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**TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY. RELATION BETWEEN THE OVERLAP DETERMINANT METHOD AND THE LEAST MOTION PRINCIPLE**

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The recently suggested approach to the study of chemical reactivity in terms of the generalized and integral similarity indices is analyzed and discussed from the point of view of its compatibility with the principle of least motion. It is shown that the formulations of the similarity approach as initially introduced on an intuitive basis are consistent with that principle.

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One of the most interesting applications of the overlap determinant method<sup>1,2</sup> concerns the possibility of formulation and subsequent practical exploitation of the so-called least-motion principle in the theory of chemical reactivity. This can be done by making use of the approach based on the so-called similarity index, suggested previously<sup>3,4</sup>. Although the potential of this approach in the analysis of pericyclic reactivity is very large indeed<sup>4,5</sup>, it has a shortcoming, namely, that the whole treatment has been formulated rather intuitively, without a profound theoretical background.

In the present paper we attempt to offer such a theoretical basis *ex post* and to demonstrate that the intuitively introduced generalization of the overlap determinant method actually expresses the requirements of the principle of least motion, so that all the subsequent applications made are generally valid.

**THEORETICAL AND DISCUSSION**

The principle of least motion was introduced into the theory of reactivity in the late 1930's by Rice and Teller<sup>6,7</sup>, who elaborated the intuitive feeling that easily proceeding are those chemical reactions associated with minimal structure changes. Within the framework of this concept, the authors made the vague notion of "minimal structure changes" somewhat more specific by identifying it with the criterion of minimal changes in the positions of the nuclei and in the electronic configuration of the reacting molecules.

Although several attempts have been made to use the principle of least motion in a systematic quantitative manner<sup>8-13</sup>, none of them is quite universal, and their importance in reactivity theory is far below that of, e.g., the Woodward-Hoffmann rules. This is due to the fact that in spite of its conceptual attractivity and simplicity, the original formulation by Rice and Teller is very difficult to quantify. This concerns, in particular, the abstract requirement of minimal changes in electronic configurations, which also has been mostly disregarded in actual applications. The only exceptions in this respect are the recently published paper by Igawa and Fukutome<sup>14</sup> and our approach based on the use of the so-called similarity index and generalizations thereof<sup>3,4</sup>, where the similarity approach is incorporated into the framework of the so-called generalized overlap determinant method<sup>2</sup>.

Since the formalism used in the present paper proceeds directly from the overlap determinant method, let us first summarize briefly the basic principles of that method to an extent necessary for the subsequent treatment.

In the overlap determinant method, a chemical reaction  $R \rightarrow P$ , where reactant  $R$  converts into product  $P$  in a concerted manner, is looked upon as an abstract transformation, described by a continuous wave function change from  $\Phi_R$  to  $\Phi_P$ . In general, such a process can be described mathematically by the equation

$$\Phi(a, b) = a\Phi_R + b\Phi_P, \quad (1)$$

where  $a$  and  $b$  are parameters, which are changed continuously when modelling the reaction process. Because of the natural requirement of normalization of the wave function,

$$\int \Phi^2(a, b) d\tau = 1, \quad (2)$$

the parameters  $a$  and  $b$  cannot be regarded independent. This implies that the transformation  $R \rightarrow P$  can be described by means of a single parameter — a generalized reaction coordinate. This can be, for instance, the angle  $\varphi$  introduced by putting  $a = \cos \varphi / N(\varphi)$  and  $b = \sin \varphi / N(\varphi)$  in Eq. (1) ( $N(\varphi)$  is the normalizing factor). In this manner, Eq. (1) transforms to the form

$$\Phi(\varphi) = (1/N(\varphi))(\Phi_R \cos \varphi + \Phi_P \sin \varphi). \quad (3)$$

Alternatively, we can use the linear transformation  $a = x/N(x)$  and  $b = (1-x)/N(x)$ , which has been also discussed.

Since Eq. (3) is only a specific case of the transformation (1), we confine ourselves to the general formalism.

In the overlap determinant method, the electron reorganization accompanying the transformation  $R \rightarrow P$  is characterized by a topological density matrix  $\Omega(a, b)$ , describing the structure of the transient species in any point of the reaction co-

ordinate<sup>2</sup>. This matrix has become the basis for the introduction of the so-called generalized and integral similarity indices as characteristics describing the extent of the electron reorganization from the local and global points of view, respectively.

