TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY. THEORETICAL JUSTIFICATION OF OVERLAP DETERMINANT METHOD

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The mutual relation of overlap determinant method and the selection rules in chemical reactivity has been analysed in terms of the technique of the configuration analysis. Such approach allows to prove the generality and the universality of the originally introduced criterion not only for thermal but also for photochemical reactions.

In our previous paper[1] a simple method was proposed allowing to analyse the nature of chemical reactions in terms of the so-called overlap determinant. The wide applicability of the method has been demonstrated on a number of examples including various types of not only thermal but also photochemical reactions[1,2]. In none of the studied examples we have succeeded so far in finding an exception from the validity of the suggested criterion. Despite of these results it is nevertheless desirable to justify the principles of the original intuitively formulated method on a more profound theoretical basis. This concerns especially the cases where the applicability of the method exceeds the range of validity of Woodward–Hoffmann approach. Within the framework of these efforts can be included our recent attempt to represent the overlap determinant method in terms of a vector model the corrected version of which[3] really suggests the expected universality. Our aim at this work is to support the conclusions of this preliminary study and to demonstrate the mutual relation of overlap determinant method and the selection rules in chemical reactivity.

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Our proof of the general validity of the overlap determinant method is based on the procedure arising from the principles of the so called configuration analysis[4]. For the simplicity only the ground state reactivity is discussed but the formalism of the proof is general enough to be extended to photochemical reaction as well. Without the loss of generality let us study therefore a simple isomerisation reaction R→P in which both the reactant and the product are closed shell molecules in the

ground electronic state. Their structure be described, in harmony with the philosophy of the overlap determinant method by the bonding functions Φ_R and Φ'_P expressed in the form of Slater determinant (Eq. (1)) constructed from the individual bonds

$$\Phi_R = \left| r_1 \bar{r}_1 r_2 \bar{r}_2 \ldots r_n \bar{r}_n \right| \tag{1}$$

$$\Phi'_P = \left| p'_1 \bar{p}'_1 p'_2 \bar{p}'_2 \ldots p'_n \bar{p}'_n \right|$$

forming in a given reaction the irreducible core[1]. The corresponding bonds are again described in terms of familiar linear combinations of some nonspecified orbitals χ and χ' localised on atoms formally connected by the classical chemical bonds. In analogy with the concept of bonding localised orbitals these combinations are required not to contain the node between the bonded centers. Going further in this analogy it is possible to assign to any classical bond r_i, p'_j the corresponding virtual bond[2] r_i^*, $p_j^{*\prime}$ characterised, like the antibonding localised orbital by the presence of the node separating the bonded atoms. This extension permits not only to generalise the original overlap determinant method for the description of photochemical reactions but opens also the possibility to use the formalism of the configuration analysis in the proof of its generality.

In formulating this proof the first step consists, similarly as in the original paper, in transforming the bonds of the product from the basis of primed atomic orbitals χ' into the basis of orbitals χ serving simultaneously to the description of the reactant bonds. This transformation schematically expressed by Eq. (2)

$$
\begin{array}{lll}
p'_1 \to p_1 & p_1^{*\prime} \to p_1^* & \\
p'_2 \to p_2 & p_2^{*\prime} \to p_2^* & \Phi'_P \to \Phi_P \\
\vdots & \vdots & \\
p'_n \to p_n & p_n^{*\prime} \to p_n^* &
\end{array}
\tag{2}
$$

can be performed using the assignment tables describing, in dependence on the actual reaction mechanism, the mutual relation of basis sets $\{\chi\}$ and $\{\chi'\}$. The detailed procedure of construction of these tables can be found in our original paper[1] and need not be repeated. The above transformation opens the possibility to employ the idea of the configuration expansion and to express the ground state bonding function Φ_R in terms of the "modified" product ground state function Φ_P and of its "excited" configurations $\Phi^*_{P,j}$ (Eq. (3))

$$\Phi_R = c_0 \Phi_P + \sum_j c_j \cdot \Phi^*_{P,j} . \tag{3}$$

Provided that the set of these functions (determinants) is constructed to be orthogonal, the individual values of the coefficients c_i are given, similarly as the coefficients

of the Fourier series, by the "overlap integrals" of the function Φ_R with the functions Φ_P, $\Phi_{P,i}^*$. (Eq. (4))

$$c_0 = \int \Phi_R \Phi_P \, d\tau , \qquad\qquad (4a)$$

$$c_i = \int \Phi_R \Phi_{P,i}^* \, d\tau . \qquad\qquad (4b)$$

Even if the above general procedure allows to determine all the coefficients of the expansion (3) such a detailed knowledge is not necessary. For the purpose of our proof it is sufficient to determine only the coefficient c_0 indicating whether and to what extent the reactant function Φ_R "resembles" the product function Φ_P. If this coefficient differs from zero and the function Φ_R "contains" the contribution of the function Φ_P the corresponding reaction can be regarded as allowed. On the other hand if $c_0 = 0$ the reaction is forbidden. Taking into the consideration the definition of the coefficient c_0 (Eq. $(4a)$) as well, as the method of modification of the product bonding function Φ_P the equivalency of the above "selection" rules with the originally introduced overlap determinant criterion is obvious. But in contrast to the original intuitive formulation the presented alternative derivation allows to estimate also the range of applicability of the new formalism. In this repect one has to realize that the above conditions represent nothing but a mathematical formulation of the intuitive general requirement according to which such a reaction is allowed in which the ground state of the reactant is converted during the transformation into the ground state of the product. Since this intuitive principle is probably entirely general there seems to be no restrictions concerning the applicability and the validity of the overlap determinant method. The same reasoning can be also used to justify the use of this method to photochemical reactions. The only difference consists in this case in that the "excited" bonding function of the reactant Φ_R^* is to be used instead of the ground state function Φ_R. The detailed procedure of selecting and constructing these "excited" functions is described in the original paper[2].

Despite of complete generality and the universality of the overlap determinant method one has to realise, however, that the method itself does not introduce into the chemical reactivity theory any new principle but that it is still based on the same physical principles as the Woodward–Hoffmann rules. The basic idea of both approaches originates in the above intuitive principle alternatively formulated by Hoffmann[5] in the form of condition requiring for the reaction to be allowed the maximum conservation of "bonding relations". While the original W–H approach identifies the conservation of these abstract "bonding relations" with the conservation of orbital symmetry the proposed topological approach gives the same requirement the physical meaning of preserving the nodal structure of the bonds. In a majority of cases both

these approaches are equivalent. The advantage of the new formalism thus consists only in its simplicity and perhaps also in a great universality allowing to formulate the selection rules even in cases in which the original technique of correlation diagrams fails *e.g.* because the conserved symmetry element does not obey the necessarry conditions required by the W–H rules.

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