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An MO-theoretical Interpretation of the Nature of Chemical Reactions. I. Partitioning Analysis of the Interaction Energy*¹

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The molecular interaction energy, without considering the nuclear configuration change, is discussed by partitioning it into the Coulomb, exchange, delocalization, and polarization terms. A succinct approximate expression for each term is derived, and its magnitude is discussed. The expressions obtained as the second-order perturbation terms for the delocalization and the polarization energies are in accord with those of the well-established reactivity indices, the delocalizability, and the self-atom polarizability respectively. The chemical reactivity can thus be measured by the combined sum of these four terms. In usual ionic reactions the Coulomb and the delocalization terms are more important than the exchange and the polarization terms respectively.

The molecular orbital (MO) approach can be used to interpret the chemical reactivity of organic molecules, both saturated¹⁾ and unsaturated.²⁾ Most of these MO criteria for the chemical reactivity are based on the use of various reactivity indices defined as the theoretical quantities of isolated reactant molecules, each based on an appropriately-assumed

model for the chemical reaction. The classification of these indices has tentatively been made by dividing them into three groups, the static, the localization, and the delocalization approaches.³⁾ The comparison of these approaches appeared promising for acquiring knowledge of the reaction mechanism.²⁾ However, the semiempirical character of calculation made an absolute comparison of the various methods difficult. In addition, as a result of the existence of several theoretical correlations among the reactivity indices,⁴⁾ no unequivocal conclusion has yet been obtained. Although the formal introduction of

*¹ The basic idea of this paper was presented by one of the present authors (K.F.) at the International Summer School of Quantum Chemistry, Istanbul, August, 1964, while a skeletal presentation was made in K. Fukui, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 794 (1966).

1) K. Fukui, "Modern Quantum Chemistry," Vol. I, ed. by O. Sinanoğlu, Academic Press, New York (1965), p. 49, and the references cited therein.

2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York (1961), Chapter 11, and the references cited therein.

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

4) K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957), and the references cited therein.

the "transition-state" concept in the absolute-rate theory has doubtless been illuminating, the basic principle of the activated complex formation is not yet clear. The nature of chemical reactions, therefore, still remains obscure in many details from the quantum-mechanical point of view.

It is the aim of the present approach to make a contribution to this problem through a formulation of the energy of chemical interaction, to derive at the same time a prototype of several reactivity indices in a unified manner, and also to discuss the characteristic features of the reaction path on the potential energy surface. The method is based chiefly on the Roothaan-type linear combination of atomic orbitals (LCAO) MO approach, with some use of the configuration interaction (CI) procedure.⁵⁾

Electron Delocalization in the Chemical Interaction. Since 1933⁶⁾ several theories were proposed one after another to explain the chemical reactivity of conjugated molecules along the static⁶⁻⁸⁾ and the localization approaches.⁹⁾ In 1952 the "frontier electron" concept¹⁰⁾ was put forth; it pointed out that the electrophilic aromatic substitution should take place at the carbon atom of the largest density of the highest energy electrons. Similarly, the nucleophilic replacement was later shown to occur at the position of the largest density of the lowest unoccupied MO. In comparison with the theoretically well-established character of the other reactivity theories then existing, the lack of a solid physical foundation for the infant frontier electron theory suggested instead the possibility of the involvement of a new principle for the mode of chemical interaction.

It was coincidentally in the same year that the elegant theory of the charge-transfer interaction was developed by Mulliken with regard to the molecular complex formation between a donor and an acceptor.¹¹⁾ In this connection, the "overlap and

orientation" principle was proposed;¹²⁾ it considered only the overlap interaction between the highest energy occupied MO of the donor and the lowest energy unoccupied MO of the acceptor.

Since the behavior of the frontier electrons was attributed to some type of electron delocalization between the reactant and the reagent,¹³⁾ it was natural for the charge-transfer mechanism and the overlap and orientation principle to be connected to the problem of ionic reactions. Brown combined the charge-transfer theory with the frontier electron concept to derive a consistent theory of chemical reactivity.¹⁴⁾ All of these treatments¹⁰⁻¹⁵⁾ together may be termed the "delocalization approach" to chemical reactivity theory.

Applying the donor and acceptor concept to the substitution reactions in conjugated molecules, the electrophilic and the nucleophilic reactions were discussed from a unified point of view. Thus, the highest occupied (HO) MO of the donor molecule and the lowest unoccupied (LU) MO of the acceptor molecule were considered to behave as frontier orbitals in ionic reactions,¹⁰⁾ not only in substitutions but also in additions, and even in multicentric reactions.⁶⁾ When the overlap and orientation principle was applied to odd-electron molecules or radicals, the half-occupied nonbonding (NB) MO was responsible for the reactive interaction. A similar behavior of these particular MO's has also been pointed out in nonplanar saturated molecules.¹¹⁾ In addition, the conspicuous property of HO and LU in determining the steric course of organic reactions has been discovered and has attracted much attention.^{8,16)}

In this view, it may be of interest to discuss the energy of reacting systems by dividing it into various kinds of interactions. Such a treatment will be useful in helping us to understand what factor is really important in the chemical reaction.

Interaction with No Nuclear Configuration Change

The energy of the interaction between two independent systems, in which, tentatively, no nuclear configuration change is considered, is defined by the following equation:

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

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

13) K. Fukui, T. Yonezawa and C. Nagata, *This Bulletin*, **27**, 423 (1954); K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **27**, 1247 (1957).

14) R. D. Brown, *J. Chem. Soc.*, **1959**, 2232; cf. K. Fukui, K. Morokuma, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **32**, 1743 (1960).

15) S. Nagakura and J. Tanaka, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 933 (1954); T. Yonezawa, K. Hayashi, C. Nagata, S. Okamura and K. Fukui, *J. Polymer Sci.*, **14**, 312 (1954), and other, related papers cited in Refs. 2 and 3.

16) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2511 (1965).

5) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951). Longuet-Higgins and Murrell applied the concept of configuration interaction in discussing the electronic spectra of composite alternant hydrocarbons. They introduced the idea of polarization and charge-transfer interaction between the two fragments of a composite molecule. H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Murrell, *ibid.*, **A68**, 969 (1955).

