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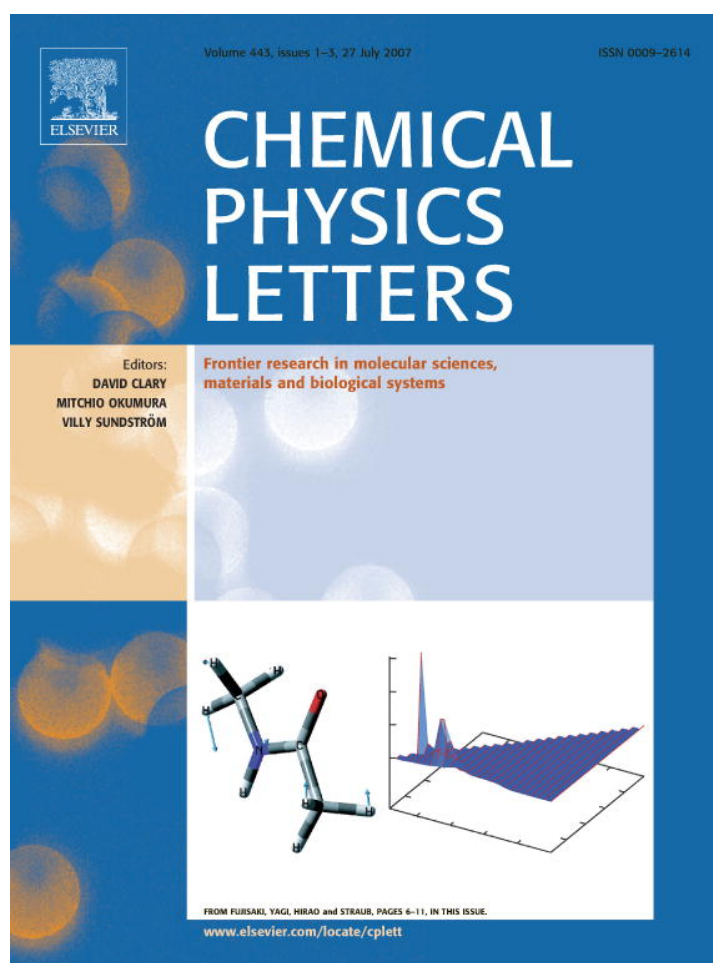


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# A theoretical scale for pericyclic and pseudopericyclic reactions

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## Abstract

A simple, unique scale based on the analysis of electron localization function (ELF) is introduced in order to categorize the degree of pericyclicity of a given electrocyclic concerted transition state. The nature of pericyclic/pseudopericyclic bonding at such type transition states becomes thus described in terms of a local measure of the Pauli repulsion. The nature of bonding of ten cycloaddition transition states associated to the reaction between ethylene and formaldehyde and buta-1,3-dien-one and simple substituted derivatives, has been discussed in this context.

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## 1. Introduction

The identification, analysis, and characterization of the pericyclic/pseudopericyclic [1–4] nature of bonding at the transition states of concerted reaction mechanisms have a primary impact on the rationalization of several organic reaction processes as well as on the development and design of novel organic electrocyclization synthetic routes [1,5,6].

A *pseudopericyclic reaction* implies a concerted electronic rearrangement through a cyclic array of atoms, where the participation of non-bonding orbitals, orthogonal to the bonding ones, yields to one or more disconnections in the cyclic array of the overlapping orbitals. Thus, all pseudopericyclic reactions are certainly orbital symmetry allowed [2,4,7,8], being able to exhibit planar geometries at the transition states and low activation energies [2,4,7,8]. In contrast, *pericyclic reactions* do not experience such orbital disconnections falling in the domain of the well-known laws of conservation of orbital symmetry [4,9,10]. Indeed, pericyclic reactions are expected to exhibit

an increasing of the *aromaticity* character (i.e., *electron delocalization*) in the region of transition state, and therefore, to exhibit quite negative values of the magnetic susceptibility. Henceforth, magnetic-based criteria such the Nucleus Independent Chemical Shift (NICS) [11,12], and/or the Anisotropy of the Current-Induced Density (ACID) [13,14] have been employed to detect the disconnections on the cyclic array of orbitals, and to distinguish between the two orbital topologies [6,15,16]. However, it should also be noted that because orbital descriptions are not unique, there does not exist in fact a definitive criterion that allows a pseudopericyclic reaction to be effectively distinguished from a normal pericyclic reaction and some controversy might arise in the description of several borderline processes [2,3,16,17]. A general scale (hopefully absolute) that accounts for the degree of pericyclicity of transition states seems to be desirable in such context.

Although the nature of bonding associated to the pericyclicity/pseudopericyclicity topologies is a concept that relies first associated to an atomic and molecular orbital formalism [4,18], it has also been shown that they can also be addressed within a topological analysis of functions depending on the electron density itself. The electron fluctuation among populations associated to domains or basins resulting from the gradient field of the Electron

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Localization Function (ELF) [19], as well as the ellipticity [20,21] of the critical points arising within the Atoms-in-Molecules (AIM) framework, have been recently explored in such context [22]. Within an ongoing study on the application of the topological analysis of ELF into such framework [17,23–26], we here propose the analysis of ELF as the basis of a general scale that allows us settle, categorize and classify the nature of pericyclic bonding at the transition state for concerted processes. The degree of pericyclicity of a given concerted transition state could be thus established on a simple and unique scale based directly on a local measure of the Pauli repulsion [27,28].

