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On the Role of Fermi and Coulomb Correlation in Pericyclic Reactions

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The recently proposed similarity approach to the systematic investigation of the changes of electron correlation during the chemical reactions was generalized by introducing the spin-resolved similarity indices allowing the separate investigation of correlation effects between electrons with parallel and antiparallel spins. The approach was applied to the investigation of several selected pericyclic reactions, both forbidden and allowed. The main attention was devoted to the evaluation of the relative role of Fermi and Coulomb correlation, especially from the point of view of the differences between the allowed and forbidden reactions.

Although the principal qualitative features of chemical reactions are usually satisfactorily described by simple MO methods based on the model of independent electrons, the achievement of quantitative agreement between the experimental and theoretical quantities usually requires the use of more sophisticated techniques taking into account the subtler effects of mutual coupling of electron motions, the so-called electron correlation. The manifestations of electron correlation in chemical reactivity are extremely heterogeneous and in addition to primary correcting effect on the heights of the activation and reaction energies *via* the so-called correlation energy, there is also a number of examples where the electron correlation affects also some other qualitative characteristics as *e.g.* the number and the nature of critical points on the potential energy hypersurface. As an example in this respect may serve some pericyclic reactions (the Diels–Alder reaction or 2 + 2 ethene dimerizations) for which the considerable differences in the predicted nature of PE critical points were reported [1–4].

Although the studies devoted to the systematic investigation of the influence of electron correlation on the character and the quality of the calculated theoretical quantities are rather numerous (for exhaustive review see *e.g.* [5]), the majority of these studies deal with this problem only from the point of view of the numerical investigation of the changes

in the quality of the calculated results with increasing quality of the methods used.

In addition to this computational effort, there appeared recently also another kind of studies, attempting to analyze the correlation effects by means of simple qualitative models. The studies of this type are usually based on the analysis of second-order or pair density matrices [6–13]. As an example in this respect it is possible to mention *e.g.* the Salem's study [11] dealing with the analysis of electron reorganization in allowed and forbidden pericyclic reactions in terms of pair correlation functions, or our own recent studies based on the analogous exploitation of the so-called second-order similarity indices [12, 13]. Since these indices are defined in terms of pair densities which inherently include the phenomenon of electron correlation, we proposed in one of our previous studies [12] to exploit these indices as a specific means for the study of correlation effects. As an example demonstrating the possibilities of the proposed similarity approach it is possible to mention *e.g.* the conclusions of recent studies [13, 14], confirming the close correspondence between the allowedness and/or forbiddenness of pericyclic reactions and the extent of electron correlation. In harmony with what could be expected, the role of electron correlation was found to be more important in forbidden reactions than in the allowed ones. In addition to this primary qualitative result, another in-

teresting information concerning the possible parallel between the contributions of Fermi and Coulomb correlation [13] was also obtained.

Our aim in this study is just to follow up the above findings of our previous study and to analyze the question of the relative role of Fermi and Coulomb correlation in a more systematic way. Our approach is based on the modification of the simple similarity model [14]. This modification is based on the decomposition of the original similarity index $g(\varphi)$ into the separate contributions of the electrons with the parallel and antiparallel spin and on the systematic investigation of the regularities in the variations of these spin-resolved similarity indices $g^{\uparrow\downarrow}(\varphi)$ and $g^{\uparrow\uparrow}(\varphi)$ along the reaction path.

THEORETICAL

Since the proposed modification is closely connected with our previous study [14] in which the original similarity model was introduced, we consider it convenient to recapitulate briefly the basic principles of the approach in the extent necessary for the purpose of this study. The basic idea of the similarity model consists in the incorporation of the second-order similarity indices [12] into the framework of the so-called generalized overlap determinant method [15], which is a simple general method of a quantitative characterization of the structural changes accompanying the transformation of the reactants into the products. Within the framework of this method the chemical reaction is regarded as a continuous transformation converting the wave function of the reactant into the wave function of the product. For this purpose a simple trigonometric formula was proposed [15], in which the role of the governing parameter describing the progress of the transformation is played by the variable φ , changing within the range $(0, \pi/2)$.