6) L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

7) T. Ri and H. Eyring, *ibid.*, **8**, 433 (1940); T. Ri, *Rev. Phys. Chem. Japan*, **17**, 1, 16 (1943); A. Pullman and B. Pullman, *Experientia*, **2**, 364 (1946); M. J. S. Dewar, *Trans. Faraday Soc.*, **42**, 764 (1946).

8) a) C. A. Coulson, *Discussions Faraday Soc.*, **2**, 9 (1947); *J. chim. phys.*, **45**, 243 (1948); b) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)* **A191**, 39; **A192**, 16 (1947); other papers cited in Ref. 3.

9) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942); M. J. S. Dewar, *ibid.*, **74**, 3357 (1952).

10) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); see also the subsequent papers: K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *ibid.*, **22**, 1433 (1954), and the papers cited in Ref. 3.

$$\Delta W = W - (W_{A0} + W_{B0}) \quad (1)$$

where ΔW is the interaction energy, W_{A0} and W_{B0} being the energies of the initial stationary states of two isolated systems, A and B , and W , the lowest total energy of the two mutually-interacting systems. The energies of all the systems were calculated in the frame of the Born-Oppenheimer approximation¹⁷⁾ and obtained in the form of the adiabatic potential.

The Hamiltonian operator of the combined system in atomic units is:

$$H = \sum_{\lambda} H(\lambda) + \sum_{\lambda < \lambda'} \frac{1}{r_{\lambda\lambda'}} + \sum_{\gamma < \gamma'} \frac{Z_{\gamma} Z_{\gamma'}}{R_{\gamma\gamma'}}$$

$$H(\lambda) = -\frac{1}{2} \Delta(\lambda) + V(\lambda)$$

$$V(\lambda) = V_A(\lambda) + V_B(\lambda)$$

$$V_A(\lambda) = -\sum_{\alpha} \frac{Z_{\alpha}}{r_{\lambda\alpha}}, \quad V_B(\lambda) = -\sum_{\beta} \frac{Z_{\beta}}{r_{\lambda\beta}} \quad (2)$$

in which:

$H(\lambda)$: One-electron Hamiltonian operator of the electron λ .

$Z_{\alpha}, Z_{\beta}, Z_{\gamma}$: The positive charges of the nuclei α, β , and γ , which specify their belonging to the system A , the system B , and the combined system, AB , respectively.

$r_{\lambda\lambda'}$: The distance between the two electrons λ and λ' .

$r_{\lambda\alpha}$, etc.: The distance of the electron λ from the nucleus α , etc.

$R_{\alpha\alpha'}$, etc.: The distance between the nuclei α and α' , etc.

The unperturbed normalized wave-functions of the A and B systems are assumed to be represented in terms of Slater determinants composed of orthonormal spin-orbitals with LCAO MO spatial functions, which are Roothaan-type SCF (self-consistent-field) MO's with respect to the *ground state* of each isolated system.¹⁸⁾ The wave-functions of an excited or charge-transferred configuration may be made up of the MO's associated with the realistic and non-realistic roots of the Fock equation for the ground state. Therefore, all of the MO's are definite and fixed, with a given nuclear configuration in each isolated system.

The spatial parts of LCAO MO are represented by:

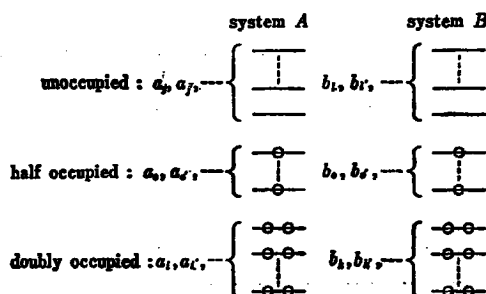
$$a(1) = \sum_i C_i t(1) \quad \text{for the system } A \quad (3a)$$

and

$$b(1) = \sum_u C_u u(1) \quad \text{for the system } B \quad (3b)$$

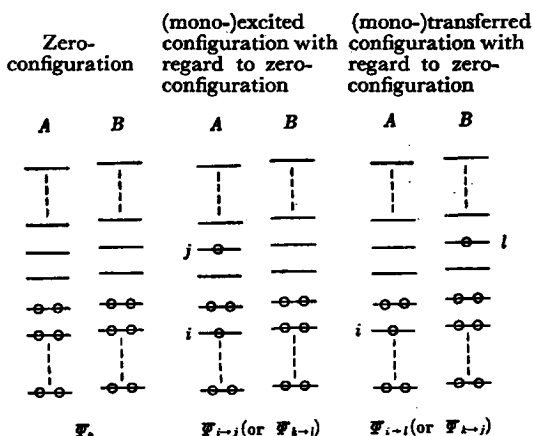
where t and u are the AO's belonging to the nuclei of A and B respectively. No particular restriction is placed on the type of these AO's. Usually they may be taken to be Slater-type or Gaussian AO's. However, it is often convenient for the later discussion of reactivity criteria to employ the valence atomic orbitals (VAO's).¹⁹⁾ Our present purpose allows us to take all functions as real.

The occupied and unoccupied MO's in the ground state are distinguished in the following way:²⁰⁾



The configurations to be taken into account are as follows:

The electron configuration of the combined system $A \cdots B$



The perturbed normalized wave-functions of the combined-system Ψ_J 's are constructed by means of

17) M. Born and J. R. Oppenheimer, *Ann. Physik*, **34**, 457 (1927).

18) Either A and B , or both, may be an odd-electron system. For such a system the "restricted" open-shell SCF MO theory (e.g., see G. Berthier, "Molecular Orbitals in Chemistry, Physics, and Biology," ed. by P.-O. Löwdin and B. Pullman, Academic Press, New York (1964), p. 57) should be applied to compose the wave-function. A calculation similar to the present one was early made by Mori (Y. Mori, *This Bulletin*, **35**, 1584 (1962)) with respect to the interaction between a molecule and a radical.

19) K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962); compare R. McWeeny, *ibid.*, **32**, 335 (1960).

