1 Atomic and Molecular Structure

Quantum theory demands a way of looking at the world of atoms and molecules very different from macroscopic world. We must abandon the idea of particles with well-defined positions and velocities. Instead we must think in terms of probabilities, superpositions and uncertainties. Combining the two basic ideas namely, de-Broglie dual nature of matter and Heisenberg Uncertainty Principle, Erwin Schrödinger introduced the differential equation that governs matter waves (electrons, protons etc.) and developed in three dimensional mechanical model of the atom. Thus, many previously unsolved problems were successfully resolved.

CHAPTER OUTLINE

For better understanding of the chapter "Atomic and Molecular Structure" the syllabus is divided into two parts:

Part A: Quantum chemistry (Atomic structure)

Part B: Chemical bonding (Molecular structure)

1.1 INTRODUCTION

The subject of chemistry cannot be understood thoroughly without a firm understanding of the principal concepts of quantum mechanics. The same is true virtually for all the spectroscopic techniques that are now so important for investigating the composition and structure. Present day techniques for studying chemical reactions have progressed to the point where the quantum chemistry has to be used in its interpretation. In fact, the structures of atoms and molecules cannot be discussed without making use of quantum chemistry concepts.

The application of quantum mechanical concepts to small objects like atoms containing particles like electrons, protons and neutrons and the molecules which are made of atoms from the chemistry point of view is called quantum chemistry and deals with the structures of atoms and molecules, their properties and chemical reactions between them. Therefore, the study of the structures of the atoms, molecules and chemical reactions between them in the light of quantum mechanics is called **quantum chemistry**.

1.2 CLASSICAL MECHANICS VERSUS QUANTUM (OR WAVE) MECHANICS

The differences between classical mechanics and quantum mechanics are as follows:

S.No.	*Classical mechanics*	*Quantum (or wave) mechanics*
1.	It is applicable to macroscopic particles.	It is applicable to microscopic particles.
2.	Newton's laws are the fundamental principles on which it is based.	Heisenberg's uncertainty principle and de Broglie's concept of dual nature of matter (particle nature and wave nature) are its foundations.
3.	Maxwell's electromagnetic wave theory is its basis. According to this theory, any amount of energy may be absorbed or emitted continuously.	Plank's quantum theory is its basis. According to this theory, energy is absorbed or emitted discontinuously only in packets, *i.e.*, quantum.
4.	The state of a system is defined with certainty. To define the state, it is required to specify all the forces acting on the particles and their positions with their velocities.	It provides the possibilities of finding the particles at different locations of space.

1.3 SCHRÖDINGER WAVE EQUATION

Erwin Schrödinger proposed that if the electron is wave-like, it should obey the same equation of motion as all other known types of wave motion obey. On the basis of this simple idea, he substituted the value of de-Broglie relation $\left(i.e., \lambda = \frac{h}{mv}\right)$ into the classical equation for wave motion. Thus, the equation obtained should describe the wave motion of the electron and is called *Schördinger wave equation*. The equation can be written in many forms. The simplest form of equation is given below:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

where E = Total energy of the electron *i.e.*, K.E. + P.E.

V = Potential energy of the electron *i.e.*, work done against the attractive force when the electron moves away from the nucleus.

m = Mass of the electron

h = Planck's constant

The ψ (Greek letter Psi) is called "*Wave function*" and is amplitude of the electromagnetic wave.

The above equation can also be expressed as

$$\nabla^2\psi + \frac{8\pi^2 m\,(E - V)}{h^2}\psi = 0$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is called **Laplacian Operator.**

1.3.1 Derivation of Schrödinger Wave Equation

The simplest form of the equation can be derived by de-Broglie idea of dual nature of matter applied to an electron within all atoms.

Total energy, (E) of an electron = Kinetic energy + Potential energy

$$= \frac{1}{2}mv^2 + V = \frac{1}{2}\frac{(mv)^2}{m} + V \qquad ...(1.1)$$

From de-Broglie equation,

$$\lambda = \frac{h}{mv} \quad \text{or} \quad mv = \frac{h}{\lambda}$$

where m is the mass of an electron, v is its velocity, and h is the Planck's constant. Substituting this value of mv in Eqn. (1.1), we get

$$E = \frac{h^2}{2\lambda^2 m} + V$$

or
$$-\frac{1}{\lambda^2} = \frac{2m}{h^2}(E - V) \qquad ...(1.2)$$

The basic principle of quantum theory is that matter can be regarded as wave and the equation for such a wave motion of a vibrating string can be represented as:

$$\psi = A \sin\frac{2\pi x}{\lambda} \qquad ...(1.3)$$

where ψ is a wave function, x is the displacement,
λ is the wave length, and A is the amplitude of the wave.

