
**TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY.
ON PHYSICAL MEANING OF THE SIMILARITY INDEX**

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The paper analyzes and discusses the detailed physical meaning of the similarity indices of the first and second orders which were introduced originally as characteristics expressing, in the sense of the least-motion principle, the extent of the electron reorganization connected with the transformation of reactants into products within a given reaction

The similarity index introduced into chemistry in the papers by Polansky¹ and Carbo² has found a number of important practical applications recently. This is manifested e.g. by gradually increasing interest shown by agrochemical and pharmaceutical firms and directed to rationalization of search for new biologically active molecules³⁻⁵. Beside this undoubtedly significant practical application, however, there appear application possibilities of no less interest in the field of chemical theory, particularly in formulation of selection rules in chemical reactivity in terms of the so-called least-motion principle^{6,7}. The decisive role in all such applications is played by the empirical statement that values of the similarity index and/or some of other quantities derived therefrom express – in a certain way – the extent of electronic reorganization needed for the transformation of a structure into another one. In spite of the fact that a number of successful concrete applications show that such an empirical statement is obviously fully justified, the fact that the proclaimed physical meaning starts only from simple intuitive ideas indicates the necessity of placing the whole approach on a more profound theoretical basis. The aim of the present paper is to give such theoretical reasoning at least additionally. In terms of the corresponding theoretical analysis it will simultaneously be shown that the similarity index can be given a very simple and clear physical meaning which confirms that its original intuitive interpretation – as a characteristics expressing the requirements of the least-motion principle – really is justified. Beside that, on the basis of the respective interpretation of the r_{RP} index the physical meaning of the similarity index of the second order⁸ is discussed too.

THEORETICAL AND DISCUSSION

As the object of the present paper is immediately connected with our previous communications^{6,7} in which we introduced (and subsequently applied to the theory of reactivity) the so-called topological similarity index, it would be useful to briefly recall the basic ideas of the mentioned communications in an extent necessary for the purposes of the present study. Our approach is based on the incorporation of the original ideas by Polansky and Carbo into the framework of the recently suggested method of the so-called overlap determinant⁹.

The topological similarity index r_{RP} is defined, on the basis of this incorporation, in terms of the density matrices of the reactant and product by Eq. (1) which can be considered a generalization of the original relationship by Polansky:

$$r_{RP} = \frac{1}{2N} \text{Tr}\{\mathbf{P}_R \bar{\mathbf{P}}_P\}, \quad (1)$$

where N means the number of electrons and Tr symbolizes the trace of resulting matrix. This generalization predominantly concerns the density matrix \mathbf{P}_P which in our approach characterized by the relation (1), appears in the form of the conjugate matrix $\bar{\mathbf{P}}_P$ determined by the similarity transformation:

$$\bar{\mathbf{P}}_P = \mathbf{T}^{-1} \mathbf{P}_P \mathbf{T}. \quad (2)$$

In this transformation the decisive role is played by the \mathbf{T} matrix whose close relation to the assignment tables⁹ of the overlap determinant method allows the whole formalism to be used in the theory of chemical reactivity, particularly for differentiation between allowed and forbidden pericyclic processes. This possibility was also really confirmed in a number of cases, the general result being formulated as the rule that the reactant and product of an allowed reaction are more similar to each other than those of a forbidden reaction. This result was interpreted very clearly on the basis of an intuitive parallel between the magnitude of similarity index and the extent of electronic reorganization in the given reaction⁶. It is obvious that the greater is the similarity between the respective reactant and product, the closer also are their electronic structures and, hence, the smaller should be the additional reorganization needed for transformation of one structure into the other. In the present paper it will be shown that the above-mentioned intuitive interpretation of the similarity index as a measure of the extent of electronic reorganization really is justified.

The basis of such theoretical justification lies in an alternative transcription of the original definition equation (1) in a form making use of the transformation of the density matrices \mathbf{P}_R and $\bar{\mathbf{P}}_P$ from the usual basis of atomic orbitals to the basis of molecular orbitals of some of the reaction components. Let this, e.g., be the basis

of the molecular orbitals of the reactant. In this basis the \mathbf{P}_R matrix has an especially simple diagonal form (3) in which 2's represent the occupation numbers of the occupied molecular orbitals and zeros correspond to the virtual orbitals:

$$\mathbf{P}_R^{(\text{MO})R} = \mathbf{C}^{-1} \mathbf{P}_R \mathbf{C}, \quad (3a)$$

$$\mathbf{P}_R^{(\text{MO})R} = \text{diag}(2, \dots, 2, 0, \dots, 0). \quad (3b)$$

The \mathbf{C} matrix which transforms the \mathbf{P}_R matrix into the diagonal form then also ensures the transformation of the $\bar{\mathbf{P}}_P$ matrix (4):

$$\bar{\mathbf{P}}_P^{(\text{MO})R} = \mathbf{C}^{-1} \bar{\mathbf{P}}_P \mathbf{C}, \quad (4a)$$

$$\bar{\mathbf{P}}_P^{(\text{MO})R} = \begin{bmatrix} \eta_{11} & \eta_{12} & \cdots & \eta_{1N} \\ \eta_{21} & & & \vdots \\ \vdots & & & \vdots \\ \eta_{N1} & & & \eta_{NN} \end{bmatrix}. \quad (4b)$$

