A PRACTICAL INDEX OF REACTIVITY
FOR ALTERNANT SYSTEMS

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This paper proposes to use the minor of the diagonal component in the squared adjacency matrix as a practical index of reactivity for alternant systems having no nonbonding orbital. This index is a closer approximation to superdelocalizability but can be evaluated much more simply than frontier electron density. It is shown that this index has a simple relation to resonance structures. A few remarks are added concerning Dewar's localization energy and the analysis by Fukui and his coworkers on approximation to superdelocalizability.

1 . Introduction

Frontier electron density is prevalently used as the simplest index of reactivity for qualitative consideration on chemical reactions, in particular, of conjugated systems. This index of reactivity has a great advantage, when it is valid, in reflecting symmetry properties of systems. It is well-known that this index can be regarded as a natural approximation to superdelocalizability which is one of the most reliable indices of reactivity in the Hückel model.

Consider an alternant system consisting of m black and m white sites. Denote the set of the black sites and that of the white by M_{+1} and M_{-1}, respectively, and define the color indicator $\sigma(r)$ of site r as

$$\sigma(r) \equiv \begin{cases} +1 & (r \in M_{+1}) \\ -1 & (r \in M_{-1}) . \end{cases} \tag{1}$$

Assume the system to have no nonbonding orbital, that is, the adjacency matrix A of the system to be invertible. Let λ_j and c_{rj} be, respectively, the j-th eigenvalue and the site-r component of the j-th normalized eigenvector (orbital) of A. For brevity of description, eigenvalues are assumed to be nondegenerate and to be numbered from 1 to $2m$ in decreasing order. Then, by virtue of the alternant symmetry that

$$\lambda_{2m-j+1} = -\lambda_j \tag{2}$$

and

$$c_{r,2m-j+1} = \sigma(r)c_{rj}, \tag{3}$$

the superdelocalizability S_r on site r (Fukui, Yonezawa, and Nagata, 1954) and the frontier electron density f_r on site r (Fukui, Yonezawa, and Shingu, 1952; Fukui, Yonezawa, Nagata, and Shingu, 1954) can be written as

$$S_r = 2\sum_{j=1}^{m} c_{rj}^2 / \lambda_j \tag{4}$$

and

$$f_r = 2c_{rm}^2 \tag{5}$$

without regard to types (electrophilic, radical, and nucleophilic) of reactions.

Because the leading term in the sum over j in S_r above is usually the term for $j=m$, frontier electron density is a reasonable one-term approximation to superdelocalizability (Fukui, Yonezawa, and Nagata, 1957). Naturally, frontier electron density is often invalid, say, when c_m vanishes, when $\lambda_{m'}$ having large $|c_{r,m'}|$ is close to λ_m, or when eigenvalues are accumulated near λ_m. Such situations can occur rather frequently in systems consisting of many sites.

This paper proposes to use the minor of the diagonal component in the squared adjacency matrix as a practical index of reactivity for alternant systems having no nonbonding orbital. This index is a closer approximation to superdelocalizability than frontier electron density and does not share the above-mentioned disadvantage of frontier electron density. Still, the evaluation of this index is much simpler than that of frontier electron density. A simple relation is shown to exist between this index and resonance structures. A lucid explanation is given to the fact that Dewar's localization energy (Dewar, 1952) works well in spite of its crudeness as an approximation to Wheland's localization energy (Wheland, 1942).

2. Resonance-Theoretic Index of Reactivity

Because the squared adjacency matrix A^2 of the system under consideration is positive definite, we can well define the matrix

$$T(\theta) \equiv (A^2)^{-\theta} \tag{6}$$

for an arbitrary real number θ. The r-th diagonal component $T_r(\theta)$ of $T(\theta)$ can be written as

$$T_r(\theta) = 2\sum_{j=1}^{m} c_{rj}^2 / \lambda_j^{2\theta} \tag{7}$$

by using the alternant symmetry mentioned above for λ_j and c_{rj}. Thus, the quantity

$$S_r(\theta) \equiv \lambda_m^{2\theta-1} T_r(\theta) = 2\sum_{j=1}^{m} w_j(\theta) c_{rj}^2 / \lambda_j \tag{8}$$

can be regarded as "weighted" superdelocalizability with weight

$$w_j(\theta) \equiv (\lambda_m / \lambda_j)^{2\theta-1} . \tag{9}$$

In this notation, the case of $\theta = 1/2$ bears S_r, where every weight is unity, while the case of $\theta = \infty$ does f_r/λ_m, where only the weight for m is unity with the others vanishing.

