CHEMICAL BONDING

Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule. Obviously there must be some force which holds these constituent atoms together in the molecules. The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond. Since the formation of chemical compounds takes place as a result of combination of atoms of various elements in different ways, it raises many questions. Why do atoms combine? Why are only certain combinations possible? Why do some atoms combine while certain others do not? Why do molecules possess definite shapes? To answer such questions different theories and concepts have been put forward from time to time. These are Kössel-Lewis approach, Valence Shell Electron Pair Repulsion (VSEPR) Theory, Valence Bond (VB) Theory and Molecular Orbital (MO) Theory. The evolution of various theories of valence and the interpretation of the nature of chemical bonds have closely been related to the developments in the understanding of the structure of atom, the electronic configuration of elements and the periodic table. Every system tends to be more stable and bonding is nature's way of lowering the energy of the system to attain stability.

TYPES OF CHEMICAL BONDS

Chemical Bond: The force which holds the atoms or ions together in a compound

The two types of chemical bonds are ionic bonds and covalent bonds.

- Ionic bonds hold ions together in ionic compounds.
- Covalent bonds hold atoms together in molecules.
- A **covalent bond** is formed when there is an equal sharing of electrons between two atoms.� The atoms forming a covalent bond must have relatively equal attraction for the electrons.� The bonds between the carbon atom and the hydrogen atoms in the compound methane CH_4 are examples of covalent bonds between two different elements.

IONIC BONDING AND STRUCTURES OF IONIC COMPUNDS

Metals lose electrons from their valence shell

→ positively charged ions = cations

Nonmetals gain electrons, adding electrons to their valence shell.

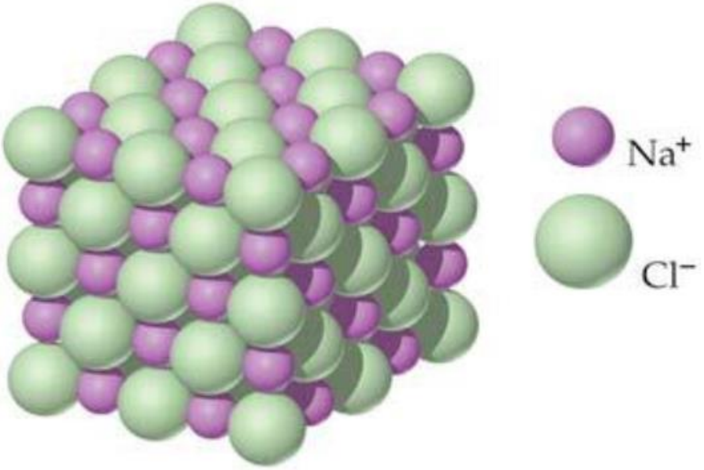
→ negatively charged ions = anions

Elements tends to gain or lose electrons, so they will have the same number of electrons as a Noble gas to become more stable.

→ Ions formed by main-group elements are usually isoelectronic with—i.e., *have the same number of electrons as*—one of the noble gases!

IONIC COMPOUNDS consist of ions (charged particles) held together by *ionic bonds*.

– ionic bond: *electrostatic attraction* holding together *positively charged metal cations* and *negatively charged nonmetal anions*



Thus, an ionic compound is actually a three-dimensional network of ions, with each cation surrounded by anions, and vice versa. Consider the molecular-level image of NaCl at the right.

formula unit: most basic entity of an ionic compound (eg. NaCl, AlCl3, etc.)

– gives the ratio of ions (not actual #) present

– In the 3D representation of NaCl at the right,

Na+ ions are shown in purple and Cl–ions are shown in green

– Note that the formula, NaCl, indicates a 1-to-1 *ratio* of Na+ ions and Cl– Ions present, *not the actual number* of each ion in the compound.

Every bond between all of the ions must be broken—requiring extremely high temperatures—to melt the substance
→ At room temperature, ionic compounds exist as solids with very high melting points.

