Localization Energy with Electronic Interaction

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The localization method by Wheland[1], in which localization energy is employed as the reactivity index, has achieved successes in interpreting chemical reactivity of conjugated molecules[2]. On the other hand, total π-electron density[3], self-polarizability[4], free valence[5], frontier electron density[6] and superdelocalizability[7] are introduced as good reactivity indexes in the approximation of the simple LCAO treatment. Regarding alternant hydrocarbons (AH's) some mathematical relations have been found between localization energy and other reactivity indexes[8].

In the previous paper[9], utilizing LCAO SCF wave function, namely, the wave function where electronic interaction is explicitly included, we have found that the total π-electron density can not predict the correct reactivity of molecules, while the frontier electron density remains a good index for both ionic and radical reactions in LCAO SCF MO treatment just as well as in usual simple LCAO MO treatment. In the present paper we have defined and calculated the localization energy under an explicit consideration of electronic interaction, and comparison of the results obtained by the present method with those in simple LCAO treatment has been made.

Theoretical

Model of Localized System.—According to Wheland's definition the localized system in the transition state has the configuration in which the attacked carbon atom is sp^3-hybridized, so that the resonance integrals between the attacked atom and the neighboring ones are taken to be zero. More precisely the integral does not completely vanish; however, in order to be faithful to the concept of the term "localization", we assume that the resonance integrals between the attacked atom and the others are always zero. This assumption may be reasonable for our approximate calculation.

Here one more problem arises: Simple treatment naturally allows us to deal with the two parts, the localized electrons and the residue, independently from each other; but when we want to take the electronic interaction into account, the interaction between the two parts, and that between those two and the attacking reagent must be considered, as well as the mutual interaction of electrons inside the residue*. Concerning this point, two approximations would be employed. As the first approximation (Approx. 1) we simply assume the two parts to be independent, that is, the only electronic interaction to be taken into account is that which acts inside the residue*. In the second approximation (Approx. 2) the interaction between the two parts shall be treated as a perturbation. The effects of attacking reagent, which do not seem essential to the localization method, are thoroughly neglected for simplicity in both approximations.

Formulation. — The wave function χ_0 of the "isolated" system consisting of $2n$ carbon atoms and $2n$ π-electrons is given as follows:

$$\chi_0 = \frac{1}{\sqrt{(2n)!}} \begin{vmatrix} (\phi_1\alpha)^1 (\phi_1\beta)^1 (\phi_2\alpha)^1 & \cdots\cdots & (\phi_n\beta)^1 \\ (\phi_1\alpha)^2 (\phi_1\beta)^2 (\phi_2\alpha)^2 & \cdots\cdots & (\phi_n\beta)^2 \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \\ (\phi_1\alpha)^{2n} (\phi_1\beta)^{2n} (\phi_2\alpha)^{2n} & \cdots\cdots & (\phi_n\beta)^{2n} \end{vmatrix}$$

$$\equiv (1/\sqrt{(2n)!}) \, [(\phi_1\alpha)^1 (\phi_1\beta)^2 (\phi_2\alpha)^3 \cdots\cdots (\phi_n\beta)^{2n}] \quad (1)$$

1) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1940).
2) M. J. S. Dewar, *J. Chem. Soc.*, **1952**, 691; H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 283 (1950); T. Yonezawa et al., *Chem. High Polymers (Kobunshi Kagaku)*, **14**, 533 (1957).
3) G. W. Wheland and L. Pauling, *J. Chem. Phys.*, **1**, 606 (1933); etc.
4) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947); **A192**, 16 (1947).
5) F. H. Burkitt et al., *Trans. Faraday Soc.*, **47**, 553 (1951).
6) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); etc.
7) K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, **27**, 423 (1954).
8) K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957); H. Baba, This Bulletin, **30**, 147, 154, (1957).
9) K. Fukui, K. Morokuma and T. Yonezawa, This Bulletin, **32**, 853 (1959).

* In electrophilic reaction, the interaction between the two localized electrons is also to be included.

where φ_i is the i-th MO, α and β are the spin functions, and the superscripts denote the numbering of electrons. Each MO should be chosen to minimize the electron energy of the system; but so far as the evaluation of localization energy with electronic interaction is concerned, it seems sufficient to use Hückel MO

$$\psi_i=\sum_\mu c_{i\mu}\phi_\mu \qquad (i=1,2,\cdots\cdots,2n) \tag{2}$$

where ϕ_μ denotes the AO on the μ-th carbon atom.