Differentiating the function, ψ, with respect to x, we get

$$\frac{d\psi}{dx} = A\left(\cos\frac{2\pi x}{\lambda}\right)\left(\frac{2\pi}{\lambda}\right)$$

$$= A \cdot \frac{2\pi}{\lambda} \cdot \cos\frac{2\pi x}{\lambda}$$

Differentiating again, we get

$$\frac{d^2\psi}{dx^2} = \frac{2\pi A}{\lambda}\left(-\sin\frac{2\pi x}{\lambda}\right)\left(\frac{2\pi}{\lambda}\right)$$

$$= \frac{4\pi^2}{\lambda^2}\left(A \sin\frac{2\pi x}{\lambda}\right)$$

From Eqn. (1.3), we get $\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi$ ...(1.4)

The Figs. 1.4(*a*) and (*b*) also suggest that greater the number of nodes more is the curvature in the particle wave. Hence, *for a potential box of fixed size, a Δ the curvature in the wave function increases, the number of nodes increases, the wavelength, therefore, decreases and the total energy in the box i.e., the potential energy has been assumed to be zero.*

These phenomena are direct consequences of the Schrödinger wave functional and so these types of behaviour are general.

It may be seen that while ψ may be either positive or negative, but ψ^2 giving probability of finding the particle at any point is always positive.

5. **The quantized wave functions are orthogonal to one another:** The orthogonality of wave functions can be shown as follows:

Consider two wavefunctions corresponding to $n = l$ and $n = m$ when $n \neq m$. Then

$$\psi_l = \sqrt{\frac{2}{a}} \sin\left(\frac{l\pi x}{a}\right)$$

$$\psi_m = \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right)$$

If $l > m$, then probability of finding the particle with the limit $x = 0$ and $x = a$, will be $\int_0^a \psi_l \, \psi_m \, dx$

Putting the values of ψ_l and ψ_m, we get

$$\int_0^a \psi_l \, \psi_m \, dx = \frac{1}{2}\int_0^a 2\sin\left(\frac{l\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx$$

$$= \frac{1}{2}\int_0^a \left[\cos(l-m)\frac{\pi x}{a} - \cos(l+m)\frac{\pi x}{a}\right]dx$$

$$= \frac{1}{2}\left[\frac{a}{\pi(l-m)}\sin(l-m)\frac{\pi x}{a} - \frac{a}{\pi(l+m)}\sin(l+m)\frac{\pi x}{a}\right]_0^a$$

Because l and m are integers, so $\sin 0 = 0$, $\sin(l-m)\pi = 0$ and $\sin(l+m)\pi = 0$. Therefore, right hand side of the above equation becomes zero. It means that $\int_0^a \psi_l \, \psi_m \, dx = 0$.

This equation is the condition for the two wavefunctions to be orthogonal to each other.

Exact solution of Schrödinger's wave equation are always orthogonal.

6. **Analysis of Nano-particles:** Nanotechnology is defined as the study of atoms and molecules at nano (one billionth) scale (1 – 100 nm) to produce device or systems having at least one novel or superior property. The materials having at least one dimension in the nano scale are called *nano-materials.* When the bulk materials is reduced to nanometer size, the properties exhibited by this nano-materials is of tremendous use. For example, opaque materials become transparent, (copper), insoluble substances become soluble, stable substances become combustable (Aluminium). In fact gold is chemically inert, but at nanoscale, gold nano-particles serves as chemical catalysts. The properties of nano-materials show strong dependency on particle size. The size at which the entire properties of materials changes, from-those in the bulk material, is said to be in the nanoscale range. This is generally observed at size below 100 nm. Reduction of system in size can change chemical reactivity because it is function of the structure and occupation of outermost electronic

energy levels. Correspondingly, the physical properties such as electrical, thermal, optical, mechanical and magnetic characteristics, which depend on the arrangement of outermost electrons, are also altered.