Although these indices have found interesting applications, particularly in the theory of pericyclic reactions<sup>3,4</sup>, their relation to the principle of least motion has so far remained at the level of a mere intuitively felt parallel. This circumstance puts no serious constraints in practice, as demonstrated by some successful applications, it is, however, important from the conceptual point of view because just in its solution is the clue to a physically feasible utilization of the least motion principle. It turns out that the principal cause limiting the general approach based on the similarity indices lies in the fact that these characteristics do not express the electronic configuration absolutely but only with respect to some reference, standard structure. For instance, the index  $r_{AB}$  expresses the "similarity" of molecule A to molecule B (or vice versa), the generalized index  $r_{RX(\varphi)}$  expresses the similarity of the general species  $X(\varphi)$  to reactant R, etc. Another drawback is in the fact that none of the characteristics involves free parameters necessary to make use of the variation nature of the principle of least motion.

For circumventing this shortcoming it is feasible, rather than to employ quantities of the similarity index type when formulating criteria of minimal changes in the electronic configuration, to use characteristics describing the electronic configuration absolutely, independent of any reference structure. A straightforward approach consists then of proceeding directly from the matrix  $\Omega(a, b)$ . It will be clear that because of its independence with respect to unitary transformations of the basis, the quantity in question should be an invariant of matrix  $\Omega$ . The simplest invariant is  $\text{Tr } \Omega(a, b)$ ; however, this quantity is unsuitable because its value is equal to the number of electrons in the system and hence, independent of the position of the species on the reaction coordinate. A next quantity both meeting the invariancy condition and respecting the effect of structure of the transient species is  $\text{Tr } \Omega^2$ . It will be demonstrated later that the requirements of the principle of least motion can really be formulated quite satisfactorily with the use of this quantity. However, instead of  $\text{Tr } \Omega^2(a, b)$  itself, we will employ the quantity  $\xi(a, b)$  defined by Eq. (5)

$$\xi(a, b) = 2 \text{Tr } \Omega(a, b) - \text{Tr } \Omega^2(a, b). \quad (5)$$

This quantity is closely related to  $\text{Tr } \Omega^2(a, b)$ , and its value, within the framework of the overlap determinant method, is

$$\begin{aligned} \xi(a, b) = & 2(a^2 + b^2)N + 4abNS_{RP} - 2(a^4 + b^4)N - \\ & - 4a^2b^2Nr_{RP} - 8(a^3b + ab^3)NS_{RP} - \\ & - 8a^2b^2S_{RP} \sum_i \sum_j (A_{ij}^{RP2} + \sum_k \sum_l A_{ij}^{RP} A_{kl}^{RP} D_{il}^{RP} D_{kj}^{RP}) \end{aligned} \quad (6)$$

which can be obtained by inserting in Eq. (5) the general identities

$$\text{Tr } \Omega_{\text{RR}} = \text{Tr } \Omega_{\text{PP}} = N \quad (9a)$$

$$\text{Tr } \Omega_{\text{RR}}^2 = \text{Tr } \Omega_{\text{PP}}^2 = 2N \quad (7b)$$

$$\text{Tr } (\Omega_{\text{RP}} + \Omega_{\text{PR}}) = 2NS_{\text{RP}} \quad (9c)$$

$$\text{Tr } \Omega_{\text{RR}}(\Omega_{\text{RP}} + \Omega_{\text{PR}}) = \text{Tr } \Omega_{\text{PP}}(\Omega_{\text{RP}} + \Omega_{\text{PR}}) = 4NS_{\text{RP}} \quad (7d)$$

$$\text{Tr } (\Omega_{\text{RP}} + \Omega_{\text{PR}})^2 = 8NS_{\text{RP}} \sum_i \sum_j (A_{ij}^{\text{RP}^2} + \sum_k \sum_l D_{il}^{\text{RP}} D_{kj}^{\text{RP}} A_{ij}^{\text{RP}} A_{kl}^{\text{RP}}) \quad (7e)$$

$$\text{Tr } \Omega_{\text{RR}} \Omega_{\text{PP}} = 2Nr_{\text{RP}}. \quad (7f)$$

Here  $N$  is the number of electrons,  $r_{\text{RP}}$  is the index of similarity between R and P, and  $S_{\text{RP}}$  is the corresponding overlap integral given by the squared overlap determinant  $D^{\text{RP}}$ ;  $D_{ii}^{\text{RP}}$  and  $D_{jk}^{\text{RP}}$  are matrix elements and  $A_{ij}^{\text{RP}}$ ,  $A_{kl}^{\text{RP}}$  are the corresponding minors of this determinant.

Now, let us discuss some general properties of this quantity. First, it is clear that in the cases  $a = 1$ ,  $b = 0$  and  $a = 0$ ,  $b = 1$ , corresponding to the reactant and product, respectively, its value is zero. This is so because in the overlap determinant method the corresponding density matrices  $\Omega_{\text{RR}}$  and  $\Omega_{\text{PP}}$  are derived from wave functions described by a single Slater determinant. Hence, Eq. (5) is nothing else than an alternative representation of the so-called idempotency relations, and  $\xi = 0$  only expresses the fact that the electronic configurations in the reactant and product involves perfect pairing of the  $N$  electrons in  $N/2$  occupied molecular orbitals.

