

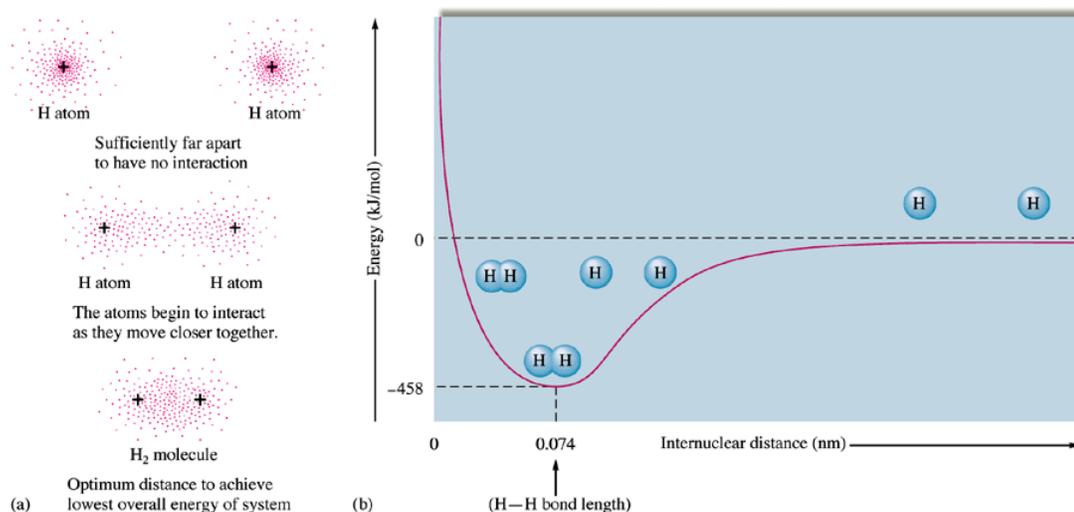
Chapter 8 Outline – Bonding: General Concepts

Types of Chemical Bonds

- Information about the strength of a bonding interaction is obtained by measuring the **bond energy**, which is the energy required to break the bond.
- Ionic bonding occurs between an element that loses electrons easily reacts with an atom that has a high affinity for electrons. Ionic compounds are formed between a metal and a non-metal.
- The energy of interaction between a pair of ions can be calculated using Coulomb's law in the form:

$$E = (2.31 \times 10^{-19} \text{ J} \cdot \text{nm}) \left(\frac{Q_1 Q_2}{r} \right);$$
 E has units of joules, r is the distance between the ion centers in nanometers, and Q_1 and Q_2 are the numerical ion charges.
- For example: in solid NaCl, the distance between Na^+ and Cl^- ions is 2.76 Å (0.276 nm), and the ionic energy per pair of ions is:

$$E = (2.31 \times 10^{-19} \text{ J} \cdot \text{nm}) \left(\frac{(+1)(-1)}{0.276} \right) = -8.37 \times 10^{-19} \text{ J}$$
 where the negative sign equals an attractive force. The ion pair has lower energy than the separated ions.
- A bond will form if the system can lower its total energy in the process.
- In a bond between two hydrogen atoms, the system will act to minimize the sum of the positive (repulsive) energy terms and the negative (attractive) energy term. The distance where the energy is minimal is called the bond length.

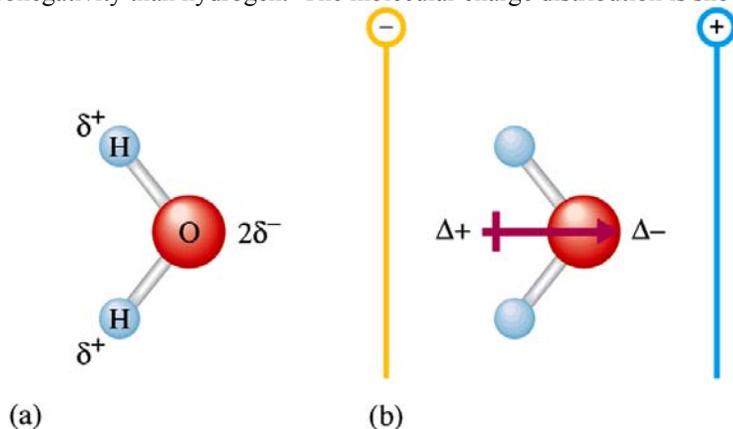


- The zero point of energy is defined with atoms at infinite separation.
- At very short distances the energy rises steeply because of the importance of the repulsive forces when atoms are very close together.
- The bond length is the distance at which the system has minimum energy.
- H_2 is a non-polar covalent bond where the two hydrogen nuclei share the valence electrons equally.
- HF exhibits a polar-covalent bond where the electrons are shared unequally, showing an attraction to the more electronegative element.