IONIC RADIUS: distance from the nucleus to the outermost electrons in an ion
– an atom loses electrons to form a cation
→ a *cation* has a *smaller radius* than its corresponding atom
– an atom gains electrons to form an anion
→ an *anion* has a *larger radius* than its corresponding atom

COULOMB'S LAW AND THE STRENGTH OF IONIC BONDS

Coulomb's law: E = Q_1Q_2 /r

where Q1 and Q2 are the charges on the ions, and r is the distance between the ions' nuclei.
– The strength of interactions between ions is directly proportional to the product of the ions' charges (Q1 and Q2) and inversely proportional to the distance between their nuclei. Thus, the *relative strength of an ionic bond* is determined by the following:

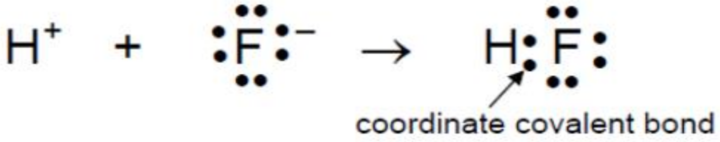
1. Charges of ions: Higher the charge → the stronger the bond
– Because the charges are higher in Ca^{+2} and O^{-2} ions, the bonds between Ca^{+2} and O^{-2} ions in CaO are stronger than the bonds between Na^+ and Cl^- ions in NaCl.
→ The melting point of CaO (2927°C) is much higher than NaCl's melting point (801°C).

2. Distance between two ions: Shorter distance → stronger the bond
– Na^+ and Cl^- have smaller radii than K^+ and Br^-
→ NaCl's melting point (801°C) is higher than KBr's (734°C).

Note: The strength of the ionic bond is generally determined foremost by the charges, and only if the charges are similar does one compare the distance between nuclei to determine the strength of the bond.

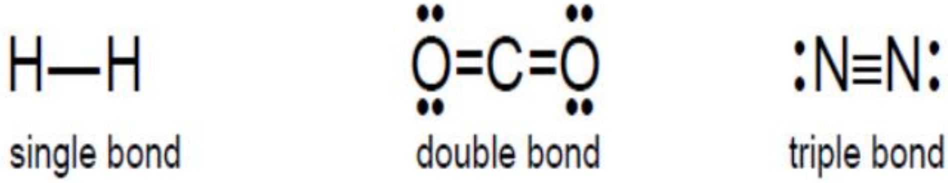
Note that there is a *positive correlation* between the melting point of an ionic compound and the strength of the ionic bonds in the compound.
→ The stronger the ionic bond → the higher the melting point.

Coordinate covalent bond: When one atom donates both electrons to make the bond



MULTIPLE BONDS: Single Bonds, Double Bonds, and Triple Bonds

- Covalent bonds can also be shown as a line to represent the pair of electrons



single bond: the sharing of ***one pair of electrons*** by two atoms (H—H in H_2)

double bond: the sharing of ***two pairs of electrons*** by two atoms (O=O in O_2)

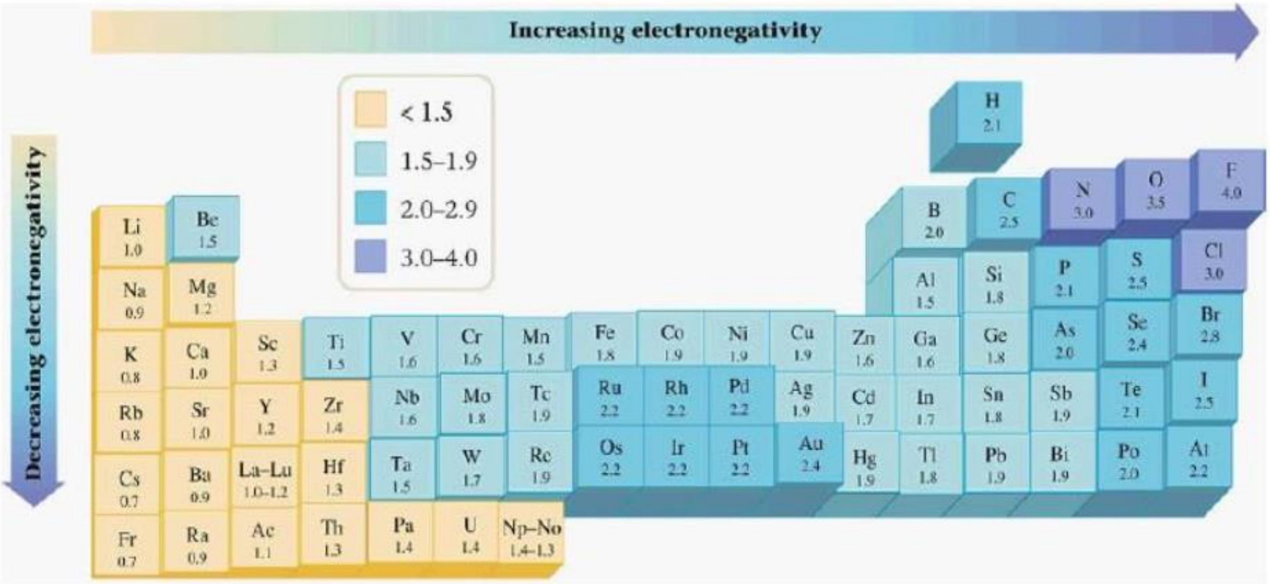
triple bond: the sharing of ***three pairs of electrons*** by two atoms (N≡N in N_2)