Particle-Size vs Surface Area

If a macroscopic (large) object is divided into smaller parts, the ratio of surface atoms to interior atoms becomes a significant number of the total fraction of atoms. For example, a cube of iron with side 10 cm long, the percentage of surface atoms is only 10^{-5}. When the same cube is cut into smaller cubes with side length 10 nm, the percentage of surface atoms increases to 10. When the cube is further cut into cube with side length 1 nm, every atom comes on the surface. This inverse relation between particle size and surface area is responsible for the remarkable changes in the physical and chemical properties of nanomaterials.

The electronic properties of nanomaterials are particularly useful in analysis of these materials. In nanomaterials, the valence electrons, which are almost free, in finite volume leads to quantification of their energy. The band gap decreases when the particle size is decreased and energy gaps gradually convert into discrete molecular electronic levels. If the particle size is less than the wavelength of the electron, the charge carriers may be treated as "particle in a box". *The spatial confinement of electrons within the crystallite boundary is referred to as quantum confinement.* Since nanomaterials are closer in size to atoms or molecules, quantum mechanical laws are used to describe their behaviour. In nanocrystals, the energy levels are well defined and the addition and substraction of one atom or electron to the nanocrystal measurably changes the electronic properties.

The properties of bulk materials change completely as their dimensions are reduced to nanoscale (< 100 nm). If one dimension is changed to nano range then ***quantum waves*** are obtained. If two dimensions are reduced, the resulting structure is called ***quantum wire.*** When all three dimensions are reduced, ***quantum dots*** are obtained, which are zero-dimensional ***semiconducting spheres.*** In quantum dot crystal, the energy gap is tunable and can be altered to produce a range of energies between the valence and conduction bands. It can be considered a semiconductor crystal with a small number of atoms and physical dimensions of the order of 10 nm. Thus, when a semiconductor crystal has discrete states, it can be defined as ***quantum dot.***

Optical properties at nanoscale arise because of quantum confinement of electrons; the size of particles being small, the electrons are restricted in their movement and hence react differently to incident light in comparison to the bulk material.

Nanostructured materials have at least one dimension lying between 1 to 100 nm. According to Siegal, nanostructued materials can be classified on the basis of the number of dimensions that are not confined to nanoscale range, that is, < 100 nm. They can be:

(*i*) **Zero dimensional (0 D):** These are nanomaterials in which each of the dimensions is in the nano-scale, for example *nanoparticles, quantum dots*.

(*ii*) **One dimensional (1 D):** These are nanomaterials in which two dimensions are in the nanoscale while the third is not. Examples are *nanowires, nanorods and nanotubes*.

(*iii*) **Two dimensional (2 D):** These are nanomaterials in which one dimension is in the nanoscal while the other two are not. Examples are *nanofilms and nanocoatings*.

(*iv*) **Three dimensional (3 D):** These are bulk materials that are not nanoscale in any of th dimensions. However, they can be composed of multiple arrangements of nanosize particl or crystals, *bundles of nanosize wires, strand or tubes*.

There is a pressing need for development methods and instrumentation techniques to observe, measure and manipulate the individual nano-materials and nano-structures. This requires development of techniques that are extremely sensitive, accurate and offer atomic level resolution.

1.5 WAVE MECHANICAL MODEL FOR HYDROGEN ATOM

Hydrogen atom and hydrogen atom like species *e.g.*, He^{+}, Li^{2+}, Be^{3+} etc., resemble with one another in having one electron around their nuclei, but they differ in their nuclear charges. The hydrogen atom consist of an electron (e^{-}) and proton of charge $+e$. Hydrogen like species have one electron with e^{-} charge and their nucleus has ze^{+} charge, where z is the atomic number of such atoms.

The Schrödinger wave equation for the motion of a single particle is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0 \qquad ...(1.23)$$

where m = mass of the particle,

E = total energy of the particle,

V = the potential energy of the particle, and

x, y, z = co-ordinates of the particle.

For hydrogen like atom reduced mass $(\mu)=\frac{m_e \times m_n}{m_e+m_n}$ replaces the mass where m_e and m_n are the masses of the electron and the nucleus respectively. It may be noted that $m_e < m_n$, the reduced mass $\mu \approx m_e$.

