Module 1 Electronic Structure and Covalent Bonding
Lecture 1 Structure and Bonding I

1.1 The Structure of an Atom

An atom consists of a tiny dense nucleus surrounded by electrons. The nucleus contains positively charged protons and neutral neutrons. A neutral atom has an equal number of protons and electrons. Atoms can gain electrons and thereby become negatively charged, or they can lose electrons and become positively charged. However, there won't be any change in the number of protons. Most of the mass of an atom is in its nucleus and most of the volume of an atom is occupied by its electrons. The atomic number of an atom equals to the number of protons and the number of electrons. The mass number of an atom is the sum of its protons and neutrons. The number of neutrons of an atom can be varied, so an atom can have different mass number.

1.2 The Distribution of Electrons in an Atom

The electrons are the greatest importance in organic chemistry. A neutral atom of each element contains an equal number of protons and electrons. According to quantum mechanics, the electrons in an atom can be thought of as occupying a set of shells. The first shell is the closest to the nucleus and subsequent shells lies farther from the nucleus. Each shell contains subshells known as atomic orbitals that have a characteristic shape and energy. They occupy a characteristic volume of the space. The atomic orbital that is close to the nucleus, is lower in its energy.

The first shell consists of only *s* atomic orbital. The second shell consists of *s* and three degenerate *p* atomic orbitals and the third shell contains, in addition, five degenerate *d* atomic orbitals. The fourth and higher shells contain, in addition, seven degenerate *f* atomic orbitals. Degenerate orbitals are orbitals that have the same energy. Each atomic orbital can have maximum of two electrons. There are only two electrons in the first shell as it has only *s* atomic orbitals. The second shell can have a total of eight electrons for one *s* and three *p* atomic orbitals. The third shell has nine atomic orbitals, one *s*, three *p*, and five *d* atomic orbitals, so eighteen electrons can occupy these nine atomic orbitals. Thirty two electrons can be occupied by the sixteen atomic orbitals of the fourth shell. When the electrons are in the available orbitals with the lowest energy, we call it as the

ground-state electronic configuration of the atom. One or more electrons can jump into a higher energy orbital, if energy is applied to the atom in the ground state. We call it as an excited-state electronic configuration.

The following principles are used to determine which orbitals occupy the electrons:

- According to the **aufbau principle**, an electron always goes into the available lower energy orbital. The relative energies of the atomic orbitals follow:

  $$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f$$

  $1s$ atomic orbital is closer to the nucleus and lower in energy than $2s$ atomic orbital, which is lower in energy and closer to the nucleus than $3s$ atomic orbital. While comparing atomic orbitals in the same shell, s atomic orbital is lower in energy than p atomic orbital, and p atomic orbital is lower in energy than d atomic orbital.

- According to the **Pauli Exclusion Principle**, only two electrons can occupy each atomic orbital, and the two electrons must be of opposite spin. The single electron of a hydrogen atom occupies $1s$ atomic orbital, the second electron of a helium atom fills the $1s$ atomic orbital, the third electron of a lithium atom occupies $2s$ atomic orbital, the fourth electron of a beryllium atom fills the $2s$ atomic orbital. The fifth electron of a boron atom occupies any one of the three degenerate $2p$ atomic orbitals.

- According to the **Hund's rule,** when there are degenerate orbitals, an electron will occupy an empty orbital before it starts to pair up.

1.3 Ionic, Covalent and Polar Bonds

According to Lewis's theory, an atom is most stable if its outer shell is either filled or contains eight electrons. So it will give up, accept, or share electrons in order to achieve a filled outer shell or an outer shell that contains eight electrons. This theory is called as **octet rule**. Lithium (Li) has a single electron in its 2*s* atomic orbital. The lithium atom ends up with a filled outer shell, a stable configuration, if it loses the 2*s* electron.

Energy released on removing an electron from an atom is called **ionization energy**. Lithium has relatively low ionization energy because loss of electron leads to stable configuration and become a positively charged. The elements in the first column of the periodic table, alkali metals, are all electropositive because they lose their outermost electron readily. Electrons in inner shells, called core electrons, do not participate in chemical bonding. Electrons in the outermost shell are called **valence electrons**, and the outermost shell is called the valence shell. Carbon, for example, has two core electrons and four valence electrons.

The chemical behavior of an element depends on its electronic configuration. Elements in the same column of the periodic table have the same number of valence electrons, and have similar chemical properties. When we draw the electrons around an atom, only valence electrons are shown as a dot. Sodium readily loses its valence electron to have stable electronic configuration and becomes positive ion. Fluorine gains one electron to achieve stable electronic configuration and becomes negative ion. Energy is released when an atom gains an electron.

$$Na\cdot \longrightarrow Na^+ + e^-$$

$$:\ddot{F}\cdot + e^- \longrightarrow :\ddot{\ddot{F}}:^-$$
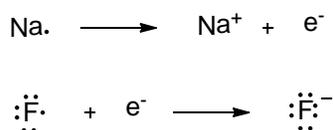
1.3.1 The Ionic Bond

A chemical compound is called an ionic compound in which the components atoms exist as ions. Crystalline KCl results when potassium metal and chlorine gas are mixed. One electron is transferred from potassium atom to chlorine.

potassium ion (K^+)
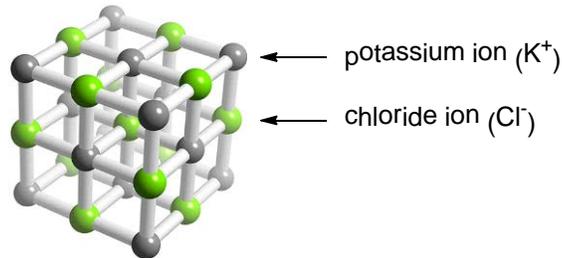
chloride ion (Cl^-)

Crystal structure of KCl

The positively charged potassium ions and negatively charged chloride ions are held together by the electrostatic attractions. An electrostatic attraction that holds ions together is called an **ionic bond**. Thus, the crystal structure of KCl is maintained by ionic bonds between potassium ions and chloride ions.

