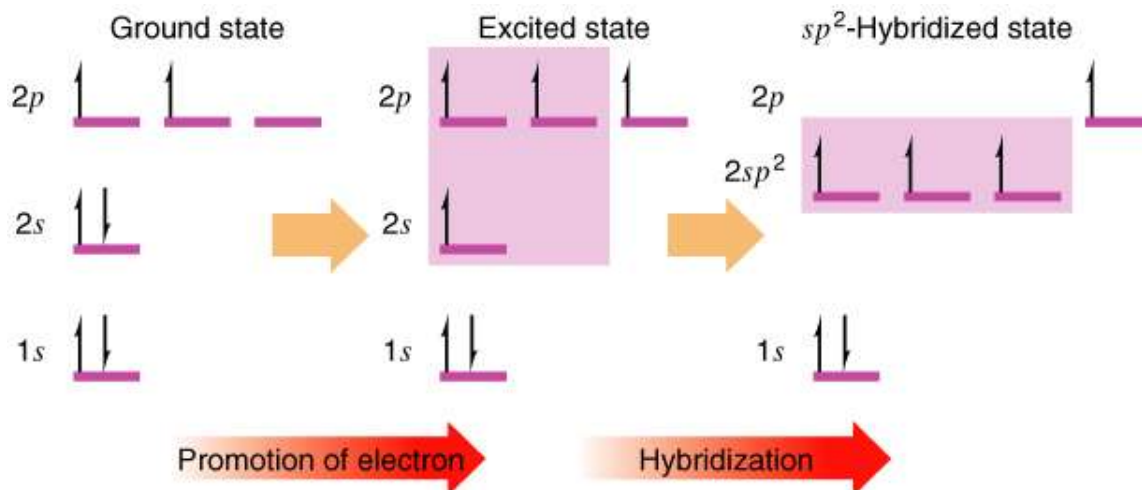
Dimethyl ether

## 1.13 THE STRUCTURE OF ETHENE (ETHYLENE): $sp^2$ HYBRIDIZATION



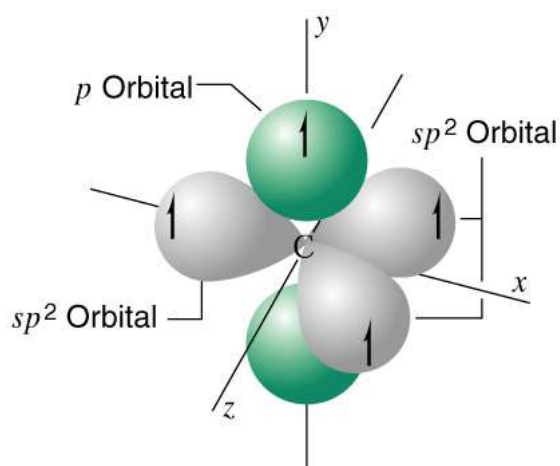
**Figure 1.19** The structure and bond angles of ethene. The plane of the atoms is perpendicular to the paper. The dashed edge bonds project behind the plane of the paper, and the solid wedge bonds project in front of the paper.



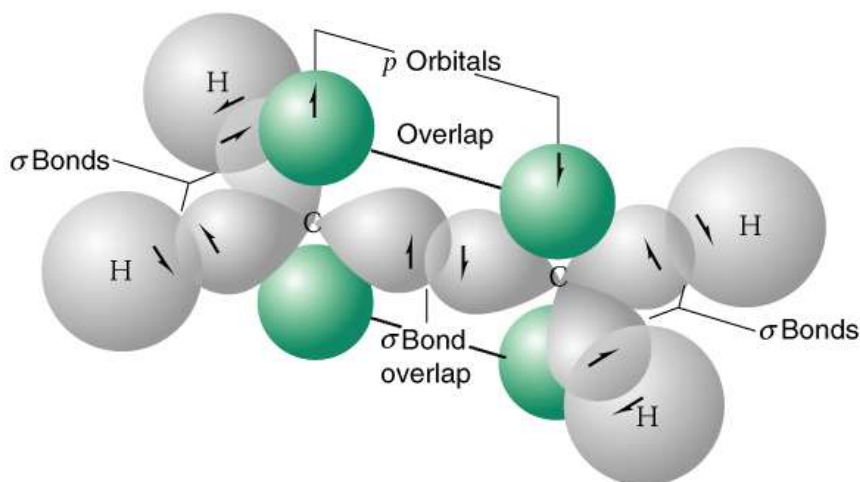


**Figure 1.20** A process for obtaining  $sp^2$ -hybridized carbon atoms.

1. One  $2p$  orbital is left unhybridized.
2. The three  $sp^2$  orbitals that result from hybridization are directed toward the corners of a regular triangle.



**Figure 1.21** An  $sp^2$ -hybridized carbon atom.



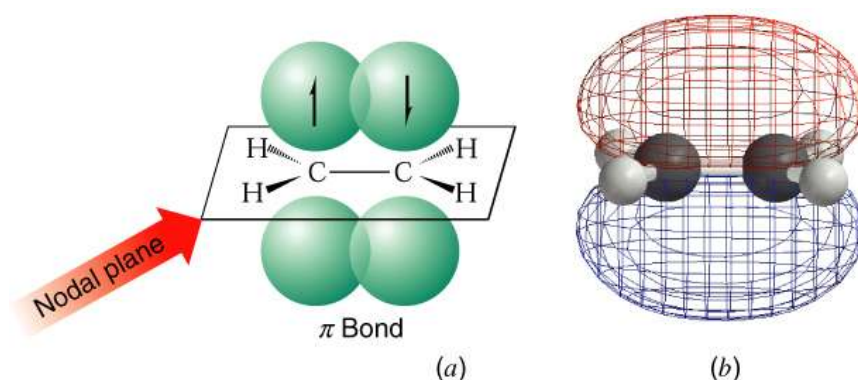
**Figure 1.22** A model for the bonding molecular orbitals of ethane formed from two

$sp^2$ -hybridized carbon atoms and four hydrogen atoms.

