

KENICHI FUKUI

4 October 1918 — 9 January 1998



Kunikida Doppo

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LIFE AND CAREER

Kenichi Fukui was born in Oshikuma, Nara, Japan, on 4 October 1918. He was the eldest of three boys of Ryoukichi, his father, and Chie, whose family name before marriage was Sugisawa. Ryoukichi Fukui, who graduated from the Tokyo Commercial Institute (later Hitotsubashi University), was a merchant who traded with foreign countries and also managed a factory making precision instruments. He liked fishing and often took Kenichi with him, and was a member of the National Geographic Society—the *National Geographic Magazine* was one of the most important magazines of Kenichi's childhood. Chie graduated from Nara Women's College and was an affectionate mother of her boys. She never forced them to study but provided a studious environment. For example, she bought for her children the complete works of Souseki Natsume, a famous Japanese novelist, whose books Kenichi was very fond of reading.

Shortly after Kenichi's birth, the family moved to their new house at Kishinosato, Osaka, and lived there until he was 18. In his childhood, he loved playing in the natural environment and spent almost every vacation at his mother's native house in Oshikuma. He liked walking near or sometimes far from the house. There were many ponds in the vicinity and he enjoyed fishing with his brothers. Even in Osaka, there was much in nature that entranced him. Kenichi liked collecting many different kinds of things, like postage stamps, match labels, leaves and buds of plants, and mineral stones. There were many beautiful butterflies and mysterious insects; the imaginative and sensitive heart of Kenichi was enchanted by their

beauty. This interest in nature remained with him even when he went abroad to give lectures at international symposia many years later; he was excited to catch a splendid cicada at Ryukabitos near Athens, and butterflies in Florida and Istanbul.

Kenichi entered Tamade Daini Primary School in 1925. He was not strong physically. He enjoyed field work in the summer school at the seashore to the south of Osaka. A beautiful *Halinga ornata* (*hana-densha* in Japanese) in seawater in bright summer sunshine enchanted Kenichi.

Kenichi moved to Imamiya Middle School in 1931. He joined the Biological Circle, whose senior members were experts and were good leaders. They went hiking in nearby mountains in the suburbs of Osaka and gathered many different kinds of insect. This introduced Kenichi to the works of Jean Henri Fabre, who continued to influence him through his book series *Entomological souvenirs*. Kenichi read it in the Japanese translation by Y. Yoshida and T. Hayashi and eagerly awaited the publication of each volume. The statements and observations written in this book were in harmony with his own experiences. This was in some sense a surprise for him because Osaka and Provence are so distant. Much later, Kenichi was elected a member of the International Academy of Quantum Molecular Science, whose headquarters are located in Menton, France. While attending an academy meeting, he enjoyed travelling in Provence with Tomoe, his wife, because this was the place where Fabre had spent his life with his insects. Kenichi and his wife dreamt of living in Provence after retirement, but this was not realized because the Nobel Prize caused him to be so busy.

Henri Fabre was a gifted chemist as well as an eminent entomologist. He succeeded in preparing alizarin dye from plant madder on an industrial scale, but this was not used because of the success of the synthetic method introduced by German chemists. Fabre devoted the last chapter of his *Entomological souvenirs* to this story and the last sentence was a declaration of starting again from the beginning: 'Laboremus!', and this impressed Kenichi. Chemistry did not seem to give happiness to Fabre. This cast a shadow on Kenichi's impression of chemistry. The chemistry course started in the third year of the middle school, but he did not like it mainly because of its dependence on memory work, but also partly because it did not give happiness to Henri Fabre.

Kenichi wrote at the age of 65 how important these boyhood experiences were in his becoming a natural scientist. However, in those early days he never thought of becoming a scientist, but rather a doctor of literature. His favourite subjects were history and literature. A reason for this is that his birthplace, Oshikuma, was located between Nara and Kyoto, where there are many historical monuments.

In 1935 Kenichi entered Osaka High School. He joined the Science Department and took German as a second language. In those days, students had to take one sport as a specialty and he took Japanese fencing (Kendo). Kenichi enjoyed doing exercises for this sport almost every day, but it made him tired so he did not do much study. When he started fencing he was unable to win, but one day his master said to him 'never expect to win, rather only do your best'. After taking this suggestion on board, he found he could win a match and he gradually got into this sport. It made him strong in body, but rather apart from his studies.