1.3.2 The Covalent Bond

The covalent bond consists of an electron pair that is shared between bonded atoms instead of giving up or gaining electrons. Two hydrogen atoms can form a covalent bond by sharing electrons. As a result of covalent bonding, each hydrogen acquires a stable, filled outer shell electronic configuration. Similarly, hydrogen and chlorine can form a covalent bond by sharing electrons.

covalent bond

covalent bond
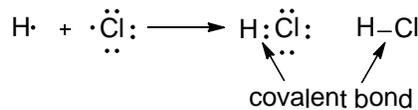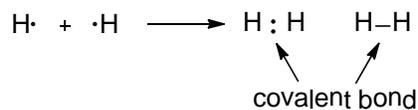
Molecular structures that use this notation for the electron pair bond are called **Lewis structures**. A hydrogen atom can achieve a completely empty shell by losing an electron and become a positively charged hydrogen ion, called proton. A hydrogen atom can achieve a filled outer shell by gaining an electron, thereby forming a negatively charged hydrogen ion, called hydride ion.

$$H\cdot \longrightarrow H^+ + e^-$$

hydrogen atom   proton

$$H\cdot + e^- \longrightarrow H\colon^-$$

hydrogen atom   hydride ion
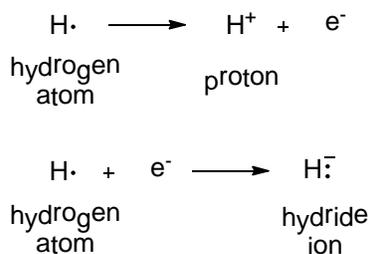
In some covalent compounds, however, some valence electrons remain unshared. For example, water (H_2O) has six valence electrons. Two of these combine with hydrogens to make two O-H covalent bonds and four of the valence electrons remain unshared.

$$H\cdot + \cdot\ddot{O}\colon \longrightarrow H\colon\ddot{O}\colon H$$

hydrogen atom   oxygen atom   water   unshared pairs
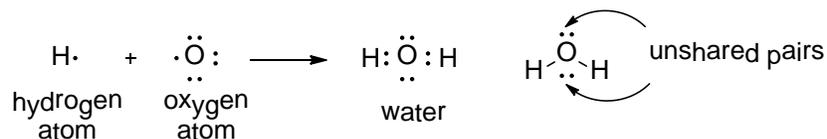
Ionic species such as $[SO_2]^{2-}$, $[NH_4]^+$ and $[BF_4]^-$ also contain covalent bonds. For an example, the tetrafluroborate anion contains covalent B-F bonds.

$$\left[\begin{array}{c} F \\ | \\ F-B-F \\ | \\ F \end{array}\right]^-$$

tetrafluroborate ion
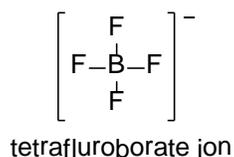
The charge on each atom is called formal charge and the sum of the formal charges on the individual atoms must be equal to the total charge on the ion.

1.3.2 Polar Covalent Bonds

In many covalent bonds the electrons are not shared equally between two bonded atoms. For example, in hydrogen chloride the electrons are unevenly distributed between the two atoms because the atoms that share the electrons in the molecule are different and have different electronegativities. *Electronegativity* is the tendency of an atom to pull bonding electrons toward it. It increases as you go from left to right across a row of the periodic table or down to up in any of the columns. A bond in which electrons are shared unevenly is called a **polar bond** or **polar covalent bond**. A polar bond has a slight positive charge on one end and a slight negative charge on the other end. The greater the difference in electronegativity between the bonded atoms, the more polar the bond will be. The direction of bond polarity can be indicated with an arrow. The head of the arrow is at the negative end of the bond; a short perpendicular line near the tail of the arrow marks the positive end of the bond.

$$\delta^+ \quad \delta^-$$
$$H-Cl \qquad\qquad H-Cl$$

In this notation, the delta can be read as "partially" that indicates the hydrogen atom of HCl is "partially positive," and the chlorine atom is "partially negative." The uneven electron distribution in a compound containing covalent bonds is measured by a quantity called the **dipole moment** (μ). The dipole moment is commonly given in derived units called *debyes*, abbreviated D. The dipole moment is defined by the following equation:

$$\mu = q\mathrm{r}$$

In this equation, q is the magnitude of the separated charge and r is a vector from the side of positive charge to the site of negative charge. For example, the HCl molecule has a dipole moment of 1.08 D. Molecules that have permanent dipole moments are called polar molecules. Some molecules contain several polar bonds. In such case, each polar bond has associated with it's a dipole moment contribution, called a **bond dipole**. The net dipole moment of such a polar molecule is the vector sum of its bond dipoles. Carbon dioxide molecule is not a polar molecule, even though it has polar bonds. Carbon dioxide is linear, and the C-O bond dipoles are oriented in opposite directions. So they cancel out each other and the dipole moment is zero.

1.4 Representation of Structure

Lewis structures represent the valence electrons of an atom as dots. By using Lewis structures one can recognize if any atoms possess lone-pair electrons or have a formal charge. For example, water and hydroxide ion can be represented by Lewis structures as shown below.

$$H:\overset{..}{\underset{..}{O}}:H \qquad H:\overset{..}{\underset{..}{O}}:^-$$

water   hydroxide ion
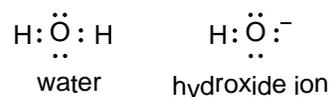
Valence electrons not used in bonding are called nonbonding electrons or lone-pair electrons. A positive or a negative charge assigned to an atom is called a formal charge; water molecule has no formal charge but the oxygen atom in the hydroxide ion has a formal charge of -1.