Introducing a SCF-like procedure proposed by Pople[10], we obtain the following expression of the total electronic energy of the system**.

$$\varepsilon_0=2nU+(\gamma_{\mu\mu}/4)\sum_\mu (P_{\mu\mu})^2+2\beta\sum_{\mu<\nu}^{*} P_{\mu\nu} +\sum_{\mu<\nu}\{(P_{\mu\mu}-1)(P_{\nu\nu}-1)-(1/2)(P_{\mu\nu})^2\}\gamma_{\mu\nu} \tag{3}$$

where U is a core matrix element and is put a constant, β is the resonance integral between the nearest neighbors, and $\gamma_{\mu\nu}$ is the coulomb repulsion integral

$$\gamma_{\mu\nu}=\int\phi_\mu^*(1)\,\phi_\nu^*(2)\frac{e^2}{r_{12}}\phi_\mu(1)\,\phi_\nu(2)\,dv_1 dv_2 \tag{4}$$

and

$$P_{\mu\nu}=2\sum_{i=1}^{n} c_{i\mu}c_{i\nu} \tag{5}$$

Summation Σ and Σ^* should cover all the atoms and the nearest neighboring atoms, respectively. In deriving Eq. 3 the same assumptions as proposed by Pople[10], for instance, of equi-bond-length, of neglecting the coulomb penetration integrals and so on, are employed.

From the assumption made in the preceding section the wave function χ_E of the "localized" system (transition complex) for electrophilic reaction, in which two electrons are localized on the carbon λ, may be written as follows:

$$\chi_E=(1/\sqrt{(2n-2)!})\,[(\psi'_1\alpha)^1(\psi'_1\beta)^2\cdots\cdots \times(\varphi'_{n-1}\alpha)^{2n-3}(\psi'_{n-1}\beta)^{2n-2}] \times(1/\sqrt{2!})\,[(\phi_\lambda\alpha)^{2n-1}(\phi_\lambda\beta)^{2n}] \tag{6}$$

where ψ'_i is the i-th Hückel MO for the residue consisting of $(2n-1)$ carbons.

$$\psi'_i=\sum_\mu c'_{i\mu}\phi_\mu \quad (i=1,2,\cdots\cdots,2n-1) \tag{7}$$

Here we refer the superscript "$'$" to the residue of the molecule. The two parts being treated separately (Approx. 1), the energy of the system, ε_{E0}, is given as follows[11]:

$$\varepsilon_{E0}=2U+\gamma_{\mu\mu}+(2n-2)U+(\gamma_{\mu\mu}/4)\sum_\mu (P^+_{\mu\mu})^2 +2\beta\sum_{\mu<\nu}^{*} P^+_{\mu\nu}+\sum_{\mu<\nu}\{(P^+_{\mu\mu}-1)(P^+_{\nu\nu}-1) -(1/2)(P^+_{\mu\nu})^2\}\gamma_{\mu\nu} \tag{8}$$

where

$$P^+_{\mu\nu}=2\sum_{i=1}^{n-1} c'_{i\mu}c'_{i\nu} \tag{9}$$

The first two terms correspond to the energy of the localized electrons and the others to that of the residue. When the interaction between the parts is taken into account in higher approximation (Approx. 2), the interaction energy ε_{E1}:

$$\varepsilon_{E1}=\sum_\mu (P^+_{\mu\mu}-1)\gamma_{\mu\lambda} \tag{10}$$

is to be added to the energy ε_{E0}.

Also for nucleophilic reaction, through the similar consideration as for electrophilic one, we easily obtain the following formulae.

$$\chi_N=(1/\sqrt{(2n)!})\,[(\psi'_1\alpha)^1(\psi'_1\beta)^2\cdots\cdots \times(\psi'_n\alpha)^{2n-1}(\psi'_n\beta)^{2n}] \tag{11}$$

$$\varepsilon_{N0}=2nU+(\gamma_{\mu\mu}/4)\sum_\mu (P^-_{\mu\mu})^2 +2\beta\sum_{\mu<\nu}^{*} P^-_{\mu\nu}+\sum_{\mu<\nu}\{(P^-_{\mu\mu}-1) \times(P^-_{\nu\nu}-1)-(1/2)(P^-_{\mu\nu})^2\}\gamma_{\mu\nu} \tag{12}$$

$$\varepsilon_{N1}=\sum_\mu (1-P^-_{\mu\mu})\gamma_{\mu\lambda} \tag{13}$$

$$P^-_{\mu\nu}=2\sum_{i=1}^{n} c'_{i\mu}c'_{i\nu} \tag{14}$$

For radical reaction,

$$\chi_R=(1/\sqrt{(2n-1)!})\,[(\psi'_1\alpha)^1(\psi'_1\beta)^2\cdots\cdots \times(\psi'_{n-1}\alpha)^{2n-3}(\psi'_{n-1}\beta)^{2n-2} \times(\psi'_n\alpha)^{2n-1}]\cdot(\phi_\lambda\alpha)^{2n} \tag{15}$$

