विचार संगम

भारतीय दर्शन, विज्ञान, साहित्य-कला और तकनीकी के विशेष संदर्भ में

सम्पादक
डॉ. दिनेश चन्द्र शर्मा

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Ph.D., D.Lit. (Sub.)

निदेशक, कॉम्पिटिशन प्लस ग्रुप ऑफ इन्स्टीट्यूशन,

अजमेर

Books n Books

51/1509, आचमन, वेदविहार,

लोहाखान, अजमेर-305001

प्रकाशक :

पुष्पा शर्मा

Books n Books

51/1509, आचमन, वेदविहार,

लोहाखान, अजमेर-305001

ई-मेल : bnbajmer@gmail.com

संस्करण

प्रथम 2025

ISBN : 978-81-993854-0-5

मूल्य - 400/-

रचना - विचार संगम-भारतीय दर्शन, विज्ञान, साहित्य-कला और तकनीकी के विशेष संदर्भ में

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मुद्रक - श्रीनिवास प्रिन्टोग्राफिक्स, अजमेर

24

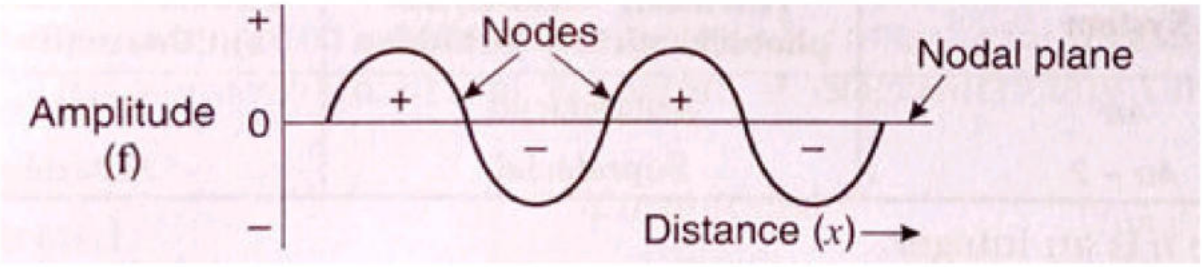
FRONTIER MOLECULAR ORBITAL AND THEIR APPLICATIONS

Dr. Ashwani Sharma
Assistant Professor (Deptt. of Science and Technology)
Hukumchand Noble Institute of Science and Technology

MOLECULAR ORBITAL

Molecular structure is best represented in terms of quantum mechanics. Quantum mechanical calculations are quite difficult. Therefore, approximation methods have been evolved which are result of mathematical simplifications. Molecular orbitals are centered around all the nuclei present in the molecule. Relative stabilities of molecules depend upon how electrons are distributed in them. In order to understand molecular symmetry; it is essential to understand wave equations, phases of waves originated by the movement of electrons if we consider them as waves and also what are bonding and antibonding molecular orbitals.

Phase: Electrons not only behave as particles but as waves as well, i.e.. they have dual nature. A stationary wave can be represented as follows.



The vertical displacement of wave is known as amplitude which increases in one direction to the maximum, then decreases to zero and then again increases in opposite direction. The points of zero amplitude are known as nodes which lie is nodal plane perpendicular to the plane of paper. Upward and downward displacements are opposite phases, to distinguish between them we assign them positive and negative signs respectively.

Wave nature of electrons can be expressed in terms of wave

equation which describes amplitude, & as a function of distance (x). Such function is known as wave function. It is important to note that electron waves are similar to string waves. When wave function gives the amplitude (6) as a function of three co-ordinates it is known as orbital. In case of orbital lobes

of opposite phases are given plus (+) and minus (-) signs or one of them is shown by shaded area; between two lobes lies nodalplane. These (+) or (-) sign have nothing to do with charge. They indicate amplitude of electron wave is of opposite sign in two lobes. The amplitude or wave function, & is the orbital. It is actually and not which have some meaning and gives the actual probablity of finding the electron is space. may be either (+) or (-) but is always positive indicating that probability can not be zero.