It is readily found that $S_r(\theta)$ decreases monotoneously as θ increases from 1/2, that is,

$$S_r \geq S_r(\theta) > S_r(\theta') > f_r / \lambda_m \qquad (1/2 \leq \theta < \theta' < \infty). \tag{10}$$

Therefore, since no $S_r(\theta)$ for nonintegral θ larger than 1/2 will be evaluated more easily than S_r itself, the best practical approximation to S_r is obviously $S_r(1)$. Fukui and his coworkers (1961) noticed the usefulness of the quantity corresponding to $T_r(1)$ as an approximation to superdelocalizability through quite a different way. However, they seem to have paid no attention to the fact that $T_r(1)$ is the r-th diagonal component of $(A^2)^{-1}$ at all. They examined the correlation between $T_r(1)$ and S_r numerically to obtain the conversion curve.

By numbering black sites from 1 to m and white sites from $m+1$ to $2m$, the adjacency matrix A can be written in the form

$$A = \begin{pmatrix} 0 & B \\ {}^tB & 0 \end{pmatrix} \tag{11}$$

with a relevant $m \times m$ submatrix B. Denote $B\,{}^tB$ and ${}^tBB$ by T_{+1} and T_{-1}, respectively, and define $\tilde{r}$ as

$$\tilde{r} \equiv \begin{cases} r & (r \in M_{+1}) \\ m - r & (r \in M_{-1}) . \end{cases} \tag{12}$$

Then, using the symbol $|X|$ for the determinant of X and the symbol $|X[r]|$ for the minor of the r-th diagonal component in X, we can express $T_r(1)$ as

$$T_r(1) = |T_{\sigma(r)}[\tilde{r}]| / |T_{\sigma(r)}| . \tag{13}$$

Here note that $|T_{+1}|$ and $|T_{-1}|$ are identical with the absolute value $\|A\|$ of $|A|$. Since $\|A\|$ as

well as λ_m is a positive constant within the system, the quantity (the minor of the diagonal component in A^2)

$$R_r \equiv |\ T_{\sigma(r)}[\tilde{r}]\ | \tag{14}$$

can be used in place of

$$S_r(1) = \lambda_m\ \|\ A\ \|^{-1}\ R_r \tag{15}$$

as a relative index of reactivity. As shown in the next section, this index is related to resonance structures in quite a simple way and seems to deserve to be named resonance delocalizability.

Resonance delocalizability takes integral values and can be evaluated simply by calculating determinants of integral components or by inverting A^2 without solving the eigenvalue problem of A. In sharp contrast to frontier electron density, resonance delocalizability contains contributions from other orbitals than the m-th orbital (frontier orbital) to some extent. In particular, contributions from orbitals belonging to eigenvalues near λ_m are almost completely taken into account in resonance delocalizability.

The best way of evaluating resonance delocalizability depends on systems. For large systems containing heavily peri-condensed structures, we have to rely on numerical calculation in general. In such cases, if one needs to compare reactivities for many sites involved, it may be suitable to calculate $T(1)$, that is, $(A^2)^{-1}$ as a whole. Calculating the inverse of A^2 is still much easier than solving the eigenvalue problem of A. This must be advantageous particularly for investigating site reactivities of the system whose eigenvalue problem is difficult to solve. Except for extremely large systems, the primitive Newton type iteration by

$$^{(i+1)}T(1) = 2\ ^{(i)}T(1) - ^{(i)}T(1)A^2\ ^{(i)}T(1) \tag{16}$$

works adequately, where $^{(i)}T(1)$ stands for the i-th guess for $T(1)$. The plain initial guess

$$^{(1)}T(1) = I\ /\ k \tag{17}$$

is relevant with $k=4$ for nonpathological conjugated systems. For systems containing no heavily peri-condensed structure, we can evaluate R_r without aid of computers by calculating appropritate minors or by enumerating appropriate Kekulé structures as shown below.

3 . Relation to Resonance Structures

The component of the inverse of the adjacency matrix is regarded as a kind of bond orders (Ruedenberg, 1954; Ham and Ruedenberg, 1958) and explicitly related to resonance structures

(Ham, 1958; Isihara, 1996). Hence, through the identity

$$(A^2)^{-1} = (A^{-1})^2 \qquad (18)$$

we can immediately relate resonance delocalizability to resonance structures in quite a simple way.