3. **The  $\sigma$ -bond framework:**

4. **Pi ( $\pi$ ) bond:**

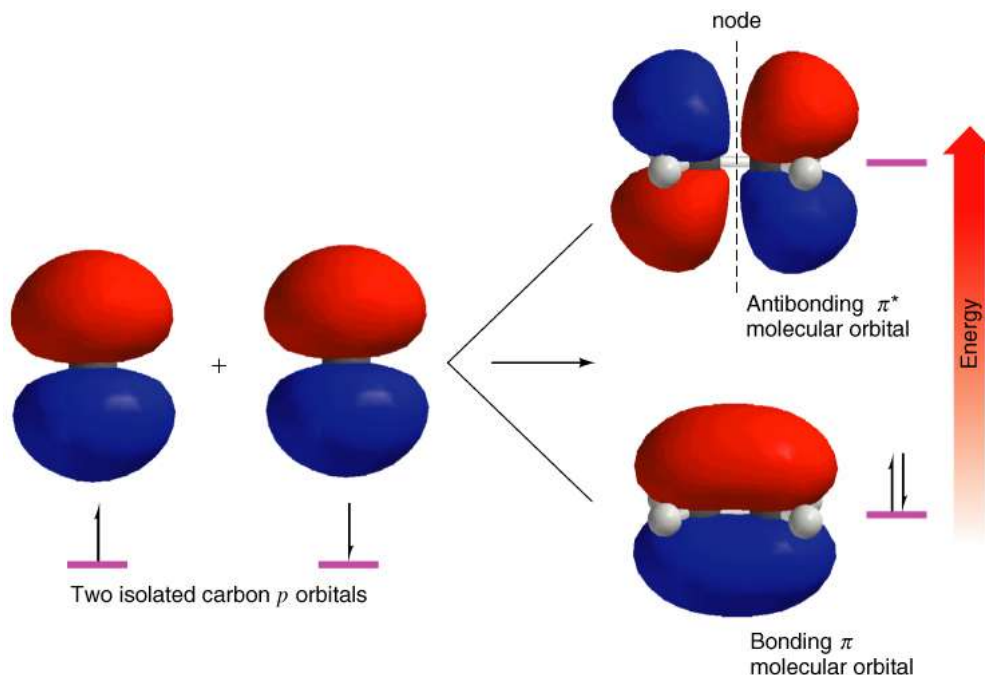
- 1) The parallel  $p$  orbitals *overlap above and below the plane of the  $\sigma$  framework*.
- 2) The sideways overlap of  $p$  orbitals results in the formation of a  $\pi$  bond.
- 3) A  $\pi$  bond has a nodal plane passing through the two bonded nuclei and between the  $\pi$  molecular orbital lobes.



**Figure 1.23** (a) A wedge-dashed wedge formula for the sigma bonds in ethane and a schematic depiction of the overlapping of adjacent  $p$  orbitals that form the  $\pi$  bond. (b) A calculated structure for ethene. The blue and red colors indicate opposite phase signs in each lobe of the  $\pi$  molecular orbital. A ball-and-stick model for the  $\sigma$  bonds in ethane can be seen through the mesh that indicates the  $\pi$  bond.

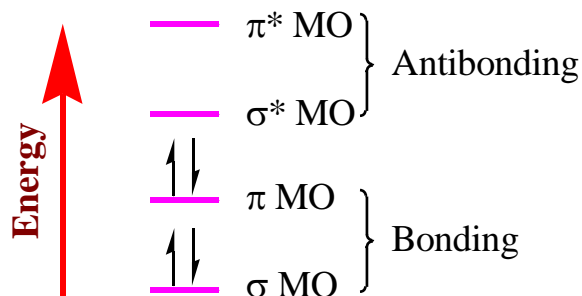
4. **Bonding and antibonding  $\pi$  molecular orbitals:**





**Figure 1.24** How two isolated carbon  $p$  orbitals combine to form two  $\pi$  (pi) molecular orbitals. The bonding MO is of lower energy. The higher energy antibonding MO contains an additional node. (Both orbitals have a node in the plane containing the C and H atoms.)

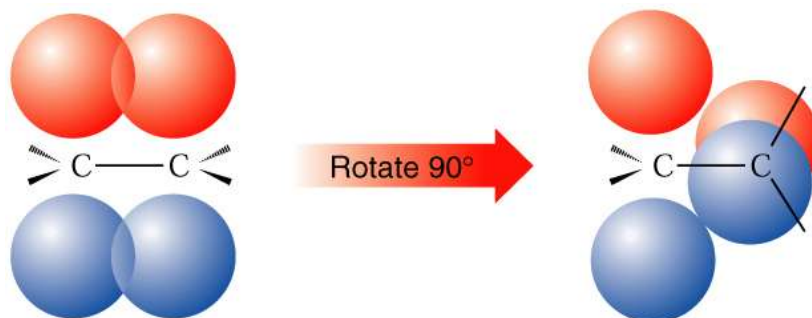
- 1) The bonding  $\pi$  orbital is the lower energy orbital and contains both  $\pi$  electrons (with opposite spins) in the ground state of the molecule.
- 2) The antibonding  $\pi^*$  orbital is of higher energy, and it is not occupied by electrons when the molecule is in the ground state.



### 1.13A. Restricted Rotation and the Double Bond

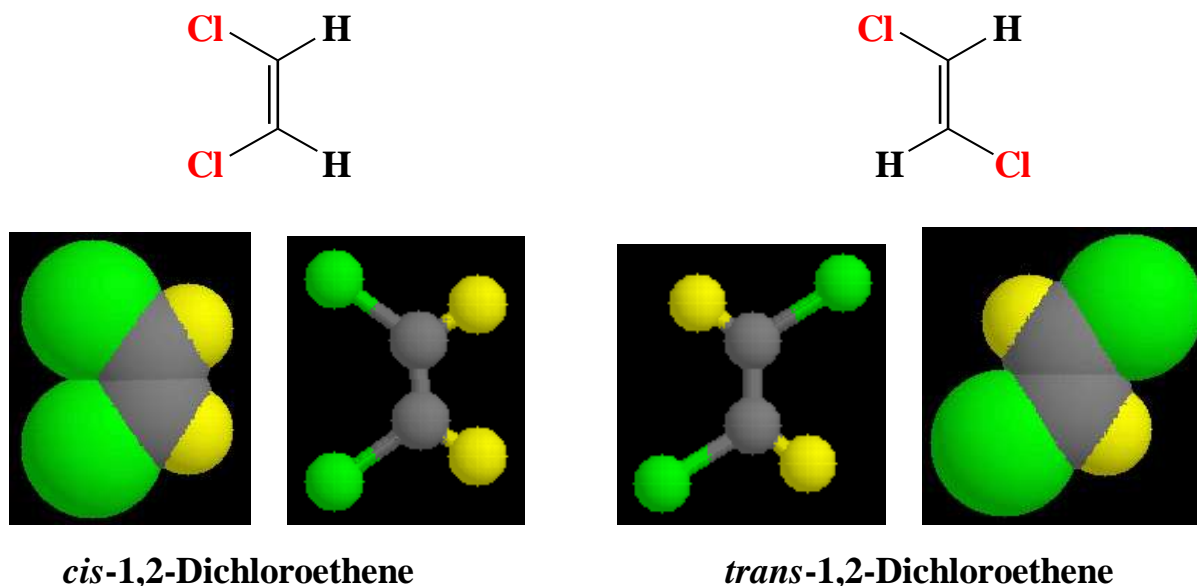
1. There is a large energy barrier to rotation associated with groups joined by a double bond.