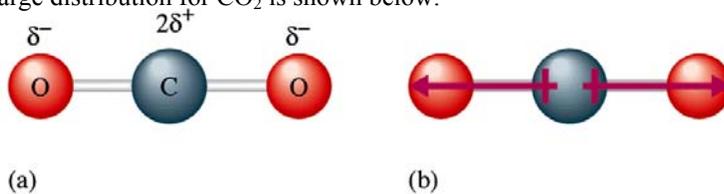
Electronegativity

- Electronegativity is the ability of an atom in a molecule to attract shared electron.
- The widely accepted method for determining electronegativity values is that of Linus Pauling (1901-1995), an American scientist who won the Nobel Prizes for both chemistry and peace.

- Any diatomic (two-atom, but not necessarily the same atoms) molecule that has a polar bond also will show a dipole moment.
- Polyatomic molecules can also exhibit dipolar behavior. For example, in water, oxygen has a higher electronegativity than hydrogen. The molecular charge distribution is shown below.



- Some molecules have polar bonds but do not have a dipole moment. This occurs when the individual bond polarities are arranged in such a way that they cancel each other out. CO_2 is an example of this behavior. The charge distribution for CO_2 is shown below.



- SO_3 is also a molecule with polar bonds but overall no dipole moment. This is due to its molecular shape. More will be covered on molecular shapes later this chapter.

