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Nature of Covalent Bonds

To explain the nature of covalent bonds, following two theories have been proposed-

(1) Valence Bond Theory (VBT)

(2) Molecular Orbital Theory (MOT)

(1) Valence Bond Theory (VBT)

This theory was for the first time proposed by **Hietler and London** and then modified by **Pauling and Slater**. It is based upon the pairing of electrons and neutralization of their spins. The main postulates of this theory are as under-

(1) The covalent bonds are formed by overlapping of atomic orbitals, but in molecule atomic orbitals do not lost their identity. Thus, shape, size and other parameters of atomic orbitals remain unchanged in the molecule.

Thus, in molecules, the electrons are found in atomic orbitals. Hence, this theory is also called **Atomic Orbital Theory (AOT).**

(2) In overlapping, there occurs pairing of electrons and neutralization of their spins.

(3) The strength of a covalent bond depends upon the extent of overlapping between the atomic orbitals. The larger the extent of Overlapping, more stronger is the bond formed.

The extent of Overlapping is given by the overlap integral "S". If ψ_A and ψ_B are the wave functions of combining atomic orbitals, then, the overlap integral "S" is given by following expression-

$$S = \int \psi_A \, . \, \psi_B \, \partial r$$

Here, if-

(i) $S > 0$ (+ve), then there occurs attraction between the atoms and stable covalent bonds are formed.

(ii) $S < 0$ (-ve), then there occurs repulsion between the atoms and covalent bonds are not formed.

(iii) $S = 0$, then there occurs neither attraction nor repulsion between the atoms. Here also, stable covalent bonds are not formed.

(5) The inter-nuclear distance after the formation of covalent bonds is called bond length of respective bond.

(6) The energy released during formation of a covalent bond is called bond energy of respective bond. It provides stability to the covalent bonds formed. The larger the value of bond energy, more stronger is the bond formed.

Limitations of VBT

This theory successfully explains the formation of molecules like H_2, Cl_2, NH_3, CH_4 etc. However, it has following limitations-

(1) It could not explain the formation of odd election molecule ions like H_2^+ molecule ion.

(2) It could not explain the magnetic behaviour of molecules. For example, according to this theory, O_2 molecule should not contain any unpaired election and therefore, it should be diamagnetic in nature. However, in practice, it is found to be paramagnetic.

(3) It does not give any idea about resonance.

Energy Profile of Covalent Bonds

The covalent bonds are formed by overlapping of atomic orbitals. Here, two half-filled atomic orbitals having elections with opposite spin, come close together, share some common space and their unpaired elections get paired up in the shared space. Thus, covalent bond gets formed.

If inter-nuclear distance (r) of combining atoms are plotted against potential energy of the system, following curves are obtained-

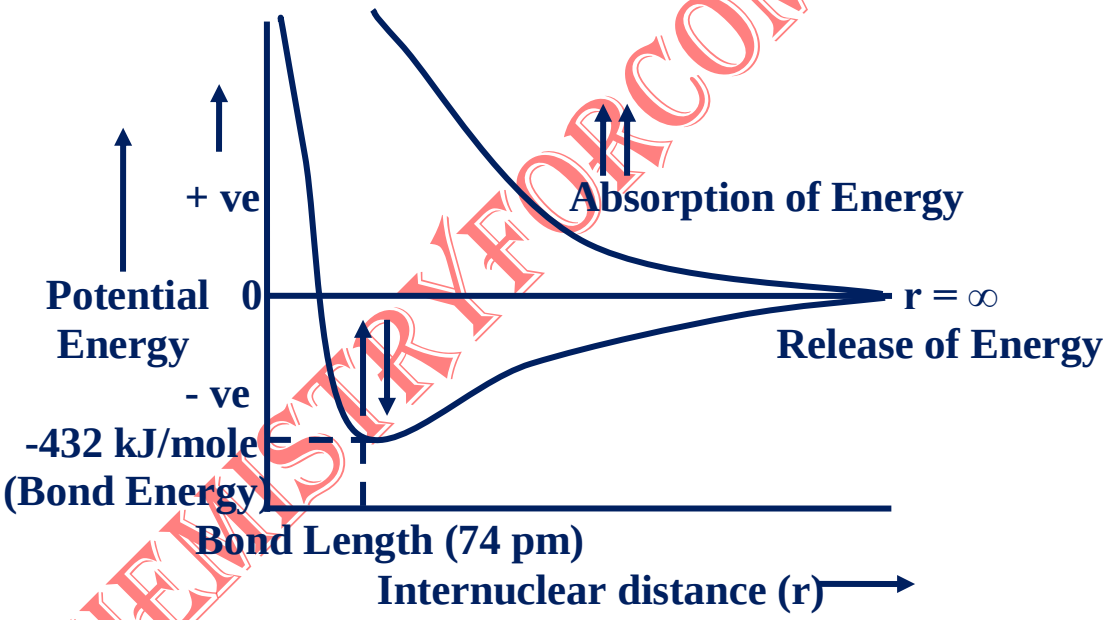

Fig.-Variation of Potential Energy with Internuclear distance (r) for H_2 molecule

From the curves, it is clear that-

(1) When r = ∞, there occurs neither attraction nor repulsion between the atoms. Hence, potential energy of the system is zero.

(2) When orbitals contain elections with opposite spin, attraction between the atoms increases with decrease of inter-nuclear distance (r). Hence,

energy is released from the system and potential energy of the system becomes negative.

(3) For a definite value of inter-nuclear distance (r), potential energy of the system takes highest negative value. This state corresponds to the state of bond formation. The energy released corresponding to this state is called **bond energy** and inter-nuclear distance corresponding to this state is called **bond length**.

(4) If inter-nuclear distance is decreased further, strong repulsion start operating between the atoms. It results in steep rise in potential energy of the system.

(5) When orbitals contain elections with same spin, repulsion between the atoms increases with decrease of inter-nuclear distance (r). Hence, energy is absorbed by the system and potential energy of the system goes on increasing continuously. Here, covalent bond is not formed.