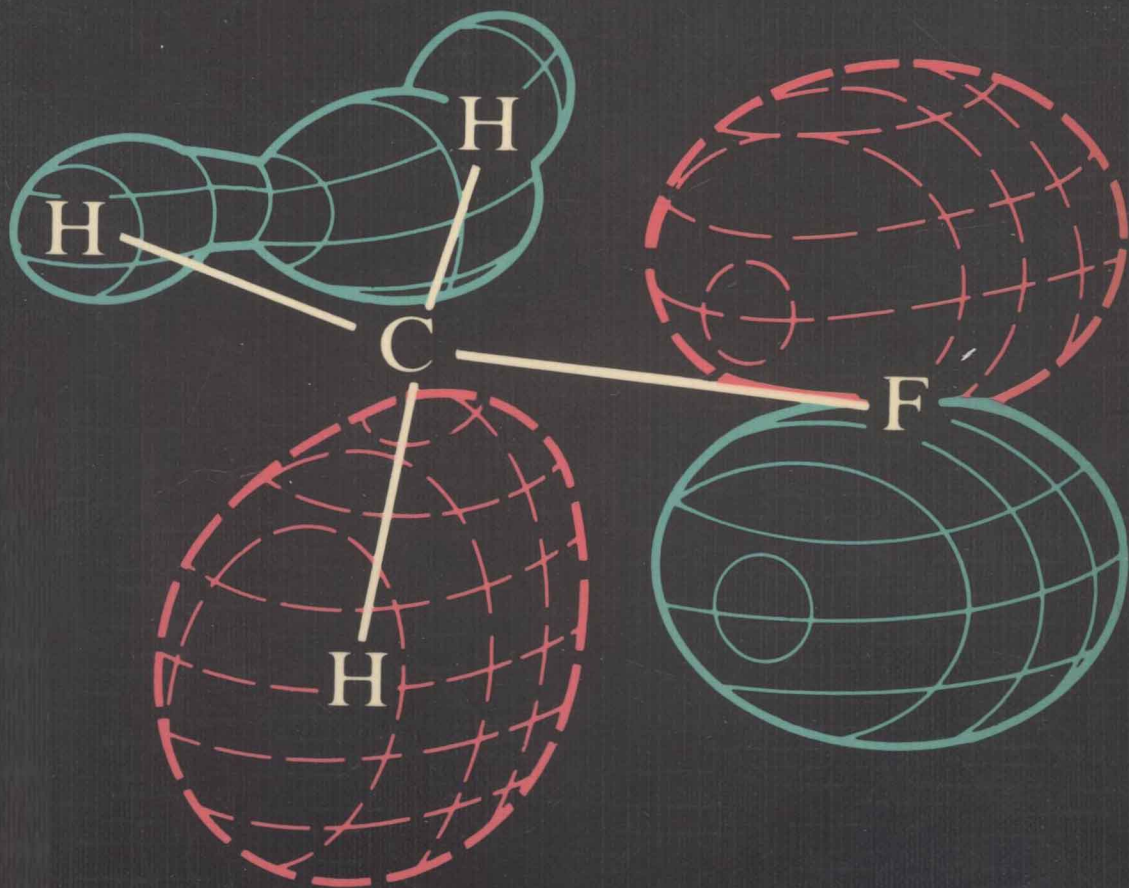# Pictorial Orbital Theory

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Pictorial Orbital Theory

Acknowledgments

The orbital contour pictures are based on those from W. J. Jorgensen and L. Salem *The Organic Chemist's Book of Orbitals*, Academic Press, New York, 1973. There are several more recent calculations available but for pictorial orbital theory Jorgensen and Salem's are more than adequate.