$$\text{formal charge} = \begin{array}{c}\text{number of}\\\text{valence electrons}\end{array} - \left(\begin{array}{c}\text{number of}\\\text{lone-pair electrons}\end{array} + \frac{\text{number of bonding electrons}}{2}\right)$$

Nitrogen has five valence electrons and the Lewis structures of ammonia, ammonium ion, and amide anion are shown below. Ammonium ion has a formal charge of +1 and amide anion has a formal charge of -1.

$$\begin{array}{ccc} & H & \\ H:\overset{..}{N}:H & H:\overset{..}{N}^+:H & H:\overset{..}{\underset{..}{N}}:H^- \\ H & H & \\ \text{ammonia} & \text{ammonium ion} & \text{amide anion} \end{array}$$
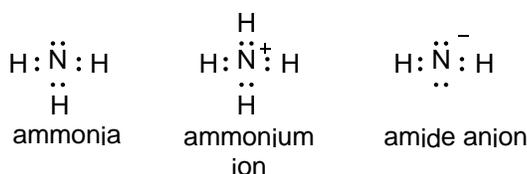
Carbon has four valence electrons and the Lewis structures of methane, methyl cation, methyl anion, and methyl radical are shown below.

$$\begin{array}{cccc} H & H & H & H \\ H:\overset{..}{\underset{..}{C}}:H & H:\overset{..}{\underset{..}{C}}+ & H:\overset{..}{\underset{..}{C}}:^- & H:\overset{..}{\underset{..}{C}}\cdot \\ H & H & H & H \\ \text{methane} & \text{methyl cation} & \text{methyl anion} & \text{methyl radical} \end{array}$$
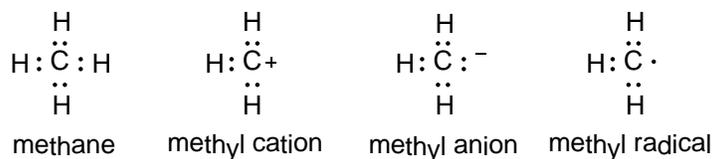
A species containing a positively charged carbon atom is called a **carbocation**, and a species containing a negatively charged carbon atom is called a **carbanion**. A species containing an atom with a single unpaired electron is called a **radical** or a **free radical**.

Hydrogen has one valence electron and each halogen (F, Cl, Br, I) has seven valence electrons, so the following species have the indicated formal charges:

$$H^+ \qquad H\colon^- \qquad H\cdot \qquad :\ddot{B}r\colon\colon\ddot{B}r\colon \qquad :\ddot{B}r\cdot \qquad :\ddot{B}r\colon^-$$

proton   hydride ion   hydrogen radical   bromine   bromine radical   bromide ion
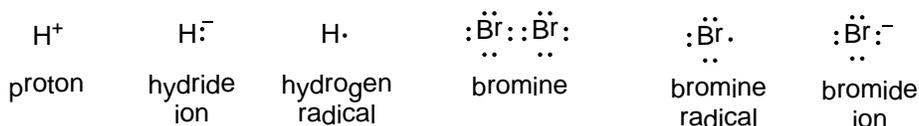
A pair of shared electrons can also be shown as a line between two atoms. The hydrogen has one covalent bond and no lone pair. The halogens have one covalent bond and three lone pairs. The oxygen of water has two covalent bonds and two lone pairs. The nitrogen of ammonia has three covalent bonds and one lone pair. Each atom has a complete octet except hydrogen which has completely filled outer shell.

$$H–H \qquad :\ddot{B}r–\ddot{B}r\colon \qquad H\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}H \qquad H\overset{\underset{|}{N}–H}{\underset{\cdot\cdot}{}}H$$

hydrogen   bromine   water   ammonia
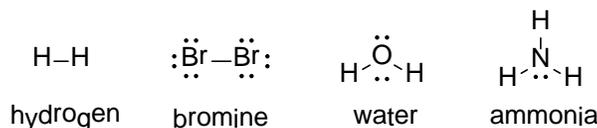
Kekulé structures represent the bonding electrons as lines and the lone-pair electrons are usually left out entirely, unless they are needed to draw a mechanism for a chemical reaction.

$$H–O–H \qquad H–N(H)–H \qquad H–C(H)(H)–H \qquad H–C\equiv N \qquad H–C(=O)–O–H$$

water   ammonia   methane   hydrogen cyanide   formic acid
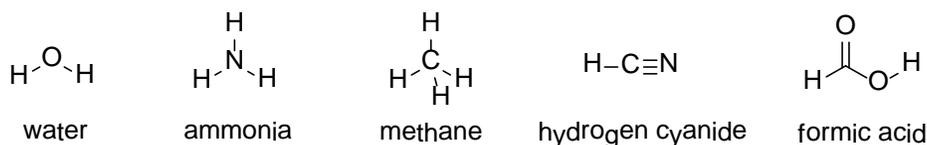
Sometimes some of the covalent bonds of the structure of a compound are omitted for simplification. These kinds of structures are called **condensed structures**.

$$H_2O \qquad NH_3 \qquad CH_4 \qquad HCN \qquad HCOOH$$

water   ammonia   methane   hydrogen cyanide   formic acid
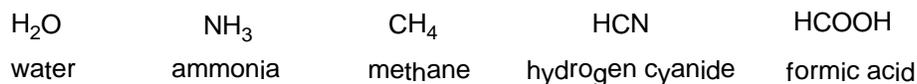
1.5 Atomic Orbitals

An orbital is a three-dimensional region around the nucleus where the probability of finding an electron is high. Mathematical calculations and experimental evidence indicate that the *s* atomic orbital is a sphere with the nucleus at its center. According to the ***Heisenberg uncertainty principle***, both the location and the momentum of an atomic particle cannot be determined simultaneously.

