

Chemical Bond

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Objectives

At the end of this, we will be able to-

- Know the chemical bonds and several intermolecular forces of attractions
- Explain various classical theory and modern theory of chemical bonds as well as related terms.
- Apply several concepts in figuring the structures, geometry of the molecules, and electronic configuration of molecules.

Contents

- Chemical Bonding
- Forces between atoms and molecules
- Forces in Solid bindings
- Ionic bond, covalent bond, metallic bond, hydrogen bond
- Lewis theory
- Hybridization
- Valence bond theory (VBT)
- VESPER theory- geometry of molecules
- Molecular orbital theory

Chemical Bonds-Forces Between Atoms and Molecules

The atoms of many elements can combine to form compounds. Individual, isolated units of compounds are considered molecules.

On the atomic or molecular scale, all particles exert both attractive and repulsive forces on each other. The nature of these forces dictate some of the important properties of matter.

Attractive Forces bring atoms or molecules together and are necessary for molecules to cohere.

They are seen as two atoms or molecules with opposite charges are brought closer together. They are either cohesion forces (attraction between molecules of the same substance) or adhesion forces (attraction between molecules of different substances). They are long range interactions.

Repulsive Forces push atoms or molecules apart and prevent the molecules from interpenetrating with each other. They are seen as the negatively charged electron clouds of the molecules are brought so close that the outer charge clouds touch, and hence the molecules will repel each other like rigid elastic bodies. These are short range interactions.

The atoms in most molecules are held together by strong attractive forces called chemical bonds. These bonds are formed through the interaction of valence electrons of the combining atoms. In addition to the very strong forces within a molecule, there are weaker forces acting between molecules. These intermolecular forces, although weaker than the intramolecular chemical bonds, are of considerable importance in understanding the properties of many substances.

Intra-molecular forces

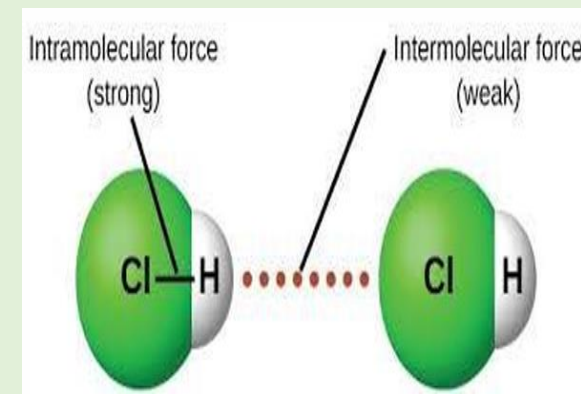
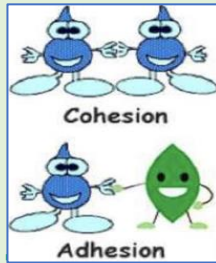
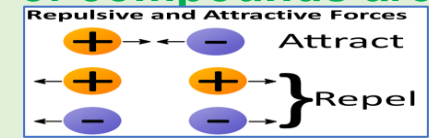
Forces of attraction between the atoms that hold an individual molecule together.

Inter-molecular forces

Forces of attractions between a molecule and its neighboring molecule.

- **Bonding Forces**
- **Exist within Molecules**
- **Determine Chemical Properties**

- **Attractive Forces (Non-bonding Forces)**
- **Exist between Molecules**
- **Determine Physical Properties**



Chemical Bonds-Forces Between Atoms and Molecules

Forces within molecules (Intra-molecular force) When two atoms of same or different elements approach each other, the energy of the combination of the atoms becomes less than the sum of the energies of the two separate atoms at a large distance. Two atoms have combined, or a bond is formed between the two. The bond is called a chemical bond.

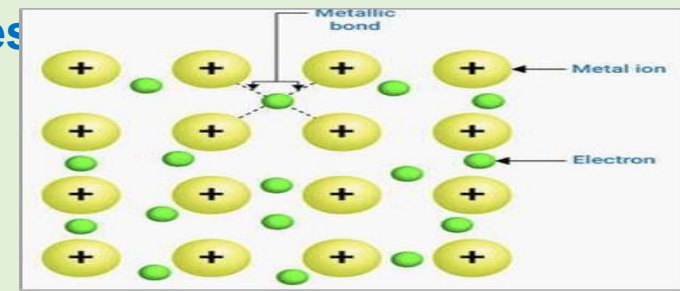
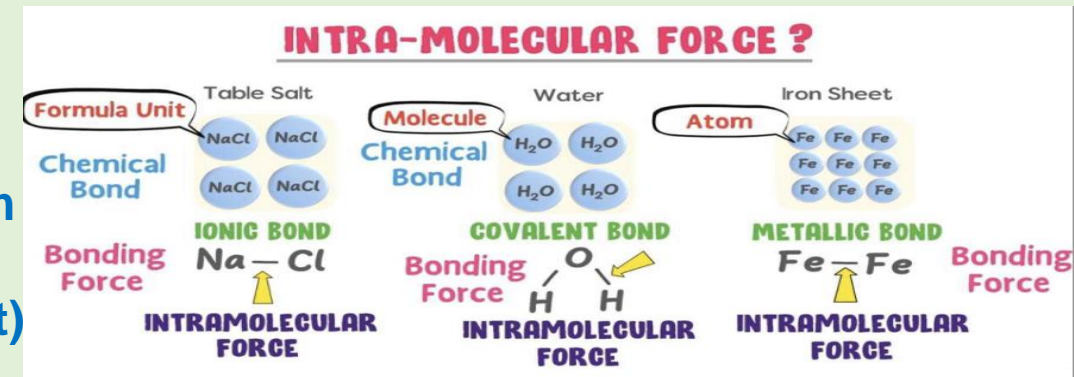
A chemical bond may be visualized as an effect that leads to the decrease in the energy. The combination of atoms leads to the formation of a molecule that has distinct properties different from that of the constituent atoms.

The formation of a bond between two atoms may be visualized in terms of their acquiring stable electronic configurations. That is when two atoms (other than that of noble gases) combine they will do so in such a way that they attain an electronic configuration of the nearest noble gas.

The stable electronic configuration of the noble gases can be achieved in a number of ways; by losing, gaining or sharing of electrons.

Different types of chemical bonds-

- **Ionic or electrovalent bond-** formed between two oppositely charged ions due to complete transfer of valence electrons from one atom to another. **Example: NaCl**
- **Covalent bond-** formed between two atoms (same or different) due to sharing of electrons. **Example: H₂, CCl₄**
- **Co-ordinate covalent bond-** A covalent bond in which a single atom contributes shared pair is called a coordinate covalent bond. **Example: NH₄⁺**
- **Metallic Bonds-** bonds formed due to sharing of free valence electrons between a group of positively charged metal ions. **Example: Gold, silver, copper**

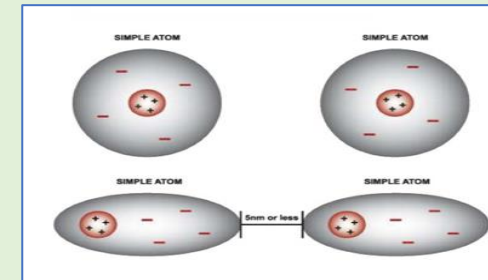


Chemical Bonds-Forces Between Atoms and Molecules

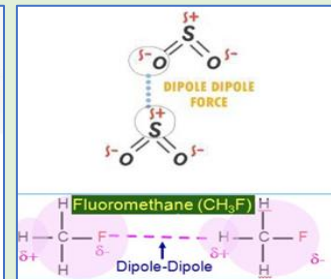
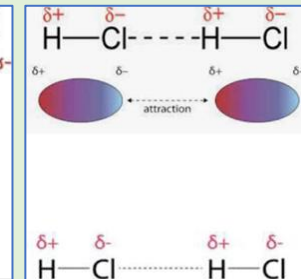
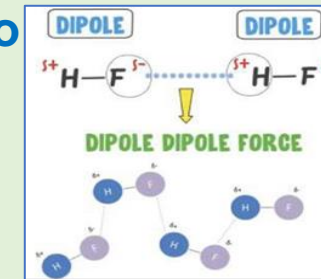
Forces within molecules (Inter-molecular force or secondary force) **is the force that mediates interaction between molecules.** These forces must exist between molecules so that such molecules can form aggregates in gases, liquids, and solids. The intermolecular forces may involve weak attractive forces due to the electron distribution in the molecules or involve specific intermolecular bonds – such as hydrogen bonds.

The common types of attractive intermolecular forces are-

- Van der Waals forces-** are relatively weak attractive forces that arise because of fluctuation in the electron density of all molecules and these cause small dipoles within the molecules. The electric polarization will attract one molecule to another. When two atoms come within 5 nanometers of each other, there will be a transient shift in electron density to one side of the nucleus, thus causing polarity and a slight attraction between the atoms.



Keesom forces (Dipole–Dipole Forces)-electrostatic attractive forces that occur between two polar molecules (molecules which have permanent dipoles, where molecules have an asymmetric distribution of electrons, i.e., they contain polar bonds). Dipolar molecules frequently tend to align themselves with their neighbors to lower the energy of the assembled molecules so that the negative pole of one molecule (δ^-) points toward the positive pole (δ^+) of the next. Thus, a large groups of molecules may be associated through weak attractions.



Energy of attraction is 1-7 Kcal/mole. The alignment could be end-to-end, resulting in a stronger interaction than a side-by-side alignment.

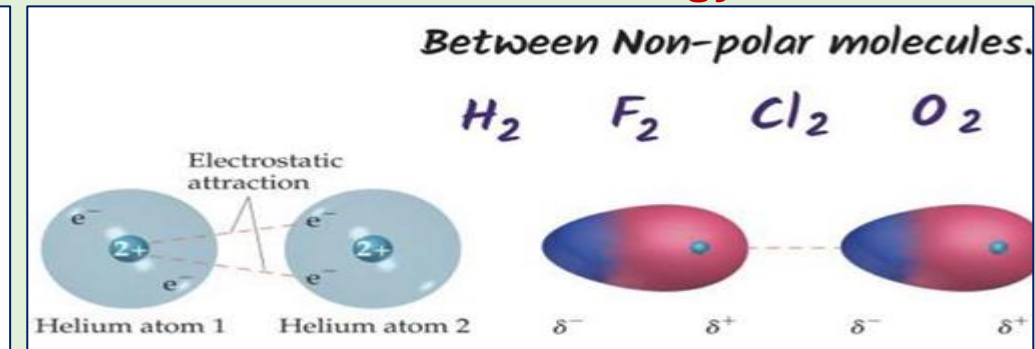
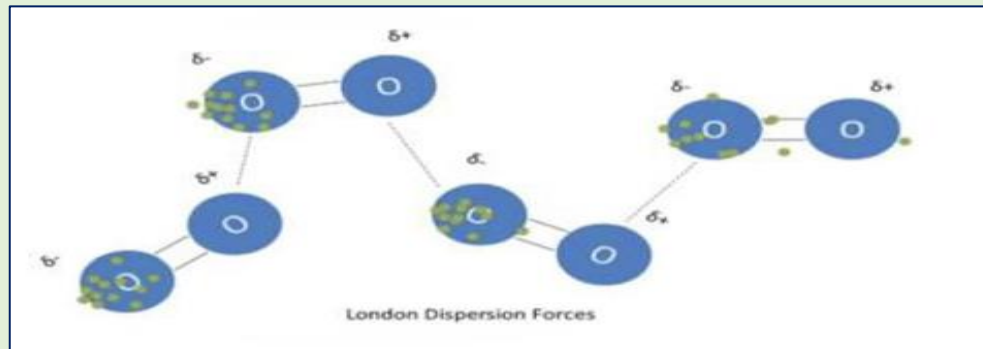
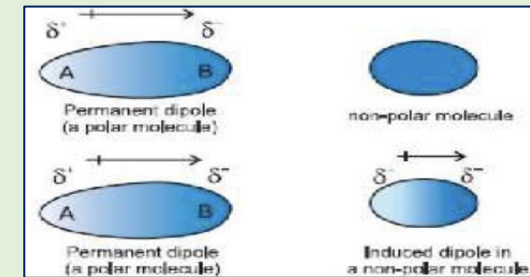
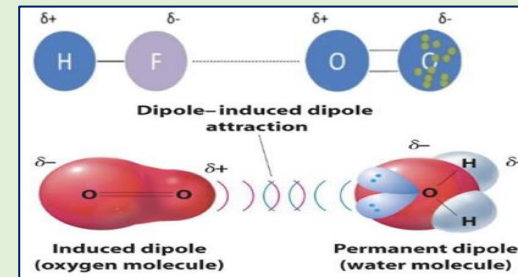
Intermolecular Forces

Dipole–Induced dipole Forces (Debye forces)- Permanent dipoles (polar molecules) are capable of inducing a temporary electric dipole in normally non-polar molecules (easily polarizable), and thus produce a net attractive force between the two particles. This attraction is usually rather weak (about half of dipole-dipole forces), but in a few cases it can lead to the formation of loosely-bound compounds.

This effect explains the observation that a wide variety of neutral molecules such as hydrocarbons, and even some of the noble gas elements, form stable hydrate compounds with water. **Energy of attraction is 1-3 Kcal/mole.**

Induced Dipole–Induced Dipole Forces (London forces)-

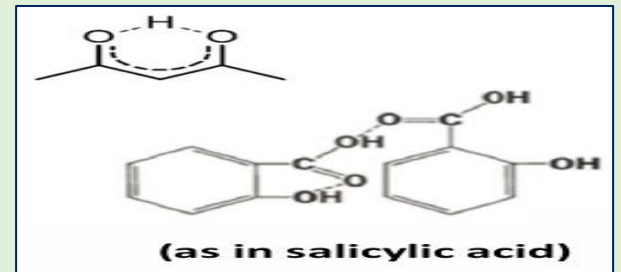
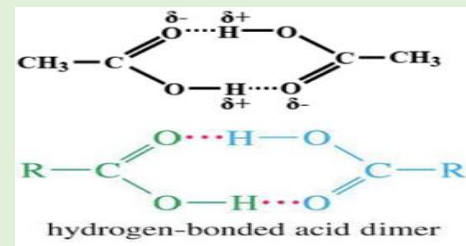
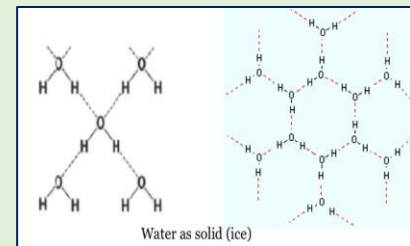
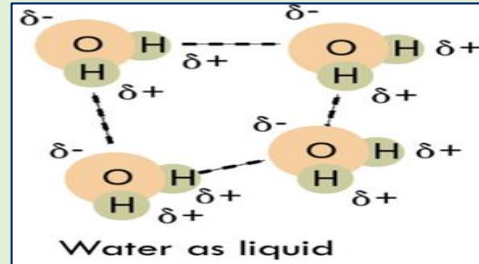
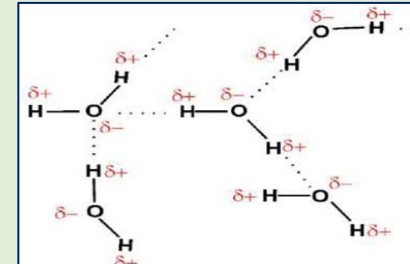
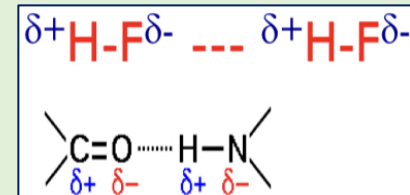
Non-polar molecules can induce polarity in one another. The distribution of negative charge around the center of an atom will not be perfectly symmetrical at every instant. On a very short time scale, every atom therefore has a weak, fluctuating dipole moment that is continually disappearing and reappearing in another direction. Although these extremely short-lived fluctuations quickly average out to zero, they can still induce new dipoles in a neighboring atom or molecule, which helps sustain the original dipole and gives rise to a weak attractive force known as the dispersion or London force. London forces are the only kind of intermolecular interaction forces seen in non polar molecules. Unlike the other two types of Van der Waals forces they are present in all molecules and are the weakest of all intermolecular forces. **Energy of attraction is 0.5-1 Kcal/mole.**



Intermolecular Forces- Hydrogen Bonding

Hydrogen bonding- occurs when a hydrogen atom bonded to an electronegative atom (Z) such as (O, N, or F) is attracted to a lone pair of electrons on an atom in another molecule. **It is not a covalent bond within the molecule, but it is a specific type of dipole-dipole interaction.** Hydrogen bonds are shown with dotted lines connecting a lone pair with the hydrogen. It is very common in nature starting from water and going to complex biological systems like DNA and proteins. It is stronger than Van der Waals interaction, but weaker than covalent or ionic bonds. **Energy of attraction is 2-8 Kcal/mole.**

- Simple hydrogen bonding between two diatomic molecules, hydrogen fluoride in the vapor state which exist as a hydrogen bonded polymer (F-H....)n, can be as large as 6.
- Hydrogen bonding between carbonyl and amide group. It can also exist between alcohol molecules, carboxylic acids, aldehydes, esters, and polypeptide.
- Hydrogen bond exists in ice and in liquid water; it accounts for many of the unusual properties of water including its high dielectric constant, abnormally low vapor pressure, and high boiling point. Ice has the very unusual property that its solid state is less dense than its liquid state. As a result, ice floats in liquid water. Ice is well ordered 3-dimensional array of regular tetrahedra with oxygen in the center and H atom at each corner.
- Hydrogen bonding between two carboxylic molecules-formic acid and acetic acid- bonds may occur sufficiently strong to yield dimers (two molecules attached together), which can exist even in the vapor state. Intramolecular hydrogen bonding within one carboxylic molecule. It is noticed that intra- as well as intermolecular hydrogen

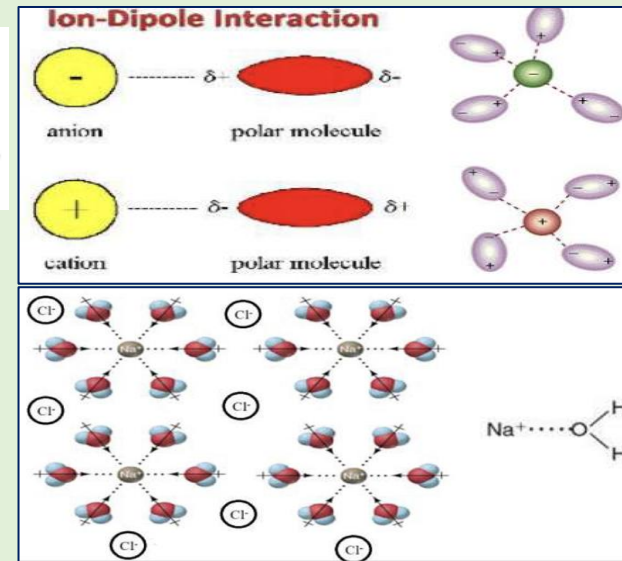
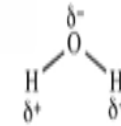


Intermolecular Forces

Ion - dipole force- A dipole that is close to a positive or negative ion will orient itself so that the end whose partial charge is opposite to the ion charge will point toward the ion. This kind of interaction is very important in aqueous solutions of ionic substances.

