

## P R E F A C E

The concept of orbital hybridisation, first introduced by Pauling and later extended by several authors, has played an important role in the development of chemical thoughts. In spite of the availability of large digital computers which makes more rigorous and sophisticated quantum chemical approach to fairly large molecules possible to-day, the concept of hybridisation has not lost its relevance to chemistry even to day. In fact, the simplicity of the concept which enables a chemist to visualize the electron distribution in the molecule in terms of familiar chemical bonds has led many authors to work out localized orbitals from delocalized orbitals obtained by SCF MO calculations.

The type of orbital hybridisation in a given atom is primarily determined by the basis set of atomic orbitals involved in its valency and the symmetry of the molecule. However, the changes in the hybridisation resulting from the change in the substituent(s) without change in its valency (isovalent hybridisation) can not be obtained easily due to loss in symmetry. Because of the role of orbital hybridisation in determining a wide variety of molecular properties, e.g., bond length, geometry, force constant, NMR coupling constants etc., the effect of the substituents on isovalent hybridisation assumes an important role. Qualitative principles

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for predicting the trends in orbital hybridisation in an atom resulting from variation in the substituent were proposed by Walsh and Bent. Apart from being qualitative, the principle proposed by these workers suffer from many drawbacks. The present work was therefore undertaken to make a critical assessment of the isovalent hybridisation principle put forward by Walsh and Bent and to develop a quantitative approach.

The thesis is divided into five chapters. The concept of orbital hybridisation and isovalent hybridisation is discussed in chapter I. In chapter II Bent's rule is critically examined and its scope and limitations are pointed out.

A quantitative approach to isovalent hybridisation is developed in chapter III. Although the general theory developed in this chapter may be applied to any basis set, i.e.,  $sp$ ,  $sp^d$ ,  $spdf$  etc., the application of the theory is restricted only to cases where the orbital hybridisation involves only  $s$  and  $p$  type orbitals.

The numerical method of computations involved in the application of the theory developed in chapter III forms the subject matter of chapter IV. Several applications of the calculated  $s$ -characters are also discussed.

In the concluding chapter a simplified approach to isovalent hybridisation is discussed and a qualitative rule

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for isovalent hybridization is proposed.

It is hoped that the present work will provide the foundations for a simple quantitative approach to orbital hybridization in the more complex case involving s, p and d type orbitals.

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