TOPOLOGICAL ASPECTS OF CHEMICAL REACTIVITY. ELECTRON CORRELATION IN THE COURSE OF CHEMICAL REACTIONS

Robert PONEC and Martin STRNAD

Institute of Chemical Process Fundamentals,
Academy of Sciences of the Czech Republic, 165 02 Prague 6-Suchdol, The Czech Republic

Received September 3, 1992
Accepted February 8, 1993

The second order similarity index g_{RP}, which has been proposed recently as a new means for a qualitative characterization of correlation effects in chemical reactivity, was generalized by incorporation into a topological model of the overlap determinant method. The resulting approach, which provides information about the variation of electron correlation during chemical reactions, was applied to the investigation of several selected pericyclic reactions. Consistent with what can be expected, the role of electron correlation was found to be the most critical for transition states or other transient species near the top of the energy barrier. The systematic differences in the extent of electron correlation between allowed and forbidden reactions are also discussed.

Electron reorganization accompanying the process of structural transformation in chemical reactions is inherently connected with the phenomenon of mutual coupling of electron motions – the so-called electron correlation. Manifestations of this phenomenon in chemical reactivity are extremely heterogeneous, and in addition to the well-known correcting effect on the activation and reaction energies (correlation energy)[1], examples are also known where electron correlation affects the number, and exceptionally also the nature, of critical points on the PE hypersurface. For instance, in the Diels–Alder reaction the C_s critical structure resulting from the synchronous approach of the ethene and butadiene moieties has been found dependent on the quality of the methods used (true transition state vs second order saddle point)[2 – 4]. As a consequence of this remarkable richness of manifestations, the spectrum of studies dealing with correlation effects is also very broad and ranges from purely computational numerical investigations of the changes in the quality of calculated results with increasing accuracy of the methods[5 – 8], to studies attempting to analyze the correlation effects in a more systematic but qualitative way[9 – 13].

Studies of this type are often based on the analysis of properties of the second order or pair density matrix[14 – 15]. Examples include Salem's study discussing the electron reorganization in pericyclic reactions in terms of pair correlation functions[11] and our recent studies dealing with the analogous use of the so-called second and third order similarity indices[12,13]. The potential of the proposed similarity approach is demonstrated, e.g., by the conclusions of the recent study[16], confirming the close correspondence between the extent of electron correlation and the forbiddenness and/or allowedness of pericyclic reactions. Although such a simple qualitative insight is certainly valuable and interesting, the potential of the similarity approach is much broader. One of the possible extensions consists in an appropriate generalization of the original indices r_{AB} and g_{AB} for taking into account not only the structures of the initial reactant and the final product but also all the transient species through which the system passes during its motion along the reaction path.

Our aim in this study was to follow the above philosophy and to propose an appropriate modification of the original formalism[16] providing a more detailed insight into the role of electron correlation during the process of structural reorganization.

THEORETICAL

The basic idea of the proposed modification consists in an incorporation of the similarity approach into the framework of the topological theory of chemical reactivity based on the generalized overlap determinant method[17]. Since the principles of that method are sufficiently described in the original study[17], we shall confine ourselves to a brief recapitulation of the basic ideas to the extent necessary for the purpose of this study. The generalized overlap determinant method is based on a simple intuitive idea which regards the chemical reaction R → P as a specific transformation converting the structure of the reactant into the structure of the product. When describing the structures of the reacting molecules R and P by the approximate electron wave functions Φ_R and Φ_P, respectively, the above idea can be mathematically expressed by an abstract mapping, converting, by a continuous change in a certain parameter, the wave function Φ_R into the function Φ_P. The actual form of this mapping is not very important as long as the criterion of continuity and mutual uniqueness is satisfied. In our previous study[17] we used for this purpose a simple trigonometric formula,

$$\Phi(\varphi) = \frac{1}{\sqrt{1 + S_{RP} \sin 2\varphi}} (\Phi_R \cos \varphi + \Phi_P \sin \varphi) , \qquad (1)$$

describing the structure of the transient species by the generalized wave function $\Phi(\varphi)$. In this formula, S_{RP} denotes the overlap between Φ_R and Φ_P and the parameter ensuring the continuous transformation R → P is represented by the variable $\varphi \in \langle 0, \pi/2 \rangle$*. On