- 1) Maximum overlap between the  $p$  orbitals of a  $\pi$  bond occurs when the axes of the  $p$  orbitals are exactly parallel  $\Rightarrow$  Rotation one carbon of the double bond  $90^\circ$  breaks the  $\pi$  bond.
- 2) The strength of the  $\pi$  bond is  $264 \text{ KJ mol}^{-1}$  ( $63.1 \text{ Kcal mol}^{-1}$ )  $\Rightarrow$  the rotation barrier of double bond.
- 3) The rotation barrier of a C–C single bond is  $13\text{-}26 \text{ KJ mol}^{-1}$  ( $3.1\text{-}6.2 \text{ Kcal mol}^{-1}$ ).



**Figure 1.25** A stylized depiction of how rotation of a carbon atom of a double bond through an angle of  $90^\circ$  results in breaking of the  $\pi$  bond.

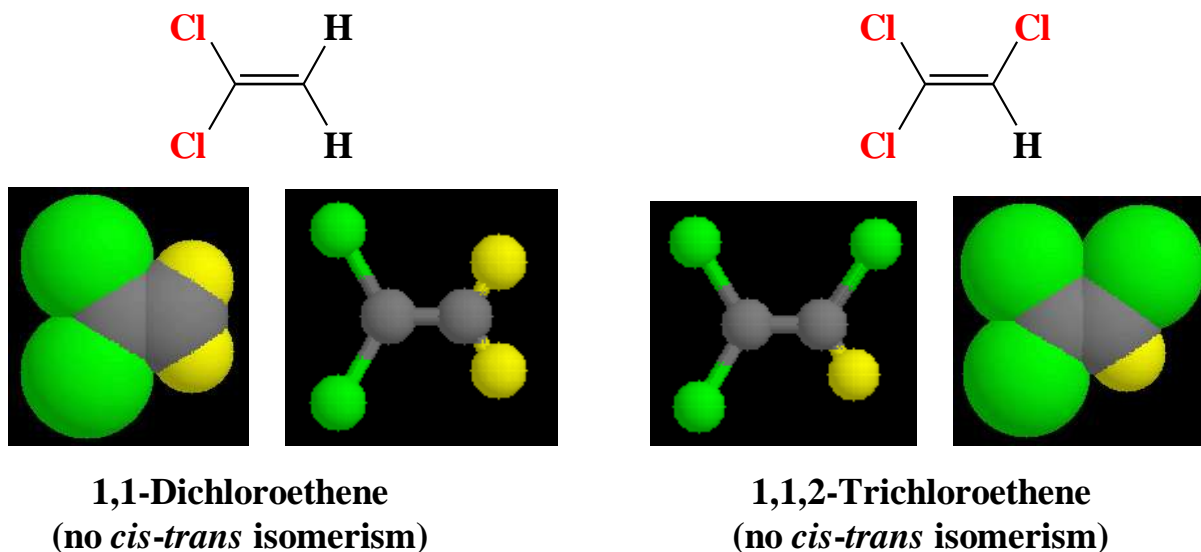
### 1.13B. *Cis-Trans* Isomerism



#### 1. Stereoisomers

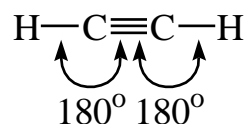
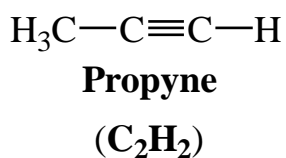
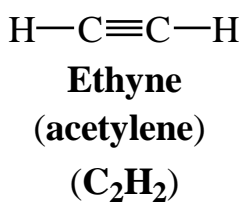
- 1) *cis*-1,2-Dichloroethene and *trans*-1,2-dichloroethene are *non-superposable*  $\Rightarrow$  Different compounds  $\Rightarrow$  *not constitutional isomers*
- 2) Latin: *cis*, on the same side; *trans*, across.

- 3) *Stereoisomers*  $\Rightarrow$  differ only in the arrangement of their atoms in space.
- 4) If one carbon atom of the double bond bears two identical groups  $\Rightarrow$  *cis-trans* isomerism is not possible.

