Chapter 1

Remembering General Chemistry:

Electronic Structure and Bonding

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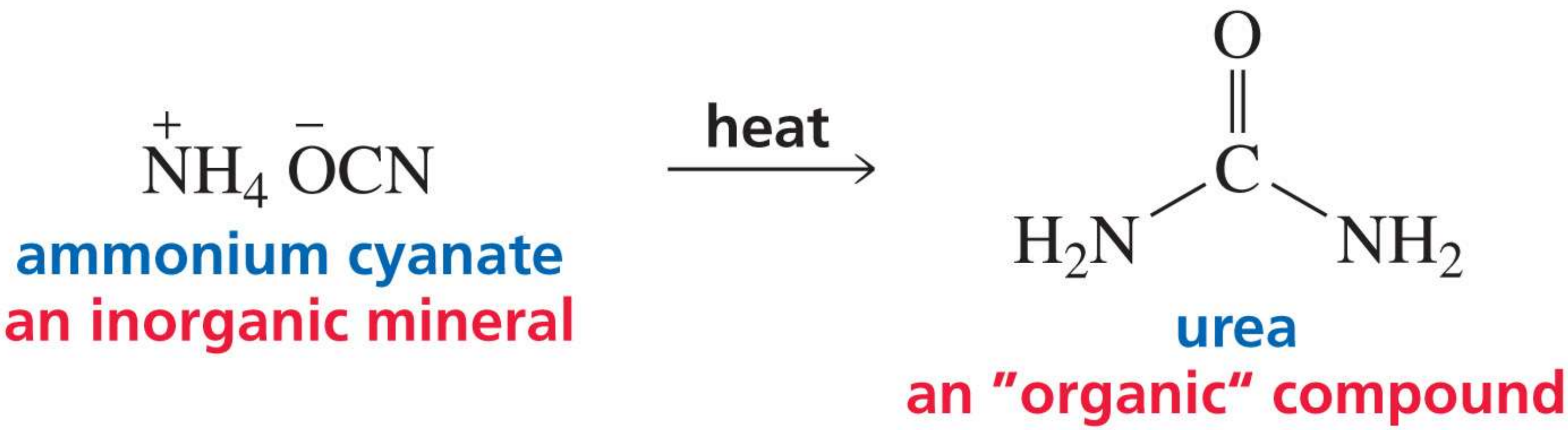
What is Organic Chemistry?

Organic compounds: from living organisms

(with a vital force)

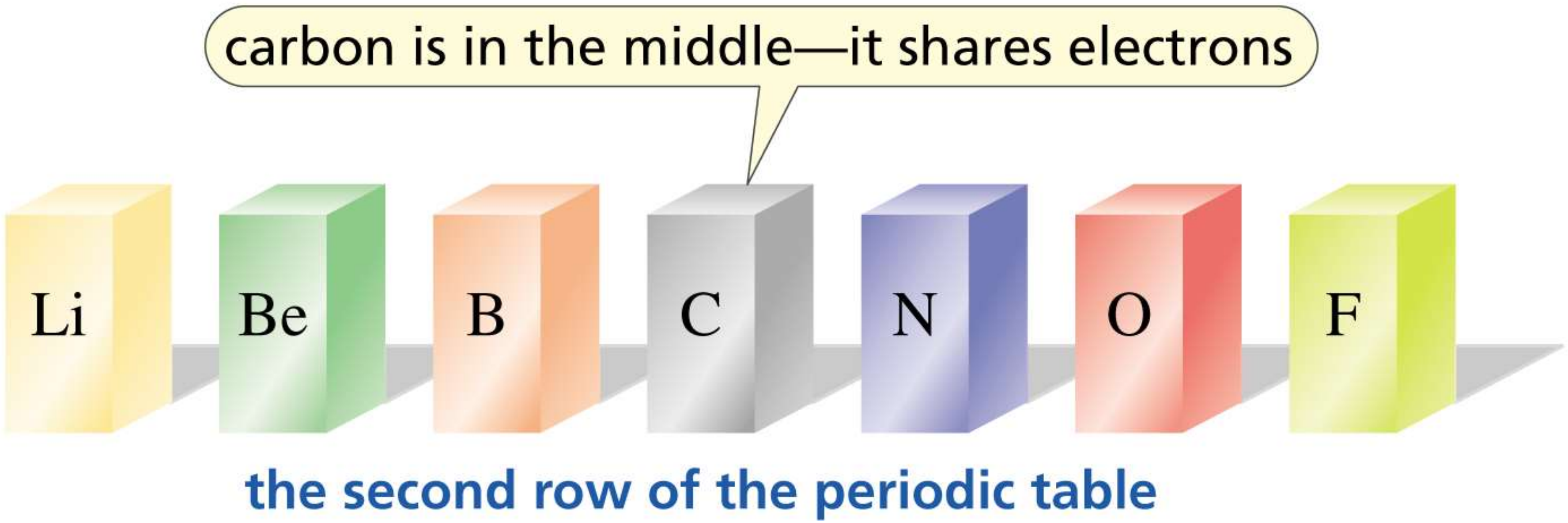
Inorganic compounds: from minerals

(without a vital force)



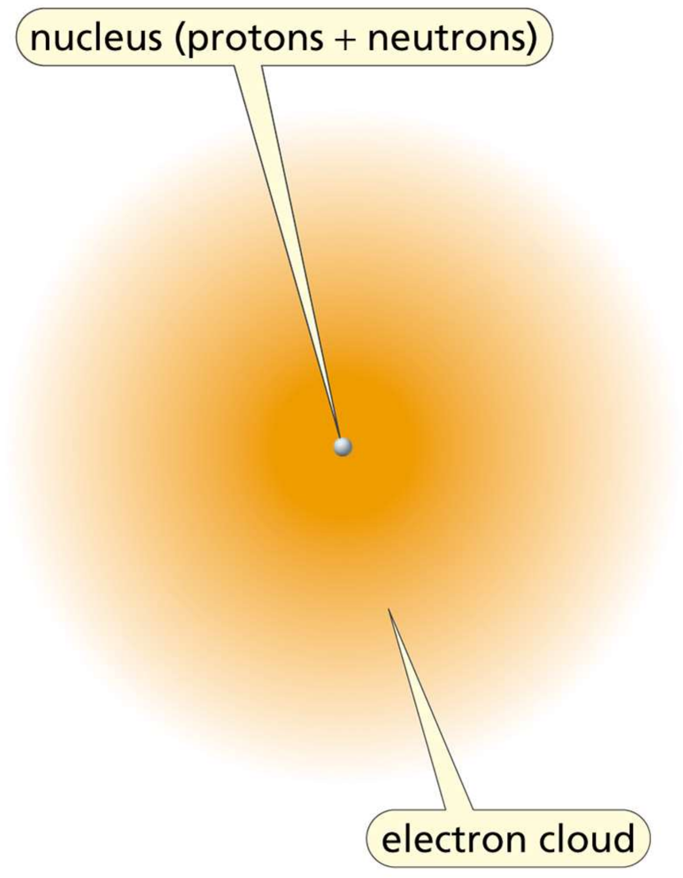
Organic compounds are compounds that contain carbon.

What Makes Carbon So Special?



- Atoms to the left of carbon give up electrons.
- Atoms to the right of carbon accept electrons.
- Carbon shares electrons.

The Structure of an Atom



an atom

Protons are positively charged.

Neutrons have no charge.

Electrons are negatively charged.

atomic number = # of protons

atomic number of carbon = 6

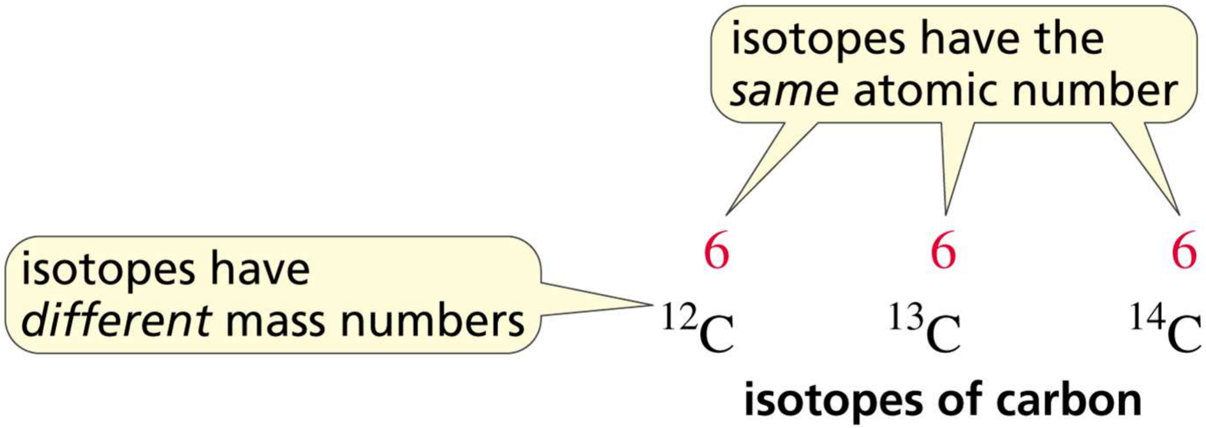
Neutral carbon has six protons and six electrons.

Isotopes

All Carbon Atoms Have the Same Atomic Number = # of protons

Carbon Atoms Can Have the Different Mass Numbers

Mass Number = # of protons + # of neutrons



The Distribution of Electrons in an Atom

Table 1.1 Distribution of Electrons in the First Four Shells

	First shell	Second shell	Third shell	Fourth shell
Atomic orbitals	*s*	*s, p*	*s, p, d*	*s, p, d, f*
Number of atomic orbitals	1	1, 3	1, 3, 5	1, 3, 5, 7
Maximum number of electrons	2	8	18	32

- The first shell is closest to the nucleus.
- The closer the atomic orbital is to the nucleus, the lower its energy.
- Within a shell, *s* < *p*.

Table 1.2 The Electronic Configurations of the Smallest Atoms

Atom	Name of element	Atomic number	1s	2s	$2p_x$	$2p_y$	$2p_z$	3s
H	Hydrogen	1	↑					
He	Helium	2	↑↓					
Li	Lithium	3	↑↓	↑				
Be	Beryllium	4	↑↓	↑↓				
B	Boron	5	↑↓	↑↓	↑			
C	Carbon	6	↑↓	↑↓	↑	↑		
N	Nitrogen	7	↑↓	↑↓	↑	↑	↑	
O	Oxygen	8	↑↓	↑↓	↑↓	↑	↑	
F	Fluorine	9	↑↓	↑↓	↑↓	↑↓	↑	
Ne	Neon	10	↑↓	↑↓	↑↓	↑↓	↑↓	
Na	Sodium	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑

- Aufbau principle: An electron goes into the atomic orbital with the lowest energy.

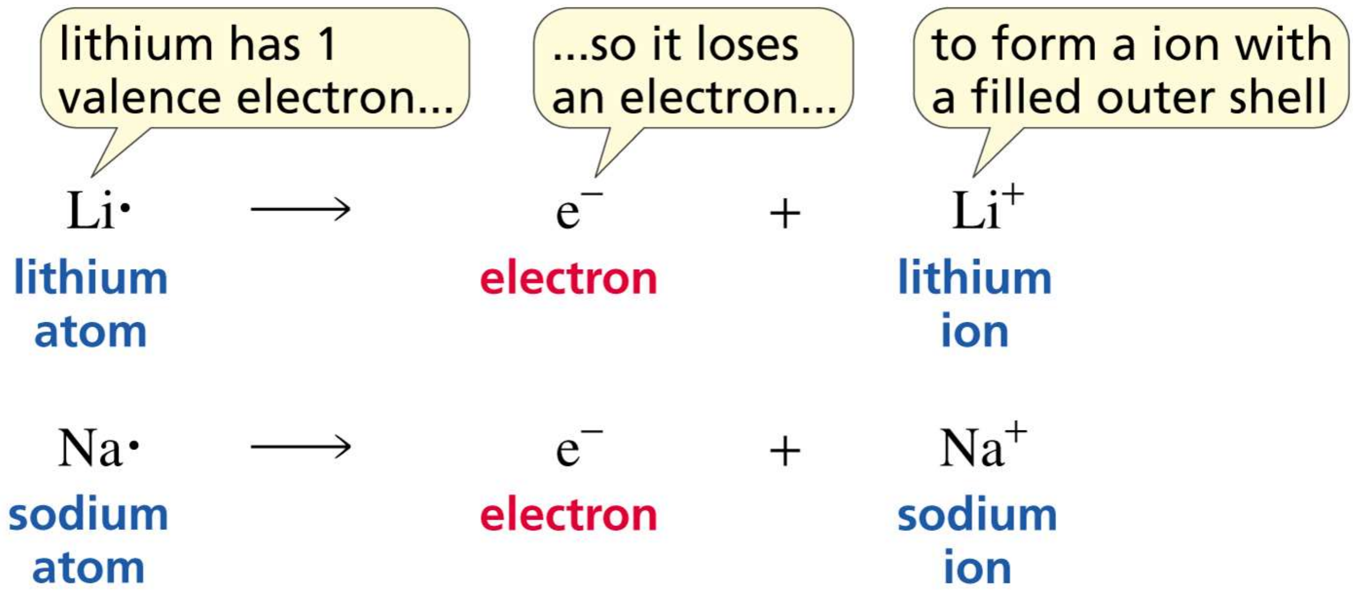
$$1s < 2s < 2p < 3s < 3p < 3d$$

- Pauli exclusion principle: No more than two electrons can be in an atomic orbital.
- Hund's rule: An electron goes into an empty degenerate orbital rather than pairing up.

Atoms in the First Column of the Periodic Table Lose an Electron

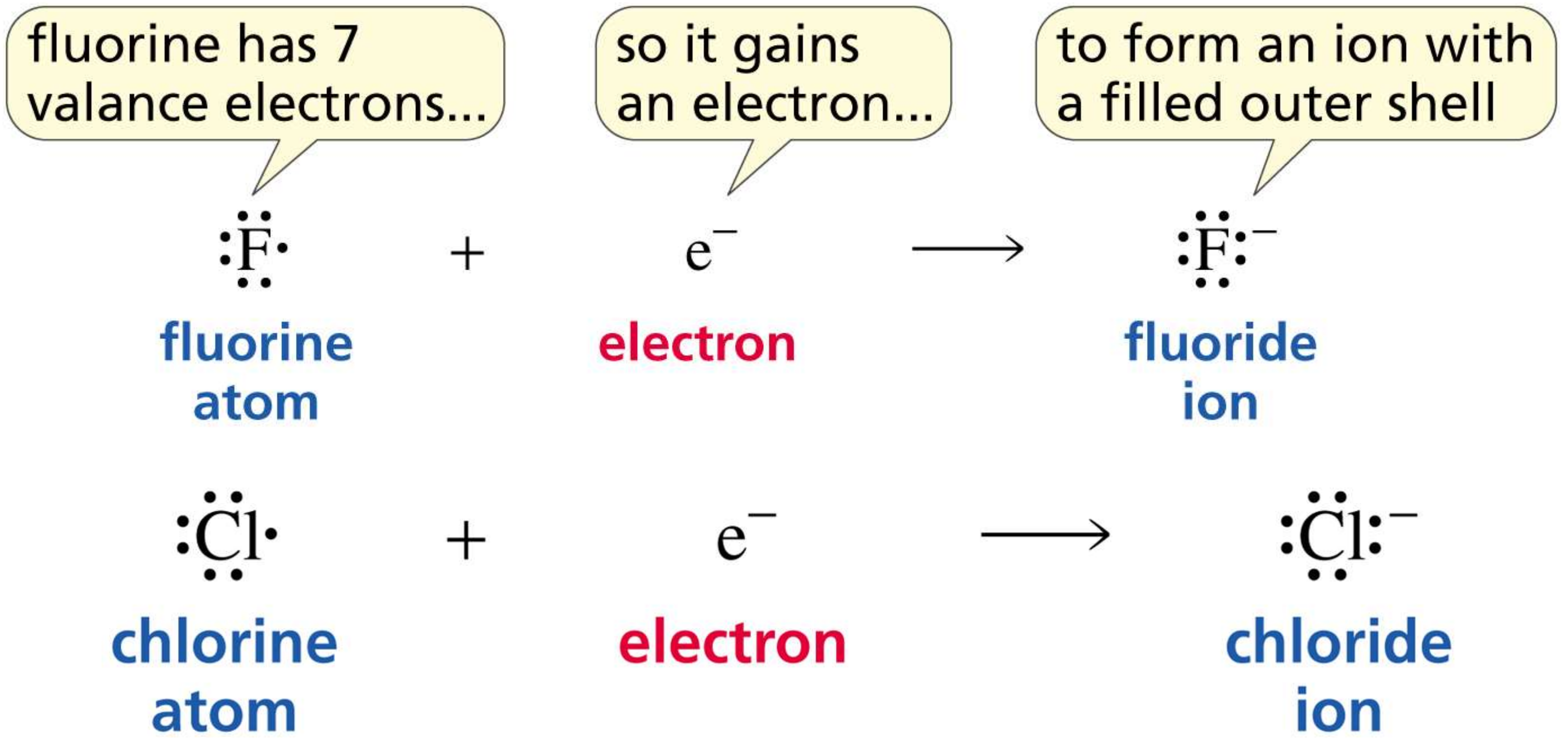
An atom is most stable if its outer shell is either filled or contains 8 electrons.

Lithium and sodium achieve a filled outer shell by losing an electron.



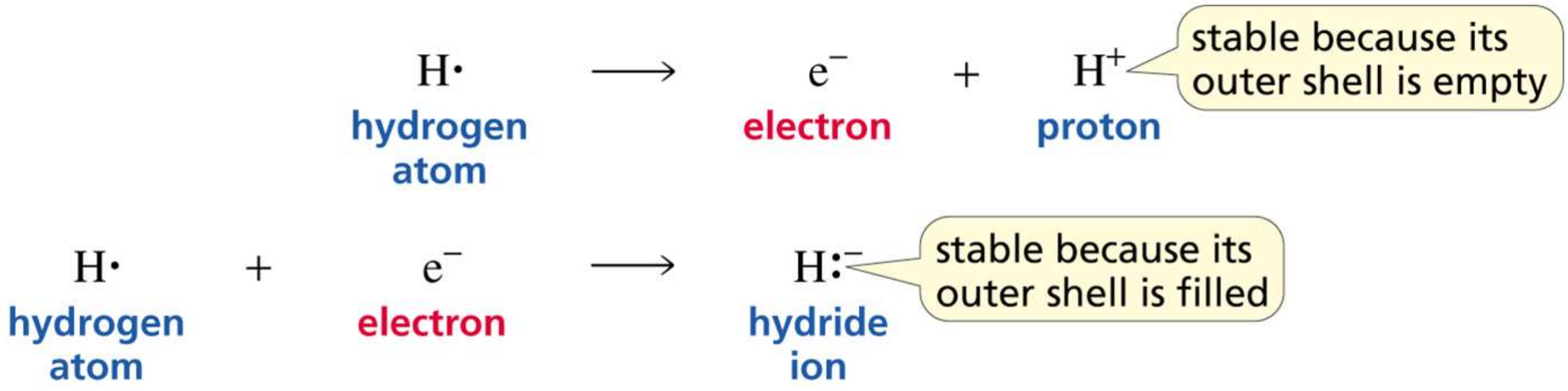
Atoms on the Right Side of the Periodic Table Readily Gain an Electron

Fluorine and chlorine achieve a filled outer shell by gaining an electron.

