The 1981 Nobel Prize in Chemistry

Kenichi Fukui and Roald Hoffmann share the 1981 Nobel Prize in Chemistry for their quantum mechanical studies of chemical reactivity. Professor Fukui was born in Nara Prefecture, Japan, in 1918 and has spent his entire professional career at Kyoto University. Professor Hoffmann was born in Zlockaw, Poland, in 1937; after graduate studies at Harvard University, he stayed at Harvard as a junior fellow during 1962 to 1965 before joining the chemistry faculty at Cornell University. Both men have played leading roles in a developing revolution in our thinking about chemical reactions of important classes of organic and inorganic molecules.

One of the goals of the chemist is to predict the course of a chemical reaction under given conditions. For simple molecules, many reactions can be understood as associated with functional groups, characteristic small groups of bonded atoms. Examples are the hydroxy and amino groups, carboxylic acid, and the carbon-carbon double bond. Many reactions, however, do not lend themselves to a simple functional group classification because they involve more complex interactions. For such systems, the reacting molecules must be regarded as a whole. For several decades theoretical considerations of such reactions have been based on molecular orbital (MO) theory, in which an MO is defined as a one-electron wave function generally encompassing the entire molecule. Each MO, ϕ_i, is given as a linear combination of atomic-like orbitals (LCAO), χ_r,

$$\phi_i = \sum_r^n c_{ir}\chi_r$$

and has an associated energy, ϵ_i. The occupancy of each MO by up to two electrons of opposite spin determines the total energy of the molecule.

Many reactions can be treated as a perturbation of the MO's as they transform from those of the reactants to those of the products. If the transition state for a given reaction is treated as a perturbation H_{rs} for interaction of atom r in R with atom s in S, the energy change for each MO of R is given by

$$\Delta\epsilon_i = \sum_k^{\substack{\text{unoccupied}\\ \text{MO of S}}} \frac{(c_{ir}c_{ks}H_{rs})^2}{\epsilon_i - \epsilon_k}$$

A similar expression is given for the MO's of S. The most important term is usually given by the interaction of the highest occupied MO (HOMO) of one reactant with the lowest unoccupied MO (LUMO) of the other; $\epsilon_{HOMO} - \epsilon_{LUMO}$ is smallest for this combination.

In the early 1950's, Fukui proposed that HOMO's and LUMO's play a dominant role in reactions, and he called these the frontier orbitals. The proposal at first was simply intuitive, but various rationalizations soon followed. About that time M. J. S. Dewar independently deduced the approximate quantitative role of such MO's in certain classes of unsaturated and aromatic hydrocarbons. R. S. Mulliken also developed his theory of donor-acceptor complexes at about the same time, and his concepts were later extended to reactions. In many reactions one reactant (donor) has a HOMO of high energy from which an electron is readily lost, whereas the other reactant (acceptor) has a LUMO of relatively low energy and can readily accept an electron. Such donor-acceptor reactions then involve charge transfer from donor to acceptor and the nature of the reaction is determined by the bonding characteristics of the HOMO and LUMO. The energy relationship between the HOMO of the donor and the LUMO of the acceptor is shown schematically in Fig. 1. Thus, Fukui's frontier orbital concept has a solid basis in modern theory and is of wide applicability.

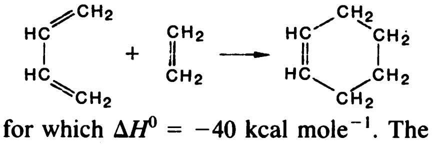
Kenichi Fukui

Electrophilic aromatic substitution such as nitration or halogenation generally involves reagents acting as acceptors. In one of his early examples, Fukui showed that such reactions with polycyclic aromatic hydrocarbons occur most readily at the position of highest HOMO electron density. Figure 2 shows the frontier electron density at different carbon atoms in benzo[*a*]pyrene as given by one MO computational procedure. The most reactive position is that having the highest frontier density. The high carcinogenicity of benzo[*a*]pyrene appears to be related in part to its high reactivity. Fukui applied his approach to a variety of reactions, including such examples as copolymerization ratios in free radical polymerizations that were difficult to explain by other theories. The frontier orbital approach is now used frequently as a guide to help understand and predict reactions. More recently, Fukui has generalized the concept and has applied it to three or more reacting molecules.