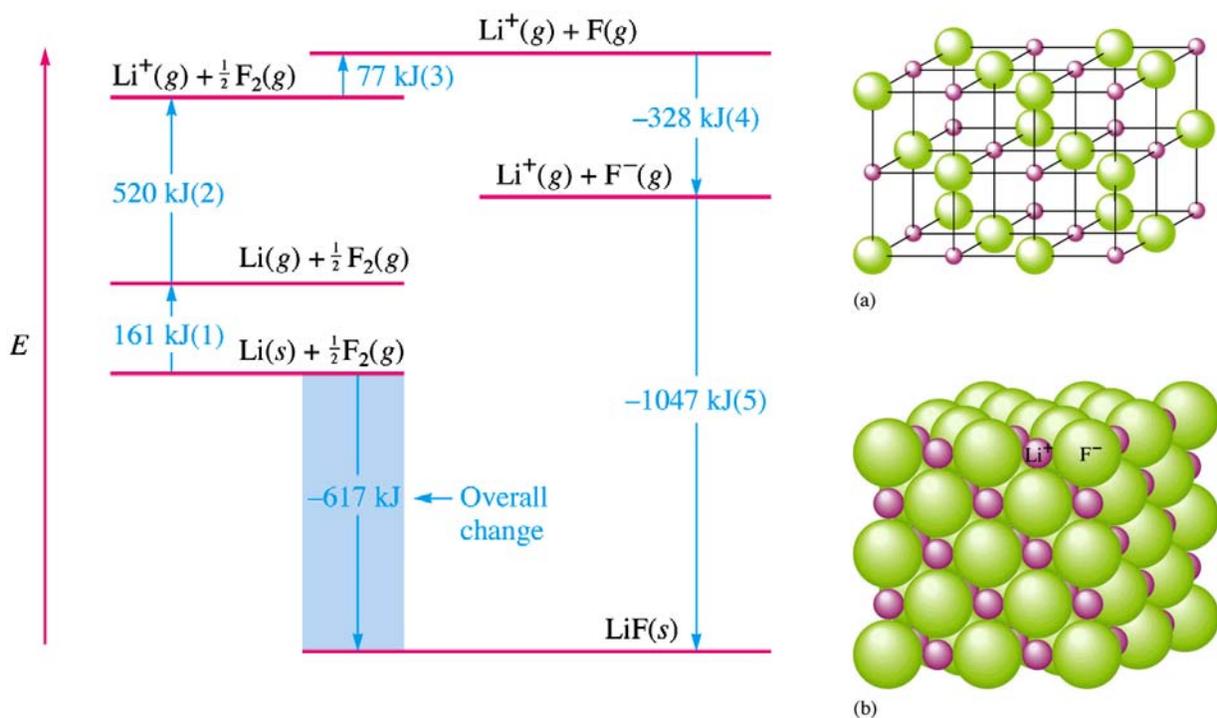
Ions: Electron Configuration and Sizes

- In virtually every case, the atoms in a stable compound have a noble gas arrangement of electrons.
- When two nonmetals react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms. Both nonmetals attain noble gas electron configurations.
- When a nonmetal and a representative-group metal react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal achieves the electron configuration of the next noble gas atom and the valence orbitals of the metal are emptied.
- There are some important exceptions to the rules above.
 - Sn forms Sn^{2+} and Sn^{4+}
 - Pb forms Pb^{2+} and Pb^{4+}
 - Bi forms Bi^{3+} and Bi^{5+}
 - Tl forms Tl^+ and Tl^{3+}
- Ion size plays an important role in determining the structure and stability of ionic solids, the properties of ions in aqueous solution, and the biological effects of ions.
- Since a positive ion is formed by removing one or more electrons from a neutral atom, the resulting cation is smaller than its parent atom. The opposite is true for negative ions; the addition of electrons to a neutral atom produces an anion significantly larger than its parent atom.
- Ion size increases going down a group. Horizontally, the trend is complicated because metals on the left side of the periodic table form cations, and nonmetals on the right side of the periodic table form anions.
- One trend worth noting involves relative sizes of a set of isoelectronic ions – ions containing the same number of electrons.
- Consider the ions O^{2-} , F^- , Na^+ , Mg^{2+} and Al^{3+} .

- Since all species have the same number of electrons, it can be assumed that as the number of protons increases, the attraction between protons and electrons will increase and make the ionic size smaller.
- **In summary, for isoelectronic ions, the greater the atomic number, the smaller the ionic radius.**
- You try: Arrange the ions Se^{2-} , Br^- , Rb^+ and Sr^{2+} in order of decreasing size.

Formation of Binary Ionic Compounds

- Ionic compounds form because the aggregated oppositely charged ions have a lower energy than the original elements.
- Just how strongly the ions attract each other in the solid state is indicated by the lattice energy – *the change in energy that takes place when separated gaseous ions are packed together to form an ionic solid*:
 - $\text{M}^+(\text{g}) + \text{X}^-(\text{g}) \rightarrow \text{MX}(\text{s})$
- Lattice energy is often defined as the amount of energy released when an ionic solid forms from its ions, so lattice energy will have a negative value.
- Consider the energy change associated with the following reaction: $\text{Li}(\text{s}) + \frac{1}{2} \text{F}_2(\text{g}) \rightarrow \text{LiF}(\text{s})$
 - Step 1: Sublimation of solid lithium. $\text{Li}(\text{s}) \rightarrow \text{Li}(\text{g})$ $\Delta E = 161 \text{ kJ/mol}$
 - Step 2: Ionization of lithium atom. $\text{Li}(\text{g}) \rightarrow \text{Li}^+(\text{g}) + \text{e}^-$ $\Delta E = 520 \text{ kJ/mol}$
 - Step 3: Dissociation of fluorine molecules. $\frac{1}{2} \text{F}_2(\text{g}) \rightarrow \text{F}(\text{g})$ $\Delta E = 77 \text{ kJ/mol}$
 - Step 4: Formation of fluoride ions. $\text{F}(\text{g}) + \text{e}^- \rightarrow \text{F}^-(\text{g})$ $\Delta E = -328 \text{ kJ/mol}$
 - Step 5: Formation of LiF from $\text{Li}^+(\text{g})$ and $\text{F}^-(\text{g})$ ions. $\text{Li}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{LiF}(\text{s})$ $\Delta E = -1047 \text{ kJ/mol}$
 - By adding the ΔE values, the $\Delta E_{\text{overall}} = -617 \text{ kJ/mol}$ of LiF. This is an exothermic reaction.



- The lattice structure of lithium fluoride is shown above. All the binary ionic compounds formed by an alkali metal (except cesium) and a halogen have the same lattice structure as lithium fluoride. It is sometimes called the sodium chloride structure.

Partial Ionic Character of Covalent Bonds

- When atoms with different electronegativities react to form molecules, the electrons are not shared equally. The possible result is a polar covalent bond or, if the electronegativity difference is great enough, a complete transfer of one or more electrons to form ions.
- Percent ionic character of a bond = (measured dipole moment of X—Y) ÷ (calculated dipole moment of X⁺Y⁻) x 100%
- Generally compounds with more than 50% ionic character are normally considered to be ionic solids.
- Since compounds such as ammonium chloride and sodium sulfate contain both ionic and covalent bonds, ionic compounds will be defined as any compound that conducts an electric current when melted.

Covalent Bond Energies and Chemical Reactions

- Consider the stepwise decomposition of methane:
 - CH₄(g) → CH₃(g) + H(g) energy required: 435 kJ/mol
 - CH₃(g) → CH₂(g) + H(g) energy required: 453 kJ/mol
 - CH₂(g) → CH(g) + H(g) energy required: 425 kJ/mol
 - CH(g) → C(g) + H(g) energy required: 339 kJ/mol
 - Total = 1652 ÷ 4 = 413 kJ/mol
 - Note that the C—H bond is somewhat sensitive to its environment
- Consider the following molecules and the measured C—H bond energy (kJ/mol)

Molecule	Measure C-H bond energy (kJ/mol)
HCB ₃	380
HCCl ₃	380
HCF ₃	430
C ₂ H ₆	410

- Again, C—H bond strength varies significantly with its environment, but the concept of an average bond energy is helpful to chemists.
- The average bond energies for various types of bonds are listed below.