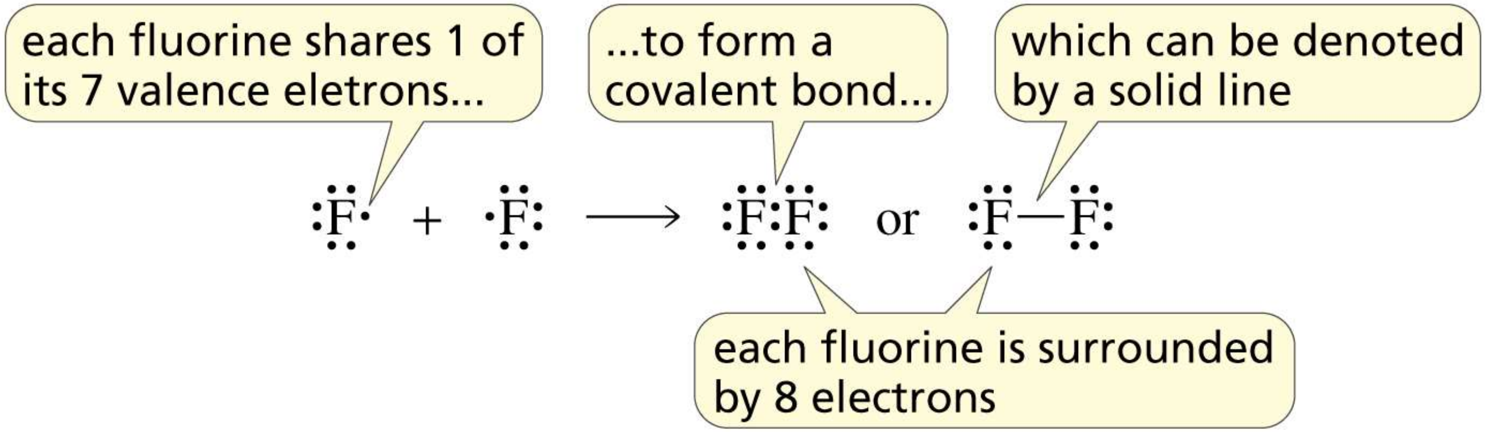


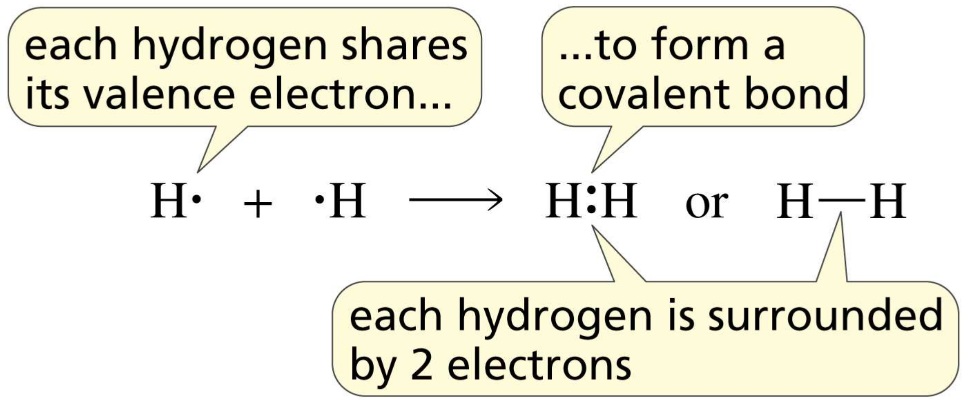
A Hydrogen Atom Can Lose or Gain an Electron

A hydrogen atom achieves an empty shell by losing an electron or a filled outer shell by gaining an electron.



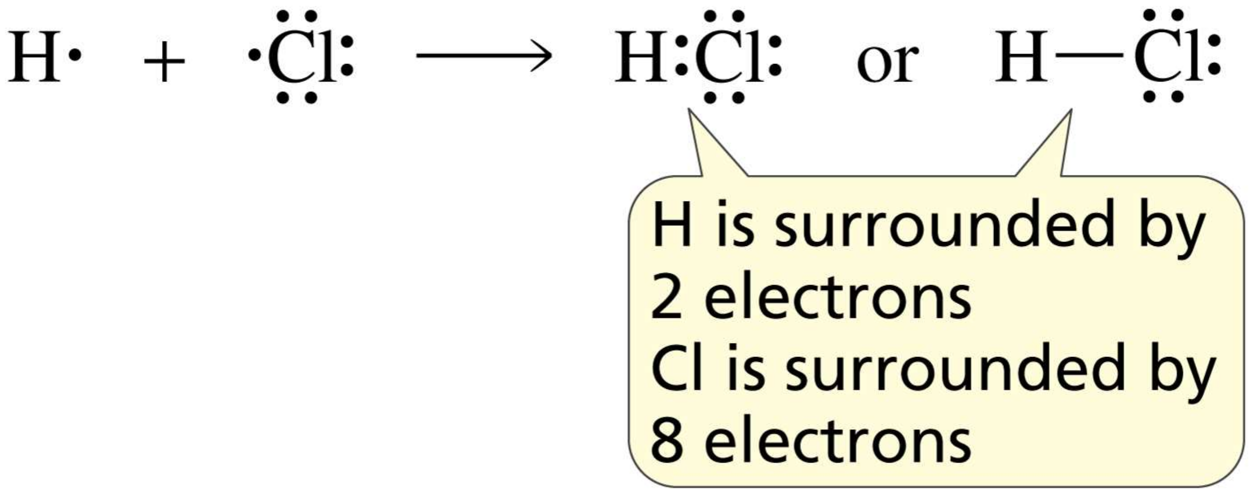
Achieving a Filled Outer Shell by Sharing Electrons



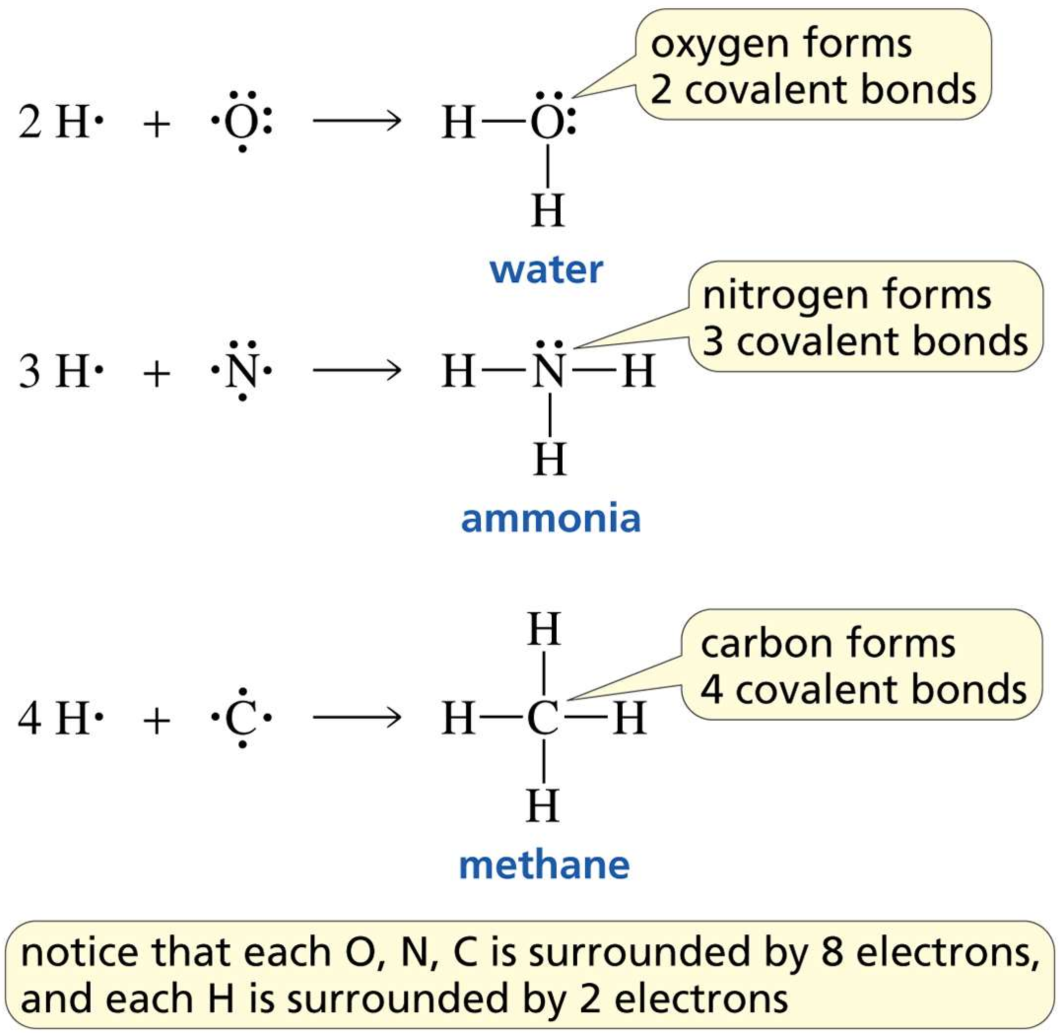


A bond formed by sharing electrons is called a covalent bond.

Achieving a Filled Outer Shell by Sharing Electrons



How Many Bonds Does an Atom Form?

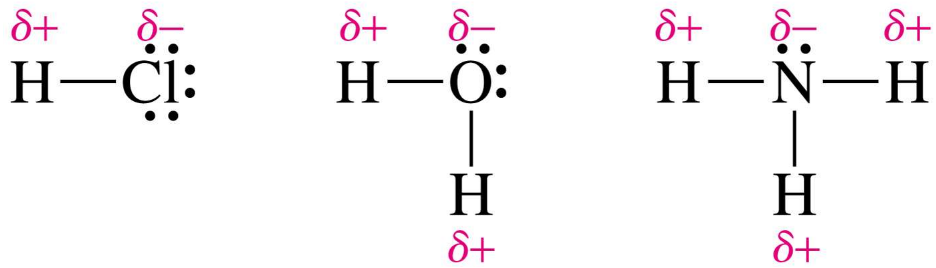


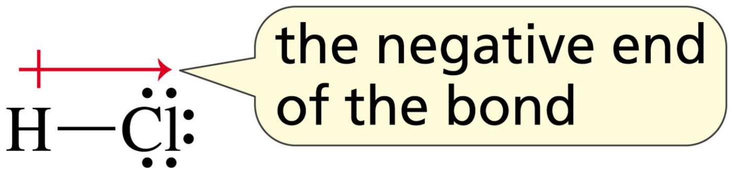
Nonpolar and Polar Covalent Bonds

Nonpolar covalent bond = bonded atoms are the same or have similar electronegativities.

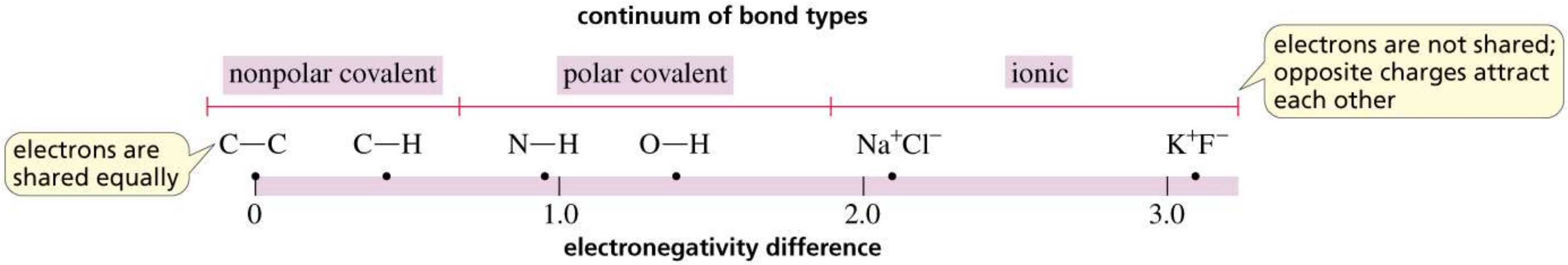
H—H F—F C—C C—H

Polar covalent bond = bonded atoms have different electronegativities.





The Greater the Difference in Electronegativity, the More Polar the Bond



Nonpolar covalent bond: electonegativity difference < 0.5

Polar covalent bond: electonegativity difference 0.5 – 1.9

Electronegativity difference > 1.9: electrons are not shared; atoms are held together by the attraction of opposite charges

Dipole Moment

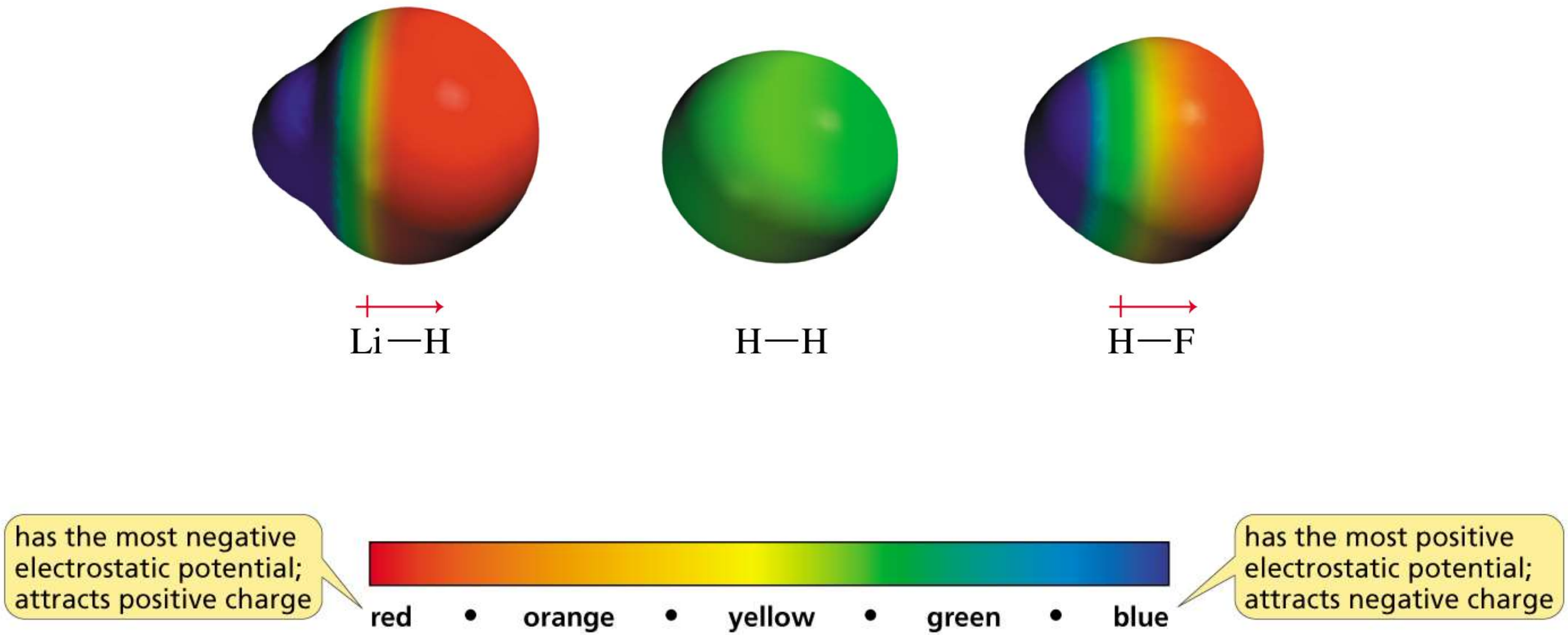
Dipole moment = size of the charge x the distance between the charges

Table 1.4 The Dipole Moments of Some Common Bonds

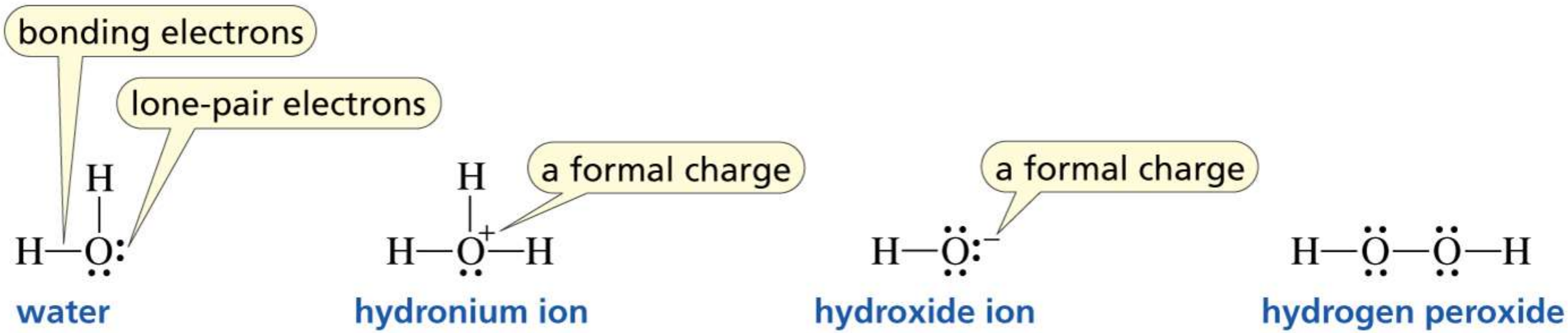
Bond	Dipole moment (D)	Bond	Dipole moment (D)
H—C	0.4	C—C	0
H—N	1.3	C—N	0.2
H—O	1.5	C—O	0.7
H—F	1.7	C—F	1.6
H—Cl	1.1	C—Cl	1.5
H—Br	0.8	C—Br	1.4
H—I	0.4	C—I	1.2

The greater the difference in electronegativity,
the greater the dipole moment and the more polar the bond.

Electrostatic Potential Maps



Lewis Structures

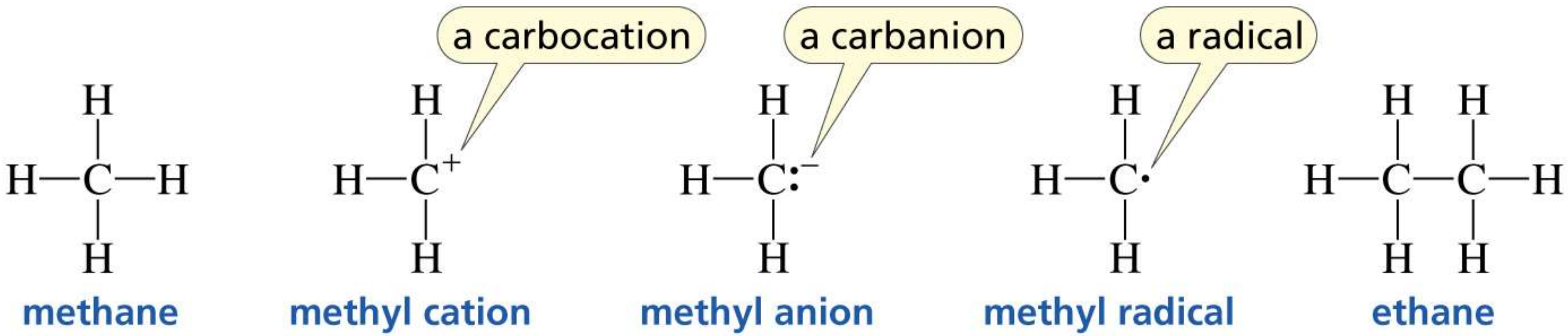


Formal Charge

Formal Charge =

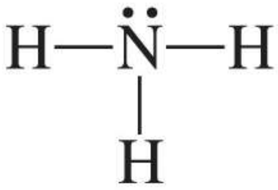
the # of valence electrons – (the # of lone-pair electrons + the # of bonds)

Carbon Forms Four Bonds

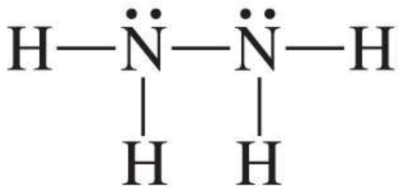


If carbon does not form four bonds,
it has a charge (or it is a radical).

Nitrogen Forms Three Bonds



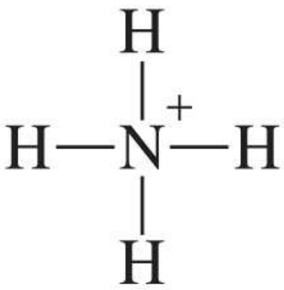
ammonia



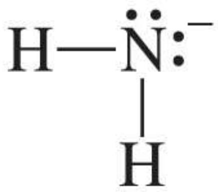
hydrazine

Nitrogen has one lone pair.

If nitrogen does not form three bonds, it is charged.

