Module 1 : Atomic Structure
Lecture 1 : Structural Chemistry

Objectives

In this Lecture you will learn the following

- The meaning of the terms molecular structure and geometry and electronic structure.

- Some interesting aspects of molecular structure through examples.

- Uncertainty principle.

- Principles of quantum mechanics, which provide a theoretical basis for structural chemistry.

1.1 What do we mean by "Structure "?

By the word "structure" we refer to the process of visualizing an object as made up of parts and relating the parts to the entire object. The structure of a galaxy refers to its shape and the arrangement of the stars (and the planets therein) in the galaxy, the distances between them and so on. The structure of a galaxy is not static or frozen as the stars are moving with great speeds relative to one another. The structure of a building refers to its height, the number of floors, rooms, room sizes, the details of its foundation and so on. The structure of a solid material refers to the arrangement of atoms/molecules in the solid, the different types of arrangements and related details. Molecular geometry refers to the arrangement of the constituent atoms relative to one another. These atoms are not "fixed" but are constantly moving (rotating and vibrating) relative to each other.

Atoms and molecules contain electrons and the "structure" or the arrangement of electrons in these is referred to as the electronic structure. You may recall that the electronic configuration of a lithium atom is 1s2 2s1. This is only one aspect of the electronic structure of an atom. To describe molecular structure, in addition to the electronic configuration, we have to identify its vibrational and rotational structure. Since electrons and nuclei are not stationary objects, their structure is inherently associated with the dynamical behaviour of these "objects".
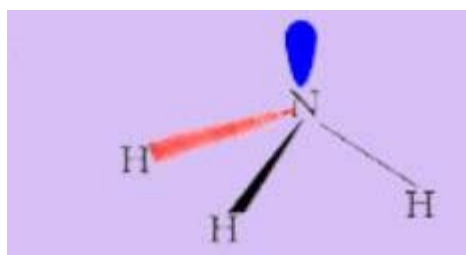
In this introductory chapter, we will give examples of several interesting structures in chemistry, describe in brief their technological applications and prepare the groundwork for the necessity of using connotation for understanding the microscopic structure of matter.

1.2 Example of molecular structures

The examples of structures considered here are structure of ammonia and its inversion, D / L configurations of molecules, C_{60} with an included atom, a micelle and a protein.

The structure of ammonia
Ammonia has a pyramidal structure with nitrogen at its apex and the three hydrogens at the base. The HNH angle is 107.3° close to the tetrahedral angle of 109° 28'. The lone pair of electrons is situated above the N atom and away from the H–atoms. An interesting feature of this structure is that the N atom can go back and forth through the triangle formed by the three hydrogens to the other side of the triangle. This is referred to as umbrella inversion or "tunneling". The action of the ammonia maser is based on this phenomenon.

Figure 1.1 Ammonia

D and L Glyceraldehydes

A carbon atom bonded to four distinct groups is referred to as an asymmetric or a chiral carbon atom. One simple example of a molecule containing an asymmetric carbon atom is d glyceraldehyde, shown in Fig 1.2. The mirror image of D glyceraldehyde, L glyceraldehyde is also shown. In the figure, H and OH groups are above the plane of paper and the CHO and CH_2OH groups are below the plane of the paper. By rotating D glyceraldehyde with respect to any axis, it cannot be converted to L glyceraldehyde. (Try this using molecular models). This is similar to a person having a mole on his left cheek. In the mirror, the mole appears on his right cheek. If one rotates the person by 180°, the mole still remains on the left cheek and the rotated person differs from the mirror image.

If you look at the carbon center, with the hydrogen atom further away form it, the groups CHO, CH_2OH and OH which are nearer to the eye than the H atom, are arranged clockwise. In the L configuration, they are arranged counterclockwise. These asymmetric molecules rotates the plane of polarization of a plane polarized light. The configuration of molecules are critical, e.g. a molecule can act as a drug only in one of the two configurations (not the always). Naturally occurring amino acids have L configurations.
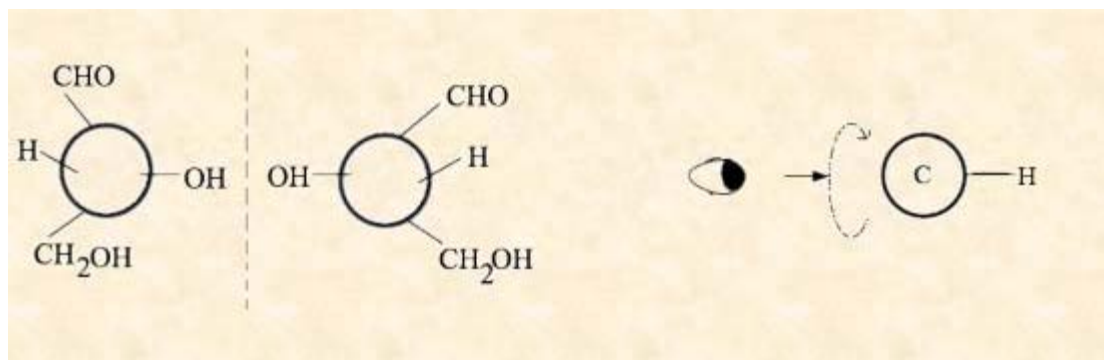