TABLE 8.4 Average Bond Energies (kJ/mol)

Single Bonds				Multiple Bonds			
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200			C=O*	745
H—I	295	N—Br	243	S—H	347	C≡O	1072
		N—O	201	S—F	327	N=O	607
C—H	413	O—H	467	S—Cl	253	N=N	418
C—C	347	O—O	146	S—Br	218	N≡N	941
C—N	305	O—F	190	S—S	266	C≡N	891
C—O	358	O—Cl	203			C=N	615
C—F	485	O—I	234	Si—Si	340		
C—Cl	339			Si—H	393		
C—Br	276	F—F	154	Si—C	360		
C—I	240	F—Cl	253	Si—O	452		
C—S	259	F—Br	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C=O(CO₂) = 799

- Note that single, double and triple bonds exist. In a single bond, one pair of electrons is shared, in a double bond, two pairs of electrons are shared and in a triple bond, three pairs of electrons are shared. Single bonds are the longest and weakest of the bonds. Triple bonds are the shortest and the strongest of the bonds.
- For bonds to be broken, energy must be added to a system – an endothermic process.
- $\Delta H = \Sigma D(\text{bonds broken}) - \Sigma D(\text{bonds formed})$, Σ represents the sum of terms and D represents the bond energy per mole of bonds
- Example: Using the bond energies from above, calculate the ΔH for the reaction of methane with chlorine and fluorine to give Freon-12 (CF_2Cl_2)
 - $\text{CH}_4(\text{g}) + 2\text{Cl}_2(\text{g}) + 2\text{F}_2(\text{g}) \rightarrow \text{CF}_2\text{Cl}_2(\text{g}) + 2\text{HF}(\text{g}) + 2\text{HCl}(\text{g})$
 - Bonds broken:
 - C—H: $4 \times 413 = 1652 \text{ kJ}$
 - Cl—Cl: $2 \times 239 = 478 \text{ kJ}$
 - F—F: $2 \times 154 \text{ kJ} = 308 \text{ kJ}$
 - Total = 2438 kJ
 - Bonds formed:
 - C—F: $2 \times 485 = 970 \text{ kJ}$
 - C—Cl: $2 \times 339 = 678 \text{ kJ}$
 - H—F: $2 \times 565 = 1130 \text{ kJ}$
 - H—Cl: $2 \times 427 = 854 \text{ kJ}$
 - Total energy released = 3632 kJ
 - $\Delta H = \Sigma D(\text{bonds broken}) - \Sigma D(\text{bonds formed})$
 - $\Delta H = 2438 \text{ kJ} - 3632 \text{ kJ} = -1194 \text{ kJ}$
- You try: Calculate the ΔH for the reaction below:

$$\text{N}\equiv\text{N}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$$

The Localized Electron Bonding Model

- The localized electron (LE) model assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using atomic orbitals of the bound atoms. Electron pairs in the molecule are assumed to be localized on a particular atom or in the space between two atoms. Those pairs of electrons localized on an atom are called lone pairs, and those found in the space between the atoms are called bonding pairs.

Lewis Structures

- The Lewis structure of a molecule shows how the valence electrons are arranged among the atoms in the molecule.
- Elements tend to follow the octet rule where there are surrounded by eight electrons.
- Hydrogen follows the duet rule and only has two electrons in a covalent bond.
- When writing Lewis structures, do not worry about which electrons come from which atoms in a molecule. The best way to look at a molecule is to regard it as a new entity that uses all available valence electrons on the atoms to achieve the lowest possible energy.

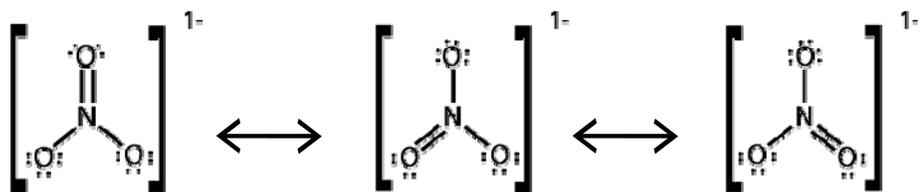
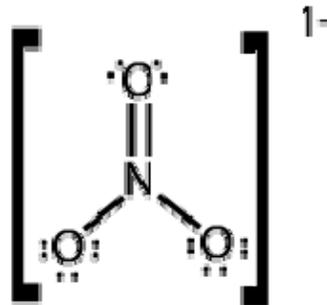
You Try: Write Lewis Structures for the following: HF, CH₄, NO⁺, CO₂, CO₃²⁻