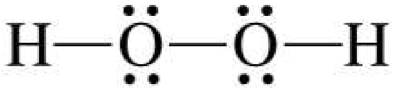


ammonium ion



amide anion

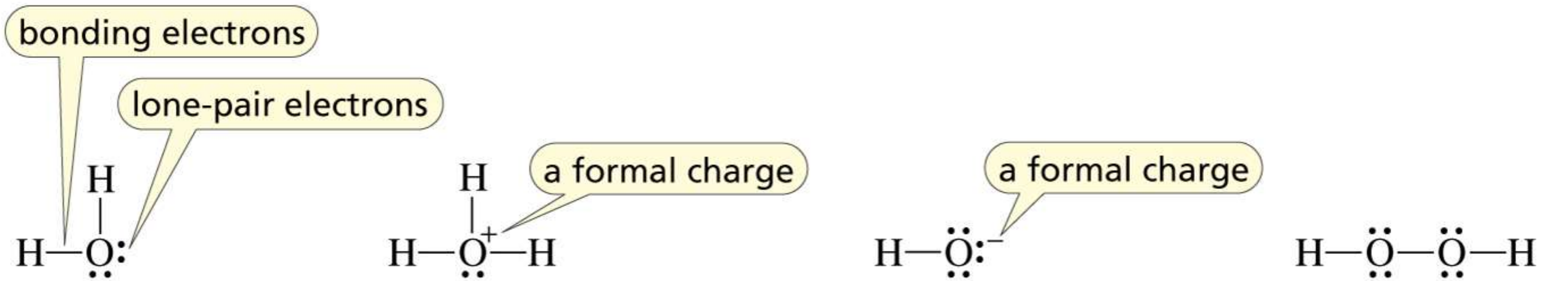
Oxygen Forms Two Bonds



hydrogen peroxide

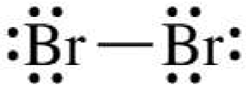
Oxygen has two lone pairs.

If oxygen does not form two bonds, it is charged.

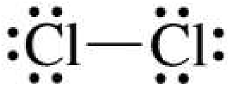


water   hydronium ion   hydroxide ion   hydrogen peroxide

Hydrogen and the Halogens Form One Bond



bromine



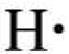
chlorine

A halogen has three lone pairs.

If hydrogen or halogen does not form one bond, it has a charge (or it is a radical).

hydrogen ion

hydride ion

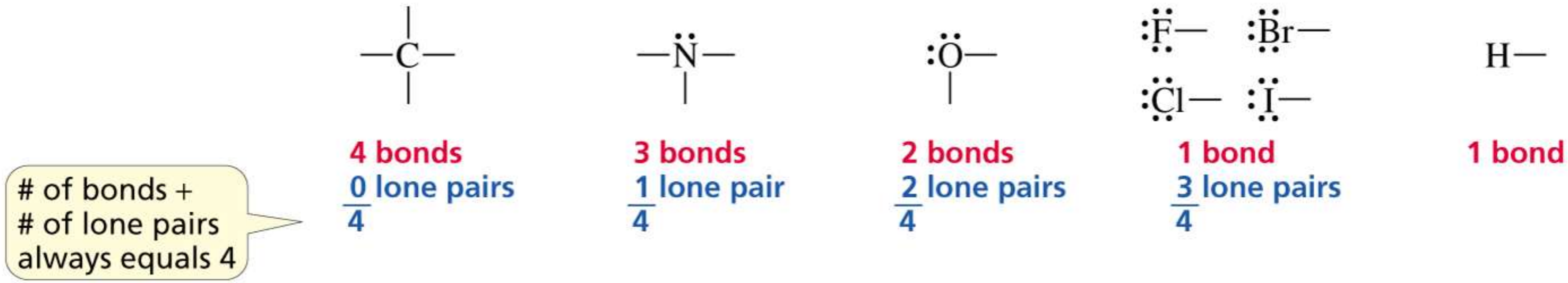


hydrogen radical

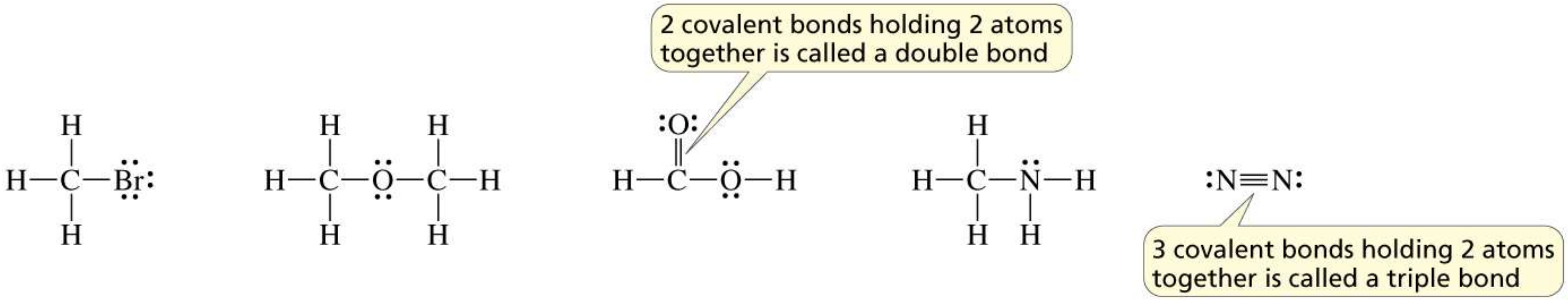
bromide ion

bromine radical

The Number of Bonds Plus the Number of Lone Pairs Equals Four



Lewis Structures

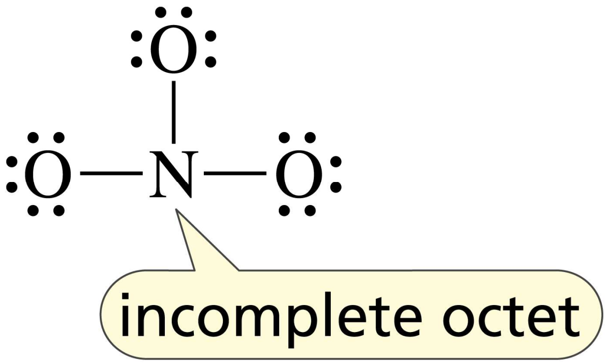


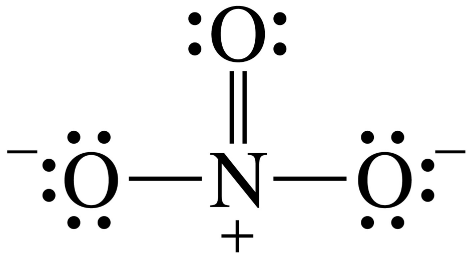
How to Draw a Lewis Structure

NO_3^-

Determine the total number of valence electrons (5 + 6 + 6 + 6 = 23).
Because they are negatively charged, add another electron = 24.

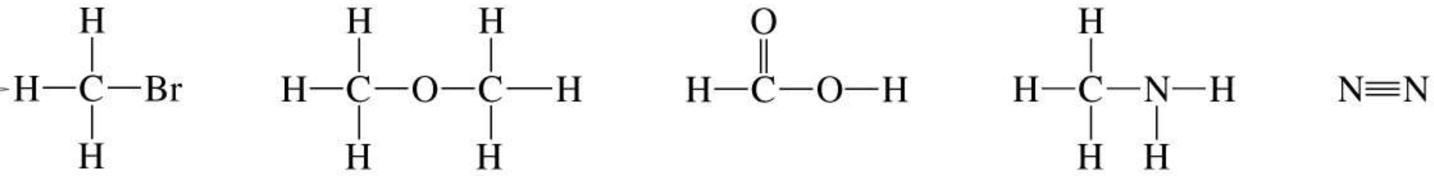
Avoid O—O bonds.
Check for formal charges.





Kekulé Structures and Condensed Structures

Kekulé structures

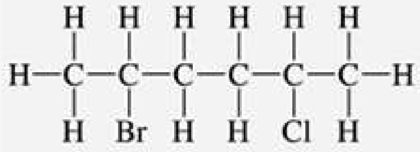
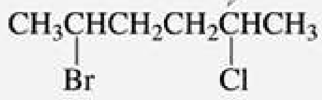
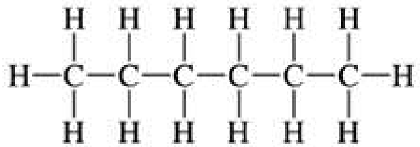
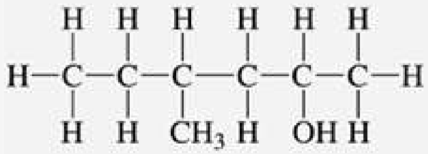
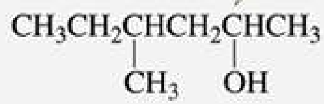
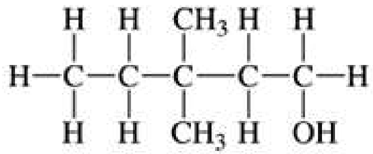
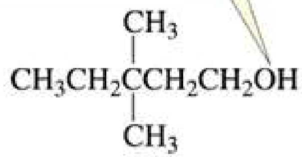


condensed structures

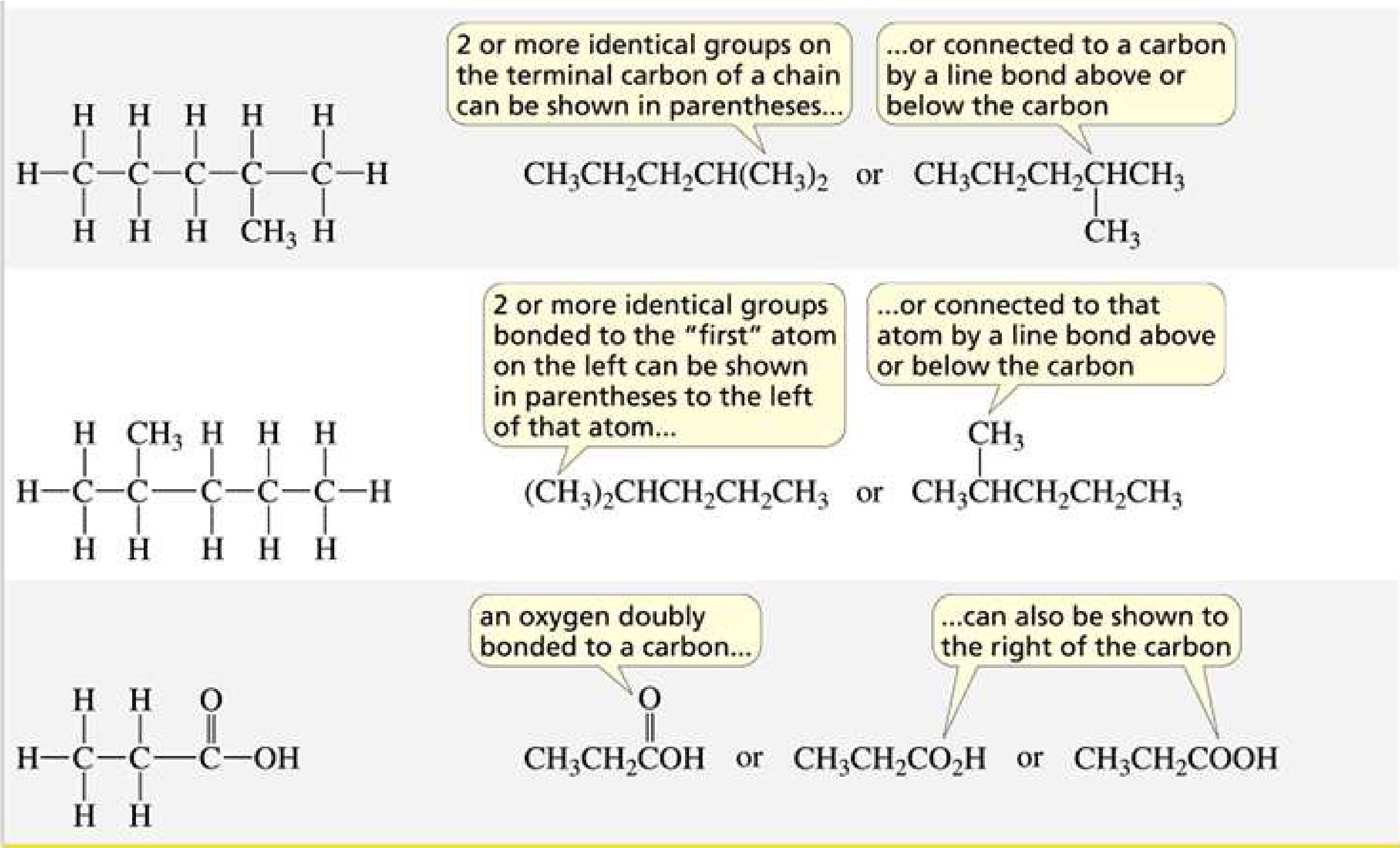
CH_3Br CH_3OCH_3 HCO_2H CH_3NH_2 N_2

Kekulé Structures and Condensed Structures

Table 1.5 Kekulé Structures and Condensed Structures

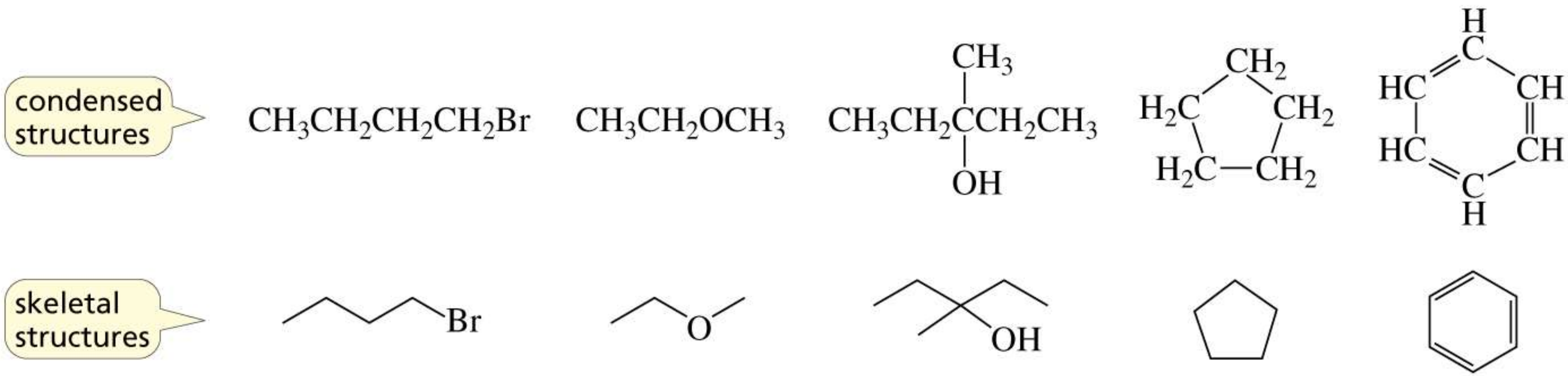
Kekulé Structures	Condensed Structures
	atoms bonded to a carbon are shown to the right of the carbon... $CH_3CHBrCH_2CH_2CHClCH_3$ or  ...or connected to a carbon by a line bond above or below the carbon
	$CH_3CH_2CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_4CH_3$ (repeating CH_2 groups can be shown in parentheses)
	groups bonded to a carbon can be shown in parentheses to the right of the carbon... $CH_3CH_2CH(CH_3)CH_2CH(OH)CH_3$ or  ...or connected to the carbon by a line bond above or below the carbon
	$CH_3CH_2C(CH_3)_2CH_2CH_2OH$ or  (a single group bonded to the terminal carbon of a chain is not put in parentheses)

Kekulé Structures and Condensed Structures



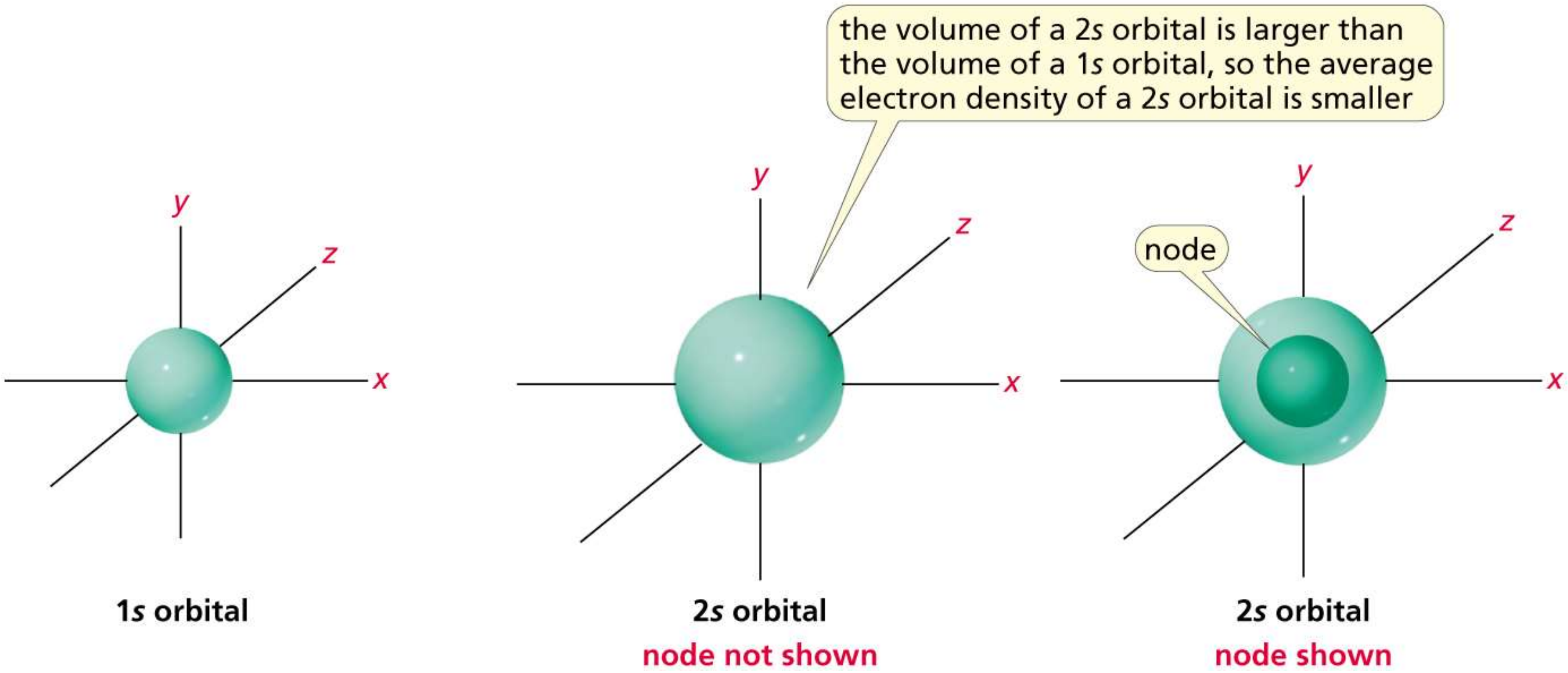
Skeletal Structures

Skeletal structures show the carbon-carbon bonds as lines,
but do not show the carbons
or the hydrogens that are bonded to the carbons.