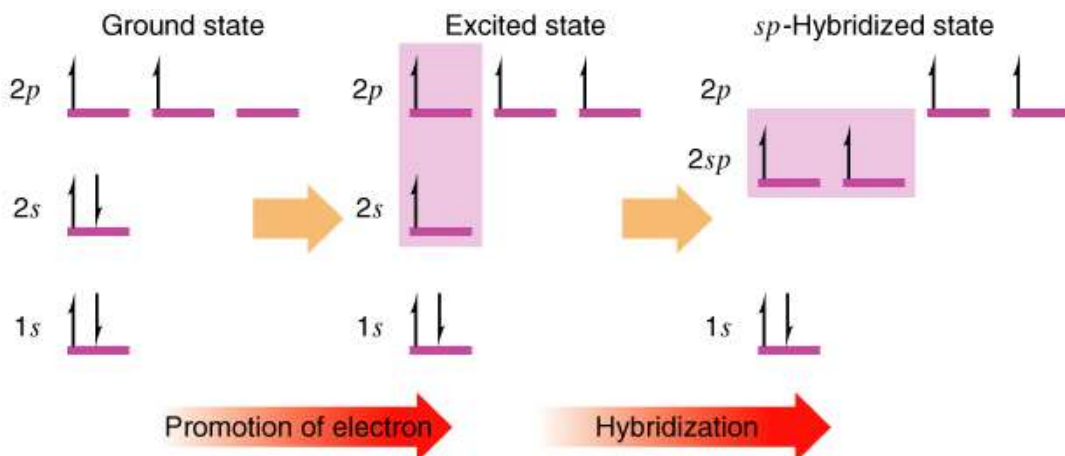


## 1.14 THE STRUCTURE OF ETHYNE (ACETYLENE): *sp* HYBRIDIZATION

### 1. Alkynes

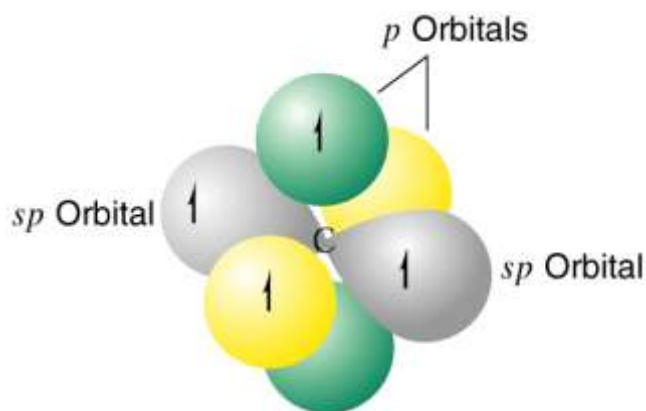


### 2. *sp* Hybridization:



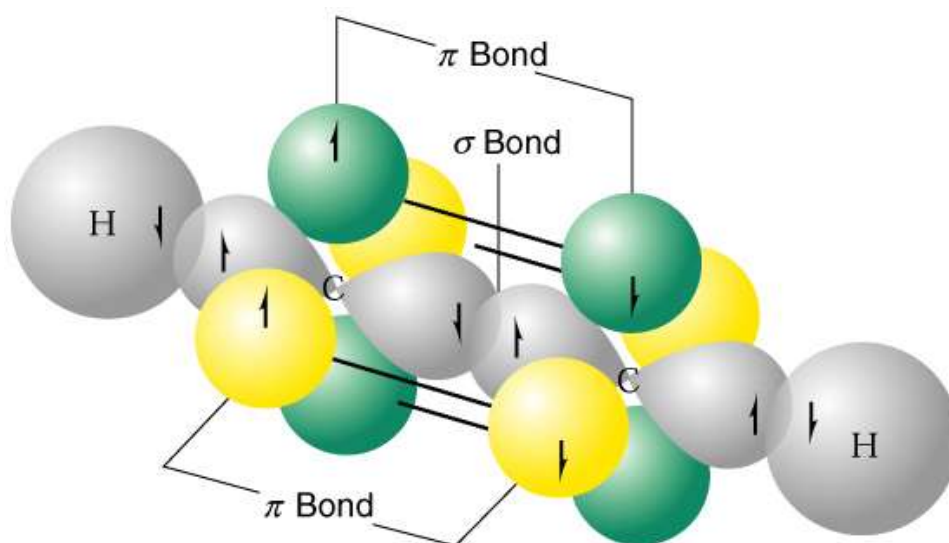
**Figure 1.26** A process for obtaining  $sp$ -hybridized carbon atoms.

3. The  $sp$  hybrid orbitals have their large positive lobes oriented at an angle of  $180^\circ$  with respect to each other.



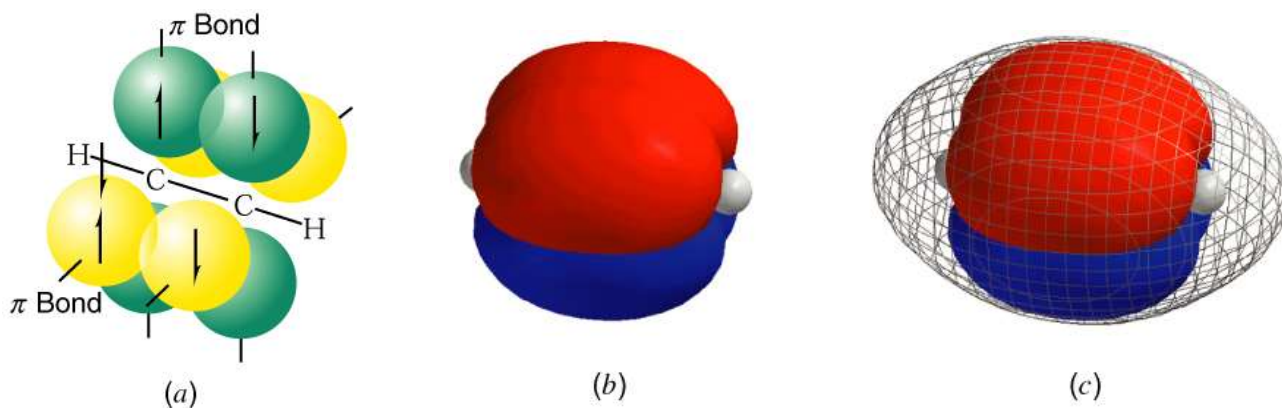
**Figure 1.27** An  $sp$ -hybridized carbon atom.

4. The carbon-carbon triple bond consists of two  $\pi$  bonds and one  $\sigma$  bond.



**Figure 1.28** Formation of the bonding molecular orbitals of ethyne from two  $sp$ -hybridized carbon atoms and two hydrogen atoms. (Antibonding orbitals are formed as well but these have been omitted for simplicity.)

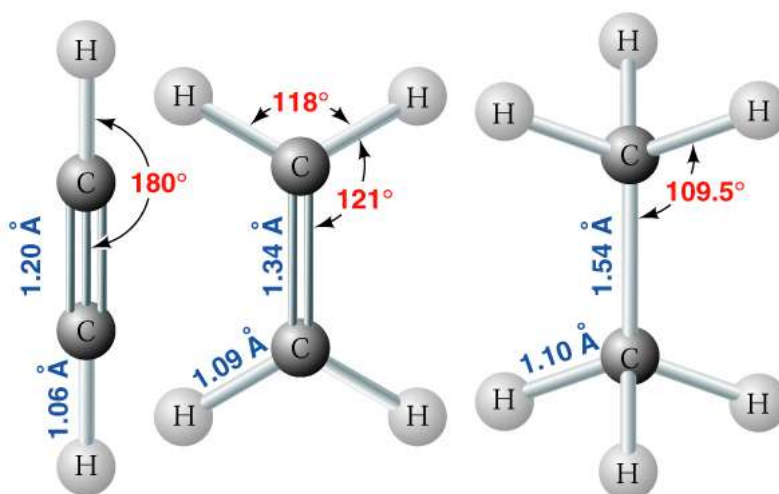
5. **Circular symmetry** exists along the length of a triple bond (**Fig. 1.29b**)  $\Rightarrow$  **no restriction of rotation** for groups joined by a triple bond.



**Figure 1.29** (a) The structure of ethyne (acetylene) showing the sigma bond framework and a schematic depiction of the two pairs of  $p$  orbitals that overlap to form the two  $\pi$  bonds in ethyne. (b) A structure of ethyne showing calculated  $\pi$  molecular orbitals. Two pairs of  $\pi$  molecular orbital lobes are present, one pair for each  $\pi$  bond. The red and blue lobes in each  $\pi$  bond represent opposite phase signs. The hydrogen atoms of ethyne (white spheres) can be seen at each end of the structure (the carbon atoms are hidden by the molecular orbitals). (c) The mesh surface in this structure represents approximately the furthest extent of overall electron density in ethyne. Note that the overall electron density (but not the  $\pi$  bonding electrons) extends over both hydrogen atoms.

### 1.14A. Bond lengths of Ethyne, Ethene, and Ethane

- The shortest C–H bonds are associated with those carbon orbitals with the greatest  $s$  character.



