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The Role of Frontier Orbitals in Chemical Reactions (Nobel Lecture)**

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Introduction

For more than a thousand years chemistry has been thought of as a complicated, hard-to-predict science. Efforts to improve even a part of its unpredictable character first bore fruit through the success of the "electronic theory". This was founded mainly by organic chemists, such as *Fry*, *Stieglitz*, *Lucas*, *Lapworth*, and *Sidgwick*, brought to a completed form by *Robinson* and *Ingold*, and later developed by many other chemists^[1]. In the electronic theory, the mode of migration of electrons in molecules is considered under various aspects. For this purpose a criterion is necessary for the number of electrons which should be assigned to an atom or to a bond in a molecule. Therefore, it can be said that the concept of the sharing of electrons, proposed by *Lewis*, gave a firm basis to the electronic theory^[2].

In the theory of organic chemistry the terms acid/base, oxidation/reduction, and so on have been profitably utilized for some time. Furthermore, there are terms centering more closely around the electron concept, such as electrophilicity/nucleophilicity and donor/acceptor.

It should be mentioned that these pairs of terms can be qualitatively related to the scale of electron density or electric charge. In the electronic theory, the static and dynamic behavior of molecules are explained by the electronic effects which are based solely on the distribution of electrons in a molecule.

The charge distribution in a molecule can be sketched to a certain extent using the electronegativity concept of

atoms, in conjunction with chemical experience. It is given foundation, made quantitative, and supported by physical measurements and theoretical calculations based on quantum theory.

The distribution of electrons or electric charge—the result is the same irrespective of which is used—in a molecule is usually represented by the total number (generally non-integer) of electrons in each atom and each bond. This concept was easily acceptable, even to experimental chemists, as having a tolerably realistic meaning. Therefore, chemists used electron density as a fundamental concept for the explanation of various phenomena. In particular, in devising novel chemical reactions researchers usually rely upon analogy through experience, and here electron density was very effectively and widely used as the basic concept.

When the magnitude of the electron density is adopted as the criterion, the electrostatic attraction and repulsion caused by the electron distribution are taken into account. Therefore, it is reasonable to infer that an electrophilic reagent will attack the center of high electron density in a molecule, whereas a nucleophilic reaction will occur at the center of low electron density. In fact, *Wheland* and *Pauling*^[3] explained the orientation of substitutions in benzene and its compounds along these lines, and analogous interpretations of the mode of many other chemical reactions followed in the same fashion.

However, the question as to why one of the long-known, simple reactions, such as the electrophilic substitution of naphthalene, *e.g.* by nitration, predominantly yields 1-substituted derivatives was not so easy to answer. This is because in many unsubstituted aromatic hydrocarbons both the electrophile and the nucleophile react at the same center. This point cast some doubt on the theory of organic reactivity, where exclusively the electron density was thought to be decisive.

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The Concept of Frontier Orbital Interactions

The solution of this reactivity problem was attempted by many people from numerous angles. Above all, *Coulson* and *Longuet-Higgins*^[4] investigated the change of electron density distribution under the influence of the approaching reagent. The explanation proposed by *Wheland*^[5] was based on the calculation of the energy required to localize electrons at the site of reaction. But I myself tried to attack this problem in a way which was at that time slightly unusual. Bearing in mind the principal role played by the valence electrons in the formation of molecules from atoms, only the distribution of the electrons occupying the highest energy π orbital of aromatic hydrocarbons was calculated. The results were more successful than expected, and an almost perfect agreement between the actual position of electrophilic attack and the site of highest electron density calculated for the highest occupied π orbital was found, as shown in Figure 1^[6].

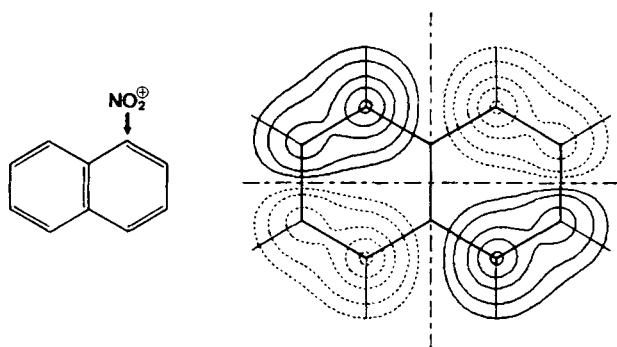


Fig. 1. Nitration of naphthalene.

The “orbital” concept, which was established and developed by many scientists—*Pauling*, *Slater*, *Mulliken*, *Roothaan*, *Löwdin*, *Hückel*, *Parr* and so on—had till then been used to construct wave functions of molecules by means of which molecular properties were usually interpreted^[7]. It also seemed that the electron distribution in an orbital was directly connected to chemical observations, and this fact was certainly felt to be interesting by many chemists.

But the result of such an “extravagant” attempt was by no means readily accepted by the majority of chemists. The publication^[6] received a number of controversial comments. This was in a sense understandable, because due to my lack of experience the theoretical foundation for our notable result was obscure or rather improperly presented. However, it was fortunate for me that the work of *Mulliken*^[8] on charge-transfer complexes was published in the same year.

The model of *Mulliken et al.* for protonated benzene was very helpful^[9]. Our work in collaboration with *Yonezawa*, *Nagata*, and *Kato* provided a simple and clear picture of the theoretical interpretation of reactions^[10]. In a similar way the “overlap and orientation” principle proposed by *Mulliken* enabled the orientation in molecular complexes^[11] to be clarified. Subsequent to electrophilic substitution, nucleophilic substitution was discussed and it was found that here the lowest unoccupied orbital was deci-

sive^[12]. In reactions with radicals, both of the two orbitals mentioned previously become the “essential” orbitals.

There was no reason to limit these essential orbitals to π orbitals, so that the method was applied not only to unsaturated but also to saturated compounds. The fact that it could be applied to saturated compounds was a substantial advantage compared to many theories of reactivity which were limited only to π electron compounds. The method displayed its particular usefulness in studying the abstraction of hydrogen from aliphatic hydrocarbons by radicals, the S_N2 and E2 reactions of halogenated hydrocarbons, the nucleophilic abstraction of α -hydrogen atoms from alkenes, and so forth^[13].