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

On the basis of the generalized wave function (1) the pair density $\Gamma_2(\mathbf{r}_1, \mathbf{r}_2 | \varphi)$ (eqn (2)) was introduced in the previous study [14] as a basic quantity, in terms of which the nature of correlation effects can be discussed.

$$\begin{aligned} \Gamma_2(\mathbf{r}_1, \mathbf{r}_2 | \varphi) &= \\ &= \frac{N(N-1)}{2} \int \Phi^2(\varphi) d\sigma_1 d\sigma_2 \dots d\sigma_N d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N \quad (2) \end{aligned}$$

The pair density itself is, however, rather complex quantity and the information from it can be extracted

in a number of various ways. One of the simplest such possibilities consists in introducing the so-called second-order similarity index $g(\varphi)$ characterizing the extent of correlation effects by comparing the true pair density (2) with the pair density $\Gamma_{\text{ref}}(\mathbf{r}_1, \mathbf{r}_2 | \varphi)$ of the hypothetical, totally noncorrelated reference standard.

$$\begin{aligned} g(\varphi) &= \\ &= \frac{\int \Gamma_2(\mathbf{r}_1, \mathbf{r}_2 | \varphi) \Gamma_{\text{ref}}(\mathbf{r}_1, \mathbf{r}_2 | \varphi) d\mathbf{r}_1 d\mathbf{r}_2}{\left(\int \Gamma_2^2(\mathbf{r}_1, \mathbf{r}_2 | \varphi) d\mathbf{r}_1 d\mathbf{r}_2 \right)^{1/2} \left(\int \Gamma_{\text{ref}}^2(\mathbf{r}_1, \mathbf{r}_2 | \varphi) d\mathbf{r}_1 d\mathbf{r}_2 \right)^{1/2}} \quad (3) \end{aligned}$$

The choice of this standard is, of course, a little bit arbitrary and from a number of possible alternatives it is possible to mention e.g. the model by *McWeeny* and *Kutzelnigg* [16], defining the pair density of the reference standard as a simple product of corresponding first-order density matrices and the model by *Hashimoto* [17] derived from the one-determinant wave functions. In order to compare the effect of the change in the nature of the standard both the above models were used in the study [14]. Using this approach we have been able to disclose some general rules governing the variation of the electron correlation in the course of pericyclic reactions as well as some systematic differences between the allowed and forbidden reactions.

In this connection it is, however, necessary to remark that the variation of φ within $(0, \pi/2)$ required for eqn (1) gives generally the correct description only of allowed reactions, whereas for the forbidden ones the interval $(0, -\pi/2)$ is generally preferred [18]. In our case, however, this required change in the direction of the reaction path has no impact on the values of similarity indices so that the original eqn (1) with φ varying within $(0, \pi/2)$ can be used to describe both types of reactions.

Our aim in this study is to extend the applicability of the above similarity model and to complement the conclusions of the previous study [14] by a more detailed discussion of the correlation effects in terms of separate contributions of electrons with parallel and antiparallel spins. For this purpose the original similarity index (3) was generalized by introducing the individual spin-resolved similarity indices $g^{\uparrow\uparrow}(\varphi)$ and $g^{\uparrow\downarrow}(\varphi)$ (eqn (4)), the variation of which with the systematic change of the parameter φ allows one to assess the relative role of Fermi and Coulomb correlation in the course of the reaction. In this connection it is perhaps convenient to recall that the analyzing of the Coulomb correlation which is not involved in one-determinant model is made possible in our approach *via* the use of multideterminant wave function (1).

$$g(\varphi)^{\uparrow\uparrow} = \frac{\int \Gamma_2^{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) \Gamma_{\text{ref}}^{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) d\mathbf{r}_1 d\mathbf{r}_2}{\left(\int \Gamma_2^{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) d\mathbf{r}_1 d\mathbf{r}_2\right)^{1/2} \left(\int \Gamma_{\text{ref}}^{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) d\mathbf{r}_1 d\mathbf{r}_2\right)^{1/2}} \quad (4a)$$

$$g(\varphi)^{\uparrow\downarrow} = \frac{\int \Gamma_2^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) \Gamma_{\text{ref}}^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) d\mathbf{r}_1 d\mathbf{r}_2}{\left(\int \Gamma_2^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) d\mathbf{r}_1 d\mathbf{r}_2\right)^{1/2} \left(\int \Gamma_{\text{ref}}^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) d\mathbf{r}_1 d\mathbf{r}_2\right)^{1/2}} \quad (4b)$$