This perfect pairing, however, is disturbed during the reaction, and as a result, the values of the parameter  $\xi$  are generally nonzero. Plotting schematically this parameter in dependence on the reaction coordinate (the argument  $\xi$  in our particular case, Fig. 1), we see that a simple parallel exists between the value of the parameter  $\xi$  and the position of the corresponding transient structure on the reaction coordinate.

The most important result following from this parallel is the existence of a critical structure  $X^*$  in which the electron reorganization attains its maximum during the reaction. This fact, along with the simple shape of the dependence, demonstrates that for characterizing the extent of electron reorganization it is sufficient to compare the  $\xi$  value in the critical point. It is clear that reactions with lower  $\xi$  values are associated with smaller electron reorganization than reactions with higher  $\xi$  values, and according to the principle of least motion, the former proceed more easily than the latter.

A basic presupposition for making use of the above criterion is localization of the critical points. Answer to this problem rests in the solution of Eqs (8),

$$\partial\xi/\partial a = 0 \quad (8a)$$

$$\partial\xi/\partial b = 0, \quad (8b)$$

is conjunction with the bonding condition (2). It can be shown that there exist two solutions, viz.

$$a = b \quad (9a)$$

and

$$a = -b. \quad (9b)$$

In the particular case of transformation (3), the corresponding values of the argument  $\varphi$  are  $\varphi = \pi/4$  and  $\varphi = -\pi/4$ . Inserting them in Eq. (3) we obtain expressions for the wave functions  $\Phi_+^*$  and  $\Phi_-^*$  of the critical species  $X_+^*$  and  $X_-^*$ , respectively, viz.

$$\Phi_+^* = (1/(2 + 2S_{RP})^{1/2}) (\Phi_R + \Phi_P) \quad (10a)$$

$$\Phi_-^* = (1/(2 - 2S_{RP})^{1/2}) (\Phi_R - \Phi_P). \quad (10b)$$

These expressions demonstrate that the structure of the functions is determined to a high extent by the overlap integral  $S_{RP}$ .

It will be shown that this integral plays a major role also in the suggested model based on the least motion criterion. To demonstrate the role of the integral  $S_{RP}$  in this relation, we will pass from the wave functions  $\Phi_+^*$ ,  $\Phi_-^*$  to the chemically more illustrative density matrices  $\Omega_+^*$ ,  $\Omega_-^*$ :

$$\Omega_+^* = [1/(2 + 2S_{RP})] [(\Omega_{RR} + \Omega_{PP}) + 2(\Omega_{RP} + \Omega_{PR})] \quad (11a)$$

$$\Omega_-^* = [1/(2 - 2S_{RP})] [(\Omega_{RR} + \Omega_{PP}) - 2(\Omega_{RP} + \Omega_{PR})]. \quad (11b)$$

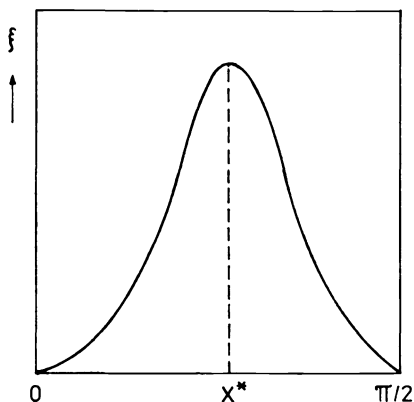


FIG. 1  
Schematic plot of changes in electronic configuration of molecules, characterized by parameter  $\xi$ , in dependence on reaction coordinate value

It appears that similarly as we can distinguish between allowed and forbidden reactions, it is convenient to distinguish between cases where  $S_{RP} = 0$  and where  $S_{RP} \neq 0$ . It is clear from the form of the matrices  $\Omega_+^*$  and  $\Omega_-^*$  that in the former case, characteristic of forbidden reactions, both critical structures are equivalent ( $\Omega_{RP} + \Omega_{PR} = 0$  for  $S_{RP} = 0$ ), whereas for allowed reactions the two critical structures are mutually different. This fact is of crucial importance, as will be shown later; really, it indicates that in contrast to forbidden reactions, for allowed reactions there exist two different reaction pathways with extremal electron reorganization.