Introduction

Our understanding of organic chemistry has depended on the use of models of increasing complexity. The representation of atoms as hard spheres joined together by sticks has been and remains an important part of the organic chemist's stock in trade. In order to understand the mechanism of many reactions, however, a more sophisticated picture was required and this was provided by Lewis Theory which was developed so successfully by the British chemists Sir Robert Robinson and C. K. Ingold. The use of curved arrows to depict electron migration during a chemical reaction led to a much better understanding of the factors which control chemical reactions. The development of resonance theory by the American Linus C. Pauling and others provided the necessary rationale to an all-embracing pictorial theory. The use of 'canonical forms' or 'resonance hybrids', together with the extensive use of curved arrows, has provided the intellectual background to much of modern organic theory. It is somewhat of a paradox that R. B. Woodward, a supreme master of 'arrow pushing', should have been a prime mover in the development of pictorial orbital theory. A number of reactions (particularly cyclic additions like the Diels–Alder reaction) did not fit very well into the curved arrow or canonical forms concept. Indeed these reactions were sometimes called 'no mechanism reactions'. Woodward and Hoffmann showed that by examining the interaction of the frontier molecular orbitals (i.e. the Highest Occupied and the Lowest Unoccupied orbitals) both the regio- and the stereospecificity could be accounted for. Woodward and Hoffmann's treatment was very quickly assimilated into general organic theory for reactions with a cyclic transition state. At present most books continue to use the 'electronic theory' supplemented by 'resonance theory' to describe the major part of organic chemistry and then develop a pictorial orbital theory especially for cyclic reactions. The purpose of this little book is to show that it is possible to use pictorial orbital theory to describe all the major transformations in organic chemistry. There is no suggestion that a stage has been reached when the 'arrow pushing' of the electronic theory can be completely displaced by the 'balloons and sausages' of

pictorial orbital theory; but there is no doubt that there is a substantial part of organic chemistry which is better accounted for by pictorial orbital theory than by conventional electronic theory. Both approaches attempt to describe in qualitative terms facts which can only be fully accounted for by rigorous mathematical treatment. Chemistry has not yet reached the stage when any but the simplest reactions can be fully analyzed on the computer.

Nomenclature

We have tried to avoid the terms of the electronic theory and in general we are concerned with orbital interaction. We will, however, have occasion to describe the movement of electrons, and to classify the groups involved we will use the terms *electron repeller* in place of $+I$, *electron donor* in place of $+R$ or $+M$, *electron attractor* in place of $-I$, and *electron acceptor* in place of $-R$ or $-M$. The electron donors and electron acceptors involve orbitals of π-symmetry. A substituent like a halogen has electrons of π-symmetry but it is also a very electronegative atom; we can call such groups *electron attracting donors* instead of using the symbol: $-I, +R$. In chemical reactions involving the transfer of electrons from the Highest Occupied Molecular Orbital (HOMO) of one species to the Lowest Unoccupied Molecular Orbital (LUMO) of another species we shall call the electron donating species the HOMO-gen and the electron accepting species the LUMO-gen (Ingold, nucleophile and electrophile).

The concerted displacement reactions (see Chapter 5) we will call 'displacement reactions' and so avoid the unfortunate term S_N2 which confuses students into believing that the nucleus takes some direct part in the reaction. The term 'unimolecular ionization' will be used where appropriate in preference to the term S_N1 (see Chapter 9).

Contents

1 Atomic and Molecular Orbitals

Atoms form molecules by sharing electrons and we regard the sharing of two electrons by two atoms as constituting a chemical bond. Atoms can share one, two or three electron pairs (these correspond to single, double and triple bonds of classical valence theory). Before we can meaningfully discuss electrons in molecules we need to remind ourselves of some qualitative ideas of the arrangement of electrons in atoms.

A hydrogen atom consists of a nucleus (a proton) with an associated electron. The exact position of the electron cannot be determined; instead we can determine the probability of finding the electron at any point in space. In the case of the ground state of a hydrogen atom the probability distribution is spherical around the nucleus and it is possible to draw a spherical boundary surface inside which there is about 95 per cent probability of finding the electron. The electron has a fixed energy and a fixed spatial distribution called an *orbital*. In the helium molecule there are two electrons associated with the helium nucleus. These two electrons have exactly the same spatial distribution and hence exactly the same energy (i.e. they occupy the same orbital) but they differ in their spin (the Pauli exclusion principle). This is quite general: electrons associated with atomic nuclei occupy orbitals of fixed energy and with determined spatial distribution, and each orbital can only contain a maximum of two electrons with anti-parallel spins.

In physics, periodic phenomena are frequently associated with a 'wave equation', and in atomic theory the relevant equation is called the 'Schrödinger Equation'. The wave equation predicts discrete solutions and in one dimension for a particle confined to a box with infinite walls, the solutions can be depicted as shown in Fig. 1.1. $\psi_1 \rightarrow \psi_4$ represents solutions of increasing energy (note also increasing number of nodes). There is no direct physical interpretation of the wave function ψ, but $\psi^2 \, d\tau$ is taken to be a measure of the probability of finding an electron in a small volume of space $d\tau$ (in one dimension as shown on p. 2 for a small value dx).