In the spring of 1938, his last high school year, his father visited Genitsu Kita, a relative and native of the same district of Nara and Professor of Chemistry at Kyoto University, at his home in Kitashirakawa and consulted him about the course for Kenichi after graduation from high school. He explained that his son had taken German and liked mathematics. Kita advised that both mathematics and German are important for chemistry, so 'please send your

son to my laboratory in Kyoto'. This advice was rather unexpected because it was thought in those days that mathematics was not necessary for chemistry. When Kenichi heard this advice from his father, namely 'if he likes mathematics, he should do chemistry', he immediately decided to do chemistry. Kenichi was very happy to have received such good advice and to have met such an excellent teacher.

Professor Kita was born in Nara in 1883, graduated from the Department of Applied Chemistry of the Imperial University of Tokyo in 1906 and became an associate professor in that department in 1908. After two years in Europe and America, he became a professor in the Department of Industrial Chemistry of Kyoto Imperial University in 1921. Kita was not only an eminent chemist who published more than 1000 articles, but also an excellent teacher who taught a number of leaders of chemistry in Japan, including J. Sakurada, S. Kodama, M. Horio and J. Furukawa. After his retirement from Kyoto University in 1944, he became President of Naniwa University (later Osaka Prefectural University) and a member of the Japan Academy.

Kenichi entered the Department of Industrial Chemistry, Faculty of Engineering, Kyoto Imperial University, in 1937. He would often visit Professor Kita at home where he and his wife, an excellent violinist who had played in a US orchestra and once performed for the Meiji Emperor, warmly welcomed him. Kita was a rather silent person and even looked rustic. His advice was, 'You must study basic science if you want to do excellent applied chemistry'. Although he never suggested an actual field, there was a clear recommendation to study fundamental chemistry. The Department of Industrial Chemistry emphasized applied fields of chemistry such as ceramic chemistry, electrochemistry, fermentation chemistry and the chemistries for synthetic dyes, fibres, rubbers and plastics. The lectures in the department were strongly application-oriented. Kenichi, who was oriented towards basic science, took lectures in the Faculty of Science, which was located nearby. In due time, Kenichi decided to study quantum mechanics, which was only about 12 years from its birth. There were almost no lectures on quantum mechanics, so he went to the library of the Physics Department and borrowed books. His policy was to try to understand all the equations, so he went back to the original literature. The world of atoms and molecules enchanted Kenichi. A problem was that he could not borrow books such as *Handbuch der Physik*, so he wrote the essence of the articles in his notebook. For recreation he enjoyed, once in a while, imported movies like *Under the roofs of Paris*. His undergraduate days in Kyoto gave him much pleasure.

Kenichi's method of study was to read deeply a small number of selected papers, rather than a lot of literature in a wide range of fields. The field of mathematical physics was already established. Courant & Hilbert's *The methods of mathematical physics* was one of his favourite books. He wondered then why 'mathematical chemistry' did not exist and thought that the empirical nature of chemistry should decrease through cultivating mathematical chemistry. 'Decreasing the empirical nature of chemistry' was a phrase that Professor Fukui was often to use in his lectures.

In the third undergraduate year he started graduate study under the guidance of Associate Professor Haruo Shingu, because Professor Kita was approaching retirement. This experimental study was important for his later theoretical study: different hydrocarbons showed different reactivities to hexachloroantimony, which was rather mysterious and interesting. Kenichi was also interested in the different reactivities in aromatic hydrocarbons, such as naphthalene and anthracene. This was the subject through which the frontier electron theory was first cultivated and to which the first applications of the theory were so

successfully made. It was perhaps fortunate that the results of his experimental studies could not be explained by existing theories.

Kenichi graduated from Kyoto University's Faculty of Engineering in March 1941 and entered the graduate school in the Department of Fuel Chemistry of the Faculty of Engineering. The supervisor of his graduate study was Professor Shinjiro Kodama, who was also a student of Professor Kita. Professor Kodama considered fundamental science to be important, probably even more so than Professor Kita. Kodama had studied in Germany from the age of 24 and owned many books on subjects such as quantum mechanics and electromagnetism. Kenichi was able to study basic physics in the free atmosphere of Professor Kodama's laboratory.

In August 1941, Kenichi went to the Fuel Institute of the Japanese Army in Tokyo. In 1943, he became a lecturer in the Department of Fuel Chemistry, Kyoto University, and in 1944 Associate Professor in the same department. Kenichi spent much time studying quantum mechanics. Particularly impressive to him were R.H. Fowler's *Statistical mechanics* (1936) and Hideki Yukawa's *Introduction to quantum mechanics* (1947) and *Introduction to particle physics* (1948).

The Fuel Institute was concerned with the synthesis of hydrocarbons that improve the performance of gasoline. In the USA they used 2,2,4-trimethylpentane, and Kenichi had to synthesize similar compounds from butanol that had been made by the fermentation of sugar. In September 1944 his team succeeded in this synthesis and was awarded a prize by the Army. After World War II, Kenichi returned to Kyoto University and engaged in chemical reaction design under the guidance of Professor Kodama. He worked on basic aspects of engineering in the high-pressure synthesis of polyethylene. From this emerged the subject of his doctoral thesis, namely the theoretical study of temperature distributions in the reactors of chemical industry. It was a volume of about 200 pages; when he showed it to Professor Kita, who had already retired, he only responded how thick it was! It was a hot summer in 1948 when he submitted his doctoral thesis. Three copies were required, all handwritten in those days. As his thesis was long, his wife, Tomoe, helped him to make a copy; her handwriting was mixed with his.

Tomoe (whose maiden name was Tomoe Horie) and Kenichi married in the summer of 1946. She had dreamt of becoming a scientist after reading the biography of Marie Curie, and graduated from the Physical Chemistry Department of the Imperial Women's University of Science in Tokyo. Before their marriage, Kenichi took her to a concert with all the scores of what was probably the Ninth Symphony of Beethoven. After the concert, he proudly pointed out that they did not play some parts of the symphony as written on the score. Her concern was with how he could spoil the pleasure of the concert. Those were difficult days in Japan, but Tomoe did her best to let him concentrate on science. Their son, Tetsuya, was born on 8 January 1948 and their daughter, Miyako, on 19 May 1954.

After completing his doctoral thesis, Kenichi turned to theoretical studies on chemical reactions. In those days, chemical reactions formed the major subject of the Department of Chemistry in the Faculty of Science of Kyoto University. In particular, S. Horiba, T. Lee and S. Sasaki were active in this field. This was in sharp contrast to the Faculty of Science of the University of Tokyo, where studies on molecular structure were favoured. In this atmosphere it was natural for him to take chemical reactions as his main subject. The experimental studies on the reactions of hydrocarbons that he did in his undergraduate study and in the Fuel Institute in Tokyo formed the backbone of his theoretical studies.

In 1951 Fukui was promoted to Professor in the Department of Fuel Chemistry. In February of that year a fire occurred at the department and as a result he had to share a laboratory with Professor Shingu and others. It was in this room that the frontier electron theory was born. He imagined that, in the course of a chemical reaction, the electron in an outermost molecular orbital should have an important role, as it is the outermost region of the molecule that meets the other molecule. This orbital was called a 'frontier orbital'.

Fukui first calculated the frontier electron density of naphthalene and found that the density was largest at the position where chemical reaction took place. He proceeded, with the help of Tejiro Yonezawa, who was at that time his graduate student, to study more complex hydrocarbons such as anthracene, pyrene and perylene. The frontier orbital theory correctly showed the positions of chemical attack by an electrophile such as NO_2^+ , thus giving confidence in the validity of the theory. Details of the theory are explained later in this memoir.

The collection of many experimental results and their interpretation were due to Professor Shingu, an organic chemist with a deep knowledge of the electron theory of organic reactions. They discussed the naming of the new theory and it was Shingu who suggested 'frontier' electron theory. In October 1951 the first paper of the frontier electron theory was submitted to the *Journal of Chemical Physics*; it appeared in April 1952 (1)*, with T. Yonezawa and H. Shingu as co-authors. Two years later, a second paper appeared and then the frontier electron theory was changed to the frontier orbital theory to include the lowest unoccupied orbitals in the frontier orbitals (2). Kenichi and his students T. Yonezawa, C. Nagata, H. Kato, K. Morokuma, A. Imamura and H. Fujimoto in particular developed frontier orbital theory and identified the special role of the frontier orbitals of molecules in the course of chemical reactions. Later, R.B. Woodward (For.Mem.R.S. 1956) and Roald Hoffmann (For.Mem.R.S. 1984) also considered the role of orbitals in chemical reactions (Woodward & Hoffmann 1965, 1969*a, b*). The orbital was the key common concept of their theories.

The frontier orbital theory explained not only the reactivities of hydrocarbons but also those of many types of molecule. This showed that the frontier orbital theory had a wider validity than the electron theory of organic reactions that had previously existed. Hammett's rule (Hammett 1940), one of the important consequences of the electron theory, was explained by the frontier orbital theory.

In the same year as the frontier orbital theory was published, the charge-transfer theory of Robert Mulliken appeared (Mulliken 1952). His theoretical formulation on the interaction of two molecules leading to a charge-transfer complex had some similarity to the frontier orbital theory. This similarity gave Kenichi much insight in the later development of frontier orbital theory. Mulliken visited Japan in 1953 and gave a series of lectures referring to the frontier orbital theory, thus enhancing the importance of this theory to Japanese chemists. It took about 10 years for the frontier orbital theory to be recognized worldwide.

In 1962 he received the Japan Academy Prize for the study of the electronic structure and chemical reactivity of conjugated compounds; this was 10 years after the first appearance of the frontier orbital theory. Yoshio Tanaka, Professor Emeritus of the University of Tokyo, who was one of his supporters, told him, 'This theory may even deserve the Nobel Prize'. Tanaka continued to ask him whether the frontier orbital theory was applicable to stereospecific reactions. That was three years before the Woodward-Hoffmann rule was published.

* Numbers in this form refer to the bibliography at the end of the text.

In 1964 he attended the Sanibel Symposium and met Roald Hoffmann for the first time. Hoffmann was 19 years younger than Fukui and was already well known for his extended Hückel method, a subject of his PhD dissertation. From that meeting a warm friendship continued until the end of Kenichi's life. After Sanibel, he travelled for almost two months in the USA and Europe with Tomoe. This was his first travel abroad and they celebrated their 19th wedding anniversary at a restaurant in Paris.

In 1964 P.-O. Löwdin and B. Pullman invited him to contribute a chapter to a book that was to be a tribute to Robert Mulliken at the age of 60. He accepted, and wrote a paper entitled 'A simple quantum theoretical interpretation of the chemical reactivity of organic compounds' (9). In this article he studied the Diels–Alder reaction and related for the first time the symmetries of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) to the selectivity of the reaction. This concept was shown to be important by Woodward and Hoffmann through their presentation of the theory of the conservation of orbital symmetry, the so-called Woodward–Hoffmann rule. This theory, presented in 1965, relating the chemical reactivities of molecules directly with the natures of their HOMOs and LUMOs, was quickly understood by chemists and opened a new field in organic chemistry. As a result, the frontier orbital theory, especially in its application to the Woodward–Hoffmann rule, became famous and was recognized by the joint award of the Nobel Prize for Chemistry in 1981. *Chemical and Engineering News*, published weekly by the American Chemical Society, commented as follows:

So if Fukui had not developed frontier orbital theory, Hoffmann and Woodward might not have hit upon their own theory when they did. And if Hoffmann and Woodward had not presented their ideas in simple, instantly usable form, Fukui might have been much longer in gaining recognition.

In 1970 Fukui was in Chicago for six months with Tomoe. He took the opportunity to visit R.B. Woodward at Harvard University. The purpose of his visit to Chicago was mainly to lecture for a semester in the graduate school at the Illinois Institute of Technology. It was his first graduate lecture course outside Japan and therefore he prepared hard. However, the reaction of the students was that his lectures were difficult to understand. This was also the general impression even for Japanese students in Kyoto. After a discussion with a group of the students, he agreed to make the lectures easier. It was disappointing for him. Nevertheless, he enjoyed life in Chicago, where it was possible to sample restaurants from all over the world. It was in Chicago that they experienced a tornado that hit their apartment—they saw a big tree pulled from the earth and several cars turned over like toys.