For the alternant system having m black and m white sites, we can assign $m!$ permutations of the symmetric group of degree m to $m!$ general resonance structures[1] having m bonds all between black and white sites, so that the parity of the permutations can be appropriated to the general resonance structures. Let us refer to the Kekulé structure including a bond between sites r and s as the rs-Kekulé structure and to the resonance structure having a nonadjacent bond between sites r and s besides $m-1$ adjacent bonds as the rs-Dewar structure. Using the number K_η of Kekulé structures of parity η and the number $J_\eta(rs)$ of rs-Kekulé or rs-Dewar structures of parity η, we can express the rs-component v_{rs} of A^{-1} as

$$v_{rs} = (J_+(rs) - J_-(rs))/(K_+ - K_-) \qquad (\sigma(r) \neq \sigma(s)) \qquad (19)$$

(Isihara, 1996). Since A^{-1} is real-symmetric, the well-known relationship

$$(K_+ - K_-)^2 = \| A \| \qquad (20)$$

(Dewar and Longuet-Higgins, 1952) immediately lead us to

$$R_r = \sum_{s \in M_{\bar{\sigma}(r)}} (J_+(rs) - J_-(rs))^2, \qquad (21)$$

where $\bar{\sigma}(r)$ stands for $-\sigma(r)$.

It will be preferable to rewrite the expression above in terms of the algebraic structure count (Wilcox, Jr., 1968; 1969). Let $ASC(rs)$ denote the algebraic structure count of the subsystem derived by deleting sites r and s. Although the algebraic structure count of each subsystem does not necessarily stand on an identical reference of parity, the squaring process removes the influence and, therefore, we have

$$R_r = \sum_{s \in M_{\bar{\sigma}(r)}} ASC(rs)^2. \qquad (22)$$

If the system contains no $4n$-membered ring, either $J_+(rs)$ or $J_-(rs)$ vanishes and the expression can be simplified to

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[1] The term "general resonance structures" here means resonance structures allowed to have bonds not only between adjacent sites but also between nonadjacent sites of different colors.

$$R_r = \sum_{s \in M_{\bar{\sigma}(r)}} K(rs)^2 \tag{23}$$

with the number $K(rs)$ of Kekulé structures of the subsystem derived by deleting sites r and s.

Through the expressions obtained above, we can understand how resonance structures contribute to reactivity on each site. It should be emphasized (rather from a conceptual point of view) that the evaluation of resonance delocalizability can be reduced, in principle, to the enumeration of resonance structures of appropriate subsystems.

4. Supplementary Remarks

Dewar's localization energy l_r for site r is originally defined in terms of nonbonding orbital coefficients of the odd-alternant subsystem derived by deleting site r (Dewar, 1952; Dewar and Longuet-Higgins, 1952), but it is not difficult to prove that the relationship

$$l_r = 2\lambda_m^{1/2} S_r(1)^{-1/2} \infty R_r^{-1/2}, \tag{24}$$

which assures that the analysis with l_r always gives the same conclusion as the analysis with R_r. Dewar's localization energy is quite a crude approximation to Wheland's localization energy and comparisons by differences in Dewar's localization energy cannot be soundly justified on the basis of Wheland's localization approach (Koutecký, Zahradnik, and Čížek, 1961). Nevertheless, Dewar's localization energy can work surprizingly well as an index of reactivity. The analysis in the second section with the relationship above provides a lucid explanation to this.

To define the condition under which frontier electron density gives the same conclusion on sites reactivities as superdelocalizability, Fukui and his coworkers (1957) examined a series of quantities $T_r(l)$'s for $l=1,2,\cdots$ in the present notation. Let $\Delta(z)$ be the secular determinant of A and let $\Delta_{rr}(z)$ be that of the matrix derived by deleting the r-th row and the r-th colum from A. Using the quantity essentially identical with

$$G_r(y) \equiv \Delta_{rr}(iy)/(iy\Delta(iy)), \tag{25}$$

they pointed out that

$$l_r = -2 G_r(0)^{-1/2} = 2 T_r(1)^{-1/2} \tag{26}$$

but affirmed that frontier electron density was the simplest to calculate. As already mentioned, they took up $T_r(1)$ as "a simple reactivity index" afterwards (1961).

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