In three dimensions the equation determines the energy and defines the spatial distribution of each electron. Solutions of the
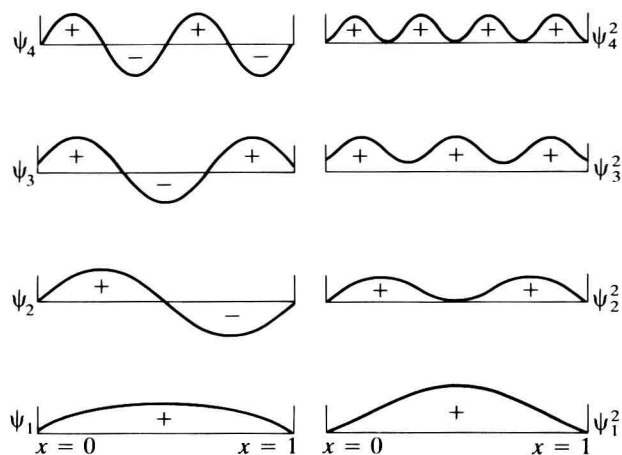
Fig. 1.1

wave equation in three dimensions enable us to calculate the 'shape' of each atomic orbital i.e. boundary surfaces inside of which there is, say, 90 per cent probability of finding the electron. Thus the first five solutions of the wave equation for an electron associated with a proton (nucleus) can be depicted as shown in Fig. 1.2.

In the hydrogen atom the 1s atomic orbital is the lowest in energy, while the remainder ($2s, 2p_x, 2p_y, 2p_z$) are of equal energy (i.e. degenerate), but for all other atoms the 2s atomic orbital is of lower energy than the $2p_x, 2p_y, 2p_z$ orbitals which are degenerate. The figure shows ψ rather than ψ^2 because as we shall see when considering valency, the sign of the wave equation is extremely important. Further review of atomic theory need not concern us.

In atoms, electrons occupy 'atomic orbitals' of specific energy and spatial distribution. In molecules, electrons occupy similar 'molecular orbitals' which embrace the molecule. The simplest molecule is hydrogen which can be considered to be made up of two separate protons and two electrons. There are two
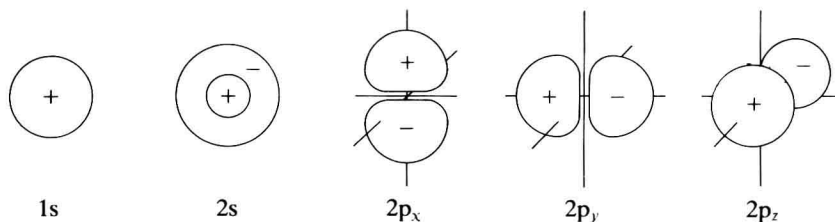

| 1s | 2s | 2p$_x$ | 2p$_y$ | 2p$_z$ |

Fig. 1.2 The first five solutions for ψ for the wave equation. The '+' and '−' signs have the same significance as they have in Fig. 1.1
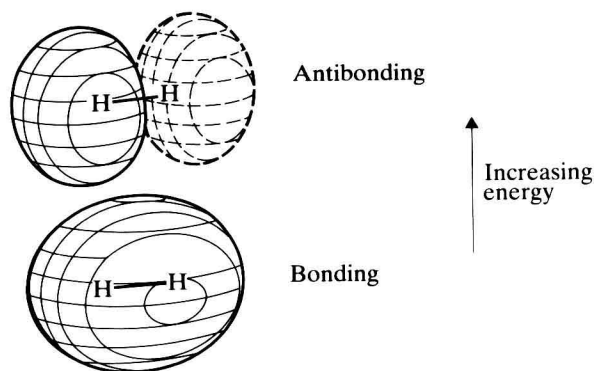
2

Fig. 1.3

molecular orbitals for hydrogen which can be depicted as shown in Fig. 1.3. The lower energy orbital has its greatest electron density between the two nuclei and a qualitative picture would be to regard the negatively charged electrons as holding the two positively charged nuclei together like jam in a sandwich. The bonding molecular orbital is of lower energy than the 1s atomic orbitals of hydrogen and is referred to as a *bonding orbital*. This orbital is more stable than two separated atomic hydrogen orbitals. In contrast, in the upper molecular orbital, there is a node in the electronic wave function and the electron density is low between the two positively charged nuclei (i.e. there is insufficient jam to overcome the mutual repulsion of the atoms and to hold the sandwich together). The energy of the upper molecular orbital is greater than that of a 1s atomic orbital. Such molecular orbitals are described as *antibonding*.

