

8.1: Introduction

There is a second major theory of chemical bonding whose basic ideas are distinct from those employed in valence bond theory. This alternative approach to the study of the electronic structure of molecules is called molecular orbital theory. The theory applies the orbital concept, which was found to provide the key to the understanding of the electronic structure of atoms, to molecular systems.

The concept of an orbital, whether it is applied to the study of electrons in atoms or molecules, reduces a many-body problem to the same number of one-body problems. In essence an orbital is the quantum mechanical description (wave function) of the motion of a single electron moving in the average potential field of the nuclei and of the other electrons which are present in the system. An orbital theory is an approximation because it replaces the instantaneous repulsions between the electrons by some average value. The difficulty in obtaining an accurate description of an orbital is the difficulty in determining the average potential field of the other electrons. For example, the 2s orbital in the lithium atom is a function which determines the motion of an electron in the potential field of the nucleus and in the average field of the two electrons in the 1s orbital. However, the 1s orbital is itself determined by the nuclear potential field and by the average potential field exerted by the electron in the 2s orbital. Each orbital is dependent upon and determined by all the other orbitals of the system. To know the form of one orbital we must know the forms of all of them. This problem has a mathematical solution; the exploitation of this solution has proved to be one of the most powerful and widely used methods to obtain information on the electronic structure of matter.

A molecular orbital differs from the atomic case only in that the orbital must describe the motion of an electron in the field of more than one nucleus, as well as in the average field of the other electrons. A molecular orbital will in general, therefore, encompass all the nuclei in the molecule, rather than being centred on a single nucleus as in the atomic case. Once the forms and properties of the molecular orbitals are known, the electronic configuration and properties of the molecule are again determined by assigning electrons to the molecular orbitals in the order of increasing energy and in accordance with the Pauli exclusion principle.

In valence bond theory, a single electron pair bond between two atoms is described in terms of the overlap of atomic orbitals (or in the mathematical formulation of the theory, the product of atomic orbitals) which are centred on the nuclei joined by the bond. In molecular orbital theory the bond is described in terms of a single orbital which is determined by the field of both nuclei. The two theories provide only a first approximation to the chemical bond.

We shall begin our discussion of molecular orbital theory by applying the theory to the discussion of the bonding in the homonuclear diatomic molecules.

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