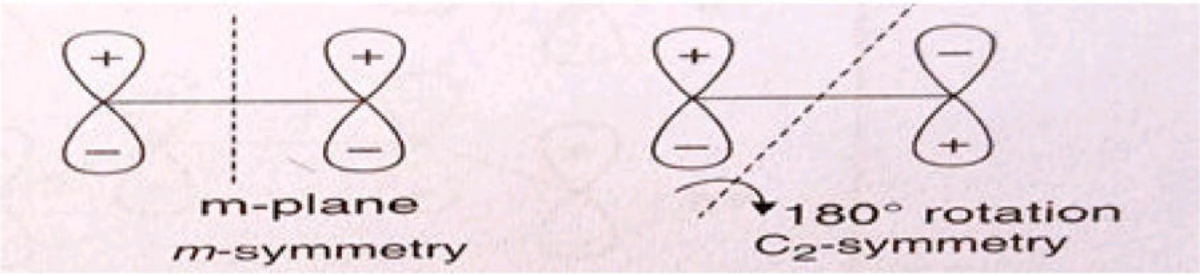
MOLECULAR ORBITAL SYMMETRY

When we think of symmetry of orbitals we mean relative disposition of phases of two lobes in space. In pericyclic reactions only p-orbitals of alkenes are involved; therefore, we consider only symmetries of p-orbitals (o-skeleton is often ignored). For a system with nn-electrons n-molecular orbitals will be there: 2 2 bonding orbitals and antibonding orbitals. In other words, we can say that in a system with na-electrons n-approximation sets of p-orbitals will be there, all of which differ in regard to their energies. Half of them with lower energies will be bonding molecular orbitals and other half with higher energies will be antibonding molecular orbitals is having m-symmetry if a line drawn perpendicular to the plane of molecule divides it in two equal halves which are mirror images of each other. On the other hand a molecular orbital is said to possess C?-axis of symmetry if rotation around its axis perpendicular to mirror plane by 360°, 2 i.e., 180° gives the arrangement identical to the original one

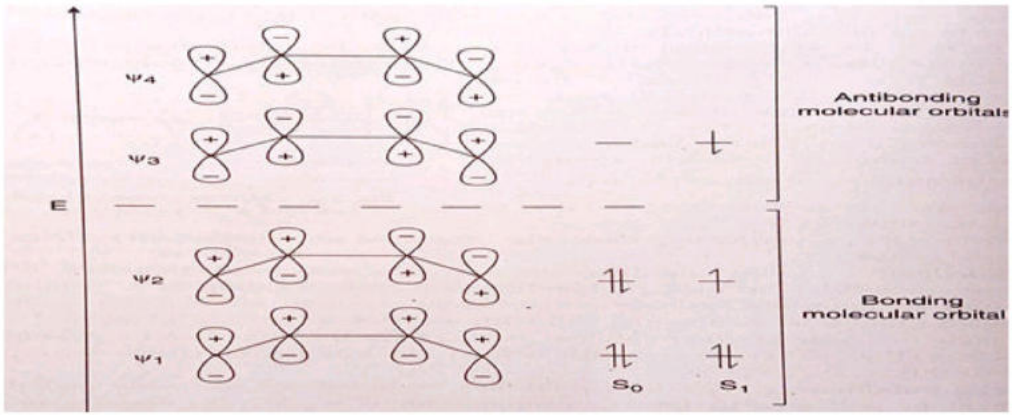
Symmetry properties of p-molecular orbitals of some important systems are discussed below:

(1) Ethylene: In ethylene, there are only two r-electrons, therefore, it has only two molecular orbitals: bonding and antibonding (*). Symmetry properties of both the orbitals are different. Ground state (G.S.) bonding molecular orbital is symmetric (S) with respect to mirror plane (m) and antisymmetric (A) w.r.t. the rotational axis (c?). On the other hand antibonding orbital of ethylene is

antisymmetric w.r.t. m plane and symmetric with respect to c?-axis



(2) 1, 3-Butadiene: The four p-orbitals in butadiene molecule and their combinations will give us four molecular orbitals psi_{1} psi_{2} Psi_{3} and psi_{4} in the increasing order of their energies out of which Psi_{1} and Psi_{2} are bonding orbitals which contain all the four -electrons, as they are lowest energy molecular orbitals and are filled first similar to the filling pattern of atomic orbitals. and Psi_{3} are antibonding orbitals and are vacant. Ground state of butadiene represented by \mathcal{S}_{0} whereas excited states by S_{1} singlet) and t_{2} (triplet) symbols. In S_{1} electron from highest occupied molecular orbital (HOMO) has jumped to lowest unoccupied molecular orbital (LUMO, antibonding) and have opposite spins but int, their spins are same.