Normally the two electrons in a hydrogen molecule occupy the bonding molecular orbital with their spins anti-parallel (i.e. the Pauli principle applies to molecules as well as atoms). If molecular hydrogen is irradiated by light from the far ultra-violet region a molecule may absorb light and one of the two electrons will be promoted to the antibonding orbital (σ^*). To a first approximation, the energy of the electron in the antibonding orbital cancels out the effect of the electron in the bonding orbital (σ) and the atoms can drift apart. This is not an important way of dissociating molecular hydrogen but it can be
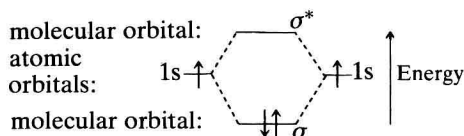

Fig. 1.4 Bonding and anti-bonding orbitals on a hydrogen molecule

very important in dissociating other molecules (for example molecular chlorine and molecular bromine are dissociated in this way). We can represent the energy levels in a hydrogen molecule by a diagram which shows how two 1s atomic orbitals combine to form two molecular orbitals, one bonding σ and one antibonding σ^* (Fig. 1.4).

Further reading

The Chemical Bond, J. H. Murrell, S. F. A. Kettle and J. M. Tedder, Wiley, Chichester, 1979.

2 Pictorial Orbital Theory

In terms of the electron pair theory (Lewis dot structure) methane consists of four hydrogens bound by four electron pairs to a central carbon atom. The innermost electrons occupying the 1s orbital of the carbon atom can be regarded as non-bonding and can be neglected for most chemical applications. There are four valence molecular orbitals in methane, but they are not identical. They consist of one orbital with no nodal plane, and three degenerate (i.e. of equal energy) orbitals, each of which contains a nodal plane. Figure 2.1 depicts the four orbitals. It is important to realize that the existence of bonding orbitals of different energy in no way conflicts with the electron pair picture in which each 'carbon–hydrogen' bond is identical. The tetrahedral disposition of the hydrogen atoms follows from the combination of the four orbitals. The only circumstance in which the presence of differing molecular orbitals is apparent is when the electron energy levels are being directly probed as in photo-electron spectroscopy. The photo-electron spectrum of methane confirms that there are two different occupied electronic levels in the valence shell of the methane molecule.
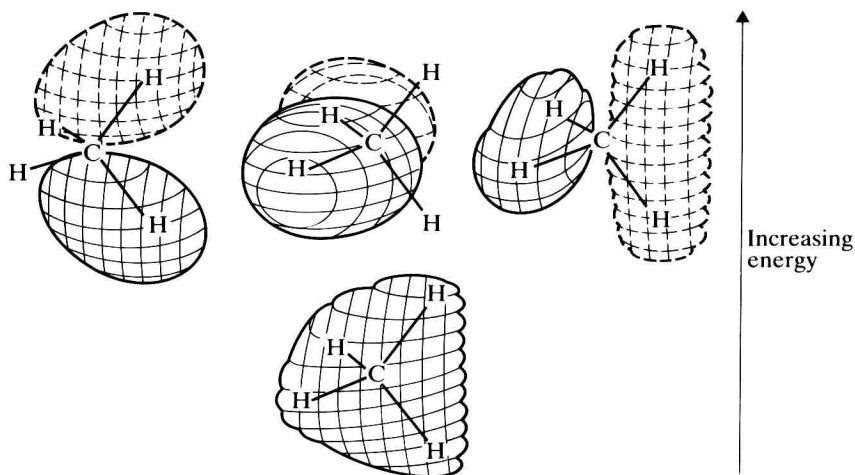

Fig. 2.1 The bonding orbitals of methane

The ethane molecule has fourteen valence electrons occupying seven bonding molecular orbitals (Fig. 2.2).