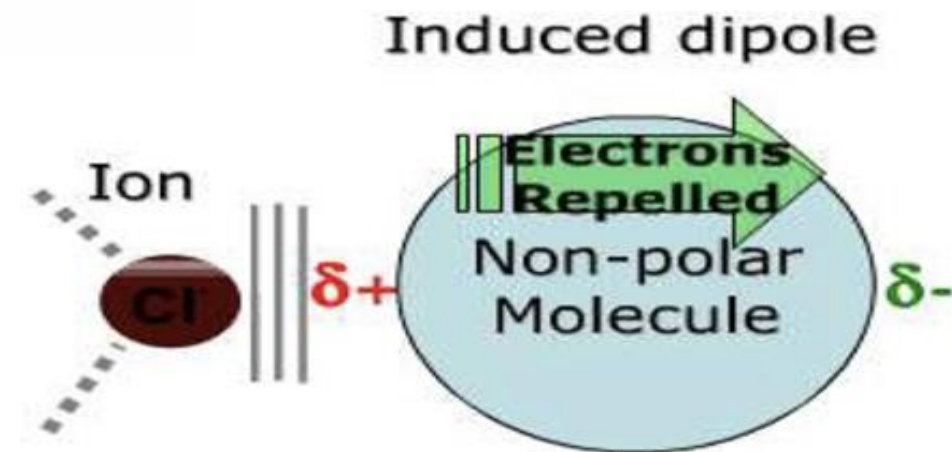
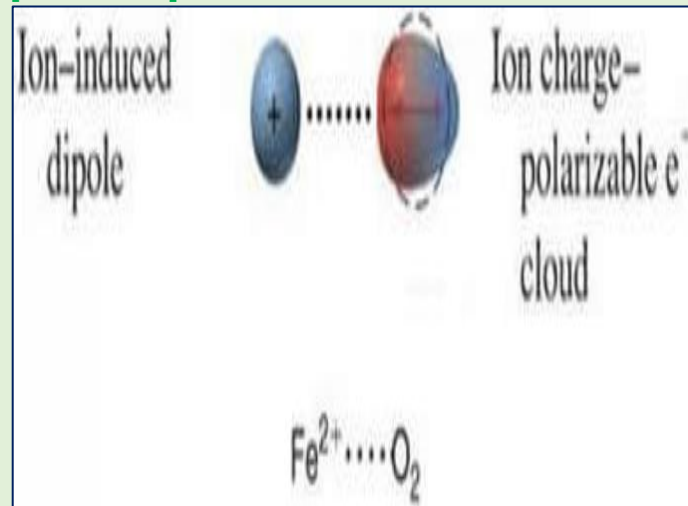
Energy of attraction is 1-7 Kcal/mole.

Example: Solubility of NaCl in water. In a solution of sodium chloride, H_2O is a highly polar molecule, and NaCl breaks up to Na^+ and Cl^- because the ion dipole with water is stronger than the attraction of Na^+ to Cl^- . The Na^+ ions will be enveloped by a shell of water molecules with their oxygen-ends pointing toward these ions, while H_2O molecules surrounding the Cl^- ions will have their hydrogen ends directed inward.



Ion – induced dipole force- attraction is a weak attraction that results when the approach of an ion induces a dipole in an atom or in a non-polar molecule by disturbing the arrangement of electrons in the nonpolar species.

Energy of attraction is 6 Kcal/mole



Various Forces and Bonding

Bond energies serve as a measure of the strength of bonds

Class		Unit 1	Unit 2	Energy (Kcal/mole)	bonding
Van der Waals forces	Keesom forces	Dipole	Dipole	1~7	Physical bonding (intermolecular interaction)
	Debye forces	Dipole	Induced dipole	1~3	
	London forces	Induced dipole	Induced dipole	0.5~1	
Ion-dipoles forces		Ion	Dipole	1~7	
Ion-induced dipole forces		Ion	Induced dipole	-	
→ Hydrogen bond	H atom	O, N, F	2~8		
Ionic bond		Ion	Ion	100~200	Chemical bonding (atomic bonding)
Covalent bond		Polar atom	Polar atom	50~150	

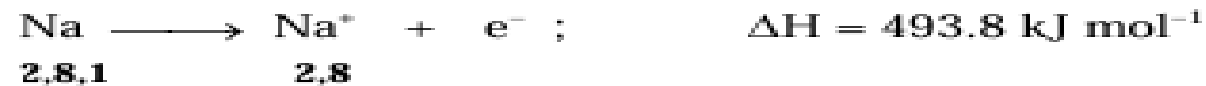
Bond strength

The strength between intermolecular bonds is a lot weaker than the strength of intramolecular bonds and the weakest form of intermolecular bond is a bond that uses Van der Waals forces or an instantaneous induced-dipole bond.

Ionic or Electrovalent Bond

According to Kossel's theory, in the process of formation of ionic bond the atoms acquire the noble gas electronic configuration by the gain or loss of electrons.

Consider the formation of NaCl in terms of Kossel's Theory. The electronic configuration of sodium atom (atomic number 11) is 2,8,1. Since it is highly electropositive, it readily loses an electron to attain the stable configuration of the nearest noble gas (neon) atom. It becomes a positively charged sodium cation (Na^+) in the process.

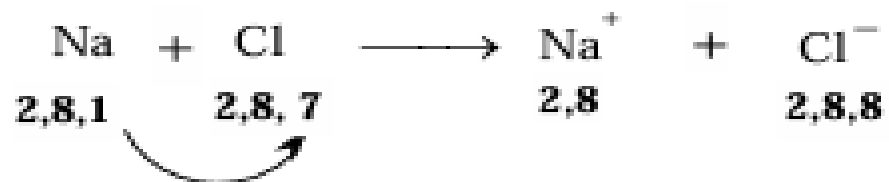


On the other hand, a chlorine atom (electronic configuration: 2,8,7) requires one electron to acquire the stable electronic arrangement of an argon atom. It becomes a negatively charged chloride anion (Cl^-) in the process.



According to Kossel's theory, there is a transfer of one electron from sodium atom to chlorine atom and both the atoms attain noble gas configuration.

The positively charged sodium ion and the negatively charged chloride ion are held together by electrostatic attractions. The bond so formed is called an electrovalent or an ionic bond. The ionic bond can be visualized as the electrostatic force of attraction that holds the cation and anion together. The compounds so formed are termed as ionic or electrovalent compounds.



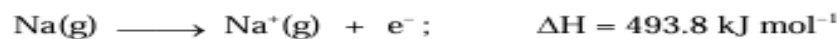
Energetics of Ionic Compound Formation

The formation of an ionic compound (NaCl) as a result of transfer of electrons as proposed by Kossel. The formation of NaCl from sodium and chlorine can be broken down into a number of steps as :

a) **Sublimation** of solid sodium to gaseous sodium atoms.



b) **Ionization** of gaseous sodium atom to give sodium ion.



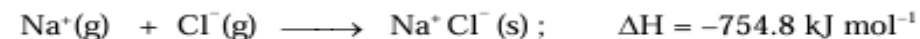
c) **Dissociation** of gaseous chlorine molecule into chlorine atoms



d) Conversion of gaseous chlorine atom to chloride ion (**addition of electron**)



e) Formation of NaCl from sodium and chloride ions. (**Crystal or lattice formation**).



The energy released in this step is **lattice energy**.

The net reaction would be



The overall energy change can be computed by taking the sum of all the energy changes:

$$\Delta H = (108.7 + 493.8 + 120.9 - 379.5 - 754.8) = -410.9 \text{ kJ mol}^{-1}$$

The net process of formation of NaCl from sodium and chlorine is accompanied by a large decrease in the energy. Sublimation and dissociation energies are generally of low values than the rest. Three energy terms i.e., ionization energy, electron affinity and lattice energy are important in determining the formation of an ionic compound. The formation of an ionic compound is favored by low ionization energy of the metal, high electron affinity of the other element (non-metal), and high lattice energy.

Properties of ionic compound

- They are crystalline solids in which the ions are arranged in a regular three-dimensional structure.
- Generally hard and brittle in nature.
- Have high melting and boiling points due to strong electrostatic interactions between the ions.
- Generally soluble in water and less soluble in non-polar solvents like ether, alcohol, etc.
- They conduct electricity when in molten state or in aqueous solutions.

Kossel's theory explains bonding only for a small class of solids composed of electropositive elements of Group 1 and 2 with highly electronegative elements. This theory is incapable of explaining the formation of compounds like, SO₂ or O₂.

Lewis Theory

- Electrons, especially those of the outermost (valence) electronic shell, play a fundamental role in chemical bonding.
- In some cases, electrons are transferred from one atom to another. Positive and negative ions are formed and attract each other through electrostatic forces called ionic bonds.
- In other cases, one or more pairs of electrons are shared between atoms. A bond formed by the sharing of electrons between atoms is called a covalent bond.
- Electrons are transferred or shared in such a way that each atom acquires an especially stable electron configuration. Usually this is a noble gas configuration, one with eight outer-shell electrons, or an octet.

Lewis Symbols and Lewis Structures

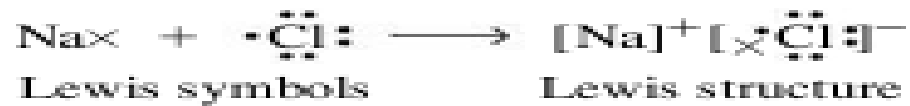
Lewis developed a special set of symbols for his theory. A Lewis symbol consists of a chemical symbol to represent the nucleus and core (inner-shell) electrons of an atom, together with dots placed around the symbol to represent the valence (outer-shell) electrons. Thus, the Lewis symbol for silicon, which has the electron configuration is $[\text{Ne}] 3s^2 3p^2$,



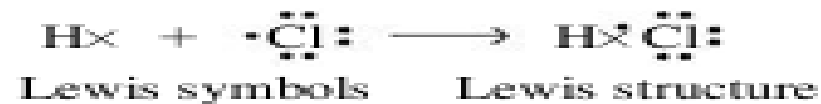
Electron spin had not yet been proposed when Lewis framed his theory. He did not show that two of the valence electrons are paired ($3s^2$), and two are unpaired ($3p^2$). Lewis placed single dots on the sides of the symbol, up to a maximum of four, then paired up dots until reach an octet. **Lewis symbols are commonly written for main-group elements but much less often for transition elements.**

A Lewis structure is a combination of Lewis symbols that represents either the transfer or the sharing of electrons in a chemical bond.

Ionic bonding
(transfer of
electrons):



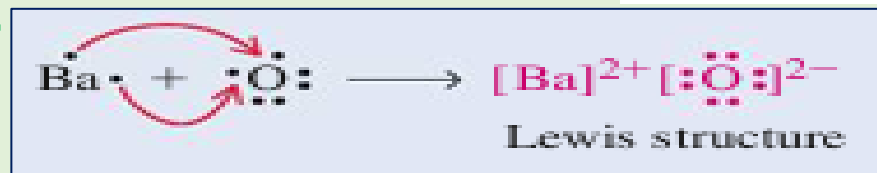
Covalent bonding
(sharing of
electrons):



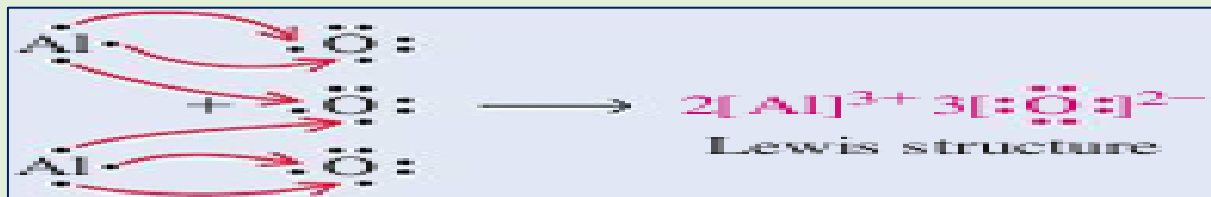
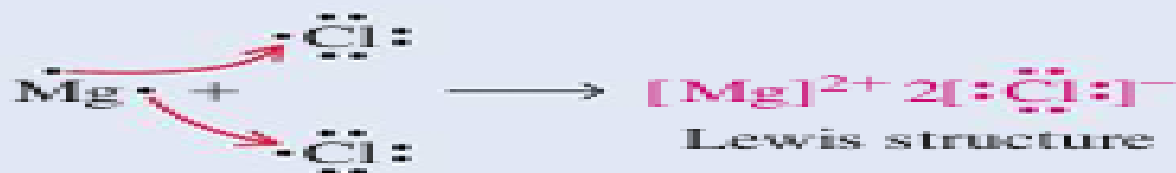
Lewis Structures of Ionic Compounds

The formula unit of an ionic compound is the simplest electrically neutral collection of cations and anions from which the chemical formula of the compound can be established. The Lewis structure of sodium chloride represents its formula unit. $[\text{Na}]^+ [\text{Cl}]^-$

Examples-



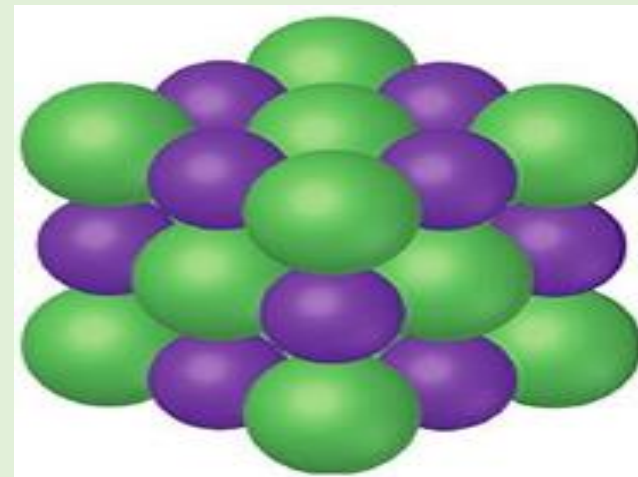
For an ionic compound of a main-group element, the Lewis symbol of the metal ion has no dots if all the valence electrons are lost, and the ionic charges of both cations and anions are shown.



The structures of ionic compounds are much more complicated than is suggested by the Lewis structure.

The compounds described are binary ionic compounds consisting of monatomic cations and monatomic anions. Commonly encountered ternary ionic compounds consist of monatomic and polyatomic ions. Bonding between atoms within the polyatomic ions is covalent.

Ion pairs, such as Na^+Cl^- , that may be found in the gaseous state, formula units of solid ionic compounds do not exist as separate entities. Each cation is surrounded by anions and each anion by cations. These very large numbers of ions are arranged in an orderly network called an ionic crystal.



Structure of alternating Na^+ and Cl^- ions extends in all directions and involves countless numbers of ions.