The two molecular orbitals which play an essential role in a wide range of chemical reactions of saturated or unsaturated compounds were referred to under the general term “frontier orbitals”, abbreviated frequently by HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital).

The validity of the theory gradually became clearer. The vein of ore discovered by chance was found to be more extensive than expected. But it was the role played by the symmetry of the “essential” orbital, pointed out in 1964 with regard to Diels-Alder reactions^[14], that broadened the utility of our studies further. It was found, as seen in Figure 2, that the symmetries of the HOMO and LUMO of dienes and of the LUMO and HOMO of dienophiles, respectively, are in an extremely favorable situation for a concerted cyclic interaction.

This led to two important aspects: Firstly, it pointed out a possible correlation between the orbital symmetry and the rule determining the occurrence or non-occurrence of a chemical reaction, which may be called the “selection rule”, in common with the selection rule in molecular spectroscopy. Secondly, it provided a clue to discuss what was the “concertedness” in a reaction which proceeds *via* a cyclic conjugation of electrons.

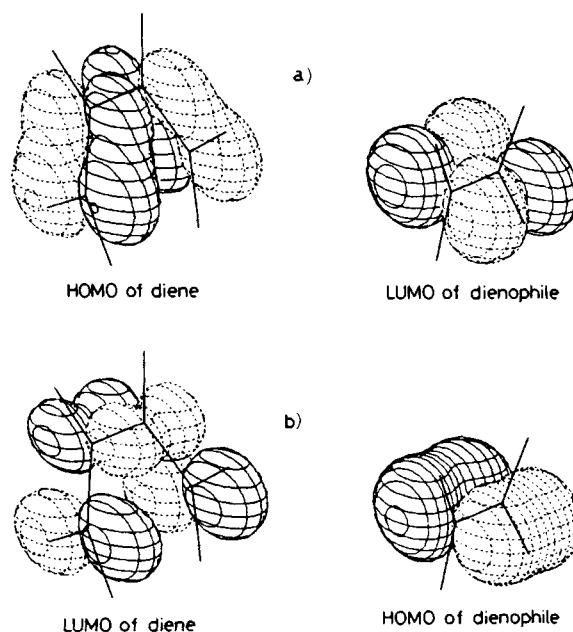


Fig. 2. The significance of orbital symmetry in the HOMO-LUMO overlap in Diels-Alder reactions.

In 1965 *Woodward* and *Hoffmann* proposed the stereo-selection rules which are known today as the “Woodward-Hoffmann” rules^[15,16]. An experimental result developed by *Havinga et al.*^[17] was, herewith, extended immensely. It was only after the appearance of the brilliant work by *Woodward* and *Hoffmann* that I became fully aware that not only the electron density distribution but also the nodal properties of the essential orbitals have significance in a wide variety of chemical reactions. In fact, we previously studied the classical $(4n+2)$ rule proposed by *Hückel*^[8], and noticed that the sign of the bond order in the highest occupied orbital of an open-chain conjugation system should be closely related to the stabilization of the corresponding conjugated rings^[19]. We did not imagine, however, that the discussion might be extended to the so-called Möbius-type ring-closure!^[20]

By considering the HOMO-LUMO interactions between the fragments of a conjugated chain divided into two parts^[21], frontier orbital theory can yield selection rules which are absolutely equivalent to those obtained from the “conservation of orbital symmetry” principle of *Woodward* and *Hoffmann*. One point I may stress here is, as suggested by *Fujimoto*, *Inagaki*, and I^[22], that the electron delocalization between the “essential” orbitals exactly expresses, in terms of orbital symmetries, the formation and breaking of chemical bonds which, I believe, should be of key importance for perceiving chemical processes.

In the cycloaddition of butadiene and ethylene shown in Figure 2, both the interaction between the HOMO of the diene and the LUMO of the dienophile, and that between the LUMO of the diene and the HOMO of the dienophile stabilize the reacting system. If one is interested in the spatial properties of interaction, however, one may recognize the clear distinction between the roles of the two types of orbital interactions. The HOMO of ethylene and the LUMO of butadiene are both symmetric with respect to the symmetry plane retained throughout the course of cycloaddition. This signifies that each of the carbon atoms of ethylene is bound to both of the terminal carbons of butadiene. The chemical bonding between the diene and dienophile thus generated may resemble that in a loosely bound complex, *e.g.*, protonation of an olefinic double bond. In contrast, the HOMO of butadiene and the LUMO of ethylene are antisymmetric. The interaction between these orbitals leads, therefore, to two separated chemical bonds, each of which links a carbon atom of ethylene and a terminal carbon atom of butadiene. Needless to say it is the interaction between the HOMO of the diene and the LUMO of the dienophile that is decisive for the occurrence of a concerted cycloaddition^[22].

In the course of time it was discovered that the electron delocalization between the HOMO and LUMO is generally the principal factor determining the ease of a chemical reaction and its stereoselective path, irrespective of whether an intra- and intermolecular processes occurs (Fig. 3). Besides our work, a number of other research groups have made contributions to this area.

First of all, the general perturbation theory of HOMO-LUMO interaction between two molecules was built up by *Salem et al.*^[23–25]. One of *Salem's* papers^[25] was in line with the theory of *Bader*^[26], which specified the mode of