Fukui completed a small but important study in Chicago (12). It was about the definition of the chemical reaction coordinate, which he called the 'intrinsic reaction coordinate (IRC)'. He thought it necessary to define the route of a chemical reaction, and the formulation itself was quickly completed. However, anxiety came over him; his idea was so simple and obvious, and it was already about 30 years from the famous book of Henry Eyring, so surely a similar idea must have been published somewhere. He did his best to look for such a publication but failed. At the apartment, which faced west, he struggled with the anxiety about the priority of this study. Later, Tomoe told him that he was like a Deva King facing sunset and trying with all his power to produce his cerebrospinal fluid. He finally decided to submit this small article to the *Journal of Physical Chemistry*. The referee's report was fun: this article had no originality but was worthy of publication. He had never before had the experience of a paper having no originality being acceptable for publication. However, it was indeed pleasing for him that this short study turned out to initiate a series of studies by other scientists.

Fukui was a scientist with plenty of ideas, most of which came early in the morning. He suddenly woke up with an inspiration that would quickly disappear if it were not put down on paper. Such papers were always beside his bed, just like a samurai's sword, and when some inspiration came he could record it without light.

Kenichi Fukui was Chairman of the third International Congress of Quantum Chemistry held in Kyoto, and Tejiro Yonezawa was its general secretary. It was in the autumn of 1979 and Kyoto was brilliantly coloured by maple trees. Many scientists gathered from both outside and inside Japan to the Congress Hall located north of the city.

It was at about 10 p.m. on 19 October 1981, soon after his 63rd birthday, that Fukui had a telephone call from a newspaper in Tokyo asking for an interview as a Nobel laureate. He was astonished but became confident when he saw his name on television with Roald Hoffmann's. That night he had many visitors at home: cameramen, newspapermen, friends and students. Kenichi and Tomoe were surrounded by newspapermen until midnight.

On 10 December 1981 Kenichi Fukui received the Diploma and Medal of the Nobel Prize for Chemistry from King Gustav of Sweden. The prize was shared with Roald Hoffmann. The pictures on the Diploma were purple crocus flowers. At that moment he recalled the favours and the benefits that he had received from Professor Genitsu Kita and Professor Yoshio Tanaka. It was impressive for him that many important events after the ceremony were held under the auspices of the Student Union of Sweden.

After the Nobel Prize, Fukui became very busy and was constantly in the public eye in Japan. This made his life less flexible, but he still liked walking among nature and he did so early in the morning. He became President of the Kyoto Institute of Technology. As this position was not a scientific one but an administrative one, he could not have a laboratory in the university. Three years later he became President of the Institute for Fundamental Chemistry that was built for him in Kyoto with funds donated by the Japanese chemical industry. He also became chairman of many important organizations and committees, leaving little time for active science.

Fukui was frequently invited to deliver lectures, not very specific but rather general ones. In such lectures, he discussed several topics. He suggested that chemistry would become one of the most popular fields of science. Although the problem of environmental pollution damaged the image of chemistry, this had also forced chemistry and chemical industry to change. Now it was clear that without chemistry the problems of resources, energy and food that the human race must face could not be resolved. Young scientists and students should study this important subject by less empiricism and through more fundamental concepts. Advances in computer science should be of great benefit in such non-empiricism in chemistry; he proposed the name 'molecular engineering' for the field that exploits the intrinsic properties of molecules. He encouraged young scientists to be creative and a source of new science and engineering.

In the winter of 1997, cancer was diagnosed in his stomach. He immediately underwent surgery but had to return to hospital in the summer. On 9 January 1998 he died at the age of 79. His tomb is on the hillside of Higashiyama, where his teacher Genitsu Kita also lies.

RESEARCH

On graduation from Kyoto Imperial University in 1941, Kenichi Fukui was engaged in experimental research on synthetic fuel chemistry. He therefore started his research career as

an experimentalist. This might be thought to have been a diversion from the path to becoming a theoretician. However, not much time was required to make up for this because he had been immersing himself since his student days in quantum mechanics, theoretical physics and mathematics. By 1956 Fukui had built up a subgroup of theoreticians in his research group. His experience in experimental chemistry and his associations with experimentalists were in fact central to his theoretical work.

The thrust of his main contribution to chemistry can be recognized in his more than 300 publications in English, of which about 230 concern the theory of chemical reactions and related subjects. Other papers relate to the statistical theory of gelation, organic synthesis by inorganic salts, and polymerization kinetics and catalytic reactions.