$$\varepsilon_{R0}=U+(2n-1)U+\gamma_{\mu\mu}\sum_\mu P^\alpha_{\mu\mu}P^\beta_{\mu\mu} +2\beta\sum_{\mu<\nu}^{*} P^0_{\mu\nu}+\sum_{\mu<\nu}\{(P^0_{\mu\mu}-1)(P^0_{\nu\nu}-1) -[(P^\alpha_{\mu\nu})^2+(P^\beta_{\mu\nu})^2]\}\gamma_{\mu\nu} \tag{16}$$

$$\varepsilon_{R1}=0 \tag{17}$$

$$\left.\begin{aligned} P^\alpha_{\mu\nu}&=\sum_{i=1}^{n} c'_{i\mu}c'_{i\nu}=(1/2)\,P^-_{\mu\nu}\\ P^\beta_{\mu\nu}&=\sum_{i=1}^{n-1} c'_{i\mu}c'_{i\nu}=(1/2)\,P^+_{\mu\nu}\\ P^0_{\mu\nu}&=P^\alpha_{\mu\nu}+P^\beta_{\mu\nu}\end{aligned}\right\} \tag{18}$$

10) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

** Core-core repulsion energies are included in all the expressions of energies in this paper.

11) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

TABLE I. LOCALIZATION ENERGIES OF ALTERNANT HYDROCARBONS

Compound	Position	Ionic ($L_N=L_E$)[a] Approx. 1	Ionic ($L_N=L_E$)[a] Approx. 2	Radical (L_R)[a] Approxs. 1 & 2	Simple[b] ($L_N=L_E=L_R$)
Ethylene	—	13.695	6.395	3.165	2.000
Butadiene (*trans*)	1	11.854	6.324	2.590	1.694
	2	14.467	7.167	3.937	2.472
Benzene	—	13.834	7.334	4.995	2.536
Naphthalene	1	12.918	7.134	4.411	2.299
	2	13.470	7.473	4.888	2.480
Anthracene	1	12.575	7.160	4.255	2.240
	2	13.233	7.676	4.755	2.423
	9	11.806	6.882	3.636	2.013
Phenanthrene	1	12.821	7.212	4.604	2.317
	9	12.872	7.147	4.361	2.297
Biphenyl	2	13.157	7.191	4.905	2.400
	4	13.196	7.483	4.944	2.447

a) In units of eV.
b) In units of $(-\beta)$.

TABLE II. LOCALIZATION ENERGIES OF NON-ALTERNANT HYDROCARBONS

Compound	Position	Electrophilic (L_E) Approx. 1[a]	Electrophilic (L_E) Approx. 2[a]	Electrophilic (L_E) Simple[b]	Nucleophilic (L_N) Approx. 1[a]	Nucleophilic (L_N) Approx. 2[a]	Nucleophilic (L_N) Simple[b]	Radical (L_R) Approxs. 1 & 2[a]	Radical (L_R) Simple[b]
Azulene	1	11.392	6.543	1.352	13.265	7.572	2.090	4.177	1.721
	2	12.521	8.100	1.728	12.734	6.694	1.728	4.500	1.728
	4	13.760	8.148	1.808	10.559	5.280	1.231	3.987	1.520
	5	12.654	6.655	1.659	12.595	8.274	1.655	4.485	1.655
	6	13.755	7.349	1.959	11.177	8.959	1.280	4.368	1.620
Fulvalene	1	12.908	5.969	1.987	9.408	5.145	1.365	3.021	1.676
	2	13.702	6.680	2.236	10.507	7.131	1.452	3.783	1.848

a) In units of eV.
b) In units of $(-\beta)$.

The first term in Eq. 16 refers to the localized electron and the others to the residue.