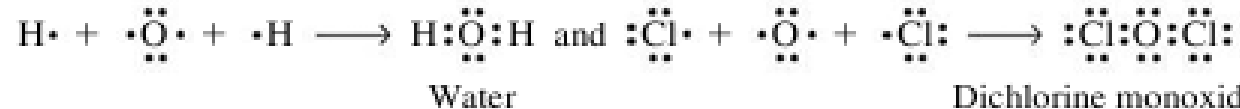
Lewis Structures- Covalent Bonding & Coordinate Covalent Bonds

Bonding between a hydrogen atom and a chlorine atom involves the sharing of electrons, which leads to a covalent bond. Lewis structure of HCl-

Lewis theory helps us to understand

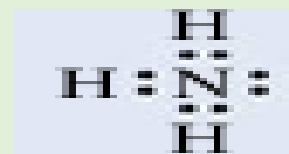
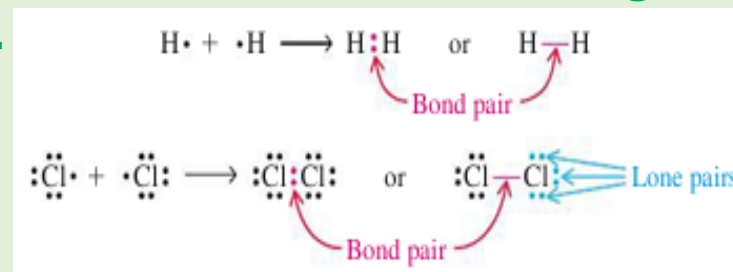
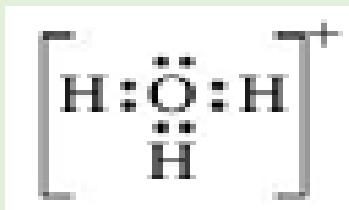
The existence of elemental hydrogen and

chlorine as diatomic molecules, H_2 and Cl_2 . The sharing of a single pair of electrons between bonded atoms produces a single covalent bond. In the Lewis theory the term bond pair applies to a pair of electrons in a covalent bond, while lone pair applies to electron pairs that are not involved in bonding. In writing Lewis structures, it is customary to replace bond pairs with lines.

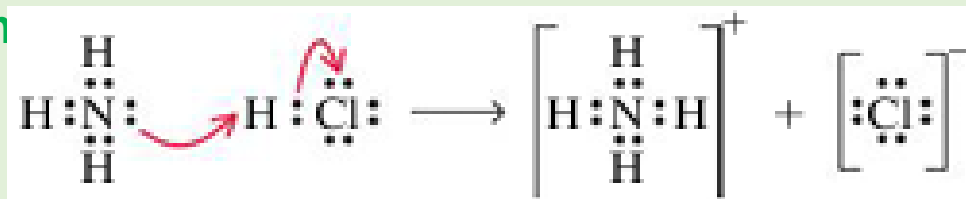


A covalent bond in which a single atom contributes both of the electrons to a shared pair is called a coordinate covalent bond. For the ammonium ion, NH_4^+ , the lone pair of electrons on a NH_3 molecule extracts an H atom from a

HCl molecule, and the electrons in the H-Cl bond remain on the Cl atom. The result is equivalent to a H^+ ion joining with the NH_3 molecule to form the NH_4^+ ion. The electron pair from the H-Cl bond remains on the Cl atom, converting it to a Cl^- ion. The bond formed between the N atom of NH_3 and the H^+ ion in structure is a coordinate covalent bond. It is important to note, however, that on covalent bond is indistinguishable from a regular covalent bond. Another example of coordinate covalent bonding is found in the familiar hydronium ion.



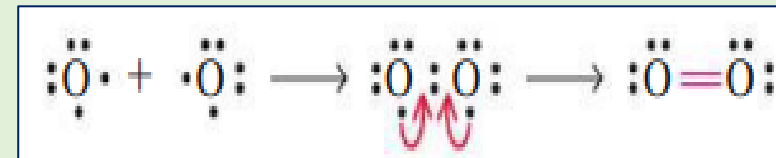
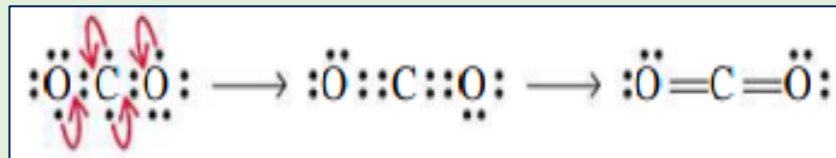
Lewis structure for ammonia



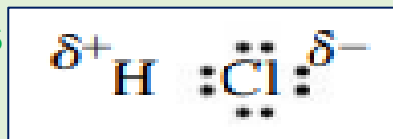
Formation of the ammonium ion, NH_4^+ The H atom of HCl leaves its electron with the Cl atom and, as H^+ , attaches itself to the molecule through the lone-pair electrons on the N atom. The ions NH_4^+ and Cl^- are formed.

Lewis Structures- Multiple Covalent Bonds & Polar Covalent Bonds

More than one pair of electrons are also shared if an atom is to attain an octet (noble gas electron configuration). For example, CO_2 , N_2 , and O_2 are molecules in which atoms share more than one pair of electrons.



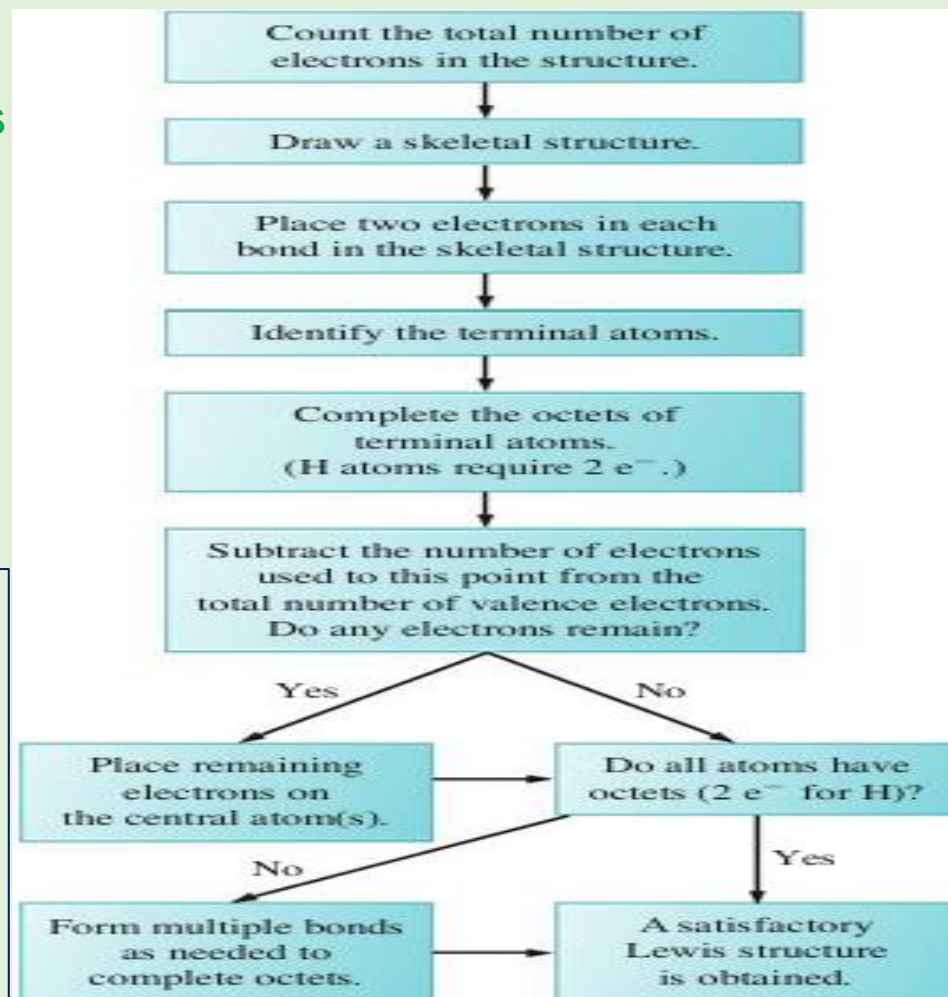
Covalent bond in which electrons are not shared equally between two atoms is called polar covalent bond. In such a bond, electrons are displaced toward the more nonmetallic element. The unequal sharing of the electrons leads to a partial negative charge on the more non-metallic element signified by δ^- , and a corresponding partial positive charge on the more metallic element, designated by δ^+ . Lewis structure of HCl is



Characteristic properties of Covalent Compounds

- The covalent compounds have low melting and boiling points due to weak forces of interaction between the molecules.
- They are poor conductors of electricity as these lack ionic species.
- Compounds are generally insoluble in water and dissolve in nonpolar solvents like benzene, carbon tetrachloride etc.

Lewis theory tells nothing about the shapes of molecules, and repulsions between valence-shell electron pairs.



Lewis Structures- Multiple Covalent Bonds & Polar Covalent Bonds

Write a plausible Lewis structure for cyanogen, C_2N_2 , a poisonous gas used as a fumigant and rocket propellant.

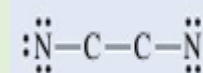
Step 1. Determine the total number of valence electrons. Each of the two C atoms (group 14) has four valence electrons, and each of the two N atoms (group 15) has five. The total number of valence electrons is $4 + 4 + 5 + 5 = 18$

Step 2. Identify the central atom(s) and terminal atoms. Because the C atoms have a lower electronegativity (2.5) than do the N atoms (3.0), C atoms are central atoms, and N atoms are terminal atoms.

Step 3. Write a plausible skeletal structure by joining atoms through single covalent bonds.
N-C-C-N

Step 4. Subtract two electrons for each bond in the skeletal structure. The three bonds in this structure account for 6 of the 18 valence electrons. This leaves 12 valence electrons to be assigned.

Step 5. Complete octets for the terminal N atoms, and to the extent possible, the central C atoms. The remaining 12 valence electrons are sufficient only to complete the octets of the N atoms.



Step 6. Move lone pairs of electrons from the terminal N atoms to form multiple bonds to the central C atoms. Each C atom has only four electrons in its valence shell and needs four more to complete an octet. Thus, each C atom requires two additional pairs of electrons, which it acquires if we move two lone pairs from each N atom into its bond with a C atom, as shown below

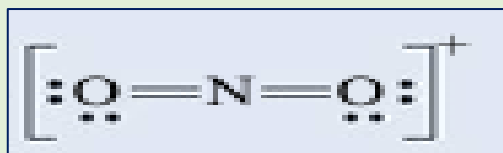


Lewis Structures- Formal Charge

Formal charges (FC) are apparent charges on certain atoms in a Lewis structure that arise when atoms have not contributed equal numbers of electrons to the covalent bonds joining them. In cases where more than one Lewis structure seems possible, formal charges are used to ascertain which sequence of atoms and arrangement of bonds is most satisfactory.

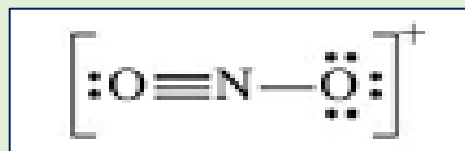
$$\text{FC} = \text{number valence } e^- \text{ in free atom} - \text{number lone-pair } e^- - \frac{1}{2} \text{number bond-pair } e^-$$

Lewis structure for the nitronium ion, NO_2^+



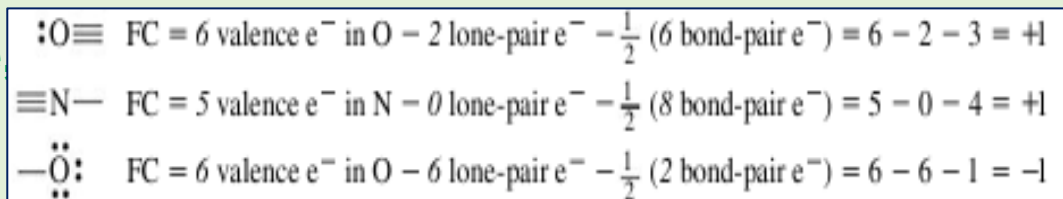
1

or



2

For 2nd structure



Formal charges in a Lewis structure can be shown by using small, encircled numbers.

General rules that can help to determine the plausibility of a Lewis structure based on its formal charges.

- The sum of the formal charges in a Lewis structure must equal zero for a neutral molecule and must equal the magnitude of the charge for a polyatomic ion. [For structure 2, this sum is $+1 + 1 - 1 = +1$.
- Where formal charges are required, they should be as small as possible.
- Negative formal charges usually appear on the most electronegative atoms positive formal charges, on the least electronegative atoms.
- Structures having formal charges of the same sign on adjacent atoms are unlikely.

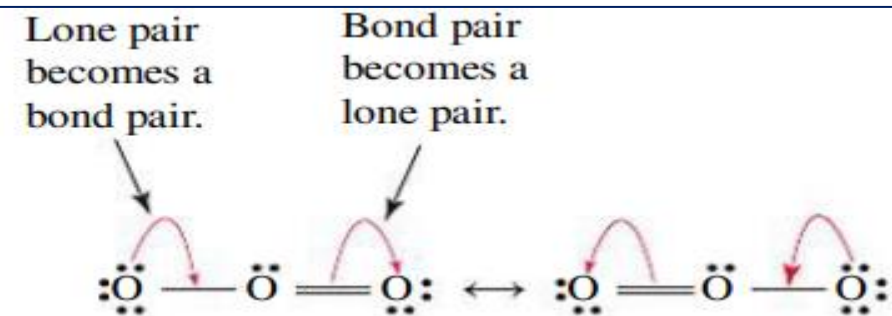


Structure 2 conforms to the first two rules. But it is not in good accordance with the third rule. Despite the fact that O is the most electronegative element in the structure, one of the O atoms has a positive formal charge. The greatest failing, though, is in the fourth rule. Both the O atom on the left and the N atom adjacent to it have positive formal charges. Structure 2 is not the most satisfactory Lewis structure. By contrast, the Lewis structure 1 has only one formal charge, +1, on the central N atom. It conforms to the rules completely and is the most satisfactory Lewis structure.

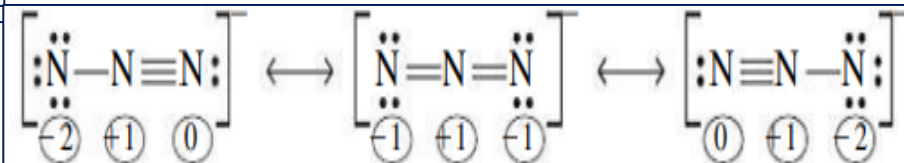
Lewis Structures- Resonance

The situation in which two or more plausible Lewis structures contribute to the correct structure is called resonance. The true structure is a resonance hybrid of plausible contributing structures. Acceptable contributing structures to a resonance hybrid must all have the same skeletal structure (the atomic positions cannot change); they can differ only in how electrons are distributed within the structure.

For ozone molecule, the two contributing structures are joined by a double-headed arrow. The arrow does not mean that the molecule has one structure part of the time and the other structure the rest of the time. It has the same structure all the time. By averaging the single bond in one structure with the double bond in the other, we might say that the **oxygen-to-oxygen bonds in ozone are halfway between a single and double bond**, that is, 1.5 bonds. The two resonance structures are equivalent; that is, they contribute equally to the structure of the resonance hybrid.



In many cases, several contributing resonance structures do not contribute equally. For example, consider the azide anion, for which three resonance structures are –
The central resonance structure avoids the unlikely large formal charge of -2 found on an N atom in the other two structures. That structure to contribute most to the resonance hybrid of the azide anion.



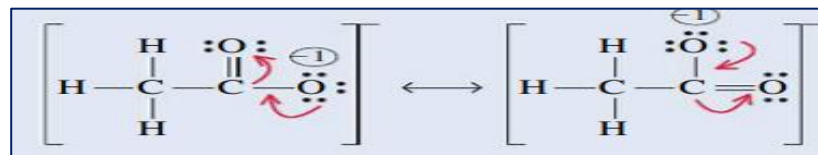
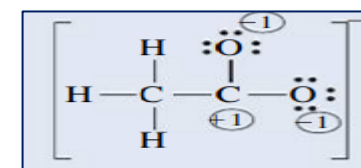
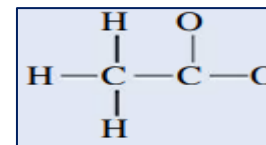
Representing the Lewis Structure of a Resonance Hybrid

Lewis structure of the acetate ion CH_3COO^-

The skeletal structure has the three H atoms as terminal atoms bonded to a C atom as a central atom. The second C atom is also a central atom bonded to the first. The two O atoms are terminal atoms bonded to the second C atom.

The number of valence electrons (dots) that must appear in the Lewis structure is 24.

The true Lewis structure is a resonance hybrid of the following two contributing structures.



Lewis Structures- Exceptions to the Octet Rule

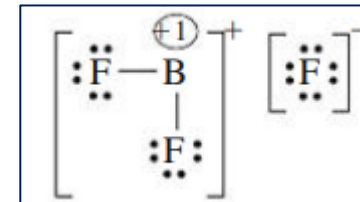
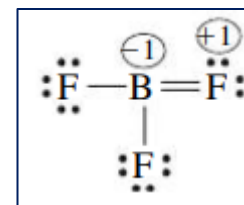
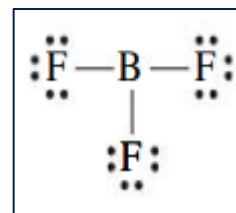
Odd-Electron Species

The molecule NO has 11 valence electrons, an odd number. If the number of valence electrons in a Lewis structure is odd, there must be an unpaired electron somewhere in the structure. Lewis theory deals with electron pairs and does not tell us where to put the unpaired electron; it could be on either the N or the O atom. To obtain a structure free of formal charges, however, we will put the unpaired electron on the N atom



Incomplete Octets

Our initial attempt to write the Lewis structure of boron trifluoride leads to a structure in which the B atom has only six electrons in its valence shell an incomplete octet. The most important contribution made by the structure with an incomplete octet. The number of species with incomplete octets is limited to some beryllium, boron, and aluminum compounds. Perhaps the best examples are the boron hydrides.