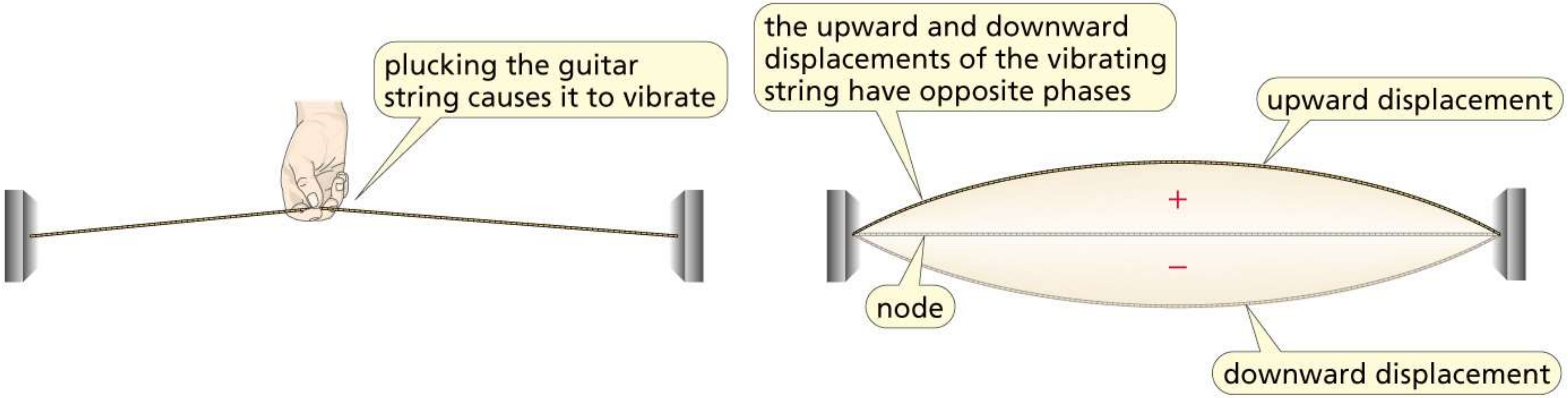


s Atomic Orbitals

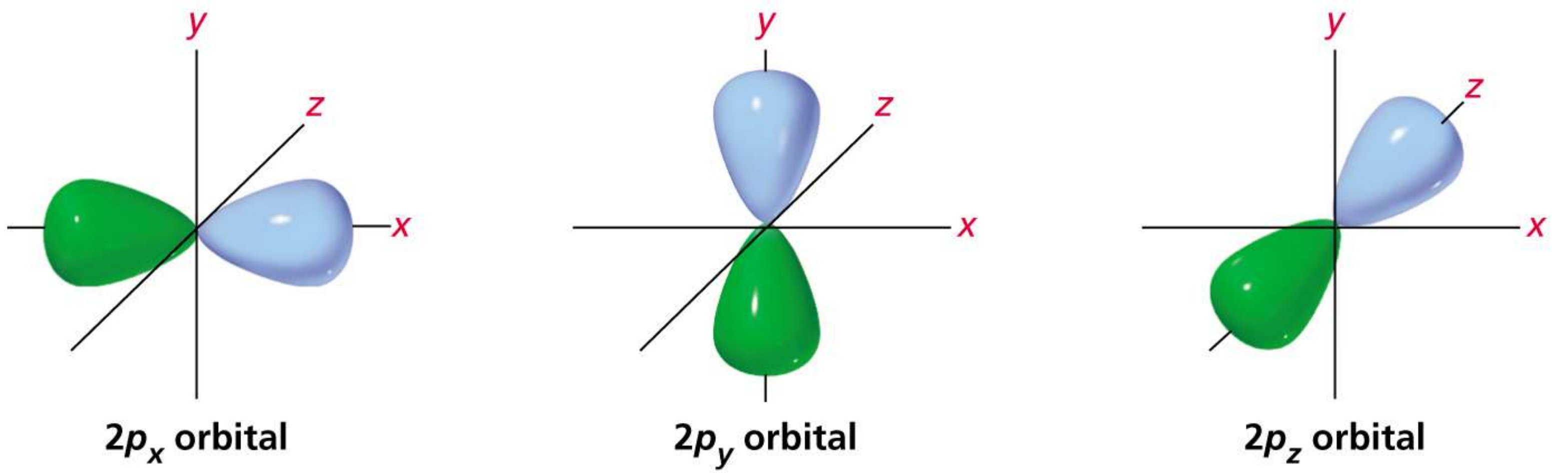
An atomic orbital is the region of space around the nucleus where an electron is most apt to be found.



An Electron Behaves Like a Standing Wave

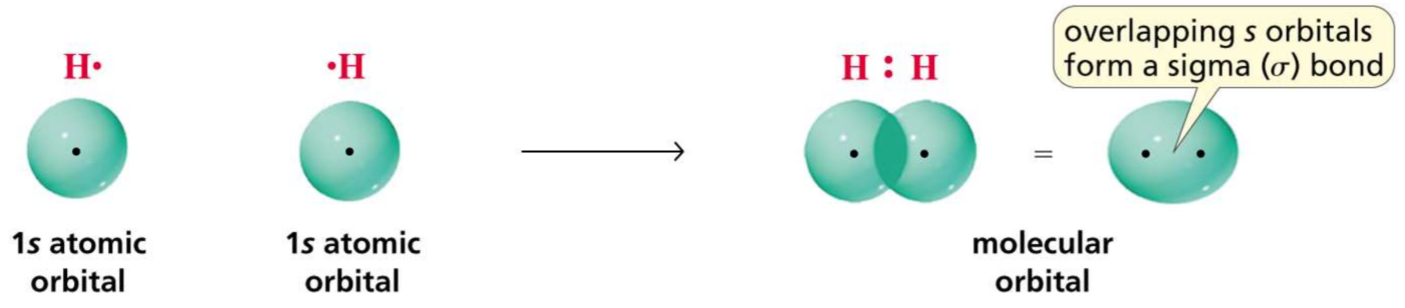


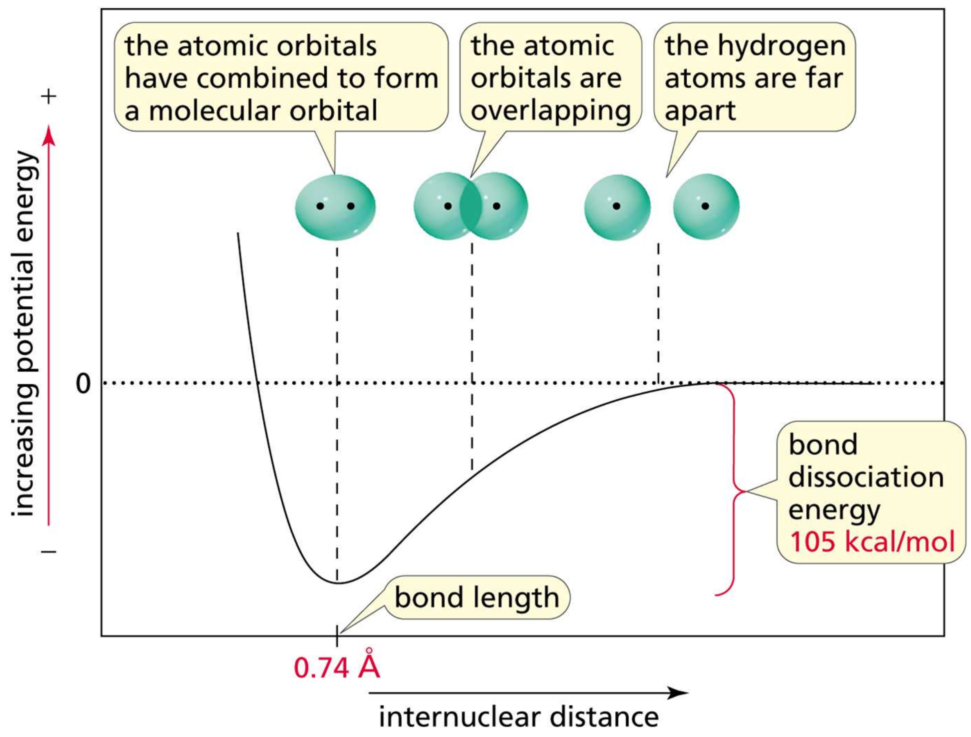
The Three *p* Orbitals



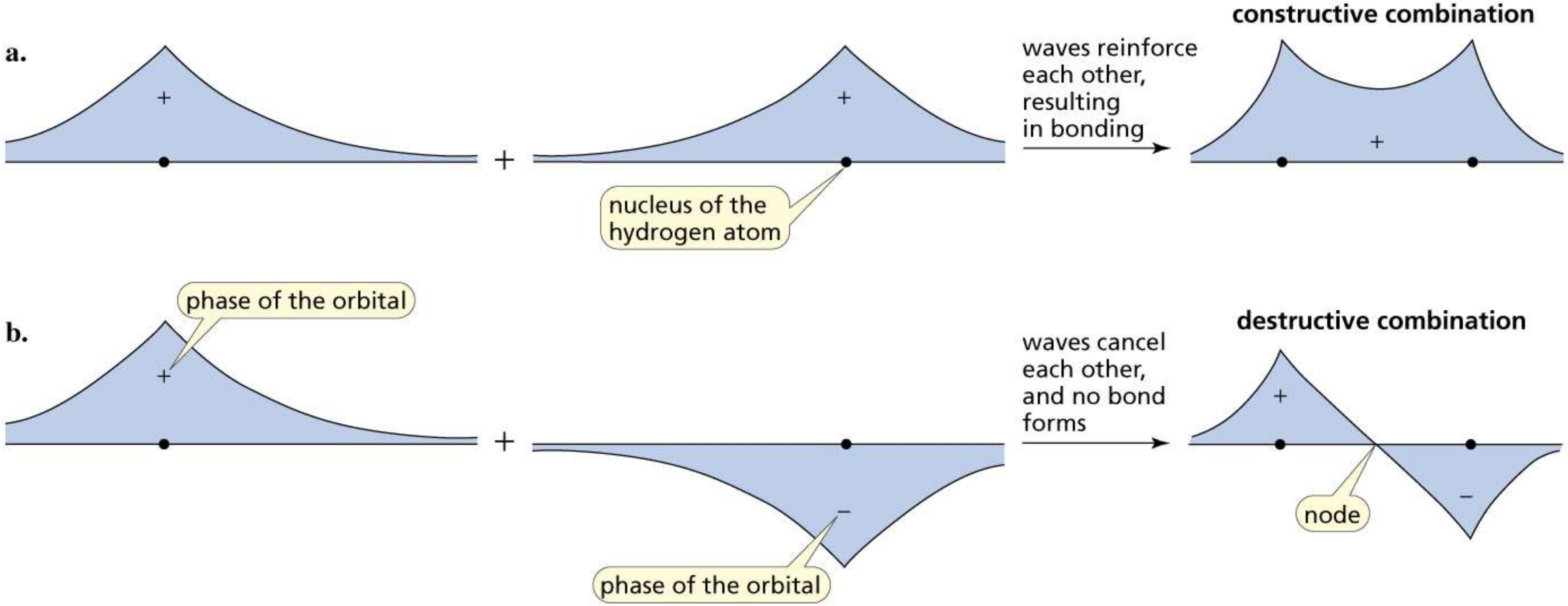
The lobes of a *p* atomic orbital have opposite phases.

Forming a Sigma Bond

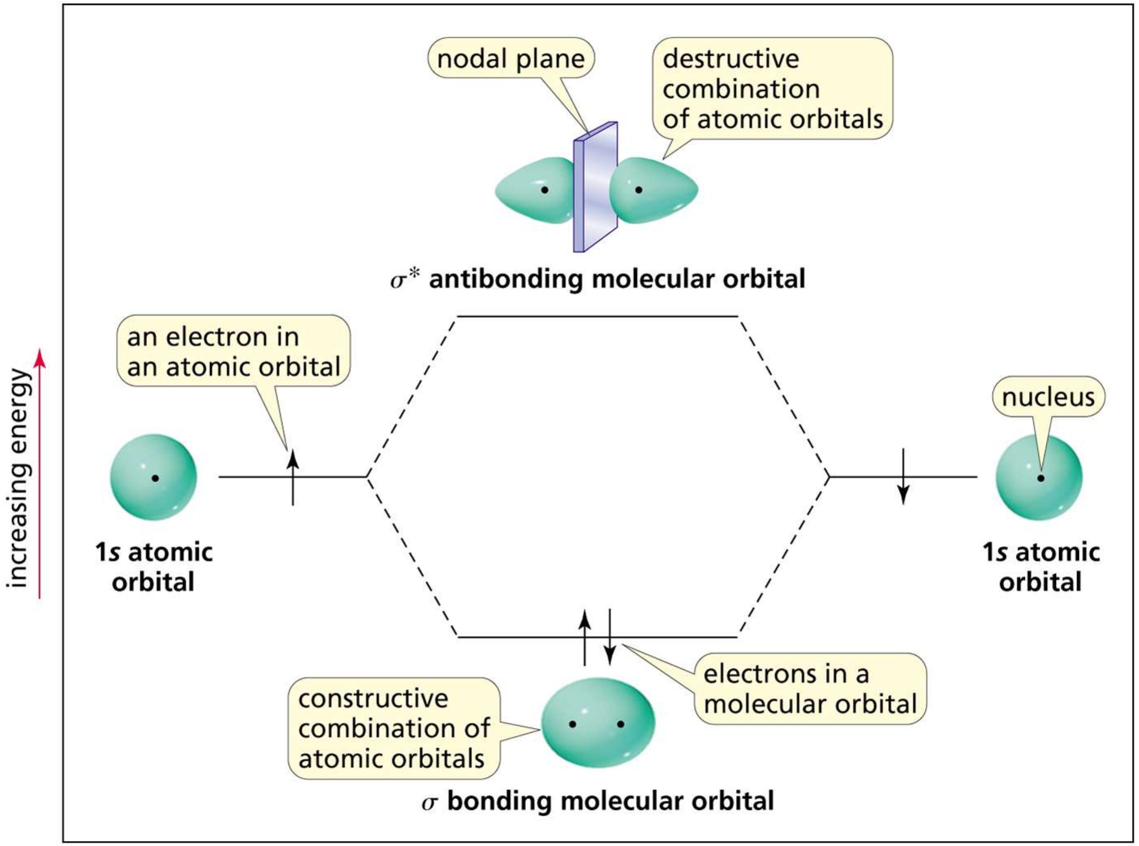




Waves Can Reinforce Each Other
Waves Can Cancel Each Other



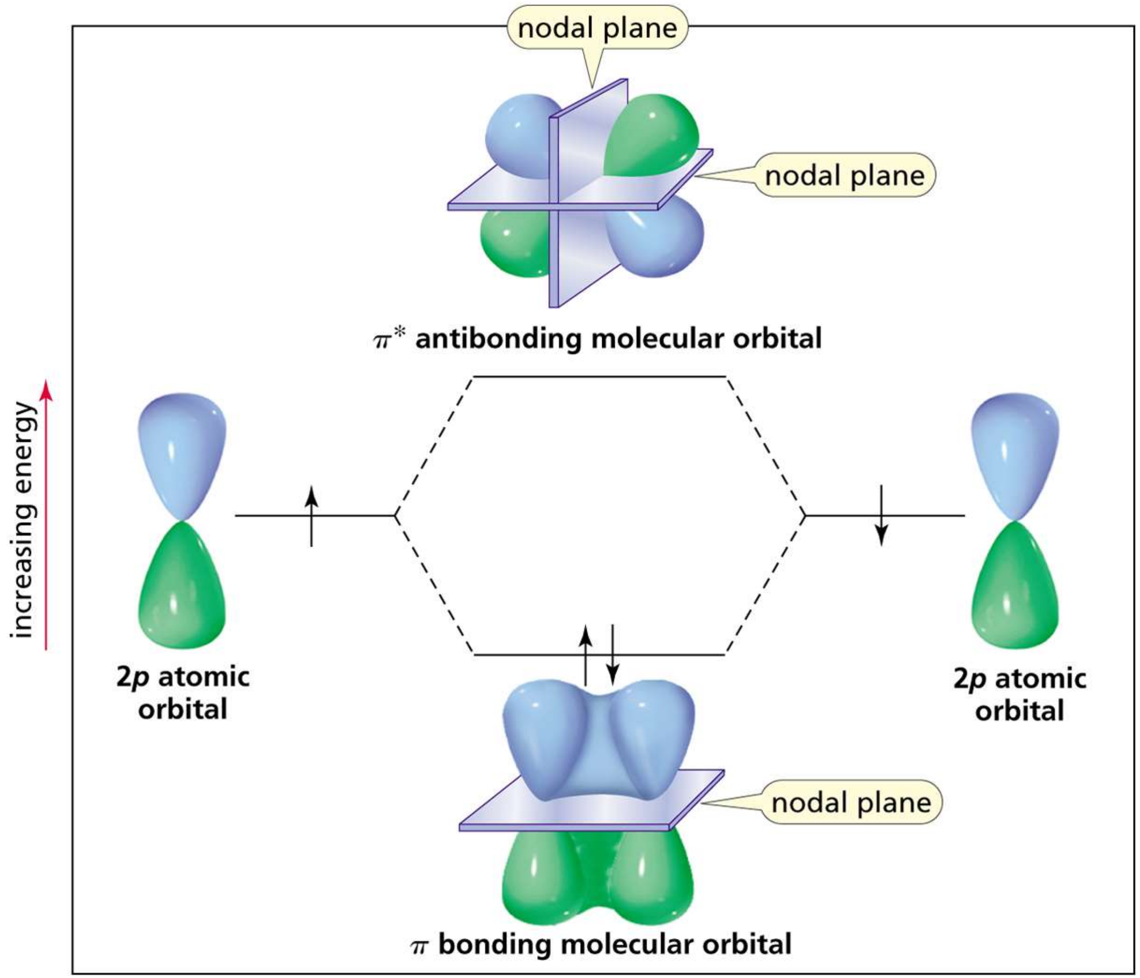
Atomic Orbitals Combine to Form Molecular Orbitals



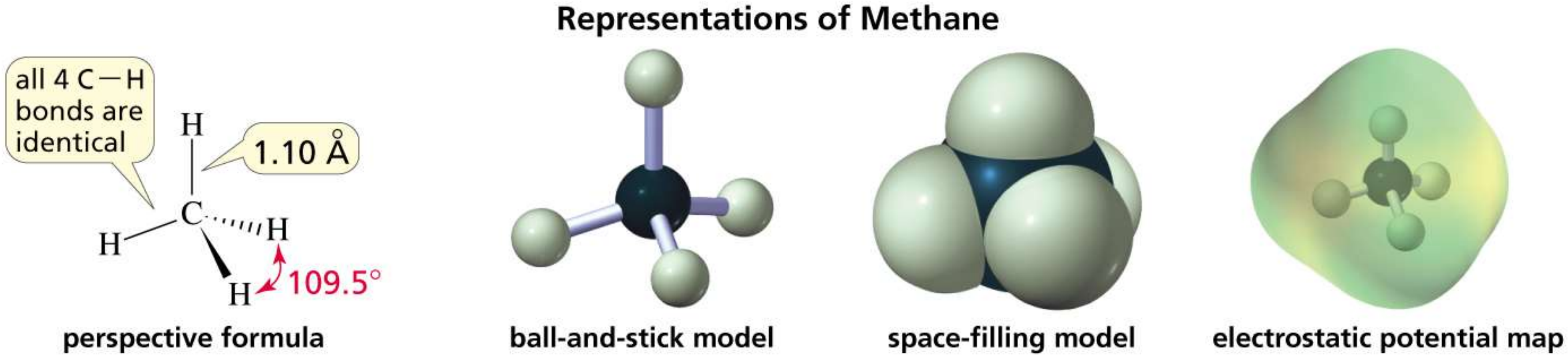
Orbitals are Conserved

\# of Molecular Orbitals = # of Atomic Orbitals Combined

Side-to-Side Overlap of In-Phase *p* Orbitals Forms a π Bond



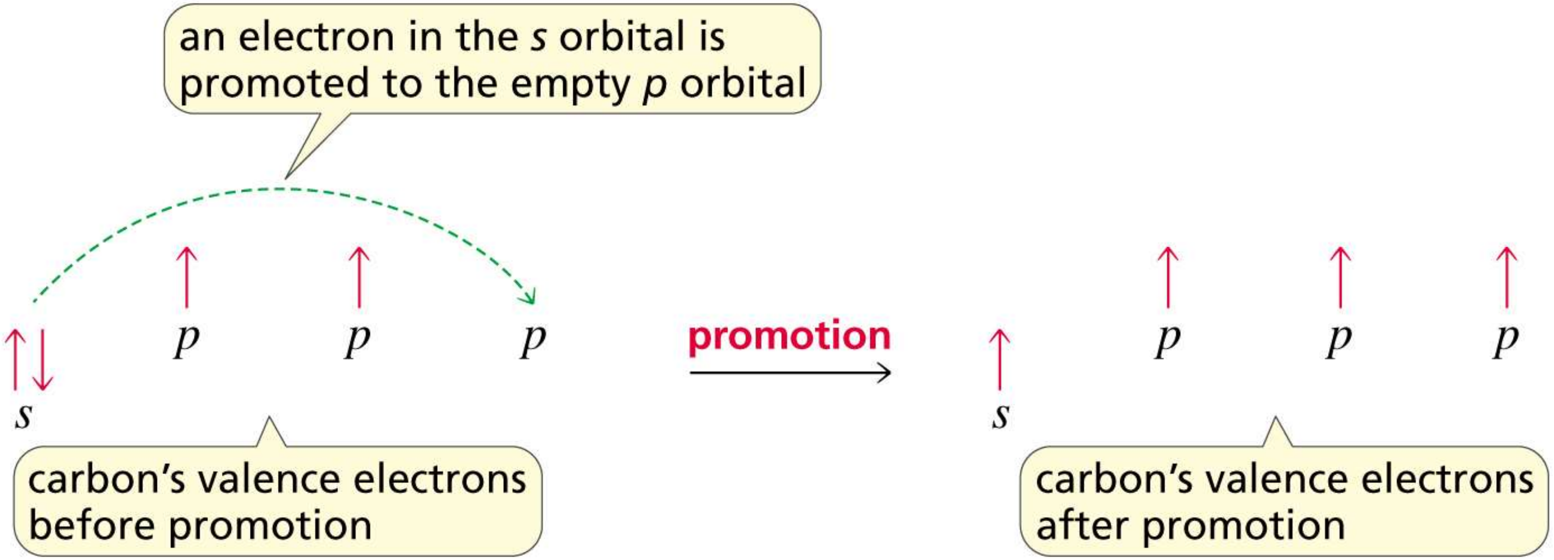
Methane (CH_4)



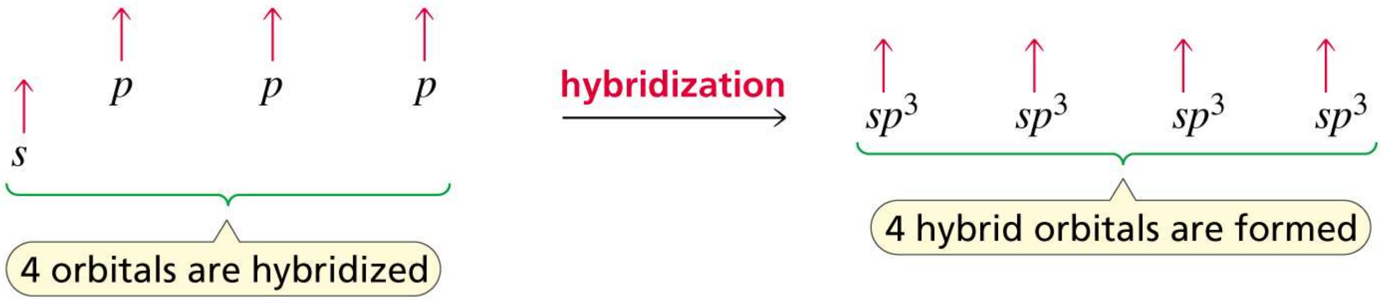
The 4 C-H bonds have the same length.

All the bond angles are the same (109.5°)

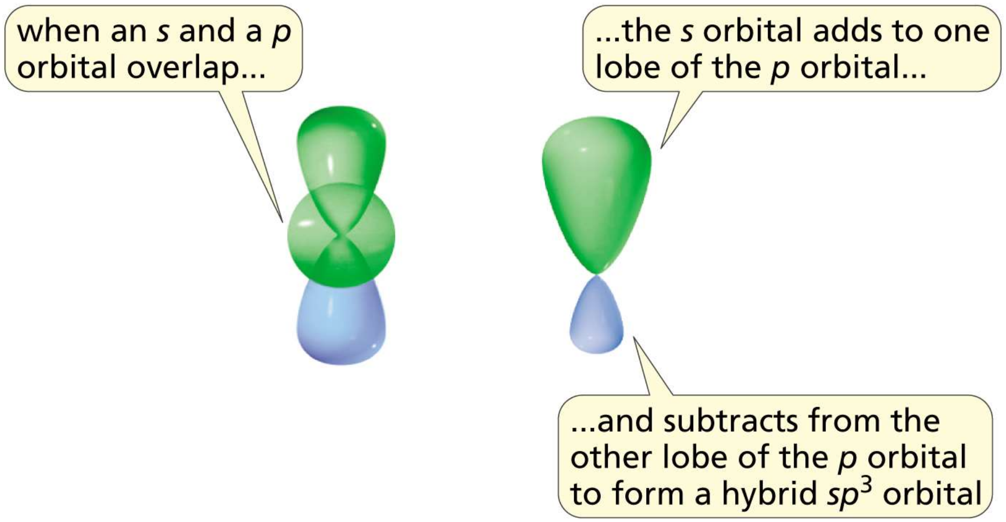
In Order to Form Four Bonds, Carbon Must Promote an Electron



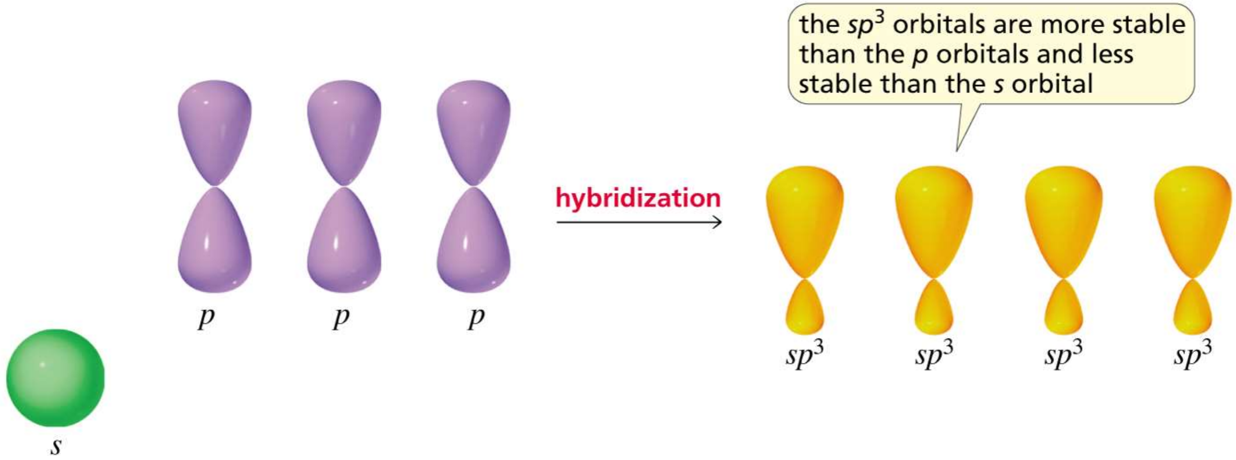
Four Orbitals are Mixed to Form Four Hybrid Orbitals



An sp^3 orbital has a large lobe and a small lobe.

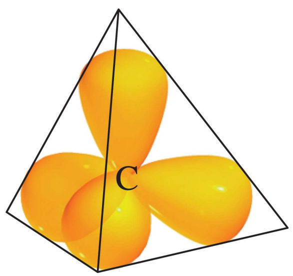


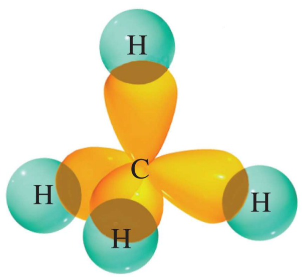
The Carbon in Methane is sp^3



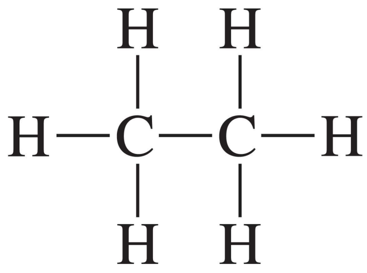
Carbon is tetrahedral.

The tetrahedral bond angle is 109.5°.

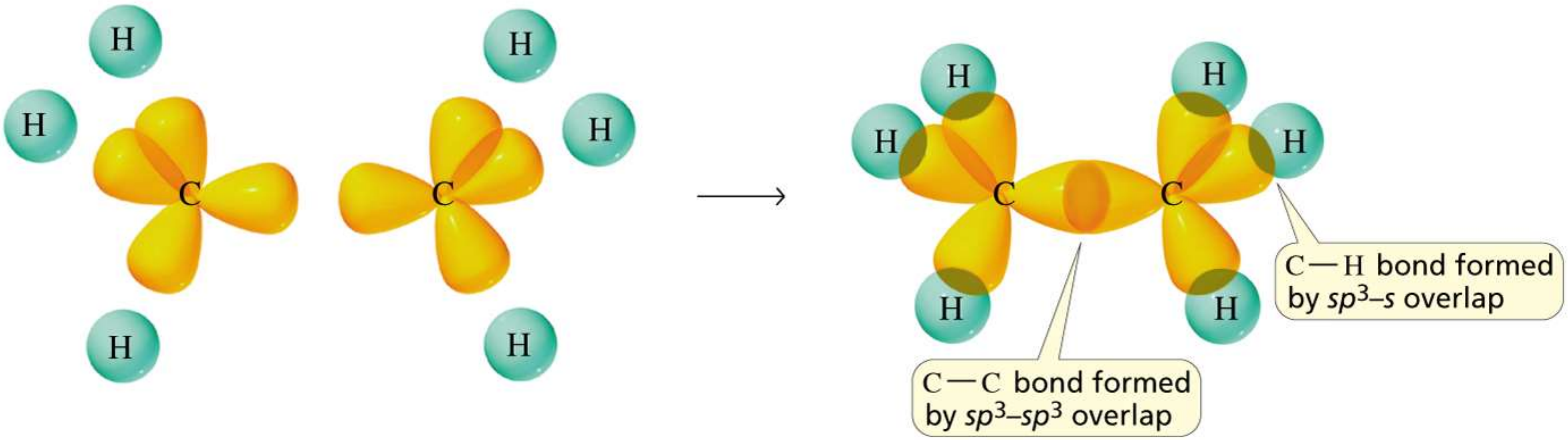




The Bonding in Ethane

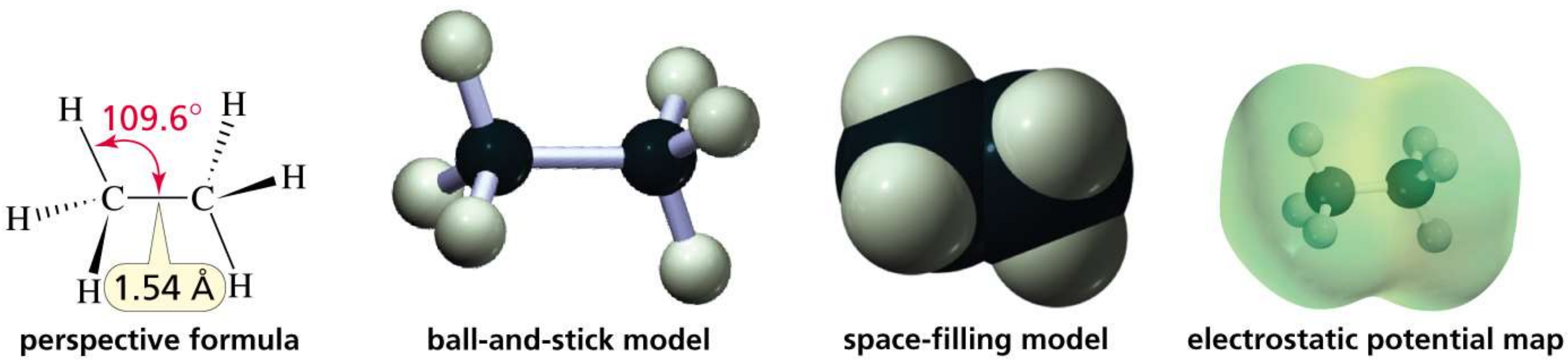


ethane

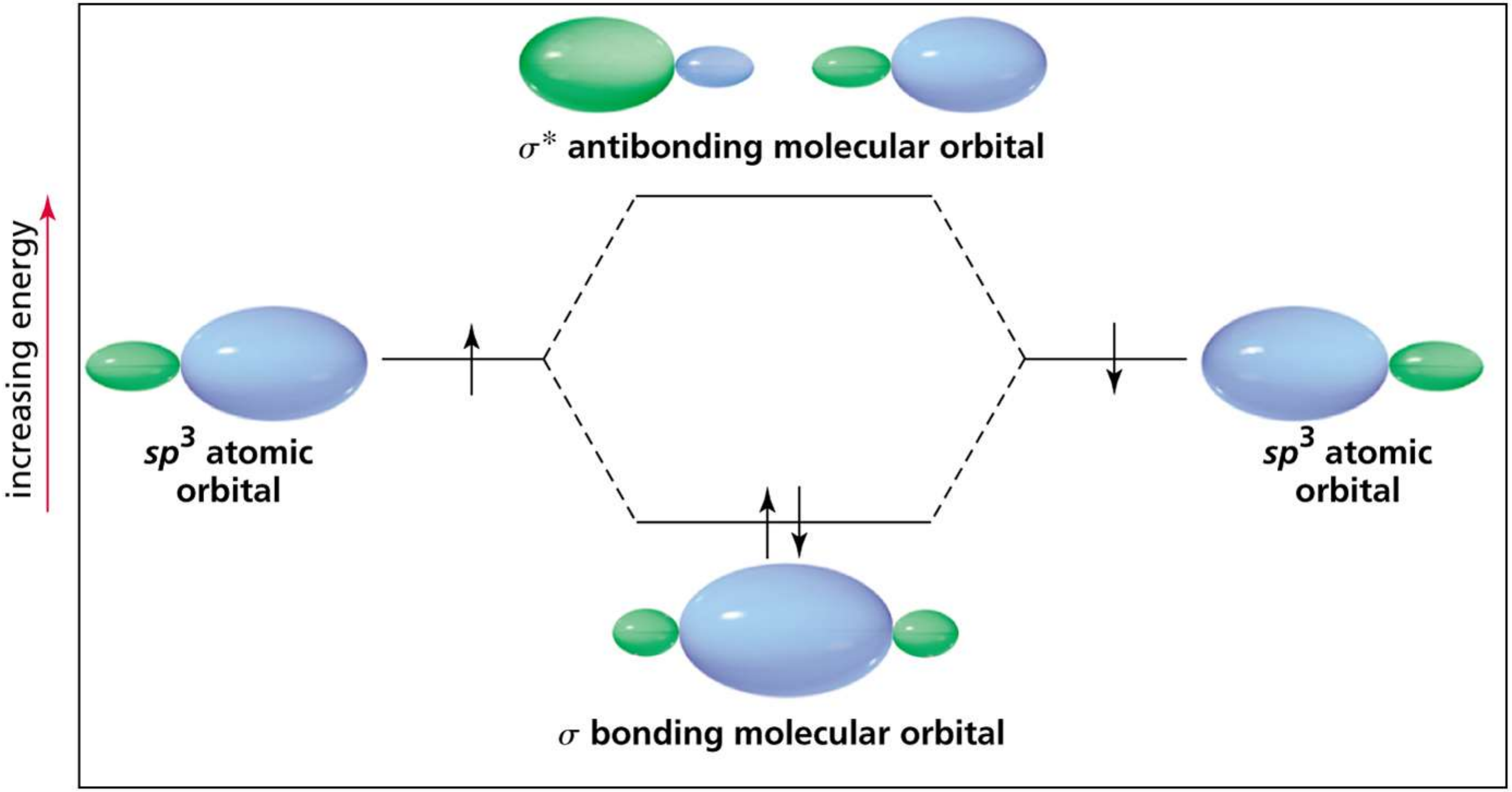


Ethane

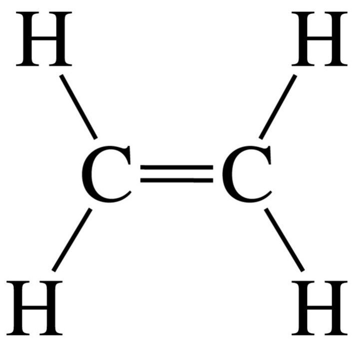
Representations of Ethane



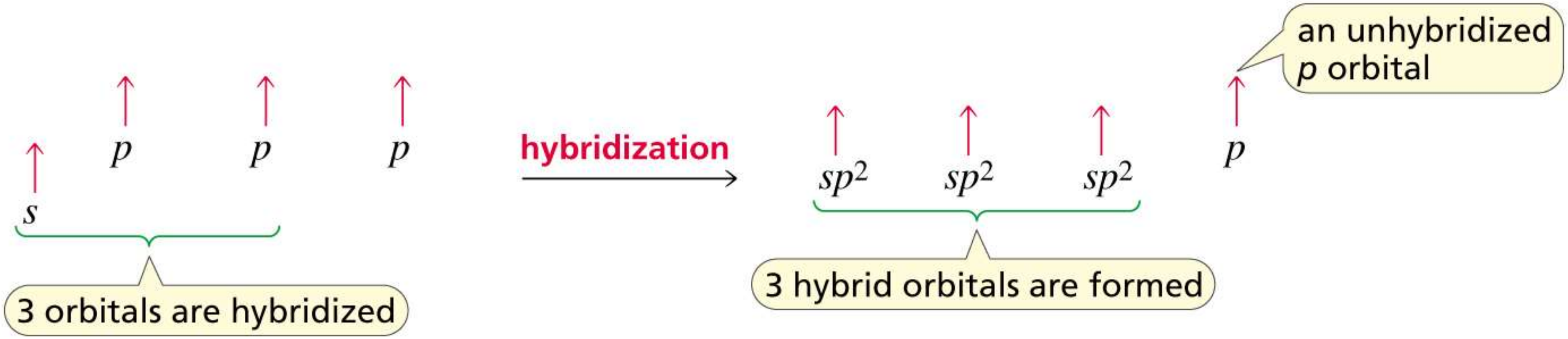
End-on Overlap of Orbitals Forms a σ Bond



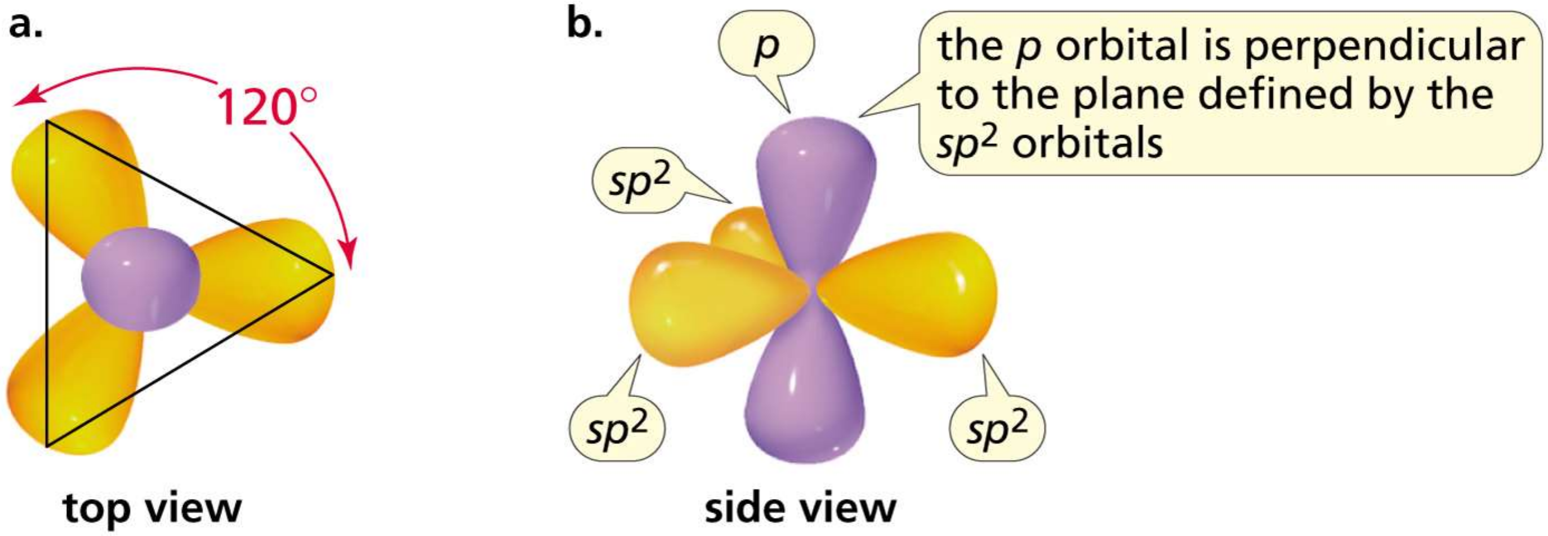
Ethene (Ethylene)



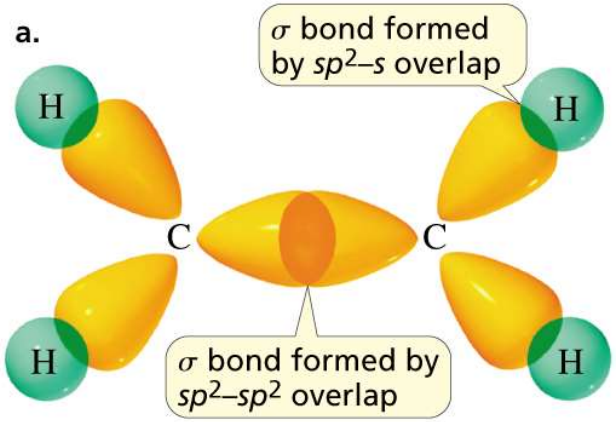
Carbon bonds to 3 atoms, so it needs to hybridize 3 atomic orbitals.

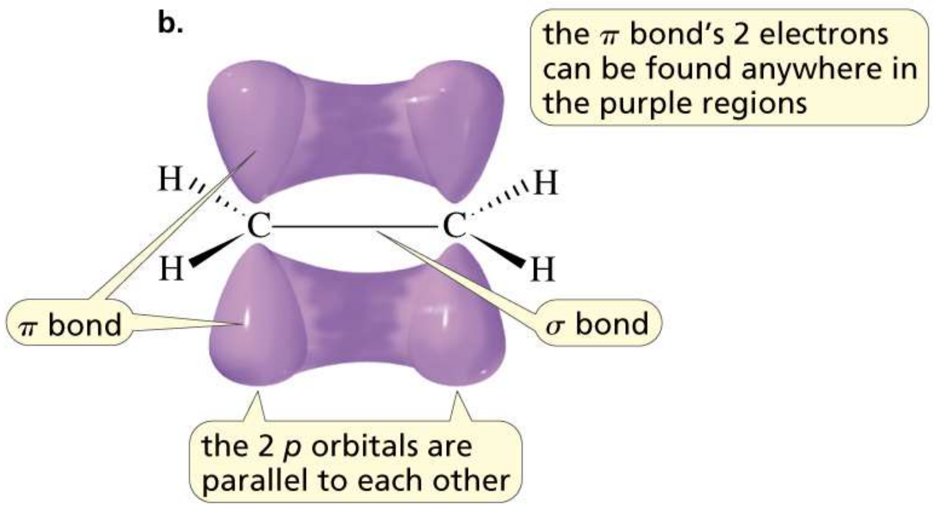


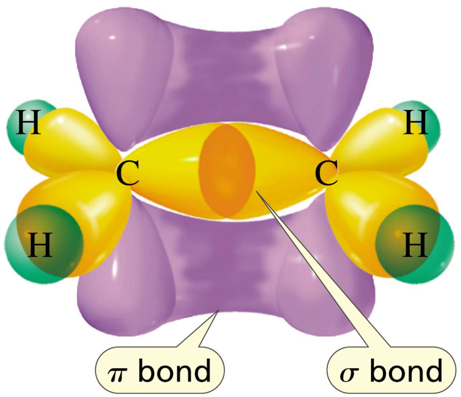
An *sp*^{2} Carbon Has Three *sp*^{2} Orbitals and One *p* Orbital



The Bonding in Ethene

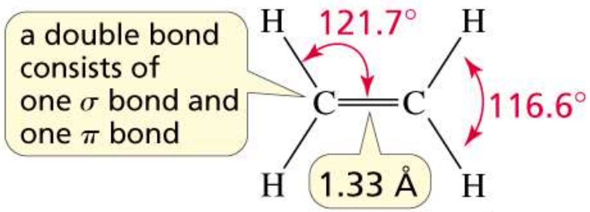




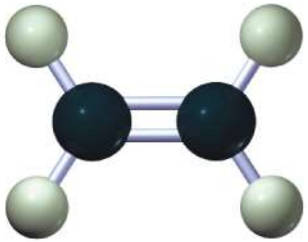


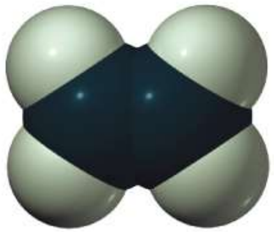
Ethene

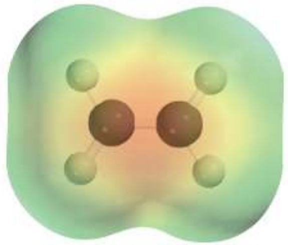
Representations of Ethene



perspective formula

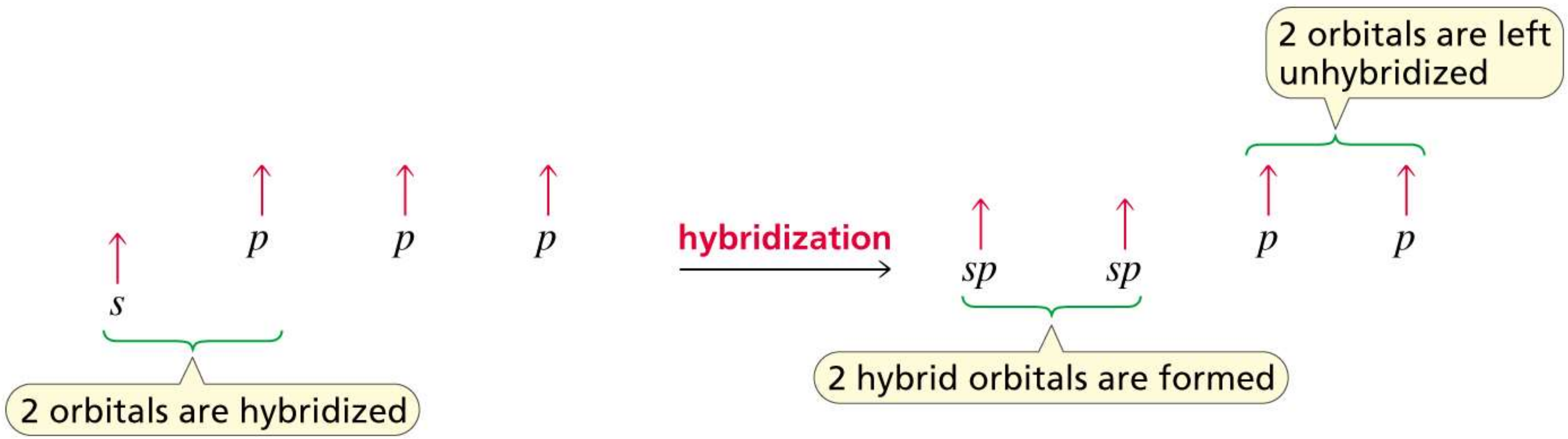

ball-and-stick model


space-filling model

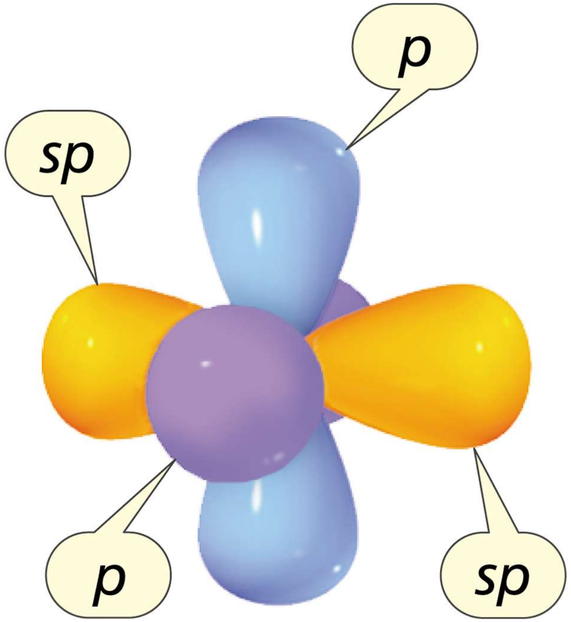

electrostatic potential map

Ethyne (Acetylene)

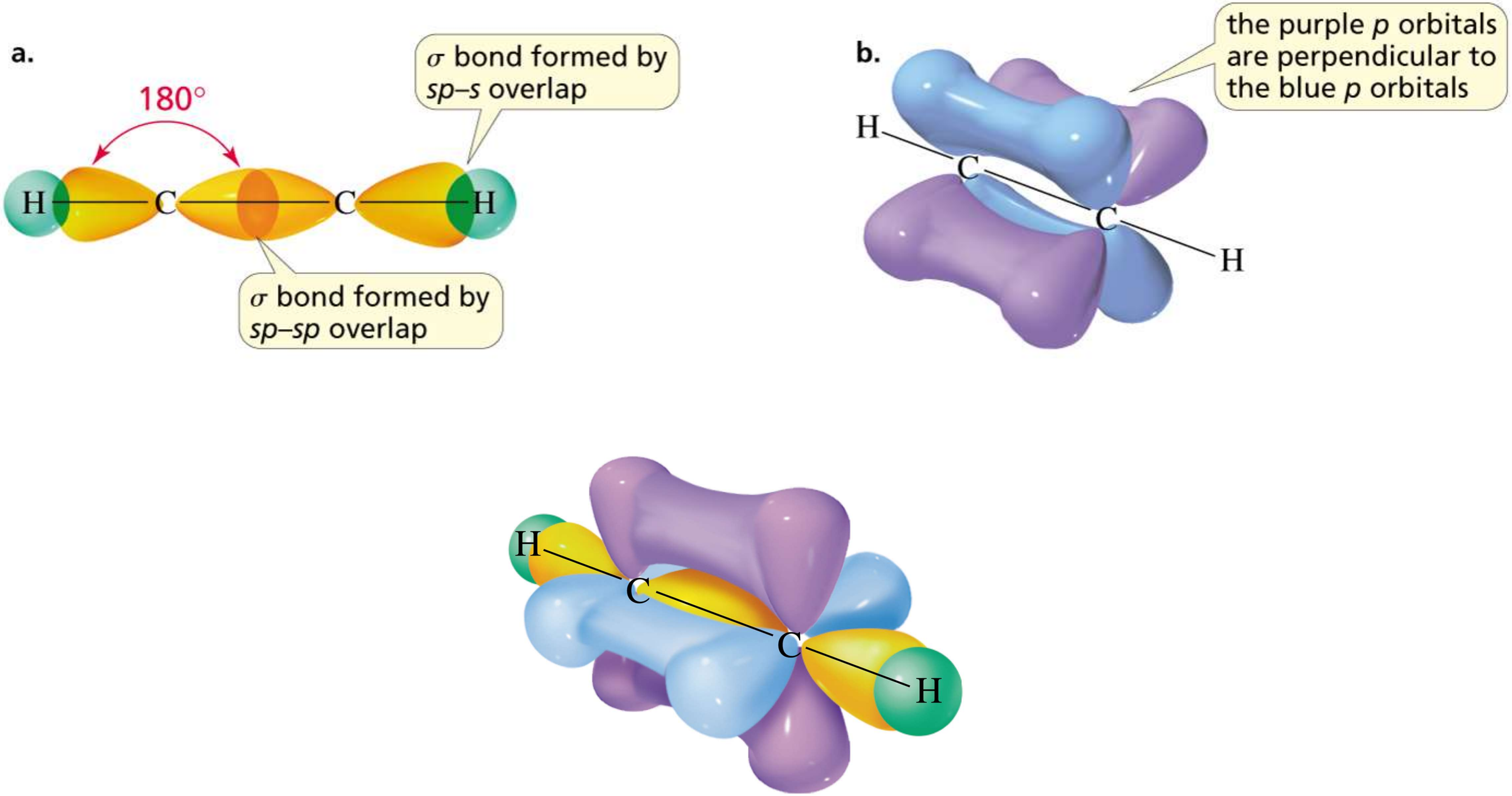
Carbon bonds to 2 atoms, so it needs to hybridize 2 atomic orbitals.



The Two *sp* Orbitals Point in Opposite Directions; The Two *p* Orbitals are Perpendicular

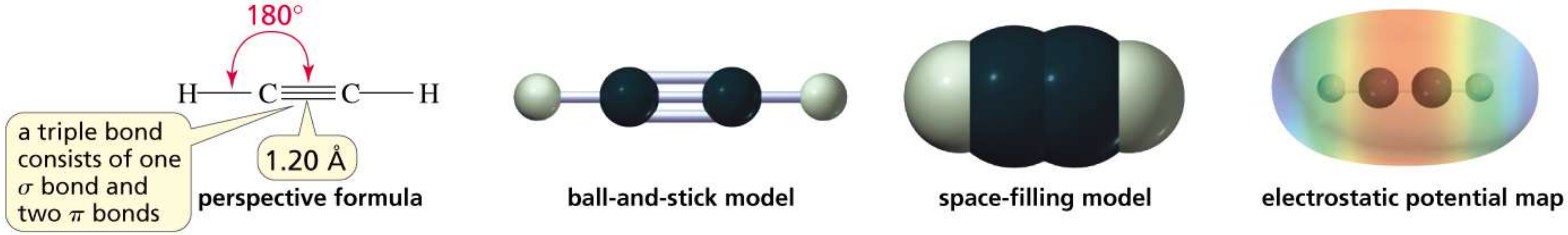


The Bonding in Ethyne



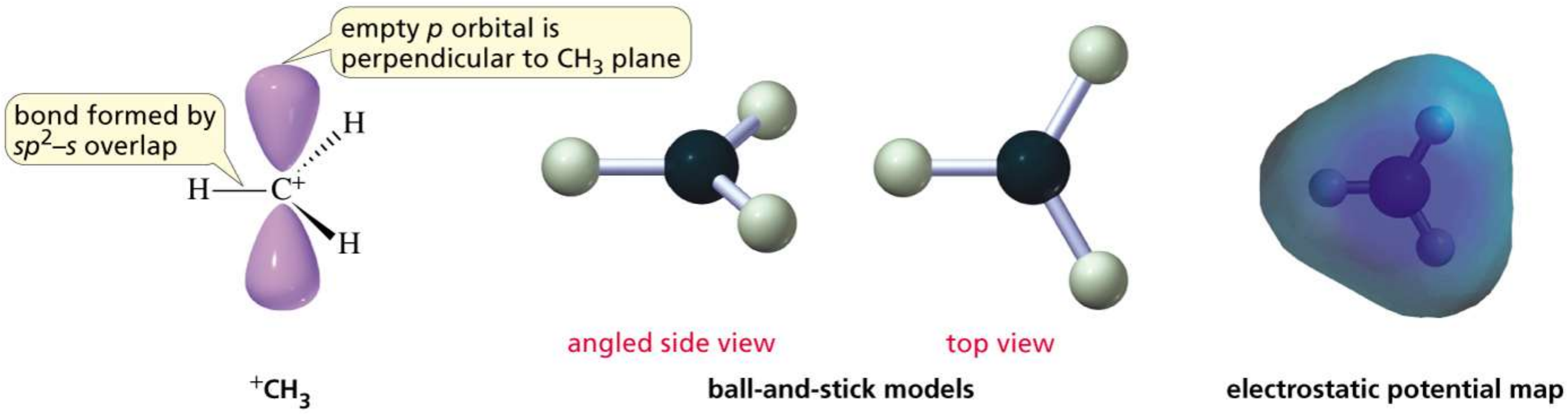
Ethyne

Representations of Ethyne

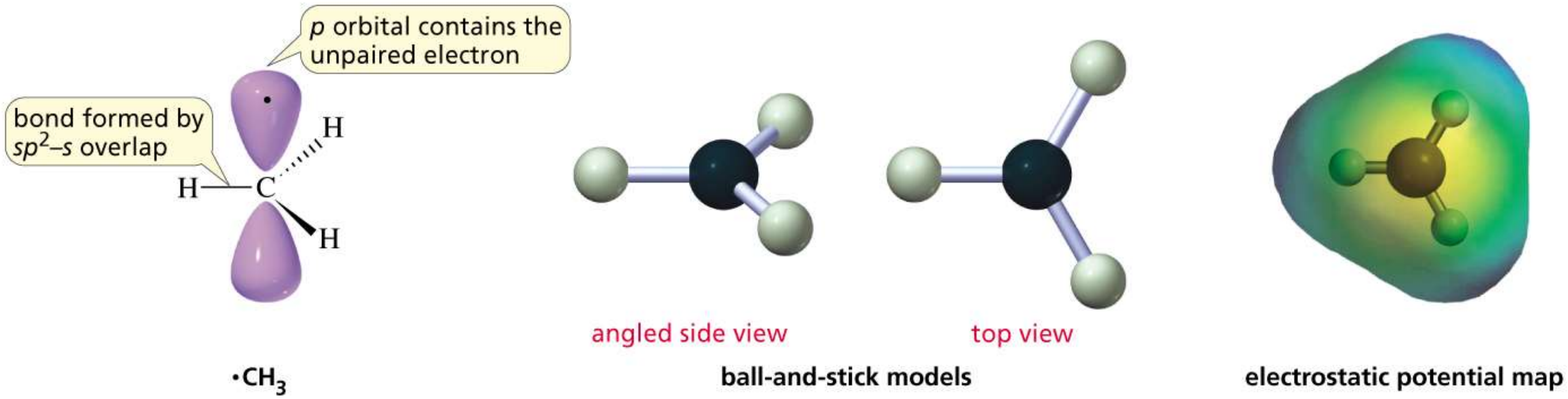


The Carbon in the Methyl Cation and in the Methyl Radical are *sp*^{2}

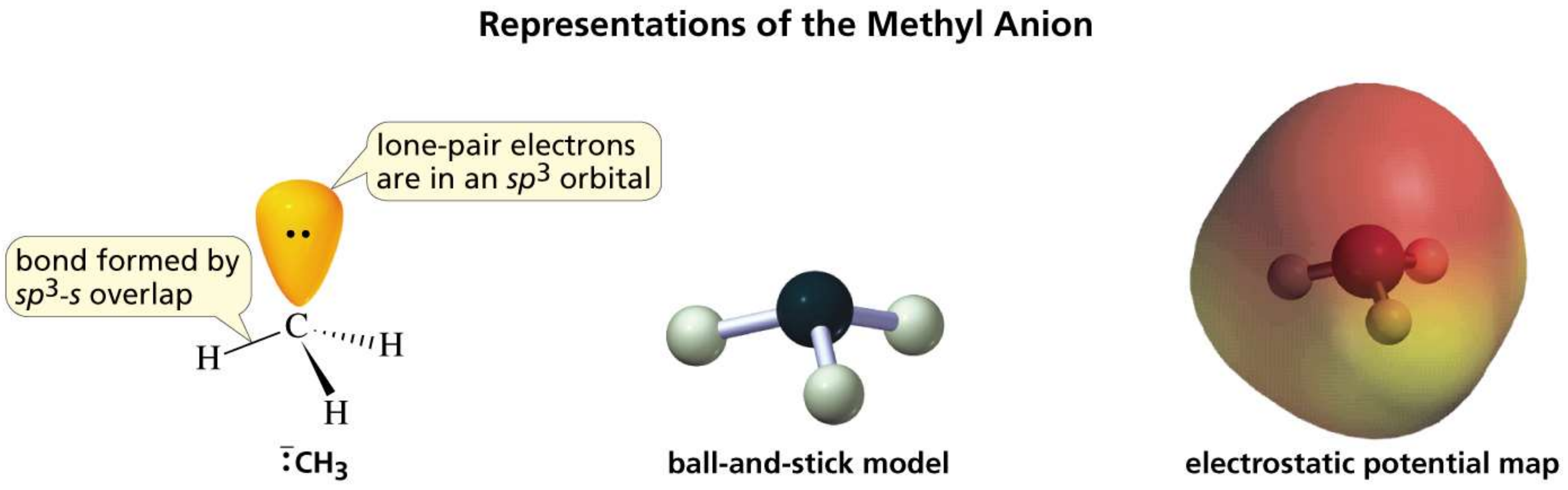
Representations of Methyl Cation



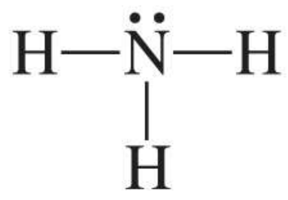
Representations of the Methyl Radical

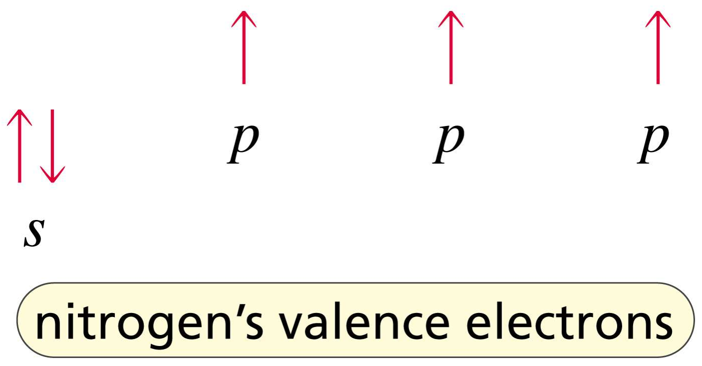


The Carbon in the Methyl Anion is *sp*^{3}



Ammonia (NH_3)





