Molecular Orbital Theory

Modern chemistry has depended upon the use of models of increasing comlexity. Atoms can be represented as spheres connected by cylinders or sticks. In order to understand the mechanism of many reactions, **Lewis Theory**, developed by Robinson and Ingold, can provide a better answer.Lewis Theory uses curly arrows to denote electron migration during a chemical reaction and has led to a greater understanding of the factors controlling chemical reactions.

Pauling with others developed Resonance Theory, which provided the rationale to an all-embracing orbital theory. The use of "canonical forms" and "resonance hybrids", along with extensive use of curvy arrows has provided the fundamental background to modern organic theory, but for *e*.g. Diels-Alder and per cyclic reactions, the curly arrow format is not very clear and in some instances the reactions are described as no-mechanism reactions. Woodward and Hoffmann showed that by examining the interaction of the frontier molecular orbitals (i.e. the Highest Occupied, **HOMO** and Lowest Unoccupied, **LUMO**) both the regio- and stereo specificity could be accounted for. Woodward and Hoffmann work was assimilated into general organic reaction theory

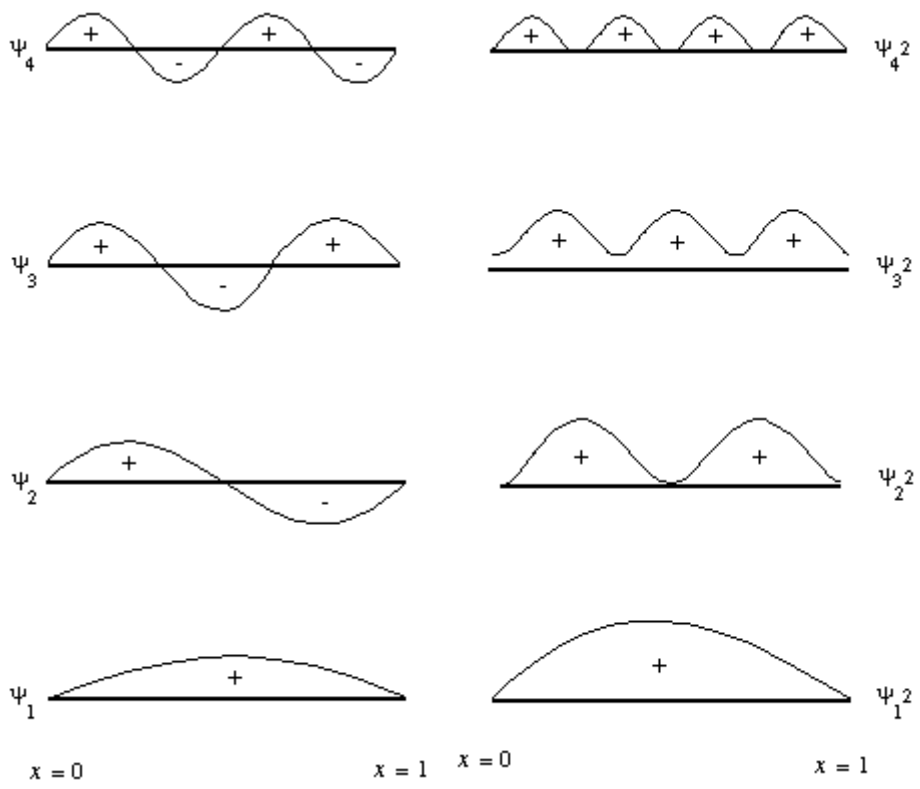
Atomic and Molecular Orbital's

By sharing electron, molecules can form bonds, and it is possible to regard the sharing of two electrons by two atoms as constituting a chemical bond. Atoms can share one, two or three electrons (forming single, double and triple bonds).

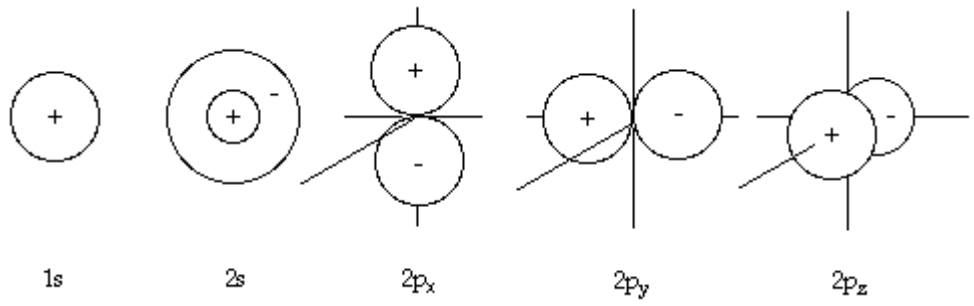
A hydrogen atom consists of a nucleus (a *proton*) and an electron. It is not possible to accurately determine the position of the electron, but it is possible to calculate the probability of finding the electron at any point around the nucleus. With a hydrogen atom the probability distribution is spherical around the nucleus and it is possible to draw a spherical boundary surface, inside which there is a 95% possibility of finding the electron. The electron has a fixed energy and a fixed spatial distribution called an *orbital*. In the helium atom there are two electrons associated with the helium nucleus. The electrons have the same spatial distribution and energy (*ie*. they occupy the same orbital), but they differ in their spin (Pauli Exclusion Principle). In general: electrons in atomic nuclei occupy orbitals of fixed energy and spatial distribution, and each orbital only contains a maximum

of two electrons with anti-parallel spins.