Note: **Single bonds** are the ***longest and weakest***,
double bonds are ***shorter and stronge***r than single bonds, and
triple bonds are the ***shortest and strongest***.

12.2 ELECTRONEGATIVITY

Electronegativity (EN): Ability of an atom in a bond to attract shared electrons to itself

- F is the most electronegative element
  - → Elements are less electronegative the farther away they are from F.
    - Except for H which has an EN between B and C.
    - Note: This trend mainly applies to elements within the same group or period.



– In some covalent bonds, both atoms have equal electronegativity values.

→ The two atoms share the bonding electrons equally.

→ nonpolar covalent bond

– Most common example is between two identical atoms: H2, O2, N2, Cl2, F2, I2, Br2

H—H

– Nonpolar covalent bonds can also occur between different atoms which have identical electronegativity values.

In some covalent bonds, one of the two atoms attracts the bonding electrons more strongly.

→ A polar covalent bond results between the two atoms.

– The bond is **polar** because it has two poles, a positive (+) end and a negative (–) end.

Polar Covalent Bond

– Because the electrons spend more time around F, they spend less time around H

→ F gets a partial negative charge (indicated with a δ–), and H gets partial positive charge (indicated with a δ+):

$$\overset{\delta+}{\mathrm{H}} — \overset{\delta-}{\mathrm{F}}$$

Polar molecules will have an overall dipole**.**

– The quantitative measure of a molecule's polarity is called its dipole moment,

Delta (δ) Notation for polar bonds:

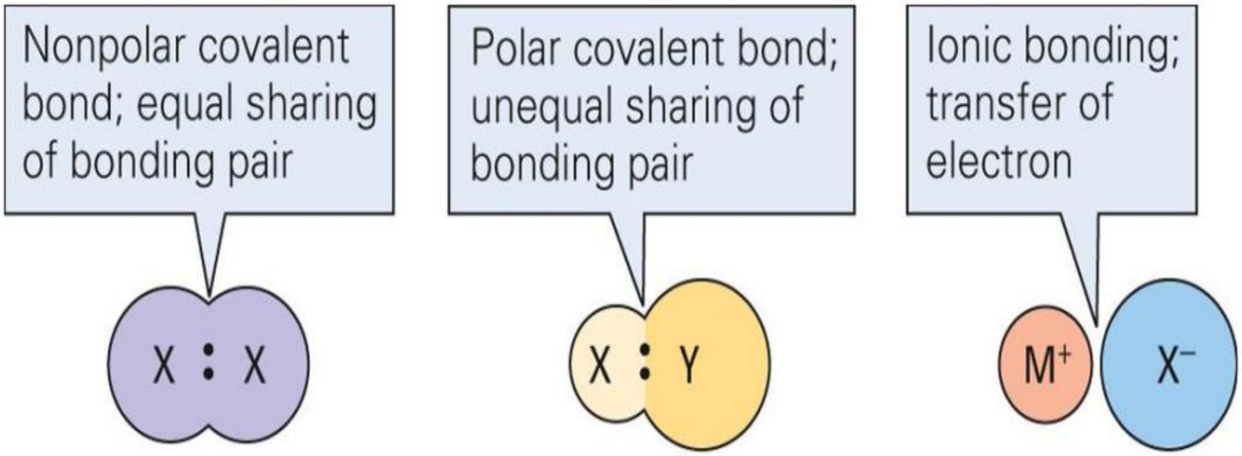
– Electrons concentrate around the more EN atom in a molecule

→ Atom gains a partial negative charge, indicated with δ–.

– Since electrons spend less time around the other atom

→ Other atom gains a partial positive charge, indicated with δ+.