20) For the presentation of an "unoccupied" MO to interact with another molecule, the Roothaan LCAO MO approach, with a basis set of a limited number of AO's chosen so as to be suitable for describing the occupied MO's is not necessarily appropriate.

the Slater determinants, composed of a_i 's, a_j 's, b_k 's, and b_l 's according to each electron configuration. The subscript J stands for all configurations, 0, $i \rightarrow j$, $k \rightarrow l$, $i \rightarrow l$, $k \rightarrow j$, and other highly-excited or transferred ones, such as $(i \rightarrow j, i' \rightarrow j')$, $(i \rightarrow j, i' \rightarrow l)$, $(i \rightarrow l, i' \rightarrow l')$, and so on.²¹⁾ The wave-function Ψ_J may further be specified by the superscript $(2S+1)$ and the subscript M_S as represented by $^{2S+1}_{M_S}\Psi_J$, where S and M_S designate the usual total spin quantum numbers. For instance, $^3\Psi_{i \rightarrow l}$ is represented by:

$$\frac{1}{\sqrt{2}}[NA|a_1\bar{a}_1a_2\bar{a}_2\cdots a_{i-1}\bar{a}_{i-1}a_ia_{i+1}\bar{a}_{i+1}\cdots \\ a_n\bar{a}_nb_1\bar{b}_1\cdots b_m\bar{b}_mb_l| + NA|a_1\bar{a}_1a_2\bar{a}_2\cdots \\ a_{i-1}\bar{a}_{i-1}\bar{a}_ia_{i+1}\bar{a}_{i+1}\cdots a_n\bar{a}_nb_1\bar{b}_1\cdots b_m\bar{b}_mb_l|]$$

where NA signifies the normalization-antisymmetrization operator; the nonbarred and barred MO's represent the spin-orbitals with spin-functions of α and β respectively, and n and m indicate the number of doubly-occupied MO's of A and B respectively in the zero-configuration.

The secular determinant is represented by:

$$\begin{vmatrix} H_{I,I} - E & H_{I,J} - S_{I,J}E \cdots \\ H_{J,I} - S_{J,I}E & H_{J,J} - E \cdots \\ \cdots & \cdots \end{vmatrix} = 0 \quad (4)$$

where the subscript I signifies the initial J , and where:

$$H_{J,J'} = \int \Psi_J^* H \Psi_{J'} d\tau \\ S_{J,J'} = \int \Psi_J^* \Psi_{J'} d\tau$$

The orders of magnitude of the overlap integrals are estimated as:

$$\begin{aligned} S_{0,i \rightarrow l} &= S_{0,k \rightarrow j} = O(s_{ab}) \\ S_{0,i \rightarrow j} &= S_{0,k \rightarrow l} = S_{i \rightarrow l, k \rightarrow j} = S_{i \rightarrow j, k \rightarrow l} = O(s_{ab}^2) \\ S_{i \rightarrow j, i' \rightarrow l} &= S_{i \rightarrow j, k \rightarrow j'} = S_{i \rightarrow l, k \rightarrow l'} \\ &= S_{k \rightarrow j, k' \rightarrow l} = O(s_{ab}^3) \\ S_{i \rightarrow j, i' \rightarrow j'} &= S_{k \rightarrow l, k' \rightarrow l'} = O(s_{ab}^4) \\ S_{i \rightarrow j, (i \rightarrow j, i' \rightarrow l)} &= S_{i \rightarrow j, (i \rightarrow j, k \rightarrow j')} \\ &= S_{i \rightarrow j, i \rightarrow l} = S_{i \rightarrow j, k \rightarrow j} = O(s_{ab}) \\ S_{i \rightarrow j, (i \rightarrow j, i' \rightarrow j')} &= S_{i \rightarrow j, (i \rightarrow j, k \rightarrow l)} \\ &= S_{i \rightarrow j, i' \rightarrow j} = O(s_{ab}^2) \end{aligned}$$

and so forth, where s_{ab} represents an overlap integral of an MO of the system A and an MO of the system B . The general relation is given by:

21) The wave-functions for these electron configurations should be regarded as those adopted to describe the perturbed wave-function in terms of that of the isolated reactant molecules, and not necessarily as corresponding to any realistic "excited" or "transferred" states.

$$S_{J,J'} = O(s_{ab}^\nu) \quad (5)$$

in which ν is the minimum number of electron transfers between A and B required to shift the electron configuration from J to J' .

In order to calculate W in Eq. (1), which is given by the lowest root of the secular equation (4), it is assumed that the lowest $H_{J,J}$ is $H_{I,I}$ and that no others are equal to $H_{I,I}$.²²⁾ On the basis of the second assumption, that $S_{J,J'}$ and $H_{J,J'}$ ($J \neq J'$) are small, W can be expanded in approximately the following form:

$$W = H_{I,I} - \left(\sum_p^{\text{monotr.}} + \sum_p^{\text{monoex.}} + \sum_p^{\text{ditr.}} + \sum_p^{\text{monotr.-monoex.}} \right. \\ \left. + \sum_p^{\text{diex.}} + \cdots \right) \frac{|H_{I,p} - S_{I,p}H_{I,I}|^2}{H_{p,p} - H_{I,I}} + \cdots \quad (6)$$

where monotr., diex., etc. imply monotr., diexcited, etc. configurations with respect to the initial configuration, I .²³⁾ The third term ($+\cdots$) designates the remaining terms, which cover the difference from the exact root of Eq. (4).

If it is assumed¹²⁾ that the interaction between A and B is not yet very strong and that $H_{I,p}$ is almost linear with $S_{I,p}$, it follows that, in light of Eq. (5), the terms from monotr., diex., etc. configurations will possess magnitudes of the order of s_{ab}^2 , and that the monoex. and the ditr. terms are of s_{ab}^4 , the monotr.-monoex. term is of s_{ab}^6 , and so on. In addition to this, if SCF MO's are employed, the well-known Brillouin theorem²⁴⁾ makes the $H_{I,p}$ values of monoex. terms small. Moreover, the denominator of the second term, $H_{p,p} - H_{I,I}$, can usually not be small in excited configuration terms, while in transferred configuration terms it can be, and sometimes, as in Eq. (7'), even a first-order term appears in place of the second-order transferred configuration terms of Eq. (6). In these circumstances the monotr.-transferred term will become uniquely important.