One of the most important papers was his first on the theory of chemical reactions (1). He found a correlation between the reactivity of aromatic hydrocarbons to electrophilic reagents and the square of the atomic orbital coefficients of the linear combination in the HOMO. The spatial distribution of electron density in the HOMO was parallel to the order of reactivity in the molecule. A little later, a similar correlation was found with respect to the reactions with nucleophilic reagents between the reactivity and the distribution of the LUMO. The reactivity with free radicals was determined by the summed density of both the HOMO and LUMO (2).

Fukui considered this result as coming from a general feature of chemical reactions, that is, a general orientation behaviour. He attempted to extend the range of compounds to which this rule was applicable to different types, namely organic and inorganic, aromatic and aliphatic, saturated and unsaturated. He found that the range of chemical reactions thus treated covered substitutions, additions, abstractions, bond fissions, eliminations and molecular complex formation.

Fukui's 1952 paper (1) was published in the same year as Mulliken's important paper on the charge-transfer interaction in donor-acceptor complexes (Mulliken 1952). Under the influence of Mulliken's paper, Fukui gave a theoretical foundation for his findings. The basic idea was essentially the consideration of the importance of the electron delocalization between the HOMO and LUMO of reacting species. These particular orbitals are known as 'frontier orbitals'.

The frontier orbital approach was developed in various directions by Fukui's own group and by other scientists, both theoretical and experimental. Useful reactivity indices, particularly 'super-delocalizabilities', (3) were derived from the theory and applied to various special topics, for example comparison of the chemical reactivity of different molecules, polymerization kinetics and copolymer structures (4, 6), antioxidants (8) and various biochemical substances (5).

However, it was after the discovery of a relation connecting the HOMO and LUMO with stereoselective phenomena that Fukui's theory attracted more attention. In 1961 the importance of the nodal property of the frontier orbital was indicated in the study of silver complexes of aromatic compounds (7). In 1964 Fukui correlated the symmetry of the HOMO and LUMO of the reactant molecules with the occurrence of a cycloaddition reaction (9). This was a result of the simple application of the frontier orbital approach to so-called 'concerted' two-centre reactions.

A more decisive illumination of Fukui's theory was brought about by Woodward & Hoffmann (1965), who pointed out a specific control by the HOMO and LUMO for the formation of stereospecific products in thermal cyclizations and photocyclizations of conjugated polyenes. This discovery was the start of their establishing rules for stereoselection

in various concerted reactions. They interpreted all of these rules in a unified manner as the consequence of 'conservation of orbital symmetry' (Woodward & Hoffmann 1969*a, b*).

All the results explained by the Woodward–Hoffmann rules were interpreted later by Fukui through the frontier orbital approach (14, 27–29). However, there is no doubt that Fukui's work became more widely understood by the chemical community through the incisive work of Woodward and Hoffmann.

The HOMO–LUMO interaction rationale of the type made by Fukui in 1964 in respect of cyclic additions was applied later by his own group and by other chemists (Houk 1973) to a variety of chemical reactions, cyclic and acyclic additions, eliminations, rehybridizations, multicyclizations, various intramolecular rearrangements, benzyne reactions, ring openings and closures, and so on, including thermally induced and photoinduced reactions (13, 14, 20, 27–29). Particular use was made of frontier orbitals with respect to complicated regioselectivities and various sorts of secondary stereochemical effects in concerted cycloadditions. These were explained in the same unified manner by the particular interaction of the frontier orbitals. The charge and spin transfers in chemical reaction paths were discussed from the same viewpoint (17).

Fukui and his co-workers extended their orbital interaction rationale from two-orbital problems to three-orbital interactions (16). The important role of orbital mixing and polarization and that of a favourable phase relation in three-orbital interactions were derived to explain various experimental results. This theory of three-species interaction was introduced to discuss the role of catalysts in terms of HOMO–LUMO analysis (19), and the concept of 'pseudoexcitation' was applied to the interpretation of several chemical phenomena (18).

In addition to these fundamental but rather qualitative successes, Fukui and his group tried to give the frontier orbital rationale a more quantitative character (10). In 1968 a general theory of intermolecular reactions was proposed to disclose the general principles governing the reaction path, pointing out the increasing importance of the HOMO–LUMO interaction with the progress of the reaction (11). The mechanism of bond interchange essential to the occurrence of the reaction and the origin of stabilization of the reacting system along the reaction path were made clear (15).