Expanded Valence Shells

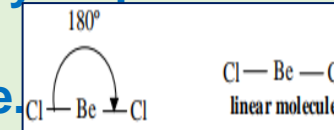
There are a few Lewis structures that break this rule by having 10 or even 12 valence electrons around the central atom, creating an expanded valence shell. Molecules with expanded valence shells typically involve nonmetal atoms of the third period and beyond that are bonded to highly electronegative atoms. For example, phosphorus forms two chlorides, PCl_3 , and PCl_5 . We can write a Lewis structure for PCl_3 with the octet rule. In PCl_5 , with five Cl atoms bonded directly to the central P atom, the outer shell of the P atom appears to have ten electrons. We might say that the valence shell has expanded to ten electrons. In the SF_6 molecule, the valence shell appears to expand to 12

Valence Shell Electron Pair Repulsion (VSEPR) Theory

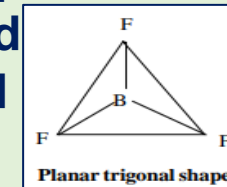
In a molecule the constituent atoms have definite positions relative to one another i.e., the molecules have a definite shape. A simple theory called VSEPR theory was put forth by Sidgwick and Powell in 1940 to explain the shapes of molecules. It was later refined and extended by Nyholm and Gillespie in 1957. This theory focuses on the electron pairs present in the valence shell of the central atom of the molecule and can be stated in terms of two postulates-

- The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion. In other words, the chemical bonds in the molecule will be energetically most stable when they are as far apart from each other as possible.

BeCl₂-the central atom, Beryllium has an electronic configuration of $1s^2 2s^2$. It has two electrons in its valence shell. In the process of covalent bond formation with two chlorine atoms two more electrons are contributed (one by each chlorine atom) to the valence shell. Thus there are a total of 4 valence electrons or two pairs of valence electrons. These electron pairs would try to keep as far away as possible. It makes the two electron pairs to be at an angle of 180° which gives the molecule a linear shape. Other molecules of this type would also have a similar shape.





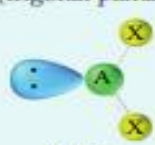
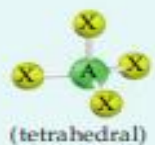







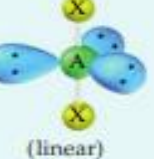






BF₃- the central atom, Boron has an electronic configuration of $1s^2 2s^2 2p^1$. It has three electrons in its valence shell. In the process of covalent bond formation with three fluorine atoms three more electrons are contributed (one by each fluorine atom) to the valence shell. There are a total of 6 valence electrons or three pairs of valence electrons. These electron pairs would try to keep as far apart as possible. It makes the three electron pairs to be located at an angle of 120° which gives the molecule a planar trigonal shape.



- Different molecules would have different shapes depending on the number of valence shell electrons involved.
- The most common situations are those in which central atoms have two, three, four, five, or six electron groups distributed around them.
- The molecular geometry is the same as the electron-group geometry only when all electron groups are bond pairs. These are for the VSEPR notation (that is, AX_2 , AX_3 , AX_4 , and so on)

Molecular Geometry as a Function of Electron-Group Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	
2	linear	0	AX_2	 (linear)	180°	$BeCl_2$	
3	trigonal planar	0	AX_3	 (trigonal planar)	120°	BF_3	
	trigonal planar	1	AX_2E	 (bent)	120°	SO_2^a	
4	tetrahedral	0	AX_4	 (tetrahedral)	109.5°	CH_4	
	tetrahedral	1	AX_3E	 (trigonal pyramidal)	109.5°	NH_3	
	tetrahedral	2	AX_2E_2	 (bent)	109.5°	H_2O	
5	trigonal bipyramidal	0	AX_5	 (trigonal bipyramidal)	$90^\circ, 120^\circ$	PCl_5	
	trigonal bipyramidal	1	AX_4E^b	 (seesaw)	$90^\circ, 120^\circ$	SF_4	
	trigonal bipyramidal	2	AX_3E_2	 (T-shaped)	90°	ClF_3	
	trigonal bipyramidal	3	AX_2E_3	 (linear)	180°	XeF_2	
6	octahedral	0	AX_6	 (octahedral)	90°	SF_6	
	octahedral	1	AX_5E	 (square pyramidal)	90°	BrF_5	
	octahedral	2	AX_4E_2	 (square planar)	90°	XeF_4	

Valence Shell Electron Pair Repulsion (VSEPR) Theory

The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is greater than that between two bond pairs.

The order of repulsive force between different possibilities is-

lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

The shapes of molecules containing a combination of lone pairs and bond pairs would be distorted.

For methane, ammonia and water. All the three contain a total of 4 electron pairs around their central atom. But the nature of these is different in the three cases. In methane molecule the central carbon atom has 4 valence electrons, and it shares 4 electrons with four hydrogen atoms. There are a total of 4 bond pairs and, it should have a tetrahedral shape. In case of ammonia also there are four pairs of electrons, but their nature is different. Three of these are bond pairs while one is a lone pair. Similarly, in case of water again there are four pairs of electrons ; two are bond pairs while two are lone pairs. Due to the differences in the mutual repulsion between bond pair - bond pair and lone pair - bond pair the molecular shape would be slightly distorted from the expected tetrahedral shape.

Applying VSEPR Theory

- Draw a plausible Lewis structure of the species (molecule or polyatomic ion).
- Determine the number of electron groups around the central atom and identify them as being either bond-pair electron groups or lone pairs of electrons.
- Establish the electron-group geometry around the central atom linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral.
- Determine the molecular geometry from the positions of the atoms bonded directly to the central atom

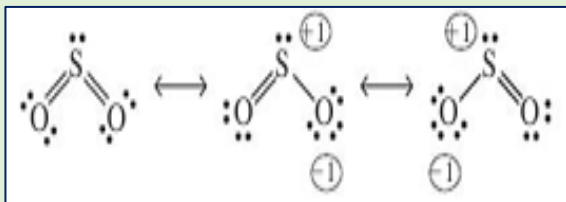
Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Molecular Shape	Bond angle (in degrees)
CH ₄	4	0	tetrahedral		109.5
NH ₃	3	1	trigonal pyramidal		107
H ₂ O	2	2	angular or bent		104.5

Molecular geometries of molecules with 4 electron pairs with different combinations of lone pairs and bond pairs.

VSEPR Theory- Structures with Multiple Covalent Bonds

In a multiple covalent bond, all electrons in the bond are confined to the region between the bonded atoms, and together constitute one group of electrons. For predicting the molecular geometry of sulfur dioxide. S is the central atom, and the total number of valence electrons is $3 \times 6 = 18$

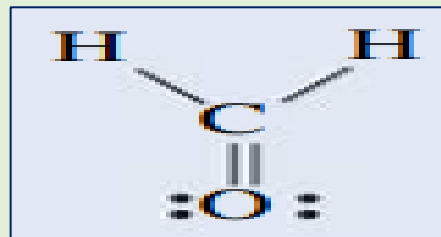
The Lewis structure is the resonance hybrid of the three contributing structures shown as-



Because we count the electrons in the double covalent bond as one group, the electron-group geometry around the central S atom is that of three electron groups trigonal-planar. Of the three electron groups, two are bonding groups and one is a lone pair. This is the case of AX_2E . The molecular shape is angular, or bent, with an expected bond angle of 120° (The measured bond angle in SO_2 is 119°)

Molecular geometry of formaldehyde, H_2CO

The Lewis structure of the molecule is shown,



There are three electron groups around the C atom, two groups in the carbon-to-hydrogen single bonds and the third group in the carbon-to-oxygen double bond. The electron-group geometry for three electron groups is trigonal-planar. Because all the electron groups are involved in bonding, the VSEPR notation for this molecule is AX_3 . The molecular geometry is also trigonal-planar

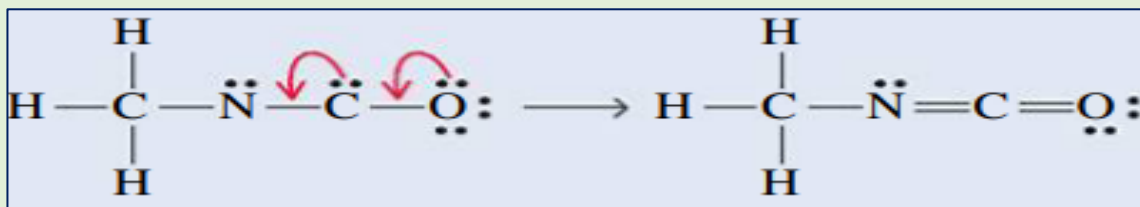
VSEPR Theory- Molecule with More Than One Central Atom

Methyl isocyanate, CH_3NCO is used in the manufacture of insecticides, such as carbaryl (Sevin). In the molecule, the three H atoms and the O atom are terminal atoms and the two C and one N atom are central atoms.

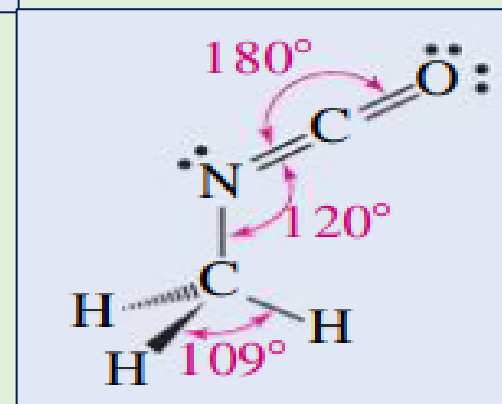
The number of valence electrons in the structure is,

From C	From N	From O	From H
(2×4)	(1×5)	(1×6)	$(3 \times 1) = 22$

In drawing the skeletal structure and assigning valence electrons, we first obtain a structure with incomplete octets. By shifting the indicated electrons, we can give each atom an octet.



The C atom on the left has four electron groups around it all bond pairs. The shape of this end of the molecule is tetrahedral. The C atom to the right, by forming two double bonds, is treated as having two groups of electrons around it. This distribution is linear. For the N atom, three groups of electrons are distributed in a trigonal planar manner. The C-N-C bond angle should be about 120°



Modern Theories of Chemical Bonding

The processes of bond formation and the bonding in simple molecules can be conveniently represented in terms of electron – dot structures. Further, the VSEPR theory provides a good idea of the shapes of the molecules. This is representing of electrons as well defined dots i.e., localized particles.

This is in contradiction with the probabilistic (orbital) representation of the electron.

The theories of chemical bonding proposed (in 1916) by Kossel and Lewis are called as classical theories of bonding. These do not take into account the wave mechanical or quantum mechanical principles.

After the development of quantum mechanical description of atomic structure two more theories were proposed to explain the bonding between atoms. These are called modern theories of chemical bonding.

These are

- Valence Bond Theory (VBT)
- Molecular Orbital Theory (MOT)

Valence Bond Theory

Valence bond theory was proposed by Heitler and London in 1927, to describe the formation of hydrogen molecule from its atoms. Linus Pauling and others further developed it.

In this approach the process of chemical bond formation can be visualized as the overlapping of atomic orbitals of the two atoms as they approach each other.

The strength of the bond depends on the effectiveness or extent of the overlapping. Greater the overlapping of the orbitals, stronger is the bond formed.

Valence Bond Theory

Bonding in hydrogen molecule to understand the VBT approach

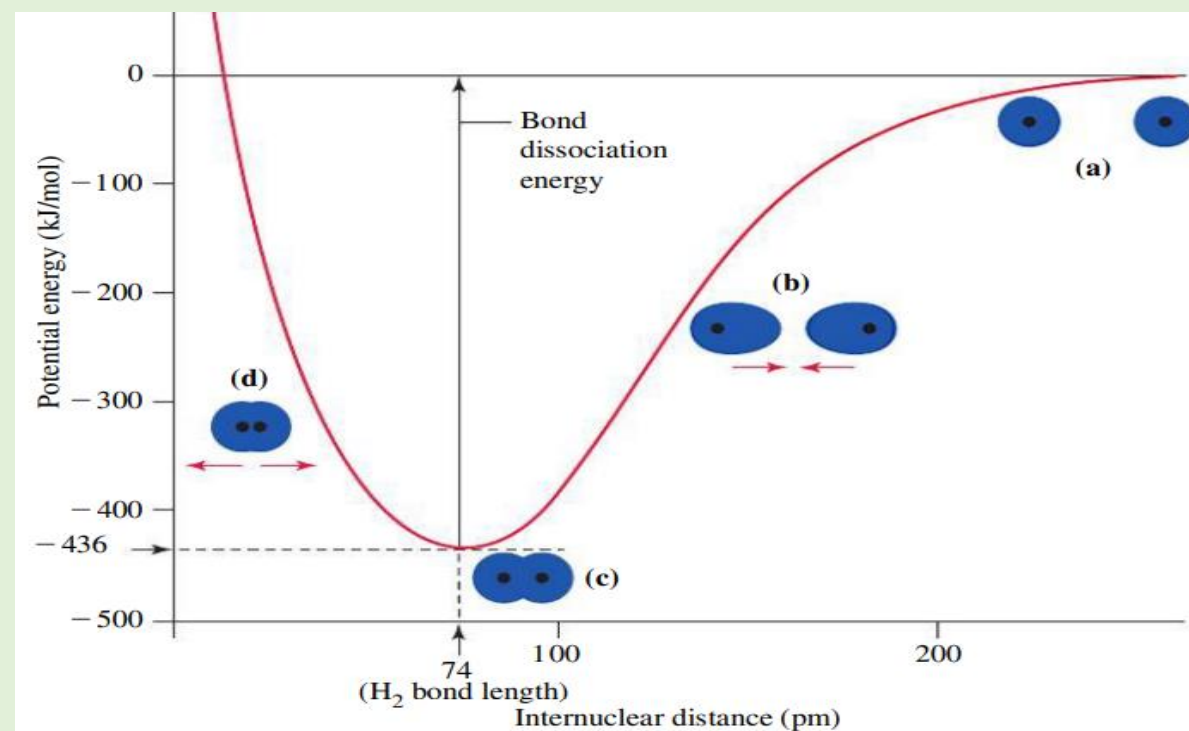
Suppose that the two hydrogen atoms are at infinite distance from each other. Their electrons are in their respective 1s orbitals and are under the influence of the corresponding nuclei. As the two atoms approach each other their 1s orbitals begin to overlap which lead to decrease in energy,. At a distance equal to the bond length the overlapping is maximum and the energy is minimum. The overlapping can be equated to the sharing of electrons between the atoms. The electrons occupying the shared region of orbitals are under the influence of both the nuclei.

(a) The potential energy is defined as zero when the two H atoms are infinitely separated.

(b) Where the curve slopes downward from right to left, the net interaction is attractive. When the interaction is attractive, the potential energy decreases as the internuclear distance, r , decreases.

(c) Where the curve is flat, at the bottom of the potential energy well, there is no tendency either to attract or to repel. The molecule is most stable at this internuclear distance (74 pm).

(d) Where the curve slopes upward from right to left, the interaction is repulsive. When the interaction is repulsive, the potential energy increases as the internuclear distance, r , decreases.

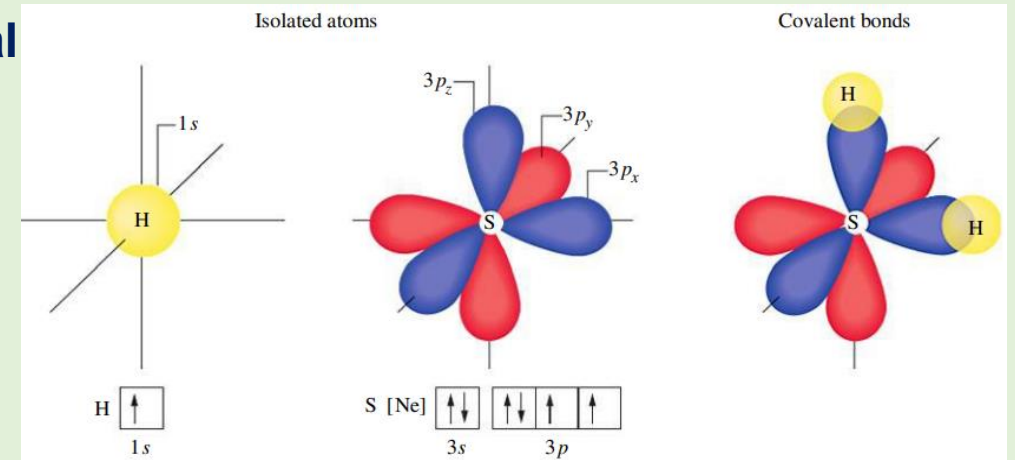


Energy of interaction of two hydrogen atoms plotted for internuclear separations from zero to infinity

Valence Bond Theory- Molecular Structure

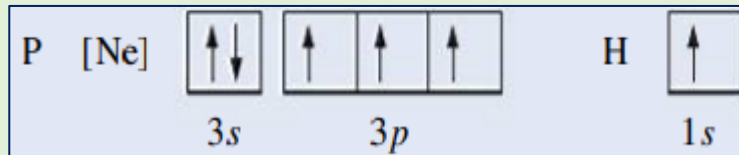
Hydrogen sulfide, H_2S

Maximum overlap between the orbital of a H atom and a p orbital of a S atom occurs along a line joining the centers of the H and S atoms.