Summary of Nonpolar Covalent Bonds, Polar Covalent Bonds, and Ionic Bonds



METALLIC BONDS

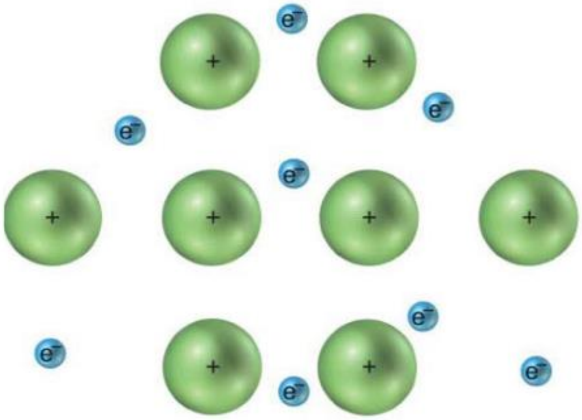
Metals exist as nuclei surrounded by a sea of electrons

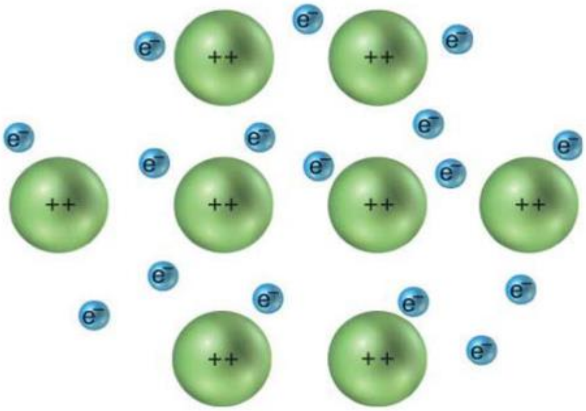
→ The electrons in a metal are shared among all the nuclei, so the electrons are delocalized (i.e., they are not fixed to a specific atom)

→ The electrons can shift throughout the entire metal.

→ Electrons are free to move throughout the solid → metals' unique properties

– e.g. metals conduct heat and electrical because electrons flow through the metal; metals are malleable and ductile because electrons act as a glue, holding the positively charged nuclei together





MOLECULAR STRUCTURE

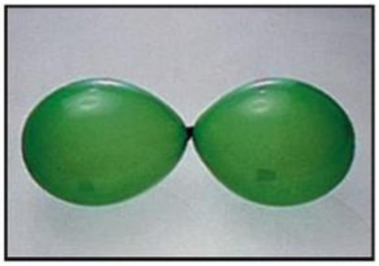
MOLECULAR STRUCTURE: THE VSEPR MODEL

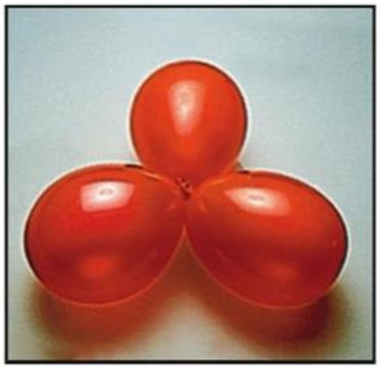
Repulsion between electrons causes them to be as far apart as possible

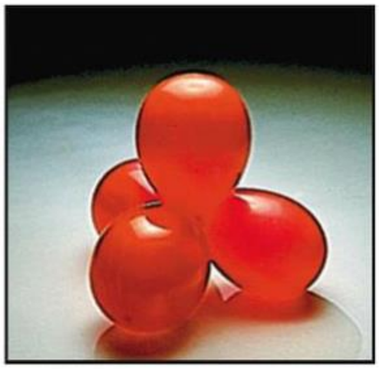
→ Valence Shell Electron Pair Repulsion (VSEPR) Model

– *repulsion* between electron pairs around a *central atom* → the *shape of molecule*

– For example, consider the following shapes resulting from balloons tied together are the same shapes that molecules will achieve.







Molecular geometry refers to three-dimensional arrangement of atoms in molecule

– responsible for many physical and chemical properties (boiling point, density, etc.)

Determining the Shapes of Molecules

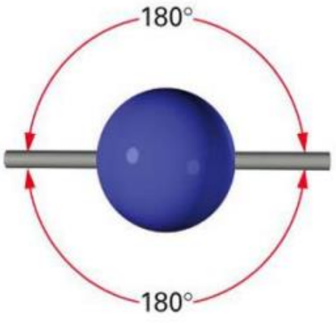
– If there are **only two atoms**, the molecule must be **linear**.

