Note on a Relationship between Self-Mutability and Superdelocalizability in Regular Alternants

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Abstract

This note presents a simple theorem expressing superdelocalizabilities solely in terms of site-site mutabilities in regular alternants. The theorem provides an explicit relationship between self-mutability and superdelocalizability and manifests similarities and differences between the two quantities, leading to a concise interpretation on the physical meaning of superdelocalizability. The theorem is also practically useful for estimating superdelocalizabilities from site-site mutabilities. An effective approximation for estimation is examined with numerical examples. Supplementary remarks are added on the expression of superdelocalizabilities between different sites.

1. Introduction

Self-mutability[1,2] and superdelocalizability[3] are the most reliable indices of reactivity in the Hückel model. These two indices behave surprizingly in parallel with each other and always provide the same conclusion regarding site reactivities in conjugated hydrocarbons. The existence of such correlations between several indices of reactivity (the above two, localization energy, free valence, and so on) has been proved mathematically under a certain condition (Condition A) fulfilled in many conjugated hydrocarbons.[4-7] However, aside from approximate relationships,[8] no explicit relationship between the indices has been found so far.

This note derives a theorem on an explicit relationship between self-mutability and superdelocalizability in regular alternants from the hypervirial condition.[9,10] Because the theorem is essentially a consequence of alternant symmetry, a few other derivations are, of course, possible and not difficult at all. Still, the present derivation seems to be the most straightforward.

2. Theorem

Consider a simple Hückel model of a regular alternant, an alternant system having no nonbonding orbital. The sites of the system are divided into the set of starred sites and that of unstarred sites with the alternant symmetry parity. Let E^{tu} be the matrix whose rs component is $\delta_{rt}\delta_{su}$, namely the matrix unit of the tu component, and define the perturbation matrix D^{tu} for site pair tu as

$$D^{tu}=(E^{tu}+E^{ut})/(1+\delta_{tu}).\tag{1}$$

Then, using the adjacency matrix A of the system and the bond order matrix $P,$[11] we can write the hypervirial condition upon the mutability matrix Π^{tu} for the perturbation on site pair tu as[9]

$$[A,\Pi^{tu}]=[P,\ D^{tu}].\tag{2}$$

This note uses what is called dimensionless mutability throughout.[12]

Suppose a normal state[13] and consider the case of site perturbations, namely, the case of $t=u$ in Eq. 2. The alternant symmetry enables us to write A, P, and Π^{tt} in the form

$$A=\begin{pmatrix} 0 & A_{*\circ} \\ A_{\circ *} & 0 \end{pmatrix},\tag{3}$$

$$P=\begin{pmatrix} 0 & P_{*\circ} \\ P_{\circ *} & 0 \end{pmatrix},\tag{4}$$

and

$$\Pi^{tt}=\begin{pmatrix} \Pi^{tt}_{**} & 0 \\ 0 & \Pi^{tt}_{\circ\circ} \end{pmatrix}\tag{5}$$

with appropriate half-size submatrices. Since we can assume site t to be starred, that is, D^{tt} to have the form

$$D^{tt}=\begin{pmatrix} D^{tt}_{**} & 0 \\ 0 & 0 \end{pmatrix}\tag{6}$$

without loss of generality, the above hypervirial condition can be rewritten as

$$\Pi_{**}^{tt}A_{*\circ}-A_{*\circ}\Pi_{\circ\circ}^{tt}=D_{**}^{tt}P_{*\circ},\tag{7}$$

which is a basis of the present derivation.

Note that the superdelocalizability on site t is given by the diagonal component s_{tt} of the matrix[14]

$$S=PA^{-1}=\begin{pmatrix} P_{*\circ}(A_{*\circ})^{-1} & 0 \\ 0 & P_{\circ*}(A_{\circ*})^{-1} \end{pmatrix}.\tag{8}$$

Therefore, multiplying $(A_{*\circ})^{-1}$ from the right in Eq. 7 and taking the trace, we obtain

$$\mathrm{Tr}(\Pi_{**}^{tt})-\mathrm{Tr}(\Pi_{\circ\circ}^{tt})=s_{tt}.\tag{9}$$

On the other hand, the number conservation condition[2,9]

$$\mathrm{Tr}(\Pi^{tu})=0 \qquad (tu \text{ arbitrary})\tag{10}$$

immediately leads to

$$\mathrm{Tr}(\Pi_{**}^{tt})+\mathrm{Tr}(\Pi_{\circ\circ}^{tt})=0.\tag{11}$$

A combination of Eqs. 9 and 11 yields

$$s_{tt}=2\mathrm{Tr}(\Pi_{**}^{tt}) \qquad (t \text{ starred}).\tag{12}$$

It will be preferable to put this result in the form of a theorem with the use of traditional notation for s_{tt} and π_{rr}^{tt}.