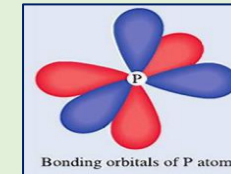


Phosphine PH_3

Draw valence-shell orbital diagrams for the separate atoms.



Sketch the orbitals of the central atom (P) that are involved in the overlap.

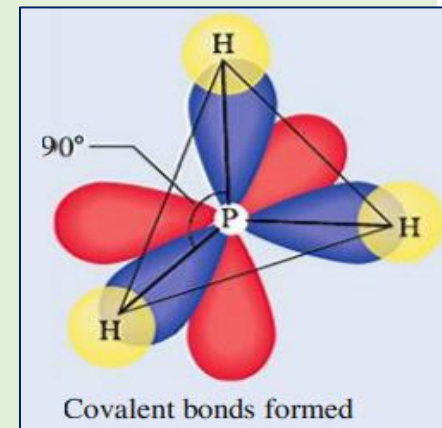


Complete the structure by bringing together the bonded atoms and representing the orbital overlap.

PH_3 is a trigonal-pyramidal molecule. The three H atoms lie in the same plane.

The P atom is situated at the top of the pyramid above the plane of the H atoms, and the three H-P-H bond angles are 90° .

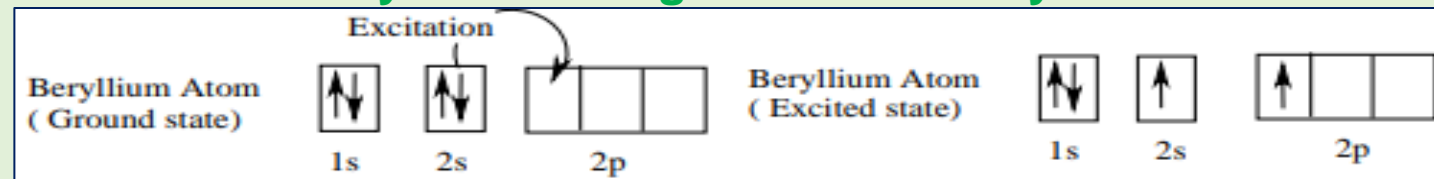
The predicted bond angle is 90° and the experimentally measured bond angles are 93° to 94° . These are in good agreement.



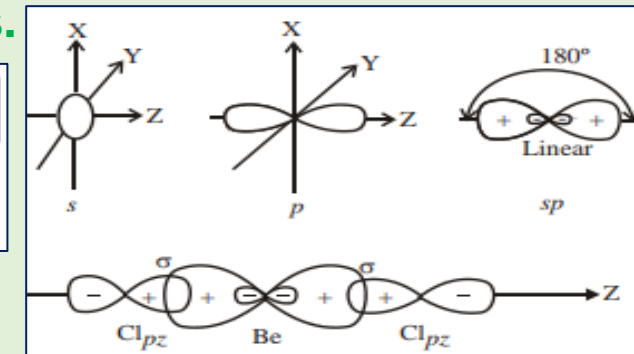
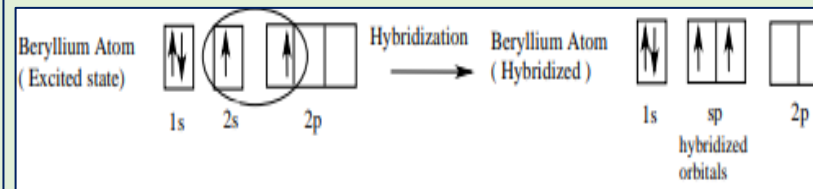
Hybridization

Bonding in a triatomic molecule, beryllium hydride (BeH_2) to understand the concept of hybridization of orbitals and the need for the same.

The atomic number of beryllium is 4. Its electronic configuration is $1s^2 2s^2$. In order to form bonds with two hydrogen atoms the valence electrons (2s) of beryllium atom must overlap with the 1s electrons of the two hydrogen atoms. **The valence shell of beryllium atom contains both the electrons in the same orbital (i.e., 2s)** it cannot overlap with the 1s orbital of hydrogen atoms containing one electron [an orbital can contain a maximum of two electrons with opposite spin]. **Pauling got over this problem by suggesting that in the process of bond formation an electron from the 2s orbital of beryllium atom gets momentarily excited to the empty 2p orbital.** Two valence electrons are in two singly occupied orbitals which can overlap with the 1s orbitals of the two hydrogen atoms and form two bonds. **The two bonds formed by these overlaps would be of different nature.** One of these would involve overlapping of 2s orbital of beryllium with 1s orbital of hydrogen while the other would involve overlapping of 2p orbital of beryllium with 1s orbital of hydrogen. **Experimentally the two bonds are found to be equivalent.** A concept called hybridization of orbitals considers to solve that. Two or more than two non equivalent orbitals (having different energies and shapes) of comparable energies mix or hybridize and give rise to an equal number of equivalent (same energies and shapes) hybrid orbitals.



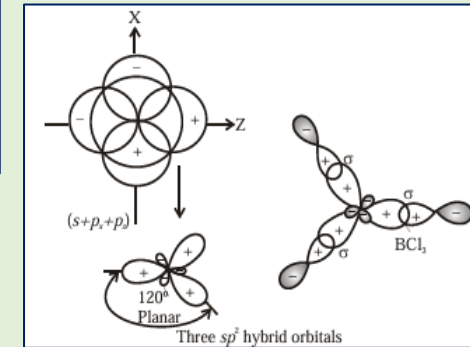
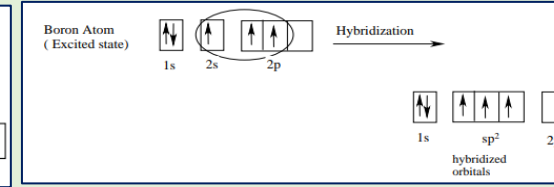
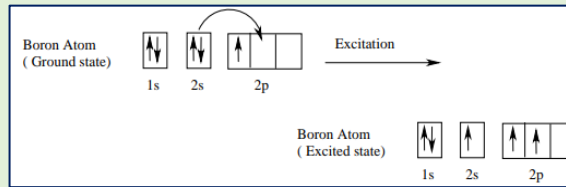
In case of BeCl_2 , the two singly occupied orbitals (2s and 2p) hybridize to give two sp hybrid orbitals. This is called sp- hybridization. These hybrid orbitals lie along the z-direction and point in opposite directions. These hybrid orbitals can now overlap with the 1s orbitals of hydrogen atoms to give the linear molecule of BeCl_2 .



Hybridization

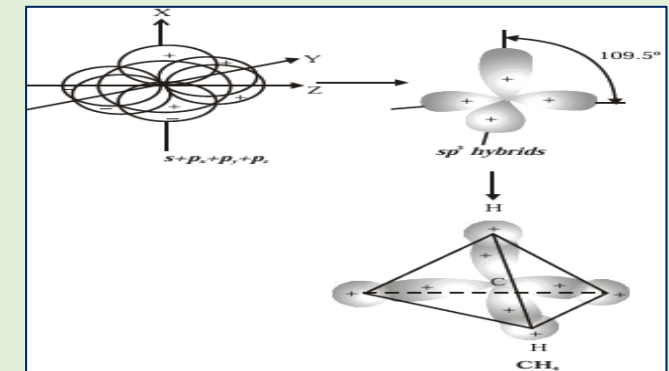
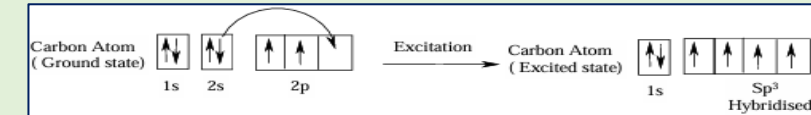
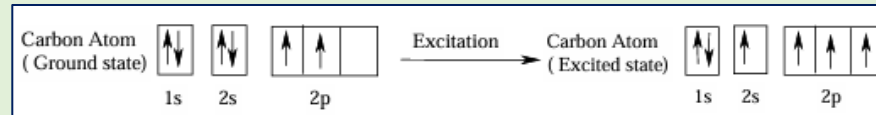
Boron trichloride (sp^2 hybridization)

In boron there are five electrons and the electronic configuration is $1s^2 2s^2 2p^1$. There are three electrons in the valence shell. In order to form bonds with three chlorine atoms one of the electrons from the 2s orbital of boron atom is excited to its 2p orbital. One 2s orbital and two 2p orbitals hybridize to give three sp^2 hybridized orbitals. This is called sp^2 - hybridization. The three hybridized orbitals are coplanar and directed towards the corners of an equilateral triangle. These hybrid orbitals then form bonds with the p-orbitals of chlorine atoms.



Methane (sp^3 hybridization)

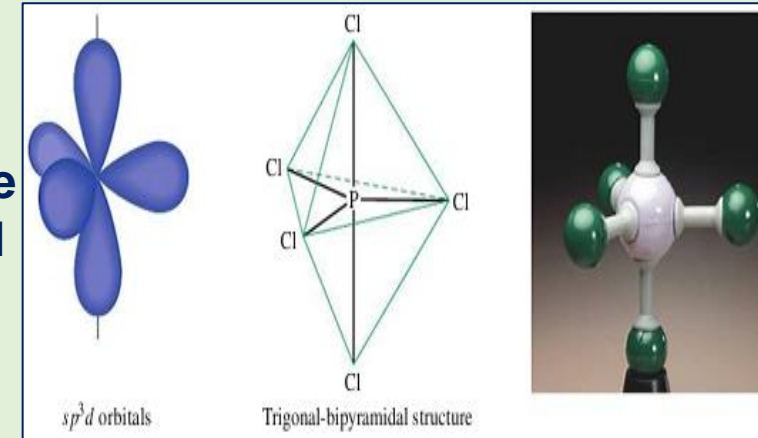
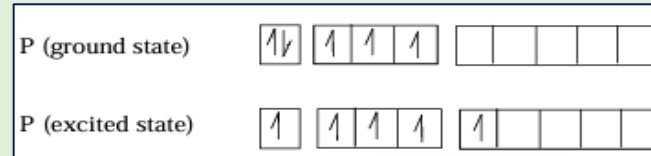
In methane the central atom, carbon, has an electronic configuration of $1s^2, 2s^2, 2p^2$. In order to form bonds with four hydrogen atoms one of the electrons from the 2s orbital of carbon atom is excited to the 2p orbital. One 2s orbital and three 2p orbitals of the carbon atom then hybridize to give four sp^3 hybridized orbitals. This is called sp^3 - hybridization. These four sp^3 hybrid orbitals are directed towards the corners of a regular tetrahedron. These hybrid orbitals then form bonds with the 1s orbitals of hydrogen atoms to give a methane molecule.



Hybridization

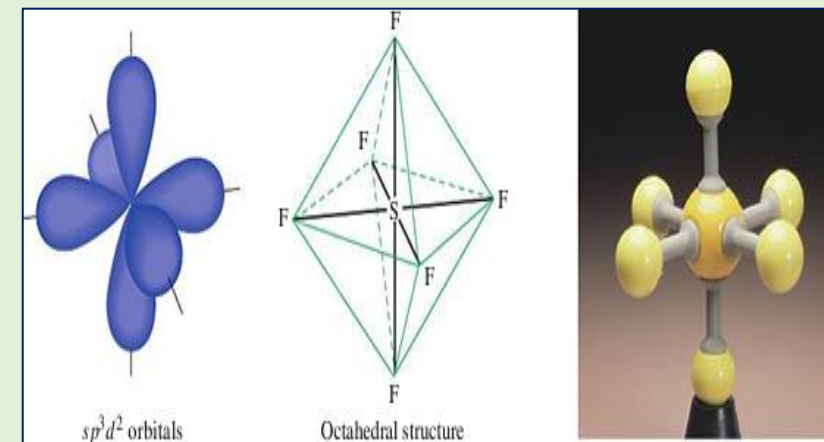
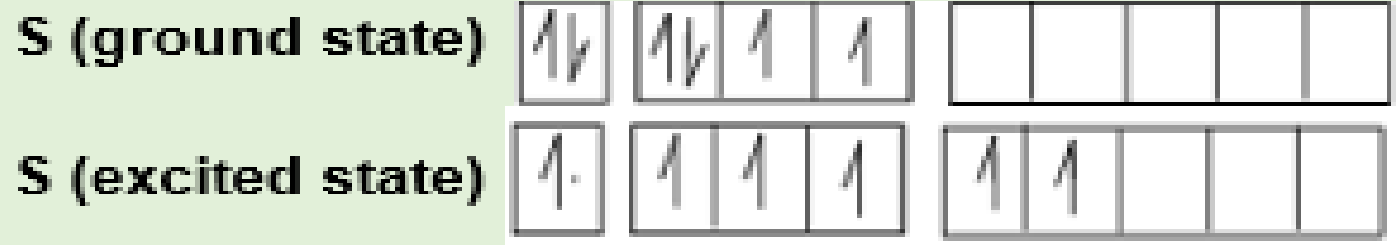
Phosphorus pentachloride (sp^3d hybridization)

Five sp^3d hybrid orbitals are formed which are directed towards the corners of a trigonal bipyramidal. These orbitals overlap with singly filled p-orbitals of five chlorine atoms and five σ bonds are formed. PCl_5 molecule has a trigonal bipyramidal geometry. Three P–Cl bonds (equatorial) make an angle of 120° with each other and lie in one plane. The other two P–Cl bonds (axial) are at 90° to the equatorial plane, one lying above and the other lying below the plane.



SF_6 (sp^3d^2 hybridization)

Six sp^3d^2 hybrid orbitals are formed which are directed towards the corners of a regular octahedron. These orbitals overlap with singly filled orbitals of six F atoms and form σ bonds giving a regular octahedral geometry.



Hybridization

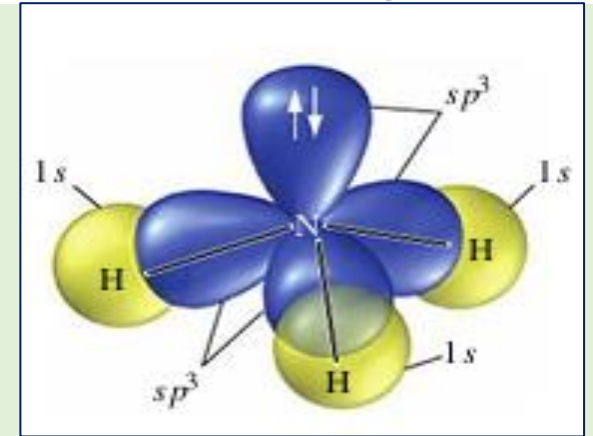
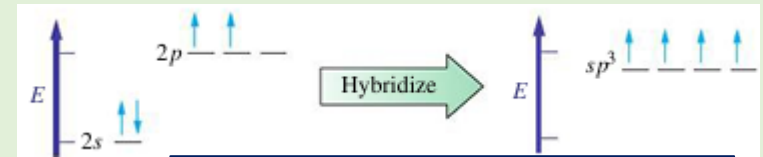
Bonding in H_2O and NH_3

Applied to H_2O and NH_3 to VSEPR theory describes a tetrahedral electron group geometry for four electron groups. This, in turn, requires a sp^3 hybridization scheme for the central atoms in H_2O and NH_3 . This scheme suggests angles of 109.5° for the H-O-H bond in water and the H-N-H bonds in NH_3 . These angles are in reasonably good agreement with the experimentally observed bond angles of 104.5° in water and 107° in NH_3 . Bonding in NH_3 , for example, can be described in terms of the following valence-shell orbital diagram for nitrogen.

Because one of the orbitals is occupied by a lone pair of electrons, only the three half-filled orbitals are involved in bond formation. This suggests the trigonal-pyramidal molecular geometry.

Even though the sp^3 hybridization scheme seems to work quite well for H_2O and NH_3 , both theoretical and experimental (spectroscopic) evidence favors a description based on unhybridized p orbitals of the central atoms. The H-O-H and H-N-H bond angle expected for 1s and 2p atomic orbital overlaps is 90° which does not conform to the observed bond angles. One possible explanation is that because O-H and N-H bonds have considerable ionic character, repulsions between the positive partial charges associated with the H atoms force the H-O-H and H-N-H bonds to open up to values greater than 90° .

The issue of how best to describe the bonding orbitals in H_2O and NH_3 is still unsettled and underscores the occasional difficulty of finding a single theory that is consistent with all the available evidence.



