CHAPTER - I

THE CONCEPT OF ORBITAL HYBRIDISATION AND ISOVALENT HYBRIDISATION

I.A. Introduction

Synthesis of chemical insight and quantum mechanics has often resulted in outstanding chemical concepts. A remarkable example of this is the concept of hybridisation which provides a very simple, yet quite elegant interpretation of chemical bonds.

That the chemical bonds are directed in space has been supported both by experimental evidences and theoretical calculations[1-3,25]. One of the consequences of the directed valency of atoms in molecules is the definite pattern in which atoms are arranged in molecular frame work. It is mainly the geometry of molecules and its variation from one molecule to another that led Pauling[5] to introduce the concept of hybridisation or mixing of intra-atomic orbital in VBMO theory. The idea of hybridisation probably stemmed from the E.Schrodinger's work on stark effect of Hydrogen where the splitting was explained using a linear combination of 2s and 2p orbital of hydrogen[4].

I.B. Salient features of the concept of 'hybridisation' :

Pauling[5] developed his hybridisation theory on the basis of following considerations.

(i) Chemical bond may be considered to be localised mainly in the region between the bond forming atoms.

(ii) The direction of chemical bond corresponds to that in which the overlap between the orbitals is maximum.

(iii) The strength of a chemical bond is proportional to the overlap between the connecting orbitals.

(iv) Orbitals used by the connected atoms in general can be a linear combination of pure atomic orbitals (s,p,d... etc) so as to satisfy the principle of maximum overlap. The orbitals constructed by a linear combination of atomic orbitals are termed the hybrid orbitals and the process is called hybridisation.

(v) The number of hybrid orbitals that may be constructed from a given set of atomic orbitals equals the number of basis orbitals in the set.

Using these criteria along with normalisation and orthogonality conditions satisfied by the atomic orbitals, Pauling[5] constructed hybrid orbitals from symmetry consideration. This approach provided an elegant explanation of the geometries of many molecules. Since then several workers[5-15,17,21] have used this maximum overlap criterion for constructing hybrid orbitals from group theoretical consideration where the molecules possess a high degree of symmetry. In table 1.1 examples of different types of hybridisation and the corresponding geometry are given.

Table 1.1

Type of hybridisation	Geometry
sp^3	tetrahedral
sd^3	"
sp^2	trigonal
sp	digonal
d^2sp^3	octahedral
dp^2	trigonal
ds^2	trigonal
dsp^2	tetragonal
d^2sp	irregular tetrahedron
d^2p^2	tetragonal
dsp^3	bipyramid
d^2sp^2	tetragonal pyramid
d^4s	tetragonal
d^4p	pyramid
d^3p^2	pentagonal
d^5	pentagonal pyramid
d^4sp	trigonal prism
d^5p	" "
d^3p^3	" antiprism
d^4sp^3	dodecahedron
d^5p^3	antiprism

I.C. Isovalent Hybridisation:

The hybridisation and the geometries given in table 1.1 are strictly applicable to molecules with equivalent substituent. Thus, sp^3 hybridisation which implies hybrid orbitals with 25 percent s-character holds only for symmetric molecules of the type CX_4 (X = H, halogen or alkyl group etc). Any substitution of the X group by a non equivalent group Y will lower the symmetry with a concomitant change in the hybridisation. In such a situation, all the orbitals do not have equal (25 percent) s-characters, some have more than 25 percent while the others less than 25 percent although the basic set remains the same, viz., one 2s orbital and the three 2p orbitals of the carbon atom. It is because of this that all tetrahedral molecules are usually classified as sp^3 hybridised though the individual hybrid orbitals in such cases differ in their s-character.

While such classification based on the basic set used in the construction of hybrid orbitals, e.g., sp^3, sp^2, sp, dsp^2, d^2sp^3 etc. given in table 1.1, often helps greatly in the understanding and interpretation of molecular properties (the use of hybridisation in the interpretation of geometries and magnetic properties of coordination compound is classic example of such applications), the variation of molecular properties with variation of substituent in a given class of molecules is of greater chemical interest. For example, the properties of the C-H bond, e.g., ^{13}C-H coupling constant, bond distance, polarity etc. show a wide variation in going from CH_4 to $CHCl_3$, though all the molecules belong to the general category of sp^3 hybridised molecules. All the properties indicate a gradual variation in the s-characters of the carbon valence orbitals along the series. CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$. Such variation of hybridisation where only the degree of mixing within the same set of atomic orbitals changes was termed as 'Isovalent (valency remaining same) Hybridisation' by Mulliken[22] to distinguish it from the type sp^3 and sp^2 where the variation in the mixing is a result of changing the basis set from s-$3p^3$ to s-$2p^2$ set.