---

* Although a correct description of forbidden reactions generally requires variation of φ within the range of $\langle 0, -\pi/2 \rangle$ (ref.[18]), the quantities introduced in this study are independent of the direction of the reaction path and both allowed and forbidden reactions can be correctly described by φ varying between $\langle 0, \pi/2 \rangle$.

the basis of the generalized wave function (*1*) describing the structure of the transient species at various points along the reaction path, the corresponding pair density function

$$\Gamma_2(\boldsymbol{x}_1, \boldsymbol{x}_2|\,\varphi) = \frac{N(N-1)}{2}\int \Phi^2(\varphi)\,\mathrm{d}\sigma_1 \ldots \mathrm{d}\sigma_N\,\mathrm{d}\boldsymbol{x}_3 \ldots \mathrm{d}\boldsymbol{x}_N \qquad (2)$$

can be introduced as a basic quantity in terms of which the electron correlation during the process of structural transformation can be analyzed. In this study, however, these pair densities will not be used directly. Instead we employ a similarity index $g(\varphi)$

$$g(\varphi) = \frac{\int \Gamma_2(\boldsymbol{x}_1, \boldsymbol{x}_2|\,\varphi)\ \ \Gamma_{\mathrm{ref}}(\boldsymbol{x}_1, \boldsymbol{x}_2|\,\varphi)\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2}{\left(\int \Gamma_2^2(\boldsymbol{x}_1, \boldsymbol{x}_2|\,\varphi)\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2\right)^{1/2}\left(\int \Gamma_{\mathrm{ref}}^2(\boldsymbol{x}_1, \boldsymbol{x}_2|\,\varphi)\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2\right)^{1/2}}\,, \qquad (3)$$

which characterizes the desired correlation effects by comparing the actual density matrix $\Gamma_2(\boldsymbol{x}_1, \boldsymbol{x}_2|\,\varphi)$ at the various points of the reaction path with the density matrix of totally uncorrelated reference standard $\Gamma_{\mathrm{ref}}(\boldsymbol{x}_1, \boldsymbol{x}_2|\,\varphi)$. The choice of such a standard is, of course, a matter of certain arbitrariness, but there are nevertheless two generally accepted definitions; both will be used and compared below.

The first is based on the proposal by McWeeny and Kutzelnigg[19] who define the pair density of the reference standard as a simple product of the corresponding first order density matrices*

$$\Gamma_{\mathrm{ref}}(\boldsymbol{x}_1, \boldsymbol{x}_2|\,\varphi) = \Gamma_1(\boldsymbol{x}_1|\,\varphi)\ \ \Gamma_1(\boldsymbol{x}_2|\,\varphi)\,, \qquad (4)$$

where

$$\Gamma_1(\boldsymbol{x}_1|\,\varphi) = N\int \Phi^2(\varphi)\,\mathrm{d}\sigma_1 \ldots \mathrm{d}\sigma_N\,\mathrm{d}\boldsymbol{x}_2 \ldots \mathrm{d}\boldsymbol{x}_N \qquad (5)$$

and similarly $\Gamma_1(\boldsymbol{x}_2|\,\varphi)$. Introducing the usual expansion of Γ_1 and Γ_2 in the basis of atomic orbitals χ_τ

$$\Gamma_1(\boldsymbol{x}_i|\,\varphi) = \sum_\alpha \sum_\beta\ [\Omega_1(\varphi)]_{\alpha\beta}\ \chi_\alpha(\boldsymbol{x}_i)\ \chi_\beta(\boldsymbol{x}_i) \qquad (i = 1, 2)\,, \qquad (6)$$