**Figure 1.30** Bond angles and bond lengths of ethyne, ethene, and ethane.

## 1.15 A SUMMARY OF IMPORTANT CONCEPTS THAT COME FROM QUANTUM MECHANICS

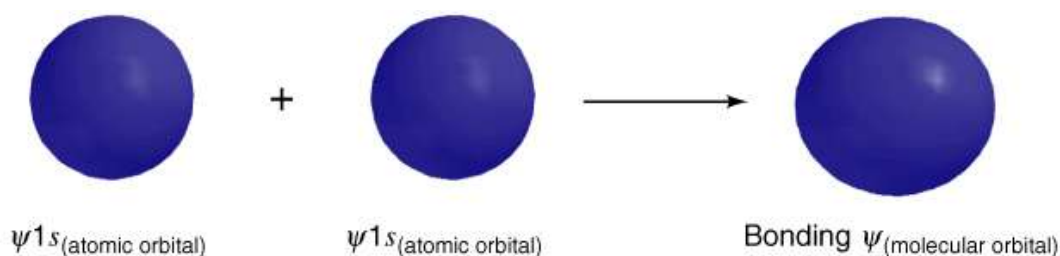
### 1.15A. Atomic orbital (AO):

1. AO corresponds to a region of space with high **probability** of finding an electron.
2. **Shape** of orbitals:  $s, p, d$
3. Orbitals can hold a maximum of two electrons when their spins are paired.
4. Orbitals are described by a wave function,  $\psi$ .
5. **Phase sign** of an orbital: “+”, “-”

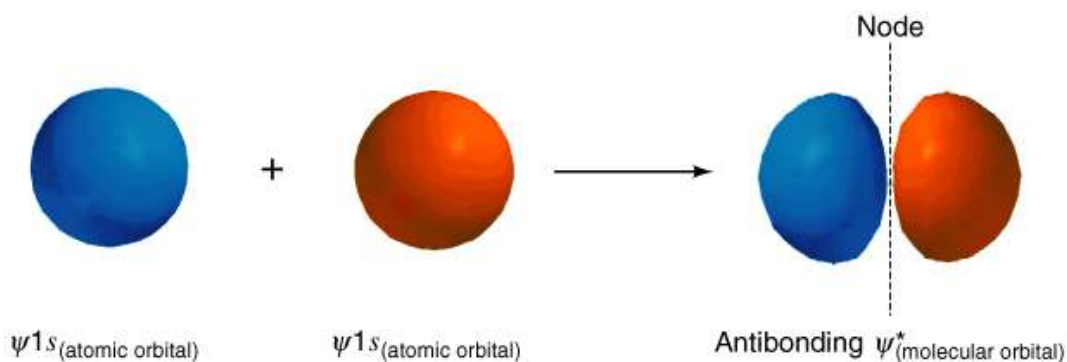
### 1.15B. Molecular orbital (MO):

1. MO corresponds to a region of space encompassing two (or more) nuclei where electrons are to be found.

#### 1) Bonding molecular orbital: $\psi$



#### 2) Antibonding molecular orbital: $\psi^*$



#### 3) Node:

#### 4) Energy of electrons:

- 5) **Number of molecular orbitals:**
- 6) **Sigma bond ( $\sigma$ ):**
- 7) **Pi bond ( $\pi$ ):**

### 1.15C. Hybrid atomic orbitals:

1.  **$sp^3$  orbitals  $\Rightarrow$  tetrahedral**
2.  **$sp^2$  orbitals  $\Rightarrow$  trigonal planar**
3.  **$sp$  orbitals  $\Rightarrow$  linear**

## 1.16 MOLECULAR GEOMETRY: THE VALENCE SHELL ELECTRON-PAIR REPULSION (VSEPR) MODEL

1. **Consider all valence electron pairs of the “central” atom — bonding pairs, nonbonding pairs (lone pairs, unshared pairs)**
2. **Electron pairs repel each other  $\Rightarrow$  The electron pairs of the valence tend to stay as far apart as possible.**
  - 1) The **geometry** of the molecule — considering “**all**” of the electron pairs.
  - 2) The **shape** of the molecule — referring to the “**positions**” of the “**nuclei (or atoms)**”.

### 1.16A Methane

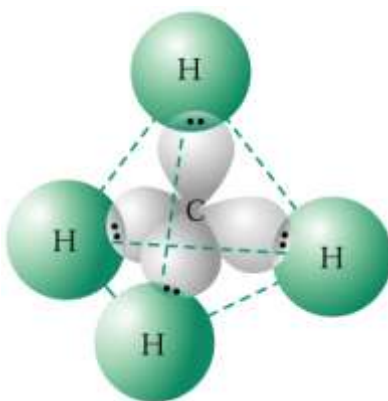


Figure 1.31 A **tetrahedral shape** for methane allows the maximum separation of



the four bonding electron pairs.

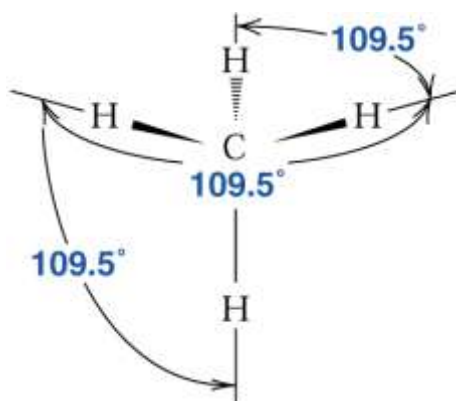


Figure 1.32 The bond angles of methane are  $109.5^\circ$ .

### 1.16B Ammonia

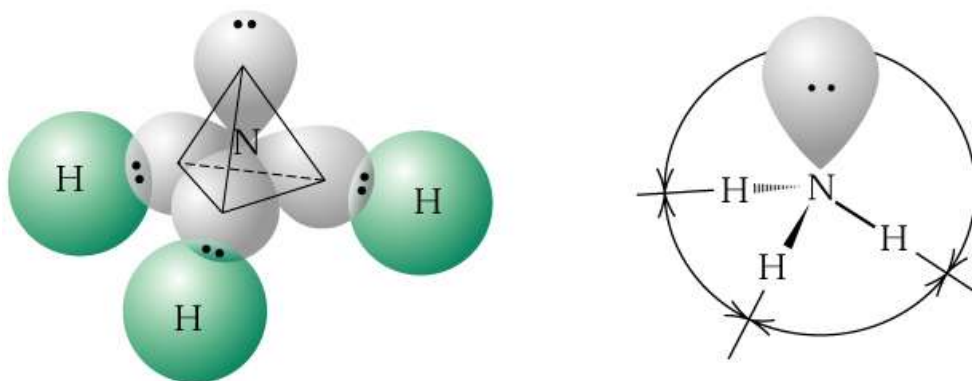


Figure 1.33 The **tetrahedral arrangement** of the electron pairs of an ammonia molecule that results when the nonbonding electron pair is considered to occupy one corner. This arrangement of electron pairs explains the **trigonal pyramidal shape** of the  $\text{NH}_3$  molecule.

