

Robert Mulliken and His Influence on Japanese Physical Chemistry

Noboru Hirota

Kyoto University, Japan

Introduction

Physical Chemistry underwent a transformation from a science based on thermodynamics to one based on quantum mechanics in the 1920s and the early 1930s. Although quantum mechanics was born in Germany and first applied to a chemical problem, understanding of the covalent bonding in H₂, by two physicists, Walter Heitler and Fritz London¹, the transformation in physical chemistry was mainly made in the US; some young American physical chemists were very active in applying quantum mechanics to chemical problems. Most notable among them were three Nobel Prize winning physical chemists, Linus Pauling, Robert Mulliken and Harold Urey. In particular, Linus Pauling and Robert Mulliken played the most important roles in the development of quantum chemistry in the 1920s and the 1930s. Both of them started as experimental physical chemists, Pauling as an X-ray crystallographer and Mulliken as a molecular spectroscopist, but they became pioneers in applying quantum mechanics to chemical problems. However, in their endeavors they took different approaches. Pauling advanced valence bond theory, applying it to explain a variety of chemical bonds. His famous book on the nature of chemical bonds was well received by chemists and became a classic.² On the other hand, Mulliken advanced molecular orbital theory in connection with the interpretation of the electronic spectra of small molecules³. Before World War II Pauling's valence bond theory was more popular and influential among chemists because of its appeal to chemical intuition. However, in the long run Mulliken's molecular orbital theory has made a much greater influence on chemistry as performance of electronic computer improved rapidly, while Pauling's valence bond theory eclipsed. Among quantum chemists Mulliken made the most important contributions to the transformation of chemistry in the period covering from the 1920s to the 1960s. He also presented a theory on charge transfer (CT) complexes in 1952 that has become very influential in a variety of areas of chemistry.⁴ This theory made a particularly strong impact on Japanese Physical Chemistry.

Introduction of quantum chemistry to Japan was also made by physicists. Yoshikatsu Sugiura who made an extension of Heitler-London calculation of the H₂ molecule at Bohr's Institute in Copenhagen returned to Riken in 1927, and introduced quantum mechanics to Japan. Masao Kotani's group in the Physics Department of the University of Tokyo started to evaluate molecular integrals involved in the quantum mechanical calculations of atoms and molecules before World War II, and continued their work after the war. Their efforts resulted in the publication of internationally known "*Table of Molecular Integrals*"⁵. However, physical chemists in Japan were not very active in doing theoretical work based on quantum

¹ Heitler, W., and London, F., *Z. Physik*, **44**, 455 - 4472 (1927)

² Pauling, F., "The Nature of Chemical Bonds, and the Structures of Molecules and Crystals.", Cornell Univ. Press, 1939.

³ Mulliken, R. S., *Phys. Rev.* **32**, 186 - 222 (1928)

⁴ Mulliken, R. S., *J. Am. Chem. Soc.* **74**, 811 - 825 (1952)

⁵ Kotani, M., Amemiya, A., Ishiguro, E., and Kimura, T., "Tables of Molecular Integrals", Maruzen, Tokyo, (1955)

mechanics before World War II, perhaps with an exception of Taikei Ri (later known as Taikyū Ree), assistant professor at Kyoto University, who published a paper with Henry Eyring at Princeton in 1940.⁶

After the war some young Japanese chemists began work based on quantum chemistry. Notable among them were Kenichi Fukui of Kyoto University and Saburo Nagakura of the University of Tokyo. Fukui and coworkers reported their “frontier electron theory” on chemical reactions in 1952⁷, the same year as Mulliken published his paper on charge transfer complexes. Fukui’s group found a support to their theory in Mulliken’s paper. Nagakura and coworkers studied electronic spectra of organic molecules that involve intra and intermolecular charge transfer interactions.^{8,9} They were inspired by Mulliken’s work. In 1954 Akamatsu, Inokuti and Matsunaga discovered high electrical conductivity in a complex formed between perylene and bromine.¹⁰ It was soon recognized that charge transfer interaction is involved in this complex. Thus studies of charge transfer complexes became a very popular research field in Japan.