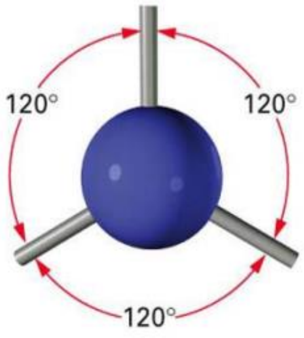
– If there are **more than two atoms** in the molecule

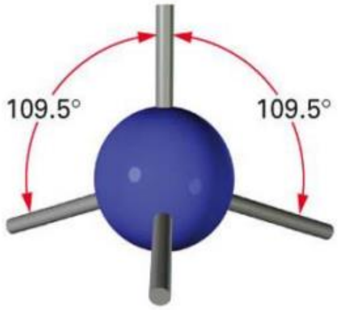
→ **the shape depends** on **number of electrons around the central atom**

– The electrons orient themselves to maximize the distance between them.

MOLECULES WHERE CENTRAL ATOM HAS NO LONE PAIRS







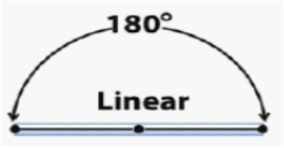
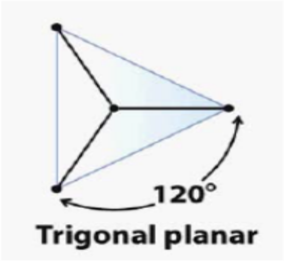
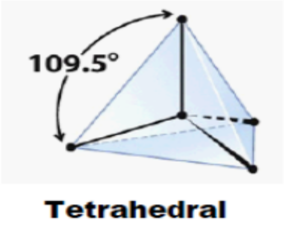
Molecular Geometries with 2 to 4 Outer Atoms on the Central Atom

(where the **Central Atom Has No Lone Pairs)**

Consider a molecule composed of only two types of atoms, A and B:

A=central atom **B=outer atoms**

Table showing Molecular Geometries(Shapes) and Bond Angles.

Steric Number	# of Outer Atoms	# of Lone Pairs on Central Atom	General Formula	MOLECULAR GEOMETRY and NAME
2	**2**	**0**	**AB_2**	
3	**3**	**0**	**AB_3**	
4	**4**	**0**	**AB_4**	

When there are lone pairs of electrons around the central atom, knowing the **steric number** for the central atoms can help determine the three-dimensional shape.

The **steric number (SN)** of the central atom is determined as follows:

$$\textbf{steric number} = \left(\begin{array}{c}\text{\# of atoms bonded}\\ \text{to the central atom}\end{array}\right) + \left(\begin{array}{c}\text{\# of lone pairs}\\ \text{on the central atom}\end{array}\right)$$

MOLECULES WHERE CENTRAL ATOM HAS ONE OR MORE LONE PAIRS

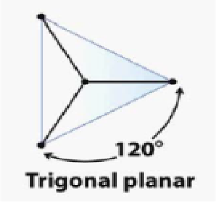
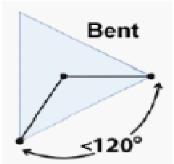
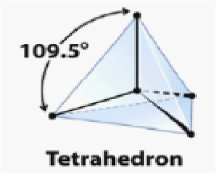
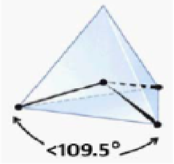
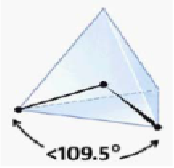
A=central atom **B=outer atoms** **E=lone pairs**

A central atom with lone pairs has three types of repulsive forces

lone-pair vs. lone-pair repulsion > **lone-pair vs. bonding-pair repulsion** > **bonding-pair vs. bonding-pair repulsion**

- **bonding pairs:** takes up less space than lone pairs since held by attractive forces exerted by nuclei of two bonded atoms
- **lone pairs:** take up more space than bonding electrons

Table II: Molecular Geometries For a Central Atom With Lone Pairs

Original Shape	General Formula	# of Outer Atoms	# of Lone Pairs on Central Atom	Molecular Shape and Name
 SN=3	AB_2E	2	1	 bent or angular
 SN=4	AB_3E	3	1	 trigonal pyramidal
	AB_2E_2	2	2	 bent or angular

ELECTRONEGATIVITY AND POLARITY

For diatomic molecules:

– **nonpolar molecules:** when the 2 atoms have equal EN values

– **polar molecules**: when the 2 atoms have different EN values

– have dipole (+ve and –ve ends)

For molecules of three of more atoms:

– polarity depend on individual bonds and geometry around central atom

– **Polar molecules** have an **overall *dipole*** (positive end and negative end)

– In **nonpolar molecules**, all the individual dipoles cancel → **no overall dipole**.

