B. Sc Part-II (Sub.), Paper-II, Grap-6 (Inorganic Chemistry)

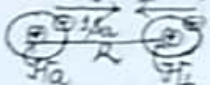
Unit-1 Chemical bonding (Valence bond theory & metallic bond)

⇒ Valence bond theory of Covalent compounds:

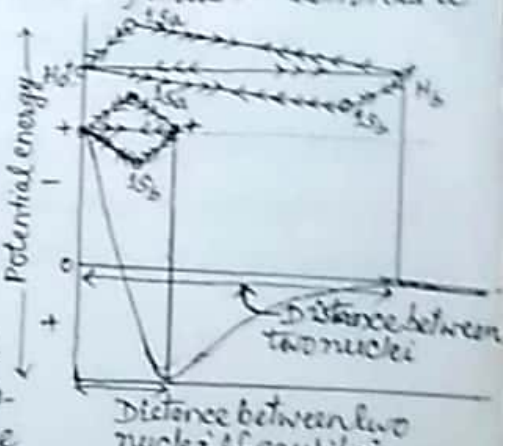
Valence bond theory was put forward by Heitler & London in 1927 and modified later in 1935 by Pauling & Slater. It explains the nature of covalent bonds/compounds. The main postulates of this theory are—

1. The atom which go to enter into chemical combination/bonding must possess one or more unpaired electrons.
2. A covalent bond is formed by sharing or pairing of two electrons with opposite spins. If more than one unpaired electrons are present, multiple (double or triple) bond is formed.
3. In the formation of covalent bond, overlapping of atomic orbitals take place. This can be done in two ways and so there are two types of covalent bond, Sigma(σ) & pie(π) bond.
4. Sigma(σ) bond is formed by co-axial/head to head overlap of two atomic orbitals while pie(π) bond is formed by lateral/sidewise overlap of two atomic orbitals. s-s, s-p, s-d overlapping always give a σ-bond but p-p overlapping give σ or π bond.
5. In the formation of covalent bond only valence electrons are involved. The atoms unite retain their identity.
6. Nature of atomic orbitals determines the bond length. Thus, H-Cl bond length is smaller than that of H-Br, since former involves 3p-orbital of Cl atom, while later 4p-orbital of Br atom overlapping with 1st orbital of H-atom.
7. Overlapping determines the strength of the bond. The greater the overlapping of atomic orbitals, greater will be the strength or stronger will be the bond. Thus, stability decreases $\sigma_{s-s} > \sigma_{p-p} > \sigma_{s-p}$, and Sigma(σ) bond is stronger than pie(π) bond.

Explanation of VBT: Formation of H_2 molecule can be shown as follows: H-atom has a single electron in 1s-orbital.

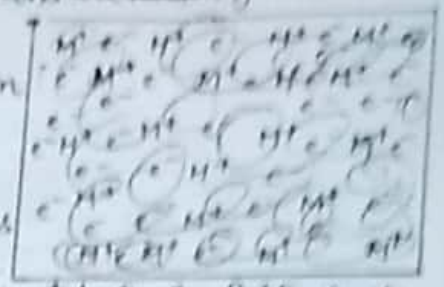


When two hydrogen atoms approaching each other to a close distance (R), two electrostatic forces acted. Firstly, the attractive force, which acts between the nucleus (H_a) and the electron associated with $1s_a$ & $1s_b$ as well as that between the nucleus H_b and the electron associated with it. Secondly, the repulsive force between H_a & H_b as well as between $1s_a$ & $1s_b$. The attractive forces are more important at a large H_a-H_b distance but, short range repulsive force becomes effective when the two atoms come much closer. The repulsive forces increase, much more rapidly when the internuclear distance becomes very short. The change in potential energy with respect to interatomic distances shown in fig. 1. When two atoms are far apart, the potential energy of each is independent of other and is arbitarily set at 0. As the two H-atoms approach, there is an attraction between them and the potential energy decreases. The potential energy decrease to minimum value beyond which it shoots up sharply.