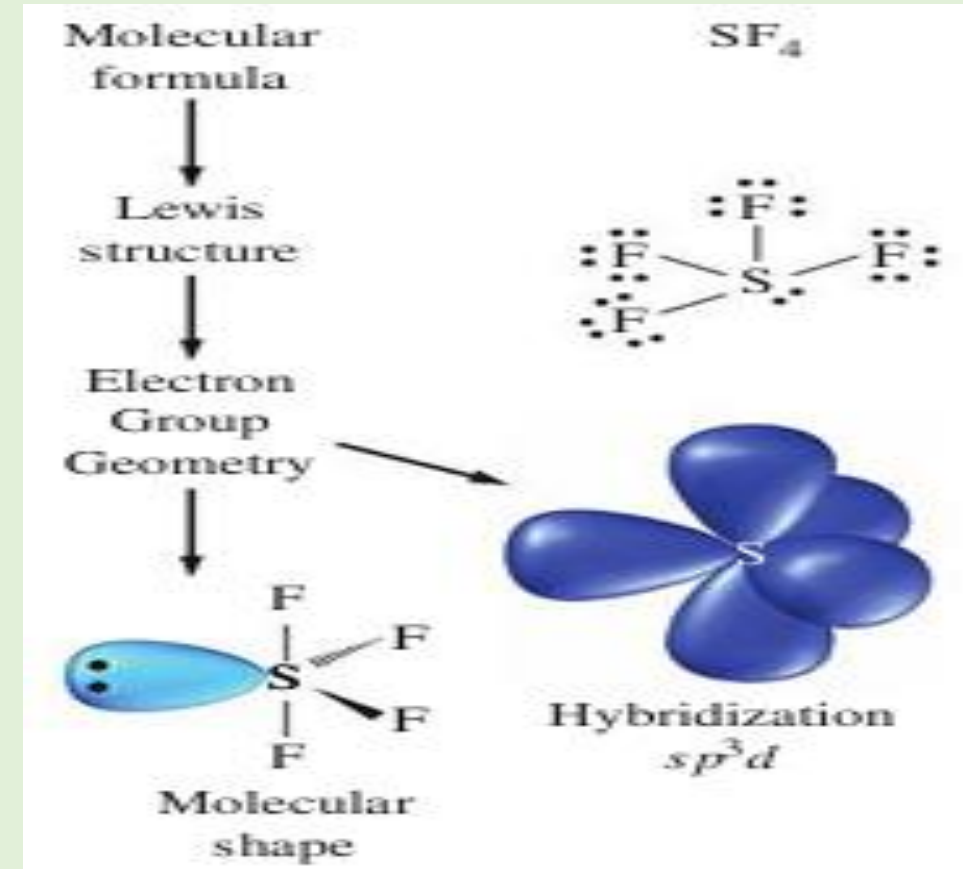
Hybrid Orbitals and the VSEPR Theory

Likely hybridization scheme for a central atom in a structure in the valence-bond method is identified by

- writing a plausible Lewis structure for the species of interest
- using VSEPR theory to predict the probable electron-group geometry of the central atom
- selecting the hybridization scheme corresponding to the electron-group geometry

Some Hybrid Orbitals and Their Geometric Orientations

Hybrid Orbitals	Geometric Orientation	Example
sp	Linear	BeCl_2
sp^2	Trigonal-planar	BF_3
sp^3	Tetrahedral	CH_4
sp^3d	Trigonal-bipyramidal	PCl_5
sp^3d^2	Octahedral	SF_6



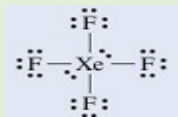
Using electron-group geometry to determine hybrid orbitals

Hybrid Orbitals and the VSEPR Theory

The shape of the XeF_4 molecule and a hybridization scheme

- **Write a plausible Lewis structure-** The Lewis structure we write must account for 36 valence electrons eight from the Xe atom and seven each from the four F atoms. To place this many electrons in the Lewis structure, we must expand the valence shell of the Xe atom to accommodate 12 electrons.

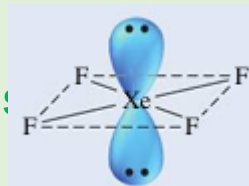
The Lewis structure is



- **Use the VSEPR theory to establish the electron-group geometry of the central atom-** From the Lewis structure, we see that there are six electron groups around the Xe atom. Four electron groups are bond pairs and two are lone pairs. The electron-group geometry for six electron groups is octahedral.

Describe the molecular geometry- The VSEPR notation for XeF_4 is AX_4E_2 , and the molecular geometry is square-planar. The four pairs of bond electrons are directed to the corners of a square, and the lone pairs of electrons are found above and below the plane of the Xe and F atoms, as shown here.

- **Select a hybridization scheme that corresponds to the VSEPR prediction-** The only hybridization consistent with an octahedral distribution of six electron groups is sp^3d^2 .



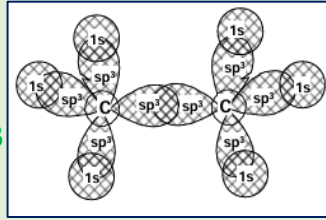
The orbital diagram for this scheme shows clearly that four of the eight valence electrons of the central Xe atom singly occupy four of the sp^3d^2 orbitals. The remaining four valence electrons of the atom occupy the remaining two sp^3d^2 orbitals as lone pairs. These are the lone pairs of electrons situated above and below the plane of the Xe and F atoms in the sketch.

Valence shell of Xe atom



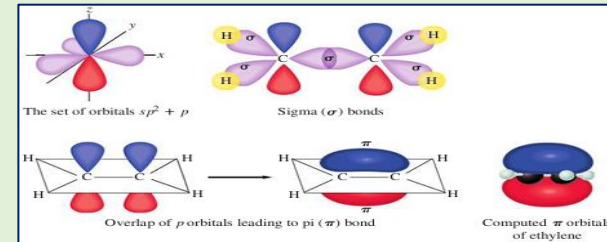
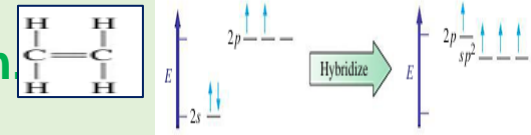
Hybridization and Multiple Bonds

Bonding in ethane (C_2H_6), two carbon atoms are bonded to each other and each carbon atom is bonded to three hydrogen atoms. In ethane each carbon atom undergoes sp^3 hybridization to give four sp^3 hybridized orbitals. The two carbon atoms form a carbon-carbon bond by $\text{sp}^3\text{-sp}^3$ overlapping. The remaining six sp^3 hybridized orbitals overlap with 1s orbitals of hydrogen atoms to give a molecule of ethane, C_2H_6 . The C-C bond so formed is along the internuclear axis. Such a bond is called a σ bond.

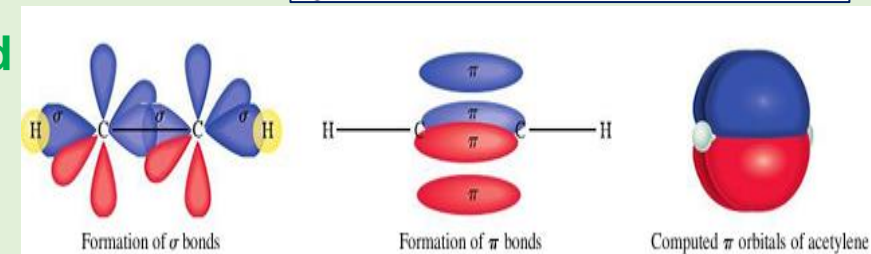
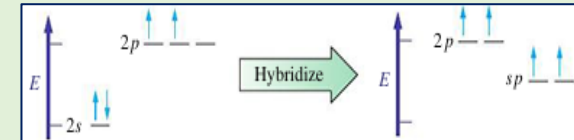


Bonding in ethene, the relevant orbitals of the carbon atoms undergo sp^2 hybridization.

Two of the three p orbitals of the carbon atoms hybridize with the 2s orbital to form three sp^2 hybrid orbitals each. The remaining p-orbitals (one on each carbon atom) do not take part in hybridization. A carbon – carbon bond is formed by overlapping of sp^2 orbital on the two carbon atoms. The remaining four sp^2 hybridized orbitals overlap with the 1s orbitals of hydrogen atoms to give the basic skeleton of the molecule. This leaves an un-hybridized p orbital each on both the carbon atoms. These are perpendicular to the molecular plane and undergo sideways overlap to give an electron cloud in the plane above and below the molecule. This is called a π - bond. In ethene there are two bonds between the carbon atoms (one sigma and one pi bond).



Bonding in ethene, Bonding can be explained in terms of sp hybridization in carbon atoms. One 2s and one 2p orbitals hybridize to give two sp Hybridized orbitals. This leaves two mutually perpendicular unhybridized p orbitals each on both the carbon atoms. Carbon – carbon bond is formed by sp- sp overlapping with each other. Remaining sp orbital on each carbon overlaps with the 1s orbital of hydrogen to give C-H bonds.

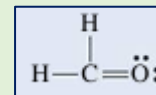


Unhybridized p orbital each on both the carbon atoms overlap sideways to give two π –bonds.

Hybridization Schemes Involving and Bonds

Molecular geometry and a bonding scheme for the Formaldehyde gas, H_2CO

Write the Lewis structure- C is the central atom, and H and O are terminal atoms. The total number of valence electrons is 12. Note that this structure requires a carbon-to-oxygen double bond.



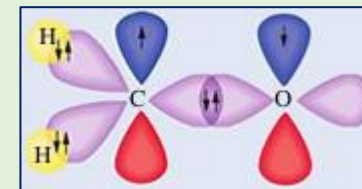
Determine the electron-group geometry of the central C atom- The σ framework is based on three electron groups around the central C atom. VSEPR theory, based on the distribution of three electron groups, suggests a trigonal-planar molecule with 120° bond angles.

Identify the hybridization scheme that conforms to the electron-group geometry-

A trigonal-planar orientation of orbitals is associated with sp^2 hybrid orbitals.

Identify the orbitals of the central atom that are involved in orbital overlap-

The C atom is hybridized to produce the orbital set $sp^2 + p$, as in C_2H_4 . Two of the sp^2 hybrid orbitals are used to form σ bonds with the H atoms. The remaining sp^2 hybrid orbital is used to form a bond with oxygen. The unhybridized p orbital of the C atom is used to form a π bond with O.

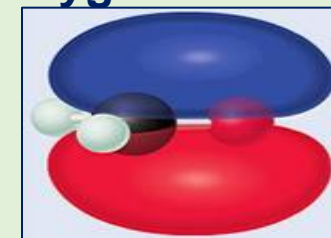
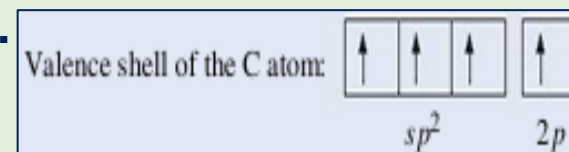


Sketch the bonding orbitals of the central and terminal atoms-

The bonding orbitals of the central C atom described above are

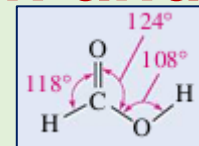
Pictured. The sp^2 hybrid orbitals are shown in lavender, and the pure p orbitals, in blue and red.

The H atoms have only 1s orbitals available for bonding. For oxygen, the half-filled 2p orbital can be used for end-to-end overlap in the σ bond to carbon, and a half-filled orbital can participate in the side-to-side overlap leading to a π bond. Thus, the valence-shell orbital diagram we can use for oxygen is



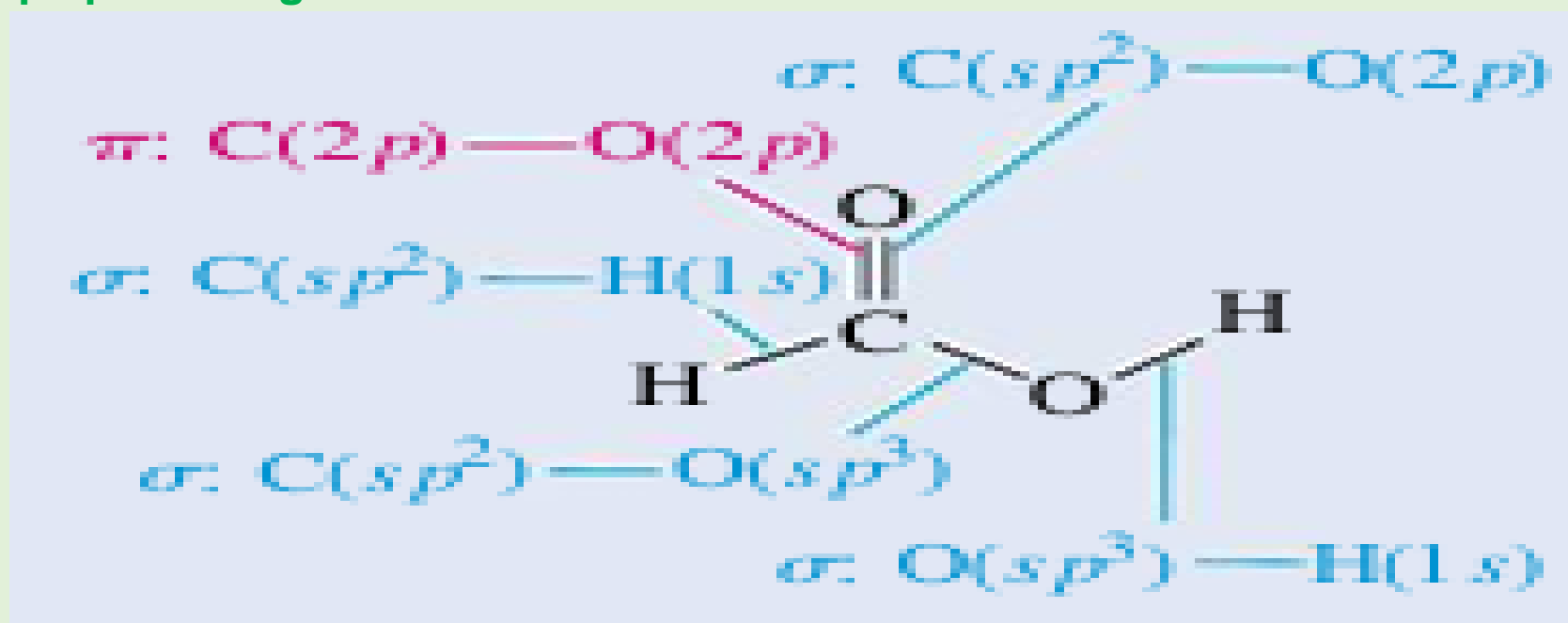
Experimental Data to Select a Hybridization and Bonding Scheme

Formic acid, HCOOH - A structural formula with bond angles is given-



Propose a hybridization and bonding scheme consistent with this structure.

The 118° H-C-O bond angle on the left is very nearly the 120° angle for a trigonal-planar distribution of three groups of electrons. This requires a sp^2 hybridization scheme for the C atom. The 124° O-C-O bond angle is also close to the 120° expected for sp^2 hybridization. The C-O-H bond angle of 108° is close to the tetrahedral angle 109.5° . The O atom on the right employs a sp^3 hybridization scheme. The four σ and one π bonds and the orbital overlaps producing them are indicated-



Molecular Orbital Theory

Lewis structures, VSEPR theory, and the valence-bond method make a potent combination for describing covalent bonding and molecular structures. They are satisfactory for most purposes. Valence bond theory describes bond formation as a result of overlapping of the atomic orbitals belonging to the constituent atoms. The overlapping region responsible for bonding is situated between the two atoms i.e., it is localized.

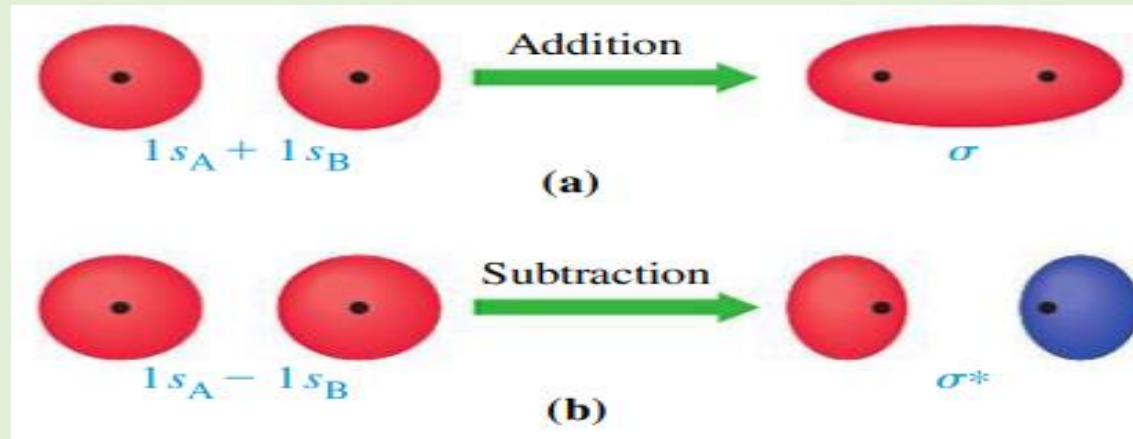
None of these methods, provides an explanation of the electronic spectra of molecules, why oxygen is paramagnetic, or why H_2^+ is a stable species.