In 1953 Kotani organized a satellite meeting on molecular physics in Nikko on the occasion of the international conference of theoretical physics held in Kyoto and Tokyo. Mulliken presented a paper on electronic spectra and molecular structures at the Nikko meeting. There he met Japanese scientists who were working on molecular electronic spectra and quantum chemistry. Since then he had close ties with Japanese physical chemists and physicists, and contributed much to the development of Japanese physical chemistry. From the mid 1950s to the 1960s a number of Japanese scientists including Nagakura worked in Mulliken’s laboratory in Chicago.

In this article we first briefly describe Mulliken’s biographical background and his work on molecular orbital theory. Then we discuss his charge transfer theory and the influence of this theory on Japanese physical chemistry.

2. Brief Summary of Mulliken’s Biographical Background^{11, 12} and Achievements¹³.

Robert Mulliken was born in Newburyport in Massachusetts on June 7, 1896. His father, Samuel P. Mulliken, was a professor of organic chemistry at the Massachusetts Institute of Technology (MIT). As a young boy Mulliken helped his father by proofreading his father’s book on organic analysis. Influenced by his father’s academic interests and the scientific ferment of the period, he developed an early interest in science. In high school, he elected the science course, which included biology, chemistry, physics, French, German, and read widely books on science. When he graduated from Newburyport High School in 1913, he was class salutatorian and delivered an essay entitled “Electrons: “What they are and what they do.” Amazingly, this topic turned out to be the target of his life-long research.

Mulliken entered MIT to study chemistry in 1913. He did senior research in organic chemistry with J. F. Norris, the result of which was published in *JACS* in 1920. He graduated from MIT in 1917, but the United States was at war and he accepted a job which later came under the Chemical Warfare Service, and worked on the poison gas research under James B.

⁶ Ri, T., and Eyring, H., *J. Chem. Phys.* **8**, 433 - 443 (1940)

⁷ Fukui, K., Yonezawa, T., and Shingu, H., *J. Chem. Phys.*, **20**, 722 - 725 (1952)

⁸ Nagakura, S., *J. Chem. Phys.* **23**, 1441- 1445 (1955)

⁹ Kuboyama, A., and Nagakura, S., *J. Am. Chem. Soc.*, **77**, 2644 - 2646 (1955)

¹⁰ Akamatsu, H., Inokuchi, H., and Matsunaga, Y., *Nature*, **173**, 168 - 169 (1954)

¹¹ Ransil, B., “Robert Mulliken” in “Nobel laureates in Chemistry 1901 - 1922”, L. K. James Ed., ACS/CHF (1993)

¹² Adams, D. L., www.chem.umass.edu/~adams/pubs/mullikenweb.pdf

¹³ Mulliken, R. S., Nobel lecture (1966), “Spectroscopy, molecular orbitals and chemical bonding” Nobelprize.org. 1966

Conant. Then after working for New Jersey Zinc Company for a while, he went to the University of Chicago to work with William Harkins in the fall of 1919. He wrote his thesis on the partial separation of mercury isotopes by irreversible evaporation. From 1922 to 1923 he continued his work on mercury isotope separation as a National Research Council Fellow. When he reapplied to the National Research Council to continue his work on the isotope separation, the Council told him to propose something different at another institution. He proposed a project to study isotope effects in molecular band spectra, especially that of BN at Harvard's Jefferson Physical Laboratory. This introduced him to the field of molecular spectroscopy. At Harvard Mulliken studied the band spectra of BN and analyzed them carefully. He found that there was a much better fit of the data with theory if the spectra were ascribed to BO rather than BN.