A hydrogen like atom can have two kind of motions:

(*i*) Revolution of electron around the nucleus, and

(*ii*) The translational motion of the system *i.e.*, centre of mass (nucleus).

Assuming that the nucleus centre of mass is not moving, we consider only the revolution of the electron around the nucleus. Hence, E represents the electronic energy.

The Eqn. (1.23) for a hydrogen-like atom takes the following form:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2\mu}{h^2}(E-V)\psi=0 \qquad ...(1.24)$$

x, y and z are the co-ordinates of the centre of mass of the system.

This equation is identical to that of a single particle of mass μ (equal to that of the electron) moving in a field of potential V.

For the hydrogen like atom electron is moving under the central field of the nucleus. By Coulomb's law, force of attraction between these particles is given as:

$$F=\frac{-Ze^2}{r} \qquad ...(1.25)$$

where 'Z' is the charge on the nucleus, 'e' is the charge on the electron and r is the distance between the two.

Force acting between the particles according to Coulomb's law.

$$F=\frac{-e\cdot Ze}{r^2}=\frac{-Ze^2}{r^2},\ V=\int_{\infty}^{r} F\cdot dr=\int_{\infty}^{r}\frac{-Ze^2}{r^2}=\frac{-Ze^2}{r} \qquad ...(1.26)$$

"The theory of chemical bond ... is still far from perfect. Most of the principles that have been developed are crude, and only rarely can they be used in making an accurate quantitative prediction. However they are the best that we have as yet, and I agree with Poincare that it is far better to foresee even without certainity than not to foresee at all." **—Linus Pauling, Noble Laureate 1954, 1962**

CHAPTER OUTLINE

2.1 INTRODUCTION

Most of the substances exist in the form of aggregated atoms called *molecules*. The attractive force which holds together the constituents (atoms or ions) in a molecule is called a *chemical bond*. The concept of covalent bond formation on sharing of electrons (Lewis concept) was purely a qualitative approach. It could not answer number of basic questions such as the following:

1. Why a covalent bond is formed at all ?
2. How electrons are arranged in the molecule ?
3. What are the forces of attractive interactions in a molecule ?

4. What is the bond energy in a covalent bond ?
5. How does the sharing of electrons explain the shapes of resluting molecules ?

The development of wave mechanics has provided answers to these questions which ultimately paved the way for the development of more comprehensive theories of covalent chemcial bonding. These theories are:

1. Valence Bond Theory (VBT)
2. Molecular Orbital Theory (MOT)

Keeping in view the revised syllabus, we shall discuss the details of Molecular Orbital Theory.

2.2 MOLECULAR ORBITAL THEORY (MOT)

A latest approach to chemical bonding known as *molecular orbital theory*, developed mainly by Mulliken (1932), explains the bonding characteristics in a better way.

The molecular orbital theory considers the entire molecule as a unit with all the electrons moving under the influence of all the nuclei present in the molecule. This approach recognizes that each electron belongs to the molecule as a whole and may move within the entire molecule.

2.2.1 Molecular Orbitals

When the atoms to be bounded come close together, the orbitals of the bonded atoms lose their individual character and fuse (overlap) to form larger orbitals called *molecular orbitals*. Thus, like atomic orbitals, there are molecular orbitals in a molecule. The only difference is that in atomic orbitals, electrons move under the influence of only one nulceus (*i.e.*, AOs are *monocentric*), while in molecular orbitals, electrons move under the influence of many nuclei (*i.e.*, MOs are *polycentric*).

Molecular orbitals may, therefore, be defined *as the regions in space associated with all the nuclei of the molecule where the probability of finding a particular electron is maximum.* As in the case of atomic orbitals, each molecular orbital can accommodate at the most *two electrons with opposite spins*.

It may be noted that electrons in molecular orbitals are not confined to an individual atom, but they belong to the *entire molecule* and are said to be *delocalized* with respect to the individual atoms.