Figure 1.2 D and L Glyceraldehydes. The left part of the figure has a mirror plane separating D and L glyceraldehydes. The right part shows the rotation of the molecule with respect to the C-H bond when the bond is directed away from the eye.

1.3 The Structure of C_{60}

Carbon is well known to exist in the forms of graphite and diamond. In graphite, the atoms are arranged in a plane, with each atom connecting three other atoms. Adjacent planes are held together by weak interactions (which are much weaker than covalent or ionic interactions). The planes can slide against each other. That is why graphite is used in pencil. In diamond, the atoms are tetrahedrally linked to one another to form a strongly knit three dimensional network. Another allotrope of carbon was discovered in the nineties. This form, buckminsterfullerene (C_{60}) has sixty atoms lying approximately on the surface of a sphere. The structure is shown in Fig 1.3. Other forms such as C_{70} have also been discovered. These units can be packed to form molecular solids.

In Fig 1.3, a C_{60} which has enclosed a potassium has been shown. This is an example of an ion or a small molecule encased in a larger molecule. The process of encasing is useful for transporting small molecules across membranes or regions wherein direct transport is chemically unfeasible.
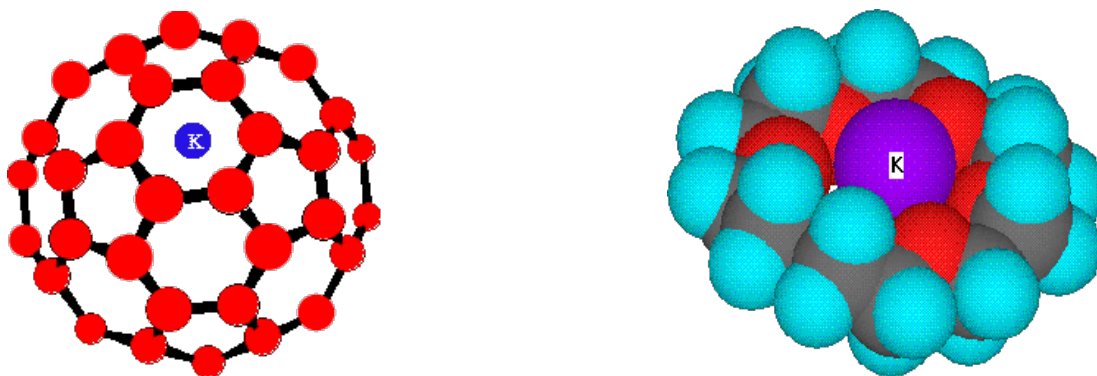
Figure 1.3: Structure of C$_{60}$ which has enclosed a potassium ion

1.4 The structure of Micelle.

Chain molecules such as soap contain hydrophilic (water loving) groups like SO$_3$H at one end and hydrophobic (water repelling) groups like alkyl groups at the other end. At very low concentrations they do not dissolve in water. Above a concentration called the critical micelle concentration (cmc) the solubility abruptly increases due to the formation of micelles. In a micelle, the hydrophobic groups come together forming a core and hydrophilic groups (which are either charged or dipolar in nature) which are outward are in contact with water molecules. An example of such a structure formed by cetyl trimethyl ammonium bromide (CTAB) is shown in Fig 1.4. It is seen that in the centre of the micelle, a hydrophobic entity has been trapped. Some water molecules which are trapped in the micelle are also shown.