Mulliken made a European tour to meet European spectroscopists in the summer of 1925. He met nearly everybody in Europe who had been doing worthwhile research on band spectra as well as important scientists working on atomic spectra and quantum theory. In particular, he extensively discussed with Friedrich Hund, who was Born's assistant at that time, about molecular spectra. In 1926 he became assistant professor at New York University. Two years later he moved to the University of Chicago as associate professor. Between 1926 and 1932 Mulliken and Hund worked independently with periodic communications with each other. They developed a molecular orbital (MO) model based on the Bohr's model of the atom in which electrons, characterized by individual quantum numbers, were distributed in molecular orbitals that permeate the entire molecule^{3,14}. Further development of the MO theory was facilitated by Lennard-Jones's introduction of linear combinations of atomic orbitals (LCAO) in 1929¹⁵. It appears that his idea of molecular orbital has its root on his attempt to interpret the band structure of the electronic spectra of diatomic molecules. When he accepted the offer of the University of Chicago, he intended to continue his experimental work, but he gradually devoted himself to theoretical studies.

From 1932 Mulliken started to publish a series of fourteen papers, all titled "Electronic structures of polyatomic molecules and valence"¹⁶. In this series Mulliken used the term "orbital". He also used Hund's symbols for σ and π bonds to describe typical single and double bonds. In Paper VI¹⁷ in this series he outlined the general method of MO theory which was developed by Hund and Mulliken in 1927-28. By these publications Mulliken established the foundation of MO treatment of the electronic structures of small molecules.

Mulliken spent World War II years as an organizer and Director of the Information Division of Manhattan Project at the University of Chicago. After the war he assembled a group of students and associates, and established the Laboratory of Molecular Structure and Spectra (LMSS). Research emphasis was divided between theoretical and experimental work on molecules. In the theoretical group C. C. Roothaan developed a self-consistent field method in which each MO is constructed as LCAO.¹⁸ This LCAO-SCF method opened a way to accurate *ab initio* calculations of atomic and molecular wave functions. With rapid progress of computer technology more and more reliable and accurate calculations on molecules became feasible using MO methods. MO calculations became widely disseminated and appreciated by chemical communities. His laboratory became an international center for molecular spectroscopy and molecular calculations with many visiting scientists, research associates and students from all over the world. A number of Japanese chemists and physicists

¹⁴ Hund, F., *Z. Physik*, **40**, 742 - 764, **42**, 93 - 120 (1927)

¹⁵ Lennard-Jones, J. E., *Trans. Faraday Soc.*, **25**, 668 - 686 (1929)

¹⁶ Mulliken, R. S., *Phys. Rev.*, **40**, 55 - 62 (1932)

¹⁷ Mulliken, R. S., *Phys. Rev.*, **43**, 279 - 302 (1933)

¹⁸ Roothaan, C. C., *Rev. Mod. Phys.* **23**, 69 - 89 (1951)

visited his laboratory. Mulliken's great contribution to the developments of molecular science in Japan was well recognized; in 1984 he was decorated by the Japanese Government for his contribution to the training of Japanese spectroscopists. He received the 1966 Nobel Prize in Chemistry for "his fundamental work concerning chemical bonds and electronic structures of molecules". Mulliken died in 1986.

3. Mulliken's Charge Transfer Theory

In addition to the monumental work on molecular orbital theory Mulliken published his seminal paper⁴ on charge transfer complexes in 1952 that has made a huge impact on various fields of chemistry. The appearance of strong color on bringing together two colorless or nearly colorless compounds had been well known for many years. In the late 1940s evidence for the formation of molecular complexes between inorganic and organic molecules attracted considerable attention; complex between benzene and iodine studied by Benesi and Hildebrand,¹⁹ those between Ag^+ and aromatic or unsaturated compounds studied by Andrews and Keefer,²⁰ and such compounds as $\text{R}_3\text{N}:\text{BF}_3$ ²¹ are these examples. Mulliken proposed a simple general quantum mechanical theory to explain the stabilities and electronic spectra of such complexes in terms of the interaction of electron acceptors and donors.⁴

The wave functions for the ground (N) state of a molecular complex A:B was given as,

$$\psi_N = a\psi_0 + b\psi_1 + \dots$$

where ψ_0 is a "no-bond" structure wave function, $\psi_A\psi_B$, product of the wave function of acceptor A and donor B. ψ_1 is the wave function for the ionic state A^-B^+ formed by electron transfer from B to A. The energy of the ground state as well as the energy of formation of the complex were calculated based on the second order perturbation theory, but he mainly treated the cases in which only the first two terms are important. Then the wave function for the excited state, ψ_E , is given as,

$$\psi_E = a^*\psi_1 - b^*\psi_0$$

The existence of an intense absorption spectrum corresponding to the transition $\psi_N \rightarrow \psi_E$ was predicted and called intermolecular charge transfer spectrum. The intensity of the charge transfer spectrum is obtained from the transition moment μ_{EN} which is given by

$$\mu_{EN} = -e \int \psi_E \sum r_i \psi_N dV = ab^*(\mu_1 - \mu_0) + (aa^* - bb^*)(\mu_{01} - S\mu_0)$$

where $\mu_1 = -e \int \psi_1 \sum r_i \psi_1 dV$, $\mu_0 = -e \int \psi_0 \sum r_i \psi_0 dV$, $\mu_{01} = -e \int \psi_1 \sum r_i \psi_0 dV$, and $S = \int \psi_0 \psi_1 dV$.

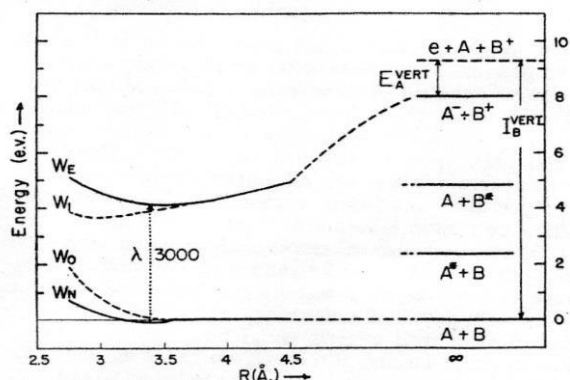


Fig.1 Potential energy curves for the benzene-iodine complex⁴.

Mulliken made detailed calculations on the stabilities and structures of the complexes and the intensities of the intermolecular charge transferred spectra for benzene-iodine (Fig. 1), Ag^+ Benzene, and $\text{BX}_3:\text{NR}_3$ type complexes. He compared the calculated results with the experimental data and showed that the agreements were satisfactory. Mulliken also reported on the hyperconjugation and the spectrum of the Benzenium ion (C_6H_7^+), prototype of aromatic carbonium ion. He

¹⁹ Benesi, H. A., and Hildebrand, J. H., *J. Am. Chem. Soc.*, **70**, 2832 - 2833 (1948), **71**, 2703 - 2707 (1949)

²⁰ Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.* **71**, 3644 - 3647 (1949), **72**, 3113 - 3116 (1950)

²¹ Brackmann, W., *Rec.trav.chim.*, **68**, 147 (1949)

calculated energy levels and spectrum, charge distribution, bond orders, resonance energy and hyperconjugation energy of the $C_6H_7^+$ ion²². This work became important in connection with Fukui's "frontier electron theory" as we see later.

4. Fukui's Frontier Electron Theory and Mulliken's Charge Transfer Theory

Kenichi Fukui, Japan's first Nobel Prize winner in chemistry, was born in Nara in 1918. He received a B.A. degree in engineering from the Department of Industrial Chemistry of Kyoto University. After two years employment in the Army Fuel Laboratory he returned to Kyoto University in 1943, and started to do applied fuel research. Gifted with mathematical ability he developed a strong interest in quantum mechanics while he was an undergraduate student, and he became a self-taught theoretical chemist. He was also interested in the reaction rate theory, and was stimulated by work being done in the Chemistry Department of the Faculty of Science. In the early 1950s, he built up a small theoretical chemistry group in the Department of Hydrocarbon Chemistry, and started to work on the electronic theory of organic reactions.

In 1952 Fukui, Yonezawa and Nagata presented the "frontier electron theory",⁷ the same year as Mulliken presented the charge transfer theory. In Fukui's first paper, they calculated the electron densities of the highest occupied π orbitals (HOMO) in fifteen aromatic hydrocarbons and examined the relationship between the electron densities and chemical reactivities, electrophilic attack of the NO_2^+ to the ring. They found that the positions at which the electron density of HOMO is the largest is most readily attacked by electrophilic or oxidizing reagents. In the subsequent paper they discussed the nucleophilic substitution reactions.²² In this case the important role of the lowest unoccupied orbitals (LUMO) in determining the reactivity was noted. HOMO and LUMO were referred as "Frontier Orbitals", and they concluded that the frontier orbitals play decisive roles in chemical reactions of hydrocarbons. However, this conclusion was radically different from the way of thinking of the leading theoretical chemists at the time including Longuet-Higgins, Coulson and Dewar; the total electron density is important in determining the chemical reactivity. In their papers theoretical arguments to justify their bold proposal were qualitative and lacked in solid theoretical foundation. Therefore, Fukui and coworkers received considerable controversial comments to their papers. In his Nobel lecture Fukui wrote as follows.²³

"But the results of such a rather "extravagant" attempt was by no means smoothly accepted by the general public of chemists. The paper received a number of controversial comments. This was in a sense understandable, because, for a lack of my experiential ability, the theoretical foundation for this conspicuous results were 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."

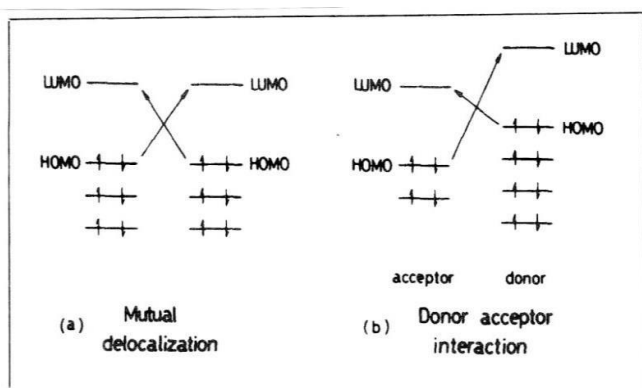


Fig 2. The mode of orbital interactions²⁴

²² Muller, N. L., Pickett, W., and Mulliken, R. S., *J. Am. Chem. Soc.*, **76**, 4770 - 4778 (1954)

²³ Fukui, K., Yonezawa, T., and Nagata, C., *Bull. Chem. Soc.* **27**, 423 - 427 (1954)

²⁴ Fukui, K., Nobel lecture, 1981, "The Role of Frontier Orbitals in Chemical Reactions", Nobelprizeorg. 1981

In both Mulliken's charge transfer theory and Fukui's frontier electron theory, HOMO – LUMO interactions shown in Fig. 2 are important. In both cases overlap of orbitals and their orientations are crucial, and HOMO and LUMO play decisive roles. Mulliken's quantum mechanical treatments must have helped Fukui to fortify the theoretical foundations of their work. In 1954 Fukui and coworkers extended frontier electron theory to explain the orientation effects in substitution and addition reactions in heteroaromatic and other conjugated molecules, including electrophilic, nucleophilic or radical type.²⁵ In the fourth paper on the frontier electron theory by Fukui and coworkers an MO-theoretical investigation on the mechanism of aromatic substitutions was presented.²⁶ Here detailed quantum mechanical calculations were made on the transition state complexes during the course of reaction which are similar to the benzenium ion discussed by Mulliken and coworkers.²² The role of charge transfer in the process of the reaction was discussed in great detail.

Though the criticism to Fukui's frontier electron theory continued through 1950s,²⁷ the theory gradually gained world-wide recognition as his group extended its applicability to a wide variety of reactions. The advent of the Woodward-Hoffman rule in 1965²⁸ was decisive in bringing complete recognition. In 1964 Fukui pointed out the importance of the symmetries of the frontier orbitals in the cyclization reaction of diene and dienophile.²⁹ This preceded the Woodward-Hoffman rule. The pioneering role that the frontier electron theory had played in the development of the electronic theory of organic reactions was fully appreciated. Fukui was awarded Nobel Prize in Chemistry in 1981 together with Roald Hoffman.

5. Influence on the Molecular Spectroscopy in Japan

Molecular spectroscopy in Japan gained international reputation under the leadership of Sanichiro Mizushima at the University of Tokyo before World War II. They developed infrared and Raman studies on molecular structures. In particular, the work done by Mizushima and Morino on the rotational isomerism of dichloroethane^{30,31} was internationally acclaimed. After World War II a group of young physical chemists in Tokyo became interested in the electronic structures of molecules, and started active research in this field. The leader of this group was Saburo Nagakura who was a student of Mizushima, but was more interested in the electronic structures of molecules rather than the geometric structures. He was interested in the colors of molecules and led to study electronic spectra of aromatic compounds. From 1952 Nagakura's group started to publish papers on the electronic spectra of substituted benzenes and unsaturated compounds containing nitro or carbonyl group.³¹ They interpreted the strong absorption bands in the near UV region as arising from the transitions between two energy levels produced by the interaction of the highest occupied levels of the electron donating group with the lowest vacant levels of the electron accepting group, which are regarded as intramolecular charge transfer bands in analogy with Mulliken's intermolecular charge transfer bands.^{32–35}

²⁵ Fukui, K., Yonezawa, T., Nagata C., Shingu, H., *J. Chem. Phys.*, **22**, 1433 - 1443 (1954)

²⁶ Fukui, K., Yonezawa, T., Nagata, C., *J. Chem. Phys.*, **27**, 1247 - 1259 (1957)

²⁷ Fukui, K., Yonezawa, T., Nagata, C., *J. Chem. Phys.* **28**, 550 -551 (1959) and references therein.

²⁸ Woodward, R., Hoffman, R., *J. Am. Chem. Soc.* **87**, 395 – 396, 396 -397, 2045 – 2046, 2046 - 2048 (1965),

²⁹ Fukui, K., in "Molecular Orbitals in Chemistry, Physics and Biology", ed. by Lowdin, P –O., Pullman, B., Academic Press, New York, p. 513 (1964)

³⁰ Mizushima, S., Morino, Y., and Takeda, M., *J. Chem. Phys.* **9**, 826 (1941)

³¹ Mizushima, S., Morino, Y., *Bull. Chem. Soc. Japan*, **17**, 94 - 99 (1942)

³² Nagakura, S., *Bull. Chem. Soc. Jpn.*, **25**, 164 - 168 (1952)

³³ Nagakura, S., and Tanaka, J., *J. Chem. Phys.* **22**, 236 - 240 (1954)

³⁴ Nagakura, S., *J. Chem. Phys.*, **23**, 1441 - 1445 (1955)

³⁵ Tanaka, J, and Nagakura, S., *J. Chem. Phys.* **24**, 1274 - 1275 (1956)

Nagakura's group also studied a variety of electron donor-accepter complexes. In 1955 he and Kuboyama reported on the determination of binding energies of molecular complexes formed between p-benzoquinone and various aromatic substances such as hydroquinone and phenol.⁹ Subsequently Nagakura studied the complex formation between iodine and triethylamine spectrophotometrically and determined thermodynamic quantities (ΔH and ΔS) for the complex formation. This work was submitted in 1957 while he was staying in Mulliken's laboratory.³⁶

Nagakura and his coworkers made numerous contributions to the studies of charge transfer complexes, but here we only mention the observation of excited triplet states of some charge transfer (CT) complexes as a particularly noteworthy contribution. In 1967 Nagakura's group reported phosphorescence spectra of the CT complexes formed between 1,2,4,5-tetracyanobenzene (TCNB) and benzene or methyl-substituted benzenes.³⁷ From the EPR spectra they could verify the existence of the excited triplet states of the CT complexes, and determined the degree of the CT character of the triplet state.³⁸

In a tribute to a collection of selected papers of Nagakura, Mulliken wrote in 1980 as follows³⁹,

“For nearly thirty years, Nagakura and his collaborators at frequent intervals have published important experimental and theoretical papers on the structure and spectra of molecules and molecular complexes. They have dealt with large variety of molecules and of complexes for themselves and both in solution at ordinary temperature and in rigid matrices and crystals. In the course of this work, Professor Nagakura has trained many good people who have afterward gone on to do notable work themselves.”