Metallic bond

In metallic crystals, metal cations are surrounded by a sea of mobile electrons. The metal cations are in their positions and mobile electrons are ~~fulfill together~~ in the interstices between them. The metal cations and mobile electrons are held together by electrostatic force of attraction known as metallic bond.



Thus, metallic bond can be defined as "the force of attraction between the metal cations and the mobile electrons and this force holds the metal atoms finally together in the metallic crystal/lattice". Most of metals, e.g. Hg, W, alkali metals, Os, Cu, Ba, Fe, Au etc. and alloys have metallic bond.

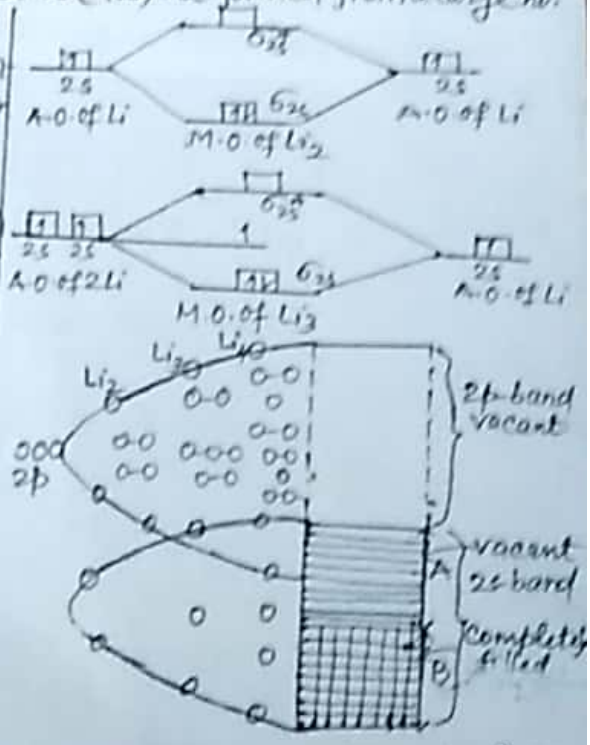
Factors affecting metallic bond: (i) Ionisation energy of the metals should be low so that the valence electrons of the metal are loosely held by the nucleus and thus become mobile (ii) The metal should have low electronegativity so that they do not accept electrons. (iii) The number of vacant orbitals in a metal should be more than the number of valence electrons in it so that the mobile electrons easily move into the vacant orbitals.

Features of metallic bond: (i) It is weaker bond than ionic & covalent bonds. (ii) It is non-directional (iii) It is electrostatic nature, i.e; electrostatic force of attraction acting between Kernels (metal cations) and mobile electrons.

→ Theories of Metallic bond: To explain nature of metallic bond, following theories have been profosed: 1. Electron Sea theory 2. Valence bond theory 3. Molecular orbital theory

Molecular orbital theory or Band model: The smallest piece of a metal would contain about 10^{20} atoms, a large number of molecular orbitals (MOs) are formed from a large no. of atomic orbitals (AOs).

Let us consider an idealised one dimensional lattice of Li-atom (Li--Li--Li--) In the formation of this chain, first of all two Li-atoms will form a Li_2 molecule. In the formation of Li_2, the two 2s atomic orbitals having unpaired electron ($2s^1$) undergo linear combination to give two MOs. The lower energy MO (σ_{2s}) is completely filled and the higher energy MO (σ^*_{2s}) is vacant. Attaching another Li-atom to Li_2 molecule gives the linear Li_3 molecule (hypothetical).



Now, as the length of the chain increases by increasing no. of Li-atoms we get a large no. of MOs closely spaced together. No. of MOs is the same as that of AOs. As the number of Li-atoms increases, the energy levels get closer & closer and ultimately become continuous. Such a group of continuous energy levels is known as a band and consequently the MOT is called band model. Here A is the upper half of the 2s-band (vacant) and B is the lower half (Completely filled). Small circles indicate AOs & MOs. This can readily explain the metallic properties.