Important features of molecular orbital theory are as follows:

1. Like an atomic orbital which is around the nucleus of an atom, molecular orbitals are around the nuclei of a molecule and are entirely different from the atomic orbitals from which they are formed.
2. The valence electrons of the constituent atoms are considered to be moving under the influence of nuclei of participating atoms in the moelcular orbital.
3. The molecular orbitals possess different energy levels like atomic orbitals in an isolated atom.
4. The shapes of molecular orbitals are dependent on the shapes of atomic orbitals from which they are formed.
5. Molecular orbitals are arranged in order of increasing energy just like atomic orbitals.
6. The number of molecular orbitals formed is equal to the number of atomic orbitals combining in bond formation.
7. Like atomic orbitals, the filling of electrons in molecular orbitals is governed by the three principles such Aufbau principle, Hund's rule and Pauli's exclusion principle.

The shape of molecular orbital formed in case of valence bond approach depicts that the identity of atomic orbitals is not lost, whereas in case of molecular orbital approach the original identity of atomic orbitals is completely lost.

The main difference between VBT and MOT is that the molecular orbitals formed in a compound are quite different from the constituent atomic orbitals. When the atomic orbitals combine to form molecular orbitals, they lose their identity and merge into each other completely.

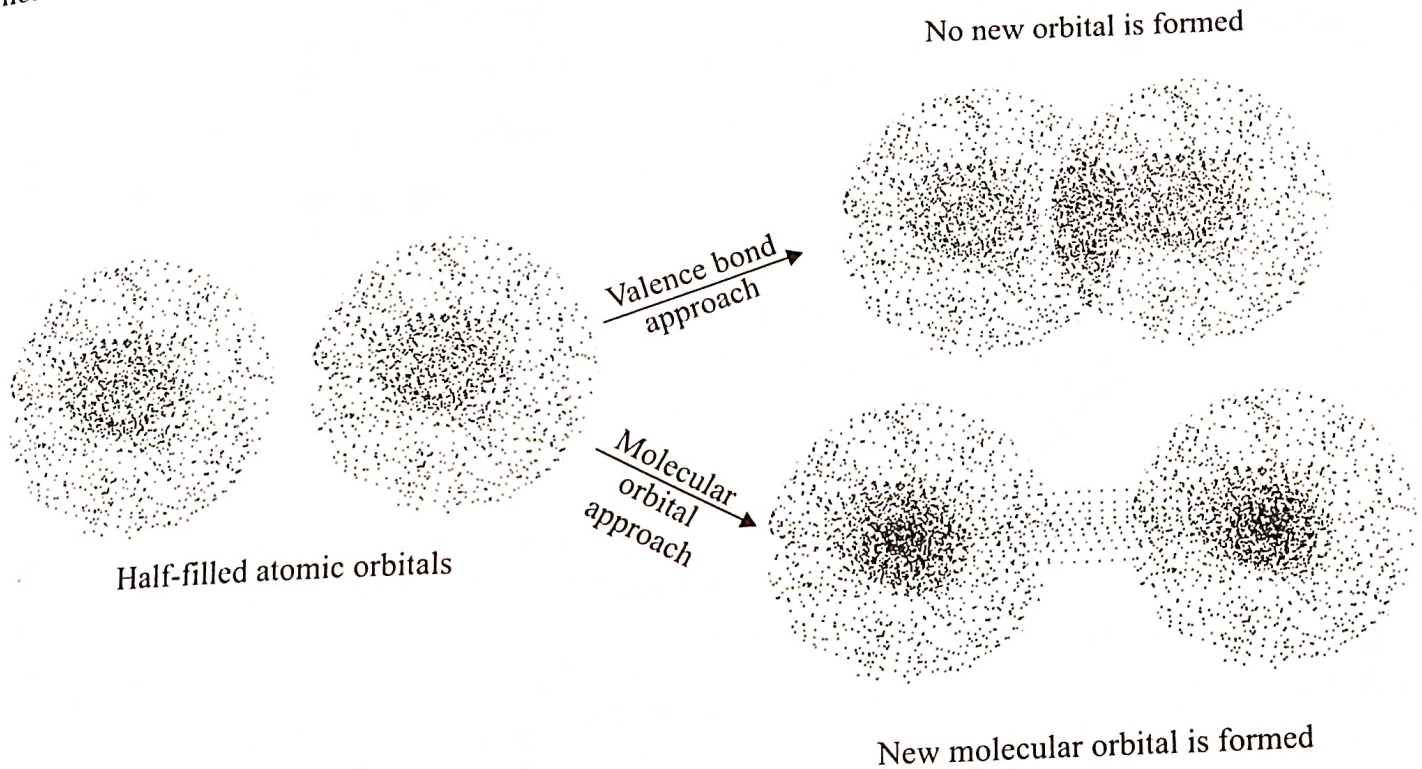

Fig. 2.1 (*a*). Comparison of valence bond approach and molecular orbital approach.