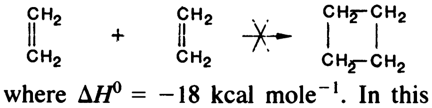
An important subsequent development involved the symmetry characteristics of the MO's of reactants and brought understanding to some puzzling observations.

Roald Hoffmann

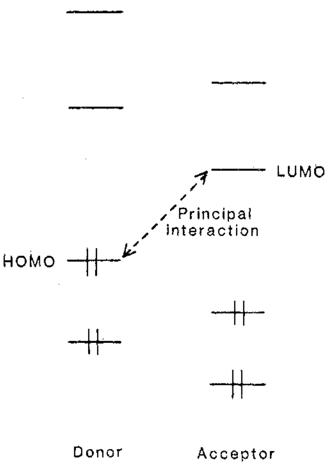
It has long been known that ethylene reacts with butadiene to give cyclohexene, a cycloaddition reaction that is the simplest example of the important Diels-Alder reaction:



for which $\Delta H^0 = -40$ kcal mole^{-1}. The reaction is highly exothermic but favorable thermodynamics is not sufficient. The comparable cycloaddition reaction of two ethylenes to give cyclobutane does not occur, despite the fact that such a reaction is also exothermic:



where $\Delta H^0 = -18$ kcal mole^{-1}. In this case the reaction has such a high energy barrier that other competing reactions intervene.



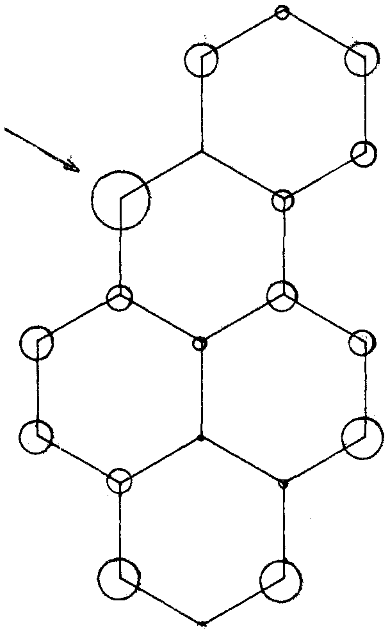


Fig. 1 (left). Molecular orbital energy levels of donor and acceptor reactants showing the principal interaction between the HOMO of the donor and the LUMO of the acceptor. Fig. 2 (right). Circles are proportional to the frontier electron density of benzo[*a*]-pyrene. The most reactive position is shown by the arrow.

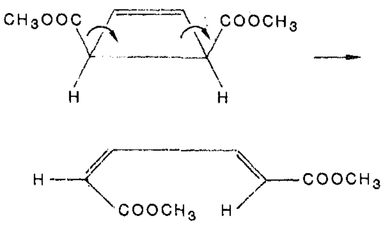
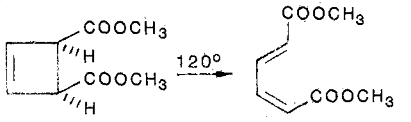


Fig. 3. Electrocyclic thermal ring opening of dimethyl *cis*-cyclobutenedicarboxylate to dimethyl *cis-trans*-muconate.

In 1958, E. Vogel observed the remarkable stereospecific thermal ring opening of dimethyl *cis*-cyclobutenedicarboxylate to the *cis-trans*-muconic ester:



This stereospecificity was subsequently shown to be general and different from that of six-membered rings.

Understanding these and a number of other reactions came with a landmark series of communications in 1965 by Hoffmann and the late R. B. Woodward of Harvard. They gave the general name of electrocyclic reaction to ring openings and closings such as the cyclobutene example. The observed stereochemistry of ring opening of the cyclobutene requires motion in the same sense (conrotation) (Fig. 3). Woodward and Hoffmann observed that interaction of the two positive orbital lobes of the HOMO of butadiene would effect ring closure in this sense (Fig. 4). Ring opening and closing occur by way of the same transition state and the same stereochemistry would hold for both reaction directions. Alternatively, inspection of the HOMO of hexatriene (Fig. 4) shows that a corresponding ring closure involves the two end groups rotating in the opposite sense (disrotation). This stereochemistry has been observed in a number of examples.