We can never say exactly where an electron is. We can only describe its probable location. If we say that an electron occupies a 1*s* atomic orbital, it means, there is a greater than 90% probability of finding the electron in the space which is defined as the sphere for *s* orbital. The average distance from the nucleus is greater for an electron in a 2*s* atomic orbital than for an electron in a 1*s* atomic orbital. Consequently, the average electron density in a 2*s* atomic orbital is less than the average electron density in a 1s atomic orbital. An electron in a 1*s* atomic orbital can be anywhere within the 1*s* sphere, but there is a node in a 2*s* atomic orbital where the probability of finding an electron is zero.

| 1*s* atomic orbital | 2*s* atomic orbital node not shown | 2*s* atomic orbital node shown |
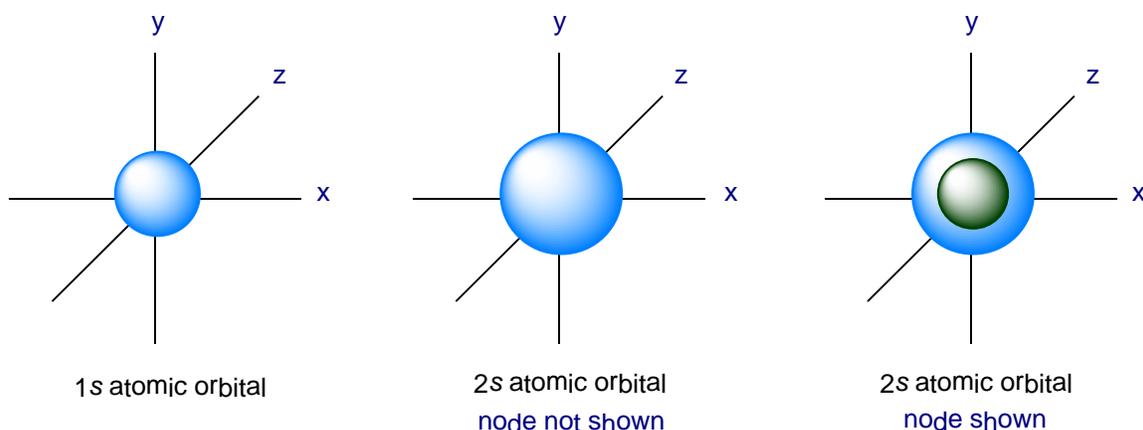
Unlike *s* atomic orbitals, *p* atomic orbitals have two lobes which are of opposite phase. These two phases can be designated by plus and minus signs.

A plane that passes through the center of the nucleus of the *p* atomic orbital is called, nodal plane that bisects the two lobes. There is zero probability of finding an electron in the nodal plane of the *p* orbital.
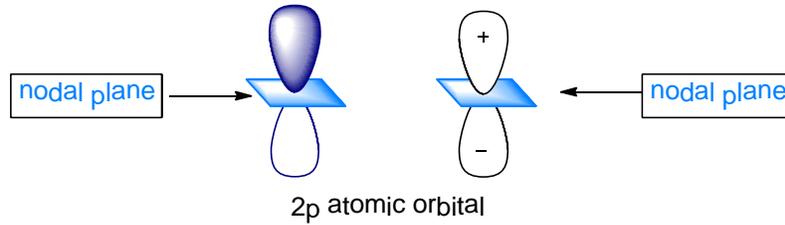
2p atomic orbital

We have seen that there are three degenerate p atomic orbitals. The p_x orbital is symmetrical about the x-axis, p_y the orbital is symmetrical about the y-axis, and p_z the orbital is symmetrical about the z-axis. All these p orbitals are perpendicular to each other. The energy of a $2p$ atomic orbital is slightly greater than that of a 2s atomic orbital.

$2p_x$ orbital $2p_y$ orbital $2p_z$ orbital
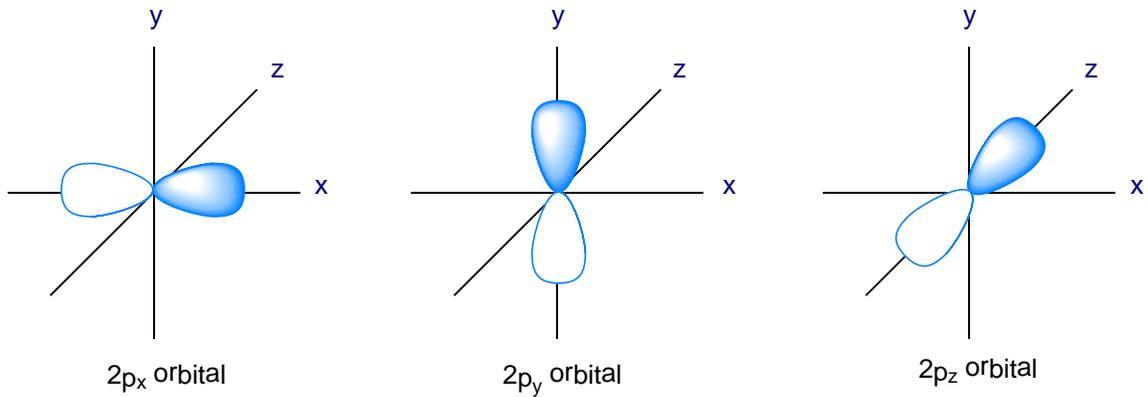
Module 1 Electronic Structure and Covalent Bonding
Lecture 2 Structure and Bonding II