Exceptions to the Octet Rule

- The localized electron model is successful but there are some exceptions that must be noted.
- The second-row elements C,N,O and F should always be assumed to obey the octet rule.
- **The second row elements B and Be often have fewer than eight electrons around them in their compounds** (know BF₃). These electron deficient compounds are very reactive.
- **Second row elements never exceed the octet rule, since their valence orbitals (2s and 2p) can accommodate only 8 electrons.**
- **Third row and heavier elements often satisfy the octet rule but can exceed the octet rule by using their empty valence d orbitals.** (PCl₅, SF₆).
- When writing the Lewis structure for a molecule, satisfy the octet rule for all atoms first. If electrons remain after the octet rule has been satisfied, then place them on the elements having available d orbitals.
- When it is necessary to exceed the octet rule for one of several third row (or higher) elements, assume that the extra electrons should be placed on the central atom.
- You try: Write the structural formula for the following: SF₆, ClF₃, RnCl₂ and BeCl₂

Resonance

- Sometimes more than one valid Lewis structure is possible for a given molecule.
- Observe the Lewis structure for nitrate to the right. It shows one double bond and two single bonds. But, experiments clearly show that only one type of N – O bond occurs with length and strength between those expected for a single and double bond.
- The structure to the right is a valid Lewis Structure but it does not correctly represent the bonding in NO_3^- .
- Resonance occurs when more than one valid Lewis structure can be written for a particular molecule.
- The resulting electron structure of the molecule is the average of the resonance structures. The three resonance structures for nitrate are shown below.



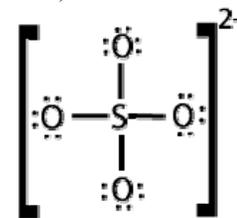
- Resonance shows that electrons are not localized to one atom but instead travel throughout the molecule.

Odd-Electron Molecules

- Few molecular compounds contain odd numbers of electrons.
- Two exceptions are nitric oxide (NO) and nitrogen dioxide (NO_2).
- The localized electron model is based on pairs of electrons; it does not handle odd-electron cases in a natural way. A more sophisticated model is needed.

Formal Charge

- The formal charge of an atom in a molecule is the difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule.
- Formal Charge = (valence e^- on free atom) – (valence e^- assigned to atom in molecule)
- Valence e^- assigned = (number of lone pair e^-) + $\frac{1}{2}$ (number of shared e^-)
- For Example: Calculate the formal charge for each element in the structural formula shown to the right.
 - Oxygen:
 - Valence e^- assigned = $(6) + \frac{1}{2} (2) = 7$
 - Formal Charge = $(6) - (7) = -1$
 - Sulfur:
 - Valence e^- assigned = $(0) + \frac{1}{2} (8) = 4$
 - Formal Charge = $(6) - (4) = +2$
- Atoms in molecules try to achieve formal charges as close to zero as possible.
- Any negative formal charges are expected to reside on the most electronegative atoms.
- You try: Above it was mentioned that NO and NO_2 have an odd number of electrons. Use your knowledge of formal charge to determine the correct Lewis structures for each of the molecules. You must show a formal charge calculation for each atom in each possible Lewis structure.



Molecular Structure: The VSEPR Model

- The term trigonal can be used instead of triangular in shapes such as trigonal planar.

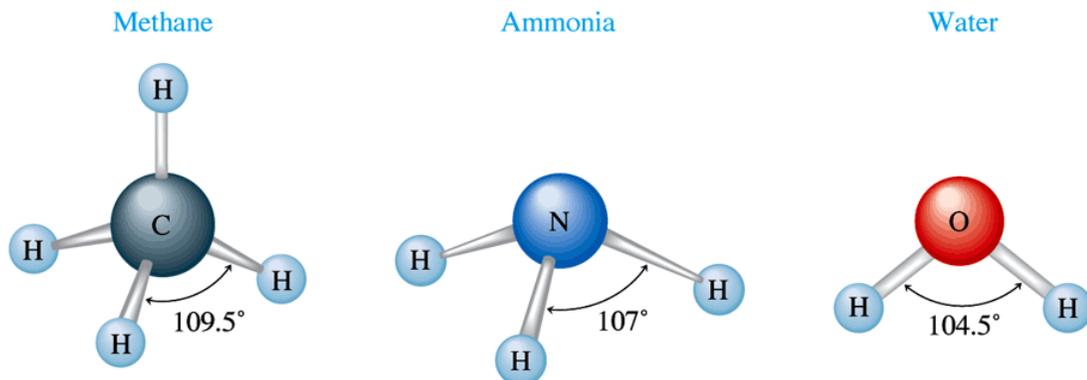
Central Atoms with Three Electron Pairs				
# of lone pair	General Formula	shape	Example	Lewis Structure
0	AX_3E_0	triangular planar	BCl_3	
1	AX_2E_1	bent (angular)	NO_2^-	