The Woodward-Hoffmann approach to electrocyclic reactions has been generalized to many different ring sizes and to carbanions and carbocations, and the observed stereochemistry is always in accord with theory. The theory, formulated originally in terms only of a frontier orbital, was subsequently made more complete by considerations of correlation diagrams. The procedure will be illustrated by their application to the

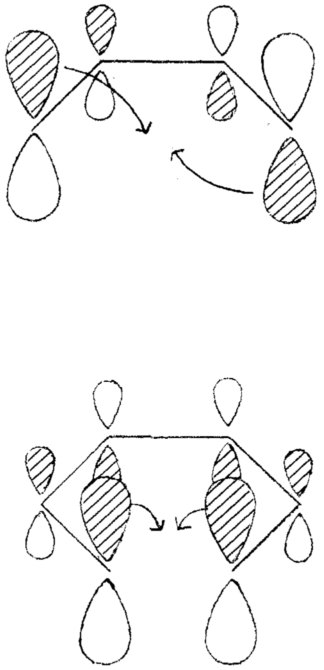
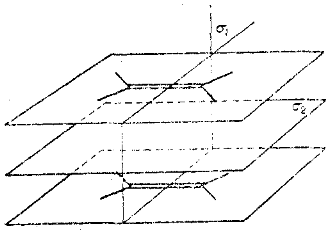
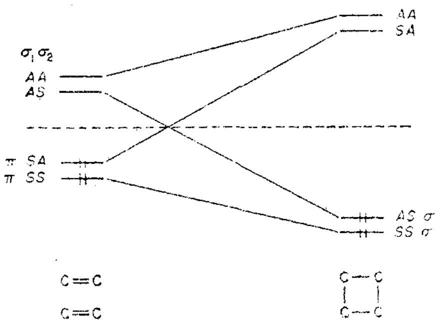
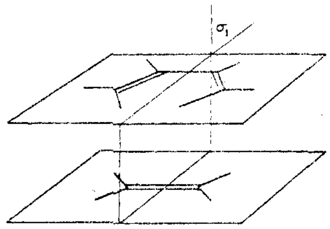


Fig. 4. HOMO of butadiene (top) and hexatriene (bottom) showing that interaction of the positive lobes in ring closure requires conrotation and disrotation, respectively.







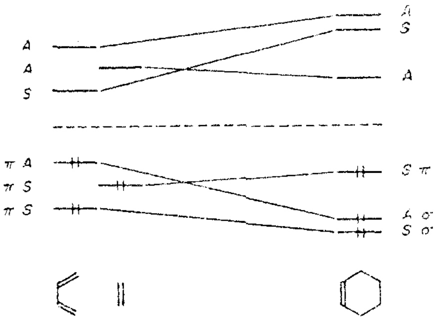


Fig. 5 (top left). Two ethylenes approaching each other in a cycloaddition reaction. Fig. 6 (top right). Correlation diagram for the significant MO's in the cycloaddition of two ethylenes. Fig. 7 (bottom left). Cycloaddition reaction of butadiene with ethylene along parallel planes. Fig. 8 (bottom right). Correlation diagram for the significant MO's in the cycloaddition of butadiene and ethylene. [Figures 5 to 8 are reprinted with permission from R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.* **87**, 2046 (1965)] cycloaddition reaction of two ethylenes. The ethylenes are allowed to approach each other in parallel planes along a symmetry plane (σ_1 in Fig. 5). The important MO's are those encompassing bonds that are made or broken in the reaction and that are symmetric (S) or antisymmetric (A) with respect to the symmetry element characteristic of the reaction. As shown in Fig. 6, the HOMO's of the reactants and products correlate not with each other but with high-energy MO's; that is, as reaction progresses this MO is transformed to a product MO having the same symmetry characteristics. At the transition state, which has some intermediate structure, this MO has high energy. The result is a high electronic energy barrier that precludes reaction, and this reaction is therefore termed symmetry-forbidden. By contrast, the comparable reaction of ethylene with butadiene (Fig. 7) involves occupied reactant MO's that correlate with occupied product MO's (Fig. 8). The result is a smooth conversion of orbitals without additional electronic barriers to reaction; the reaction is symmetry-allowed.