1.6 Molecular Orbital Theory

According to molecular orbital theory, covalent bonds result from the combination of two atomic orbitals to form molecular orbitals. For example, in hydrogen molecule the 1*s* atomic orbital of one hydrogen atom overlaps with the 1*s* atomic orbital of a second hydrogen atom to give a molecular orbital. The covalent bond that is formed when the two *s* atomic orbitals overlap is called a cylindrically symmetrical *σ*-bond.
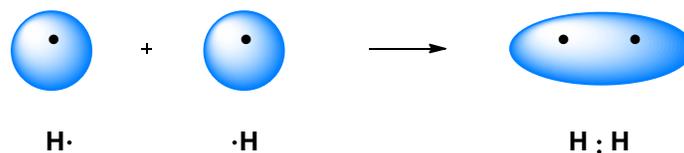
- During bond formation, energy is released as the two orbitals start to overlap. More energy released as increases the overlap of orbitals. When the atoms approach each other, their positively charged nuclei repel each other. This repulsion causes a large increase in
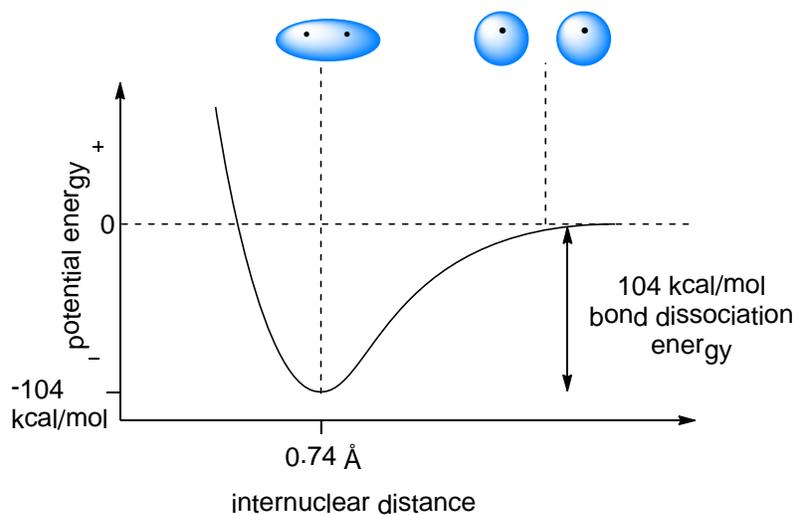
Figure 1

energy. We see that maximum stability is achieved when the nuclei are a certain distance apart. This distance is the bond length of the covalent bond which is 0.74 Å for hydrogen molecule (Figure 1). When the bond forms, 104 kcal/mol of

energy is released and the same amount of energy has to be given for breaking the bond. The energy required to break a bond is called the ***bond dissociation energy***.

- Atomic orbitals can combine in two different ways. For example, the $1s$ orbitals of two hydrogen atoms approach each other and combine constructively, when they are in phase and have the same sign, to give a σ bonding molecular orbital (Figure 2).

Constructive Interaction

The two $1s$ orbitals are in phase

σ bonding molecular orbital
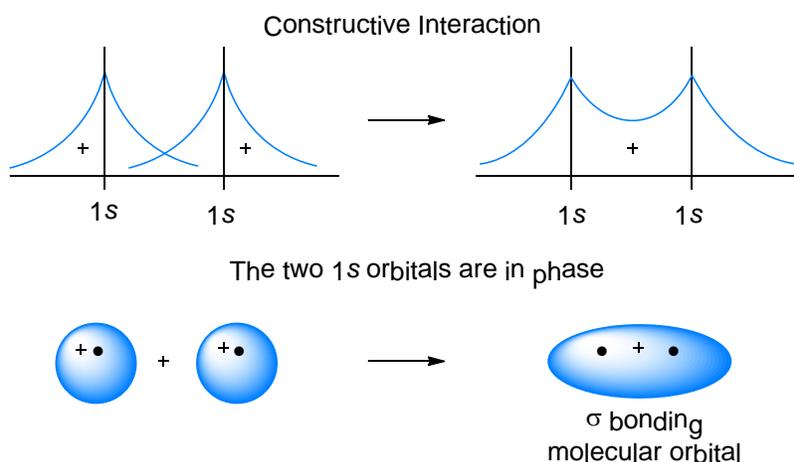
Figure 2

- When two hydrogen $1s$ orbitals overlap out of phase with each other, an σ^* antibonding molecular orbital results. When the two $1s$ orbitals have opposite signs, they tend to cancel out where they overlap. The result is a node that separates the two atoms (Figure 3).

- The relative energies of the atomic orbitals and the molecular orbitals of the system are shown in the molecular orbital diagram (Figure 4). In the MO diagram, the energies are represented as horizontal lines; the bottom line is the lowest energy level, the top line the highest energy level. When the $1s$ orbitals are in phase, the resulting molecular orbital is an σ-bonding molecular orbital which is lower in energy than that of a $1s$ atomic orbital.

Destructive interaction

node

+

−

+

−

The two 1s orbitals are out of phase

+ • + − •

+ • • −

σ* antibonding
molecular orbital

Figure 3

node

σ* antibonding molecular orbital

energy

1s atomic
orbital

1s atomic
orbital

σ bonding molecular orbital
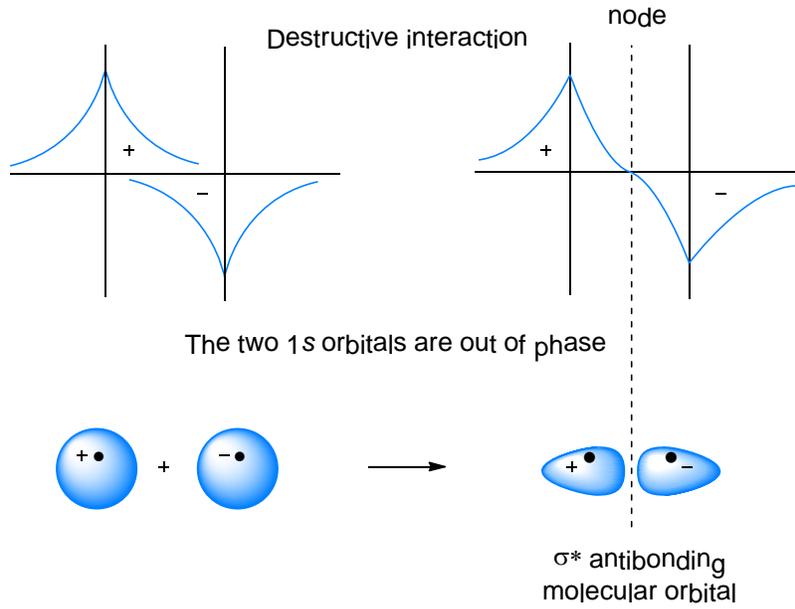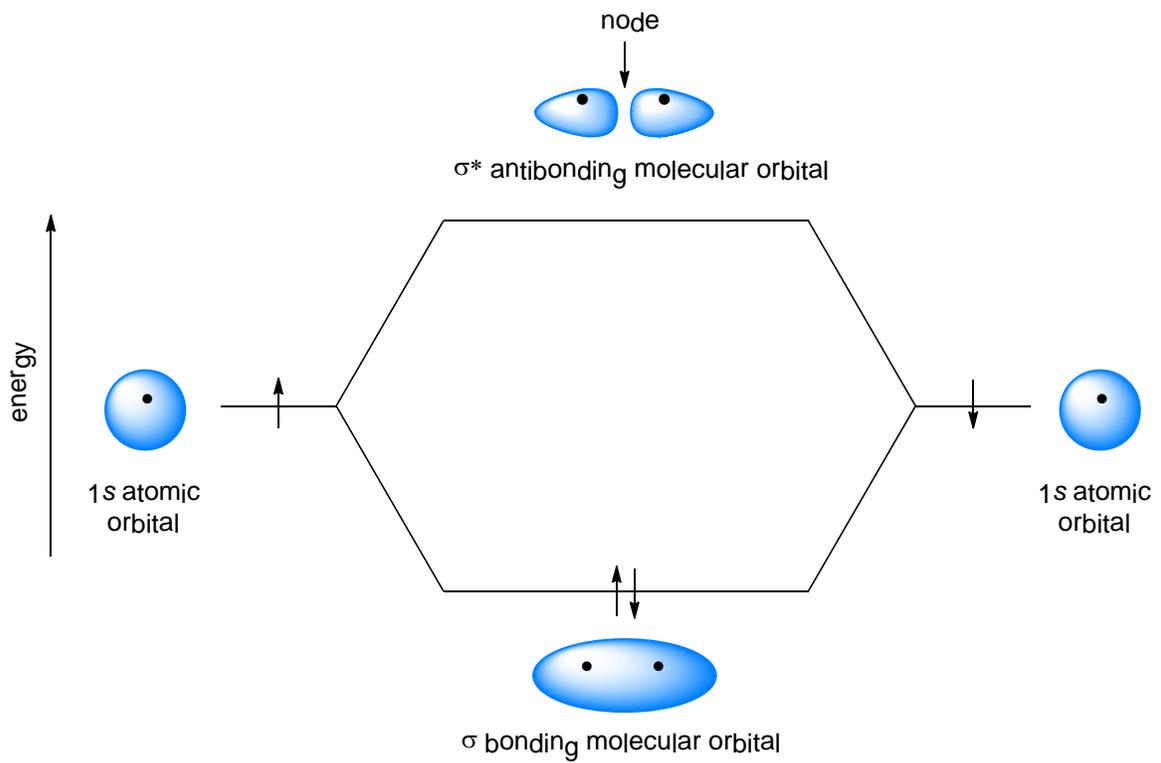
Figure 4

- When two 1s orbitals overlap out of phase, they form an antibonding orbital which is higher in energy than that of a 1s atomic orbital. After the MO diagram is constructed, the electrons are assigned to the molecular orbitals according to the *Aufbau Principle* and the *Pauli Exclusion Principle* which state that electrons always occupy available the lower energy orbitals and no more than two electrons can occupy one molecular orbital.

- We can also predict whether a compound is stable to exist. For example, helium would have four electrons. Two of them can be filled in the lower energy bonding molecular orbital and the remaining two can be filled in the higher energy antibonding molecular orbital. The two electrons in the antibonding molecular orbital would cancel the advantage to bonding gained by the two electrons in the bonding molecular orbital.

- Two p atomic orbitals can overlap either end-on or side-to-side (Figure 5). First, let us consider end-on overlap. If the overlapping lobes of the p orbitals are in-phase, an σ bonding molecular orbital is formed. The electron density of the bonding molecular orbital is concentrated between the nuclei, which causes the back lobes of the molecular orbital to be quite small. The bonding molecular orbital has two nodes.

- If the overlapping lobes of the p orbitals are out-of-phase, an σ^* antibonding molecular orbital is formed. The antibonding molecular orbital has three nodes.

- Side-to-side overlap of two p atomic orbitals forms a π-bond (Figure 6). Side-to-side overlap of two in-phase p atomic orbitals forms a π bonding molecular orbital, whereas side-to-side overlap of two out-of-phase p orbitals forms an π^* antibonding molecular orbital.

- The bonding molecular orbital has one nodal plane that passes through both nuclei. The antibonding molecular orbital has two nodal planes.