Central Atoms with Four Electron Pairs				
# of lone pair	General Formula	shape	Example	Lewis Structure
0	AX_4E_0	tetrahedral	CCl_4	
1	AX_3E_1	triangular pyramidal	NH_3	
2	AX_2E_2	bent (angular)	H_2O	

Central Atoms with Five Electron Pairs				
# of lone pair	General Formula	shape	Example	Lewis Structure
0	AX_5E_0	triangular bipyramidal	PF_5	
1	AX_4E_1	seesaw	SF_4	
2	AX_3E_2	T-shaped	ClF_3	
3	AX_2E_3	linear	XeF_2	

Central Atoms with Six Electron Pairs				
# of lone pair	General Formula	shape	Example	Lewis Structure
0	AX_6E_0	octahedral	SF_6	
1	AX_5E_1	square pyramidal	BrF_5	
2	AX_4E_2	square planar	XeF_4	

- Note in the chart below that even though CH_4 , NH_3 and H_2O are composed of central atoms with 4 electron pair, the bond angles between atoms varies in the different molecules.



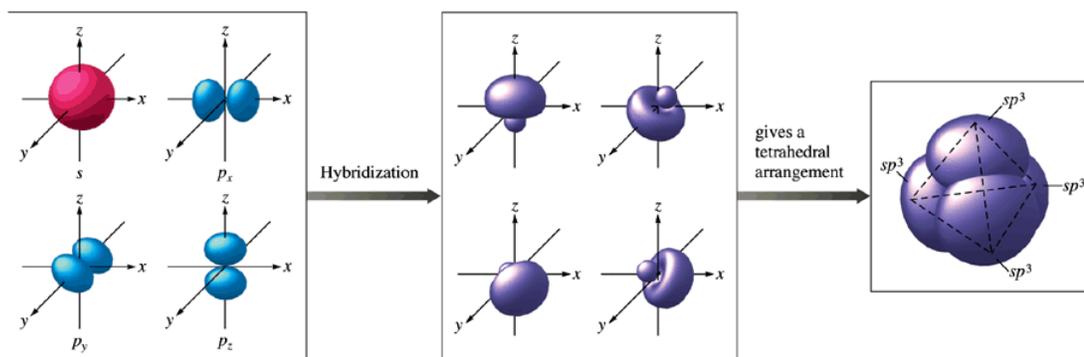
- These observations provide evidence that lone pairs of electrons need more room than bonding pairs and tend to compress the angles between the bonding pairs.**

Chapter 9 Outline – Covalent Bonding: Orbitals

Hybridization and the Localized Electron Model

• sp^3 Hybridization

- In general we assume that bonding only involves valence electrons.
- Consider methane (CH_4).
 - The valence electrons of hydrogen use 1s orbitals.
 - The 2p and 2s atomic orbitals of carbon will lead to two different type of C—H bonds: those from the overlap of the carbon 2p orbital with the 1s orbital of hydrogen and those from the overlap of a carbon 2s orbital with the 1s orbital of hydrogen.
 - This is not the case. The methane molecule is tetrahedral with bond angles of 109.5° . So either the localized electron model is wrong or carbon adopts a set of orbitals other than its “native” 2s and 2p orbitals to bond to the hydrogen atoms in forming the methane molecule.
 - The 2s and 2p orbitals present on an isolated carbon atom may not be the best set of orbitals for bonding. It makes sense to assume that the carbon atom has four equivalent atomic orbitals arranged tetrahedrally.
 - Such a set of orbitals can be obtained by combining the carbon 2s and 2p orbitals as shown below.