In physics, periodic phenomena are associated with a "wave equation", and in atomic theory the relevant equation is called the "Schrödinger Equation". The wave equation predicts discrete solutions in one dimension for a particle confined to a box with infinite walls, The solutions can be shown as in the figure below:



ψ_1 - ψ_4 represent solutions of increasing energy. In three dimensions, the equation determines the energy and defines the spatial distribution of each electron. A solution of the wave equations in three-dimensions allows calculation of the "shape" of each orbital. The first five solutions of the wave equation for an electron associated with a proton can be shown in the figure below:



In the hydrogen atom, the *1s* atomic orbital has the lowest energy, while the remainder (*2s, $2p_x$, $2p_y$ and $2p_z$*) are of equal energy (*ie*.**degenerate**), but for all other atoms, the *2s*atomic orbital is of lower energy than the *$2p_x$, $2p_y$ and $2p_z$* orbital's, which are degenerate.

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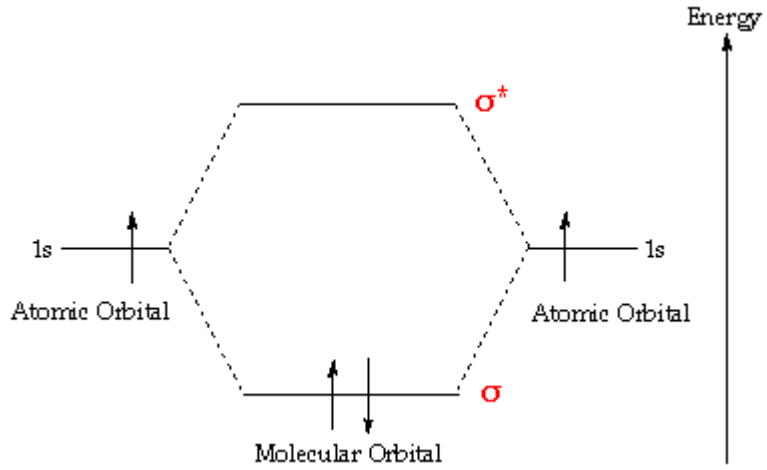
Normally, the two electrons in hydrogen occupy the bonding molecular orbital, with anti-parallel spins. If molecular hydrogen is irradiated by ultra-violet (UV) light, the molecule may absorb the energy, and promote one electron into its antibonding orbital (σ^*), and the atoms will separate. The energy levels in a hydrogen molecule can be represented in a diagram - showing how the two 1s atomic orbital's combine to form two molecular orbital's, one bonding (σ) and one antibonding (σ^*). This is shown below - by clicking upon either the σ orσ^* molecular orbital in the diagram - it will show graphically in a window to the right:

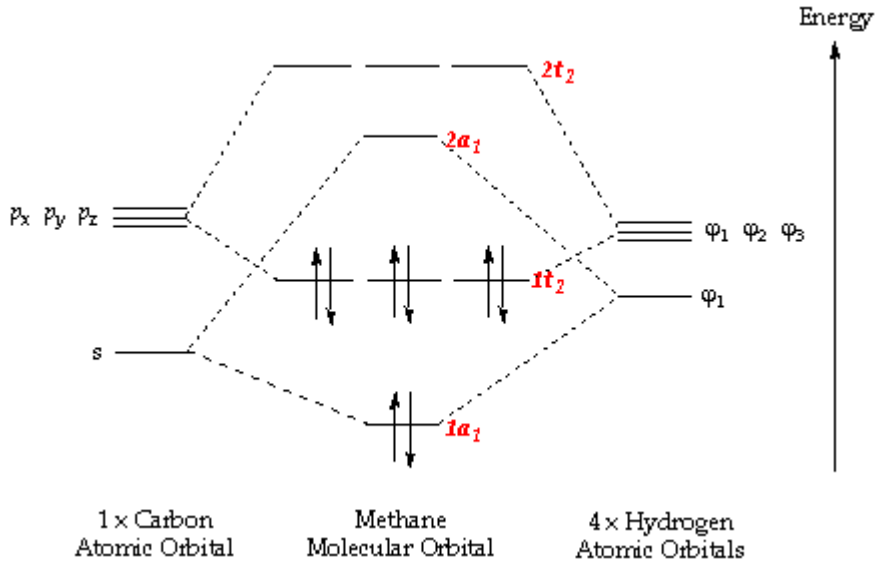


Saturated molecules

These are molecules in which all valence electrons are involved in the formation of single bonds. There are no non-bonded lone pairs. These molecules are generally less reactive than either electron-rich or electron-deficient species, with all occupied orbital's having relatively low energies.

Methane:

The valence molecular orbital's of methane are delocalized over the entire nuclear skeleton - that is, it is not easy to assign any one orbital to a particular **C-H** bond. It is possible to see how complex the orbital structure becomes with the increase in energy. Methane has four valence molecular orbital's (bonding), consisting of one orbital with one nodal plane (lowest occupied) and three degenerate (equal energy) orbital's that do have a nodal plane. For the energy diagram and pictorial view of the orbitals - please see below:



Ethane:

The ethane molecule has fourteen valence electrons occupying seven bonding molecular orbitals. As can be seen from the energy diagram - four of the molecular orbitals occur as degenerate pairs. Like in methane - the molecular orbitals of ethane show increasing nodal structure with increasing orbital energy.
For the energy diagram and pictorial view of the orbitals - please see below: