THE ROLE OF FRONTIER ORBITALS IN CHEMICAL REACTIONS

by
KENICHI FUKUI

Department of Hydrocarbon Chemistry, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Since the 3rd century 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 are said to have born fruit first of all in 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 developed later by many other chemists.[1] In the electronic theory, the mode of migration of electrons in molecules is noted and is considered under various judgements. For that purpose, a criterion is necessary with respect to the number of electrons which should originally exist in an atom or a bond in a molecule. Therefore, it can be said to be the concept by Lewis of the sharing of electrons that has given a firm basis to the electronic theory.[2]

In the organic electronic theory, the chemical concepts such as acid and base, oxidation and reduction and so on, have been conveniently utilized from a long time ago. Furthermore, there are terms centring closer around the electron concept, such as electrophilicity and nucleophilicity, and electron donor and acceptor both being pairs of relative concepts.

One may be aware that these concepts can be connected qualitatively to the scale of electron density or electric charge. In the electronic theory, the static and dynamic behaviours of molecules are explained by the electronic effects which are based on nothing but the distribution of electrons in a molecule.

The mode of charge distribution in a molecule can be sketched to some extent by the use of the electronegativity concept of atoms through organic chemical experience. At the same time, it is given foundation, made quantitative, and supported by physical measurements of electron distribution and theoretical calculations based on quantum theory.

The distribution of electrons or electric charge - with either use the result is unchanged - in a molecule is usually represented by the total numbers (generally not integer) of electrons in each atom and each bond, and it was a concept easily acceptable even to empirical chemists as having a tolerably realistic meaning. Therefore, chemists employed the electron density as a fundamental concept to explain or to comprehend various phenomena. In particular, for the purpose of promoting chemical investigations, researchers usually rely upon the analogy through experience, and the electron density was very effectively and widely used as the basic concept in that analogy.

When the magnitude of electron density is adopted as the criterion the electrostatic attraction and repulsion caused by the electron density are taken into account. Therefore, it is reasonable to infer that an electrophilic reagent will attack the position of large electron density in a molecule while a nucleophilic reaction will occur at the site of small electron density. In fact, Wheland and Pauling[3] explained the orientation of aromatic substitutions in substituted benzenes along these lines, and theoretical interpretations of the mode of many other chemical reactions followed in the same fashion.

However, the question why one of the simple reactions known from long before, the electrophilic substitution in naphthalene, for instance, such as nitration, yields α-substituted derivatives predominantly was not so easy to answer. That was because, in many of such unsubstituted aromatic hydrocarbons, both the electrophile and the nucleophile react at the same location. This point threw some doubt on the theory of organic reactivity, where the electron density was thought to do everything.

THE CONCEPT OF FRONTIER ORBITAIL INTERACTIONS

The interpretation of this problem was attempted by many people from various different angles. Above all, Coulson and Longuet-Higgins[4] took up the change of electron density distribution under the influence of approaching reagent. The explanation by Wheland[5] was based on the calculation of the energy required to localize electrons forcibly to the site of reaction. But I myself tried to attack this problem in a way which was at that time slightly unusual, Taking notice of the principal role played by the valence electrons in the case of the molecule formation from atoms, only the distribution of the electrons occupying the highest energy π orbital of aromatic hydrocarbons was calculated. The attempt resulted in a better success than expected, obtaining an almost perfect agreement between the actual position of electrophilic attack and the site of large density of these specified electrons as exemplified in Fig. 1.[6]
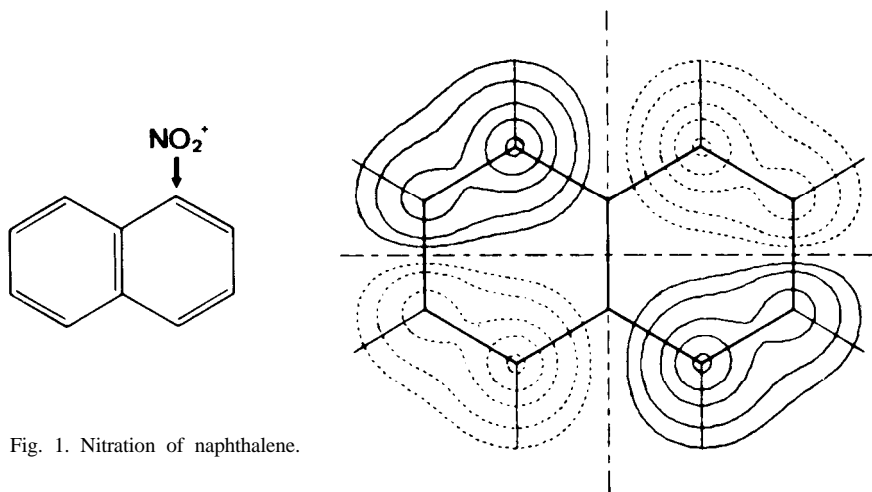

Fig. 1. Nitration of naphthalene.

The "orbital" concept, which was established and developed by many scientists, such as Pauling, Slater, Mulliken, Roothaan, Löwdin, Hückel, Parr and so on, had till then been employed to construct the wave function of a molecule, through which molecular properties were usually interpreted.[7] It 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 results of such a rather "extravagant" attempt was by no means smoothly accepted by the general public of chemists. That paper received a number of controversial comments. This was in a sense understandable, because, for lack of my experiential ability, the theoretical foundation for this conspicuous result was obscure or rather improperly given. However, it was fortunate for me that the paper on the charge-transfer complex of Mulliken was published in the same year as ours.

The model of Mulliken et al. for protonated benzene was a good help.[9] Our work in collaboration with Yonezawa, Nagata and Kato provided a simple and pointed picture of theoretical interpretation of reactions," as well as the "overlap and orientation" principle proposed by Mulliken with regard to the orientation in molecular complexes.[11] Subsequent to the electrophilic substitution, the nucleophilic substitution was discussed and it was found that in this case the lowest energy vacant orbital played this particular part.[12] In reactions with radicals, both of the two orbitals mentioned above, became the particular orbitals.

There was no essential reason to limit these particular orbitals to π orbitals, so that this method was properly applied not only to unsaturated compounds but also to saturated compounds. The applicability to saturated compounds was a substantial advantage in comparison with many theories of reactivity which were then available only for π electron compounds. The method displayed its particular usefulness in the hydrogen abstraction by radicals from paraffinic hydrocarbons, the S_N2 and E2 reactions in halogenated hydrocarbons, the nucleophilic abstraction of α–hydrogen of olefins, and so forth[13]

These two particular orbitals, which act as the essential part in a wide range of chemical reactions of various compounds, saturated or unsaturated, were referred to under the general term of "frontier orbitals", and abbreviated frequently by HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital).

In this way, the validity of the theory became gradually clearer. The vein of ore discovered by chance was found to be hopefully more extensive than expected. But it was attributed to the role of the symmetry of particular orbitals pointed out in 1964 with regard to Diels-Alder reactions[14] that the utility of our studies was further broadened. It was remarked that as is seen in Fig. 2, the symmetries of HOMO and LUMO of dienes and those of LUMO and HOMO of dienophiles, respectively, were found to be in a situation extremely favourable for a concerted cyclic interaction between them.

This signified the following important aspects: First, it pointed out a possible correlation between the orbital symmetry and the rule determining the sub-

HOMO of diene   LUMO of dienophile   a)

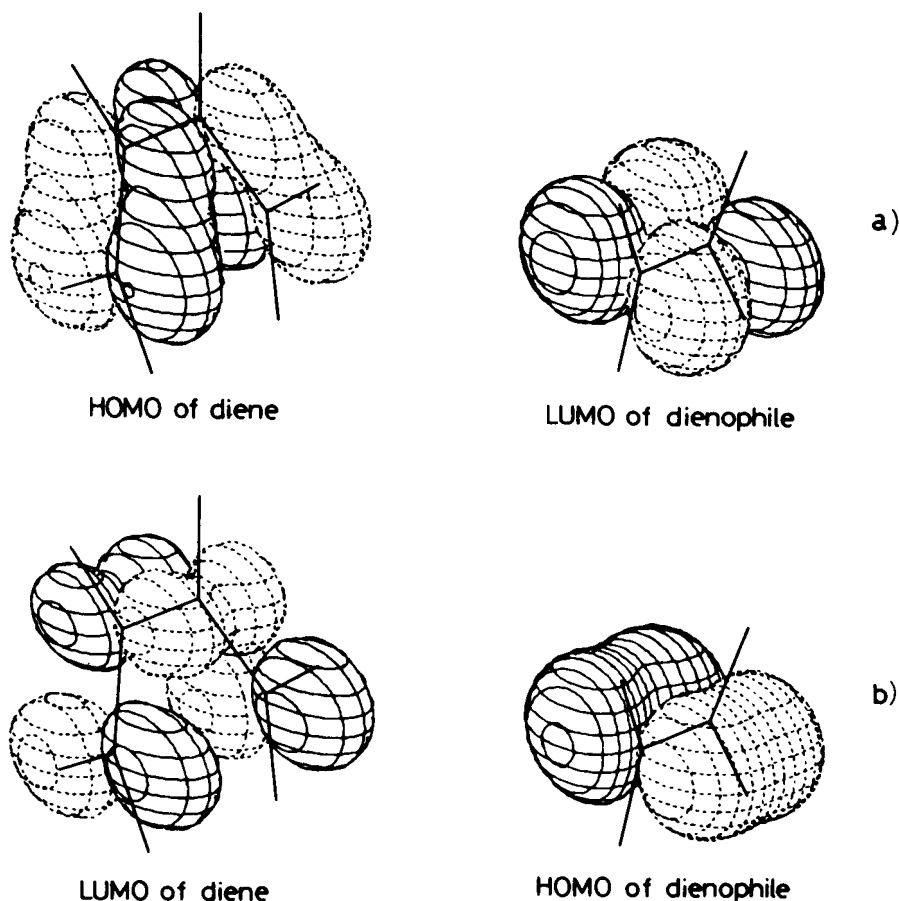LUMO of diene   HOMO of dienophile   b)

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

stantial occurrence or non-occurrence of a chemical reaction, which may be called the "selection rule", in common with the selection rule in molecular spectroscopy. Second, it provided a clue to discuss the question concerning what was the "concertedness" in a reaction which forms a cycle of electrons in conjugation along the way.

In 1965 Woodward and Hoffmann proposed the stereoselection rules which are established today as the "Woodward-Hoffmann" rules.[15,16] An experimental result developed in Havinga's important paper" was extended immensely. It is only after the remarkable appearance of the brilliant work by Woodward and Hoffmann that I have become fully aware that not only the density distribution but also the nodal property of the particular orbitals have significance in such a wide variety of chemical reactions. In fact, we studied previously the noted (4n+2) rule proposed by Hückel[18] and noticed that the sign of the bond order in the highest energy electron orbital of an open-chain conjugation should be closely related to the stabilization of the corresponding conjugated rings.[19] We did not imagine, however, on that occasion that the discussion might be extended to the so-called Mobius-type ring-closure![20]

By considering the HOMO-LUMO interactions between the fragments of a conjugated chain divided into parts,[21] the frontier orbital theory can yield selection rules which are absolutely equivalent to those obtained from the principle called "the conservation of orbital symmetry" by Woodward and Hoffmann. One point that I may stress here is, as was pointed out by Fujimoto, Inagaki and myself,[22] that the electron delocalization between the particular orbitals interprets definitely in terms of orbital symmetries the formation and breaking of chemical bonds which, I believe, should be a key for perceiving chemical reaction processes.

In the cycloaddition of butadiene and ethylene shown in Fig. 2, both the interaction between the HOMO of diene and the LUMO of dienophile and that between the LUMO of diene and the HOMO of dienophile stabilize the interacting system. If one is interested in the local property 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 regards to the symmetry plane retained throughout the course of cycloaddition. This signifies that each of the carbon atoms of ethylene are bound to both of the terminal carbons of butadiene. The chemical bonding between the diene and dienophile thus generated may be something like the one in a loosely bound complex, e.g., protonation to an olelinic double bond. On the contrary, 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 combines a carbon atom of ethylene and a terminal carbon atom of butadiene. Needless to say it is the interaction between the HOMO of diene and the LUMO of dienophile that is of importance for the occurrence of concerted cycloaddition.[22]

In this way, it turned out in the course of time that the electron delocalization between HOMO and LUMO generally became the principal factor determining the easiness of a chemical reaction and the stereoselective path, irrespective of intra- and intermolecular processes, as illustrated in Fig. 3. Besides our own school, a number of other chemists made contributions. I want to refer to several names which are worthy of special mention.

First of all, the general perturbation theory of the HOMO-LUMO interaction between two molecules was built up by Salem.[23-25] One of Salem's papers[25] was in line with the important theory of Bader,[26] which specified the mode of decomposition of a molecule or a transition complex by means of the symmetry of the normal vibration. Furthermore Pearson[27] investigated the relation between the symmetry of reaction coordinates in general and that of HOMO and LUMO.

The discussion so far may seem to be an overestimation of these selected orbitals, HOMO and LUMO. This point was ingeniously modified by Klopman.[28] He carefully took into account the factors to be considered in the perturbation theory of reacting systems and classified reactions into two cases: the one was "frontier-controlled" case in which the reaction was controlled by the particular orbital interaction, and the other was the "charge-controlled"
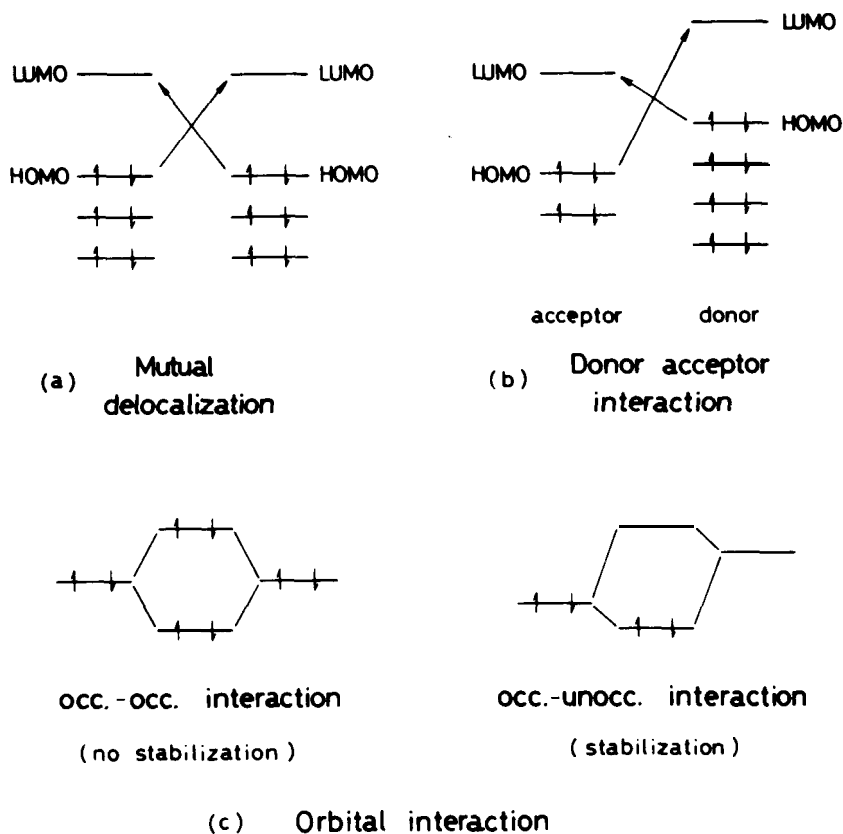
Fig. 3. The mode of interaction between orbitals of two molecules

case, where it was controlled by the electrostatic interaction of charges. This classification was conveniently used by many people. In this context the review articles of Herndon[29] and of Hudson[30] appeared to be very useful. The names of Coulson[4] and Dewar[31] should also be noted here as those who contributed to the development of reactivity theories.

Returning to the subject again, let us assume that two molecules approach each other and orbital overlapping takes place. The perturbation theory[32] of this sort of interaction indicates that, the larger the orbital overlapping is and the smaller the level separation of two overlapping orbitals is, the larger is the contribution of the orbital pair to the stabilization of an interacting system. Accordingly, at least at the beginning, a reaction will proceed with a mutual nuclear configuration which is most favourable for the HOMO-LUMO overlapping.

Now let us suppose an electron flow from the HOMO of molecule I to the LUMO of molecule II. In each molecule the bonds between the reaction centre - the place at which the orbitals overlap with those of the other molecule - and the remaining part of the molecule are weakened. On this occasion, in molecule I the bonds which are bonding in HOMO are weakened and those

antibonding in HOMO are strengthened, while in molecule II the bonds which are antibonding in LUMO are weakened and those bonding in LUMO are strengthened. Consequently, the HOMO of molecule I particularly destabilizes as compared with the other occupied orbitals, and the LUMO of molecule II discriminatively stabilizes among unoccupied orbitals, so that the HOMO-LUMO level separation between the two molecules is decreased. Such a circumstance is clearly understandable in Fig. 3.

The following tendency is further stressed. When the bond weakenings specified above have arisen, the HOMO and the LUMO tend to become more localized at these weakened bonds in each molecule. Besides, the weakening of the bonds between the reaction centre and the remaining part causes an increase of the amplitudes of HOMO and LUMO at the reaction centres, resulting in a larger overlapping of HOMO and LUMO.[33] Such a trend of the characteristic change in the orbital pattern is made numerically certain by actual calculations. The role of interaction between HOMO and LUMO turns out in this way to become more and more important as the reaction proceeds.

A series of studies on chemical interactions were attempted in which the interaction of reactants was divided into the Coulomb, the exchange, the polarization, and the delocalization interactions, and their magnitude of contribution to the interaction energy was quantitatively discussed[32,34] The interactions discussed by this method were the dimerization[35] and the addition to ethylene[36] of methylene and the dimerization of BH_3,[37] and also several donor-acceptor interactions-BH_3-NH_3,[38] BH_3-CO,[39] NH_3-HF,[40] etc. The method was applied also to reactions of radicals, such as the abstraction of a methane hydrogen by methyl radical, the addition of methyl radical to ethylene[41] and recombinations, disproportionations, and self-reactions of two radicals.[42] In these calculations, the configuration analysis proposed originally by Baba[43] was also utilized conveniently. We could show numerically the mode of increase of the electron delocalization from HOMO to LUMO along with the proceeding of reaction, the increasing weight of contribution of such a delocalization to the stabilization of the reacting system, the driving force of the reaction in terms of orbital interactions, and so on.

The question "Why HOMO and LUMO solely determine the reaction path?" was one which I very frequently received from the audiences in my lectures given in the past in different places. The discussion so far made here is thought to correspond, at least partly, to that answer. But one may not adhere so strictly to the HOMO and LUMO. In one-centre reactions like substitutions, which the orbital symmetry has nothing to do with, any occupied orbitals which are very close to HOMO should properly be taken into account.[12] In large paraffin molecules a number of HOMO's (high-lying occupied MO's), and furthermore as will shortly be referred to later, in metal crystals, even "HOMO-band" must be taken along the line of reactivity argument. If HOMO or LUMO happens to be inadequate owing to its extension, the symmetry, or the nodal property, the next orbital should be sought for. One of the simplest examples of such an instance is the protonation of pyridine. In this case, the nitrogen lone-pair orbital is not HOMO, but the addition of proton to

the nitrogen lone-pair so as not to disturb the π conjugation will evidently be more advantageous than the addition to higher occupied π orbitals which may intercept the π conjugation. Thus, the reason why proton dare not add to the positions of large amplitude of π HOMO in this case will easily be understood. It is not completely satisfactory to dispose of a disagreement between the HOMO-LUMO argument and the experimental fact formally as an *exception* to the theory. A so-called exception does possess its own reason. To investigate what the reason is will possibly yield a novel finding.

The HOMO-LUMO interaction argument was recently pointed out[44] to be in an auxiliary sense useful for the interpretation of the sign of a reaction constant and the scale of a substituent constant in the Hammett rule[45] which has made an immeasurable contribution to the study of the substituent effect in chemical reactivity. In the cyclic addition, like Diels-Alder reactions and 1,3-dipolar additions, the relative easiness of occurrence of reactions, various subsidiary effects, and interesting phenomena like regioselection and periselection were interpreted with considerable success simply by the knowledge of the height of the energy level of HOMO and LUMO, the mode of their extension, their nodal structure, etc.[46] - I defined these in a mass: 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 biradicals and excited molecules,[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. included in the theory the polarization effect in HOMO and LUMO due to the mixing in of other orbitals and gave an elucidation for a number of organic chemical problems which were not always easy to explain. The unique stereoselection in the transannular cross-bond formation, the lone-pair effect, the d orbital effect, and the orbital polarization effect due to substituents were the cases.[52]

As was partly discussed above, the method of orbital interaction was applied not only to the ground electronic state but to the excited states, giving an explanation of the path of even complicated photochemical isomerizations.[13] [21] In a 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 in of 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 if there were no influence of the acceptor (or donor), becomes important in stabilizing the interacting system.*'

The problems so far discussed have been limited to chemical reactions. However, the HOMO-LUMO interaction must come into relation also with other chemical phenomena in almost the same mechanism - with the exception of one different point that they usually do not bring about so remarkable a change in the nuclear configuration as in the case of chemical reactions. Now let us examine the possibility of applying the theory to so-called "aromaticity"- one of the simplest, but the hardest-to-interpret problems. There seem to be few problems so annoying to theoreticians as the explanation of this

chemically classical concept. I greatly appreciate the contribution of Dewar's theory [53, 54] based on a quantitative energy values argument. Here, however, I want to give a quality comment through a totally different way of consideration.

It is easily ascertained [55] in Fig. 4 that in benzene, naphthalene, phenanthrene, etc., any virtual division of the molecule into two always produces the parts in which their HOMO and LUMO overlap in-phase at the two junctions.
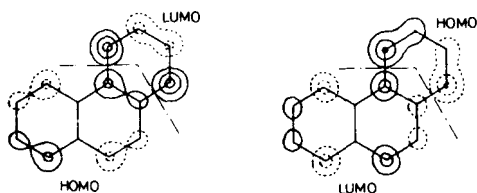
Benzene
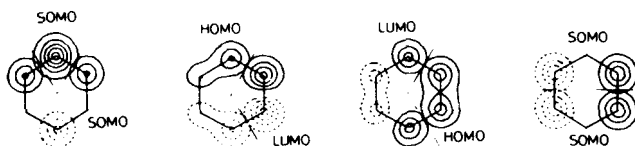
Naphthalene
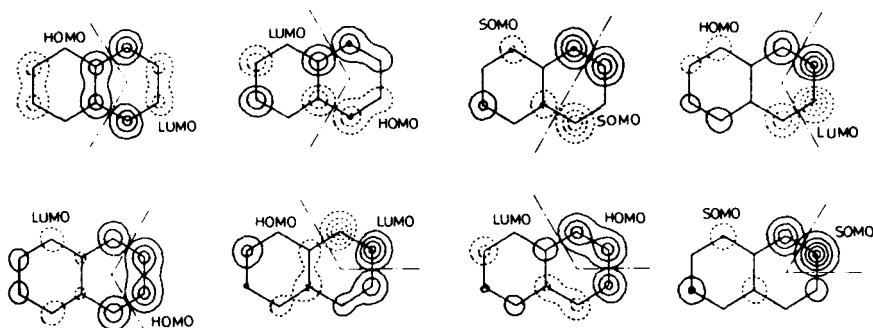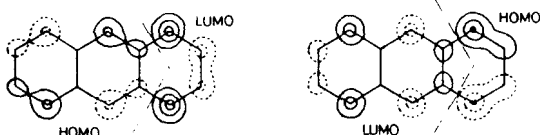

Phenanthrene


Anthracene

Fig. 4. The HOMO-LUMO phase relationship in virtual division of aromatic hydrocarbons. (SOMO: a singly occupied MO of a radical)

But these circumstances are not seen in anthracene which is usually looked upon as one of the typical representatives of aromatic compounds. Hosoya[55] pointed out from the comparison with phenanthrene indicated in Fig. 4, that the ring growth of type (II) was less stable than that of (I),

(I)   (II)
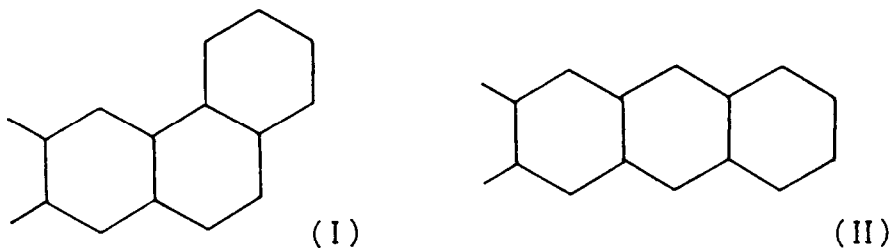
It is well known that anthracene occasionally exhibits a reactivity of olefin-like additions.

In view of so-called Hückel's (4n+2)-rule mentioned above, an anthracene molecule has 14π electrons and fulfils the stability condition for "aromaticity." Actually, if one considers a molecule of anthracene with the two inside bonds deleted,
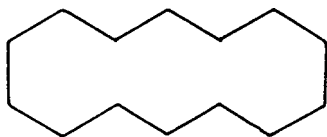
it is really seen that the HOMO and the LUMO of the two parts overlap in an in-phase manner at both of the junctions:
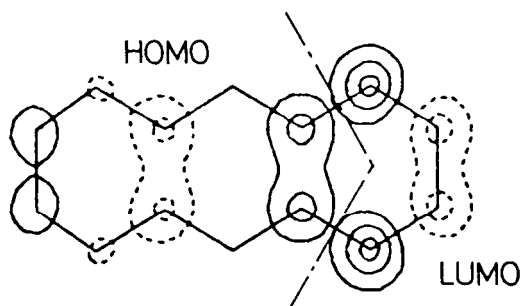
In this way, it is understood that the two bonds which were deleted above exerted a certain unfavourable influence for aromaticity. Such an influence bears a close resemblance to that of impurity scattering in the wave of a free electron moving in a metal crystal.

This discussion seems to be a digression but, as a matter of fact, it relates to the essential question as to how an electron in a molecule can delocalize. As will be mentioned later, Anderson[56] solved the question how an electron in a

random system can localize. In a molecule, there are potential barriers between atoms which should be got over by the aid of a certain condition to be satisfied, in order for an electron to move around it freely. Although the question how valence electrons can delocalize in a molecule have not yet been solved satisfactorily under the condition of unfixed nuclear configuration, the in-phase relation of HOMO and LUMO at the junctions of the two parts of the molecule seems to be at least one of the conditions of intramolecular delocalization of electrons.

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

You may be doubtful 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 the expectation based on the simple orbital interaction argument mentioned above.

CHEMICAL REACTION PATHWAYS

It has already been pointed out that the detailed mechanism of a chemical reaction was discussed along the reaction path on the basis of the orbital interaction argument. For that purpose, however, it is required that the problem as to how the chemical reaction path is determined should have been solved. The method in which the route of a chemical reaction was supposed on the potential energy surface and the rate of the reaction was evaluated by the aid of a statistical-mechanical formulation was established by Eyring.[63] Many people wrote papers where the rate expression was derived wave-mechanically with the use of the potential energy function. Besides, the problem of obtaining the trajectory of a given chemical reaction with a given initial condition was treated by Karplus.[64]

The centre line of the reaction path, so to speak, the idealized reaction coordinate - which I called "intrinsic reaction coordinate" (IRC)[65] - seemed to have been, rather strangely, not distinctly defined till then. For that reason, I began with the general equation which determines the line of force mathemat-

i c a l l y . [34, 66, 67] Although my papers themselves were possibly not very original, they turned out later to develop in a very interesting direction. [68-74] These papers opened the route to calculate the quasistatic change of nuclear configuration of the reacting system which starts from the transition state proceeding to a stable equilibrium point. [66] I termed the method of automatic determination of the molecular deformation accompanying a chemical reaction as "reaction ergodography." [34, 67] This method was applied to a few definite examples by Kato and myself[67] and by Morokuma. [72, 73] Those examples were: abstraction and substitution of methane hydrogen by hydrogen atom,[67] nucleophilic replacement in methane by hydride anion,[72] and isomerization of methylcarbylamine to acetonitrile. [73] All of these reactions thus far treated are limited to the simplest cases, but there seems to be no principal difficulty in extending the applicability to larger systems. Once 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 the reacting system with no angular momentum it is possible to obtain the IRC by the use of the space-fixed Cartesian coordinate system. All of the calculated examples mentioned above belong to this case. However, in the reaction in which rotational motion exists, it is required to discuss the IRC after separating the nuclear configuration space from the rotational motion.[74-77] For that purpose, it is essential to derive the general classical Hamiltonian of the reacting systems and then to separate the internal motion which is deter-mined only by the internal coordinates. The nuclear configuration space thus separated out is in general a Riemannian space. The classical Lagrangian form to be obtained in that process of constructing the Hamiltonian is used to deriye the IRC equation in the presence of rotational motion. It is thus understood that the rotational motion of the reacting system generally causes a deviation of I R C .[74]

   Once the method of determining unique reaction pathways is obtained, the next problem we are concerned with is to see if the calculated pathways are interpreted in terms of the frontier orbital interactions. A method referred to as the "interaction frontier orbitals" or "hybrid molecular orbitals" has been developed very recently by Fujimoto and myself in order to furnish a lucid scheme of frontier orbital interactions with the accuracy of nonempirical calcu-lations now and in the future. [78-80] By including properly contributions of other MOs than the HOMO and the LUMO, we realized in terms of orbital diagrams how ingenious the empirically established chemical concepts - "reac-tion sites" and "functional groups"- and the empirical concept of reaction pathways could be. Fig. 5 compares the HOMO of styrene and its interaction frontier orbital for protonation to the olelinic double bond. The latter is seen to be localized very efficiently in the frontier 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 people to make it useful for one of our ultimate targets: theroretical design of molecules and chemical reactions.
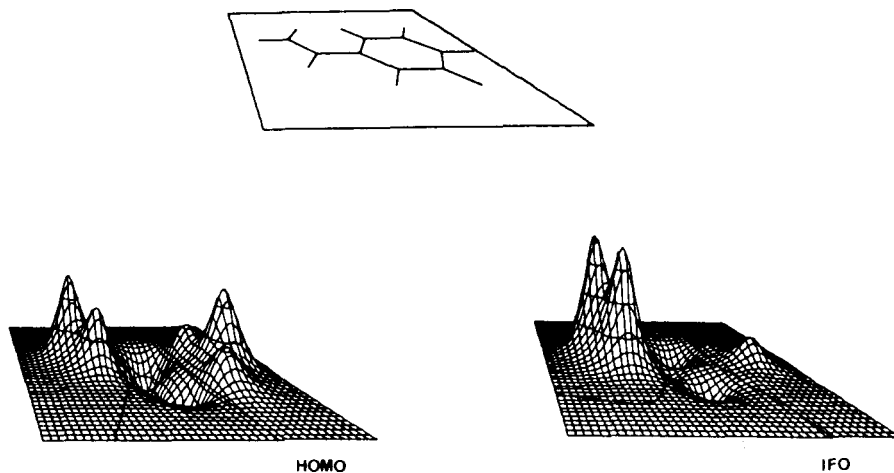
Fig. 5. A comparison of HOMO and the interaction frontier orbital for protonation in styrene.

FRONTIER ORBITALS IN RELATED FIELDS

Theoretical treatments of the property of solid crystals, or chemisorption on a solid surface, appear to have hitherto been almost monopolistically treated by the methodology of physics. But the orbital pattern technique has also advanced gradually in this field.

The "cluster approach," [81, 82] in which a portion of the metal crystal is drawn out as the form of a cluster of atoms and its catalytic actions or other properties are investigated, has contributed to the development of the orbital pattern approach, because the physical methods mentioned above can hardly be applied to such sizable systems. It is expected that, if clusters of various sizes and various shapes are studied to look into 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 reaction, and several related subjects of interest can be investigated theoretically.

As is the case of molecular interactions in usual chemical reactions, only the HOMO- and LUMO-bands lying in the range of several electron volts near 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 can be concerned in forming electron pairs as the result of interaction with lattice vibration. In the case of solid catalysts mentioned above, the discrimination of particular orbitals and electrons from the others have made the situation much easier.

Consider a system composed of a regular repetition of a molecular unit, for instance, a one-dimensional high 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 that place. One such technique was proposed by Tanaka, Yamabe and myself.[83] This method is expected to be in principle applied to a local discussion of such problems as the adsorption of a molecule on the two-dimensional surface of catalysts, surface reactions, and related matters. This approach may be called a little more chemical than the method using the function of local density of states[84] or similar ones, in that the former can be used for the argument of the reactivity of molecules on a catalyst surface in terms of the phase relationship of localized orbitals.

What is called 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 the high-polymerization to $(SN)_x$[86] were discussed, and the energy band structure of $(SN)_x$ polymer chain was analyzed to investigate the stable nuclear arrangement and the mode of inter-chain interactions.[87]

The modern technique employed in solid state physics to interpret the interesting characteristic behaviours of noncrystalline materials, in particular of amorphous materials, in which the nuclear arrangements were not regular, was certainly striking. Anderson showed generally that in a system of random lattice the electron localization should take place.[56] Mott, stating in his 1977 Nobel lecture that he thought is the first prize awarded for the study of amorphous materials, answered the question, "How can a localized electron be conducted?" with the use of the idea of hopping. Here, too, the HOMO-LUMO interaction - in this case the consideration of spin is essential - would play an important part.

Here in a few words, I want to refer to the meaning and the role of virtual orbitals. The LUMO, which has been one of the stars in orbital arguments hitherto discussed, is the virtual orbital which an external electron is considered to occupy to be 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 complex eigenvalue problem. The idea of resonant states will take a principal part in chemical reactions, particularly in high-energy reactions which will be developed more in the future.

PROSPECT

In introducing above a series of recent results of the studies carried out mainly by our group, I have ventured to make those things the object of my talk which are no more than my prospective insight and are not yet completely established. This is just to stimulate, by specifying what are the fields I believe promising in the future, the intentional efforts of many younger chemists in order to develop them further.

In my opinion, quantum mechanics has two different ways of making participations in chemistry. One is the contribution to the nonempirical comprehen-

sion of empirical chemical results just mentioned. However, we should not overlook another important aspect of quantum mechanics in chemistry. That is the promotion of empirical chemistry from the theoretical side. But, also for this second purpose, as a matter of course, reliable theoretical foundations and computational methods are required. The conclusions of theories should be little affected by the degree of sophistication in approximations adopted.

On the other hand, for theoreticians to make the second contribution, the cases where predictions surpassing the experimental accuracy are possible by very accurate calculations are for the present limited to those of a very few, extremely simple molecules. In order to accomplish this object in regard to ordinary chemical problems, it becomes 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 with respect to each problem, one can not be said to be making the most of quantum mechanics for the development of chemistry. It is certainly best that the underlying concepts are as close to experience as possible, but the sphere of chemical experience is steadily expanding. Quantum chemistry has then to perform its duty by furnishing those concepts with the theoretical basis in order to make them chemically available and serviceable for the aim of promoting empirical chemistry.

Even the same atoms of the same element, when they exist in different molecules, exhibit different behaviours. The chemical symbol H even 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 compounds" that is of chemical interest. On account of this formidable complexity, chemistry possesses inevitably one aspect of depending on the analogy through experience. This is in a sense said to be the fate alloted to chemistry, and the source of a great difference in character from physics. Quantum chemistry, too, so far as it is chemistry, is required to be useful in promoting empirical chemistry as mentioned before.

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mental results. Furthermore, many other collaborators are now distinguishing themselves in other important fields of chemistry, which, however, have not been the object of the present lecture.

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REFERENCES

I. For instance, see Ingold, C. K., Structure and Mechanism in Organic Chemistry, Cornell University Press (1953), Ithaca, N.Y.

2. For instance, see Lewis, G. N., Valence and the Structure of Atoms and Molecules, Chemical Catalog Co. (1923), New York, N.Y.

3. Wheland, G. W. and Pauling, L., J. Am. Chem Soc. 57, 2086 (1935).

4. Coulson, C. A. and Longuet-Higgins, H. C., Proc. Roy. Soc. (London) **A191, 39; A192,** 16 (1947).

5. Wheland, G. W., J. Am. Chem. Soc. 64, 900 (1942).

6. Fukui, K., Yonezawa, T. and Shingu, H., J. Chem. Phys. 20, 722 (1952).

7. For instance, see Parr, R. G., The Quantum Theory of Molecular Electronic Structure, Benjamin (1963), New York, N.Y. and references cited therein.

8. Mulliken, R. S., J. Am. Chem. Soc. 74, 811 (1952).

9. Picket, L. W., Muller, N. and Mulliken, R. S., J. Chem. Phys. 21, 1400 (1953).

10. Fukui, K., Yonezawa, T. and Nagata, C., Bull. Chem. Soc. Jpn. 27, 423 (1954); Fukui, K., Kato, H. and Yonezawa, T., ibid. 34, 1112 (1961).

11. Mulliken, R. S., Rec. Trav. Chim. 75, 845 (1956).

12. Fukui, K., Yonezawa, T., Nagata, C. and Shingu, H., J. Chem. Phys. 22, 1433 (1954).

13. For instance, see Fukui, K., Theory of Orientation and Stereoselection, Springer (1970), Berlin.

14. Fukui, K. In: Molecular Orbitals in Chemistry, Physics and Biology, Löwdin, P.-O. and Pullman, B. eds., Academic (1964), New York, N.Y., p. 513.

15. Woodward, R. B. and Hoffmann, R., Angew. Chem. 81, 797 (1969); The Conservation of Orbital Symmetry, Academic Press (1969), New York, N.Y.; see papers In: Orbital Symmetry Papers, Simmons, H. E. and Bunnett, J. F., eds., ACS (1974), Washington D.C.

16. Woodward, R. B. and Hoffmann, R., J. Am. Chem. Soc. 87, 395 (1965).

17. Havinga, E., de Kock, R. J. and Rappoldt, M. P., Tetrahedron 11, 276 (1960); Havinga, E. and Schlatmann, J. L. M. A., ibid. 15, 146 (1961).

18. Hückel, E., Z. Phys. 70, 204 (1931); 76,628 (1932).

19. Fukui, K., Imamura, A., Yonezawa, T. and Nagata, C., Bull. Chem. Soc. Japan 33, 1501 (1960).

20. Heilbronner, E., Tetrahedron Lett., 1964, 1923.

21. Fukui, K., Acc. Chem. Res. 4, 57, (1971).

22. Fujimoto, H., Inagaki, S. and Fukui, K., J. Am. Chem. Soc. 98,2670 (1976).

23. Salem, L., J. Am. Chem. Soc. 90, 543, 553 (1968).

24. Devaquet, A. and Salem, L., J. Am. Chem. Soc. **91, 3743** (1969).

25. Salem, L., Chem. Brit. 5,449 (1969).

26. Bader, R. F. W., Can., J. Chem. 40, 1164 (1962).

27. Pearson, R. G., Symmetry Rules for Chemical Reactions, John Wiley (1976), New York, N.Y. and references cited therein.

28. Klopman, G., J. Am. Chem. Soc. 90, 223 (1968). Also see Klopman, G., Chemical Reactivity and Reaction Paths, John Wiley (1974), New York, N.Y.

29. Herndon, W. C., Chem. Rev. 72, 157 (1972).

30. Hudson, R. F., Angew. Chem. Int. Ed. Eng. **12,36** (1973).

31. For instance, see Dewar, M. J. S. and Dougherty, R. C., The PMO Theory of Organic Chemistry, Plenum (1975), New York, N.Y. and many papers cited therein; see also Dewar, M. J. S., Thetrahedron S8, Part I, p. 85 (1966).

32. Fukui, K. and Fujimoto, H., Bull. Chem. Soc. Japan 41, 1989 (1968).

33. Fukui, K. and Fujimoto, H., Bull. Chem. Soc. Japan 42, 3392 (1969).

34. Fukui, K. In: The World of Quantum Chemistry, Daudel, R. and Pullman, B. eds., Reidel (1974), Dordrecht, p. 113.

35. Fujimoto, H., Yamabe, S. and Fukui, K., Bull. Chem. Soc. Japan 45, 1566 (1972).

36. Fujimoto, H., Yamabe, S. and Fukui, K., Bull. Chem. Soc. Japan 45, 2424 (1972).

37. Yamabe, S., Minato, T., Fujimoto, H. and Fukui, K., Theoret. Chim. Acta (Berl.) 32, 187 (1974).

38. Fujimoto, H., Kato, S., Yamabe, S. and Fukui, K., J. Chem. Phys. 60, 572 (1974).

39. Kato, S., Fujimoto, H., Yamabe, S., Fukui, K., J. Am. Chem. Soc. 96, 2024 (1974).

40. Yamabe, S., Kato, S., Fujimoto, H. and Fukui, K., Bull. Chem. Soc. Japan 46, 3619 (1973); Yamabe, S., Kato, S., Fujimoto, H. and Fukui, K., Theoret. Chim. Acta (Berl.) 30, 327 (1973).

41. Fujimoto, H., Yamabe, S., Minato, T. and Fukui, K., J. Am. Chem. Soc. 94, 9205 (1972).

42. Minato, T., Yamabe, S., Fujimoto, H. and Fukui, K., Bull. Chem. Soc. Japan **51,** 1 (1978); Minato, T., Yamabe, S., Fujimoto, H. and Fukui, K., Bull. Chem. Soc. Japan **51, 682 (1978).**

43. Baba, H., Suzuki, S. and Takemura, T., J. Chem. Phys. 50, 2078 (1969).

44. Henri-Rousseau, O. and Texier, F., J. Chem. Education 55,437 (1978).

45. For instance, see Hammett, L. P., Physical Organic Chemistry, McGraw-Hill (1940), New York, N.Y.

46. Houk, K. N., Acc. Chem. Res. 8, 361 (1975) and references cited therein.

47. Inagaki, S., Fujimoto, H. and Fukui, K., J. Am. Chem. Soc. 97,6108 (1975).

48. See Fleming, I., Frontier Orbitals and Organic Chemical Reactions, John Wiley (1976), New York, N.Y.; Gilchrist, T. L. and Storr, R. C., Organic Reactions and Orbital Symmetry, Cambridge Univ. Press, 2nd ed. (1979), London.