The density matrices $\Gamma_2^{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi)$ and $\Gamma_2^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi)$ appearing in the definition of these indices are derived from the decomposition of the total pair density (2) into the individual spin components

$$\Gamma_2(\mathbf{r}_1, \mathbf{r}_2|\varphi) = \Gamma_2^{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) + \Gamma_2^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) \quad (5)$$

and $\Gamma_{\text{ref}}^{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi)$, $\Gamma_{\text{ref}}^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi)$ are the corresponding pair densities of noncorrelated reference standards. In the case of electrons with antiparallel spins such a standard can be naturally defined in terms of the *McWeeny* and *Kutzelnigg* model [16] by the following equation

$$\Gamma_{\text{ref}}^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) = \Gamma_1^{\uparrow\downarrow}(\mathbf{r}_1|\varphi) \Gamma_1^{\uparrow\downarrow}(\mathbf{r}_2|\varphi) \quad (6)$$

where

$$\Gamma_1^{\uparrow\downarrow}(\mathbf{r}_1|\varphi) = \Gamma_1^{\uparrow\uparrow}(\mathbf{r}_1|\varphi) = \frac{1}{2} \Gamma_1(\mathbf{r}_1|\varphi) \quad (7)$$

$$\Gamma_{\text{ref}}^{\uparrow\downarrow}(\mathbf{r}_1|\varphi) = \int \Phi^2(\varphi) d\sigma_1 d\sigma_2 \dots d\sigma_N d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N \quad (8)$$

and similarly $\Gamma_1(\mathbf{r}_2|\varphi)$.* Situation is, however, slightly more complicated for electrons with the parallel spins since the Fermi correlation operates in this case even for the one-determinant wave functions. For this reason, the use of the reference pair density in the form of simple product of the first-order densities would not be very realistic. In order to take this inherent Fermi coupling into account we consider it more convenient to approximate the reference pair density $\Gamma_{\text{ref}}^{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi)$ by eqn (9) directly derived from the one-determinant *Hashimoto* model [17].

$$\Gamma_{\text{ref}}^{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) = \Gamma_1(\mathbf{r}_1|\varphi) \Gamma_1(\mathbf{r}_2|\varphi) - \Gamma_1^2(\mathbf{r}_1, \mathbf{r}_2|\varphi) \quad (9)$$

This choice of the standard, even if slightly different from the one for the electrons with the antiparallel spins is, however, quite natural and has some important consequences. First of them is that the simi-

larity indices $g^{\uparrow\uparrow}(0)$ and $g^{\uparrow\uparrow}(\pi/2)$ equal unity just as the indices $g^{\uparrow\downarrow}(0)$ and $g^{\uparrow\downarrow}(\pi/2)$. As a consequence of this coincidence, the scales for both types of indices are identical and the corresponding values can be directly compared. Another interesting property arising from the following coincidence

$$g^{\uparrow\uparrow}(0) = g^{\uparrow\downarrow}(0) = g^{\uparrow\uparrow}(\pi/2) = g^{\uparrow\downarrow}(\pi/2) \quad (10)$$

is that the reference standard in both cases corresponds to one-determinant wave function so that all correlation effects reflected in the deviations of the indices from the unity inherently originate from the use of general multideterminant wave function (1).

Introducing now the usual expansion of Γ_1 and Γ_2 in the basis of atomic orbitals (11)

$$\Gamma_1(\mathbf{r}_1|\varphi) = \sum_{\alpha} \sum_{\beta} [\Omega_1(\varphi)]_{\alpha\beta} \chi_{\alpha}(\mathbf{r}_1) \chi_{\beta}(\mathbf{r}_1) \quad (11a)$$

$$\Gamma_2^{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} [\Omega_2(\varphi)]_{\alpha\beta\gamma\delta}^{\uparrow\uparrow} \times \chi_{\alpha}(\mathbf{r}_1) \chi_{\beta}(\mathbf{r}_1) \chi_{\gamma}(\mathbf{r}_2) \chi_{\delta}(\mathbf{r}_2) \quad (11b)$$

$$\Gamma_2^{\uparrow\downarrow}(\mathbf{r}_1, \mathbf{r}_2|\varphi) = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} [\Omega_2(\varphi)]_{\alpha\beta\gamma\delta}^{\uparrow\downarrow} \times \chi_{\alpha}(\mathbf{r}_1) \chi_{\beta}(\mathbf{r}_1) \chi_{\gamma}(\mathbf{r}_2) \chi_{\delta}(\mathbf{r}_2) \quad (11c)$$

and using the same topological approximation as in the case of previously derived indices r_{RP} and g_{RP} [14, 20], the original definition equations (4) can be rewritten in the form (12), allowing the immediate calculation of the corresponding spin-resolved similarity indices for various values of the variable φ^* .

$$g^{\uparrow\uparrow}(\varphi) = \frac{\sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} [\Omega_2(\varphi)]_{\alpha\beta\gamma\delta}^{\uparrow\uparrow} [\Omega_{\text{ref}}(\varphi)]_{\alpha\beta\gamma\delta}^{\uparrow\uparrow}}{\left(\sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} [\Omega_2^2(\varphi)]_{\alpha\beta\gamma\delta}^{\uparrow\uparrow}\right)^{1/2} \left(\sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} [\Omega_{\text{ref}}^2(\varphi)]_{\alpha\beta\gamma\delta}^{\uparrow\uparrow}\right)^{1/2}} \quad (12a)$$

$$g(\varphi)^{\uparrow\downarrow} = \frac{\sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} [\Omega_2(\varphi)]_{\alpha\beta\gamma\delta}^{\uparrow\downarrow} [\Omega_1(\varphi)]_{\alpha\beta} [\Omega_1(\varphi)]_{\gamma\delta}}{\text{Tr } \Omega_1^2(\varphi) \left(\sum_{\alpha} \sum_{\beta} \sum_{\gamma} \sum_{\delta} [\Omega_2^2(\varphi)]_{\alpha\beta\gamma\delta}^{\uparrow\downarrow}\right)^{1/2}} \quad (12b)$$

*Due to the relations (3, 4), the normalization factor $(N - 1)/N$ usually present on the right side of eqn (6) [19] is irrelevant and can be omitted.

*The necessary expressions defining the matrix elements of the corresponding spin-resolved pair densities are given in the appendix.

Table 1. Calculated Dependence of Spin-Resolved Similarity Indices $g^{\uparrow\uparrow}(\varphi)$ and $g^{\uparrow\downarrow}(\varphi)$ on the Change of the Reaction Coordinate φ for a Series of Allowed and Forbidden Electrocyclic Transformations

Reaction	φ°	Allowed		Forbidden	
		$g^{\uparrow\uparrow}(\varphi)$	$g^{\uparrow\downarrow}(\varphi)$	$g^{\uparrow\uparrow}(\varphi)$	$g^{\uparrow\downarrow}(\varphi)$
Butadiene to cyclobutene	0	1.0000	1.0000	1.0000	1.0000
	15	0.9985	0.9988	0.9978	0.9894
	30	0.9957	0.9966	0.9730	0.9451
	45	0.9945	0.9956	0.9428	0.9045
	60	0.9957	0.9966	0.9730	0.9451
	75	0.9985	0.9988	0.9978	0.9894
	90	1.0000	1.0000	1.0000	1.0000
Hexatriene to cyclohexadiene	0	1.0000	1.0000	1.0000	1.0000
	15	0.9991	0.9991	0.9992	0.9955
	30	0.9972	0.9970	0.9915	0.9773
	45	0.9961	0.9960	0.9831	0.9619
	60	0.9972	0.9970	0.9915	0.9773
	75	0.9991	0.9991	0.9992	0.9955
	90	1.0000	1.0000	1.0000	1.0000

Table 2. Calculated Dependence of Spin-Resolved Similarity Indices $g^{\uparrow\uparrow}(\varphi)$ and $g^{\uparrow\downarrow}(\varphi)$ on the Change of the Reaction Coordinate φ for a Series of Allowed and Forbidden Cycloaddition Reactions

