NOBEL PRIZES

The course of chemical reactions

APPLIED theory finally got its long awaited share of recognition: the 1981 Nobel Prize in chemistry has been awarded to Prof. Roald Hoffmann, of Cornell University, USA, and Prof. Kenichi Fukui, of Kyoto University, Japan, for "their theories, developed independently, concerning the course of chemical reactions". Fukui's major contribution is known to the chemical world as the Frontier Orbital Theory and that of Hoffmann as the Woodward-Hoffmann rules, named after Hoffmann and the late Prof. Woodward. Since their theoretical results are expressed in the framework of Molecular Orbital (MO) Theory, an attempt is made here to make the terminology of MO theory familiar.

Electrons in atoms are arranged in shells or atomic orbitals (AOs), such as s, p, d, f, each AO taking up to two electrons. The simplest atom, hydrogen, has only one electron occupying the lowest energy AO, $1s$. The carbon atom, however, has six electrons. Two of them go to the $1s$ orbital while the remaining four have to occupy higher energy orbitals, $2s, 2p_x, 2p_y$ and $2p_z$. The approximate shape of these orbitals is obtained as the wave functions of the atom from quantum mechanical calculations (Fig. 1). As two hydrogen atoms approach each other to form a hydrogen molecule, H_2, the two $1s$ orbitals interact with each other to give two new orbitals, the so-called molecular orbitals (MOs) which can be conveniently

described in terms of a linear combination of atomic orbitals (LCAO). The lower energy MO obtained by the addition of the AOs has bonding character and the higher energy MO obtained by taking the difference of the AOs has antibonding character. The two electrons in a hydrogen molecule occupy the lowest bonding MO. In larger molecules, the problem becomes more complex. It suffices here to say that the MOs can be similarly constructed as LCAOs. If we construct the MOs of ethylene, C_2H_4, from two carbon atoms $(1s, 2s, 2p_x, 2p_y, 2p_z)$ and four hydrogen $(1s)$ atoms, we get 14 MOs, the lowest eight of which will be occupied by the 16 electrons available. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of ethylene are shown in Fig. 3a. The HOMO and LUMO of butadiene, $H_2C = CH - CH = CH_2$, are shown in Fig. 3b.

In 1952, Fukui suggested that the HOMO and LUMO (together he called them frontier orbitals) control the reactivity of molecules. An electrophilic reagent, which normally has a low-lying orbital vacant, interacts strongly with the HOMO, that too at the atom having the highest frontier electron density. A nucleophilic reagent, with a high-lying electron pair, interacts strongly with the LUMO of the system. The importance ascribed to frontier orbitals seemed to be correct at that time since the HOMO and

LUMO can be compared to the valence orbitals of an atom. Several theoretical justifications followed. The Frontier Orbital method has been used successfully in solving numerous problems, for example, reactivity in polycondensed aromatic systems, the position of attack in Diels-Alder reactions, aromatic substitution reactions, copolymerisation ratios in free radical polymerisations, etc.

While the frontier orbital concept was developing, observations of a set of reactions (Fig. 4) with puzzling reactivity were also accumulating. Consider the reactions 1 to 4. Reactions 1 and 2 proceed thermally but the stereochemistry of the products (arrangement of the substituents A and B in relation to the plane formed by the carbon atoms) is different. The two A's are above the plane of the four-membered ring in 2 but on
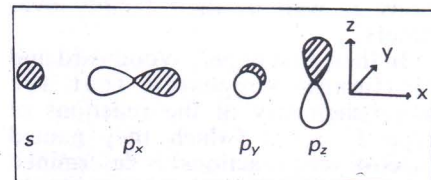

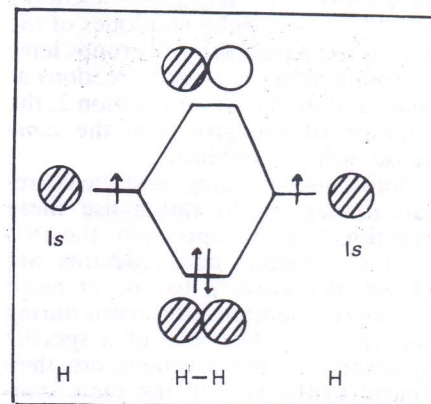Fig. 1. Shape of atomic orbitals s, p_x, p_y, and p_z