49. Fukui, K. and Tanaka, K., Bull. Chem. Soc. Japan 50, 1391 (1977).

50. Fukui, K. and Inagaki, S., J. Am. Chem. Soc. 97,4445 (1975) and many papers cited therein.

51. Inagaki, S., Fujimoto, H. and Fukui, K., J. Am. Chem. Soc. 98,4693 (1976).

52. Inagaki, S. and Fukui, K., Chem. Lett. 1974, 509; Inagaki, S., Fujimoto, H. and Fukui, K., J. Am. Chem. Soc. 98, 4054 (1976).

53. Dewar, M. J. S., The Molecular Orbital Theory of Organic Chemistry, McGraw-Hill (1969), New York, N.Y.

54. Dewar, M. J. S., Angew. Chem. 83,859 (1971).

55. Fukui, K., Kagaku to Kogyo 29,556 (1976); Hosoya, H., Symposium on Electron Correlation in Molecules, Res. Inst. for Fund. Phys., Dec. 18, 1976.

56. Anderson, P. W., Phys. Rev. 109, 1492 (1958); cf. 1977 Nobel Lectures in Physics by Anderson, P. W., and by Mott, N. F.

57. Goldstein, M. J., J. Am. Chem. Soc. 89,6357 (1967).

58. Simmons, H. E. and Fukunaga, T., J. Am. Chem. Soc. 89, 5208 (1967).

59. Goldstein, M. J. and Hoffmann", R., J. Am. Chem. Soc. 93,6193 (1971).

60. Hoffman", R., Imamura, A. and Zeiss, G., J. Am. Chem. Soc. 89, 5215 (1967).

61. For instance, see Hehre, W. J. and Pople, J. A., J. Am. Chem. Soc. 97,694l (1975).

62. Hehre, W. J., Acc. Chem. Res. 8, 369 (1975).

63. For instance, see Glasstone, S., Laider, K. J. and Eyring, H., The Theory of Rate Processes, McGraw-Hill (1941), New York, N.Y. and references cited therein.

64. Wang, I. S. Y. and Karplus, M., J. Am. Chem. Soc. 95, 8060 (1973) and references cited therein.
65. Fukui, K., J. Phys. Chem. 74, 4161 (1970).
66. Fukui, K., Kato, S. and Fujimoto, H., J. Am. Chem. Soc. 97, 1 (1975).
67. Kato, S. and Fukui, K., J. Am. Chem. Soc.98,6395 (1976).
68. Tachibana, A. and Fukui, K., Theoret. Chim. Acta (Berl.) 49, 321 (1978).
69. Tachibana, A. and Fukui, K., Theoret. Chim. Acta (Berl.) 51, 189, 275 (1979).
70. Tachibana, A. and Fukui, K., Theoret. Chim. Acta (Berl.) 5, (1979).
71. Fukui, K., Rec. Trav. Chim., Pays-Bas 98, 75 (1979).
72. Joshi, B. D. and Morokuma, K., J. Chem. Phys. 67,488O (1977).
73. Ishida, K., Morokuma, K. and Komornicki, A., J. Chem. Phys. 66, 2153 (1977).
74. Fukui, K., Tachibana, A. and Yamashita, K., Intern. J. Quant. Chem., Quant. Chem. Symp. 15,621 (1981).
75. Miller, W. H., Handy, N. C. and Adams, J. E., J. Chem. Phys. 72, 99 (1980); Gray, S. K., Miller, W. H., Yamaguchi, Y. and Schaefer, H. F., III., ibid. 73, 2732 (1980).
76. Fukui, K., Intern. J. Quant. Chem., Quant. Chem. Symp. *15,633* (1981).
77. Fukui, K., Act. Chem. Res. 14, 363 (1981).
78. Fukui, K., Koga, N. and Fujimoto, H., J. Am. Chem. Soc. *103,* 196 (1981).
79. Fujimoto, H., Koga, N., Endo, M. and Fukui, K., Tetrahedron Letters 22, 1263; 3427 (1981).
80. Fujimoto, H., Koga, N. and Fukui, K., J. Am. Chem. Soc. 103, 7452 (1981).
81. For instance, see Johnson, K. H. In: The New World of Quantum Chemistry, Pullman, B. and Parr, R. G. eds., Reidel (1976), Dordrecht, p. 317 and references cited therein.
82. Kobayashi, H., Kato, H., Tarama, K. and Fukui, K., J. Catalysis 49, 294 (1977); Kobayashi, H., Yoshida, S., Kato, H., Fukui, K. and Tarama, K., Surface Science 79, 189 (1979).
83. Tanaka, K., Yamabe, T. and Fukui, K., Chem. Phys. Letters 48, 141 (1977).
84. For instance, Schrieffer, J. R. In: The New World of Quantum Chemistry, Pullman, B. and Parr, R. G. eds., Reidel, D., Dordrecht (1976), p. 305; Danese, J. B. and Schrieffer, J. R., Intern. J. Quant. Chem., Quant. Chem. Symp. 10, 289 (1976).
85. Tanaka, K., Yamabe, T., Noda, A., Fukui, K. and Kato, H., J. Phys. Chem. 82, 1453 (1978).
86. Yamabe, T., Tanaka, K., Fukui, K. and Kato, H., J. Phys. Chem. 81, 727 (1977).
87. Tanaka, K., Yamabe, T. and Fukui, K., Chem. Phys. Letters 53, 453 (1978).
88. For instance, see Ishimaru, S., Yamabe, T., Fukui, K. and Kato, H., J. Phys. Chem. 78, 148 (1974); Ishimaru, S., Fukui, K. and Kato, H., Theoret. Chim. Acta (Berl.) 39, 103 (1975).
89. Tachibana, A., Yamabe, T. and Fukui, K., J. Phys. B. Atom. Molec. Phys. *10,* 3175 (1977); Adv. Quant. Chem. II, 195 (1978).