The interior of a micelle is like an oil drop. Micelles can be of various shapes. Micelles are used as detergents and drug carriers and find applications in froth flotation and petroleum recovery. In the action of a detergent, the dust particle to be removed is carried away in the hydrocarbon interior (hydrophobic) of a micelle.
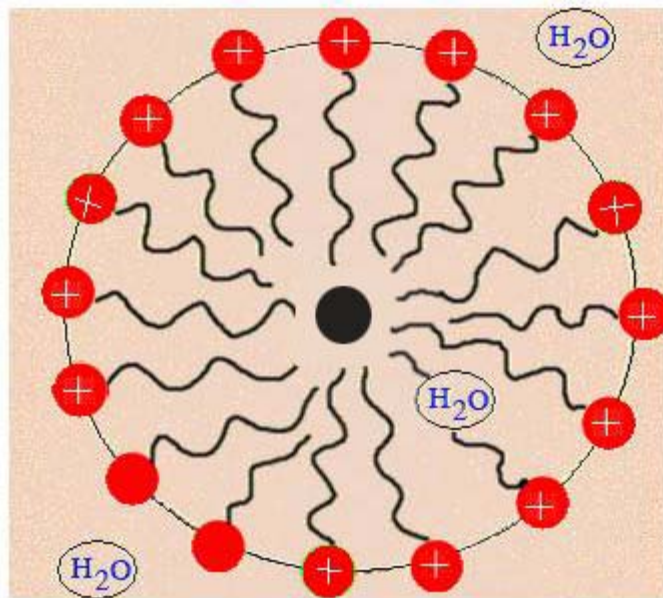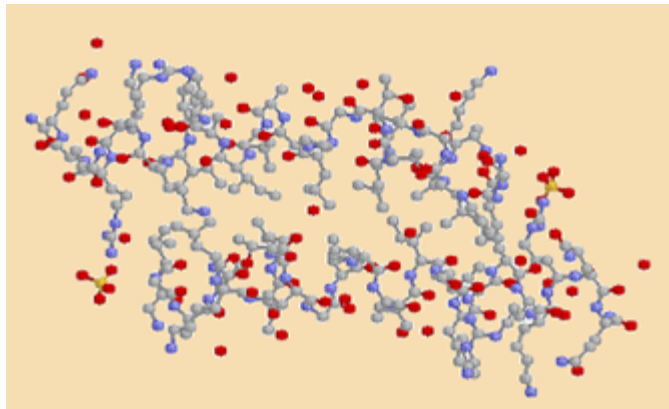

Figure 1.4: Micelle formed by cetyl trimethyl ammonium bromide (CTAB).

1.5 The Structure of Insulin

Fig 1.5 shows the structure of the protein insulin which helps in carbohydrate metabolism and stimulates protein synthesis. A protein consists of a sequence of polypeptide chains. The building blocks are amino acids which contain an amino group (NH$_2$, NH) and a carboxylic acid group (-COOH). There are 20 amino acids commonly found in proteins. The amino acids can from polypeptide chains when an NH$_2$ group of one amino acid combines with the COOH group of an adjacent amino acid by forming an amide linkage -CO-NH by eliminating a water molecule. Proteins constitute a complex class of macromolecules exhibiting versatile structures and they are

fundamental to biology since they are the instruments through which genetic information is expressed. The sequence (of the covalent linkages through amide bonds) of amino acids forms the primary structure of protein. The geometrical arrangements of polypeptide chains along their axis constitute their secondary structure. (e.g., helical structures)

The tertiary structure refers to the packing of the primary and secondary structural units in three dimensions. Many globular (spherical) proteins having a molecular weight greater than 50000 consist of two or more polypeptide chains (oligomers). Quaternary structure refers to the native confirmation of an oligomeric protein in which different polypeptide chains fit relative to one another. Bovine insulin consists of two chains of amino acids. (A chain with 21 amino acids and B chain of 30 amino acids). There are two disulphide (-S-S-) bonds that connect to A and B chains one at 7th amino acid of A chain and the 7th amino acid of another and the second disulphide bond between the 20th amino acid of A and 19th amino acid of B. There is an additional disulphide bond between the 6th and 11th amino acid of chain A. The structure of insulin is shown in Fig. 1.5.

Structure of Insulin

Figure 1.5 The Structure of Insulin dimer and hexamer

After looking at the previous structures, two questions are automatic. How are these determined? What is the theoretical basis of understanding these structures? The experimental basis is spectroscopy, which will be discussed in later chapters. We turn to the theoretical basis first. From the theoretical basis which is given by quantum mechanism, all the above structures can be "derived" or understood.