As regards the AH, whose MO has special simplifying properties, Eqs. 8, 10, 12, 13 and 16 can be reduced to simpler ones, that is,

$$\varepsilon_{N0}=\varepsilon_{E0}=2nU+(\gamma_{\mu\mu}/4)\,[(n-1)+\sum_{\mu\nu}^{st}\{1+(c'_{n\mu})^2\}^2]+2\beta\sum_{\mu<\nu}^{*}P^0{}_{\mu\nu}-\{-\sum_{\mu<\nu}^{st,st}(c'_{n\mu}c'_{n\nu})^2+\sum_{\mu,\nu}^{st,unst}(P^0{}_{\mu\nu})^2\}(\gamma_{\mu\nu}/2) \tag{19}$$

$$\varepsilon_{N1}=\varepsilon_{E1}=-\sum_{\mu}^{st}(c'_{n\mu})^2\gamma_{\mu\lambda} \tag{20}$$

$$\varepsilon_{R0}=2nU+(\gamma_{\mu\mu}/4)\{(2n-1)-\sum_{\mu}^{st}(c'_{n\mu})^4\}+2\beta\sum_{\mu<\nu}^{*}P^0{}_{\mu\nu}-\{\sum_{\mu<\nu}^{st,st}(c'_{n\mu}c'_{n\nu})^2+\sum_{\mu,\nu}^{st,unst}(P^0{}_{\mu\nu})^2\}(\gamma_{\mu\nu}/2) \tag{21}$$

Summation $\sum^{st}$ and $\sum^{unst}$ should cover all the starred and the unstarred atoms, respectively.

The localization energies, L, of the λ-th carbon atom are, therefore, obtained from the following equations.

$$\left.\begin{array}{ll}\text{Electrophilic Reaction} & \\ \quad\text{(Approx. 1)} & L_E=\varepsilon_{E0}-\varepsilon_0 \\ \quad\text{(Approx. 2)} & L_E=\varepsilon_{E0}+\varepsilon_{E1}-\varepsilon_0 \\ \text{Nucleophilic Reaction} & \\ \quad\text{(Approx. 1)} & L_N=\varepsilon_{N0}-\varepsilon_0 \\ \quad\text{(Approx. 2)} & L_N=\varepsilon_{N0}+\varepsilon_{N1}-\varepsilon_0 \\ \text{Radical Reaction} & \\ \quad\text{(Approxs. 1 \& 2)} & L_R=\varepsilon_{R0}+\varepsilon_0\end{array}\right\} \tag{22}$$

Evaluation of Atomic Integrals. — For numerical evaluation of β and $\gamma_{\mu\nu}$ are utilized the semi-empirical formulae introduced by Pariser and Parr[12]. For simplicity, as partly stated above, all the

12) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

C–C bond distances are assumed the same, 1.39Å, and all the carbon rings (five- and seven-membered rings for azulene and fulvalene, six-membered rings for the other molecules now considered) are supposed to be regular, and polyenyl bond angles to be 120°.

Results and Discussion

The calculated results of localization energy, which is defined in the preceding section, of seven AH's and two non-AH's are listed in Tables I and II***, together with those obtained by simple LCAO treatment.

As is seen from Eq. 20, the interaction energy between the localized electrons and the residue in nucleophilic and in electrophilic reactions is necessarily negative for the AH, namely, there rises some stabilization of the system from the interaction, this seeming true also for the non-AH (cf. Eqs. 10 and 13); and accordingly the values of the localization energies, L_E and L_N, in Approx. 1 are larger than in Approx. 2. For all that we can see in Tables I and II that in both approximations we obtain nearly the same intramolecular orientation, which will be discussed in the later paragraph in detail. In radical reaction, on the other hand, the interaction energy formally vanishes (cf. Eq. 17), and therefore both approximations give the same value of localization energy.

It will be seen in Tables I and II that the magnitude of L_R is generally much smaller than those of L_N and L_E in both approximations, whereas in the simple LCAO treatment the magnitude of L_R lies between those of L_N and L_E. This by no means admits that the activation energy of radical reaction is smaller than those of the others, because effects of reagents and changes in the σ-system are conventionally set aside from this argument. Especially for the AH Eqs. 19 and 20 show the relation $L_E = L_N$ within each approximation in accordance with the result obtained by the simple treatment.

It may be valuable to notice that both approximations indicate the same intramolecular orientation as the simple treatment for all the reactions of the molecules now concerned, except for the ionic reactions of phenanthrene in Approx. 1. Accordingly, its agreement with experimental results is mostly good, but the facts that azulene reacts at the position 1 in radical reaction[13] (L_R is the smallest at 4) and that the position 4 of biphenyl is more reactive than the position 2 both in radical and electrophilic reactions[14] (L_R and L_E indicate 2-orientation) can not be explained on the basis of the localization energy, whether the electronic interaction is taken into account or not. In fulvalene the position 1 is shown to be the most susceptible to attack by localization energies and the position 2 is so by frontier electron density[15], superdelocalizability[16] and total π-electron density[17],