---

* By virtue of relation (*3*), the normalization factor[20] $(n-1)/n$, which is usually present on the right side of Eq. (*4*), is irrelevant and can be omitted.

$$\Gamma_2(\boldsymbol{x}_1, \boldsymbol{x}_2 | \varphi) = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} [\Omega_2(\varphi)]_{\alpha\beta\gamma\delta}\, \chi_\alpha(\boldsymbol{x}_1)\, \chi_\beta(\boldsymbol{x}_1)\, \chi_\gamma(\boldsymbol{x}_2)\, \chi_\delta(\boldsymbol{x}_2) \qquad (7)$$

and using the analogous topological approximations as in the case of the previously introduced indices[12,21] r_{RP} and g_{RP} the above general expression (*3*) can be rewritten in the form

$$g(\varphi) = \frac{\sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} [\Omega_1(\varphi)]_{\alpha\beta}\, [\Omega_1(\varphi)]_{\gamma\delta}\, [\Omega_2(\varphi)]_{\alpha\beta\gamma\delta}}{\mathrm{Tr}\, \Omega_1^2(\varphi) \left(\sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} [\Omega_2(\varphi)]^2_{\alpha\beta\gamma\delta} \right)^{1/2}}\,, \qquad (8)$$

where symbol Tr denotes the trace of the matrix*.

Another choice of the reference standard was proposed by Hashimoto[9], who derived the pair density $\Gamma_{\mathrm{ref}}(\boldsymbol{x}_1, \boldsymbol{x}_2 | \varphi)$ directly from the single determinant wave function. Using this alternative, the final expression for the pair density Γ_{ref} (see also ref.[12] and Appendix) in the basis of atomic orbitals is given by the relation

$$\Gamma_{\mathrm{ref}}(\boldsymbol{x}_1, \boldsymbol{x}_2 | \varphi) = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} \Big([\Omega_1(\varphi)]_{\alpha\beta}\, [\Omega_1(\varphi)]_{\gamma\delta} - \frac{1}{4} [\Omega_1(\varphi)]_{\alpha\gamma}\, [\Omega_1(\varphi)]_{\beta\delta} -$$

$$- \frac{1}{4} [\Omega_1(\varphi)]_{\alpha\delta}\, [\Omega_1(\varphi)]_{\beta\gamma} \Big)\, \chi_\alpha(\boldsymbol{x}_1)\, \chi_\beta(\boldsymbol{x}_1)\, \chi_\gamma(\boldsymbol{x}_2)\, \chi_\delta(\boldsymbol{x}_2)\,. \qquad (9)$$

Using this standard, the similarity index $\tilde{g}(\varphi)$ can be introduced as in Eq. (*8*).

In the following part, application of the above indices will be demonstrated on several selected pericyclic reactions, both forbidden and allowed. Attention will be paid to a systematic investigation of the changes in the extent of electron correlation during the motion of the system along the reaction path, particularly from the point of view of the differences between the allowed and forbidden reactions. In order to maintain a close continuity with our previous studies[12,13,16,21] we shall also confine ourselves to the same (or only slightly extended) series of reactions, owing to which the presentation of technical details can be reduced. The conjugated skeletons were described by a simple

---

* The necessary expressions defining matrices $\Omega_1(\varphi)$ and $\Omega_2(\varphi)$ are given in the Appendix.

HMO model compatible with the topological nature of the approach, whereas in the remaining cases the localized π and σ bonds were described by strictly localized orbitals. The calculated values of the similarity indices g and $\tilde{g}$ for the continuously changing parameter φ are summarized in Tables I and II and, for the specific case of 2 + 2 ethene dimerization, shown in Fig. 1.