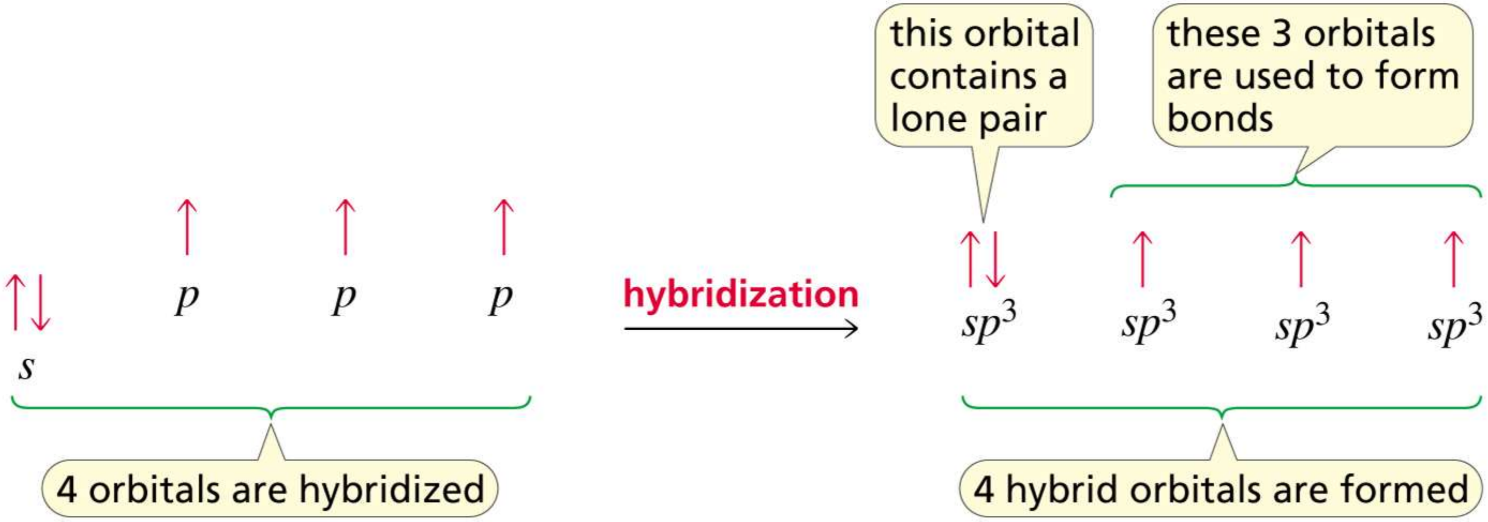
Nitrogen has 3 unpaired valence electrons and forms 3 bonds.

Nitrogen does not have to promote an electron.

The Bonds in Ammonia (NH_3)

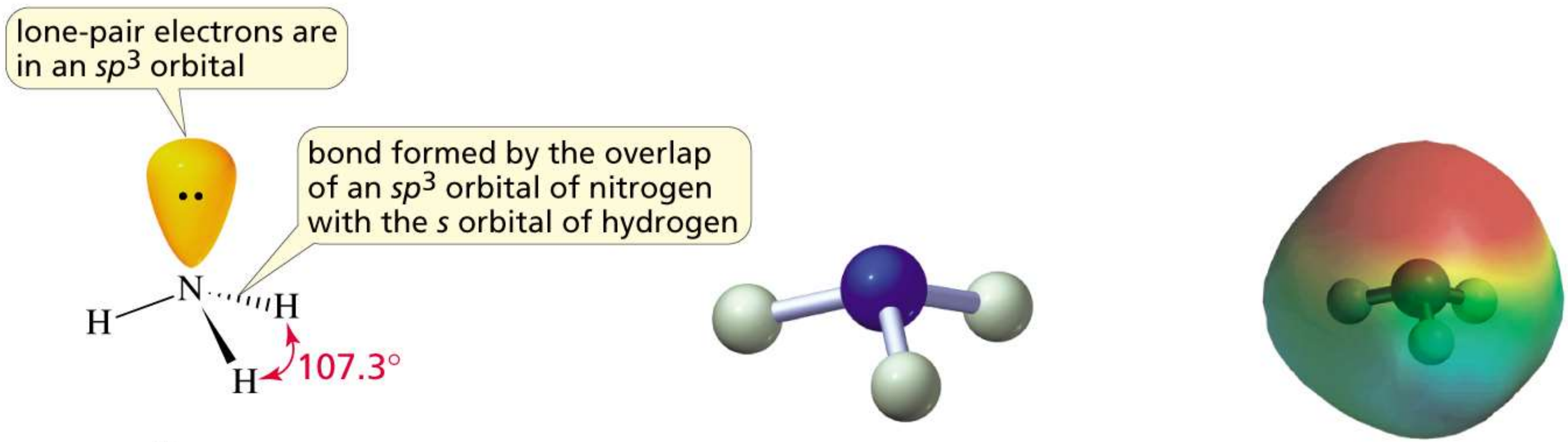
If N used *p* orbitals to form bonds, the bond angles would be 90°.

The observed bond angles are 107.3°,
so nitrogen must used hybridized orbitals.



Ammonia

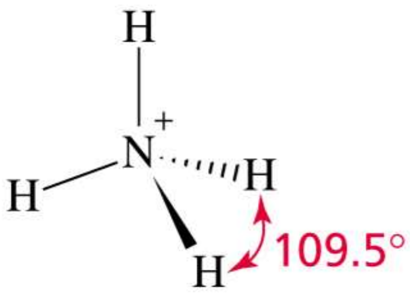
Representations of Ammonia



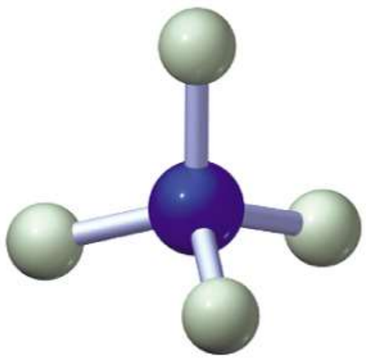
$\ddot{N}H_3$ | ball-and-stick model | electrostatic potential map

The Ammonium Ion ($^{+}NH_4$)

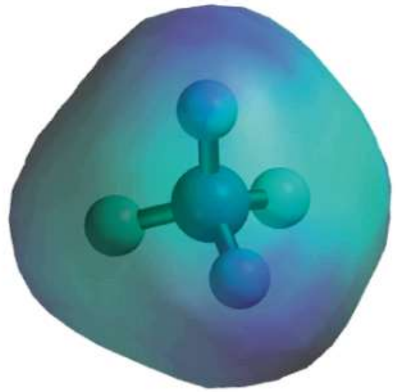
Representations of the Ammonium Ion



$^{+}NH_4$

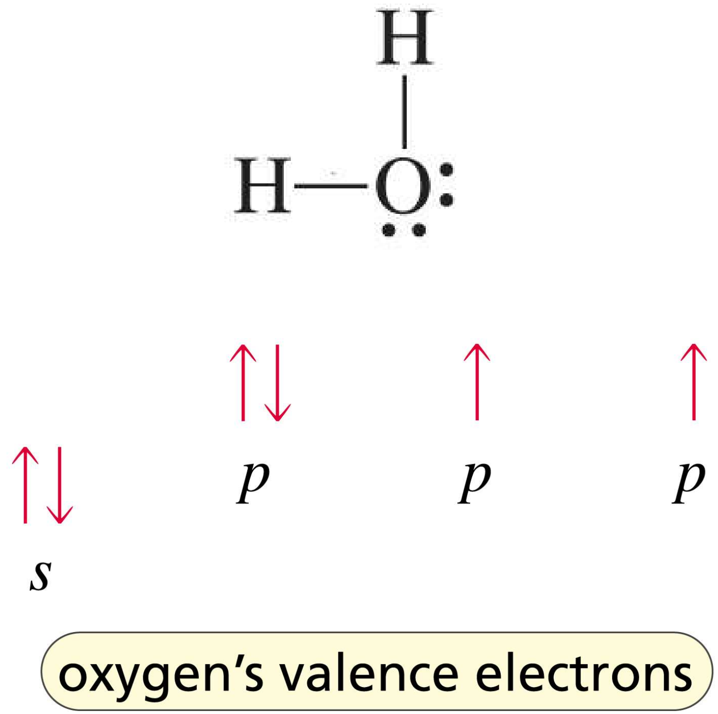


ball-and-stick model



electrostatic potential map

Water (H_2O)

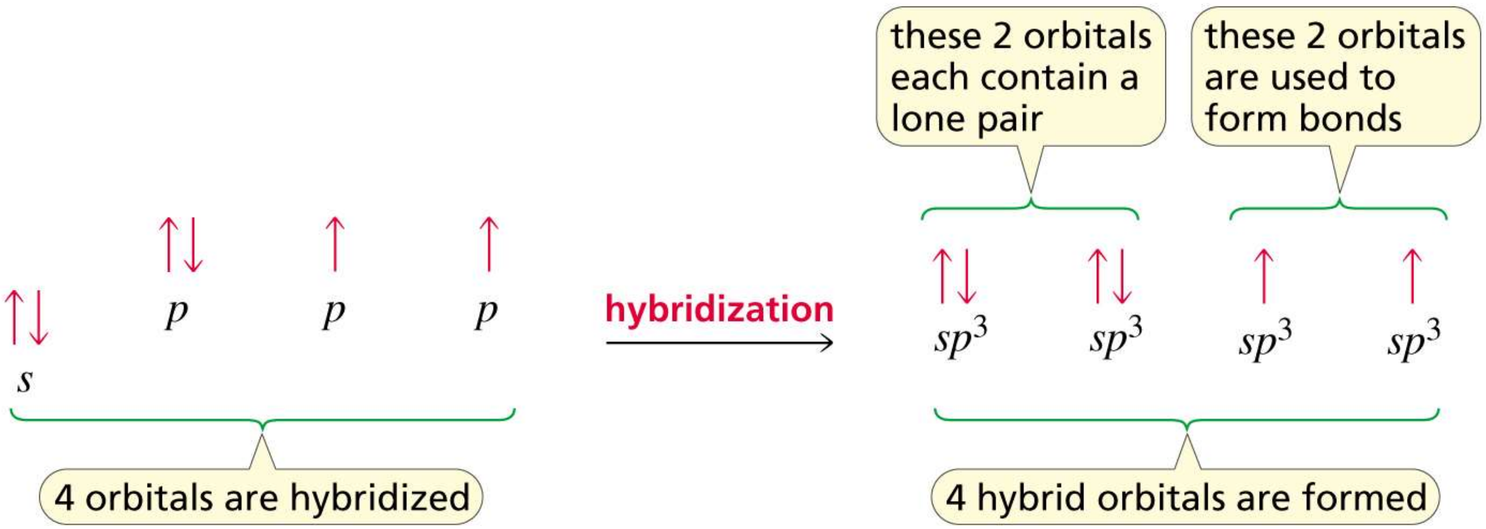


Oxygen has 2 unpaired valence electrons and forms 2 bonds.

Oxygen does not have to promote an electron.

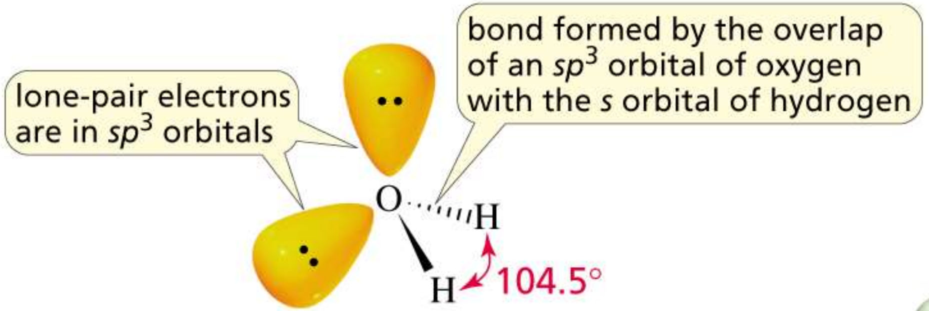
The Bonds in Water (H_2O)

The observed bond angles are 104.5°,
so oxygen must used hybridized orbitals.

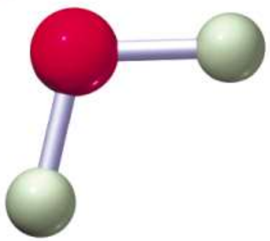


Water

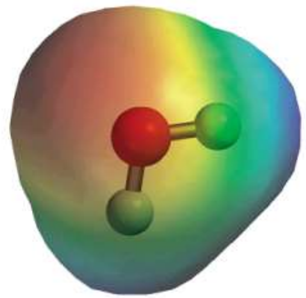
Representations of Water



H_2O

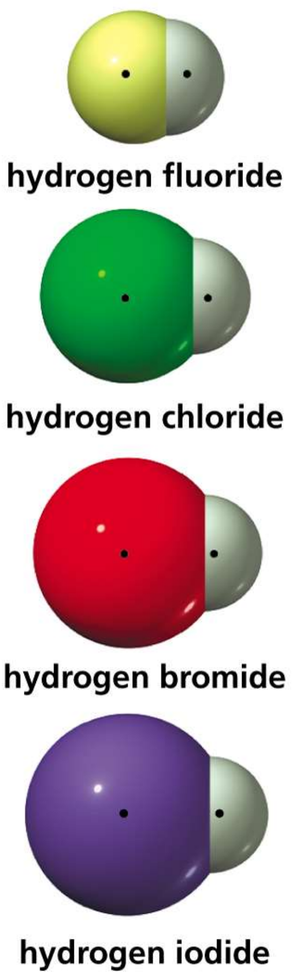


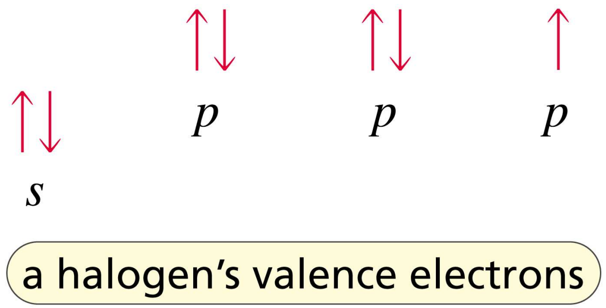
ball-and-stick model



electrostatic potential map

The Bond in a Hydrogen Halide

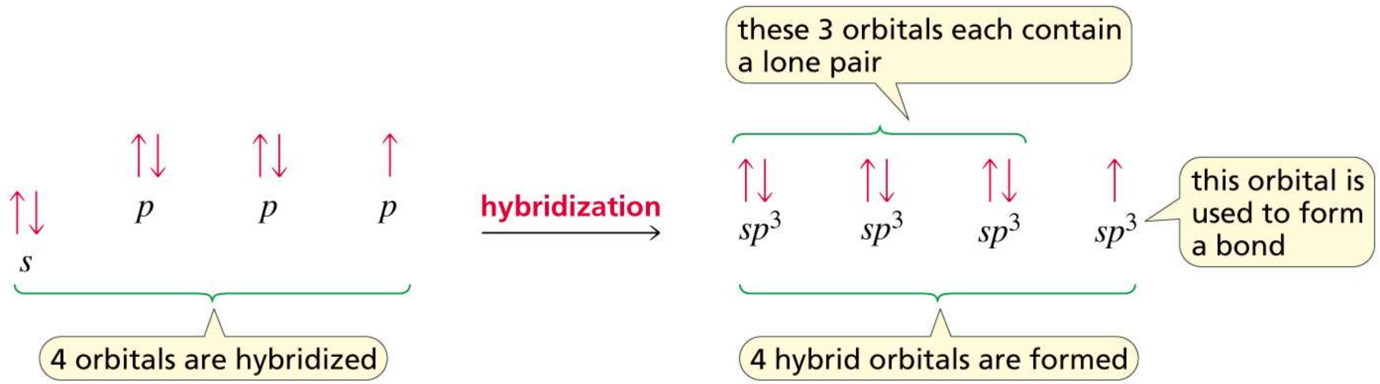




A halogen has 1 unpaired valence electron and forms 1 bond.

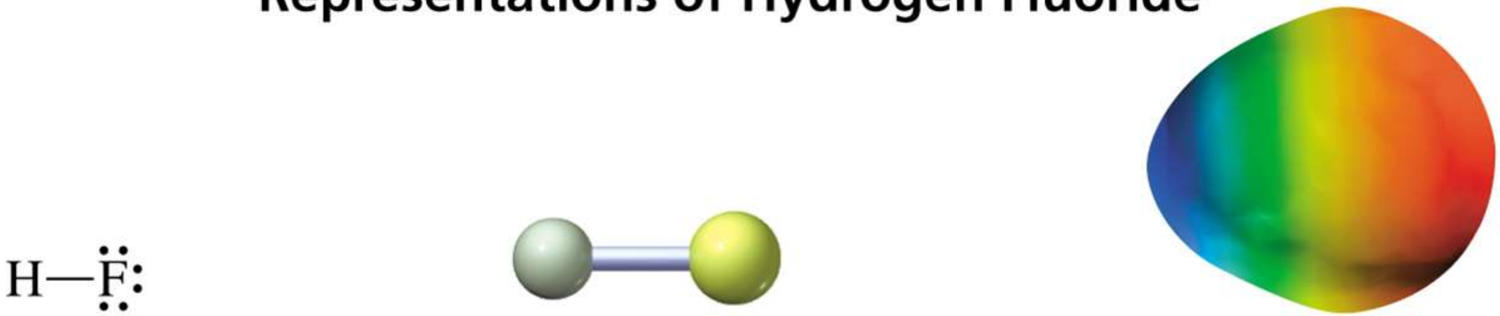
A halogen uses hybrid orbitals.

- The 3 lone pairs are energetically identical.
- Lone pairs position themselves to minimize electron repulsion.