Reaction	φ°	Allowed		Forbidden	
		$g^{\uparrow\uparrow}(\varphi)$	$g^{\uparrow\downarrow}(\varphi)$	$g^{\uparrow\uparrow}(\varphi)$	$g^{\uparrow\downarrow}(\varphi)$
Ethene dimerization	0	1.0000	1.0000	1.0000	1.0000
	15	0.9953	0.9963	0.9978	0.9894
	30	0.9778	0.9832	0.9730	0.9451
	45	0.9658	0.9742	0.9428	0.9045
	60	0.9778	0.9832	0.9730	0.9451
	75	0.9953	0.9963	0.9978	0.9894
	90	1.0000	1.0000	1.0000	1.0000
Diels—Alder reaction	0	1.0000	1.0000	1.0000	1.0000
	15	0.9977	0.9977	0.9984	0.9964
	30	0.9848	0.9855	0.9818	0.9755
	45	0.9739	0.9754	0.9628	0.9544
	60	0.9848	0.9855	0.9818	0.9755
	75	0.9977	0.9977	0.9984	0.9964
	90	1.0000	1.0000	1.0000	1.0000

On the basis of these spin-resolved similarity indices the relative role of the Fermi and Coulomb correlation can be discussed from the analysis of dependences $g^{\uparrow\uparrow}(\varphi)$ and $g^{\uparrow\downarrow}(\varphi)$ vs. φ , respectively. In the following part the practical application of the above approach will be demonstrated by several examples of selected pericyclic reactions. In order to maintain the close continuity with our previous related studies [12–14, 20] we also confine ourselves to the same series of reactions. This circumstance allows us to reduce the presentation of necessary technical details for which the reference can be found in the original studies. Hence we will give here only the most basic information, *viz.* that the conjugated skeletons were described by a simple HMO model compatible with the topological nature of the approach. In remaining cases the localized π and σ bonds were described by strictly localized orbitals. The calculated values of similarity indices $g^{\uparrow\uparrow}(\varphi)$, $g^{\uparrow\downarrow}(\varphi)$ in dependence on the continuous

change of the parameter φ are collected in Tables 1–3.

RESULTS AND DISCUSSION

Let us discuss now some principal conclusions which can be deduced from the calculated data. The most important effect reflected in the tables concerns the remarkable parallel in the values of similarity indices for electrons with parallel and antiparallel spins. This parallel manifests itself not only in the equality of the values of $g^{\uparrow\uparrow}(\varphi)$ and $g^{\uparrow\downarrow}(\varphi)$ for $\varphi = 0$ and $\pi/2$ (corresponding to the reactant and the product of a given process), but considerable similarity is observed for the whole dependence $g^{\uparrow\uparrow}(\varphi)$ and/or $g^{\uparrow\downarrow}(\varphi)$ vs. φ . This implies that both Coulomb and Fermi correlation apparently act in parallel. This result is very interesting since the major contribution to electron correlation has been so far regarded to originate from

Table 3. Calculated Dependence of Spin-Resolved Similarity Indices $g^{\uparrow\uparrow}(\varphi)$ and $g^{\uparrow\downarrow}(\varphi)$ on the Change of the Reaction Coordinate φ for the Cope Rearrangement as a Representative of Sigmatropic Reactions and Butadiene to Bicyclobutane Valence Isomerization

Reaction	φ°	Allowed		Forbidden	
		$g^{\uparrow\uparrow}(\varphi)$	$g^{\uparrow\downarrow}(\varphi)$	$g^{\uparrow\uparrow}(\varphi)$	$g^{\uparrow\downarrow}(\varphi)$
Cope rearrangement of 1,5-hexadiene	0	1.0000	1.0000	1.0000	1.0000
	15	0.9971	0.9973	0.9976	0.9967
	30	0.9747	0.9772	0.9712	0.9709
	45	0.9518	0.9570	0.9398	0.9421
	60	0.9747	0.9772	0.9712	0.9709
	75	0.9971	0.9973	0.9976	0.9967
	90	1.0000	1.0000	1.0000	1.0000
Butadiene to bicyclobutane	0	1.0000	1.0000	1.0000	1.0000
	15	0.9962	0.9957	0.9978	0.9917
	30	0.9791	0.9803	0.9776	0.9599
	45	0.9661	0.9695	0.9560	0.9333
	60	0.9791	0.9803	0.9776	0.9599
	75	0.9962	0.9957	0.9978	0.9917
	90	1.0000	1.0000	1.0000	1.0000