Fig. 2. Interaction diagram for the formation of H_2 molecule from two hydrogen atoms

opposite sides of the six-membered ring in 1. On the other hand, under similar conditions reaction 3, the Diels-Alder reaction, proceeds thermally while the apparently similar reaction 4 does not. Though such puzzling transformations were known for long, they did not attract enough attention until Woodward's research group at Harvard University found striking stereospecificity in reactions directed to the synthesis of Vitamin B_{12}. As an experimentalist interested in theory Woodward did not ignore these observations. At the same time, Hoffmann, a theoretician interested in experiments, had just finished his PhD. It was only natural that they got together, and, in 1965,
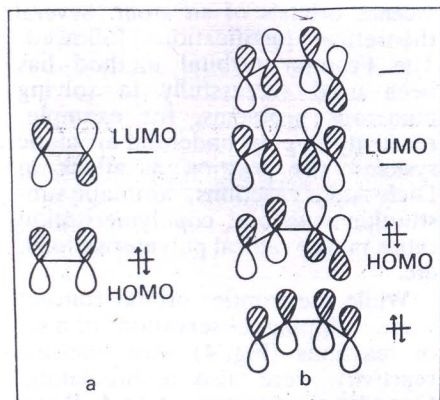
Kenichi Fukui

Roald Hoffmann

Fig. 3. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of (a) ethylene and (b) butadiene

they published a series of communications explaining how the symmetry of the MOs of the reactants determine the stereochemistry of some reactions as well as their facility over others.

In their first paper, Woodward and Hoffmann suggested that the stereochemistry of the reactions of type 1 and 2 (which they named electrocyclic reactions) is determined by the symmetry of the HOMO. In order to initiate a bonding interaction between the termini in reaction 1 (that is, to bring the end lobes of the HOMO in phase), the end groups have to rotate along *opposite* directions as indicated in Fig. 5; for reaction 2, the rotation of end groups in the *same* sense will be stabilising.

Subsequently, they used the correlation diagram to rationalise these reactions. In this approach, the MOs of the products and reactants are classified according to one or more symmetry elements preserved during the reaction. The MOs of a specific symmetry of the reactants are then traced to the MOs of the same symmetry of the products, allowing for the quantum mechanical condition that orbitals of the same symmetry cannot cross. If the occupied MOs of the reactants correlate to the occupied MOs of the products, the reaction is said to conserve orbital symmetry during reaction. Such reactions will have low activation energy. For example, an MO correlation diagram for reaction 3 constructed using a plane of symmetry perpendicular to and passing through the C-C bond in ethylene shows that all occupied orbitals correlate to occupied orbitals in the product (Fig. 6). The Diels-Alder reaction is thus said to be an athermally allowed reaction. A similar treatment for reaction 4 indicates, however, that it does not conserve symmetry; the occupied orbital correlates to an empty orbital. Hence the large barrier for the seemingly similar thermal reaction.

A more complete approach, also used by Woodward and Hoffmann, correlates the various electronic states (obtained as a product of symmetry of the occupied orbitals) of the reactant to those of the products. This is all the more important for photochemical reactions. Several alternative suggestions have now been evolved out of these principles. Whatever the language, all these treatments emphasise the difference in the reactivity of a 4n+2 system as in reaction 1, and that of a 4n system as in reaction 2.

Orbital symmetry-based ideas had so strong an impact on organic chemistry that within a few years they became part of undergraduate chemistry programmes. They owe most of their popularity to the ease with which they can be applied to everyday problems because numerical calculations are seldom necessary. It is now possible, for example, to predict the preferred product of a reaction and its rate of formation relative to another reaction without doing any calculation. All one needs to know is the nodal properties of MOs and notions based on the perturbation theory about changes in MOs and their energies caused by substituents.