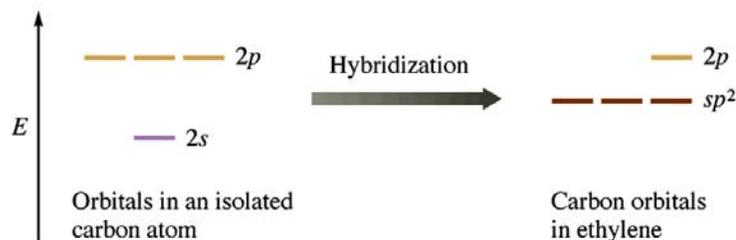
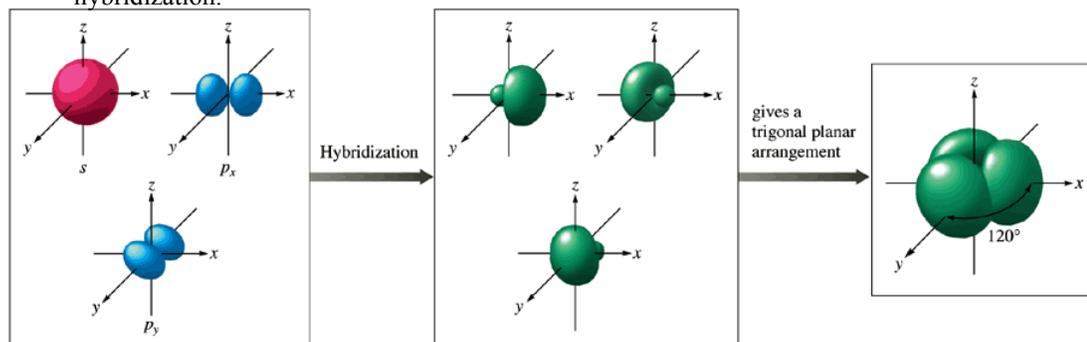
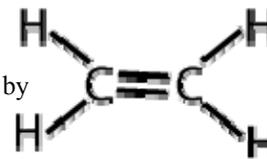


- This mixing of the native atomic orbitals to form special orbitals for bonding is called hybridization.
- The four new orbitals are called sp^3 orbitals because they are formed from one 2s orbital and three 2p orbitals (s^1p^3).
- We say that the carbon atom undergoes sp^3 hybridization or is sp^3 hybridized.
- Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, this model assumes that the atom adopts a set of sp^3 orbitals; the atom becomes sp^3 hybridized.
- What the atoms in a molecule were like before the molecule was formed is not as important as how the electrons are best arranged in the molecule. This model assumes that the individual atoms respond as needed to achieve the minimum energy for the molecule.

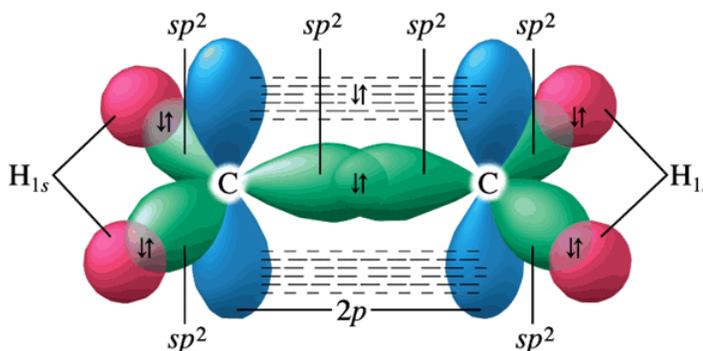


- **sp² hybridization**

- Ethylene (C₂H₄) is an important material in the manufacture of plastics.
- A double bond acts as one effective pair, so the ethylene is surrounded by three effective pair.
- This requires a trigonal planar arrangement with bond angles of 120°.
- Since one 2s and two 2p orbitals are used to form these hybrid orbitals, this is called sp² hybridization.



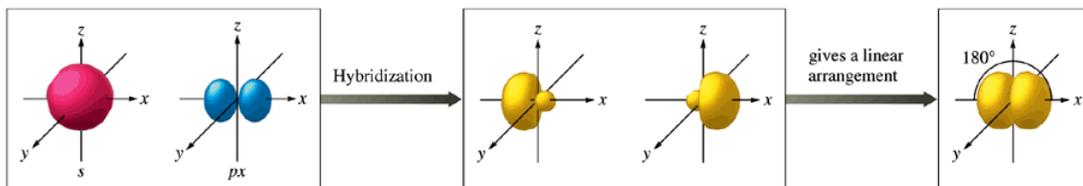
- In forming the sp² orbitals, one 2p orbital on carbon has not been used. This remaining p orbital (p_z) is oriented perpendicular to the plane of the sp² orbitals.
- The three sp² orbitals on each carbon can be used to share electrons, as shown below.