### 1.16C Water

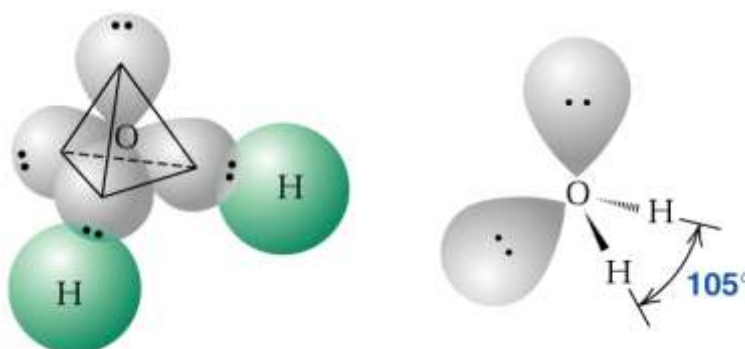


Figure 1.34 An approximately **tetrahedral arrangement** of the electron pairs for a molecule of water that results when the pair of nonbonding electrons are considered



to occupy corners. This arrangement accounts for the **angular shape** of the  $\text{H}_2\text{O}$  molecule.

### 1.16D Boron Trifluoride

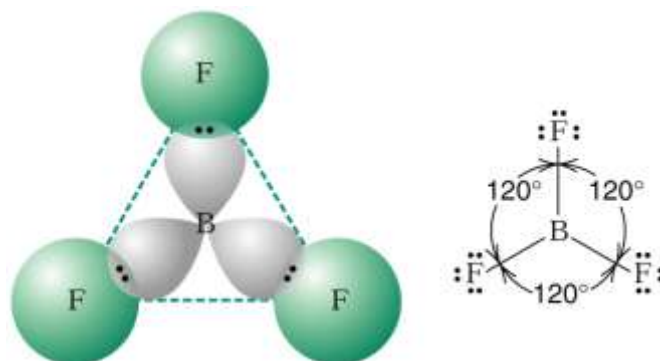
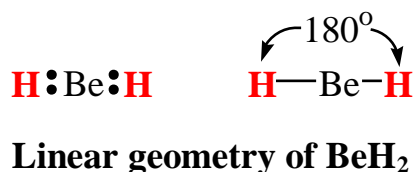


Figure 1.35 The **triangular (trigonal planar) shape** of boron trifluoride maximally separates the three bonding pairs.

### 1.16E Beryllium Hydride



### 1.16F Carbon Dioxide

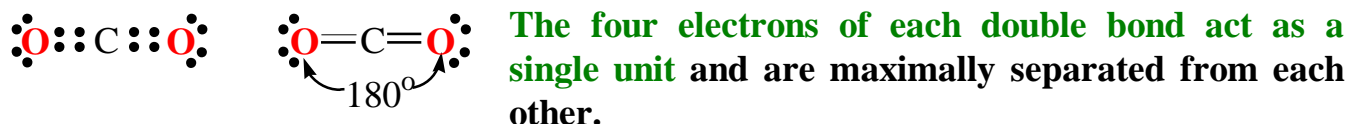


Table 1.4 Shapes of Molecules and Ions from VSEPR Theory

Number of Electron Pairs at Central Atom			Hybridization State of Central Atom	Shape of Molecule or Ion <sup>a</sup>	Examples
Bonding	Nonbonding	Total			
2	0	2	$sp$	Linear	$\text{BeH}_2$
3	0	3	$sp^2$	Trigonal planar	$\text{BF}_3$ , $\text{CH}_3^+$
4	0	4	$sp^3$	Tetrahedral	$\text{CH}_4$ , $\text{NH}_4^+$
3	1	4	$\sim sp^3$	Trigonal pyramidal	$\text{NH}_3$ , $\text{CH}_3^-$
2	2	4	$\sim sp^3$	Angular	$\text{H}_2\text{O}$

<sup>a</sup> Referring to positions of atoms and excluding nonbonding pairs.

## 1.17 REPRESENTATION OF STRUCTURAL FORMULAS

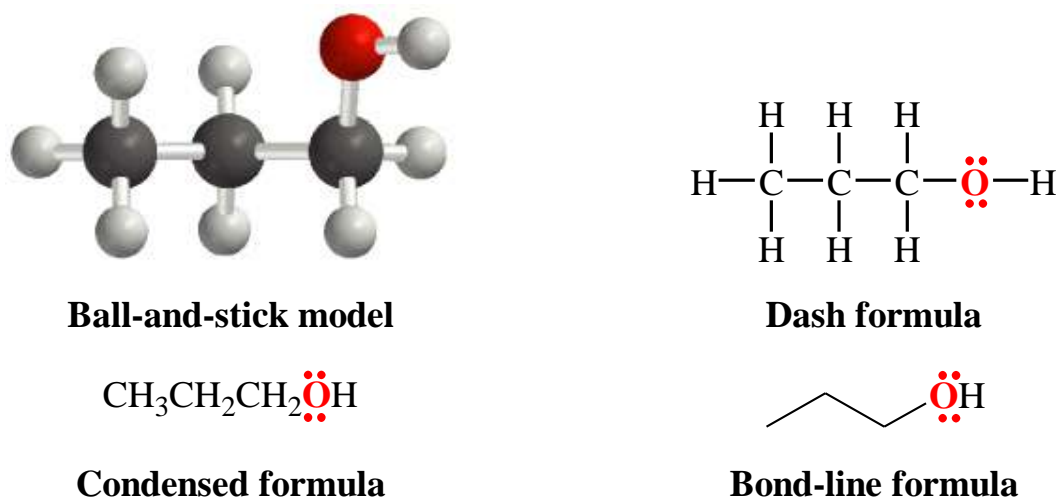
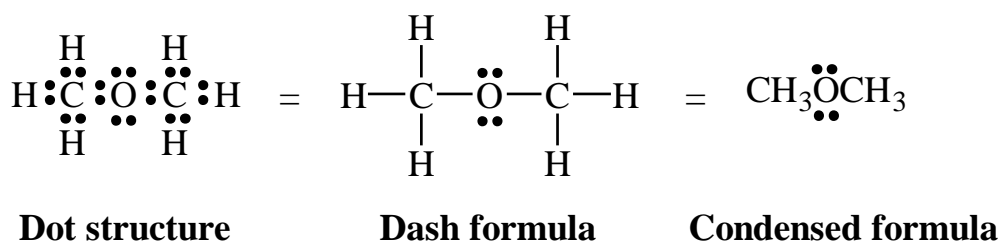
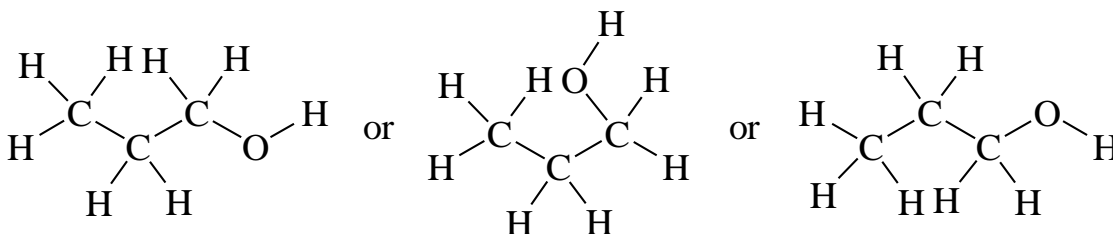


Figure 1.36 Structural formulas for propyl alcohol.