RESULTS AND DISCUSSION

Let us discuss now some general conclusions that can be derived from the calculated results. First what can be deduced from the two tables is that irrespective of the choice of the reference standard, the calculated dependences are qualitatively similar and differences only appear in the particular numerical values of corresponding indices. These differences can be best demonstrated by comparing the indices g and $\tilde{g}$ for the initial reactant and the final product, where the difference $\tilde{g}(0) = \tilde{g}(\pi/2) = 1$ vs $g(0) = g(\pi/2) < 1$ reflects perfectly the difference in the definition of the corresponding reference standard. The above difference is then also reflected in the whole dependence where the $g(\varphi)$ values are systematically lower than the $\tilde{g}(\varphi)$ values for any φ. A typical form of the $g(\varphi)$ vs φ dependence for both the allowed and forbidden ethene dimerization is shown in Fig. 1. This figure immediately suggests several facts concerning the role of electron correlation in the reaction. The most interesting is the very form of these dependences, which demonstrates that the role of electron correlation during the chemical reaction is not constant but systematically varies so that the mutual coupling is largest for the critical structures $X(\pi/4)$ which play in the generalized overlap determinant method a role which is analogous to the transition state on the PE hypersurface. This result is very interesting since a question arises as to whether the predicted greater role of electron correlation for transition states can also be interpreted in a sense that the electron correlation affects predominantly the activation rather than reaction energies.

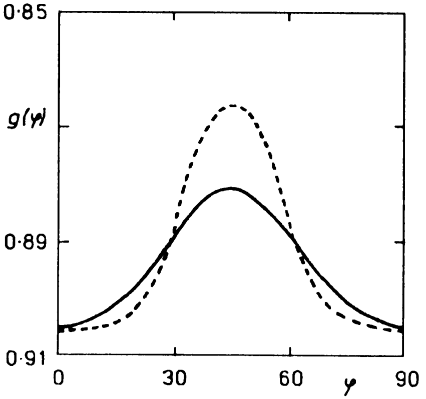


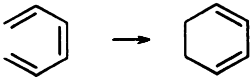
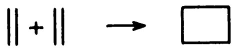
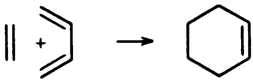
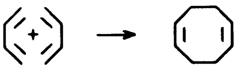
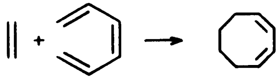
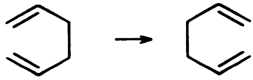
FIG. 1
Calculated dependences of the similarity indices g vs φ for the allowed s + a (full line) and forbidden s + s (broken line) ethene dimerization

In this connection it is, however, necessary to be aware of the fact that without a direct proof of the relation between the value of the similarity index and the magnitude of the correlation energy, the above intuitive interpretation is to be taken with caution.

Another conclusion that can be deduced from the comparison of the $g(\varphi)$ and $\tilde{g}(\varphi)$ vs φ dependences concerns the differences in the role of electron correlation between the allowed and forbidden reactions. In general it again holds that irrespective of the choice of the reference standard, the role of the correlation is higher in forbidden reac-

TABLE I

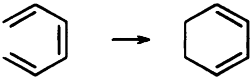
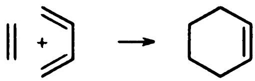
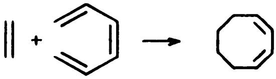
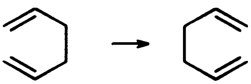
Calculated values of similarity index g in dependence on change in the reaction coordinate φ for selected pericyclic reactions. In the column rm (reaction mechanism) the upper and lower values correspond to the allowed and forbidden reaction mechanisms, respectively

Reaction	rm	φ, deg						
		0	15	30	45	60	75	90
	con	0.905	0.903	0.901	0.900	0.901	0.903	0.905
	dis	0.905	0.904	0.888	0.867	0.888	0.904	0.905
	dis	0.913	0.912	0.911	0.910	0.911	0.912	0.913
	con	0.913	0.913	0.907	0.899	0.907	0.913	0.913
	con	0.919	0.919	0.918	0.917	0.918	0.919	0.919
	dis	0.919	0.919	0.916	0.912	0.916	0.919	0.919
	s + a	0.905	0.901	0.889	0.881	0.889	0.901	0.905
	s + s	0.905	0.904	0.888	0.867	0.888	0.904	0.905
	s + s	0.913	0.912	0.902	0.894	0.902	0.912	0.913
	s + a	0.913	0.912	0.901	0.886	0.901	0.912	0.913
	s + a	0.919	0.918	0.910	0.901	0.910	0.918	0.919
	s + s	0.919	0.919	0.909	0.897	0.909	0.919	0.919
	s + a	0.919	0.919	0.913	0.907	0.913	0.919	0.919
	s + s	0.919	0.919	0.912	0.903	0.912	0.919	0.919
	s, s	0.913	0.912	0.896	0.879	0.896	0.912	0.913
	s, a	0.913	0.912	0.893	0.870	0.893	0.912	0.913

tions than in allowed ones. Actually, this result is not very surprising because a greater role of the electron correlation in forbidden reactions can also be expected from the existence of the orbital crossing between the occupied and empty orbitals. Nevertheless, the fact that the above approach complements the original intuitive considerations with a quantitative estimate of the extent of the correlation effects is certainly valuable, and it can also be useful in practice, e.g. in a systematic investigation of changes in electron correlation in a series of related reactions. An example of such use is the

TABLE II

Calculated values of similarity index $\tilde{g}$ in dependence on change in the reaction coordinate φ for selected pericyclic reactions. In the column rm (reaction mechanism) the upper and lower values correspond to the allowed and forbidden reaction mechanisms, respectively

Reaction	rm	φ, deg						
		0	15	30	45	60	75	90
	con	1.000	0.999	0.996	0.995	0.996	0.999	1.000
	dis	1.000	0.993	0.950	0.905	0.950	0.993	1.000
	dis	1.000	0.999	0.997	0.996	0.997	0.999	1.000
	con	1.000	0.998	0.984	0.970	0.984	0.998	1.000
	con	1.000	0.999	0.998	0.997	0.998	0.999	1.000
	dis	1.000	0.999	0.992	0.986	0.992	0.999	1.000
	s + a	1.000	0.996	0.979	0.968	0.979	0.996	1.000
	s + s	1.000	0.993	0.950	0.905	0.950	0.993	1.000
	s + s	1.000	0.998	0.985	0.974	0.985	0.998	1.000
	s + a	1.000	0.997	0.977	0.955	0.977	0.997	1.000
	s + a	1.000	0.998	0.987	0.976	0.987	0.998	1.000
	s + s	1.000	0.998	0.984	0.969	0.984	0.998	1.000
	s + a	1.000	0.999	0.991	0.984	0.991	0.999	1.000
	s + s	1.000	0.999	0.987	0.976	0.987	0.999	1.000
	s, s	1.000	0.997	0.975	0.952	0.975	0.997	1.000
	s, a	1.000	0.997	0.969	0.936	0.969	0.997	1.000

comparison of the $g(\pi/4)$ or $\tilde{g}(\pi/4)$ indices for allowed and forbidden reactions. When using these indices as a measure of the maximal extent of correlation effects, the corresponding differences between allowed and forbidden reactions are observed to decrease regularly with increasing size of the system. This result is again very interesting since it confirms another expected result, viz blurring of the differences between the allowed and forbidden reactions as the systems increase in size. This suggests a decrease in the strictness of the selection rules for larger systems.

Another interesting result that can be deduced from the calculated $g(\pi/4)$ and $\tilde{g}(\pi/4)$ values concerns the comparison of the specific differences between the allowed and forbidden processes according to the kind of the system. When comparing systems of the same size, the difference between allowed and forbidden reactions is generally lower for sigmatropic and cycloaddition reactions, which belong to the broad class of multibond processes[22], than for electrocyclic ones. This fact is also noteworthy because it demonstrates that the specific position, or a certain subtlety, of these reactions arises from the fact that they are apparently more sensitive to the inclusion of the electron correlation than "normal" electrocyclic reactions are. The origin of the various contradictory conclusions of the quantum chemical analyses of the mechanism of pericyclic reactions thus apparently lies just here, or more precisely, in the apparently insufficient inclusion of the electron correlation into some of the calculations[3,4,8].

In conclusion, even though some of the facts are not altogether new, the remarkable simplicity of the approach allows it to be applied to broader classes of reactions and opens up the opportunity to systematically investigate general trends and tendencies that are difficult to disclose by ordinary quantum chemical calculations. We thus believe that its systematic use in the future may contribute to a better understanding of the intriguing problem of the role of electron correlation in chemical reactions.

The authors thank Professor M. Urban (Department of Physical Chemistry, Comenius University, Bratislava) for critical reading of the manuscript and for valuable comments.

APPENDIX

Describe the structures of the reactant and the product of a given reaction by approximate wave functions Φ_R, Φ_P, respectively, constructed in the standard Slater determinant form ($n = N/2$)

$$\Phi_R = |r_1 \bar{r}_1 r_2 \bar{r}_2 \dots r_n \bar{r}_n| , \qquad (A.1a)$$

$$\Phi_P = |p_1 \bar{p}_1 p_2 \bar{p}_2 \dots p_n \bar{p}_n| , \qquad (A.1b)$$

where the individual molecular orbitals r_i, p_i are transformed into the common basis of atomic orbitals χ_τ as required by the overlap determinant method[17] for discrimination between the allowed and forbidden reaction mechanisms

$$r_i = \sum_\mu \rho_{\mu i}\, \chi_\mu \,, \qquad (A.2a)$$

$$p_i = \sum_\mu \pi_{\mu i}\, \chi_\mu \,. \qquad (A.2b)$$

Within the framework of the model described by Eqs (*1*), (*2*) and (*5*), the density matrices $\Omega_1(\varphi)$ and $\Omega_2(\varphi)$ can be expressed in the form

$$\Omega_i(\varphi) = \frac{1}{1 + S_{\mathrm{RP}} \sin 2\varphi} \left[\Omega_i^{\mathrm{RR}} \cos^2 \varphi + \Omega_i^{\mathrm{PP}} \sin^2 \varphi + \left(\Omega_i^{\mathrm{RP}} + \Omega_i^{\mathrm{PR}}\right) \sin\varphi \cos\varphi\right]$$

$$(i = 1, 2)\,, \qquad (A.3)$$

$$[\Omega_1^{\mathrm{RR}}]_{\alpha\beta} = 2 \sum_{i=1}^{\mathrm{occ}} \rho_{\alpha i}\, \rho_{\beta i}\,, \qquad (A.4a)$$

$$[\Omega_1^{\mathrm{PP}}]_{\alpha\beta} = 2 \sum_{i=1}^{\mathrm{occ}} \pi_{\alpha i}\, \pi_{\beta i}\,, \qquad (A.4b)$$

$$[\Omega_1^{\mathrm{RP}} + \Omega_1^{\mathrm{PR}}]_{\alpha\beta} = 2\, D_{\mathrm{RP}} \sum_{i=1}^{\mathrm{occ}} \sum_{j=1}^{\mathrm{occ}} A_{ij}\, (\rho_{\alpha i}\, \pi_{\beta j} + \rho_{\beta i}\, \pi_{\alpha j}\,, \qquad (A.5)$$

$$[\Omega_2^{\mathrm{QQ}}]_{\alpha\beta\gamma\delta} = [\Omega_1^{\mathrm{QQ}}]_{\alpha\beta}\, [\Omega_1^{\mathrm{QQ}}]_{\gamma\delta} - \frac{1}{4} \left([\Omega_1^{\mathrm{QQ}}]_{\alpha\gamma}\, [\Omega_1^{\mathrm{QQ}}]_{\beta\delta} + [\Omega_1^{\mathrm{QQ}}]_{\alpha\delta}\, [\Omega_1^{\mathrm{QQ}}]_{\beta\gamma}\right)$$

$$(\mathrm{Q} = \mathrm{R}, \mathrm{P})\,, \qquad (A.6)$$

$$[\Omega_2^{RP} + \Omega_2^{PR}]_{\alpha\beta\gamma\delta} = \frac{1}{2\,D_{RP}^2}\,[\Omega_1^{RP} + \Omega_1^{PR}]_{\alpha\beta}\,[\Omega_1^{RP} + \Omega_1^{PR}]_{\gamma\delta} +$$

$$+ \sum_{i=1}^{occ} \sum_{j=1}^{occ} \sum_{k=1}^{occ} \sum_{l=1}^{occ} A_{ij}\,A_{kl}\,(\rho_{\alpha i}\,\pi_{\beta l} + \rho_{\beta i}\,\pi_{\alpha l})\,(\rho_{\gamma k}\,\pi_{\delta j} + \rho_{\delta k}\,\pi_{\gamma j})\,, \qquad (A.7)$$

where D_{RP} is the overlap determinant constructed from orbitals r_i and p_i and related to the overall overlap S_{RP} by

$$S_{RP} = D_{RP}^2 \qquad (A.8)$$

and where A_{ij} is the corresponding minor.

REFERENCES

1. Čársky P., Urban M.: *Ab initio Calculations. Methods and Applications in Chemistry, Lecture Notes in Chemistry 16*. Springer, Berlin 1980.
2. Houk K. N., Lin Y., Brown F. K.: J. Am. Chem. Soc. *108*, 554 (1986).
3. Bernardi F., Bottoni F. A., Field M. J., Guest M. F., Hillier I. H., Robb M. A., Venturini A.: J. Am. Chem. Soc. *110*, 3050 (1988).
4. Dewar M. J. S., Olivella S., Rzepa H.: J. Am. Chem. Soc. *100*, 5650 (1978).
5. Dewar M. J. S., Healy F. E.: Chem. Phys. Lett. *141*, 521 (1987).
6. Osamura Y., Kato S., Morokuma K., Feller D., Davidson E. R., Borden W. T.: J. Am. Chem. Soc. *106*, 3362 (1984).
7. Janoschek R., Kachler J.: Int. J. Quantum Chem. *38*, 653 (1990).
8. Borden W. T., Loncharich R. J., Houk K. N.: Annu. Rev. Phys. Chem. *39*, 213 (1988).
9. Hashimoto K.: Int. J. Quantum Chem. *21*, 861 (1982).
10. Karafiloglou P.: Chem. Phys. *104*, 383 (1986).
11. Salem L.: Nouv. J. Chim. *2*, 559 (1978).
12. Ponec R., Strnad M.: Collect. Czech. Chem. Commun. *55*, 896 (1990).
13. Ponec R., Strnad M.: Collect. Czech. Chem. Commun. *55*, 2583 (1990).
14. Mc Weeny R.: Rev. Mod. Phys. *32*, 335 (1960).
15. Mc Weeny R., Mizuno Y.: Proc. R. Soc. London, A *259*, 554 (1961).
16. Ponec R. Strnad M.: Int. J. Quantum Chem. *42*, 501 (1992).
17. Ponec R.: Collect. Czech. Chem. Commun. *50*, 1121 (1985).
18. Ponec R., Strnad M.: J. Phys. Org. Chem. *5*, 764 (1992).
19. Mc Weeny R., Kutzelnigg W.: Int. J. Quantum Chem. *2*, 187 (1968).
20. Kutzelnigg W.: Top. Curr. Chem. *41*, 31 (1973).
21. Ponec R.: Collect. Czech. Chem. Commun. *52*, 555 (1987).
22. Dewar M. J. S.: J. Am. Chem. Soc. *106*, 209 (1984).

Translation revised by P. Adámek.