2.2.2 Conditions of Formation of Molecular Orbitals

1. For the atomic orbitals to combine and form molecular orbitals, the following conditions must be satisfied:

   (*a*) The combining atomic orbitals should be of a comparable energy. For example, 1*s* atomic orbitals of two atoms can combine but 1*s* orbital of one atom cannot combine with 2*s* orbital of the other. Similarly 2*s* orbitals cannot combine with 2*p* orbital. Such combinations are possible only for the heteronuclear diatomic molecular of the type AB.

   (*b*) The combining atomic orbitals must overlap to a large extent; greater the overlap, stable is the molecule formed. The combining atomic orbitals must have proper orientation so that they are able to overlap to a considerable extent.

2.7 MOLECULAR ORBITAL CONFIGURATIONS

While writing electronic configurations of molecules or ions, the following points must be kept in mind:

(*i*) To begin with, the formula of the molecule or ion is written followed by the square bracket starting with the symbol.

(*ii*) For molecules of the second period such as Li_2, Be_2, B_2, N_2, O_2, F_2 etc., the letters 'K.K' are written for the first shell of both the combining atoms. The letter 'K' denotes the filled inner K shell of each combining atom. These electrons do not take part in bonding. For H_2 and He_2 molecules, KK letters are not used.

(*iii*) The number of electrons in any molecular orbital are written on the right hand corner above a closed bracket ( ). For example, if s_{1s} molecular orbital has one electron, it is represented as $(\sigma_{1s})^1$.

(*iv*) After writing the complete molecular orbital configuration, the square bracket is closed with the symbol.

Keeping in view above rules, the molecular orbital configuration for oxygen molecule can be written as follows:

As there are six valence electrons in each oxygen atom, the distribution of 12 electrons in molecular orbitals will be as shown below:

$$O_2[KK(\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\sigma_{2pz})^2\ \pi(2p_x)^2\ (\pi_{2py})^2\ (\pi^*_{2px})^1\ (\pi^*_{2py})^1]$$

Also presence of unpaired electron in O_2 molecules states that oxygen is paramangnetic in nature.

2.7.1 Bonding in Some Homonuclear Diatomic Molecules and Ions

Based on the above principles, we would proceed to learn how to draw the molecular orbital pictures of some diatomic homonuclear molecules and ions.

1. **Hydrogen molecular ion, H_2^+:** This is simplest molecule that can exist. Its presence can be detected *spectroscopically* by passing an electric discharge through hydrogen gas under low pressure.

Hydrogen molecular ion is formed by the combination of one hydrogen atom having one electron and a hydrogen positive ion having no electron.

$$H + H^+ \longrightarrow H_2^+$$

In this ion, *only one electron is available to hold two protons together.* The *single available electron occupies the lowest energy* σ_{1s} *bonding molecular orbital while the anti-bonding orbital remains vacant* (*Fig. 2.11*).