- The bond formed by the end-on overlap of p orbitals is stronger than a bond formed by the side-to-side overlap of p orbitals. So an σ bonding molecular orbital is more stable than a π bonding molecular orbital.
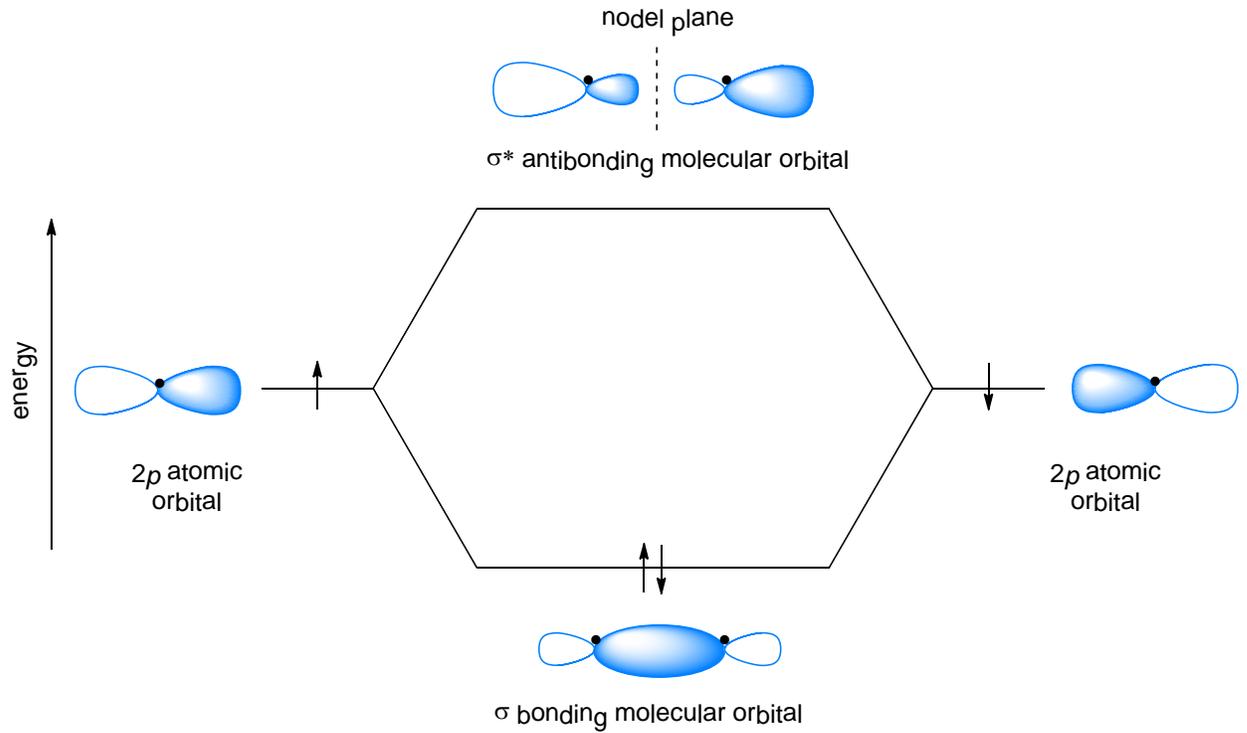
Figure 5
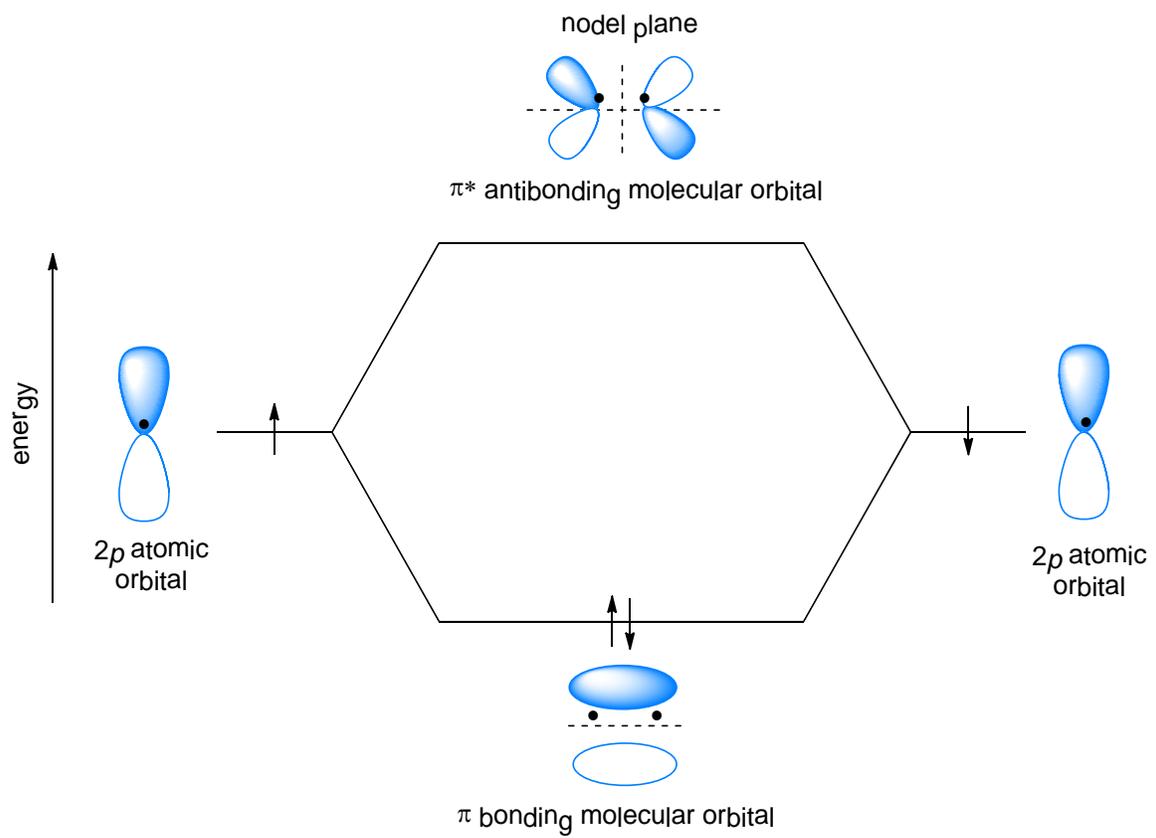
Figure 6

1.7 Hybridization and Molecular Shapes

If we consider the bond angles of organic molecules using *s* and *p* orbitals, we expect bond angles of about 90° because *s* orbitals are nondirectional, and the *p* orbitals are oriented at 90° to one another. But experimental evidence shows, however, that bond angles in most of organic compounds are close to 109°, 120° or 180°.

According to ***valence-shell electron-pair repulsion theory*** (VSEPR theory), the bonds pair and the lone pair electrons repel each other and attain the largest possible angles. An angle of 109.5° is the largest possible separation for four pairs of electrons, 120° is the largest separation for three pairs, and 180° is the largest separation for two pairs.