Although the form of this matrix is not formally simplified by such a transformation (it still contains both diagonal and nondiagonal elements) nevertheless, the work in the basis of molecular orbitals is very advantageous. On this basis it is possible to transform the original equation (1) into the alternative form (5) from which the sought physical meaning of similarity index is quite obvious:

$$r_{RP} = \sum_i^{\text{occ}} \eta_{ii} / N. \quad (5)$$

If one realizes that the matrix elements η_{ii} correspond to the "electron density" which is — in the description of the product molecule — formally accumulated in the molecular orbitals of the reactant, then the numerator of the fraction at the right-hand side of Eq. (5) gives the portion of the overall number N of electrons which during transformation $R \rightarrow P$ remain "formally nonexcited" in the subspace of the occupied molecular orbitals of the reactant. The "excitation" extent is thus quite naturally given by subtraction of this numerator from the value N . Its formal normalization by the overall number N of the electrons gives the relationship (6) which immediately confirms not only the legitimacy of the original intuitive interpretation of similarity index but also simultaneously imparts detailed precision to the physical meaning of this index:

$$(N - \sum_i^{\text{occ}} \eta_{ii}) / N = 1 - r_{RP}. \quad (6)$$

In context with this relationship it is interesting also to mention some further con-

sequences following from the given interpretation of the similarity index. First of all it can be seen that in the characterization of extent of electron reorganization this index only utilizes the diagonal elements η_{ii} . However, these elements involve only a part of information contained in the whole density matrix. The rest contained in the nondiagonal elements will not make itself felt in the similarity index. Although the diagonal elements η_{ii} perhaps are decisive for the characterization of electron configuration, the information involved in the nondiagonal elements η_{ij} can be significant in some cases as well. A typical example of such situation is encountered e.g. with the cycloaddition reactions where (as it was shown in the original communication⁶) the r_{RP} values do not allow any discrimination between allowed and forbidden processes. As it can easily be seen from the detailed form of the corresponding density matrices for the model cases ($s + s$) and ($s + a$) dimerization of ethene (Eqs (7a) and (7b), respectively), the reason consists just in the differences between nondiagonal elements of the respective matrices which, however, are not considered in the similarity index:

$$\bar{P}_{P(s+s)}^{(MO)R} = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 \end{bmatrix}, \quad (7a)$$

$$\bar{P}_{P(s+a)}^{(MO)R} = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & -1 & 0 \\ 0 & -1 & 1 & 0 \\ 1 & 0 & 0 & 1 \end{bmatrix}. \quad (7b)$$

Hence it is seen that the simple and clear physical meaning of the similarity index, on the other side, is redeemed by a certain loss of information. In this context there naturally arises the question whether it would be possible to introduce – for the characterization of electron configuration – some other characteristics which would eliminate the above-mentioned drawbacks.

In our previous paper we were led by just these reasons and suggested the so-called second order similarity index, g_{RP} , (ref.⁸) defined quite analogously as the r_{RP} index with the only difference that the spinless reduced density matrices of the second order, \tilde{q} , are used in Eq. (8) for the characterization of electron structure of both the molecules compared:

$$g_{RP} = \frac{\int \tilde{q}_R(1, 2) \tilde{q}_P(1, 2) d\tau_1 d\tau_2}{\left[\int [\tilde{q}_R(1, 2)]^2 d\tau_1 d\tau_2 \right]^{1/2} \left[\int [\tilde{q}_P(1, 2)]^2 d\tau_1 d\tau_2 \right]^{1/2}} \quad (8)$$

In ref.⁸ it was shown that this general relationship can be expressed by means of the reduced density matrices of the first order (Eq. (9)):

$$g_{RP} = \frac{9 [\text{Tr} \{ \mathbf{P}_R \bar{\mathbf{P}}_P \}]^2 - 7 \text{Tr} \{ \mathbf{P}_R \bar{\mathbf{P}}_P \mathbf{P}_R \bar{\mathbf{P}}_P \}}{4N(9N - 14)} \quad (9)$$

If now also in this case we apply the transformation of the density matrices from the basis of atomic orbitals to that of molecular orbitals, it can be shown that this relationship will be changed into the alternative form (10) from which it can be seen that the expected increase in the information content and, hence, in the discrimination ability of the g_{RP} index is attained just as a consequence of involvement of the nondiagonal elements η_{ij} :

$$g_{PR} = \frac{9 \left[\sum_i^{\text{occ}} \eta_{ii} \right]^2 - 7 \sum_i^{\text{occ}} \sum_j^{\text{occ}} \eta_{ij}^2}{N(9N - 14)} \quad (10)$$

However, the resulting relation itself is more complex as compared with Eq. (5), hence it cannot be given as simple and clear physical meaning as in the case of the r_{RP} index.

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