22) This assumption reflects the adiabaticity requirement for the interaction. There are two other possibilities. In one the lowest $H_{J,J}$ is $H_{I,I}$ and the other $pH_{J,J}$'s ($H_{1,1}$, $H_{2,2}$, ..., $H_{q,q}$, ..., $H_{p,p}$) are equal to $H_{I,I}$, where the suffix q stands for one of the monotr. configurations with reference to I . In this case the equation corresponding to Eq. (7) becomes:

$$W = H_{I,I} - \left\{ \sum_{q=1}^p |H_{I,q} - S_{I,q}H_{I,I}|^2 \right\}^{1/2} + \cdots \quad (7')$$

The other is the case in which the lowest $H_{J,J}$ is not $H_{I,I}$ but $pH_{C,C}$'s (H_{C_1,C_1} , H_{C_2,C_2} , ..., H_{C_q,C_q} , ..., H_{C_p,C_p} , ...) of an equal energy, where C_q stands for one of the monotr. configurations of I . In this case

$$W = H_{C,C} - \frac{\sum_{q=1}^p |H_{I,C_q} - S_{I,C_q}H_{C,C}|^2}{H_{I,I} - H_{C,C}} + \cdots \quad (7'')$$

23) When the initial configuration is an excited one, the term "excited" configuration should include "di"-excited configurations, too.

24) L. Brillouin, *Actualités sci. et ind.*, **71** (1933); **159** (1934).

Thus, if we take only the terms not smaller than s_{ab}^2 , namely, the monotr transferred terms in the second term of Eq. (6), we get:

$$W = H_{I,I} - \sum_{p=1}^N \frac{|H_{I,p} - S_{I,p}H_{I,I}|^2}{H_{p,p} - H_{I,I}} \quad (7)$$

where p stands for the p th monotr transferred configuration with reference to I , and where N is the number of monotr transferred configurations.

Combined Reactivity Index

The interaction energy, ΔW , in Eq. (1), appropriately calculated with respect to a given nuclear configuration, will serve as a reasonable measure of

the stability of that configuration. A comparison of ΔW with the various nuclear configurations which are possible in a given chemical interaction will make it possible to discuss the preferred orientation theoretically. Thus, ΔW can be a general scale of reactivity. The singlet interaction energy,²⁵ ΔW , of Eq. (1), which has reference to the initial state, with a zero-configuration composed of two even-electron ground-state systems, is written by Eq. (6) as:

$$\Delta W = \varepsilon_0 - D - \Pi \quad (8)$$

where:

$$\varepsilon_0 = H_{0,0} - (W_{A0} + W_{B0}) \quad (8a)$$

$$D = \sum_i^{\text{occ}} \sum_l^{\text{uno}} \frac{|H_{0,i \rightarrow l} - S_{0,i \rightarrow l}H_{0,0}|^2}{H_{i \rightarrow l, i \rightarrow l} - H_{0,0}} + \sum_k^{\text{occ}} \sum_j^{\text{uno}} \frac{|H_{0,k \rightarrow j} - S_{0,k \rightarrow j}H_{0,0}|^2}{H_{k \rightarrow j, k \rightarrow j} - H_{0,0}} \quad (8b)$$

$$\Pi = \sum_i^{\text{occ}} \sum_j^{\text{uno}} \frac{|H_{0,i \rightarrow j} - S_{0,i \rightarrow j}H_{0,0}|^2}{H_{i \rightarrow j, i \rightarrow j} - H_{0,0}} + \sum_k^{\text{occ}} \sum_l^{\text{uno}} \frac{|H_{0,k \rightarrow l} - S_{0,k \rightarrow l}H_{0,0}|^2}{H_{k \rightarrow l, k \rightarrow l} - H_{0,0}} \quad (8c)$$

Coulomb and Exchange Interaction Terms. Among the three terms on the right side of Eq. (8), ε_0 is a first order term which arises from the Coulomb and the exchange interaction terms between A and B : it can be calculated easily as:

$$\varepsilon_0 = \varepsilon_Q + \varepsilon_K \quad (9)$$

where the Coulomb interaction energy, ε_Q , is:

$$\varepsilon_Q = 2 \sum_i V_{Bii} + 2 \sum_k V_{Akk} + 4 \sum_i \sum_k (ii|kk) + \sum_\alpha \sum_\beta \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \quad (10)$$

and where the exchange interaction energy, ε_K , is:

$$\varepsilon_K = -2 \sum_i \sum_k [(ik|ki) + s_{ik}[V_{ik} + \sum_{i'} \{2(ik|i'i') - (ii'|i'k)\} + \sum_{k'} \{2(ik|k'k') - (ik'|k'k)\}]] \quad (11)$$

in which:

$$V_{Bii} = \int a_i(1)V_B(1)a_i(1)dv(1), \text{ etc.}$$

$$V_{ik} = \int a_i(1)V(1)b_k(1)dv(1), \text{ etc.}$$

$$(ij|kl) = \int a_i(1)b_k(2) \frac{1}{r_{12}} a_j(1)b_l(2)dv(1)dv(2), \text{ etc.}$$

$$s_{ik} = \int a_i(1)b_k(1)dv(1), \text{ etc.}$$

If we here employ the Mulliken approximation:²⁶

$$\int \dots \int t(1)t'(1)f \dots dv(1) \dots \cong \frac{1}{2}s_{tt'} \left\{ \int \dots \int t(1)t(1)f \dots dv(1) \dots + \int \dots \int t'(1)t'(1)f \dots dv(1) \dots \right\}$$

we can easily obtain:²⁷

$$\varepsilon_Q \cong \sum_i N_{Ai} v_{Bii} + \sum_u N_{Bu} v_{Auu} + \sum_i \sum_u N_{Ai} N_{Bu} (ti|uu) + \sum_\alpha \sum_\beta \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \quad (12)$$

25) The term "singlet interaction" signifies an interaction of two systems, A and B , with a conservation of the total spin zero. Similarly, "doublet interaction" and "triplet interaction" will later be used in the cases of the interaction of a radical with a molecule or with a radical.

26) R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949).