Molecular orbital theory (MOT) developed by F. Hund and R. S. Mulliken in 1932, is based on the wave mechanical model of atom. In contrast to the localized bonding in VBT, the molecular orbital theory visualizes the bonding to be delocalized in nature i.e., spread over the whole molecule. According to MOT, in the process of bond formation

- The atomic orbitals of the constituent atoms combine to generate new types of orbitals (called molecular orbitals). These are spread over the whole molecule i.e., they are delocalized. In other words these new orbitals, do not “belong” to any one atom but extend over the entire region of the bonded atoms.
- These molecular orbitals are created by Linear Combination of Atomic Orbitals (LCAO) approach in which, the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals.
- The available electrons then fill these orbitals in the order of increasing energy as in the Aufbau principle used in the electron configurations of atoms.

Molecular Orbital Theory-Formation of H₂ Molecule

As the hydrogen atoms approach, two 1s wave functions combine by interfering constructively or destructively. Constructive interference corresponds to adding the two mathematical functions (the positive sign puts the waves in phase), while destructive interference corresponds to subtracting the two mathematical functions (the minus sign puts the waves out of phase). These two types of combination are illustrated in Figure.

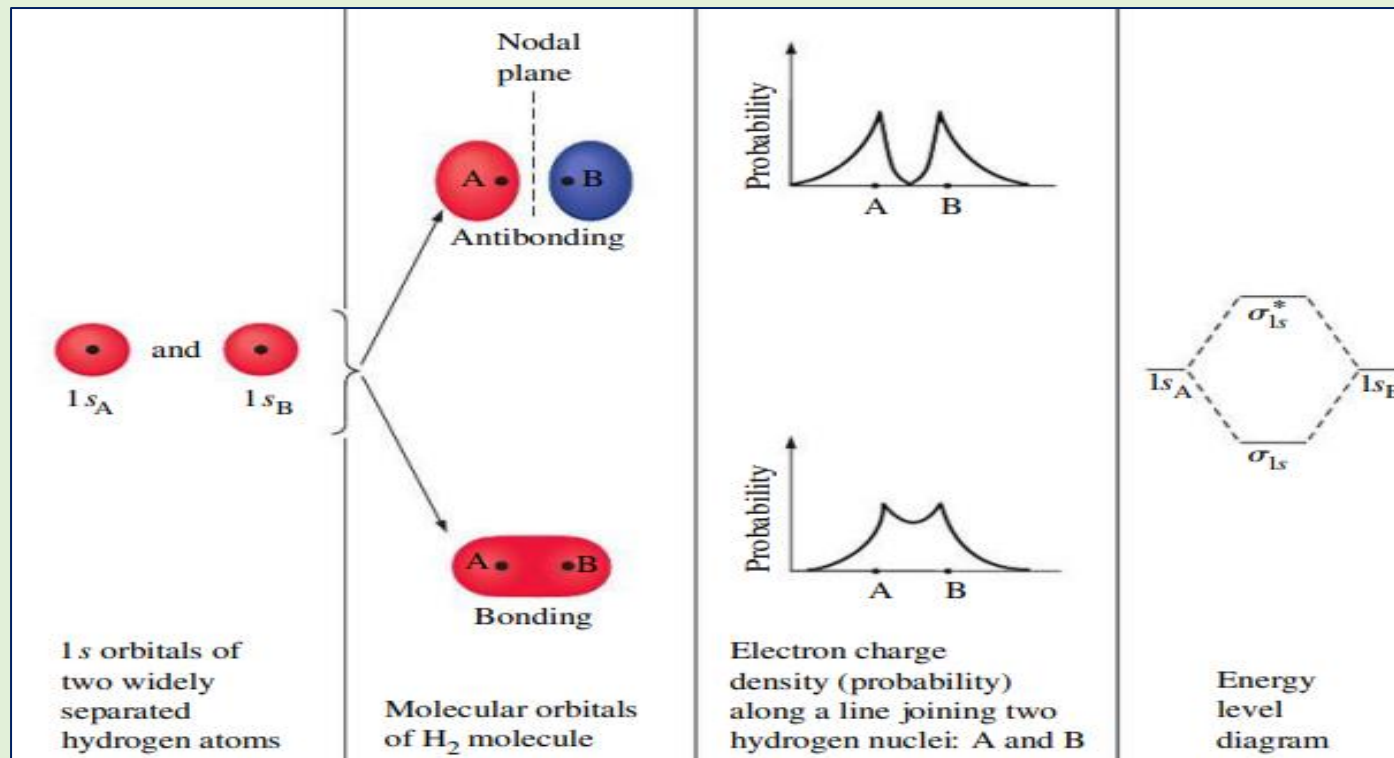


- (a) The addition of two 1s orbitals in phase to form a σ_{1s} molecular orbital. This orbital produces electron density between the nuclei, leading to a chemical bond.
- (b) The addition of two 1s orbitals out of phase to produce a σ_{1s}^* antibonding orbital. This orbital has a nodal plane perpendicular to the internuclear axis, as do all antibonding

The constructive interference (addition) of the two wave functions leads to a greater probability of finding the electron between the nuclei. The increased electron charge density between the nuclei causes them to draw closer together, forming a chemical bond. The electron probability or electron charge density in the σ_{1s} is $(1s_A + 1s_B)^2$ the square of the new function $(1s_A + 1s_B)$, where $1s_A$ and $1s_B$ are the two orbitals on the two H atoms. The square is $1s_A^2 + 1s_B^2$ plus the extra term $2 \times 1s_A 1s_B$, which is the extra charge density between the nuclei. The result of this constructive interference is a bonding molecular orbital because it places a high electron charge density between the two nuclei. A high electron charge density between atomic nuclei reduces repulsions between the positively charged nuclei and promotes a strong bond. This bonding molecular orbital, designated σ_{1s} , is at a lower energy than the 1s atomic orbitals.

Molecular Orbital Theory-Formation of H₂ Molecule

The molecular orbital formed by the destructive interference (subtraction) of the two orbitals leads to reduced electron probability between the nuclei. This produces an antibonding molecular orbital, σ_{1s}^* , because it places a very low electron charge density between the two nuclei. The electron probability or electron charge density in the σ_{1s}^* orbital is $(1s_A - 1s_B)^2$ the square of the new function $(1s_A - 1s_B)$, where $1s_A$ and $1s_B$ are the two orbitals on the two H atoms. The square is $1s_A^2 + 1s_B^2$ minus the extra term $2 \times 1s_A 1s_B$, which is the loss charge density between the nuclei. With a low electron charge density between atomic nuclei, the nuclei are not screened from each other, strong repulsions occur, and the bond is weakened (hence the term 'antibonding'). This antibonding molecular orbital, designated, σ_{1s}^* is at a higher energy than the $1s$ atomic orbitals.



The interaction of two hydrogen atoms according to molecular theory

Molecular Orbital Theory- Basic Ideas

Ideas about molecular orbitals & electron distribution

- The number of molecular orbitals (MOs) formed is equal to the number of atomic orbitals combined.
- Of the two MOs formed when two atomic orbitals are combined, one is a bonding MO at a lower energy than the original atomic orbitals. The other is an antibonding MO at a higher energy.
- In ground-state configurations, electrons enter the lowest energy MOs available
- The maximum number of electrons in a given MO is two (Pauli exclusion principle).
- In ground-state configurations, electrons enter MOs of identical energies singly before they pair up (Hund's rule).

A stable molecular species has more electrons in bonding orbitals than in antibonding orbitals. For example, if the excess of bonding over antibonding electrons is two, this corresponds to a single covalent bond in Lewis theory. In molecular orbital theory, we say that the bond order is 1. Bond order is one half the difference between the number (no.) of bonding and antibonding electrons (e^-) that is,

$$\text{bond order} = \frac{\text{no. of } e^- \text{ in bonding MOs} - \text{no. of } e^- \text{ in antibonding MOs}}{2}$$

Diatomic Molecules of the First-Period Elements

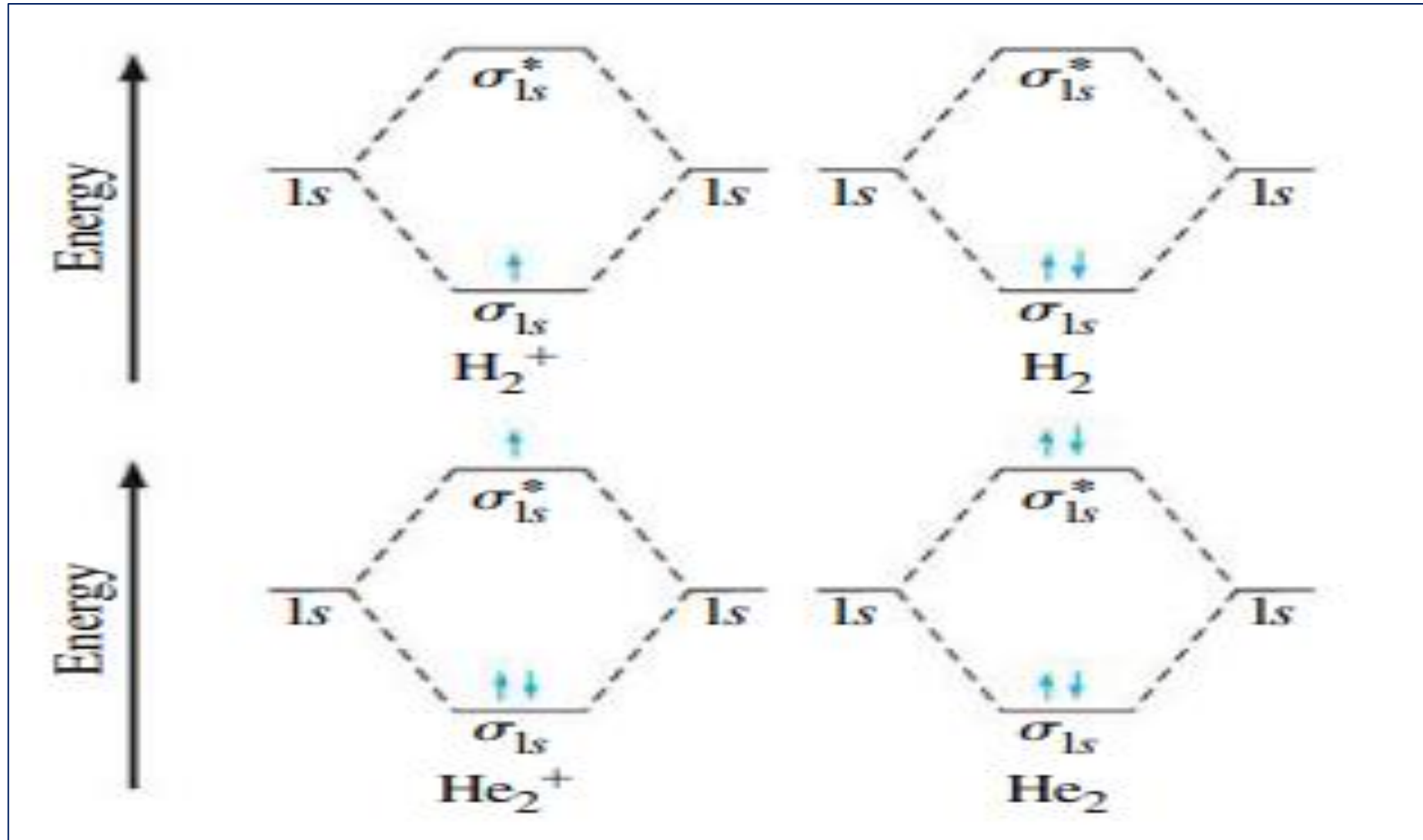
H_2^+ , This species has a single electron. It enters the orbital, a bonding molecular orbital. The bond order is $\frac{1}{2}$. This is equivalent to a one-electron, or half, bond, a bond type that is not easily described by the Lewis theory.

H_2 , This molecule has two electrons, both in the σ_{1s} orbital. The bond order is 1. With Lewis theory and the valence-bond method, we describe the bond as single covalent.

He_2^+ , This ion has three electrons. Two electrons are in the σ_{1s} orbital, and one is in the σ_{1s}^* orbital. This species exists as a stable ion with a bond order of $\frac{1}{2}$.

He_2 , Two electrons are in the σ_{1s} orbital, and two are in the σ_{1s}^* . The bond order is 0. No bond is produced. He is not a stable species.

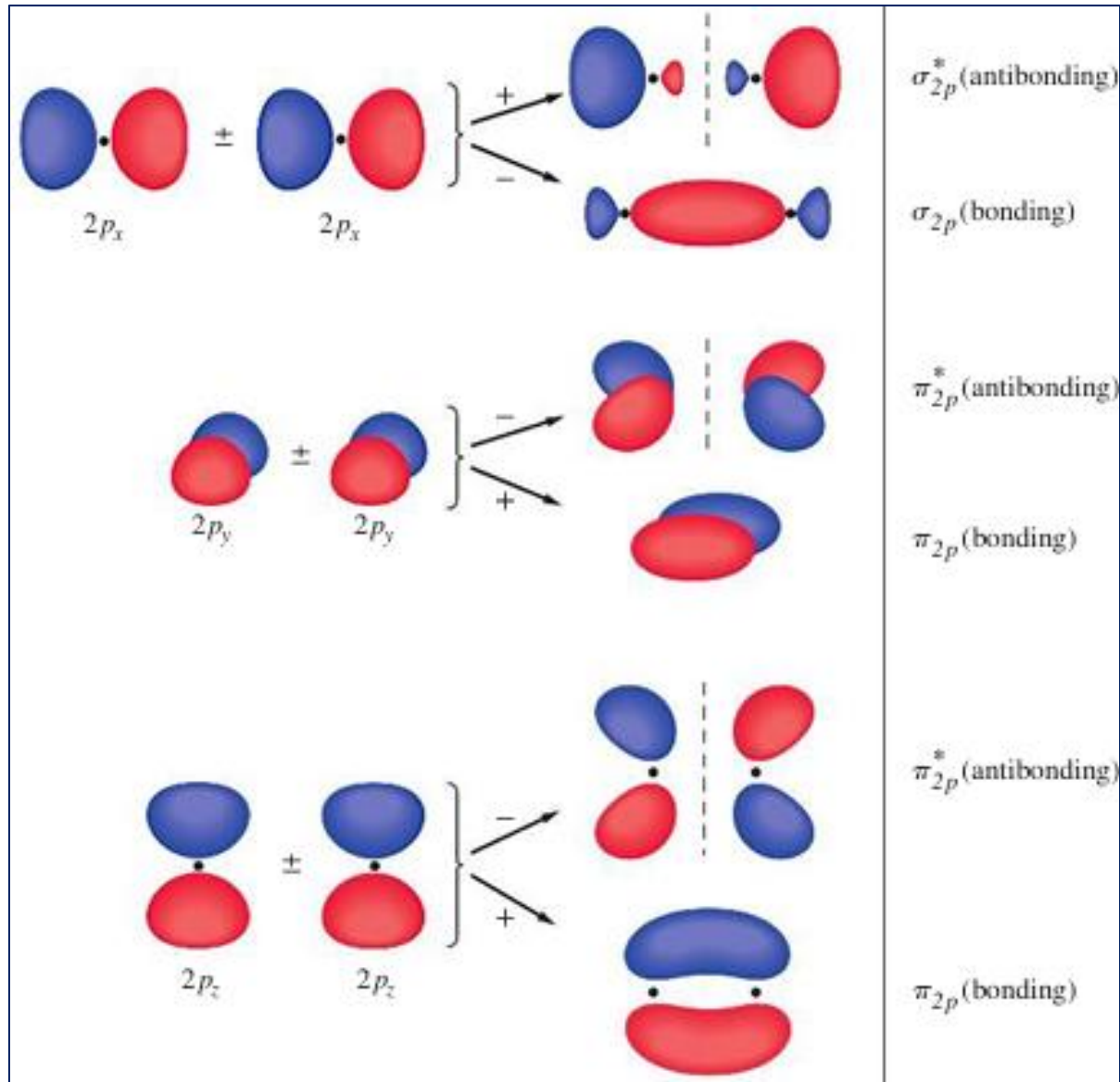
Molecular orbital- Diatomic Molecules and Ions (First-Period Element)