The actual sign of the wave function and the presence of nodal planes is better illustrated by the pictorial diagram Fig. 2.3. Four of the molecular orbitals occur as degenerate pairs, a simplification which is not shown by the molecular orbitals of propane. (A
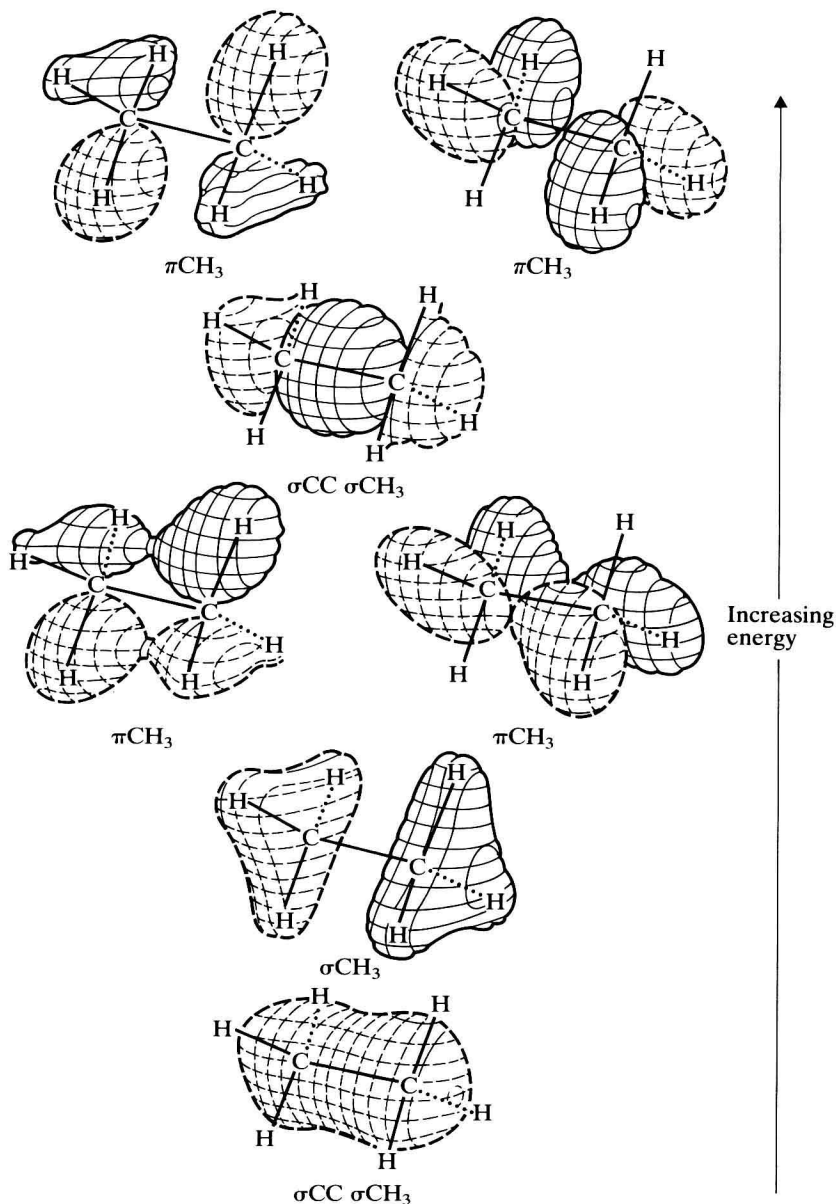