27) In the doublet interaction between an even-electron system (A) and an odd-electron system (B), a similar equation is obtained:

$$\begin{aligned} \varepsilon_Q &= 2 \sum_i V_{Bii} + 2 \sum_k V_{Akk} + V_{A0'0'} \\ &+ 4 \sum_i \sum_k (ii|kk) + 2 \sum_i (ii|o'o') \\ &+ \sum_\alpha \sum_\beta \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \cong \sum_\alpha \sum_\beta \frac{(Z_\alpha - N_\alpha)(Z_\beta - N_\beta)}{R_{\alpha\beta}} \end{aligned} \quad (12')$$

The singlet and the triplet interactions between two odd-electron systems give an analogous relation.

where N_{At} is the population of the t th AO of the isolated system, A , and is given by:

$$N_{At} = 2 \sum_i^{\text{occ}} \sum_{i'} C_i^{(i)} C_{i'}^{(i)} s_{ti'}$$

and:

$$v_{Btt} = \int t(1) V_B(1) t(1) dv(1) = \sum_{\beta} v_{\beta tt}, \text{ etc.},$$

in which $C_i^{(i)}$ means the coefficient of Eq. (3a) for MO a_i , and in which

$$s_{ti'} = \int t(1) t'(1) dv(1)$$

$$v_{\beta tt} = - \int t(1) \frac{Z_{\beta}}{r_{1\beta}} t(1) dv(1), \text{ etc.}$$

Further approximation which puts

$$v_{\beta tt} \cong - \frac{Z_{\beta}}{R_{\alpha\beta}}$$

etc., where α denotes the nucleus to which the t th AO belongs, may be possible if the distance between A and B is not very short. This approximation at once gives rise to the succinct expression:

$$\epsilon_Q \cong \sum_{\alpha} \sum_{\beta} \frac{(Z_{\alpha} - N_{\alpha})(Z_{\beta} - N_{\beta})}{R_{\alpha\beta}} \quad (13)$$

where N_{α} is the population of the atom α , that is, it is equal to $\sum_i^{(\alpha)} N_{At}$.²⁸⁾ This equation is very convenient for grasping the meaning of the Coulomb interaction term, since $(Z_{\alpha} - N_{\alpha})$ and $(Z_{\beta} - N_{\beta})$ represent the net plus charge of the atom α of A and of the atom β of B respectively. In neutral non-polar molecules, therefore, ϵ_Q is not very important.

The exchange interaction term, ϵ_K , is almost solely responsible for the multiplet separation. In the ground-state interactions it is usually repulsive except for the singlet interaction of two ground-state odd-electron systems.²⁹⁾

The case of single-site overlapping, namely, when

overlapping between only one AO (say r) of A and one AO (say r') of B is appreciable, may often be important. This is nearly the case in the aromatic substitution by a reagent with essentially one AO. If VAO's are employed as the basis AO's, the MO overlapping with reagent orbitals becomes single-sited in many cases.

In the case of single-site overlapping, Eq. (11) becomes, by the use of the Mulliken approximation:

$$\epsilon_K \cong -\frac{1}{8} s_{rr'}^2 P_{rr} P_{r'r'} [2v_{rr} + 2v_{r'r'} + (rr|rr) + (r'r'|r'r') + 2(rr|r'r') + P_{rr}\{(rr|rr) + (rr|r'r')\} + P_{r'r'}\{(r'r'|r'r') + (rr|r'r')\}] \quad (14)$$

in which:

$$v_{rr} = v_{Arr} + v_{Brr}, \text{ etc.},$$

$$P_{rr} = 2 \sum_i^{\text{occ}} C_i^{(i)} C_i^{(i)}, \text{ etc.}$$

indicating that the exchange interaction varies with the square of the overlap integrals and is, accordingly, less important than the Coulomb interaction at the initial stage of interaction in polar reactions.

Charge-transfer Interaction Term. The second term appearing on the right side of Eq. (8) comes from the electron-delocalization interaction due to the mixing of monotransferred configurations. The calculation of the matrix elements and overlap integrals gives:

$$H_{i \rightarrow l, i \rightarrow l} - H_{0,0} = -(E_{Bl} + \Delta E_{Bl}) + (I_{Ai} + \Delta I_{Ai}) + a_{il} \quad (15)$$

in which:³⁰⁾

$$E_{Bl} = -[H_{Bll} + \sum_k \{2(l|kk) - (lk|kl)\}]$$

$$I_{Ai} = -[H_{Aii} + \sum_{i'} \{2(ii|i'i') - (ii|i'i')\}]$$

28) If we put $s_{ti'}$'s and $s_{ui'}$'s equal to zero, Eq. (13) becomes identical to the equation obtained by Rein and Pollak (R. Rein and M. Pollak, *J. Chem. Phys.*, **47**, 2039 (1967)). They also assumed $s_{ab}=0$ in obtaining the exchange interaction energy. See also G. Klopman and R. F. Hudson, *Theoret. chim. Acta (Berl.)*, **8**, 165 (1967).

29) In this case

$$\begin{aligned} \epsilon_K = & -2 \sum_i \sum_k [(ik|ki) + s_{ik}[V_{ik} + \sum_{i'} \{2(ik|i'i') - (ii|i'i')\} + \sum_{k'} \{2(ik|k'k') - (ik'|k'k)\}]] \\ & - \sum_i \sum_k s_{ik} [\{2(ik|oo) - (io|ok)\} + \{2(ik|o'o') - (io'|o'k)\}] - \sum_i [(io'|o'i) + s_{io'}[V_{io'} \\ & + \sum_{i'} \{2(io'|i'i') - (ii|i'i')\} + \sum_k \{2(io'|kk) - (ik|ko')\} + (io'|oo) + (io|oo')] - \sum_k [(ok|ko) \\ & + s_{ok}[V_{ok} + \sum_{i'} \{2(ok|ii) - (oi|ik)\} + \sum_{k'} \{2(ok|k'k') - (ok'|k'k)\} + (ok|o'o') + (oo'|o'k)] + \delta_{oo'} \end{aligned}$$

where:

$$\delta_{oo'} = (oo'|o'o') + s_{oo'}[V_{oo'} + \sum_{i'} \{2(oo'|ii) - (oi|io')\} + \sum_k \{2(oo'|kk) - (ok|ko')\}]$$

Since the magnitude of ϵ_K is essentially determined by the orbital overlapping between the two systems, the attractive term, $\delta_{oo'}$, is in this case dominant, as is the case of hydrogen molecule formation from two hydrogen atoms.

30) The terms of the s_{ab} ($cd|ef$) type are omitted in order to avoid intricacy of expression in the subsequent equations, where a, b, \dots denote MO's. These are obtainable in a manner similar to that of 29). The terms of s_{ab}^2 are all neglected.

$$\begin{aligned}\Delta E_{Bl} &= -\{V_{Ail} + 2 \sum_{i'} \langle ii' | i' i' \rangle\} \\ &\quad + \sum_{i'} \{V_{i' i' s_{il}} + \langle ii' | i' i' \rangle\} \\ \Delta I_{Al} &= -\{V_{Bil} + 2 \sum_k \langle ii | kk \rangle\} \\ &\quad + \sum_k \{V_{ik s_{ik}} + \langle ik | ki \rangle\} \\ a_{il} &= -\langle ii | ll \rangle + 2\{V_{iis_{il}} + \langle il | li \rangle\} \\ H_{Ail} &= \int a_i(1) H_A(1) a_l(1) dv(1), \text{ etc.} \\ H_A(\lambda) &= -\frac{1}{2} \Delta(\lambda) + V_A(\lambda), \text{ etc.}\end{aligned}$$

and:

$$H_{0, i \rightarrow l} - S_{0, i \rightarrow l} H_{0,0} = \sqrt{2} [Q_{il} + K_{il}] \quad (16)^{31,2}$$

where

$$\begin{aligned}Q_{il} &= \{V_{Bil} + 2 \sum_k \langle il | kk \rangle\} \\ &\quad - s_{il} \{V_{Bil} + 2 \sum_k \langle ii | kk \rangle\}\end{aligned}$$

is the Coulomb interaction part, and where

$$K_{il} = -\sum_k \{ \langle ik | kl \rangle - s_{il} \langle ik | ki \rangle \}$$

is the exchange interaction part.

The Koopmans theorem³² makes a possible physical interpretation of the quantities in Eq. (15). The quantity I_{Al} is the vertical ionization potential, with no rearrangement of the nuclear configuration, of the isolated system A with respect to the electron in the i th MO; similarly, E_{Bl} is the vertical "electron affinity"³³ of the isolated system B with respect to the l th MO, while ΔI_{Al} is the change in I_{Al} due to the approach of the system B , and ΔE_{Bl} is the change in E_{Bl} due to the approach of the system A . With regard to a_{il} , the following relations hold:

$$a_{il} = I_{Al}^{(B+I)} - I_{Al}^{(B)} = E_{Bl}^{(A)} - E_{Bl}^{(A-I)}$$

where:

$$\begin{aligned}I_{Al}^{(B)} &= I_{Al} + \Delta I_{Al} \\ E_{Bl}^{(A)} &= E_{Bl} + \Delta E_{Bl}\end{aligned}$$

where $I_{Al}^{(B+I)}$ is the value of I_{Al} in the case of the approach of the system B with an additional electron occupying the l th unoccupied MO, and where $E_{Bl}^{(A-I)}$ is the value of E_{Bl} in the case of the approach

of the system A in which one electron occupying the i th MO is subtracted.

Then, we derive the useful equation:

$$\begin{aligned}H_{i \rightarrow l, i \rightarrow l} - H_{0,0} &= I_{Al}^{(B)} - E_{Bl}^{(A-I)} \\ &= I_{Al}^{(B+I)} - E_{Bl}^{(A)}\end{aligned} \quad (17)$$

which shows that this quantity is not simply written as $(I_{Al} - E_{Bl})$. As a matter of fact, Eq. (17) is self-evident, as is directly elucidated by the following diagram:

$$\begin{aligned}H_{i \rightarrow l, i \rightarrow l} - H_{0,0} &= \left[\begin{array}{c} \overline{\uparrow} \quad \overline{\uparrow} \quad \overline{\uparrow} \\ \downarrow \quad \downarrow \quad \downarrow \\ \uparrow \quad \uparrow \quad \uparrow \end{array} \right] - \left[\begin{array}{c} \overline{\uparrow} \quad \overline{\uparrow} \quad \overline{\uparrow} \\ \downarrow \quad \downarrow \quad \downarrow \\ \uparrow \quad \uparrow \quad \uparrow \end{array} \right] - \left[\begin{array}{c} \overline{\uparrow} \quad \overline{\uparrow} \quad \overline{\uparrow} \\ \downarrow \quad \downarrow \quad \downarrow \\ \uparrow \quad \uparrow \quad \uparrow \end{array} \right] - \left[\begin{array}{c} \overline{\uparrow} \quad \overline{\uparrow} \quad \overline{\uparrow} \\ \downarrow \quad \downarrow \quad \downarrow \\ \uparrow \quad \uparrow \quad \uparrow \end{array} \right] \\ &= I_{Al}^{(B)} - E_{Bl}^{(A-I)} \\ &= \left[\begin{array}{c} \overline{\uparrow} \quad \overline{\uparrow} \quad \overline{\uparrow} \\ \downarrow \quad \downarrow \quad \downarrow \\ \uparrow \quad \uparrow \quad \uparrow \end{array} \right] - \left[\begin{array}{c} \overline{\uparrow} \quad \overline{\uparrow} \quad \overline{\uparrow} \\ \downarrow \quad \downarrow \quad \downarrow \\ \uparrow \quad \uparrow \quad \uparrow \end{array} \right] - \left[\begin{array}{c} \overline{\uparrow} \quad \overline{\uparrow} \quad \overline{\uparrow} \\ \downarrow \quad \downarrow \quad \downarrow \\ \uparrow \quad \uparrow \quad \uparrow \end{array} \right] - \left[\begin{array}{c} \overline{\uparrow} \quad \overline{\uparrow} \quad \overline{\uparrow} \\ \downarrow \quad \downarrow \quad \downarrow \\ \uparrow \quad \uparrow \quad \uparrow \end{array} \right] \\ &= I_{Al}^{(B+I)} - E_{Bl}^{(A)}\end{aligned}$$

Relations of such a kind are completely general in character (cf. Eq. (21)).