(3) 1, 3, 5-Hexatriene: The six melectrons of hexatriene are accomodated in first three molecular orbitals w?. W2 and 3: while remaining three molecularorbitals 4.5 and we are unoccupied. Symmetry properties of 1, 3, 5-hexatriene along with their electron occupancy in ground state and excited state are described

Tabular representation of symmetry properties of molecular orbitals of 1, 3, 5-hexatriene :

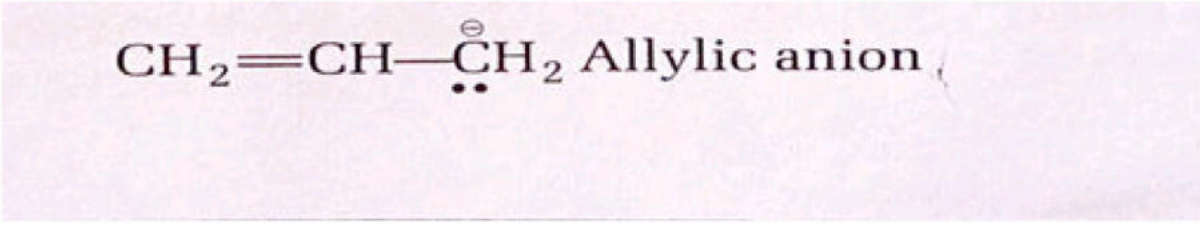
Molecular Orbital	*m*	C_2
ψ_6	A	S
ψ_5	S	A
ψ_4	A	S
ψ_3	S	A
ψ_2	A	S
ψ_1	S	A

Symmetry properties of a linear conjugated molecular orbital can he predicted on the basis of number of nodes in it. A Psi_{R} m.o. has (n - 1) nodes, II (n - 1) is zero or even integer molecular orbital is symmetrical w.r.t. mirror plane antisymmetrical w.r.t. two fold axis. On the other hand if (n - 1) is odd integer m.o. is antisymmetric with respect to mirror plane but contains c?-axis of Symmetry.

Allylic Systems For conjugated systems with even number of carbon atoms such as butadiene or 1, 3, 5-hexatriene, the nodes occur between carbon atoms. But in conjugated systems with odd number of C-atoms, nodes can coincide with one or more of C-atoms. Same is the case with allylic systems. The middle non-bonding orbital; which is singly occupied in allyl radical and doubly occupied in anion has a single nodal plane which precludes any contribution of 2p-orbital at central carbon atom. The orbital of highest energy possess two nodes. Nodes falling on carbon atom may be represented by a dot () and those falling between carbon atom by broken lines (3).It has been found that unbranched conjugated cations, anions and free radicals possess odd number of carbon atoms. Two such simplest systems are allylic systems and 2, 4-pentadienyl systems. One important characterstic of these systems is that corresponding cations, anions and free radicals though have same number of molecular orbitals with same symmetry properties; but they differ in electron occupancy. Secondly, in some of their molecular orbitals nodes lie on one or more C-atoms. Occupancy characterstics of allylic cation, anion and free radicals are as follows:

(a) Allylic cation:

(b) Allylic anion contains one -bond and one p-orbital with lone pair of electrons:



(c) Allylic free radical possess three p-orbitals: out of which two form one -bond and third one contains one electron.

$CH_2 = CH - CH$, Allylic free radical

2. 4-Pentadienyl System 2. 4-pentadienyl system possesses five

molecular orbitals.

FRONTIER MOLECULAR ORBITALS (FMO)

Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are frontier molecular orbitals. They are different for different olefins as well as depend upon species, i.e., whether it is cation, free radical or anion. For example:

(i) In ethylene HOMO is and LUMO is $\prod^*$.

(ii) In 1, 3-butadiene 2 is HOMO, whereas 3 is LUMO. But is excited state becomes HOMO and 4 LUMO.

(iii) For 1, 3, 5-hexatriene 3 is HOMO and 4 is LUMO; but upon irradiation, becomes HOMO and vs LUMO.

(iv) HOMO and LUMO of allylic systems have already been discussed in previous article.

(v) HOMO and LUMO of 2, 4-penta-dienyl systems are diagramatically represented.