Electronic structure

With electronic structure we cannot associate "geometries" such as molecular geometry or geometrical arrangements corresponding to other objects. Electrons are neither point objects nor stationary objects. Associated with a "stable" arrangement of electrons around one or more nuclei are

a)   a set of discrete energy levels.

b)   an electronic configuration resulting form the occupation of electrons in these energy levels.

c)   an electronic charge density which can be measured experimentally.

d)   an energy spectrum resulting from the transitions between these levels.

By electronic structure, we mean all of a), b), c) and d) above and this will be illustrated in the next few chapters.
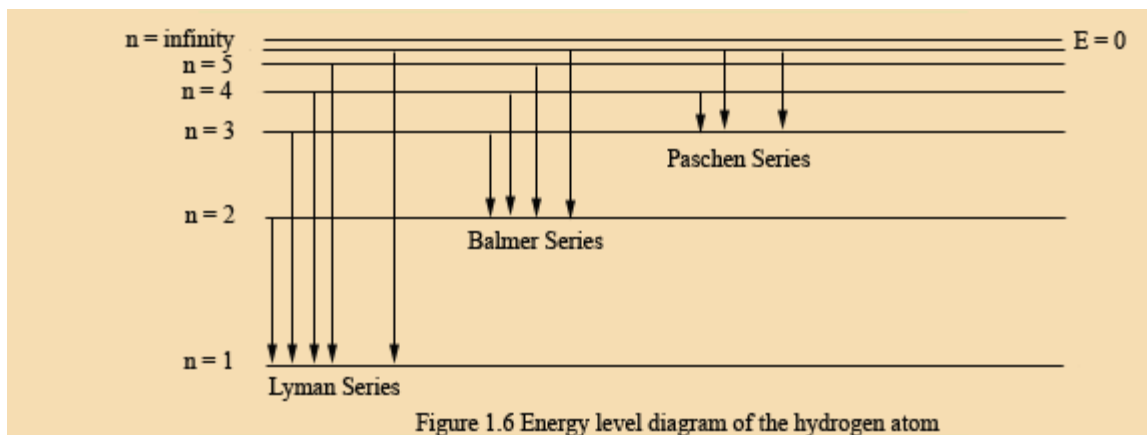
1.6 Foundations of Quantum Theory

Bohr attempted to explain atomic structure by certain postulates, which deviated in several ways from the classical or Newtonian mechanics. In Newtonian mechanics, the position and the momentum (or the velocity) of the particle (or a collection of particles) can be simultaneously determined at each instance of time. By an analogy to the orbits of planets in planetary motion, Bohr postulated that an electron of an atom exists in "*stationary*" states in these orbits, which he assumed to be circular.

Since this postulate alone was not sufficient to explain the spectral lines obtained by Balmer, Lyman, Paschen and others, he further postulated that the angular momentum of the electron in these orbits (given by mvr, where m is the electron mass, v, its velocity and r, its radius in the circular orbit) was quantized and was equal to $n\hbar$ where $\hbar = h/2\pi$ with h = Planck's constant = 6.626×10^{-34} Js, and n can take on only integer values. Whenever the atom absorbed an energy E which was equal to the difference of energy between any two levels of the atom, there was a change of state of the atom from one stationary state to another stationary state. Using these postulates, the following formula for the energy difference between the two levels can be easily derived.

$$E_2 - E_1 = - R_H (1/n_2{}^2 - 1/n_1{}^2) \qquad\qquad (1.1)$$

where R_H = 109737 cm^{-1} is called the Rydberg constant and E_2 and E_1 are the energy levels of the second and the first stationary state, respectively.

Using this formula, Bohr could obtain all the lines of the spectrum of H-atom which is shown in the Figure 1.6.

Figure 1.6 Energy level diagram of the hydrogen atom

While this theory explained the structure of the hydrogen atom well, it could not explain the structures of other atoms and molecules.

1.7 The Uncertainty Principle

In the newer and more accurate theory of matter given by Heisenberg, Schrödinger and Dirac, the description of matter is not based on the simultaneous specification of positions and momenta of particles. This implies that we cannot speak of the trajectories of these subatomic particles at all. Indeed, the Heisenberg uncertainty principle states that the position and the momentum of a particle cannot be determined simultaneously and the product of the uncertainty of the position Δx and the uncertainty of momentum Δp_x is given by

$$\Delta x\, \Delta p_x \geq \hbar \tag{1.2}$$

Here the motion has been considered only in the x-direction.