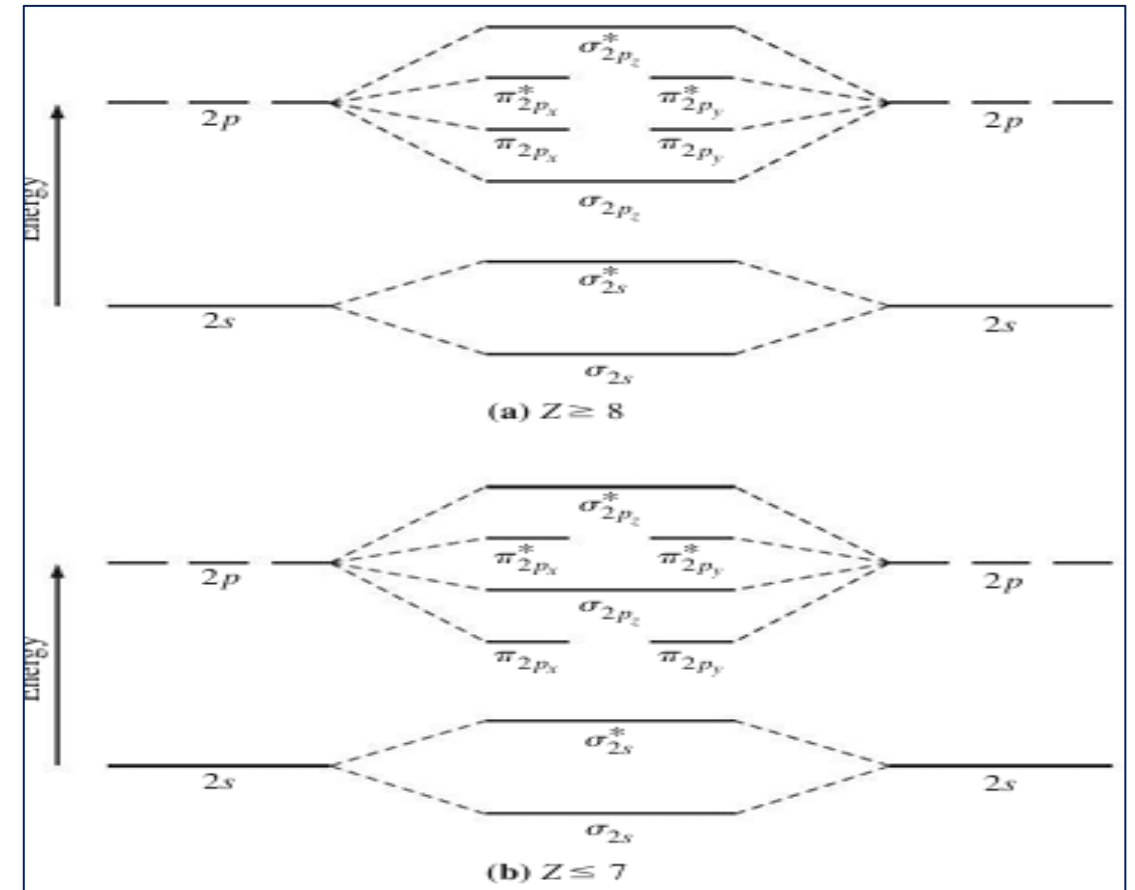
Molecular Orbitals of the Second-Period Element

The molecular orbitals formed by combining atomic orbitals are similar to those from atomic orbitals, except they are at a higher energy. For combining 2p atomic orbitals to molecular orbitals, two possible combinations are end-to-end and side-to-side. The best overlap for p orbitals is along a straight line (that is, end-to-end). This combination produces σ type molecular orbitals: σ_{2p} and σ_{2p}^* . In forming the bonding and antibonding combinations along the internuclear axis, the phase of the 2p orbitals are considered since the wave functions are in phase. The addition of the two wave functions leads to an increase of electron density in the internuclear region and produces a σ_{2p} orbital. When the two atomic orbitals are with lobes of opposite phase pointing into the internuclear region, a nodal plane midway between the nuclei is formed, leading to an σ_{2p}^* antibonding orbital. Only one pair of p orbitals can combine in an end-to-end fashion. The other two pairs must combine in a parallel or side-to-side fashion to produce molecular orbitals: π_{2p} and π_{2p}^* . The two possible ways for the side-to-side combination of a pair of 2p orbitals. The bonding orbital is formed by adding the p orbital on one nucleus to a p orbital on the other nucleus, in such a way that the positive and negative lobes of one orbital are in phase with the positive and negative lobes of the other p orbital on the other nucleus. This produces additional electron density between the nuclei, but in a much less direct way than in the σ orbital because the additional electron density is not found along the internuclear axis. Typically, the π_{2p} bond is weaker than the σ_{2p} bond. The π_{2p}^* antibonding orbital is formed by subtracting the two p orbitals perpendicular to the internuclear axes. In addition to the nodal plane that contains the nuclei, a node is formed between the nuclei, and this is a characteristic of antibonding character. There are actually four π type molecular orbitals (two bonding and two antibonding) because there are two pairs of atomic orbitals arranged in a parallel fashion. Bonding molecular orbitals place a high electron charge density between the atomic nuclei. In antibonding molecular orbitals, there are nodal planes between the nuclei, where the electron charge density falls to zero.

Molecular Orbitals of the Second-Period Element



Combining 2p atomic orbitals



The two possible molecular orbital energy level schemes for diatomic molecules of the second-period elements (a) The expected ordering when σ_{2p} lies below the π_{2p} . This is the ordering for elements with $Z \geq 8$. (b) The modified ordering due to s and p orbital mixing when σ_{2p} lies above the π_{2p} . This is the ordering for elements with $Z \leq 7$. Here, the z-axis is the internuclear axis.

MO Electronic Configuration and Properties of the Molecule

The MO energy level diagram can be used to find out the MO electronic configuration of the molecule which provides the information about some properties of the molecule.

For nitrogen molecule. An atom of nitrogen has five valence electrons; since there are two atoms, we have a total of ten valence electrons that need to be filled in the MO's. MO electronic configuration can be written as σ_{2s}^2 , σ_{2s}^{*2} , π_{2px}^2 , π_{2py}^2 , σ_{2pz}^2

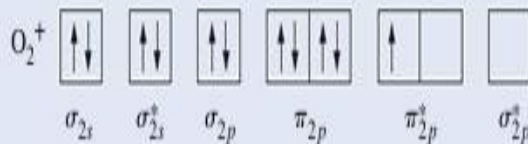
Bond order : $\frac{1}{2} [n_b - n_a] = \frac{1}{2} [8 - 2] = \frac{1}{2} [6] = 3$; this means that in nitrogen molecule, a triple bond exists between the two nitrogen atoms.

Magnetic nature: Molecules show magnetic behavior depending on their MO electronic configuration. If all the MOs are doubly occupied the substance shows diamagnetic behavior. In case one or more MOs are singly occupied, the substance shows paramagnetic behavior. The MO electronic configuration of O_2 (with 12 valence electrons) is σ_{2s}^2 , σ_{2s}^{*2} , σ_{2pz}^2 , π_{2px}^2 , π_{2py}^2 , π_{2px}^{*1} , π_{2py}^{*1} . Since it contains unpaired electrons, oxygen shows paramagnetic behavior.

The bond order and the magnetic behavior of the molecular cations and anions can also be obtained in the same way. In such cases we add one electron for every negative charge and for every +ve charge we subtract an electron. For example, O_2^{2-} (oxygen molecule dianion) would have a total of 14 valence electrons (12 + 2).

Bonding in O_2^+ with a molecular orbital diagram & the bond order

In the following diagram, there is an excess of five bonding electrons over antibonding ones. The bond order is 2.5.



	Li ₂	Be ₂	B ₂	C ₂	N ₂
Bond order	1	0	1	2	3
Magnetism	Diamagnetic	–	Paramagnetic	Diamagnetic	Diamagnetic

	O ₂	F ₂	Ne ₂
Bond order	2	1	0
Magnetism	Paramagnetic	Diamagnetic	–

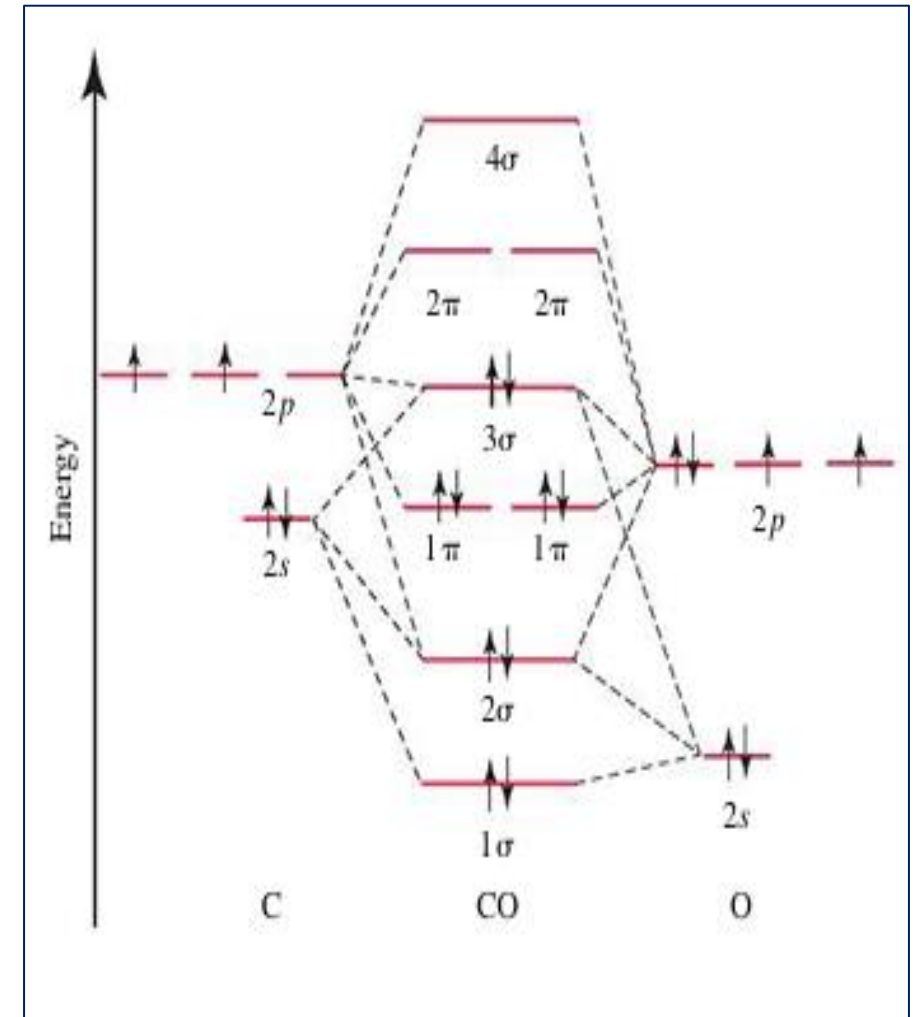
Molecular orbital occupancy diagrams for the homonuclear diatomic molecules of the second-period elements In all cases, the σ_{1s} and σ_{1s}^* molecular orbitals are filled but not shown.

Heteronuclear Diatomic Molecules

Consider the molecule carbon monoxide, CO.

First task is to decide whether or not there is 2s-2p mixing, based on our knowledge of how Z_{eff} varies across the period. The Z_{eff} of carbon is much lower than that of oxygen, and so the 2s and 2p orbitals of carbon are higher in energy than those of oxygen. This means that the contributions by each atom to the molecular orbitals will be unequal. In addition, the 2s-2p separation in carbon is much lower than in oxygen, and so we expect 2s-2p mixing to occur in the σ orbitals. As a result of 2s and 2p orbital mixing, the third σ orbital, 3σ has an orbital energy greater than that of the π_{2p} orbitals, and therefore the highest occupied molecular orbital (HOMO) is 3σ .

HOMO 3σ is dominated by the oxygen 2s orbital and is essentially nonbonding. 1σ orbital is dominated by the oxygen 2s orbital and is also essentially nonbonding. A nonbonding molecular orbital has the same energy as the atomic orbitals from which it is formed, and it neither adds to nor detracts from bond formation. The bonding in CO comes from two electrons in the 2σ orbital and two electron pairs in the degenerate 1π orbitals, producing an effective bond order of 3. The configuration of CO (ignoring the 1s orbitals) can therefore be written as follows:



The molecular orbital diagram of CO
The σ orbitals for CO are labeled 1σ , 2σ , 3σ , and 4σ , because these orbitals are mixtures of 2s and 2p orbitals from both C and O.

MO Configuration of Heteronuclear Diatomic Molecules

Molecular orbital for the cyanide ion, CN^- , and the bond order

The number of valence electrons to be assigned to the molecular orbitals is $10(4 + 5 + 1)$. Because of the $2s-2p$ mixing, we use the modified order of molecular orbitals and write the configuration of CN^- as

$$1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$$

Or, as an approximation,

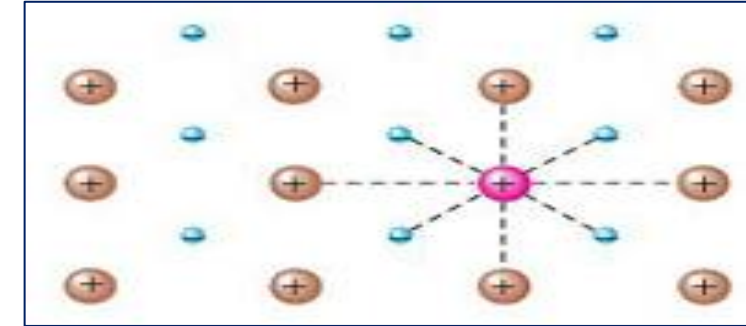
$$\sigma_{2s}^2 \sigma_{2s}^{*2} 1\pi^4 \sigma_{2p}^2$$

which gives a bond order of $(2 + 4 + 2 - 2)/2 = 3$.

Bonding in Metals

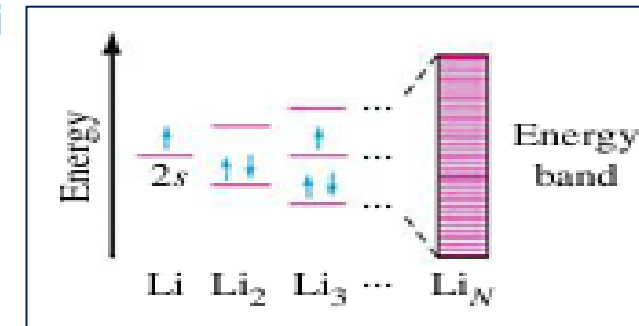
The Electron Sea Model- pictures a solid metal as a network of positive ions immersed in a sea of electrons. In lithium, for instance, the ions are Li^+ and one electron per atom is contributed to the sea of electrons. Electrons in the sea are free (not attached to any particular ion), and they are mobile. Thus, if electrons from an external source enter a metal wire at one end, free electrons pass through the wire and leave the other end at the same rate. In this way, electrical conductivity is explained. Free electrons (those in the electron sea) are not limited in their ability to absorb photons of visible light as are electrons bound to an atom. Thus, metals absorb visible light; they are opaque.

Electrons at the surface of a metal are able to reradiate at the same frequency light that strikes the surface, which explains the lustrous appearance of metals. The ease of deformation of metals can be explained as follows: If one layer of metal ions is forced across another, perhaps by hammering, no bonds are broken, the internal structure of the metal remains essentially unchanged, and the sea of electrons rapidly adjusts to the new situation.



Band Theory- the theory of metallic bonding used is a form of molecular orbital theory called band theory.

Consider the formation of molecular orbitals and the bonding between two Li atoms. Each Li atom contributes one 2s orbital to the production of two molecular orbitals σ_{2s} and σ_{2s}^* . Electrons fill the σ_{2s} orbital and leave the σ_{2s}^* empty. If we extend this combination of Li atoms to a third Li atom, three molecular orbitals are formed, containing a total of three electrons. Again, the set of molecular orbitals is half filled. We can extend this process to an enormously large number (N) of atoms the total number of atoms in a crystal of Li. Here is the result we get: a set of N molecular orbitals with an extremely small energy separation between each pair of successive levels. This collection of very closely spaced molecular orbital energy levels is called an energy band. In the band just described, there are N electrons (a 2s electron from each Li atom) occupying, N/2 molecular orbitals of Lowest energy. These are the electrons responsible for bonding the Li atoms together. They are valence electrons, and the band in which they are found is called a valence band.



Molecular orbital theory, in the form called band theory, can be applied to metals, semiconductors, and insulators. Band theory explains thermal and electric conductivity, the ease of deformation, and the characteristic luster of metals. It also explains the colors of semiconductors and the fact that their electric conductivities increase with temperature.

Check List

1. Describe the intermolecular forces occurring in the following molecules: H_2O , NH_3 , Hexane, NaCl in H_2O .
2. Write Lewis symbols for the following elements: (a) N, P, As, Sb, Bi; (b) Al, I, Se, Ar
3. Write Lewis structures for the following compounds: (a) BaO ; (b) MgCl_2 ; (c) aluminum oxide.
4. Write a Lewis structure for the ammonia molecule, NH_3 .
5. Write plausible Lewis structures for (a) CS_2 , (b) HCN , and (c) COCl_2 .
6. Write plausible Lewis structures for (a) formic acid, HCOOH , and (b) acetaldehyde, CH_3CHO
7. Write plausible Lewis structures for the following ions: (a) NO^+ ; BF_4^- ; (b) N_2H_5^+ ; (c) NH_3OH^+ ; O_2^- .
8. Write the most plausible Lewis structure of nitrosyl chloride, NOCl (using formal charge).
9. Write the Lewis structure of the acetate ion, Analyze CH_3COO^- .
10. Using VSEPR theory, predict the molecular geometry of the polyatomic anion ICl_4^- .
11. What is VSEPR theory ? predict the shape of SF_6 molecule using this theory.
12. Why do we need the concept of hybridization ? How does it help in explaining the shape of methane.
13. Be_2 molecule does not exist. Explain on the basis of molecular orbital theory.
14. Write down the molecular orbital electronic configuration of the following species and compute their bond orders. O_2 ; O_2^+ ; O_2^- ; O_2^{2-}
15. Describe the molecular geometry and propose a plausible hybridization scheme for the central atom in the ion Cl_2F^+ .
16. Write the electron configuration for CN^+ , and determine the bond order.
17. Explain the metallic bonding in sodium applying band theory.