Within the model (3), these pathways can be quantitatively described by the equations

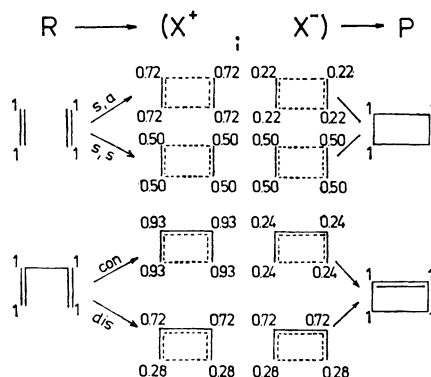
$$\Phi_+(\varphi) = (1/(1 + S_{RP} \sin 2\varphi)^{1/2}) (\Phi_R \cos \varphi + \Phi_P \sin \varphi) \quad (12a)$$

$$\Phi_-(\varphi) = (1/(1 - S_{RP} \sin 2\varphi)^{1/2}) (\Phi_R \cos \varphi - \Phi_P \sin \varphi). \quad (12b)$$

These equations demonstrate that the difference between the two pathways consists in the phase with which the wave functions  $\Phi_R$ ,  $\Phi_P$  combine in a general point of the reaction coordinate. Now, the question arises as to which of the two pathways corresponds to the minimal reorganization as required by the least motion principle. For solving this problem, the values of the parameters  $\xi_+$  and  $\xi_-$  for the critical points of the two reaction pathways must be compared; it is clear that the reaction pathway for which the  $\xi$  value is lower will proceed with the minimal reorganization whereas the other pathway, with regard to the extremal character of the two pathways, will correspond to the maximal reorganization.

We will attempt now to apply the above criterion to some particular pericyclic reactions. The reactions, along with the  $\xi$  values calculated for the corresponding two types of critical structures, are given in Table I. Let us discuss some general conclusions following from this table. First, we see that in the case of thermally forbidden reactions the above equivalence of the critical structures  $X_+^*$ ,  $X_-^*$  is associated with the equality  $\xi_+ = \xi_-$ . In the case of allowed reactions, on the other hand, the two  $\xi$  values differ, namely so that  $\xi_+ < \xi_-$ ; hence, the pathway via structure  $X_+^*$  is the minimal reorganization pathway, whereas structure  $X_-^*$  is associated with the maximal reorganization.

Justification of the above interpretation of the quantity  $\xi$  as characteristics of the electron reorganization can be also demonstrated in an illustrative way by comparing values of the so-called topological valencies<sup>15</sup>. The values corresponding to the structures  $X_+^*$  and  $X_-^*$  for some selected pericyclic reactions are given in Scheme 1. Again, of interest is particularly the case of allowed reactions, where the valencies for structure  $X_+^*$  really are not very different from those in the reactant or product, so that the corresponding electron reorganization is relatively small. In the case of structure  $X_-^*$ , on the other hand, the differences are substantial because the resulting patterns correspond to a species composed of very weakly interacting fragments



SCHEME 1

whose bonding capacity is concentrated principally in unsaturated so-called free valencies. Interpretation of these structures as those with the maximal reorganization thus seems natural also from the chemical point of view.

In relation to the discussion of the valency values it is of interest to include also forbidden reactions in the comparison. In this manner we find, in addition to the expected equivalence of the structures  $X_+^*$  and  $X_-^*$ , another interesting fact, namely

TABLE I  
Calculated values of parameter  $\xi$  for critical structures  $X^+$ ,  $X^-$  in some types of pericyclic reactions

Reaction	Mechanism	$\xi_+$	$\xi_-$
	S, A S, S	1.12 2.0	3.12 2.0
	con dis	0.30 2.00	3.00 2.00
	dis con	0.54 2.05	3.05 2.05
	S, S S, A	1.10 2.56	3.22 2.56

that from the point of view of the electron reorganization these structures for the forbidden reactions lie between those for the allowed reactions. In other words, allowed reactions are only convenient if they occur in accordance with the principle of least motion; the path of maximum reorganization via structure  $X_-^*$ , if occurring, would be even less advantageous than the forbidden reaction pathway.

It is noteworthy that the assignment of the structures  $X_+^*$  and  $X_-^*$  to the minimal and maximal reorganization, respectively, is only valid for reactions of closed shell molecules; this is so because the inequality  $\xi_+ < \xi_-$ , underlying this assignment, holds for positive values of the overlap  $S_{RP}$ . Where this overlap is negative, the reverse inequality holds true and  $X_-^*$  is the structure with the minimal reorganization. Such a situation, however, cannot occur for the most frequent case of closed shell molecules, where  $S_{RP}$  is given by the overlap determinant squared and so, the structure  $X_+^*$  is the one with the minimal reorganization. This is of prime importance for our purposes, because so the transformation (12a), describing the minimal electron reorganization pathway, is equivalent to the transformation (3) used on an intuitive basis in our previous work<sup>2</sup>. Thus, we can see that in the generalized and integral indices introduced by means of density matrices derived from the transformation equation (3), the principle of least motion is implicitly involved. Owing to this, all the applications of the generalized and integral similarity indices made previously can be considered warranted.

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