Born in 1937 in Zlockaw, then a part of Poland and now in Russia, Hoffmann migrated to the USA during the Second World War. After undergraduate studies at Columbia, Hoffmann obtained Ph D in chemical physics from Harvard University and continued there as a junior fellow and collaborated with Wood-
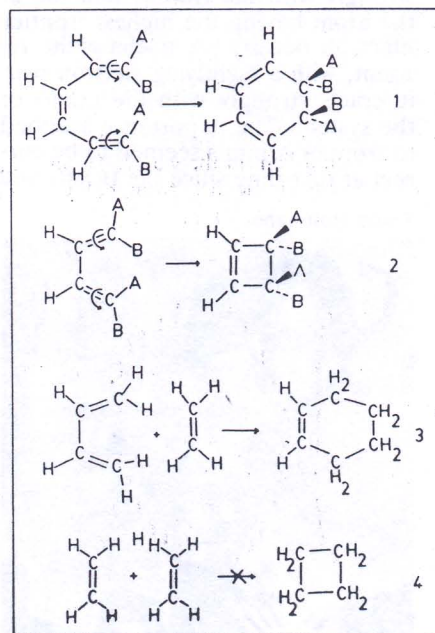

Fig. 4. Reactions 1 and 2 seemingly dissimilar, are equally favourable; and reactions 3 and 4 are seemingly similar but under similar conditions reaction 3 occurs but 4 does not
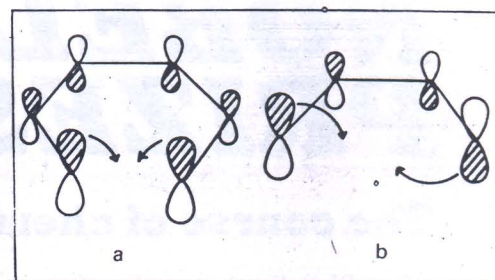

Fig. 5. The HOMOs of hexatriene and of butadiene indicating the preferred directions of ring closure giving maximum bonding during the reaction. Since the opposite placement of substituents corresponds to the opposite requirements, the reactions are equally favourable
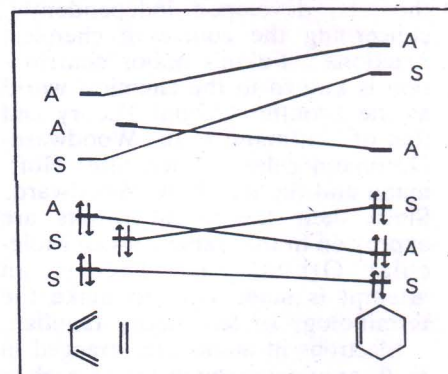

Fig. 6. Correlation diagram for reaction 3 connecting orbitals of the same symmetry of reactants and products. 'S' indicates that the MO is symmetric with respect to the plane passing through the midpoint and perpendicular to the C-C bond in ethylene. 'A' denotes the corresponding antisymmetric orbitals. In spite of the similarity, bonding in reaction 3 is S-S and A-A, so the reaction proceeds, but for reaction 4 it is S-A and the reaction does not occur

ward. In 1965, he came to Cornell University where he is currently the chairman of the department. He is married to Eva Borjesson from Sweden, and the Hoffmanns visit Sweden every summer. The research group at Cornell used to kid him: "When do you get to Sweden in *winter*?" Well, the time has come— this December.

Fukui was born in Nara Prefecture, Japan, in 1918. Even though he spent his entire professional carrier in Kyoto, the theories he developed have not met any bounds. In fact, he often says that his novel ideas got more recognition abroad than at home. Though coming rather late, the Nobel Prize will bring his contribution to the front in Japan.

E. D. JEMMIS

Dr. Jemmis is with the School of Chemistry, Central University of Hyderabad. After obtaining his Ph D from Princeton University in 1978, he worked for two years with Prof. Hoffmann at Cornell University before joining the University of Hyderabad in 1980.