Coulomb correlation solely and the role of Fermi correlation was usually ignored. In this connection it is interesting to remark that the important role of Fermi correlation, as well as its parallel with the Coulomb correlation was already stressed in our previous study [13], and the above results thus provide a direct physically more transparent proof in favour of our previous conclusion. In addition to this direct proof of the global similarity in the effects of Fermi and Coulomb correlation, the reported dependences of $g^{\uparrow\uparrow}(\varphi)$ and $g^{\uparrow\downarrow}(\varphi)$ vs. φ allow to obtain also some other interesting conclusions. Thus *e.g.* it is possible to see that the greatest deviations from the limiting value of unity, indicating the greatest mutual coupling of electron motions, are observed for critical structure corresponding to $\varphi = \pi/4$, which plays in the overlap determinant method [15] the analogous role as the transition state on the potential energy hypersurface. This seems to correspond well with the generally accepted experience of practical quantum-chemical calculations that the requirements on the inclusion of electron correlation are usually higher for transition states or for another structures near the top of the energy barrier than for the stable molecules of the reactant and the product.

Taking now the values of $g^{\uparrow\uparrow}(\pi/4)$ and $g^{\uparrow\downarrow}(\pi/4)$ as a quantitative measure of the maximal extent of electron correlation in a given process, further interesting conclusions concerning the systematic differences between the allowed and forbidden reactions can be deduced. Thus the first general trend manifesting itself within the whole series of reactions is that the electron coupling is apparently more important in forbidden reactions than in the allowed ones. This result is not, of course, too surprising since the same behaviour could be expected already from the presence of orbital crossing between the occupied and empty orbitals, but the fact that the above ap-

proach complements the original intuitive ideas by a certain quantitative estimate of the extent of correlation effects is certainly valuable and could be also practically useful, *e.g.* for the systematic investigations of the role of electron correlation in a series of related reactions. As an example in this respect may serve the interesting quantitative estimate of the relative role of Fermi and Coulomb correlation in allowed and forbidden reactions. Thus *e.g.* the comparison of corresponding similarity indices suggests, with the only exception of Cope rearrangement, that the forbidden reactions are generally more sensitive to the Coulomb correlation, while for the allowed ones the Fermi correlation dominates. This result is very interesting since as far as we know it is for the first time that such a detailed specification of the relative role of Fermi and Coulomb correlation in various types of allowed and forbidden pericyclic reactions is reported.

Other interesting and generally valid conclusions can be deduced also from the comparison of corresponding values of similarity indices according to the type of the reaction. Such a comparison reveals that the whole reaction series can be dissected into two classes differing in their sensitivity to the effects of electron correlation. For the first group, formed by the electrocyclic reactions, the sensitivity to electron correlation is relatively small, while for the other group the role of electron correlation is much more profound. Also this result is very interesting since it confirms another conclusion of our previous studies [12, 13, 21] that a certain delicateness of these reactions, which all belong to the so-called multibond processes [22], is directly related to the fact that they are inherently more sensitive to electron correlation than the "normal" electrocyclic ones. Just here, or more precisely in the apparently insufficient inclusion of electron correlation into some of the calculations

thus apparently lies the origin of various contradictory conclusions concerning the mechanisms of multibond reactions [1–4].

APPENDIX

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

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

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

where the individual molecular orbitals r_i , p_j are transformed into the common basis of atomic orbitals χ_n required by the overlap determinant method [15] for the discrimination between the allowed and forbidden reaction mechanisms.