Theorem Let S_t be the superdelocalizability on site t and $\pi_{r,t}$ be the site-site mutability for sites r and t in a regular alternant. Let T be the set of sites having the same parity as t. Then, the relationship

$$S_t=2\sum_{r\in T}\pi_{r,t}\tag{13}$$

holds.

3. Significance

In this section, site-site mutabilities are referred to simply as mutabilities. Let δq_r be the change of the electron density q_r on site r caused by the infinitesimal perturbation $\delta \eta_t$ on site t. The definition of mutability means

$$\sum_{r \in T} \delta q_r = \sum_{r \in T} \pi_{r,t} \, \delta \eta_t. \tag{14}$$

Hence, while self-mutability concerns only the change of the electron density on a perturbed site, superdelocalizability does the total change of the electron densities on all the sites having the same parity as a perturbed site. Let T be the set of sites having the parity opposite to the parity of t and let Q_X be the total electron density on all the sites of X;

$$Q_X = \sum_{r \in X} q_r \qquad (X = T \text{ or } \bar{T}). \tag{15}$$

Then, we can write S_t as

$$S_t = 2 \frac{\partial Q_T}{\partial \eta_t} \bigg|_{\eta_t = 0} \tag{16}$$

or, going back to Eq. 9,

$$S_t = \frac{\partial Q_T}{\partial \eta_t} - \frac{\partial Q_{\bar{T}}}{\partial \eta_t} \bigg|_{\eta_t = 0}. \tag{17}$$

We can thus interpret S_t as the index showing how greatly electron clouds move from the sites of T to the sites of $\bar{T}$ by the perturbation on t.

The topological distance d_{rt} between sites r and t is defined as the shortest path, namely, the minimum number of bonds between r and t. Though we have no sufficient quantitative theory of mutabilities, the general inclination is known that $\pi_{r,t}$ decreases in absolute value alternating the sign as d_{rt} increases.[15] In particular, $\pi_{r,t}$ for $d_{rt} = 2$ is already remarkably smaller than $\pi_{t,t}$ in conjugated hydrocarbons.[16] Hence, neglecting all but the term for distance zero in Eq. 13, we have

$$S_t \sim 2\pi_{t,t} , \tag{18}$$

which explains the strong correlation between the two indices most simply. The smallness of the neglected terms suggests that the correlation must be retained extensively beyond Condition A.[7,17)]

The theorem also has some practical significance besides the conceptual one mentioned above. The computation of superdelocalizabilities is rather easier than that of mutabilities. If one intends to evaluate only superdelocalizabilities but not mutabilities, one may use data of Hückel orbitals directly. However, when one evaluates mutabilities as well as superdelocalizabilities, or when one evaluates superdelocalizabilities for systems whose mutabilities are already known, the theorem is quite helpful; it enables us to compute superdelocalizabilities from data of mutabilities even without the use of computers.

Let T_d and $\bar{T}_{d'}$ denote the sets of sites apart from site t by even distance d and by odd distance d' respectively. Because of the reason already mentioned, "the second neighbor approximation"

$$S_t \sim 2(\pi_{t,t} + \sum_{r \in T_2} \pi_{r,t}) \tag{19}$$

is expected to be effective unless the system is peculiarly enormous. Table 1 shows numerical examples of this approximation for several conjugated hydrocarbons, where the approximation is successful in reproducing superdelocalizabilities, at least, with over 93 percent accuracy. It should be noted that the approximation works well even when the contribution from $2\pi_{t,t}$ is only about 80 percent of S_t. If the number conservation condition is not employed, or if mutabilities for sites of the same parity are eliminated, we have the series

$$S_t = \pi_{t,t} - \sum_{r \in \bar{T}_1} \pi_{r,t} + \sum_{r \in T_2} \pi_{r,t} - \sum_{r \in \bar{T}_3} \pi_{r,t} + \cdots \tag{20}$$
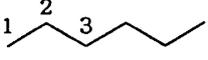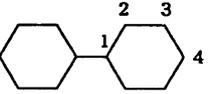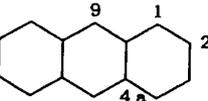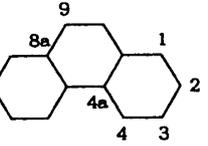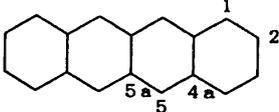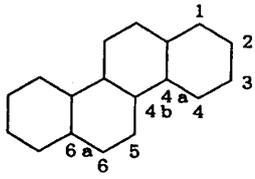
or the series

$$S_t = -2(\sum_{r \in \bar{T}_1} \pi_{r,t} + \sum_{r \in \bar{T}_3} \pi_{r,t} + \sum_{r \in \bar{T}_5} \pi_{r,t} + \cdots). \tag{21}$$

However, these do not seem to yield any efficient approximation, because $-\pi_{r,t}$ for odd d_{rt} does not decrease so rapidly as $\pi_{r,t}$ for even d_{rt} as d_{rt} increases. The decrease in $-\pi_{r,t}$ from $d_{rt}=1$ to 3 is not very large in conjugated hydrocarbons and
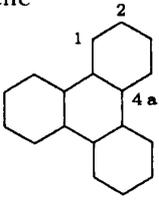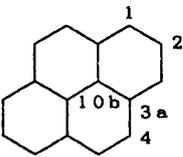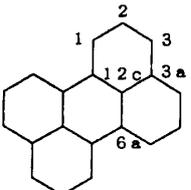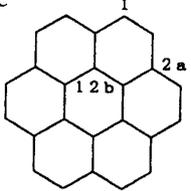
$-\pi_{r,t}$ for $d_{rt}=3$ is always larger and often much larger than $\pi_{r,t}$ for $d_{rt}=2$. Even $-\pi_{r,t}$ for $d_{rt}=5$ sometimes exceeds $\pi_{r,t}$ for $d_{rt}=2$.[16]

Table 1. Second Neighbor Approximation of Superdelocalizabilities

system numbering[*]	t	$2\pi_{t,t}$	(%)	$2(\pi_{t,t}+\sum\limits_{r\in T_2}\pi_{r,t})$	(%)	S_t
Hexatriene	1	1.369	(87.7)	1.532	(98.2)	1.560
	2	0.784	(90.0)	0.843	(96.8)	0.871
	3	0.950	(81.0)	1.173	(100)	1.173
Biphenyl	1	0.688	(89.1)	0.761	(98.6)	0.772
	2	0.847	(93.1)	0.907	(99.7)	0.910
	3	0.792	(95.4)	0.826	(99.5)	0.830
	4	0.822	(92.0)	0.881	(98.5)	0.894
Anthracene	1	0.908	(84.6)	1.043	(97.1)	1.073
	2	0.822	(89.1)	0.883	(95.8)	0.922
	9	1.051	(80.1)	1.257	(95.7)	1.313
	4a	0.663	(92.1)	0.713	(99.0)	0.720
Phenanthrene	1	0.878	(89.9)	0.968	(99.1)	0.977
	2	0.806	(93.6)	0.851	(98.9)	0.860
	3	0.817	(91.5)	0.872	(97.7)	0.893
	4	0.859	(91.4)	0.927	(98.6)	0.939
	9	0.885	(88.7)	0.973	(97.5)	0.997
	4a	0.699	(89.4)	0.774	(99.1)	0.781
	8a	0.667	(91.2)	0.721	(98.5)	0.732
Naphthacene	1	0.915	(81.6)	1.069	(95.3)	1.121
	2	0.828	(86.1)	0.895	(93.2)	0.961
	5	1.112	(73.9)	1.400	(93.0)	1.505
	4a	0.667	(88.9)	0.728	(97.0)	0.751
	5a	0.663	(92.5)	0.707	(98.7)	0.717
Chrysene	1	0.882	(88.9)	0.978	(98.5)	0.992
	2	0.806	(93.3)	0.853	(98.7)	0.864
	3	0.818	(91.2)	0.874	(97.4)	0.897
	4	0.863	(90.4)	0.935	(98.0)	0.954
	5	0.861	(90.3)	0.926	(97.1)	0.954
	6	0.902	(86.4)	1.004	(96.2)	1.044
	4a	0.696	(90.0)	0.768	(99.4)	0.773
	4b	0.712	(86.1)	0.808	(97.7)	0.827
	6a	0.665	(92.3)	0.716	(99.3)	0.720

*) IUPAC Nomenclature

Table 1. *Continued*

system numbering[*]	t	$2\pi_{t,t}$	(%)	$2(\pi_{t,t}+\sum_{r\in T_2}\pi_{r,t})$	(%)	S_t
Triphenylene	1	0.854	(92.0)	0.920	(99.1)	0.928
	2	0.811	(92.7)	0.860	(98.4)	0.875
	4a	0.700	(89.0)	0.774	(98.3)	0.787
Pyrene	1	0.932	(83.6)	1.072	(96.2)	1.115
	2	0.790	(95.3)	0.822	(99.2)	0.828
	4	0.889	(86.6)	0.987	(96.2)	1.026
	3a	0.672	(89.2)	0.731	(97.0)	0.753
	10b	0.700	(92.1)	0.757	(99.5)	0.761
Perylene	1	0.915	(82.0)	1.041	(93.2)	1.117
	2	0.796	(93.0)	0.834	(97.3)	0.856
	3	0.952	(79.7)	1.119	(93.7)	1.195
	3a	0.657	(93.7)	0.700	(99.7)	0.702
	6a	0.717	(82.3)	0.816	(93.7)	0.871
	12c	0.699	(92.4)	0.755	(99.8)	0.757
Coronene	1	0.879	(88.9)	0.965	(97.5)	0.989
	2a	0.684	(87.2)	0.757	(96.5)	0.784
	12b	0.705	(90.0)	0.767	(97.8)	0.784

*) IUPAC Nomenclature

Mutability is obviously a much simpler concept than superdelocalizability both physically and mathematically. It is not improbable for an effective approximation of mutabilities to be found. The theorem gives us a natural way of applying it to superdelocalizabilities. There exists, at present, no approximation of mutabilities sufficient to give a fine estimation of superdelocalizabilities.

4. Supplementary Remarks

The superdelocalizability between different sites t and u of the same parity is well defined as the tu component s_{tu} of the matrix S. The assumption of $t\neq u$ in Eq. 2

readily leads us to

$$\mathrm{Tr}\,(\Pi_{**}^{tu}) - \mathrm{Tr}\,(\Pi_{\circ\circ}^{tu}) = 2s_{tu} \tag{22}$$

and the preceding interpretation of S_t can be applied to s_{tu} as well. Using the number conservation condition and the traditional notation for π_{rr}^{tu}, we obtain

$$s_{tu} = \sum_{r \in T} \pi_{r,tu} \qquad (u \in T,\ u \ne t). \tag{23}$$

Since the right hand side contains no term so dominant as self-mutabilities, this relationship clarifies that superdelocalizabilities between different sites must be much smaller than superdelocalizabilities on sites. However, we have so little knowlege of site-site pair mutabilities either theoretically or empirically that we cannot proceed further at present.

References and Notes

1) The term "mutability" is used in place of "polarizability"; J. Lennard-Jones, *Proc. R. Soc, London, Ser. A*, **207**, 75 (1951); atom atom mutability is renamed site-site mutability. Self-mutability means the self-mutability on a site throughout this note.

2) C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A*, **191**, 39 (1947).

3) K. Fukui, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jpn.*, **27**, 423 (1957).

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

5) H. Baba, *Bull. Chem. Soc. Jpn.*, **30**, 147 (1957).

6) H. Baba, *Bull. Chem. Soc. Jpn.*, **30**, 154 (1957).

7) It should be noted that Condition A is sufficient but not necessary.

8) For example, for self-mutability and free valence, R. McWeeny, *Proc. R. Soc. London, Ser. A*, **237**, 355 (1956); for Brown's Z value and superdelocalizability, K. Fukuki, K. Morokuma, T. Yonezawa, and C. Nagata, *J. Chem, Phys.*, **32**, 1743 (1960); for hyperconjugation energy and superdelocalizability, see Ref. 4.

9) M. Isihara, *Bull. Chem. Soc. Jpn.*, **64**, 559 (1991).

10) M. Isihara, *Bull. Chem. Soc. Jpn.*, **62**, 2284 (1989).

11) The bond order matrix differs from the p-density matrix by the unit matrix (representing electron densities on sites), which does nothing in commutators.

12) Dimensionless mutability is the mutability multiplied by the resonance integral of the system, being opposite to the original one in sign.

13) A normal state means an m-electron ground state for a system of m sites.

14) The three kinds of superdelocalizabilities for electrophilic, radical, and nucleophilic reactions are identical in regular alternants. The spectral representation easily proves PA^{-1} to be the matrix bearing superdelocalizabilities in its diagonal components.

15) C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc, London, Ser. A,* **192**, 16 (1947).

16) C. A. Coulson and A. Streitwieser Jr., "Dictionary of π-Electron Calculations," Pergamon Press, Oxford, (1965).

17) In phenanthrene, as pointed out by Fukui and his coworkers (Ref. 4), we have $S_9 > S_1$, $\pi_{9,9} > \pi_{1,1}$, and $-L_9 > -L_1$ for localization energies, but $F_9 < F_1$ for free valences.