Equation (16) indicates that the numerator of each term on the right side of Eq. (8b) consists of two parts, the Coulomb interaction part and the exchange interaction part. Since the latter is small compared with the former, except in a perfectly nonpolar case, we will consider only the case in which the exchange part can be neglected.

The approximation of *multiple-site overlapping*, in which the paired AO's are denoted by the r of A and the r' of B , leads to the expression:

$$H_{0, i \rightarrow l} - S_{0, i \rightarrow l} H_{0,0} \cong \sqrt{2} \sum_r C_r^{(i)} C_{r'}^{(l)} \gamma_{rr'}^{(i)} \quad (18)$$

where:

$$\begin{aligned}\gamma_{rr'}^{(i)} &\cong s_{rr'} \left[\frac{1}{2} (v_{Brr} + v_{Brr'}) + \frac{1}{2} \sum_u N_{Bu} \{ \langle rr | uu \rangle \right. \\ &\quad \left. + \langle r'r' | uu \rangle \} + \sum_\alpha \sum_\beta \frac{n_\alpha^{(ii)} (Z_\beta - N_\beta)}{R_{\alpha\beta}} \right] \quad (19)\end{aligned}$$

in which:

$$n_\alpha^{(ii)} = \sum_i \sum_{i'} C_i^{(i)} C_{i'}^{(i)} s_{ii'}$$

Eq. (19) indicates a linear relationship of the right side of Eq. (16) with orbital overlapping. Equation (19) can also be written:

$$\begin{aligned}\gamma_{rr'}^{(i)} &\cong - \int r(1) \left(\sum_\beta \frac{Z_\beta - N_\beta}{r_{1\beta}} \right) r'(1) dv(1) \\ &\quad + s_{rr'} \sum_\alpha \sum_\beta \frac{n_\alpha^{(ii)} (Z_\beta - N_\beta)}{R_{\alpha\beta}} \quad (19')\end{aligned}$$

which shows the remarkable characteristic that the charge-transfer interaction is large with the local net

31) To derive this equation, it must be remembered that the MO's are assumed to satisfy the Fock equation for the isolated system.

32) T. Koopmans, *Physica*, **1**, 104 (1933).

33) With respect to the physical significance of the energy level of a Fock-Roothaan unoccupied MO, one should in any event be cautious. To connect E_{Bl} with any experimental value, it is recommended that one adopts an extended-basis set of AO's in the Roothaan LCAO. This point will be discussed in a subsequent paper.

charge near the reaction center of the acceptor molecule.

Thus, we can obtain this approximate expression of D :

$$D \cong 2 \left\{ \sum_i^{\text{occ}} \sum_l^{\text{uno}} \frac{(\sum_r C_r^{(i)} C_{r'}^{(l)} \gamma_{rr'}^{(i)})^2}{I_{Ai}^{(B)} - E_{Bl}^{(A-i)}} + \sum_k^{\text{occ}} \sum_j^{\text{uno}} \frac{(\sum_r C_r^{(j)} C_{r'}^{(k)} \gamma_{rr'}^{(j)})^2}{I_{Bk}^{(A)} - E_{Aj}^{(B-k)}} \right\} \quad (20)$$

in which:

$$\gamma_{rr'}^{(k)} \cong - \int r(1) \left(\sum_a \frac{Z_a - N_a}{r_{1a}} \right) r'(1) dv(1) + s_{rr'} \sum_a \sum_\beta \frac{n_{\beta}^{(kk)} (Z_a - N_a)}{R_{a\beta}}$$

If we consider the special case of a single-site interaction between the r th AO of the reactant, A , and a reagent, B , assuming that the reagent possesses only one AO (designated as r') and, accordingly, only one MO to be taken into account, and that $C_r^{(i)} \gamma_{rr'}^{(i)} (= \gamma_r)$ and $C_{r'}^{(k)} \gamma_{rr'}^{(k)} (= \gamma_{r'})$ are constant with respect to a given reagent, then it follows that:

$$D \cong \begin{cases} 2 \sum_i^{\text{occ}} \frac{C_r^{(i)^2}}{\epsilon_B - \epsilon_{Ai}} \gamma_r^2 & \text{when the reagent orbital is unoccupied} \\ 2 \sum_j^{\text{uno}} \frac{C_{r'}^{(j)^2}}{\epsilon_{Aj} - \epsilon_B} \gamma_{r'}^2 & \text{when the reagent orbital is occupied,} \end{cases} \quad (20')$$

in which:

$$\epsilon_{Ai} = -I_{Ai}^{(B)}, \quad \epsilon_{Aj} = -E_{Aj}^{(B-k)}$$

and

$$\epsilon_B = \begin{cases} -E_B^{(A-i)} & \text{when the reagent orbital is unoccupied} \\ -I_B^{(A)} & \text{when the reagent orbital is occupied} \end{cases}$$

The quantity on the right side of Eq. (20') is nothing but *superdelocalizability*³³⁾ and *delocalizability*³⁴⁾ previously defined by one of the present authors in discussing the reactivity of unsaturated and saturated compounds. These relations are useful for estimating the value of the quantities employed in semi-empirical reactivity theories.

The same equations as in Eqs. (17)–(19') hold in the interaction of an even-electron system and an odd-electron system. In this case, however, Eq. (20) becomes:

$$D \cong 2 \left\{ \sum_i^{\text{occ}} \sum_l^{\text{uno}} \frac{(\sum_r C_r^{(i)} C_{r'}^{(l)} \gamma_{rr'}^{(i)})^2}{I_{Ai}^{(B)} - E_{Bl}^{(A-i)}} \right.$$

$$\left. + \sum_k^{\text{occ}} \sum_j^{\text{uno}} \frac{(\sum_r C_r^{(j)} C_{r'}^{(k)} \gamma_{rr'}^{(j)})^2}{I_{Bk}^{(A)} - E_{Aj}^{(B-k)}} \right\} + \left\{ \sum_i^{\text{occ}} \frac{(\sum_r C_r^{(i)} C_{r'}^{(o')} \gamma_{rr'}^{(i)})^2}{I_{Ai}^{(B)} - E_{Bo'}^{(A-i)}} + \sum_j^{\text{uno}} \frac{(\sum_r C_r^{(j)} C_{r'}^{(o')} \gamma_{rr'}^{(j)})^2}{I_{Bo'}^{(A)} - E_{Aj}^{(B-o')}} \right\} \quad (21)$$