$$r_i = \sum_{\mu} \rho_{\mu} \chi_{\mu} \quad (\text{A. 2a})$$

$$p_j = \sum_{\nu} \pi_{\nu} \chi_{\nu} \quad (\text{A. 2b})$$

Within the framework of the model described by eqns (1–4), the density matrices $\Omega_1(\varphi)$ and $\Omega_2(\varphi)$ can be expressed in the form

$$\Omega_i(\varphi) = [\Omega_i^{\text{RR}} \cos^2 \varphi + \Omega_i^{\text{PP}} \sin^2 \varphi + (\Omega_i^{\text{RP}} + \Omega_i^{\text{PR}}) \sin \varphi \cos \varphi] \quad (i = 1, 2) \quad (\text{A. 3})$$

$$[\Omega_1^{\text{RR}}]_{\alpha\beta} = 2 \sum_i^{\text{OCC}} \rho_{\alpha i} \rho_{\beta i} \quad (\text{A. 4})$$

$$[\Omega_1^{\text{PP}}]_{\alpha\beta} = 2 \sum_i^{\text{OCC}} \pi_{\alpha i} \pi_{\beta i} \quad (\text{A. 5})$$

$$[\Omega_1^{\text{RP}} + \Omega_1^{\text{PR}}]_{\alpha\beta} = 2D_{\text{RP}} \sum_i^{\text{OCCOCC}} \sum_j^{\text{OCCOCC}} A_{ij} (\rho_{\alpha i} \pi_{\beta j} + \rho_{\beta i} \pi_{\alpha j}) \quad (\text{A. 6})$$

$$[\Omega_2^{\text{QQ}}]_{\alpha\beta\gamma\delta} = [\Omega_1^{\text{QQ}}]_{\alpha\beta} [\Omega_1^{\text{QQ}}]_{\gamma\delta} - \frac{1}{4} \left([\Omega_1^{\text{QQ}}]_{\alpha\gamma} [\Omega_1^{\text{QQ}}]_{\beta\delta} + [\Omega_1^{\text{QQ}}]_{\alpha\delta} [\Omega_1^{\text{QQ}}]_{\beta\gamma} \right) \quad (\text{A. 7})$$

(Q = R, P)

$$[\Omega_2^{\text{RP}} + \Omega_2^{\text{PR}}]_{\alpha\beta\gamma\delta} = \frac{1}{2D_{\text{RP}}^2} [\Omega_1^{\text{RP}} + \Omega_1^{\text{PR}}]_{\alpha\beta} [\Omega_1^{\text{RP}} + \Omega_1^{\text{PR}}]_{\gamma\delta} - \sum_i^{\text{OCCOCCOCCOCC}} \sum_j^{\text{OCCOCCOCCOCC}} \sum_k^{\text{OCCOCCOCCOCC}} \sum_l^{\text{OCCOCCOCCOCC}} A_{ij} A_{kl} (\rho_{\alpha i} \pi_{\beta j} + \rho_{\beta i} \pi_{\alpha j}) (\rho_{\gamma k} \pi_{\delta l} + \rho_{\delta k} \pi_{\gamma l}) \quad (\text{A. 8})$$

where D_{RP} denotes the overlap determinant constructed from the orbitals r_i and p_j and A_{ij} is the corresponding minor.

In harmony with the philosophy of the study, the expression for the global pair density $\Omega_2(\varphi)$ is further decomposed into contributions corresponding to electrons with parallel and antiparallel spins. The resulting contributions are given by eqns (A. 9–A. 12), which are directly used in the calculation of the corresponding spin-resolved similarity indices.

$$[\Omega_2^{\text{QQ}}]_{\alpha\beta\gamma\delta}^{\uparrow\downarrow} = \frac{1}{2} [\Omega_1^{\text{QQ}}]_{\alpha\beta} [\Omega_1^{\text{QQ}}]_{\gamma\delta} \quad (\text{Q} = \text{R}, \text{P}) \quad (\text{A. 9})$$

$$[\Omega_2^{\text{QQ}}]_{\alpha\beta\gamma\delta}^{\uparrow\uparrow} = \frac{1}{2} [\Omega_1^{\text{QQ}}]_{\alpha\beta} [\Omega_1^{\text{QQ}}]_{\gamma\delta} - \frac{1}{4} \left([\Omega_1^{\text{QQ}}]_{\alpha\gamma} [\Omega_1^{\text{QQ}}]_{\beta\delta} + [\Omega_1^{\text{QQ}}]_{\alpha\delta} [\Omega_1^{\text{QQ}}]_{\beta\gamma} \right) \quad (\text{A. 10})$$