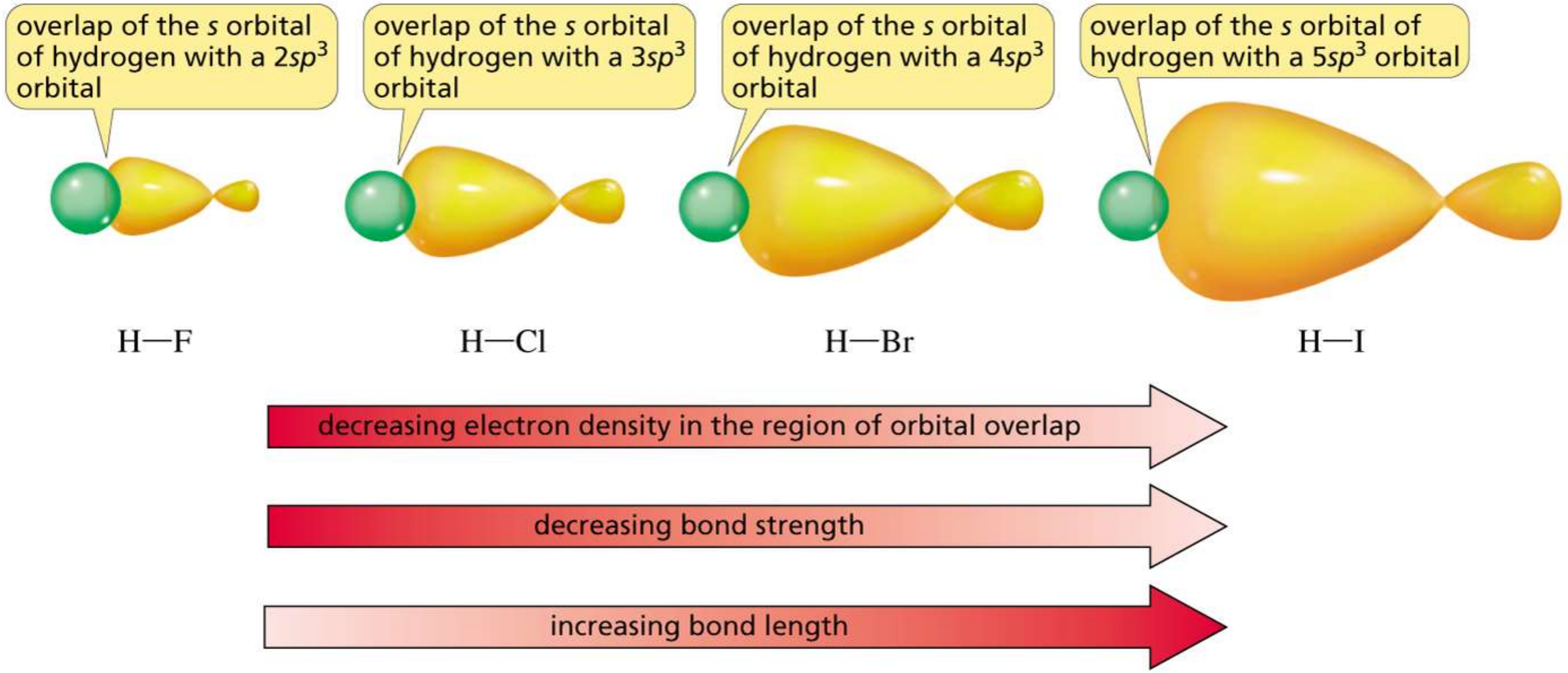
Hydrogen Fluoride

Representations of Hydrogen Fluoride



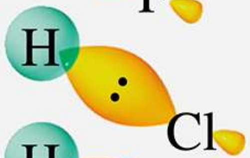
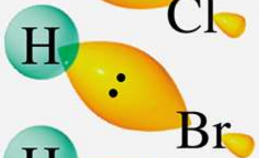
perspective formula ball-and-stick model electrostatic potential map

Overlap of an *s* Orbital with an sp^3 Orbital

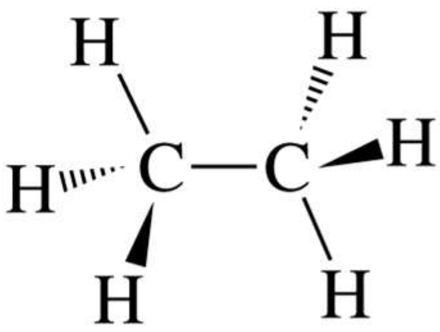


The Length and Strength of a Hydrogen Halide Bond

Table 1.6 Hydrogen–Halogen Bond Lengths and Bond Strengths

Hydrogen halide		Bond length (Å)	Bond strength (kcal/mol)
H—F		0.917	136
H—Cl		1.275	103
H—Br		1.415	87
H—I		1.609	71

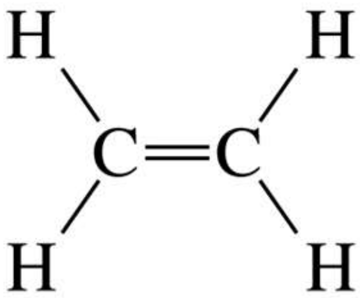
Hybridization and Molecular Geometry



sp^3

109.5°

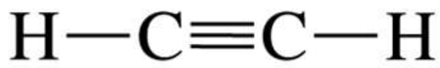
tetrahedral



sp^2

120°

trigonal planar



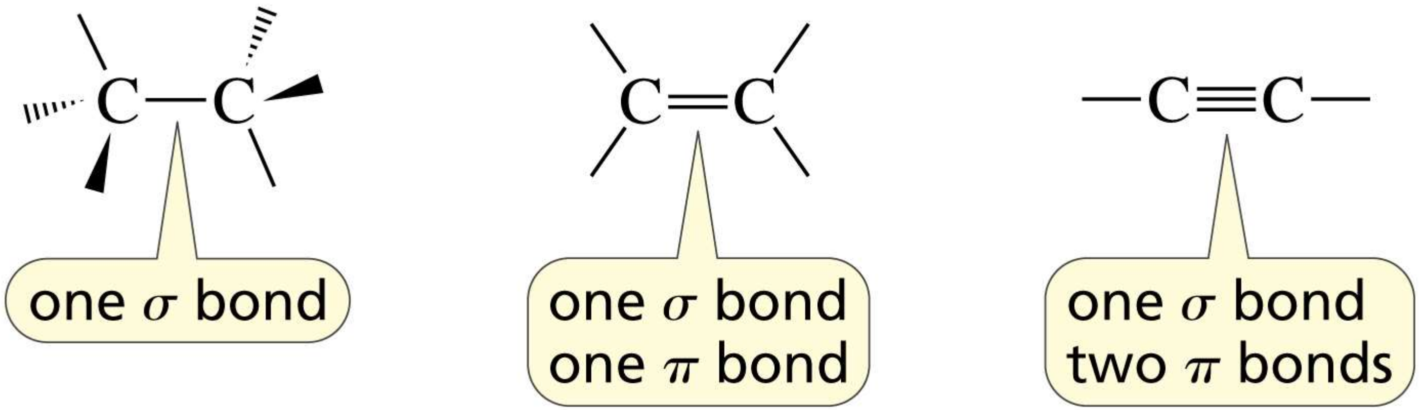
sp

180°

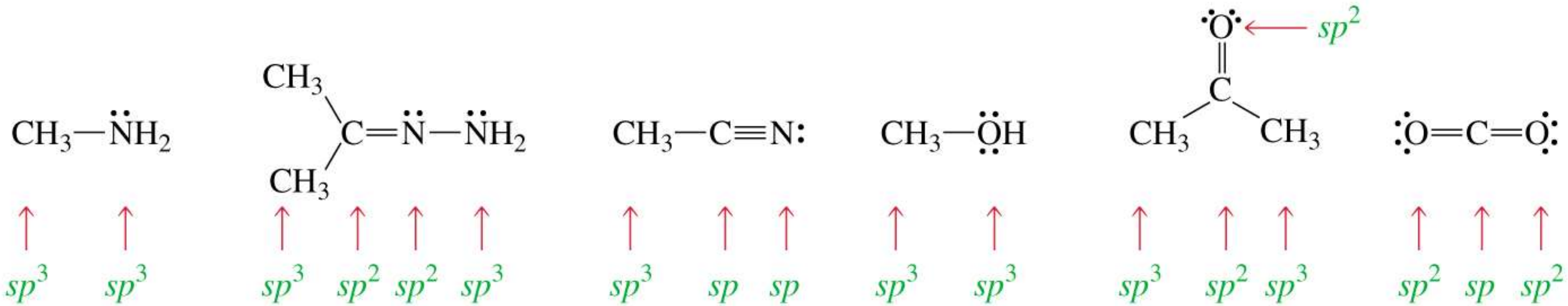
linear

The orbitals used in bond formation determine the bond angle.

Single Bond: 1 σ Double Bond: 1 σ + 1 π
Triple Bond: 1 σ + 2 π

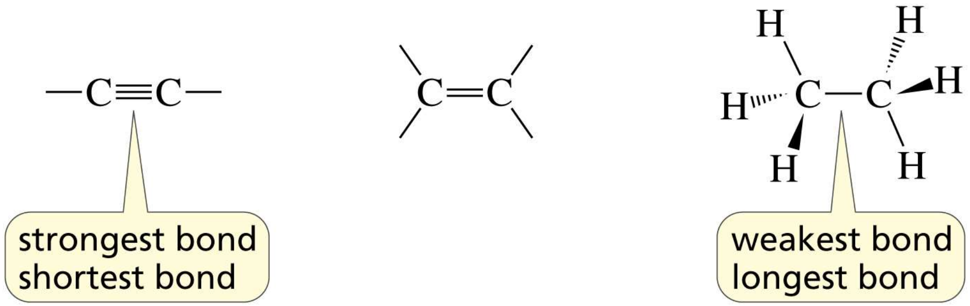


Hybridization of C, N, and O



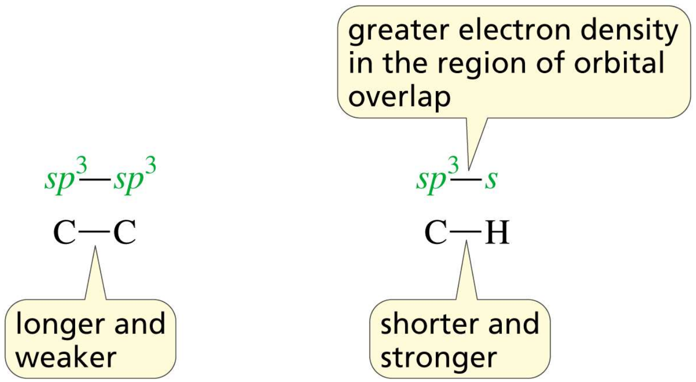
Bond Strength and Bond Length

The more bonds holding 2 atoms together,
the stronger and shorter it is.



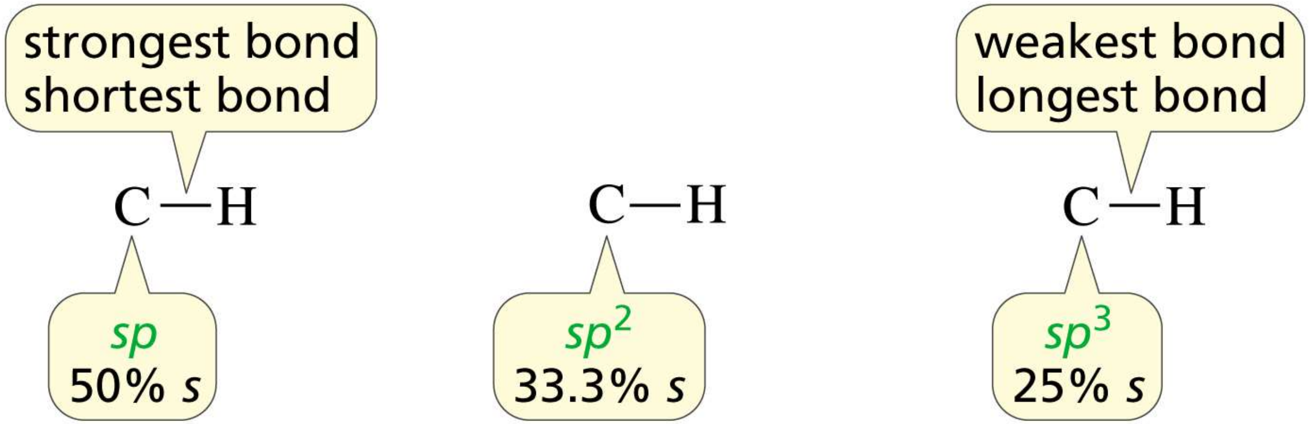
bond strength decreases as bond length increases

The greater the electron density in the region of overlap,
the stronger and shorter the bond.



the greater the electron density in the region of orbital overlap, the stronger and shorter the bond

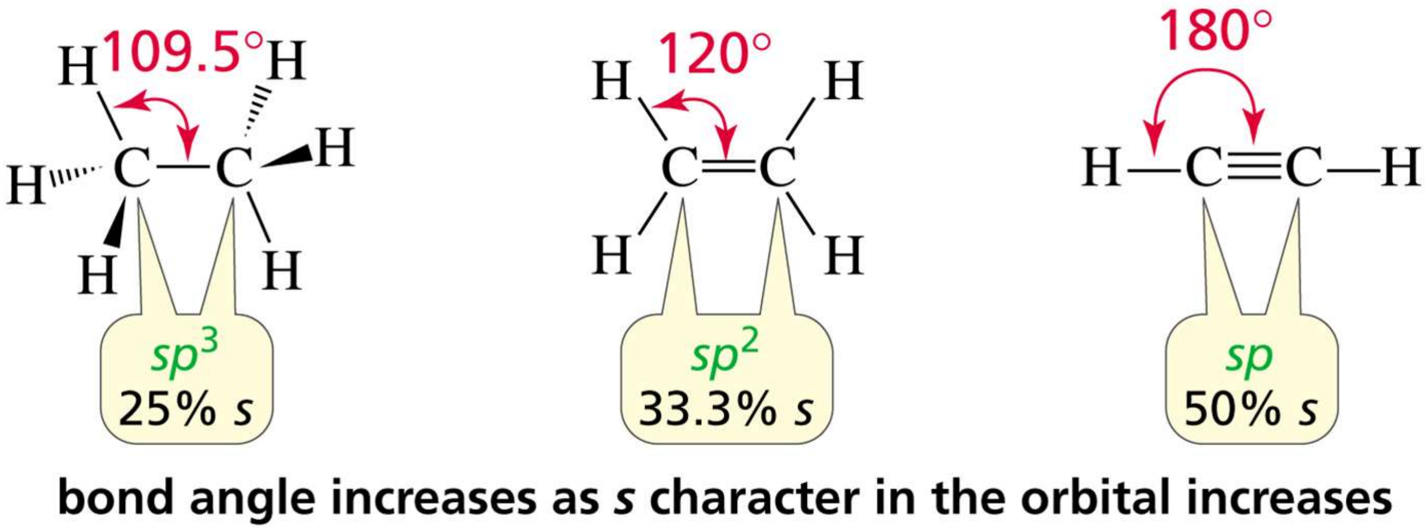
Hybridization Affects Bond Length and Bond Strength



bond strength increases as bond length decreases

The more *s* character in the orbital,
the stronger and shorter is the bond.

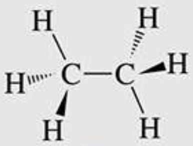
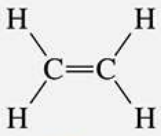
Hybridization Affects the Bond Angle



The more *s* character, the greater the bond angle.

Hybridization, Bond Angle, Bond Length, Bond Strength

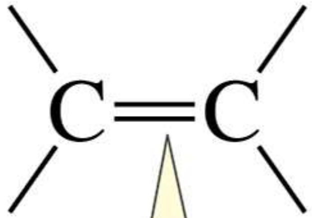
Table 1.7 Comparison of the Bond Angles and the Lengths and Strengths of the Carbon–Carbon and Carbon–Hydrogen Bonds in Ethane, Ethene, and Ethyne

Molecule	Hybridization of carbon	Bond angles	Length of C—C bond (Å)	Strength of C—C bond (kcal/mol)	Length of C—H bond (Å)	Strength of C—H bond (kcal/mol)
 ethane	*sp*^{3}	109.5°	1.54	90.2	1.10	101.1
 ethene	*sp*^{2}	120°	1.33	174.5	1.08	110.7
H—C≡C—H ethyne	*sp*	180°	1.20	230.4	1.06	133.3

Summary

- The shorter the bond, the stronger it is.
- The greater the electron density in the region of
- orbital overlap, the stronger the bond.
- The more *s* character, the shorter and stronger the bond.
- The more *s* character, the larger the bond angle.

A π Bond is Weaker Than a σ Bond



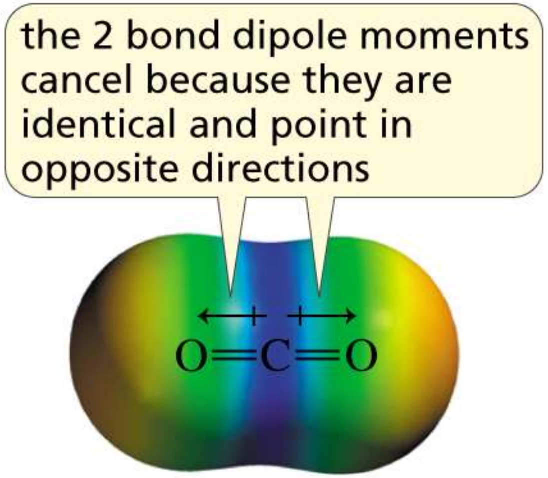
strength of the double bond = 174 kcal/mol

strength of the sp^2—sp^2 σ bond = −112 kcal/mol

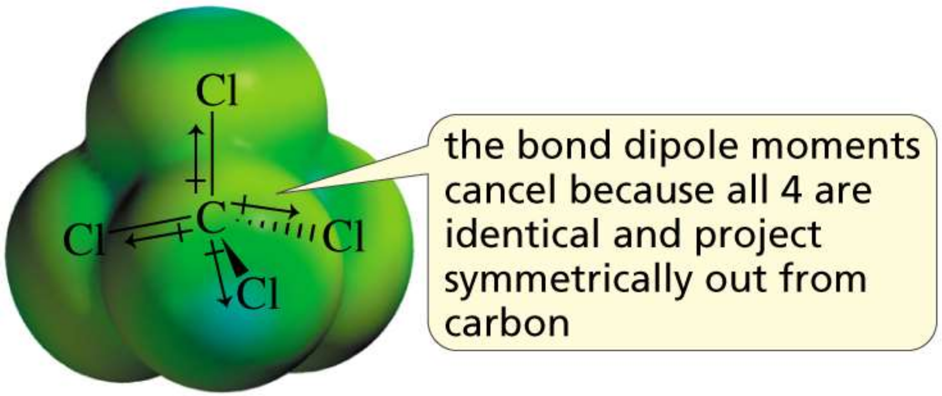
strength of the π bond = 62 kcal/mol

a π bond is weaker than a σ bond

Dipole Moments of Molecules

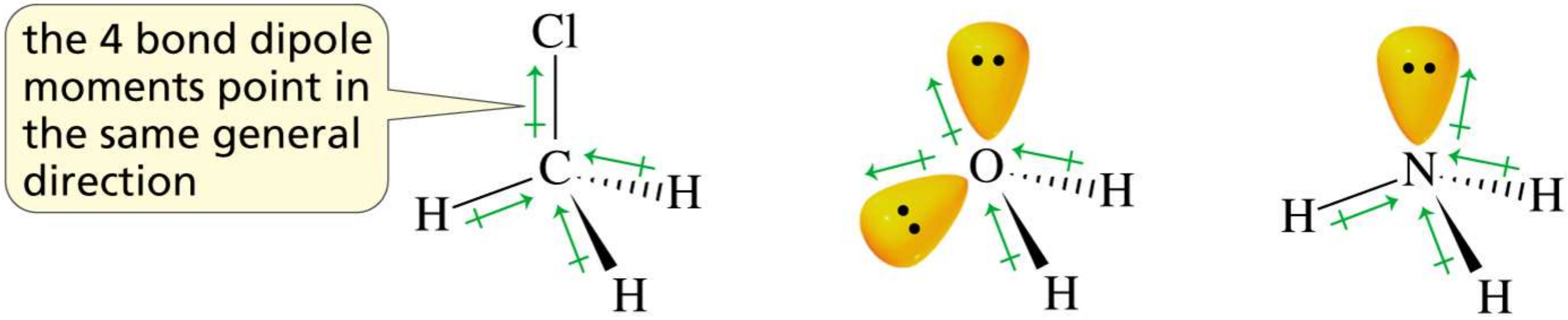


carbon dioxide
$\mu = \mathbf{0\ D}$



carbon tetrachloride
$\mu = \mathbf{0\ D}$

Dipole Moments of Molecules



chloromethane
$\mu = 1.87$ D

water
$\mu = 1.85$ D

ammonia
$\mu = 1.47$ D