There is thus a fundamental difference in the description of observables such as position, momentum and even others such as energy. The uncertainty in position is akin to the error in measuring the position and can be taken as the root mean square deviation in the position of the particle which is given by

$$\left[<x^2> - <x>^2 \right]^{1/2}$$

where the angular brackets < > refer to the average values.

The new description of matter can be formulated in terms of postulates or laws, which will replace Newton's laws. The new description goes over to or becomes equivalent to the classical description when the particle size is "macroscopic", e.g., 0.01g or greater in mass. These postulates are summarized in the next paragraph. You may wonder about the justification of these seemingly strange postulates. The final justification is the agreement of the results of the theory with experiments. We are forced to seek these and other newer descriptions whenever old laws such as Newton's laws fail to explain phenomena involving electrons, atoms and molecules and other microscopic objects such as protons, neutrons, photons and so on. If the new description fails to explain all the observed phenomena, we have no choice but to replace the new postulates by more appropriate laws as and when they are discovered. It turns out that with the present postulates, a fairly accurate description of molecular structures can be obtained.

The dynamical variables (which characterize and describe the motion of an object) such as position, momentum, angular momentum and energy are replaced by "operators". These operators operate on functions. When these operators operate on functions, new functions may result. However, in special cases, the result may be the original function multiplied by a constant. As an example, consider the operator d/dx (the derivative operator) and functions sin(ax) and exp (ax). The result of operating the operator on the two functions is shown below.

$$\frac{d}{dx} \sin\,(ax) = a\cos\,(ax) \tag{1.3}$$

$$\frac{d}{dx}\exp(ax) = a\,\exp(ax) \qquad (1.4)$$

In the second example, we get a constant multiplied by the original function. The function exp (ax) is called an eigenfunction of the operator d/dx with an eigenvalue a. The function sin (ax) is not an eigenfunction of d/dx because on operating on the function by the operator d/dx, we do not get a constant multiplied by the same function. An understanding of atomic and molecular structure and dynamics is based on the successful application of the following postulates.

1) The dynamical variables are replaced by operators. e.g.,

a) Position x replaced by x.

b) x-component of momentum p_x replaced by $\left(\dfrac{\hbar}{i}\right)\dfrac{\partial}{\partial x}$ where $i = \sqrt{(-1)}$

c) x component of kinetic energy $p_x^2 / 2m$ replaced by $-\left(\dfrac{\hbar^2}{2m}\right)\dfrac{\partial^2}{\partial x^2}$ where m is the mass of the particle.

2) Experimental observations on the dynamical variables yield the eigenvalues of the corresponding dynamical variables. When the energy of a system (atom, molecule or a cluster of molecules) is measured, the result will be an eigenvalue of the energy operator.

3) All the possible microscopic information of the system can be obtained from the wavefunction of the system which is a solution of the Schrödinger equation.
$H\Psi = E\Psi$, where H is the operator for the total energy of the system. The energy of the system is a sum of the kinetic energies of all the particles and the potential energy of interaction between all the particles. Ψ (which is called the wavefunction) is a function of the coordinates of all the particles of the system.

4) The probability of finding a particle in a given volume element ($d\tau$) of space is given by $|\Psi|^2 d\tau$, where $|\Psi|$ denotes the absolute value of ψ

1.8 Problems

1.1) Distinguish between the structures of trees, buildings, bridges, the earth and the nucleus of an atom. Identify the building blocks and the forces that bind them.

1.2) The angular momentum **L** of a particle is given by **r** x **p** where **r** x **p** are position and momentum vectors respectively. The x component of angular momentum L_x equals $y\,p_z - z\,p_y$. What is the operator for L_x? (Hint: The operator for the sum of two dynamical variables is the sum of the operators for the dynamical variables.)

1.3) What is the energy required to excite 1 mole of hydrogen atoms from the n = 2 state to the n = 7 state? Express the values of energy in eV, kJ, kJ/mol and cm^{-1}.

Recap
In this lecture you have learnt the following

Summary
In this lecture we have quantified the meaning of electronic structure and contrasted it with structures and geometries of a few interesting molecules. These geometries include NH_3 , D/L isomers of an optically active compound, a potassium ion trapped inside a C_{60}, a protein molecule and a micellar aggregate. Electronic structure was associated with an energy level diagram with electrons "occupying the lower levels, a charge density of electrons associated with these levels and a spectrum which is a signature of these levels. Quantum theory began with the works of Planck (who gave the formula $E = nh\nu$), where ν is the frequency of light and n = number of photons. It was further developed by Bohr, Heisenberg, Schrödinger and Dirac.