(Q = R, P)

$$[\Omega_2^{\text{RP}} + \Omega_2^{\text{PR}}]_{\alpha\beta\gamma\delta}^{\uparrow\downarrow} = \frac{1}{4D_{\text{RP}}^2} [\Omega_1^{\text{RP}} + \Omega_1^{\text{PR}}]_{\alpha\beta} \times [\Omega_1^{\text{RP}} + \Omega_1^{\text{PR}}]_{\gamma\delta} \quad (\text{A. 11})$$

$$[\Omega_2^{\text{RP}} + \Omega_2^{\text{PR}}]_{\alpha\beta\gamma\delta}^{\uparrow\uparrow} = \frac{1}{4D_{\text{RP}}^2} [\Omega_1^{\text{RP}} + \Omega_1^{\text{PR}}]_{\alpha\beta} \times [\Omega_1^{\text{RP}} + \Omega_1^{\text{PR}}]_{\gamma\delta} -$$

$$- \sum_i^{\text{OCC}} \sum_j^{\text{OCC}} \sum_k^{\text{OCC}} \sum_l^{\text{OCC}} A_{ij} A_{kl} (\rho_{\alpha i} \pi_{\beta j} + \rho_{\beta i} \pi_{\alpha j}) \times (\rho_{\gamma k} \pi_{\delta l} + \rho_{\delta k} \pi_{\gamma l}) \quad (\text{A. 12})$$

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Kinetics of the Reduction of Tetraaza Macrocyclic Complex $\text{Cu}(\text{TAAB})^{2+}$ by Glutathione

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The reduction of a copper(II) complex with the macrocyclic ligand tetrabenzob[*b,f,j,n*]-[1,5,9,13]-tetraazacyclohexadecine by glutathione in aqueous solution has been investigated spectrophotometrically in both anaerobic and aerobic conditions. The reaction rate is first-order with respect to the concentration of reactants. According to the values of activation parameters and the course of spectral change during the reaction, an outer-sphere redox mechanism has been suggested. The copper complex initiates the catalytic oxidation of glutathione by dioxygen. The results are compared with the catalytic effect of $\text{Cu}(\text{TAAB})^{2+}$ at the oxidation of ascorbic acid and hydroxylamine.

In connection with modelling the natural redox processes under the participation of copper-containing proteins, a systematic attention is paid to the kinetic study of the reduction of copper(II) coordination compounds by different reducing agents. Synthetic macrocyclic complexes are widely used in the investigations because of an excellent possibility of systematic changing the ligand structure and, consequently, the physicochemical properties and chemical reactivity of the Cu(II) redox centre.

The ligand TAAB (tetrabenzob[*b,f,j,n*]-[1,5,9,13]-tetraazacyclohexadecine, Fig. 1) is characterized by rather flexible geometry around the copper atom and a highly delocalized electronic structure which lead to an easy and reversible Cu(II) to Cu(I) reduction [1]. In our previous studies the reduction of $\text{Cu}(\text{TAAB})^{2+}$ by ascorbic acid [2] and hydroxylamine [3] was investigated. An influence of the substrate concentration and pH on the reaction mechanism was observed. This complex acts as a catalyst at the radical oxidation of ascorbic acid by dioxygen in

weak acidic medium [4]. However, in neutral and weak alkaline solutions the catalytic effect is lowered due to the deprotonation of $\text{Cu}(\text{TAAB})^{2+}$ as well as HO_2^\bullet radical [1].

Among reducing agents utilized in biomimetic studies the sulfur-containing bioreductant glutathione (GSH) is commonly used. The formation of Cu(II)—SG adducts was shown at the reduction of copper(II) tetrathia as well as diazadithia macrocyclic complexes [5, 6]. Such intermediates might be very useful for modelling the function of active centres of "blue" copper proteins. We were, therefore, interested in extending the previous investigations to the system $\text{Cu}(\text{TAAB})^{2+}$ and GSH in order to determine the kinetic parameters of the redox reaction, to propose the type of reagents interaction and to examine a possibility of the catalytic effect of copper complex on the autooxidation of GSH. The results are presented which allow us to describe in more detail the reactivity of both the $\text{Cu}(\text{TAAB})^{2+}$ complex and glutathione.