πCH_3

πCH_3

$\sigma CC \; \sigma CH_3$

πCH_3

πCH_3

Increasing energy

σCH_3

$\sigma CC \; \sigma CH_3$

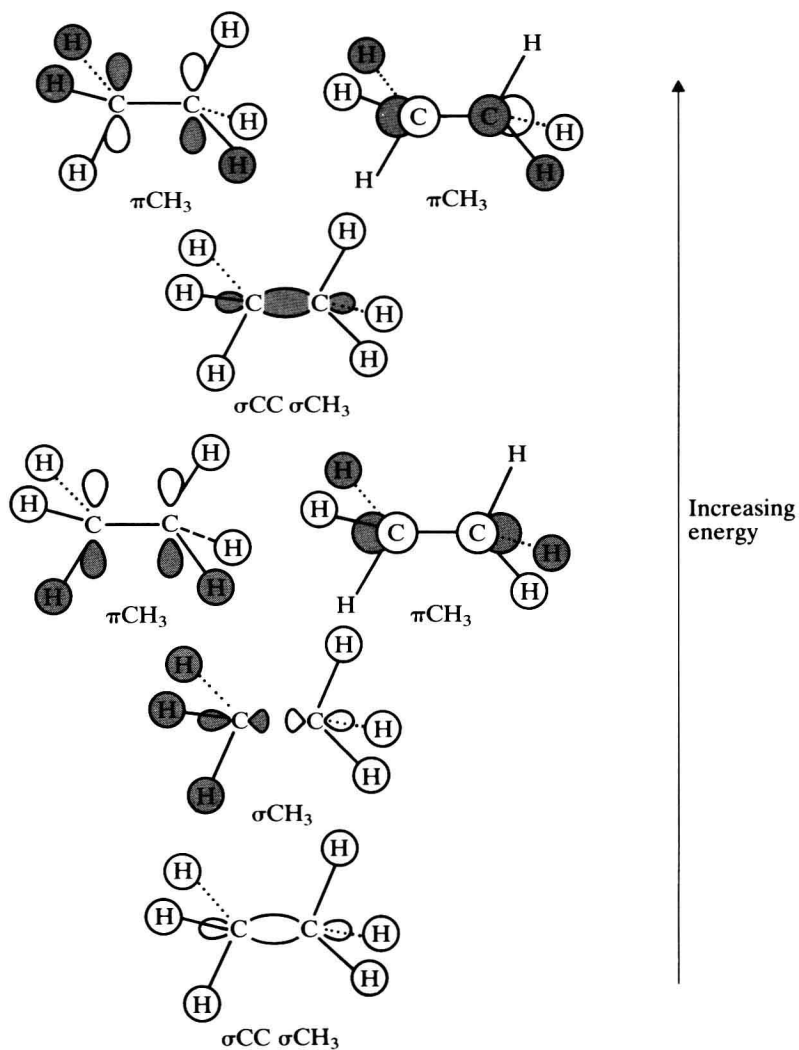**Fig. 2.2**   The bonding orbitals of ethane (staggered conformation)

Fig. 2.3 The bonding orbitals of ethane (symmetry)

π orbital has a nodal plane containing the bond axis while a σ orbital has no nodal plane.)

In propane there are ten bonding molecular orbitals with twenty valence electrons to go in them, and although there is no degeneracy, the energies of the three highest occupied orbitals are very similar.

Molecules with lone pairs

A simple diatomic molecule with different nuclei is hydrogen fluoride (Fig. 2.4). There are eight valence electrons which go