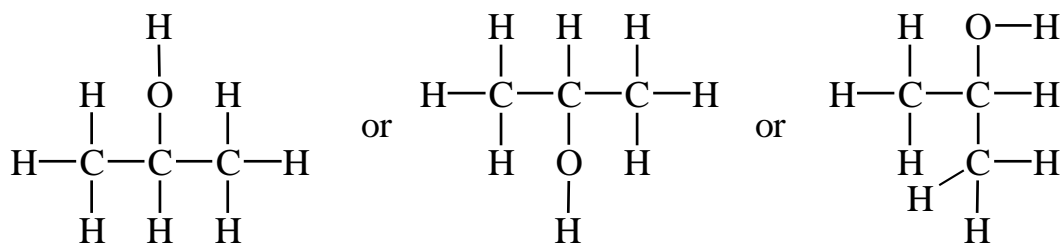
### 1.17A Dash Structural Formulas

1. **Atoms joined by single bonds can rotate relatively freely with respect to one another.**



Equivalent dash formulas for propyl alcohol  $\Rightarrow$  same **connectivity** of the atoms

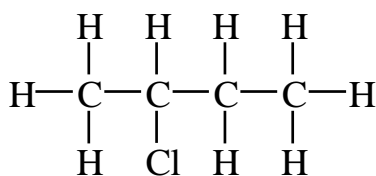
2. *Constitutional isomers have different connectivity and, therefore, must have different structural formulas.*
3. Isopropyl alcohol is a **constitutional isomer** of propyl alcohol.



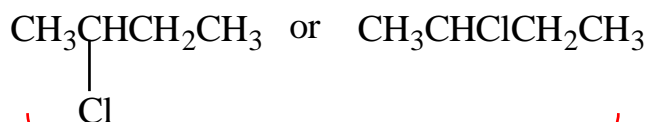
Equivalent dash formulas for isopropyl alcohol  $\Rightarrow$  same connectivity of the atoms

#### 4. Do not make the error of writing several equivalent formulas.

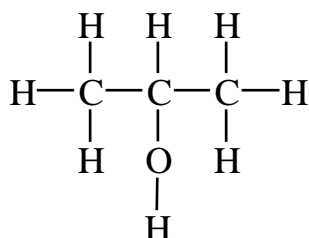
### 1.17B Condensed Structural Formulas



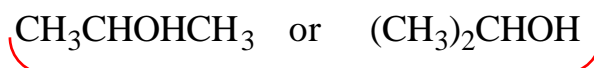
Dash formulas



Condensed formulas

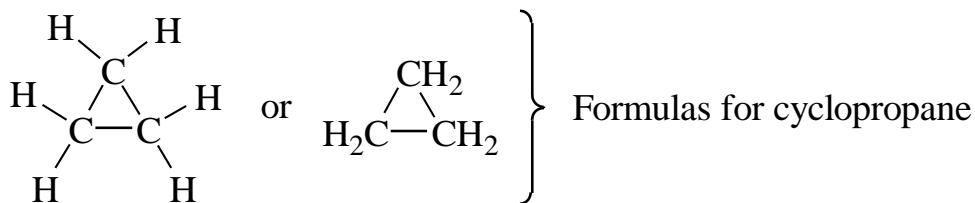


Dash formulas



Condensed formulas

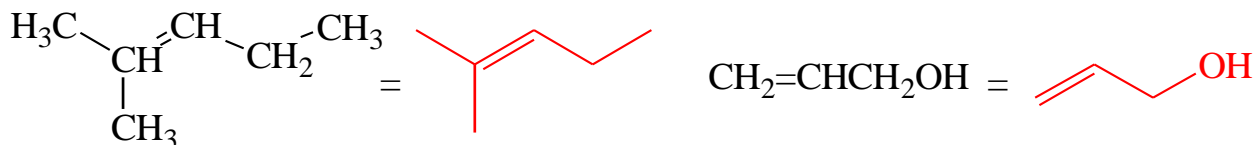
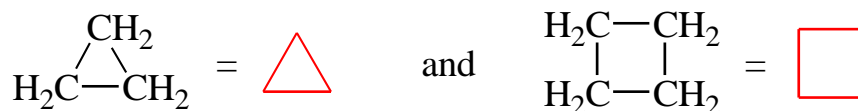
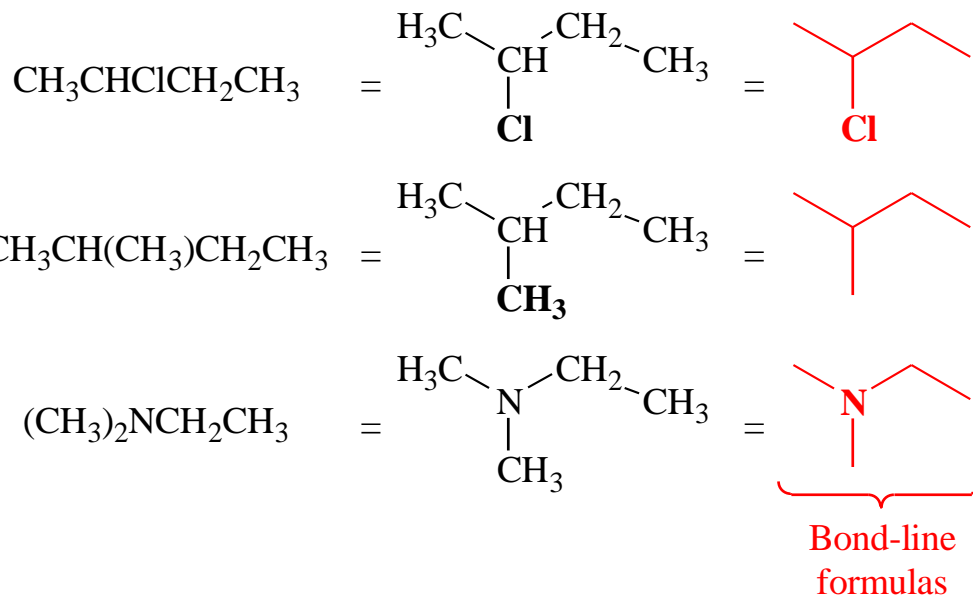
### 1.17C Cyclic Molecules



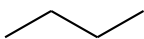
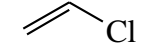
### 1.17D Bond-Line Formulas (shorthand structure)