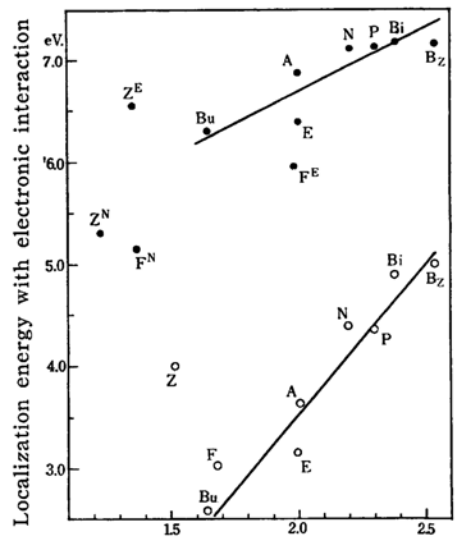

Fig. 1. Relationship between localization energies in simple treatment and with electronic interaction.
○: Radical reaction, ●: Ionic reaction (Approx. 2); E: ethylene, Bu: butadiene, Bz: benzene, N: naphthalene, A: anthracene, P: phenanthrene, F: fulvalene (F^N: nucleophilic, F^E: electrophilic), Z: azulene (Z^N: nucleophilic, Z^E: electrophilic). Only the position of the smallest localization energy of each molecule is plotted. The straight lines are only for AH's.

*** For the position 2 of butadiene, the wave functions of the localized system are expressed in the product of wave functions of three parts, as follows:

$$\chi_E = (1/\sqrt{2})[(\varphi_1'\alpha)^1(\varphi_1'\beta)^2] \times (1/\sqrt{2})[(\phi_2\alpha)^3(\phi_2\beta)^4]$$
$$\chi_R = (1/\sqrt{2})[(\varphi_1'\alpha)^1(\varphi_1'\beta)^2]\cdot(\phi_2\alpha)^3\cdot(\phi_1\alpha)^4$$
$$\chi_N = (1/\sqrt{2})[(\varphi_1'\alpha)^1(\varphi_1'\beta)^2] \times (1/\sqrt{2})[(\phi_1\alpha)^3(\phi_1\beta)^4]$$

In Approx. 1 three parts are treated independently, whereas their mutual interactions are taken into account in Approx. 2.

13) H. Arnold and K. Pahls, *Chem. Ber.*, **89**, 121 (1956).
14) G. Schults, H. Schmidt and H. Strasser, *Ann.*, **207**, *352 (1881); etc.*
15) To be published.
16) To be published.
17) R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949).

further experiments being awaited at this point.

It seems also interesting that, except for the mutual coincidence of the most reactive position, the order of reactivity of each position in azulene does not coincide with one another in the three treatments; in electrophilic reaction, for instance, the reactivity of each position decreases in the order $1>5>2>4>6$ in the simple treatment, $1>2>5>6>4$ in Approx. 1, and $1>5>6>2>4$ in Approx. 2.

As it is seen in Fig. 1, agreement of the intermolecular order of reactivity predicted by the simple treatment with that obtained with electronic interaction is not so good in Approx. 2; and in Approx. 1 the agreement is a little worse. Non-AH's, azulene and fulvalene, largely deviate from the linear relationship of Fig. 1, but unfortunately there are no available data to check which result is correct.

From the above discussion it might be concluded that the localization energy, in which the electronic interaction is taken into account, can be a pretty good index of chemical reactivity.

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Added in Proof:

It is easily proved that the following wave functions χ'_E and χ'_R, instead of Eqs. 6 and 15, directly lead to the same energy expressions that were derived in Approx. 2, ε'_E and ε'_R respectively.

$$\chi'_E=(1/\sqrt{(2n)!})[(\psi'_1\alpha)^1(\psi'_1\beta)^2\cdots(\psi'_{n-1}\alpha)^{2n-3}\times(\psi'_{n-1}\beta)^{2n-2}(\phi_\lambda\alpha)^{2n-1}(\phi_\lambda\beta)^{2n}]$$

$$\varepsilon'_E=\varepsilon_{E0}+\varepsilon_{E1}$$

$$\chi'_R=(1/\sqrt{(2n)!})[(\psi'_1\alpha)^1(\psi'_1\beta)^2\cdots(\psi'_{n-1}\alpha)^{2n-3}\times(\psi'_{n-1}\beta)^{2n-2}(1/\sqrt{2})\times\{(\psi'_n\alpha)^{2n-1}(\phi_\lambda\beta)^{2n}-(\psi'_n\beta)^{2n-1}(\phi_\lambda\alpha)^{2n}\}]$$

$$\varepsilon_R'=\varepsilon_{R0}$$