$E = -410 \text{ kcal mol}^{-1}$

$E = -410 \text{ kcal mol}^{-1}$

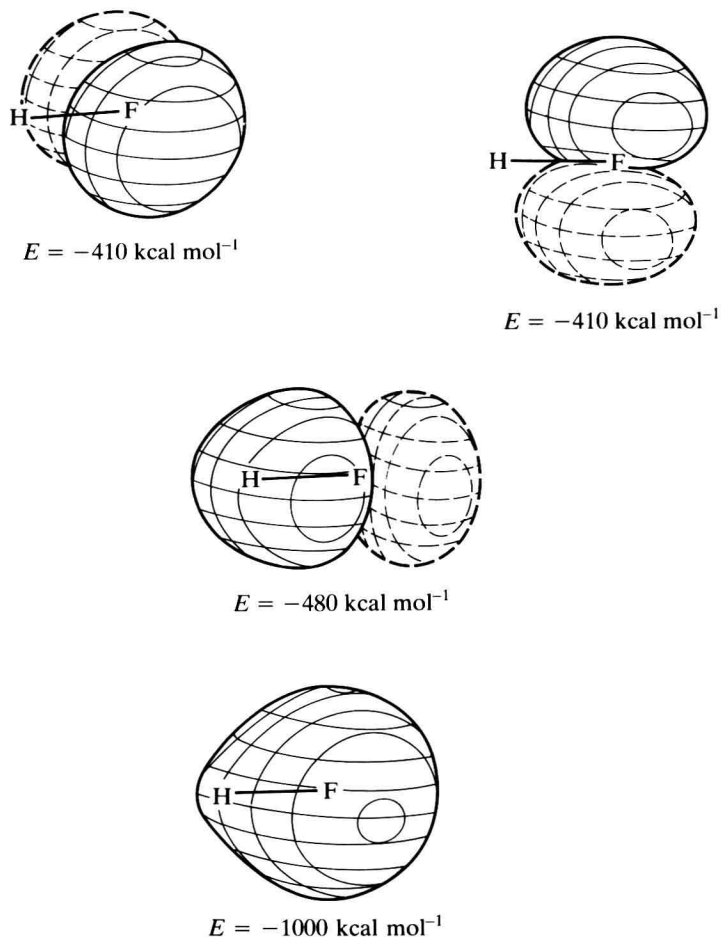$E = -480 \text{ kcal mol}^{-1}$

$E = -1000 \text{ kcal mol}^{-1}$

Fig. 2.4 The occupied molecular orbitals of hydrogen fluoride

into four molecular orbitals. The two orbitals with the highest energy are degenerate; they are of the π-type and have no electron density associated with the hydrogen atom, i.e. they are 'Non Bonding Orbitals' (NBO) and in Lewis Theory are represented as two 'lone pairs'. The second important difference between hydrogen fluoride and the molecules we have discussed so far is that the valence electron density is not distributed equally about the molecule. There is much greater electron density around the fluorine atom. This is because fluorine is the most electronegative of all the elements.* This means that in each bonding molecular orbital fluorine takes a larger share of the electron density.

* For a precise definition of electronegativity, see Chapter 4; for the present it can be regarded as the intrinsic property of an atom to attract electrons to itself when it is bonded.
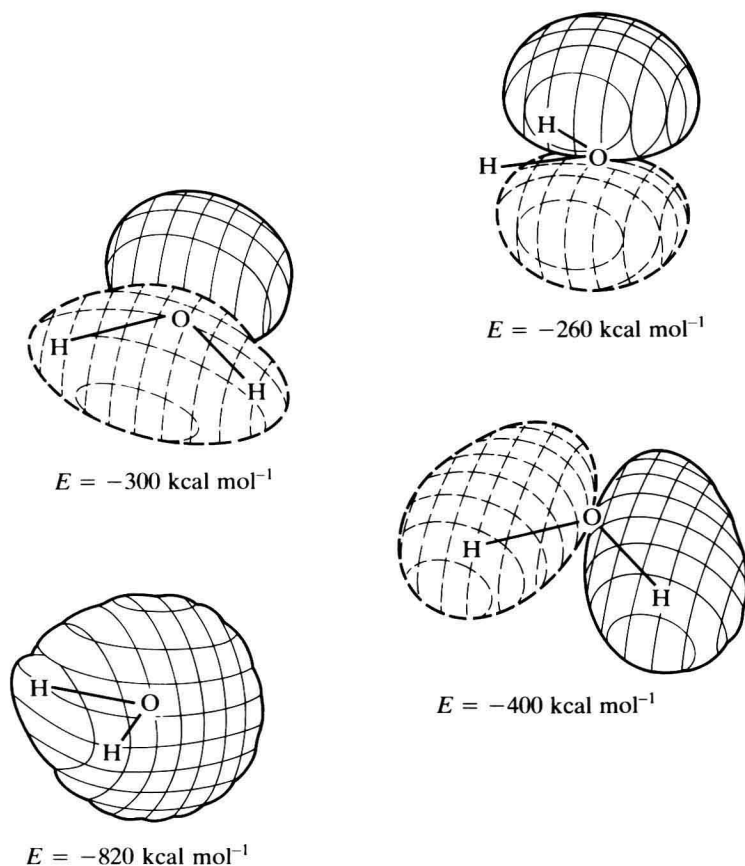
$E = -260$ kcal mol^{-1}

$E = -300$ kcal mol^{-1}

$E = -400$ kcal mol^{-1}

$E = -820$ kcal mol^{-1}

Fig. 2.5   The occupied molecular orbitals of water

In the water molecule (Fig. 2.5) there is no degeneracy, but the highest occupied orbital is non-bonding and localized on the heavy atom, oxygen, like the non-bonding orbitals of hydrogen fluoride. The next lowest orbital is also non-bonding and has a lobe pointing away from the two hydrogens corresponding to the second 'lone pair' of Lewis Theory. Again we see oxygen takes more than its 'fair share' of the total electron density. The other important feature of the water molecule is that all the bonding molecular orbitals are of higher energy than the corresponding orbitals in hydrogen fluoride.

Ammonia (Fig. 2.6) has a degenerate pair of bonding orbitals, and like hydrogen fluoride and water there is a non-bonding orbital. The highest occupied orbital has a lobe which points away from the hydrogen atoms and corresponds to the 'lone pair' of Lewis Theory. Notice that this is the molecular orbital with the highest energy of the three molecules; we shall