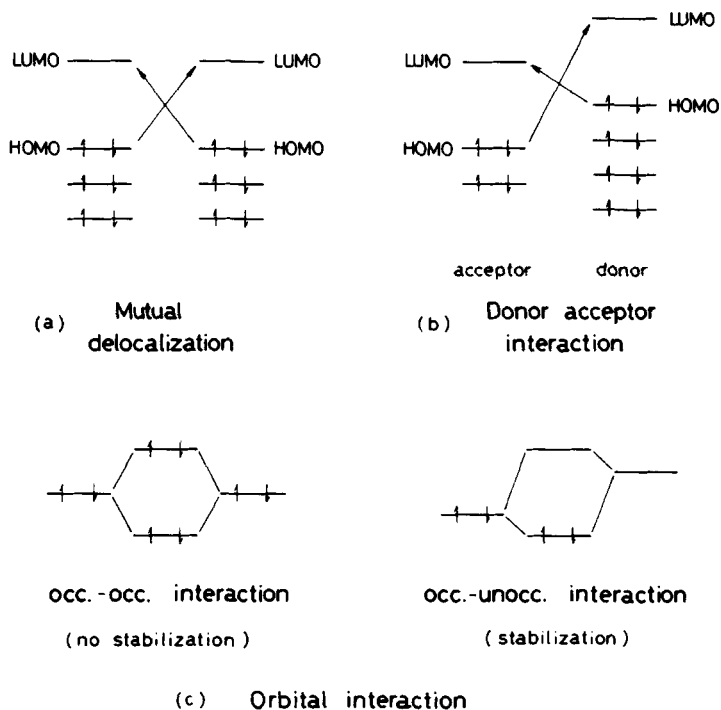


Fig. 3. The mode of interaction between orbitals of two molecules.

decomposition of a molecule or of a transition complex by means of the symmetry of the normal vibration. Furthermore, *Pearson*^[27] investigated the relationship between the symmetry of reaction coordinates and that of the HOMO and LUMO.

The discussion so far may seem to overestimate the importance of these selected orbitals, HOMO and LUMO. This point was ingeniously modified by *Klopman*^[28]. He carefully took account of the factors to be considered in the perturbation theory of reacting systems, and classified reactions into two types

- the first was the “frontier-controlled” case, in which the reaction was controlled by the “essential” orbital interaction, and
- the second was the “charge-controlled” case, where it was controlled by the electrostatic interaction of charges.

This classification was widely and successfully used. In this context, the review articles of *Herndon*^[29] and of *Hudson*^[30] proved to be very useful. The names of *Coulson*^[4] and *Dewar*^[31] should also be mentioned here as having made contributions to the development of theories of reactivity.

Returning to the subject again, let us imagine that two molecules approach each other and that orbital overlap takes place. Application of perturbation theory^[32] to this sort of interaction indicates that the larger the orbital overlap and the smaller the energy level separation of the two overlapping orbitals, the larger is the contribution of the orbital pair to the stabilization of an interacting system. Accordingly, at least initially, a reaction will proceed with

a mutual nuclear configuration which is most favorable for the HOMO-LUMO overlap.

Now let us suppose that a flow of electrons occurs from the HOMO of molecule I to the LUMO of molecule II. In each molecule the bonds between the reaction center—the site at which the orbitals overlap with those of the other molecule—and the remaining part of the molecule are weakened. In this case, the bonding relationships in the HOMO of molecule I are weakened and the antibonding strengthened, while in molecule II the antibonding relationships in the LUMO are weakened and those bonding strengthened. Consequently, the HOMO of molecule I is particularly destabilized relative to the other occupied orbitals, and among the unoccupied orbitals the LUMO of molecule II is selectively stabilized, so that the HOMO-LUMO level separation between the two molecules is decreased. Such a set of circumstances is clearly seen in Figure 3.

When such bond weakenings have arisen the HOMO and the LUMO tend to become more localized at these weakened bonds in each molecule. In addition, the weakening of the bonds between the reaction center and the remaining part of the molecule causes an increase in the amplitudes of the HOMO and the LUMO at the reaction centers, resulting in a larger overlap of the HOMO and the LUMO^[33]. Such a trend of the characteristic change in the orbital pattern is confirmed by numerical calculations. The role of the interaction between the HOMO and the LUMO turns out to become more and more important as the reaction proceeds.

A series of studies on chemical interactions was attempted in which the interaction of reactants was divided into the Coulombic, the exchange, the polarization, and the delocalization interactions, and their respective contributions to the interaction energy were quantitatively discussed^[32,34]. In this way the dimerization^[35] and the addition of methylene to ethylene^[36], the dimerization of BH₃^[37], and also several donor-acceptor interactions, *e.g.* BH₃-NH₃^[38], BH₃-CO^[39], NH₃-HF^[40], *etc.*, were discussed. The method was also applied to reactions of radicals, such as the abstraction of a hydrogen atom from methane by a methyl radical, the addition of a methyl radical to ethylene^[41], and recombinations, disproportionations, and self-reaction of two radicals^[42]. In these calculations, the configurational analysis proposed originally by *Baba et al.*^[43] was also found to be useful. We were able to show numerically the increase in electron delocalization from the HOMO to the LUMO as the reaction proceeded, the increasing importance of the contribution of such a delocalization to the stabilization of the reaction system, and the driving force of the reaction in terms of orbital interactions, among others.

The question: "Why do the HOMO and the LUMO solely determine the reaction path?" was one which I was frequently posed by audiences at my lectures. The discussion so far should correspond, at least in part, to that answer. But one may not overestimate the importance of the HOMO and the LUMO. In one-center reactions, such as substitutions, in which the orbital symmetry plays no role, any occupied orbitals which are very close in energy to the HOMO should properly be taken into account^[12]. In

large alkane molecules a number of HOMO's (high-lying occupied MO's) and furthermore, as will be referred to later, in metal crystals even the "HOMO-band" must be taken into account. If the HOMO or the LUMO happens to be inadequate owing to its extension, symmetry, or nodal properties, the next orbital should be sought. One of the simplest examples of such an instance is the protonation of pyridine. In this case, the nitrogen lone-pair orbital is not the HOMO, but the addition of a proton to the nitrogen lone-pair so as not to disturb the π conjugation, will evidently be more advantageous than addition to higher occupied π orbitals, which may interrupt this. The reason why the proton dare not add to the positions of high amplitude of the π HOMO in this case is thus understood. It is not satisfactory to treat a disagreement between the HOMO-LUMO argument and an experimental result formally as an *exception* to the theory. A so-called exception has its own causes, and the investigation of these causes may possibly yield a novel result.

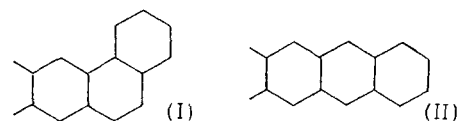
The HOMO-LUMO interaction argument was recently pointed out^[44] to be useful, in an auxiliary sense, for interpreting the sign of a reaction constant and the substituent constant scale in the Hammett rule^[45], which has made an immeasurable contribution to the study of substituent effects upon chemical reactivity. In cyclic additions, such as Diels-Alder reactions and 1,3-dipolar additions, the relative ease of occurrence of reactions, various subsidiary effects and interesting phenomena, such as regioselectivity and periselectivity, were interpreted with considerable success simply by knowing the height of the energy level of the HOMO and the LUMO, the mode of their extension, and their nodal structure, *etc.*^[46]—I defined these as the *orbital pattern*.

Other topics that have been discussed in terms of HOMO-LUMO interactions are thermal formation of excited states^[47], singlet-triplet selectivity^[48], the chemical property of diradicals and excited states^[49], the interaction of the central atom and ligands in transition-metal complexes^[50], the interaction of three or more orbitals^[51], and so forth. *Inagaki et al.* extended the theory to include the polarization effect on the HOMO and the LUMO due to mixing with other orbitals, and gave an elucidation of a number of problems in organic chemistry which were not always easy to explain: the unique stereoselectivity in transannular bond formation, the lone-pair effect, the d orbital effect, and the orbital polarization effect due to substituents^[52].

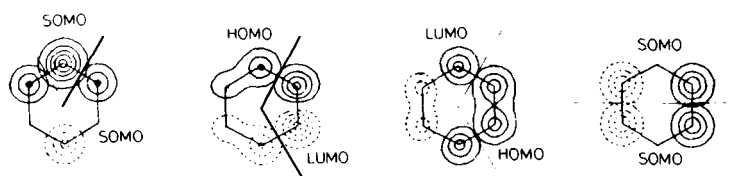
As previously discussed, the method of orbital interaction was applied not only to the ground electronic state but also to excited states, giving rise to an explanation of the path of even complicated photochemical isomerizations^[13,21]. In the majority of cases the HOMO and the LUMO of the ground-state molecule were also found to be the essential orbitals. Even the ground-state reaction of a strong electron acceptor (or donor) causes a mixing with an ionized electron configuration or an excited electron configuration in another molecule. In consequence, a partial HOMO-HOMO or LUMO-LUMO interaction, which would be trivial without the influence of the acceptor (or donor), becomes important in stabilizing the interacting system^[47].

The problems so far discussed have been limited to chemical reactions. However, the HOMO-LUMO interaction must also come into bearing in other chemical phenomena in almost the same way—with the exception that they usually do not bring about such a remarkable change in the nuclear configuration. Now let us examine the possibility of applying the theory to “aromaticity”—one of the simplest, but hardest-to-interpret problems. There seem to be few problems so frustrating to theoreticians as the explanation of this classical chemical concept. I greatly appreciate the contribution of *Dewar's theory*^[53, 54] based on quantitative energy calculations. Here, however, I want to give a qualitative comment from an entirely different point of view.

It is easily ascertained^[55] from Figure 4 that in benzene, naphthalene, and phenanthrene, *etc.*, any conceivable division of the molecule into two fragments always produces segments whose HOMO and LUMO overlap in-phase at the original two junctions. But these circumstances are not observed in anthracene, which is usually viewed as one of the typical examples of an aromatic compound. *Hosoya*^[55] pointed out from comparison with phenanthrene (see Fig. 4) that annelation of type (II) is less stable than that of type (I).



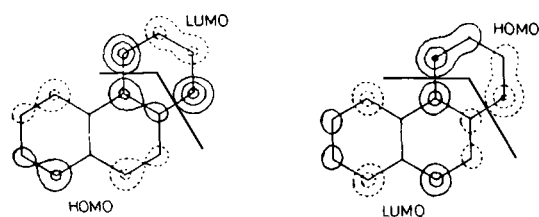
Benzene



Naphthalene



Phenanthrene



Anthracene

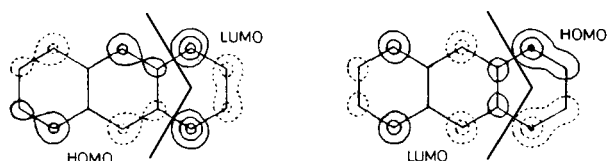
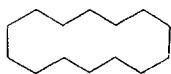


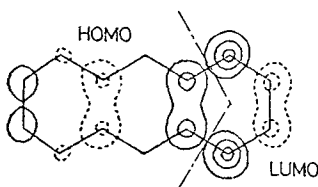
Fig. 4. The HOMO-LUMO phase relationship upon random division of aromatic hydrocarbons (SOMO = singly occupied MO of a radical).

It is well known that anthracene occasionally undergoes reactions similar to additions to olefins.

According to *Hückel's* $(4n + 2)$ -rule, mentioned previously, the anthracene molecule has 14π electrons and fulfils the stability condition for "aromaticity". Actually, if one considers a molecule of anthracene with the two internal bridging bonds deleted,



it is readily seen that the HOMO and the LUMO of each fragment overlap in an in-phase manner at both of the junctions:



In this way, it is clear that the two bonds which were deleted exert an unfavorable influence on the aromaticity. Such an influence bears a close resemblance to that of impurity scattering of the wave of a free electron moving in a metal crystal.

This discussion seems to be a digression but, as a matter of fact, it is related to the crucial question as to how an electron delocalizes in a molecule. As will be mentioned later, *Anderson*^[56] solved the question of how an electron localizes in a random system. In a molecule, there are potential barriers between atoms which must be overcome when certain conditions are satisfied, in order for an electron to move freely around it. Although the question of how valence electrons delocalize in a molecule may not yet have been solved satisfactorily for nonfixed nuclear configurations, the in-phase relationship of the HOMO and the LUMO at the junctions of the two molecular fragments seems to be at least one of the important conditions for the intramolecular delocalization of electrons.

Generally speaking, electron delocalization gives rise to stabilization due to "conjugation", which is an old concept in chemistry. If so, similar stabilization mechanisms must be detected in systems other than aromatic compounds. The discussion of this delocalization stabilization at the transition state or along the reaction path is nothing other than the reactivity theory discussed previously. The term "delocalizability" was attached to the reactivity indices we derived^[10], and our reactivity theory itself was sometimes called the "delocalization approach"^[14]. Various sorts of "hyperconjugation" can be explained in the same manner. Stabilization due to homoaromaticity or the bicycloaromaticity of *Goldstein*^[57], the stability of spirocycles, pericycles^[58], of the "laticycles" and "longicycles" of *Goldstein* and *Hoffmann*^[59], that of the spirarenes of *Hoffmann* and *Imamura*^[60], and so on are all comprehensible as examples of stabilization due to delocalization between HOMO and LUMO, although other explanations may also be possible.

One might ask to what extent such a qualitative consideration is reliable. In many cases, however, a considerably accurate nonempirical determination of the stable conformation of hydrocarbon molecules^[61, 62] results in a conclusion qualitatively not much different from expectations based on the simple orbital interaction argument mentioned here.

Chemical Reaction Pathways

It has already been pointed out that the detailed mechanism of a chemical reaction along the reaction path can be discussed on the basis of the orbital interaction argument. For this purpose, however, it is necessary that the problem of how the chemical reaction path is determined be solved. The evaluation of the route of a chemical reaction and its rate in terms of the potential energy surface is performed using a statistical-mechanical formulation established by *Eyring*^[63]. Many other papers appeared in which the rate expression was derived wave-mechanically using the potential energy function. In addition, the problem of obtaining the trajectory of a given chemical reaction with a given initial condition was treated by *Karplus*^[64].

The center line of the reaction path, so to speak, the idealized reaction coordinate—which I called the "intrinsic reaction coordinate" (IRC)^[65]—seemed to have been, rather strangely, not specifically defined until then. For that reason, I began with the general mathematical equation which determines the driving force^[34, 66, 67]. Although my papers themselves were possibly not very original, they later turned out to develop in a very interesting direction^[68–74], and opened up the method of calculating the quasistatic change of nuclear configuration of the reacting system starting from the transition state and proceeding to a stable equilibrium point^[66]. I termed the method of automatic determination of the molecular deformation accompanying a chemical reaction, "reaction ergodography"^[34, 67]. This method was applied to a few specific examples by *Kato* and I^[67], and by *Morokuma*^[72, 73]: abstraction and substitution of methane hydrogen by hydrogen atoms^[67], nucleophilic substitution of methane hydrogen by hydride anions^[72], and isomerization of methyl isocyanide to acetonitrile^[73]. All of these are very simple reactions, but there seems to be no principal difficulties in extending the applicability to larger systems. Once the IRC was determined in this way, the driving force of a chemical reaction was analyzed on the basis of the orbital interaction argument^[66].

In a reacting system with no angular momentum it is possible to obtain the IRC by the use of a space-fixed Cartesian coordinate system. All of the calculated examples mentioned previously belong to this case. However, in a reaction in which rotational motion exists, it is necessary to discuss the IRC after separating the nuclear configuration space from the rotational motion^[74–77]. For this purpose it is essential to derive the general classical Hamiltonian of the reacting systems and then to separate the internal motion, which is determined only by the internal coordinates. The nuclear configuration space thus separated

out is, in general, a Riemann space. The classical Lagrangian form obtained in this process of constructing the Hamiltonian is used to derive the IRC equation for the case of rotational motion. It is thus understood that the rotational motion of the reacting system generally causes a deviation from the IRC^[74].

Once the method of determining unique reaction pathways is available, the next problem we are concerned with is to see if the pathways calculated can be interpreted in terms of frontier orbital interactions. A method referred to as "interaction frontier orbitals" or "hybrid molecular orbitals" has been developed very recently by *Fujimoto* and I in order, once and for all, to provide a lucid scheme of frontier orbital interactions with the accuracy of nonempirical calculations^[78-80]. By properly including contributions from MO's other than the HOMO and the LUMO, we realized in terms of orbital diagrams how ingenious the empirically established chemical concepts—"reaction sites" and "functional groups"—and the empirical concept of reaction pathways could be.

various sizes and shapes are studied, the characteristic feature of their HOMO's (high-lying occupied MO's) and LUMO's (low-lying unoccupied MO's), the nature of chemisorption and catalytic action, the mode of surface chemical reactions, and several related subjects of interest will be able to be investigated theoretically.

As is the case with molecular interactions in normal chemical reactions, only the HOMO and LUMO bands lying in the range of several electron volts around the Fermi level can participate in the adsorption of molecules and surface reactions on solid crystals. You may recollect here that in the BCS (Bardeen-Cooper-Schrieffer) theory of superconductivity, too, only the HOMO's and LUMO's in close proximity to the Fermi surface are involved in the formation of electron pairs as the result of interactions with lattice vibrations. For solid catalysts the discrimination of particular orbitals and electrons from the others makes the situation much easier.

Consider a system composed of a regular repetition of a molecular unit, for instance, a one-dimensional high-po-

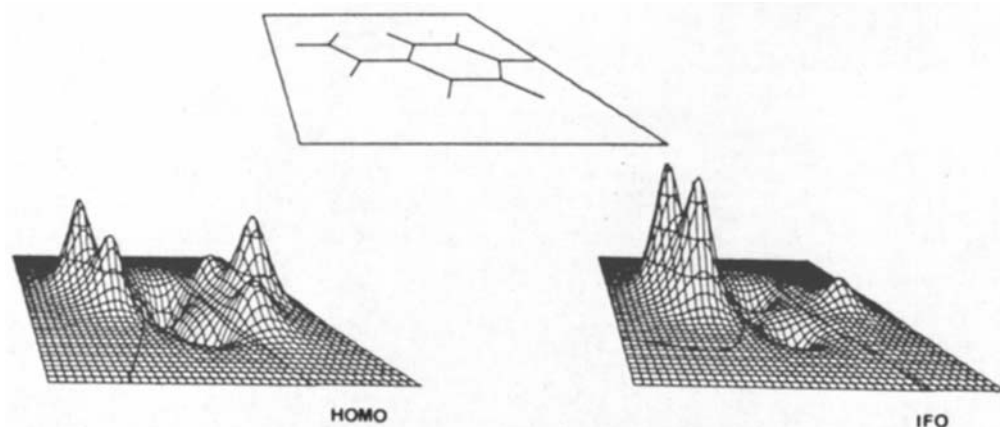


Fig. 5. Comparison of the HOMO and the IFO (interaction frontier orbital) for protonation of styrene.

Figure 5 compares the HOMO of styrene and its interaction frontier orbital (IFO) for protonation of the olefinic double bond. The latter is seen to be localized very efficiently at the site of chemical interaction. The double bond is evidently the functional unit in this case.

Innovation of the frontier orbital concept will hopefully be continued by young scientists to make it useful for one of our ultimate targets: theoretical design of molecules and chemical reactions.

Frontier Orbitals in Related Fields

Theoretical treatments of the properties of solid crystals, or chemisorption on a solid surface appear hitherto to have been almost a monopolistic domain of physics. But the orbital pattern technique has also advanced gradually into this field.

The "cluster approach"^[81,82], in which a portion of the metal crystal in the form of a cluster of atoms is selected and its catalytic action or other properties investigated, has contributed to the development of the orbital pattern approach, because purely physical methods can hardly be applied to such large systems. It is expected that if clusters of

polymer chain or a one-dimensional lattice, in which a certain perturbation is imposed at a definite location. Sometimes it is convenient to discuss the influence of this perturbation by transforming the orbitals belonging to the HOMO band to construct the orbitals localized at this site. One such technique was proposed by *Tanaka, Yamabe* and I^[83]. This method is expected, in principle, to be applicable to a discussion of such "local" problems as the adsorption of a molecule on the two-dimensional surface of catalysts, surface reactions, and related matters. This approach may be a little more "chemical" than the method using the function of local density of states^[84] or similar functions, in that the former can be used for the discussion of the reactivity of molecules on a catalyst surface in terms of the phase relationship of localized orbitals.

Low-dimensional semiconductors and some superconductors have also been the objects of application of the orbital argument. In these studies, the dimerization of S_2N_2 to S_4N_4 ^[85] and its polymerization to high-polymeric $(SN)_x$ ^[86] were discussed, and the energy band structure of the $(SN)_x$ polymer chain analyzed to investigate the stable nuclear arrangement and the mode of inter-chain interactions^[87].

The modern techniques used in solid-state physics to interpret the interesting characteristic behavior of noncrystalline materials, in particular of amorphous materials in which the nuclear arrangements are not regular, are certainly striking. *Anderson* showed generally that in a random lattice system electron localization should take place^[56]. *Mott* in his 1977 Nobel lecture, stated that he thought it the first prize awarded for the study of amorphous materials, and answered the question, "How can a localized electron become conducting?" using the concept of "hopping". Here, too, the HOMO-LUMO interaction—in this case the consideration of spin is essential—plays an important role.

In a few words I want to refer to the importance of virtual orbitals. The LUMO, which has held a key position in the orbital arguments hitherto discussed, is the virtual orbital which an external electron is considered to occupy if captured by a molecule to form an anion. Virtual orbitals always play an essential part in producing metastable states of molecules by electron capture^[88]. To discuss such problems generally *Tachibana et al.*^[89] systematized the theory of resonant states from the standpoint of the complex eigenvalue problem. The idea of resonant states will play a principal role in chemical reactions, particularly in high-energy reactions, which will be developed more in the future.

Prospects

In this article I have presented a series of recent results, largely from the studies carried out by our group, and have ventured to make those things the object of my talk which appear promising, but which are not yet completely established. In doing this my intention has been to stimulate the efforts of many younger chemists by specifying what fields I believe to be promising for the future.

In my opinion, quantum mechanics can make two different contributions to chemistry. Firstly, it permits non-empirical comprehension of experimental results. However, we should not overlook another important aspect: the promotion of empirical chemistry from the theoretical side. Here, also, reliable theoretical foundations and computational methods are required. The conclusions provided by theoretical considerations should be little affected by the degree of sophistication of the approximations used.

On the other hand, the contributions, made by theoreticians to the second aspect mentioned, in which predictions surpassing experimental accuracy are possible by very accurate calculations, are for the present limited to a very few, extremely simple molecules. In order to accomplish this objective for ordinary chemical problems, it is sometimes necessary to provide qualitative theories which can be used even by experimental chemists. If one can contribute nothing to chemistry without carrying out accurate calculations for each specific problem, one cannot be said to be making optimal use of quantum mechanics. It is certainly most favorable when the underlying concepts are as close to chemical experience as possible, but this sphere of experience is steadily expanding. Quantum chemistry has

thus the task of furnishing useful concepts on a theoretical basis and of making them available to the experimental chemist.

Even the same atoms of the same element in different molecules show different behavior: the chemical symbol H seems to signify atoms of a completely different nature. In chemistry, this terrible individuality should never be avoided by "averaging", and, moreover, innumerable combinations of such atoms form the subject of chemical research, where it is not the "whole assembly of compounds of different kinds but each individual kind of compound" that is of chemical interest. As a consequence of this formidable complexity, chemistry inevitably depends on analogy through experience. This is in a sense the fate allotted to chemistry, and the source of its great difference from physics. Quantum chemistry, too, in so far that it is chemistry, is required to be useful in promoting experimental chemistry.

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- [1] Cf. C. K. Ingold: *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, NY 1953.
- [2] Cf. G. N. Lewis: *Valence and the Structure of Atoms and Molecules*, Chemical Catalog, New York 1923.
- [3] G. W. Wheland, L. Pauling, *J. Am. Chem. Soc.* 57 (1935) 2086.
- [4] C. A. Coulson, H. C. Longuet-Higgins, *Proc. R. Soc. London A* 191 (1947) 39; *ibid.* A 192 (1947) 16.
- [5] G. W. Wheland, *J. Am. Chem. Soc.* 64 (1942) 900.

- [6] K. Fukui, T. Yonezawa, H. Shingu, *J. Chem. Phys.* 20 (1952) 722.
- [7] Cf. R. G. Parr: *The Quantum Theory of Molecular Electronic Structure*, Benjamin, New York 1963, and literature cited therein.
- [8] R. S. Mulliken, *J. Am. Chem. Soc.* 74 (1952) 811.
- [9] L. W. Pickett, N. Muller, R. S. Mulliken, *J. Chem. Phys.* 21 (1953) 1400.
- [10] K. Fukui, T. Yonezawa, C. Nagata, *Bull. Chem. Soc. Jpn.* 27 (1954) 423; K. Fukui, H. Kato, T. Yonezawa, *ibid.* 34 (1961) 1112.
- [11] R. S. Mulliken, *Recl. Trav. Chim. Pays-Bas* 75 (1956) 845.
- [12] K. Fukui, T. Yonezawa, C. Nagata, H. Shingu, *J. Chem. Phys.* 22 (1954) 1433.
- [13] Cf. K. Fukui: *Theory of Orientation and Stereoselection*, Springer, Berlin 1970.
- [14] K. Fukui in P.-O. Löwdin, B. Pullman: *Molecular Orbitals in Chemistry, Physics and Biology*, Academic Press, New York 1964, p. 513.
- [15] R. B. Woodward, R. Hoffmann, *Angew. Chem.* 81 (1969) 797; *Angew. Chem. Int. Ed. Engl.* 8 (1969) 781; cf. also H. E. Simmons, J. F. Bunnett: *Orbital Symmetry Papers*, Am. Chem. Soc., Washington, DC 1974.
- [16] R. B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.* 87 (1965) 395.
- [17] E. Havinga, R. J. de Kock, M. P. Rappoldt, *Tetrahedron* 11 (1960) 276; E. Havinga, J. L. M. A. Schlattmann, *ibid.* 15 (1961) 146.
- [18] E. Hückel, *Z. Phys.* 70 (1931) 204; 76 (1932) 628.
- [19] K. Fukui, A. Imamura, T. Yonezawa, C. Nagata, *Bull. Chem. Soc. Jpn.* 33 (1960) 1501.
- [20] E. Heilbronner, *Tetrahedron Lett.* 1964, 1923.
- [21] K. Fukui, *Acc. Chem. Res.* 4 (1971) 57.
- [22] H. Fujimoto, S. Inagaki, K. Fukui, *J. Am. Chem. Soc.* 98 (1976) 2670.
- [23] L. Salem, *J. Am. Chem. Soc.* 90 (1968) 543, 553.
- [24] A. Devaquet, L. Salem, *J. Am. Chem. Soc.* 91 (1969) 3743.
- [25] L. Salem, *Chem. Br.* 5 (1969) 449.
- [26] R. F. W. Bader, *Can. J. Chem.* 40 (1962) 1164.
- [27] R. G. Pearson: *Symmetry Rules for Chemical Reactions*, Wiley, New York 1976, and literature cited therein.
- [28] G. Klopman, *J. Am. Chem. Soc.* 90 (1968) 223; cf. also G. Klopman: *Chemical Reactivity and Reaction Paths*, Wiley, New York 1974.
- [29] W. C. Herndon, *Chem. Rev.* 72 (1972) 157.
- [30] R. F. Hudson, *Angew. Chem.* 85 (1973) 63; *Angew. Chem. Int. Ed. Engl.* 12 (1973) 36.
- [31] Cf. M. J. S. Dewar, R. C. Dougherty: *The PMO Theory of Organic Chemistry*, Plenum, New York 1975, and literature cited therein; cf. also M. J. S. Dewar, *Tetrahedron* S8, Part I (1966) 85.
- [32] K. Fukui, H. Fujimoto, *Bull. Chem. Soc. Jpn.* 41 (1968) 1989.
- [33] K. Fukui, H. Fujimoto, *Bull. Chem. Soc. Jpn.* 42 (1969) 3392.
- [34] K. Fukui in R. Daudel, B. Pullman: *The World of Quantum Chemistry*, Reidel, Dordrecht 1974, p. 113.
- [35] H. Fujimoto, S. Yamabe, K. Fukui, *Bull. Chem. Soc. Jpn.* 45 (1972) 1566.
- [36] H. Fujimoto, S. Yamabe, K. Fukui, *Bull. Chem. Soc. Jpn.* 45 (1972) 2424.
- [37] S. Yamabe, T. Minato, H. Fujimoto, K. Fukui, *Theor. Chim. Acta* 32 (1974) 187.
- [38] H. Fujimoto, S. Kato, S. Yamabe, K. Fukui, *J. Chem. Phys.* 60 (1974) 572.
- [39] S. Kato, H. Fujimoto, S. Yamabe, K. Fukui, *J. Am. Chem. Soc.* 96 (1974) 2024.
- [40] S. Yamabe, S. Kato, H. Fujimoto, K. Fukui, *Bull. Chem. Soc. Jpn.* 46 (1973) 3619; *Theor. Chim. Acta* 30 (1973) 327.
- [41] H. Fujimoto, S. Yamabe, T. Minato, K. Fukui, *J. Am. Chem. Soc.* 94 (1972) 9205.
- [42] T. Minato, S. Yamabe, H. Fujimoto, K. Fukui, *Bull. Chem. Soc. Jpn.* 51 (1978) 1; T. Minato, S. Yamabe, H. Fujimoto, K. Fukui, *ibid.* 51 (1978) 682.
- [43] H. Baba, S. Suzuki, T. Takemura, *J. Chem. Phys.* 50 (1969) 2078.
- [44] O. Henri-Rousseau, F. Texier, *J. Chem. Educ.* 55 (1978) 437.
- [45] Cf. L. P. Hammett: *Physical Organic Chemistry*, McGraw-Hill, New York 1940.
- [46] K. N. Houk, *Acc. Chem. Res.* 8 (1975) 361, and literature cited therein.
- [47] S. Inagaki, H. Fujimoto, K. Fukui, *J. Am. Chem. Soc.* 97 (1975) 6108.
- [48] Cf. I. Fleming: *Frontier Orbitals and Organic Chemical Reactions*, Wiley, New York 1976; T. L. Gilchrist, R. C. Storr: *Organic Reactions and Orbital Symmetry*, 2nd edition, Cambridge University Press, London 1979.
- [49] K. Fukui, K. Tanaka, *Bull. Chem. Soc. Jpn.* 50 (1977) 1391.
- [50] K. Fukui, S. Inagaki, *J. Am. Chem. Soc.* 97 (1975) 4445, and literature cited therein.
- [51] S. Inagaki, H. Fujimoto, K. Fukui, *J. Am. Chem. Soc.* 98 (1976) 4693.
- [52] S. Inagaki, K. Fukui, *Chem. Lett.* 1974, 509; S. Inagaki, H. Fujimoto, K. Fukui, *J. Am. Chem. Soc.* 98 (1976) 4054.
- [53] M. J. S. Dewar: *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York 1969.
- [54] M. J. S. Dewar, *Angew. Chem.* 83 (1971) 859; *Angew. Chem. Int. Ed. Engl.* 10 (1971) 761.
- [55] K. Fukui, *Kagaku To Kogyo (Tokyo)* 29 (1976) 556; H. Hosoya, Symposium on Electron Correlation in Molecules, Res. Inst. Fundam. Phys., Dec. 18, 1976.
- [56] P. W. Anderson, *Phys. Rev.* 109 (1958) 1492; cf. the Nobel Lectures in Physics 1977 by P. W. Anderson and N. F. Mott.
- [57] M. J. Goldstein, *J. Am. Chem. Soc.* 89 (1967) 6357.
- [58] H. E. Simmons, T. Fukunaga, *J. Am. Chem. Soc.* 89 (1967) 5208.
- [59] M. J. Goldstein, R. Hoffmann, *J. Am. Chem. Soc.* 93 (1971) 6193.
- [60] R. Hoffmann, A. Imamura, G. Zeiss, *J. Am. Chem. Soc.* 89 (1967) 5215.
- [61] Cf. W. J. Hehre, J. A. Pople, *J. Am. Chem. Soc.* 97 (1975) 6941.
- [62] W. J. Hehre, *Acc. Chem. Res.* 8 (1975) 369.
- [63] Cf. S. Glasstone, K. J. Laidler, H. Eyring: *The Theory of Rate Processes*, McGraw-Hill, New York 1941, and literature cited therein.
- [64] I. S. Y. Wang, M. Karplus, *J. Am. Chem. Soc.* 95 (1973) 8060, and literature cited therein.
- [65] K. Fukui, *J. Phys. Chem.* 74 (1970) 4161.
- [66] K. Fukui, S. Kato, H. Fujimoto, *J. Am. Chem. Soc.* 97 (1975) 1.
- [67] S. Kato, K. Fukui, *J. Am. Chem. Soc.* 98 (1976) 6395.
- [68] A. Tachibana, K. Fukui, *Theor. Chim. Acta* 49 (1978) 321.
- [69] A. Tachibana, K. Fukui, *Theor. Chim. Acta* 51 (1979) 189, 275.
- [70] A. Tachibana, K. Fukui, *Theor. Chim. Acta* 57 (1980) 81.
- [71] K. Fukui, *Recl. Trav. Chim. Pays-Bas* 98 (1979) 75.
- [72] B. D. Joshi, K. Morokuma, *J. Chem. Phys.* 67 (1977) 4880.
- [73] K. Ishida, K. Morokuma, A. Komornicki, *J. Chem. Phys.* 66 (1977) 2153.
- [74] K. Fukui, A. Tachibana, K. Yamashita, *Int. J. Quantum Chem. Symp.* 15 (1981) 621.
- [75] W. H. Miller, N. C. Handy, J. E. Adams, *J. Chem. Phys.* 72 (1980) 99; S. K. Gray, W. H. Miller, Y. Yamaguchi, H. F. Schaefer III, *ibid.* 73 (1980) 2732.
- [76] K. Fukui, *Int. J. Quantum Chem. Symp.* 15 (1981) 633.
- [77] K. Fukui, *Acc. Chem. Res.* 14 (1981) 363.
- [78] K. Fukui, N. Koga, H. Fujimoto, *J. Am. Chem. Soc.* 103 (1981) 196.
- [79] H. Fujimoto, N. Koga, M. Endo, K. Fukui, *Tetrahedron Lett.* 22 (1981) 1263, 3427.
- [80] H. Fujimoto, N. Koga, K. Fukui, *J. Am. Chem. Soc.* 103 (1981) 7452.
- [81] Cf. K. H. Johnson in B. Pullman, R. G. Parr: *The New World of Quantum Chemistry*, Reidel, Dordrecht 1976, p. 317, and literature cited therein.
- [82] H. Kobayashi, H. Kato, K. Tarama, K. Fukui, *J. Catal.* 49 (1977) 294; H. Kobayashi, S. Yoshida, H. Kato, K. Fukui, K. Tarama, *Surf. Sci.* 79 (1979) 189.
- [83] K. Tanaka, T. Yamabe, K. Fukui, *Chem. Phys. Lett.* 48 (1977) 141.
- [84] Cf. J. R. Schrieffer in B. Pullman, R. G. Parr: *The New World of Quantum Chemistry*, Reidel, Dordrecht 1976, p. 305; J. B. Danes, J. R. Schrieffer, *Int. J. Quantum Chem.* 10S (1976) 289.
- [85] K. Tanaka, T. Yamabe, A. Noda, K. Fukui, H. Kato, *J. Phys. Chem.* 82 (1978) 1453.
- [86] K. Tanaka, T. Yamabe, K. Fukui, H. Kato, *J. Phys. Chem.* 81 (1977) 727.
- [87] K. Tanaka, T. Yamabe, K. Fukui, *Chem. Phys. Lett.* 53 (1978) 453.
- [88] Cf. S. Ishimaru, T. Yamabe, K. Fukui, H. Kato, *J. Phys. Chem.* 78 (1974) 148; S. Ishimaru, K. Fukui, H. Kato, *Theor. Chim. Acta* 39 (1975) 103.
- [89] A. Tachibana, T. Yamabe, K. Fukui, *J. Phys. B* 10 (1977) 3175; *Adv. Quantum Chem.* 11 (1978) 195.