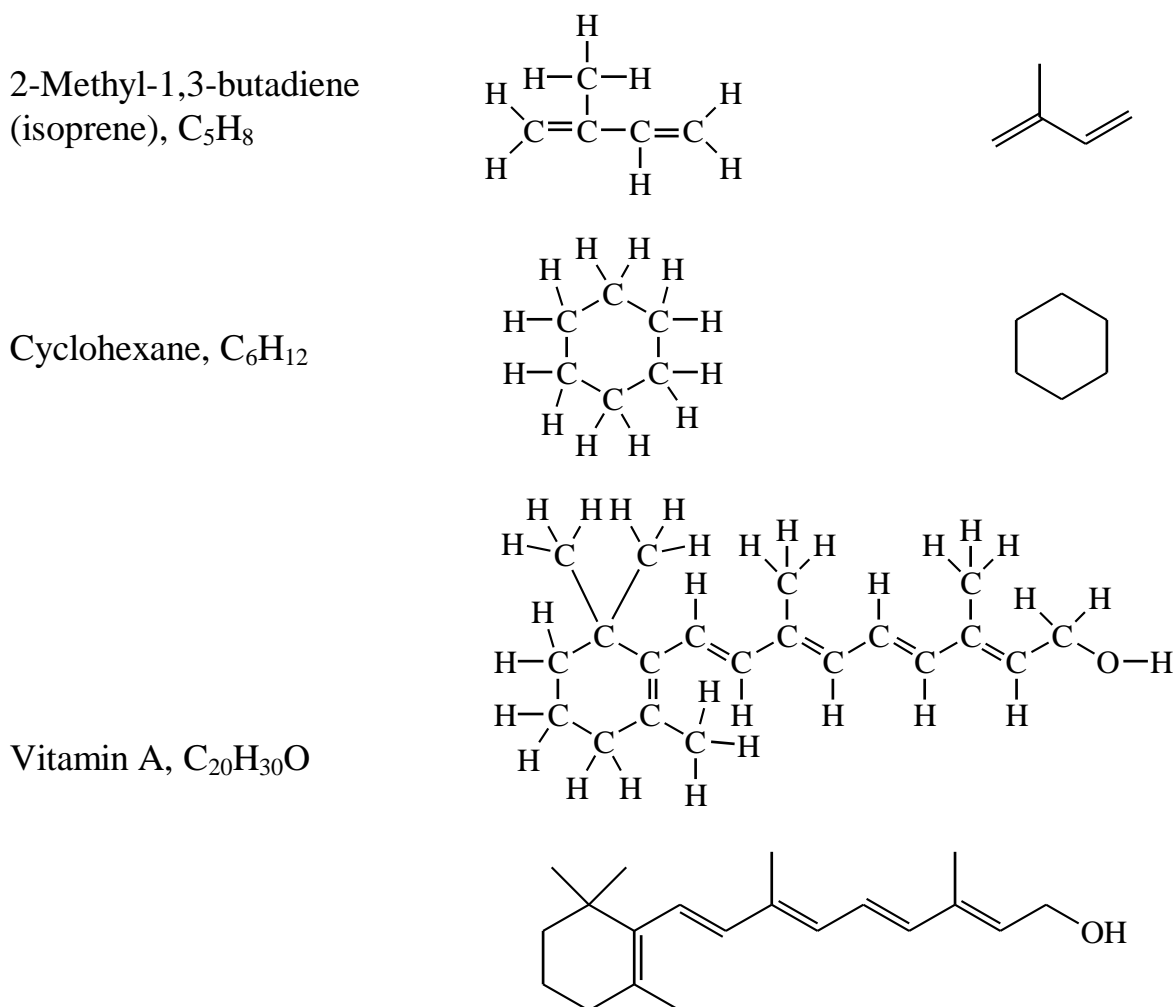
#### 1. Rules for shorthand structure:

- 1) Carbon atoms are not usually shown  $\Rightarrow$  intersections, end of each line
- 2) Hydrogen atoms bonded to C are not shown.
- 3) All atoms other than C and H are indicated.



**Table 1.5** Kekulé and shorthand structures for several compounds

Compound	Kekulé structure	Shorthand structure
Butane, C <sub>4</sub> H <sub>10</sub>	$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   &   &   &   \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	 (C-C-C-C)
Chloroethylene (vinyl chloride), C <sub>2</sub> H <sub>3</sub> Cl	$\begin{array}{cc} \text{H} & \text{H} \\ & \diagdown \quad \diagup \\ & \text{C}=\text{C} \\ & \diagup \quad \diagdown \\ \text{H} & \text{Cl} \end{array}$	 (C=C-Cl)



### 1.17E Three-Dimensional Formulas

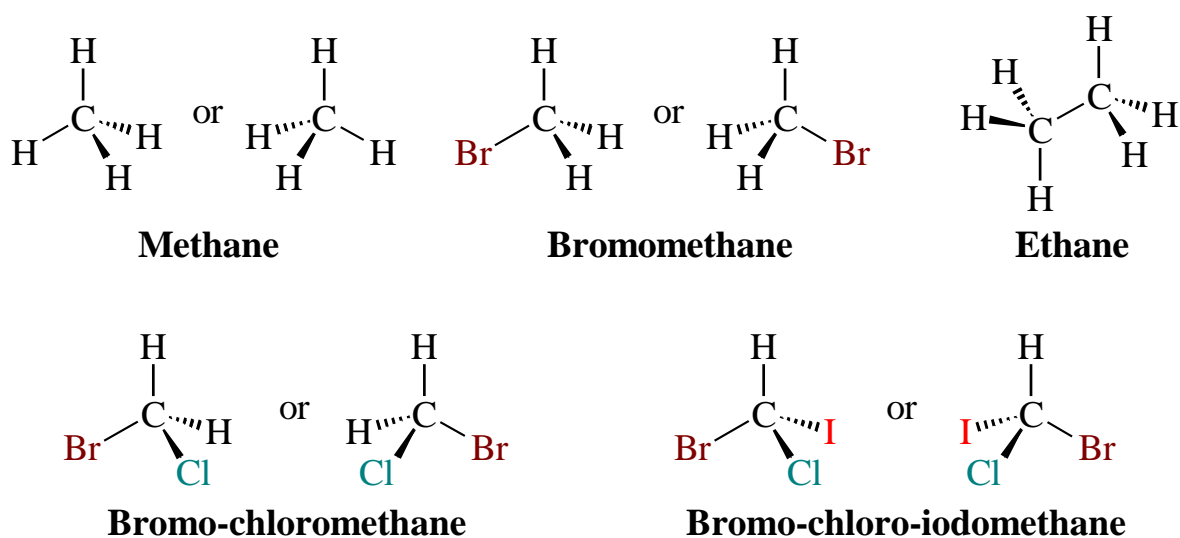


Figure 1.37 Three-dimensional formulas using wedge-dashed wedge-line formulas.