To explain the shapes of common organic molecules, we assume that the *s* and *p* orbitals combine to form hybrid orbitals that separate the electron pairs more widely in space. Hybrid orbitals are mixed orbitals that they result from combining orbitals. The concept of combining orbitals is called hybridization.

1.7.1 sp^3 Hybrid Orbitals

Methane is the simplest example of *sp*^{3} hybridization. Methane has four covalent bonds with same length. The bond angles of all the covalent bonds are same (109.5°) which gives a tetrahedron shape. So the four bonds in methane are identical.

methane
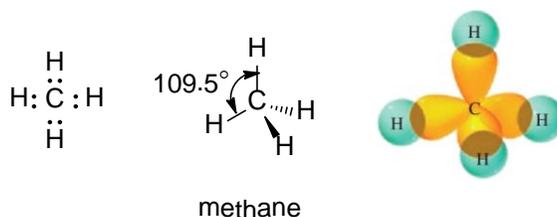
These four degenerate orbitals are called *sp*^{3} hybrid orbitals formed by the combination of one *s* orbital and three *p* orbitals. Each orbital has 25% *s* character and 75% *p* character.
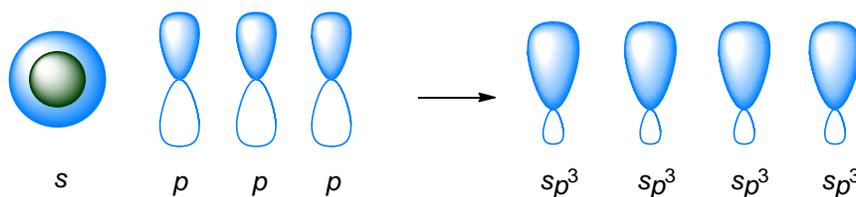
A sp^3 orbital has two lobes with different size because the s orbital adds to one lobe of the p orbital and subtracts from the other lobe of the p orbital. The larger lobe of the orbital is used in covalent bond formation. The four orbitals arrange themselves as far away as possible in space to minimize the repulsion. They point toward the corners of a regular tetrahedron.

The negatively charged carbon in the methyl anion has three pairs of bonding electrons and one lone pair. The four pairs of electrons, three bond pair and two electrons, point toward the corners of a tetrahedron. In the methyl anion, three of carbon's sp^3 orbitals overlap with the s orbital of a hydrogen and forms covalent bonds, and the fourth sp^3 orbital holds the lone pair.

$\bar{C}H_3$
methyl anion
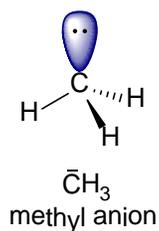
1.7.2 sp^2 Hybrid Orbitals

When an s orbital combines with two p orbitals, three hybrid orbitals results that are oriented at 120° angles to each other. These orbitals are called sp^2 hybrid orbitals. The remaining unhybridized p orbital perpendicular to the plane of the three sp^2 hybrid orbitals. The 120° arrangement is called trigonal geometry.

sp^2 hybrid carbon atom
(viewed from the side)

structure of
BH$_3$ molecule
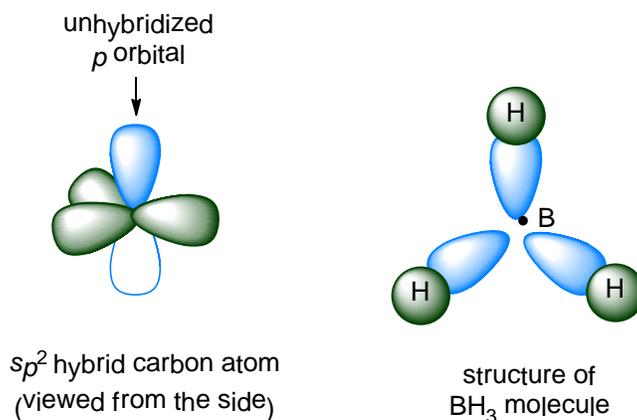
For example, each carbon atom of ethene has three sp^2 hybridized orbital and one unhybridized p orbital. The sp^2 hybridized orbital of each carbon atom forms two σ-bonds by overlapping with s orbitals of two hydrogens and one σ-bond by overlapping with sp^2 orbital of the other carbon atom. The sidewise overlap of the unhybridized p orbital of each carbon atom gives a π-bond.
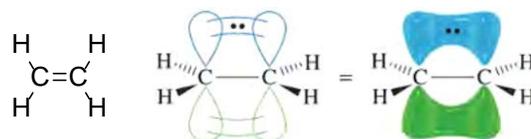
The positively charged carbon in the methyl cation is sp^2 hybridized. It forms three covalent bonds using sp^2 orbitals by overlapping with s orbital of hydrogen atom. Its unhybridized p orbital stands perpendicular to the plane and remains empty.
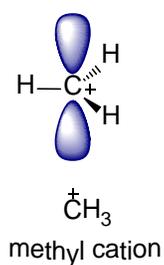
The carbon atom in the methyl radical is also sp^2 hybridized. The methyl radical has one unpaired electron. That electron is in the unhybridized p orbital.
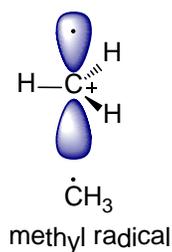
1.7.3 sp Hybrid Orbitals

When an *s* orbital and a *p* orbital of an atom combine, a *sp* hybridized orbital is formed. For example, each carbon atom of ethyne has one *sp* hybridized orbital and two unhybridized *p* orbitals. The two unhybridized *p* orbitals are perpendicular to each other. One end of the *sp* hybridized orbital overlap with *s* orbital of hydrogen and the other end overlap with *sp* hybridized orbital of the other carbon atom. Sidewise overlap of two unhybridized p orbitals gives a π-bond. So ethyne molecule has one σ-bond and two π-bonds. These hybrid orbitals give a bond angle of 180° that leads to linear arrangement.

$H–C{\equiv}C–H$

overlap of *p*-orpitals