Guidelines for Determining if a Molecule is Polar or Nonpolar

1. Use a dipole arrow to indicate which atom in a nonpolar bond is more electronegative.

2. Determine if there is an overall dipole:

– If two arrows point in opposite directions, all arrows point in, or all arrows point out, then the dipoles cancel → **nonpolar molecule.**

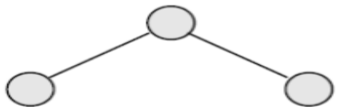
– If all arrows point towards the same direction and don't cancel, there is an **overall dipole** for the molecule → **polar molecule.**

– A **dipole moment** is the quantitative measure of the separation of charges in a molecule → The higher the dipole moment, the more polar the molecule.

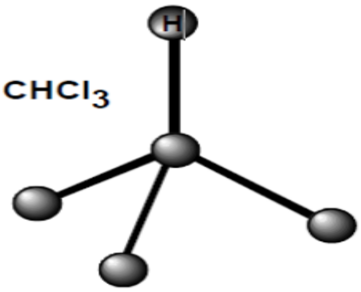
Example: Determine whether the following molecules are polar or nonpolar:

CO_2:

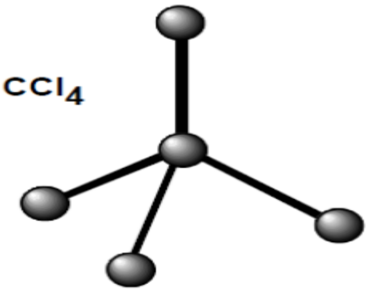
H_2O:



$CHCl_3$



CCl_4



The Valence Shell Electron Pair Repulsion Theory (VSEPR) VSEPR theory is an improved and extension of Lewis model but predicts the shapes of polyatomic molecules. This model was first suggested by Nevil Sidgwick and Herbet Powell in 1940 and later improved by Ronald Gillespie and Ronald Nyholm. Prediction of molecular shapes and geometries was made easy by this model through the following simple steps.

1. Draw the Lewis structure.
2. Count the total number of bonds and lone pairs around the central atom. (Each single bond would involve one pair of electrons).
3. Arrange the bonding pairs and lone pairs in one of the standard geometries to minimize the electron-electron repulsion.

i. Lone pair electrons stay closer to the nucleus and also they spread out over a larger space than bond pairs and hence large angles between lone pairs.

ii. The repulsion follows the order LP—LP > LP—BP > BP—BP.

4. Multiple bonds should be considered as a single bonding region.

Steric numbers:

Another term called steric number is often used in VSEPR theory.

Steric number (SN) = No. of attached atom + No. of lone pairs. Since the lone pair—lone pair repulsions are maximum, the most stable geometry can be obtained by maximizing the distance between steric numbers on the central atom.

Molecular shapes are eventually determined by two parameters: Bond distance, separation between the nuclei of two bonded atoms in a straight line and the bond angle, the angle between any two bonds containing a common atom.

While mentioning the molecular shapes lone pairs may be ignored, however, while defining the geometry both the lone pairs and bond pairs should be considered.

For example: in water molecule the central oxygen atom is in tetrahedral environment with two lone pairs and two O—H bonds (or two bond pairs). The shape of the water molecule is therefore bent (two lone pairs are ignored).

Similarly, in ammonia, the nitrogen atom is in tetrahedral environment with three bonded pairs (three N —H bonds) and one lone pair. The shape of NH3 molecule is pyramidal.

Predicting the molecular geometries

To begin with, draw the Lewis structure. Count the number of bonding pairs and lone pairs around the central atom.

Arrange the bonding pairs and the lone pairs in one of the standard geometries thereby minimizing electron—electron repulsion.

Multiple bonds count as a single bonding region