In this connection the formulation of the reaction coordinate made by Fukui in 1970 (12) was important. The concept of the IRC was defined as the steepest-descent path from the transition state. In this way, a method was proposed for discussing the origin of the favourable or unfavourable character of a reaction path by an analysis of the potential gradient along the reaction coordinate. A method of investigating qualitatively the contribution of frontier orbitals along the reaction coordinate was provided by this formulation. By the use of the IRC concept the geometry change of reacting systems could be calculated. The process was named 'reaction ergodography' (21).

The IRC approach was extended to a wave-mechanical estimation of the absolute rate of chemical reactions (24). The case of proton migration in the enol form of malonaldehyde was used as an example (23). In relation to the IRC approach a differential geometrical study of the configuration space of chemically reacting systems was developed. 'Normal coordinates' of reacting systems were defined in a coordinate-transformation-invariant form. The 'cell' structure of that space was indicated in relation to the absolute rate calculation (24). Variational principles, including the geodesic principle implicitly involved in chemical reactions, were elucidated (25). Thus, a particular Riemannian space could be defined for any reacting system (23).

Fukui tried to combine the frontier orbital concept with the IRC approach. This attempt was successful in obtaining the frontier orbitals of interacting molecules—the interaction frontier orbitals (IFOs) (26).

The range of Fukui's research extended to many fields of molecular science that are related to chemical reactivity. These included the theories of biradicals, the behaviour of crown ether complexes, chemisorption on a solid metal surface, the formation of charge-transfer complexes, the role of solvent molecules, interatomic long-range forces, solvated electrons and the theoretical interpretation of nuclear magnetic resonance and electron spin resonance spectra. They also included the nature of some intramolecular and intermolecular bonds, electronic structures and spectra of compounds including high polymers, a theory of resonant states, the problem of complex eigenvalues and quasistationary molecular systems, some vibronic problems, and some polymers of practical importance such as linear superconductors and semiconductors and chalcogenides.

Fukui's work, particularly the frontier orbital approach, exerted a strong influence on chemists. The term 'frontier orbital' is now used in many papers without a citation of Fukui's paper. The book by Ian Fleming (F.R.S. 1993) has the title *Frontier orbitals and organic chemical reactions* (Fleming 1976). Fukui and Fujimoto summarized selected papers of Fukui in a book (33) that is useful for understanding Fukui's contributions to chemistry. A memorial volume for Fukui was published in *Theoretical Chemistry Accounts* (1999) and included a complete list of Fukui's publications in English.

Fukui did not stop studying after he retired from Kyoto University. His recent work on the IRC and IFO approaches should be mentioned (24, 26). With his co-workers he applied the IRC theory to an analysis of chemical laser systems as well as to mode-selective chemical reactions by using vibrational correlation diagrams (30). A succession of IFO plots—'IFO correlation diagrams'—is useful for visualizing the mode of formation and the breaking of chemical bonds in a reaction through a completely non-empirical calculation.

Fukui also tried to extend his theories of chemical reactions to more general rate processes. He named the resultant equation of the rate process the 'equation of wandering mutation', which was presented at the Fifth Institute for Fundamental Chemistry (IFC) Symposium in 1989 and was summarized in Japanese and English (32). This was probably the last systematic scientific study he made.

Fukui's name is appropriately associated with a useful function in density functional theory (Parr & Yang 1984). If the nuclei in a molecule give rise to a potential $V(r)$ acting on N electrons and the total ground-state electronic energy is $E[N, V(r)]$, then

$$dE = \mu dN + \langle \rho(r) dV(r) \rangle,$$

where $\mu = (\partial E / \partial N)_V$ is the chemical potential and $\rho(r)$ the electron density; the angle brackets $\langle \rangle$ denote an integral over all r ;

$$d\mu = \eta dN + \langle f(r) dV(r) \rangle,$$

where $\eta = (\partial^2 E / \partial N^2)_V$ is the hardness (equal to the inverse of the softness) and

$$f(r) = (\partial \rho(r) / \partial N)_V = \partial^2 E / \partial N \partial V(r) = (\partial \mu / \partial V(r))_N$$

is the Fukui function (Parr & Yang 1984; Parr & Parr 1999), which can be used as a reactivity index.

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We end this memoir by quoting from Kenichi Fukui's Nobel Lecture (28):

In my opinion, quantum mechanics has two different ways of making contributions in chemistry. One is the contribution to the nonempirical comprehension 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 that 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 cannot 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.

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