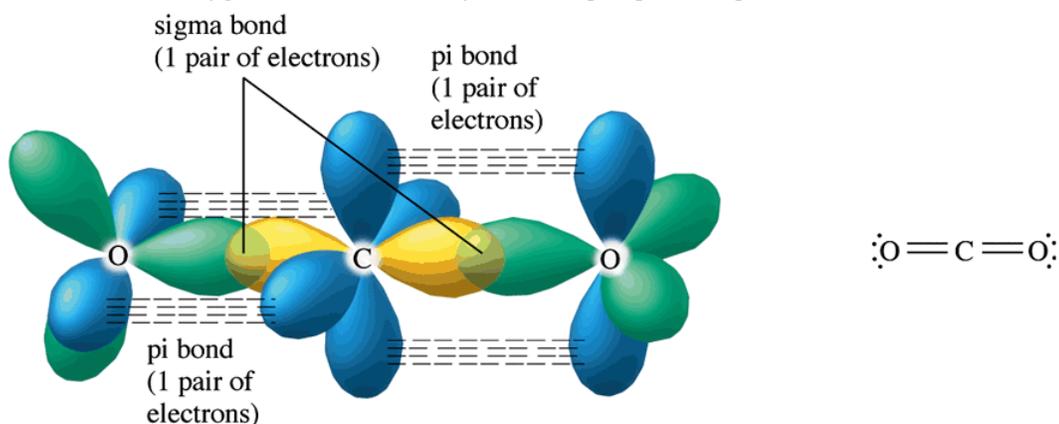
- In each of these bonds, the electron pair is shared in an area centered on a line running between the atoms. This type of covalent bond is called a sigma(σ) bond. In the ethylene molecule, the σ bonds are formed using sp² orbitals on each carbon atom and the 1s orbital on each hydrogen atom.
- The second bond must therefore result from sharing an electron pair in the space above and below the σ bond.
- The parallel p orbitals can share an electron pair, to form a pi(π) bond.
- σ bonds are formed from orbitals whose lobes point toward each other, but π bonds result from parallel orbitals. A double bond always consists of one σ bond where the electrons are located between the atoms and one π bond which occupies the space above and below the σ bond.

- **sp hybridization**

- In the CO₂ molecule the carbon has two effective pair that will be arranged at an angle of 180°.
- To obtain two hybrid orbitals arranged at 180° requires sp hybridization, involving one s orbital and one p orbital.



- Two effective pairs around an atom will always require sp hybridization of that atom.
- In CO₂ the sp orbitals on carbon form σ bonds with the sp² orbitals on the two oxygen atoms. The remaining sp² orbitals on the oxygen atoms hold lone pair. The π bonds between the carbon atom and each oxygen atom are formed by the overlap of parallel 2p orbitals.



- **dsp³ hybridization**

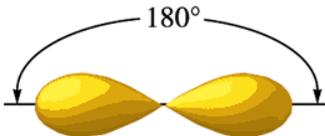
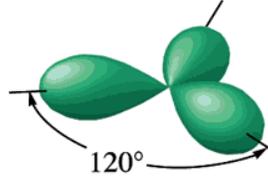
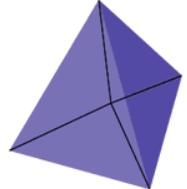
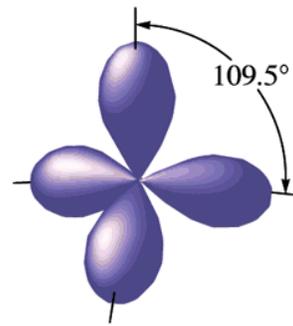
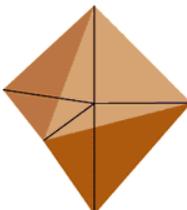
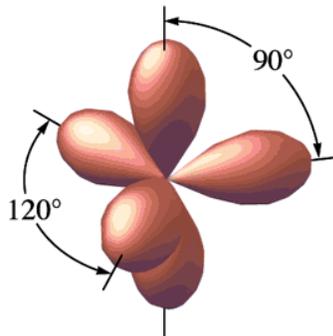
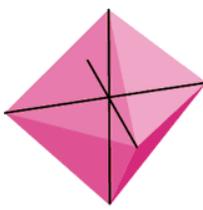
- Since 5 pairs of electrons are needed for atoms such as phosphorus in PCl₅, a dsp³ hybridization is necessary.
- The dsp³ hybridized phosphorus atom in PCl₅ molecule uses its 5 dsp³ orbitals to share electrons with five chlorine atoms.
- A set of five effective pairs around a given atom always requires a trigonal bipyramidal arrangement which in turn requires dsp³ hybridization of that atom.

- **d²sp³ hybridization**

- Since 6 pairs of electrons are needed for atoms such as sulfur in SF₆, a d²sp³ hybridization is necessary.
- A set of six effective pairs around a given atom always requires an octahedral arrangement which in turn requires d²sp³ hybridization of that atom.

Paramagnetism

- Most materials have no magnetism until they are placed in a magnetic field. However, in the presence of such a field, magnetism of two types can be induced.
- Paramagnetism causes a substance to be attracted to the inducing magnetic field.
- Diamagnetism causes the substance to be repelled from inducing magnetic field.
- Studies have shown that paramagnetism is associated with unpaired electrons and diamagnetism is associated with paired electrons.
- The O₂ molecule is known to be paramagnetic.

Number of Effective Pairs	Arrangement of Pairs		Hybridization Required	
2		Linear	sp	
3		Trigonal planar	sp^2	
4		Tetrahedral	sp^3	
5		Trigonal bipyramidal	dsp^3	
6		Octahedral	d^2sp^3	