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, H₂, 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, C₂H₄, 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, H₂C = CH – CH = CH₂, 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 polycrystalline aromatic systems, the position of attack in Diels-Alder reactions, aromatic substitution reactions, copolymerisation ratios in free radical polymerizations, 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 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 B₁₂. 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.
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 Zlockow, 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 Woodward. 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 career 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.

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