Studies of electronic spectra and electronic structures of molecules were also pursued by many other groups and became a very active field of physical chemistry research in Japan in the 1950s and the 1960s.

6. Studies of Organic Conductors

In concluding this article we briefly discuss the work on the organic conducting material that is also related to Mulliken's charge transfer work. In 1954 H. Akamatsu, H. Inokuchi and Y. Matsunaga reported in *Nature* that the complex formed between perylene and bromine shows high electric conductivity comparable to that of some metals.¹⁰ This was an epoch making discovery in the studies of organic conductors. It is interesting to note that their paper did not refer to Mulliken's 1952 paper explicitly, and only stated that the high electric conductivity was ascribed to “some particular electronic state”, though Mulliken is now considered as the pioneer in the field of organic conductors. Therefore, it appears that their finding was made during the course of research on organic semiconductors without paying attention to the charge transfer process. However, the charge transfer character of the complex must have been recognized soon. Unfortunately, the perylene-bromine complex was unstable, and the studies of conducting charge-transfer complexes did not progress much until the discovery of high conductivity of TCNQ (tetracyanoquinodimethane) complexes in 1972³⁹. Organic metals made of charge transfer complexes have been investigated extensively in Japan since then. This area of research attracted many researchers as an interesting interdisciplinary area between physics and chemistry. The discovery that some organic metals

³⁶ Nagakura, S., *J. Am. Chem. Soc.*, **80**, 520 - 524 (1958)

³⁷ Iwata, S., Tanaka, J., and Nagakura, S., *J. Chem. Phys.* **47**, 2203 - 2209 (1967)

³⁸ Hayashi, H., Iwata, S., and Nagakura, S., *J. Chem. Phys.* **50**, 993 - 1000 (1969)

³⁹ Selected Papers of Saburo Nagakura (1981): A commemorative volume published on the occasion of his retirement from the University of Tokyo and Riken.

⁴⁰ Ferraris, J. P., Cowen, D. O., Walaska, V., Perlstein, J. H., *J. Am. Chem. Soc.*, **95**, 948 - 949 (1973)

become superconductive at very low temperature further stimulated the research activity of this area.

The 2000 Nobel Prize in Chemistry was awarded to A. Heeger, A. McCdiarmid and H. Shirakawa for their discovery of conducting polymers. Although the success of the production of trans-polyacetyrene film by Shirakawa⁴¹ was the first key step to the development of the conductive polymers, the breakthrough was brought about by the doping of bromine to the polyacetyrene film that was done in collaboration with McCdiarmid and Heeger in the US.⁴² This is the case in which collaboration among researchers in different fields resulted in an excellent result. However, this collaboration was spurred when McCdiarmid accidentally met Shiwakawa on his visit to Tokyo Institue of Technology where Shirakawa was working at the time. This author feels that the doping experiment could have been done earlier in Japan, if the communication between synthetic polymer chemists and physical chemists was much better in Japan at that time, because the doping of bromine to polyacetyrene was so closely related to the pioneering work done by Akamatsu, Inokuchi and Matsunaga in 1954.

7. Concluding Remarks

In this article we mainly focused on the influence exerted by Mulliken's charge transfer theory on the work by Fukui and Nagakura in the 1950s and the 1960s. The charge transfer theory has become the key concept in understandig many phenomena in wide areas of chemistry. It played a major role in the tranformation of chemistry in the 1950s and 1960s. Mulliken's work on the charge transfer theory was not mentioned explicitly in the Nobel citation, but its impact was enormous.

⁴¹ Ito, T., Shirakwa, H., Ikeda, S., *J. Polym. Sci., Poly. Chem.Ed.* **12**, 11 (1974)

⁴² Shirakawa, H.,Loius, E. J., MacDiarmid, A. G.,Chiang, C. K., and Heeger, A. J., *J. Chem.Soc. Chem. Comm.* 578 - 580 (1977)