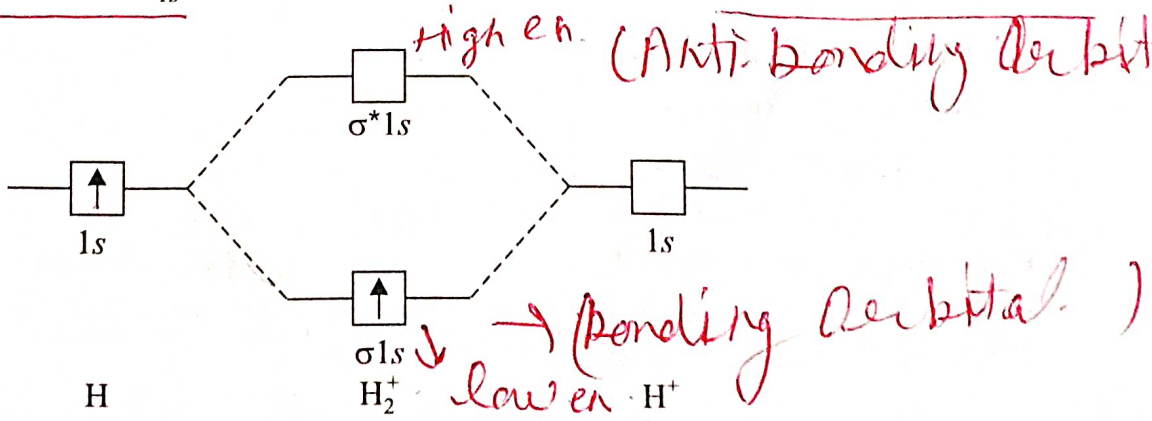

Fig. 2.11. Molecular orbital energy level diagram for H_2^+ ion.

Therefore, the electronic configuration of H_2^+ molecule ion can be represented as:

$$H_2^+ = (\sigma_{1s})^1$$

Thus,

(*i*) **Bond order.** The bond order in $H_2^+ = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[1 - 0] = \frac{1}{2}$

(*ii*) **Stability.** The positive value of the bond order means that the hydrogen molecular ion has some stability.

(*iii*) **Magnetic character.** Due to the presence of an unpaired electron in the bonding orbital, the molecule ion should, be paramagnetic. The H_2^+ molecule ion has actually been found to be stable and paramagnetic.

2. **Hydrogen molecule H_2:** Hydrogen molecule is made up of two hydrogen atoms, each of which possesses one electron in 1*s* atomic orbital.

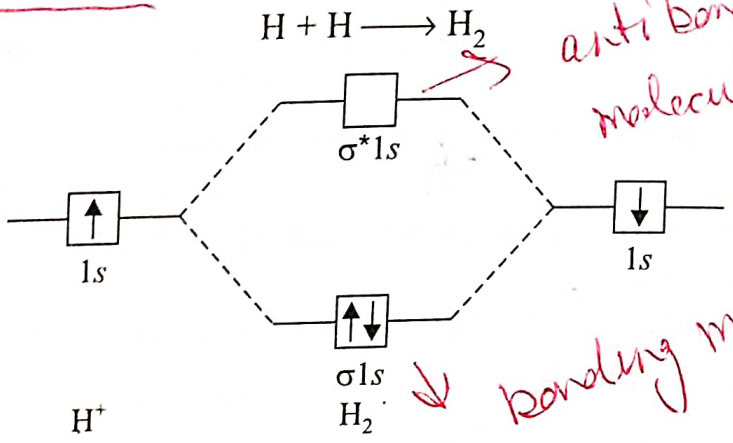

Fig. 2.12. Molecular orbital energy level diagram for H_2 moelcule.

When the two atomic orbitals overlap, two available electrons in H_2 molecule occupy the lowest energy σ_{1s} bonding molecular orbital while the anti-bonding orbital remains unoccupied. In accordance with Pauli exclusion principle, the two electrons in σ_{1s} molecular orbital must have opposite spin (Fig. 2.12).

Therefore, the electronic configuration of H_2 molecule can be represented as:

$$H_2 = (\sigma_{1s})^2$$

Thus

(*i*) The *bond order* in $H_2 = \frac{1}{2}[N_b - N_a] = \frac{1}{2}[2 - 0] = 1$

(*ii*) Since the bond order value is positive, hydrogen molecule is stable. The bond order 1 shows that the two hydrogen atoms are bonded through a single covalent bond in H_2 molecule.

Bond dissociation energy of $H_2 = 433$ kJ mol^{-1},

Bond length = 74 pm

(*iii*) Since there is no unpaired electron in any of its molecular orbitals. H_2 molecule is diamagnetic.

3. **Hydrogen molecule ion, H_2^-:** This can be formed by the combination of one hydrogen atom having one electron and a hydrogen negative ion having two electrons in their 1*s* orbitals respectively. Thus, the ion involves three electrons.

$$H + H^- \longrightarrow H_2^-$$

The two electrons occupy the lowest energy σ_{1s} bonding molecular orbital while the third electron goes to the higher energy anti-bonding σ_{1s}^* molecular orbital according to Aufbau and Pauli exclusion principles (Fig. 2.13).