The importance of isovalent hybridisation in understanding the chemical and physical properties of molecules was pointed out by Walsh[23] with reference to carbon compounds. He deduced a qualitative rule showing the dependence of the degree of mixing (s or p-character of the hybrid orbital) with the electronegativity of the substituents connected to carbon atom. His principle is often called the 'Walsh Rule'.

The idea that the substituent electronegativity plays a major role in determining the degree of hybridisation of an atom in a molecule was developed more thoroughly by Bent[24] by an analysis of available experimental data on large number of molecules. The qualitative rule that emerged from his studies is as follows:

'The atomic s-character tends to concentrate in an orbital directed toward electro positive substituents'.

This rule is known as Bent's rule or Walsh-Bent[23-24] Rule. Although this rule has found wide application in various fields of chemistry because of its simplicity, it has several drawbacks and limitations. These are discussed fully in the next chapter.

I.D. Construction of Hybrid Orbitals:

The construction of suitable hybrid orbitals is the most important first step in the localised description of chemical bonds in a molecule. Because of this the problem has received the attention of many workers[5-24]. Though the construction of the hybrid orbitals for atoms in molecules with high degree of symmetry e.g. CH_4, C_2H_4, etc. is relatively simple[1-2,5-6,15,25], construction of the best hybrid orbitals in molecule with no symmetry or very little symmetry is rather difficult. The construction of the best or optimum hybrid orbitals in such molecules has been discussed by Murrell[7], Golebiewsky[8] and many other workers[9-12,14,17,21].

The criterion that has been almost always used for the construction of the best hybrid orbitals is the 'principle of maximising overlap'. The basic argument underlying the use of this principle is that the strength of a chemical bond is qualitatively proportional to the overlap and therefore maximization of overlap is qualitatively expected to lead to the most stable geometry. It should be borne in mind that the essential criterion for the construction of optimum hybrid orbitals is not 'the principle of maximization of overlap', but the principle of minimization of the energy[5]. Because of the difficulty of having reliable explicit functions for the bond energy in terms of basis orbitals, it is normally difficult to use this criterion. However, computation of the overlaps poses no difficulty and the principle of maximization of the overlap is generally adopted due to the simplicity of the procedure.

The concept of hybridisation is so appealing to chemists that a number of workers[15,16,18-20] have attempted to determine the orbital hybridisation from the fully delocalised molecular orbitals using some localization criterion, e.g. orbital localization, bond population maximization (bond index) etc. It should, however, be mentioned that the concept of hybridisation in delocalized MO theory is not an essential requirement and therefore, not unambiguously definable in the fully delocalized LCAO MO theory.

I.E. Assumptions involved in the concept of Hybridisation:

Like all quantum chemical concepts which have resulted from a synthesis of chemical intuition and quantum mechanics, the concept of hybridisation involved certain assumptions and therefore this concept is applicable only when the assumptions involved are valid.

The basic assumption underlying the concept of hybridisation has been excellently highlighted by Trindle and Sinanoglu[16].

The idea of hybridisation rests on the following assumptions.

(i) An atom retains its identity within a molecule and makes slight adjustment to the molecular environment so that the total molecular wave function may be represented in terms of orbitals formed by combination of atomic orbitals.

(ii) Each hybrid orbital may be associated with only one localized bond and its interaction with other orbitals may be neglected.

Obviously, the concept of hybridisation has relevance only if these conditions are at least approximately fulfilled. For example, molecular orbitals constructed from floating gaussian orbitals or a one centre expansion can not be understood in terms of hybridisation. Again, in fully delocalized system, e.g., conjugated π -bonds, where the idea of localized bonding has little meaning, the concept hybridisation loses its significance.

In conclusion it may be said that the concept of hybridisation is an extremely useful artifice in understanding molecular properties in systems where the molecule can be adequately represented by local bond or chemical bond concept.

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