and, corresponding to Eq. (20'), we obtain:

$$D \cong \sum_i^{\text{occ}} \frac{C_r^{(i)^2}}{\epsilon_B - \epsilon_{Ai}} \gamma_r^2 + \sum_j^{\text{uno}} \frac{C_{r'}^{(j)^2}}{\epsilon_{Aj} - \epsilon_B} \gamma_{r'}^2 \quad (21')$$

in which ϵ_B is equal to $(-E_{Bo'}^{(A-i)})$ and $\epsilon_{B'}$ is equal to $(-I_{Bo'}^{(A)})$. This equation is similar to the form of superdelocalizability and that of delocalizability for this case of interaction. It is noteworthy that, even in the interaction of a neutral molecule with a neutral radical, the local charge of atoms determines the magnitude of D .³⁵⁾

Polarization Term. The third interaction term corresponds to the polarization due to the mutual approach of A and B . The necessary matrix elements to calculate are as follows:

$$H_{i \rightarrow j, i \rightarrow j} - H_{0,0} = I_{A+j,i}^{(B)} - E_{Aj}^{(B)} = I_{Ai}^{(B)} - E_{A-i,j}^{(B)} \quad (22)$$

where $I_{A+j,i}^{(B)}$ is the ionization potential of an electron of the i th MO of the system A , with one additional electron occupying the j th MO, in the approach of the system B , and $E_{A-i,j}^{(B)}$ is the electron affinity with respect to the j th unoccupied MO of the system A , with one electron of the i th MO subtracted, in the approach of the system B . Moreover,

$$H_{0,i \rightarrow j} - S_{0,i \rightarrow j} H_{0,0} = \sqrt{2} [V_{Bi,j} + 2 \sum_k (ij|kk)] + O(s_{ab}^2) \quad (23)$$

This reduces, by the aid of the Mulliken approximation, to:

$$H_{0,i \rightarrow j} - S_{0,i \rightarrow j} H_{0,0} \cong -\sqrt{2} \zeta_{AB}^{(ij)} \quad (23')$$

in which:

$$\zeta_{AB}^{(ij)} = \sum_a \sum_\beta \frac{n_a^{(ij)} + n_\beta^{(ji)}}{2} \cdot \frac{Z_\beta - N_\beta}{R_{a\beta}} \quad (24)$$

where:

$$n_a^{(ij)} = \sum_i^{(a)} \sum_{i'} C_i^{(i)} C_{i'}^{(j)} s_{ii'}$$

The case of a single-site interaction between the atom α of A and the atom β of B is taken for the

35) This fact does not imply that the term D is not important in the radical interaction of a molecule. One must note that a majority of radicals involve a polar character, so the Coulomb interaction part of Eq. (16) still remains important.

34) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 1111 (1961).

sake of simplicity, in which the overlap integrals are neglected. This is a case of aromatic substitution in which only the $2p\pi$ AO's are taken into account. Then, we have :

$$\zeta_{AB}^{(ij)} \cong C_r^{(i)} C_r^{(j)} \frac{Z_\beta - N_\beta}{R_{r\beta}} \quad (24')$$

which is proportional to the net charge of the atom β of the system B . This equation is useful for understanding the physical meaning of Eq. (23). The approximate formula of Π can be obtained by using Eq. (23'):

$$\begin{aligned} \Pi \cong 2 \left\{ \sum_i^{\text{occ}} \sum_j^{\text{uno}} \frac{(\zeta_{AB}^{(ij)})^2}{I_{Ai}^{(B)} - E_{A-i,j}^{(B)}} \right. \\ \left. + \sum_k^{\text{occ}} \sum_l^{\text{uno}} \frac{(\zeta_{BA}^{(kl)})^2}{I_{Bk}^{(A)} - E_{B-k,l}^{(A)}} \right\} \quad (25) \end{aligned}$$

If we consider that the quantity $(Z_\beta - N_\beta)/R_{r\beta}$ in Eq. (24') for a definite distance of approach is constant with regard to a given reagent, B , and denote it by δ_r , we obtain as the first half of Π :

$$\Pi \sim \frac{1}{2} \pi_{Arr} (\delta_r)^2$$

in which:

$$\begin{aligned} \pi_{Arr} = 4 \sum_i^{\text{occ}} \sum_j^{\text{uno}} \frac{C_r^{(i)2} C_r^{(j)2}}{\epsilon_{Aj} - \epsilon_{Ai}} \bar{\beta} \quad (26) \\ (\epsilon_{Aj} = -E_{A-i,j}^{(B)}, \epsilon_{Ai} = -I_{Ai}^{(B)}; \bar{\beta} \text{ is an ap-} \\ \text{propriately-chosen energy unit}) \end{aligned}$$

is of the same form as the well-known *self-atom polarizability* defined by Coulson and Longuet-Higgins in discussing the property of conjugated molecules.^{8a)}

In this way, it has been demonstrated that the generalized scale of reactivity for an interaction between two chemical systems breaks up into the Coulomb interaction term of the atomic charge, the exchange interaction term, the delocalizability term, and the polarizability term. In some chemical reactions, some of these terms may be less important than the others. As has been discussed earlier, the polarizability term is usually less important than the delocalizability term in ionic reactions, and the exchange interaction term is not important except in special cases. In a case in which one of the charge-transfer configurations possesses nearly the same energy as the initial one, the corresponding term becomes particularly important, whereas none of excited configurations can be important since none of them can possess the same energy as the initial one. The Coulomb interaction of the atomic charge is appreciable in a long-range interaction, but it will become less and less important as the reaction proceeds and as an appreciable amount of charge is transferred from the donor to the acceptor, which thus "neutralize" each other.

The nuclear configuration change which is caused by the interaction described above and which is left out of account in the present paper will be discussed in a forth coming paper with reference to the general features of the chemical reaction.