The results of orbital symmetry correlation diagrams lend themselves to alternative formulations that are frequently easier to apply. One is the perturbation charge-transfer approximation that involves only Fukui's frontier orbitals. Another treats the transition states in terms of their aromatic bonding character. This approach has its beginnings in the 1939 work of M. G. Evans, who recognized the relationship between the transition state for the reaction of ethylene with butadiene and the electronic structure of benzene. The idea was later generalized by M. J. S. Dewar and constitutes a simple and equivalent representation of the orbital symmetry approach. A characteristic feature in these methods is a cyclic orbital system having the stabilization of filled electronic shells for $4n$ or $4n + 2$ (n is an integer) electrons, depending on the phase relationships of the interacting orbitals. This concept of aromaticity goes back to the pioneering work of the late Erich Hückel, who first recognized the almost magical properties of some cyclic systems of $4n + 2$ electrons. His simple MO method, now generally known as the Hückel MO (or HMO) method, was used by Fukui in his early work, and an extension (the extended Hückel theory) was developed by Hoffmann and has received much use. The properties of the $4n$ and $4n + 2$ electronic cycles allowed Hoffmann and Woodward to formulate their orbital symmetry results as a set of simple rules.

An important feature of the frontier orbital and orbital symmetry approaches is that one can often derive the important results without involved computations. Even in these days of large high-speed computers and sophisticated quantum mechanical calculations, the essential features of this chemistry can be derived from the nodal properties of orbitals and their associated symmetries. The nodal properties in turn can often be related to the simplest form of electron-on-a-circle exercises familiar to most chemistry students. In a broad sense, this view of reactions has provided understanding and predictions for a large class of reactions, now called pericyclic reactions, that involve an electronic cycle in some form. The examples include many rearrangement reactions, additions, and eliminations. Frontier orbitals and orbital symmetry have generated other ideas and concepts and have led to new organic and organometallic structures. The reaction classification scheme of Woodward and Hoffmann has spawned new reactions that have entered the active repertoire of the synthetic chemist. More recent work of Roald Hoffmann is showing that the same ideas can also be applied to inorganic compounds and reactions.—ANDREW STREITWIESER, JR.

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The 1981 Nobel Prize in Physics

The 1981 Nobel Prize in Physics was awarded to three scientists. Half of the prize went to Kai M. Siegbahn at the University of Uppsala. The other half was awarded to Nicolaas Bloembergen of Harvard University and Arthur L. Schawlow of Stanford University.

Electron spectroscopy has been employed in the past decade by chemists and physicists for a wide and growing range of applications. These include basic research in molecular chemistry and surface physics, chemical characterization of atmospheric particulate matter in environmental studies, and analysis of the performance of catalysts in industrial processes. The success of this technique is due largely to the pioneering work of Kai M. Siegbahn, professor at the Physics Institute of the University of Uppsala, Sweden. During the 1950's and 1960's, Siegbahn and his collaborators in Uppsala combined instrumentation development with scientific discovery to transform electron spectroscopy from a laboratory method of limited use into a practical and powerful research tool. In recent years, many commercial electron spectrometers have become available, and electron spectroscopy is now applied in various forms at university and industrial research laboratories throughout the world. Appropriately, Siegbahn's "contribution to the development of high-resolution electron spectroscopy" has been recognized by the award of half of the 1981 Nobel Prize in Physics.

Electron spectroscopy (or, more precisely, photoelectron spectroscopy) is based on the high-resolution analysis of the kinetic energy distributions of electrons emitted from solid, liquid, or gaseous substances upon irradiation with a beam of monoenergetic x-rays or ultraviolet radiation. In recent years, monochromatized synchrotron radiation from electron storage rings has also become important as a tunable photon source. The physical quantity measured is the electron binding energy, B, which is given by Einstein's relation

$$h\nu = B + K$$

where $h\nu$ is the (known) photon energy and K is the (measured) photoelectron kinetic energy. Chemical information is obtained from chemistry-induced changes in the binding energies. In principle, all electron orbitals from the K shell out to the valence levels can be studied. When x-ray excitation is employed, the technique is usually referred to as x-ray photoelectron spectroscopy