## 2. Towards a general scale of pericyclicity based on ELF

The electron localization function,  $\eta(\mathbf{r})$ , has been probed as an useful tool to give a deeper insight into the nature of the chemical bonding in a variety of stationary and reacting systems [29]. As the details concerning the topological analysis of  $\eta(\mathbf{r})$  are widely available [27,28], we briefly recall only the general aspects directly related to our aim in the establishment of such a scale. The electron localization function can be conveniently written (and interpreted) [28] in terms of the excess of local kinetic energy density due to the Pauli repulsion,  $t(\mathbf{r})$ , and it is written for single determinantal wave functions as:  $\eta(r) = [1 + (t(r)/t_h(r))^2]^{-1}$ , where the Thomas–Fermi kinetic energy density,  $t_h(\mathbf{r})$ , is taken as a reference for comparison. Hence, in those regions where the relative probability of finding electrons with parallel spin close together is high (i.e., where the local Pauli repulsion is strong), then  $\eta(\mathbf{r}) \rightarrow 0$ ; whereas  $\eta(\mathbf{r}) \rightarrow 1$  in regions with a high probability of finding a single electron or a pair of opposite spin electrons. The analysis of the gradient field  $\nabla\eta(\mathbf{r})$  yields basins of attractors (i.e., maxima) that can be associated to units of chemical meaning (i.e., core, valence, bonding, and non-bonding regions), whose density-integrated properties can be associated to chemical properties, including those related to localization and delocalization [27,28].

The set of points in space with  $\eta(\mathbf{r}) > f$  defines a *f-localization domain*, which is *reducible* if it contains more than one attractor or *irreducible* otherwise [30]. As the value *f* is increased, all different localization domains become eventually separated. This allows us to establish a hierarchy of the electron localization basins in connection to

the concept of synaptic order [30], the basins becoming ordered with respect to the ELF values at the critical points,  $\eta^*$ , that determine such reduction of the localization domains. This value corresponds to the saddle point on the separatrix between the two regions. Indeed, these are the regions that can be finally associated to chemical units of significance (i.e., bonds, lone pairs, or atomic cores) [31,32]. We can associate the number of attractors within a particular reducible *f-localization domain* to all maxima that can be considered *still under interaction* at such given ELF value [30]. The higher  $\eta^*$  value, the higher the degree of localization of electron pairing between these domains is, and hence a higher interaction between the two regions can be expected. The corresponding basins interact as a sole chemical unit as compared to other regions that have been already separated. This is the basis for the building up of our present scale. Note also that the delocalization (i.e., covalent) nature of bonding between two given domains varies in the range zero to one (i.e., the lower the difference between the saddle point of splitting and the ELF maxima). For instance, the bifurcation analysis has been found a useful tool to rationalize the nature of chemical bonding of aromatic substitution and reactive sites, pericyclic reactions, radical systems through the analysis of the  $\alpha$ - $\beta$  spin components, and the definition of an aromaticity scale for organic molecules and clusters via the analysis of  $\sigma$ - $\pi$  contributions to density [17,23,24,26,29].

With the aim to further examine the usefulness of ELF analysis in the context of analysis of pericyclicity/pseudo-pericyclicity nature of bonding, and within the principles above described, we focus here on the cycloaddition reactions of ethylene and formaldehyde to buta-1,3-dien-one and simple substituted derivatives, an important example of electrocyclic reactions that have also been recently studied within the framework of magnetic analysis based on NICS and ACID criteria [33] (see Fig. 1). The topological analysis of ELF has been performed with the TopMod program [34]. Wave function information for the transition states in Fig. 1 were obtained, following Ref. [33], from the optimized and characterized geometries at the B3LYP/6-31+G(d) level of theory using the package of programs GAUSSIAN 03 [35].

Hereafter, we introduce here a relative delocalization index,  $\xi_i \equiv \eta_i^*/\eta_{\text{ref}}^*$ , intended to be a measure of the pericyc-

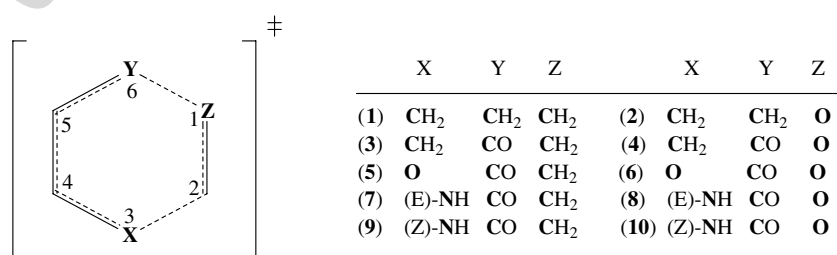


Fig. 1. Model of cycloaddition transition state of ethylene ( $Z=\text{CH}_2$ ) and formaldehyde ( $Z=\text{O}$ ) to buta-1,3-dien-one ( $X=\text{CH}_2$ ,  $Y=\text{O}$ ) and simple substituted derivatives.

licity/pseudopericyclicity degree at concerted transition states, where  $\eta_i^*$  stands for the first bifurcation occurring in the cyclic array at the reaction center of the concerted process  $i$ , and  $\eta_{\text{ref}}^*$  is the corresponding bifurcation value for a selected reference system (ref). In the present case, the reference system has been set up to be the simplest Diels–Alder reaction between 1,4-butadiene and ethane (1) for which  $\eta_{\text{ref}}^* = 0.495$ , at the current level of theory. Fig. 2 presents a type of arrangement based on the  $\xi_i$  index,

allowing us to categorize, within a unique absolute scale, the degree of pericyclicity/pseudopericyclicity of the cycloaddition transition states for the reaction between ethylene and formaldehyde and buta-1,3-dien-one and simple substituted derivatives. A careful examination of the bonding pattern in related systems [17,23,24,26,29] as well as in the present structures reveals that within such scale, a pseudopericyclic character can be associated to the range  $0 < \xi_i < 0.25$ , borderline cases belong to the range

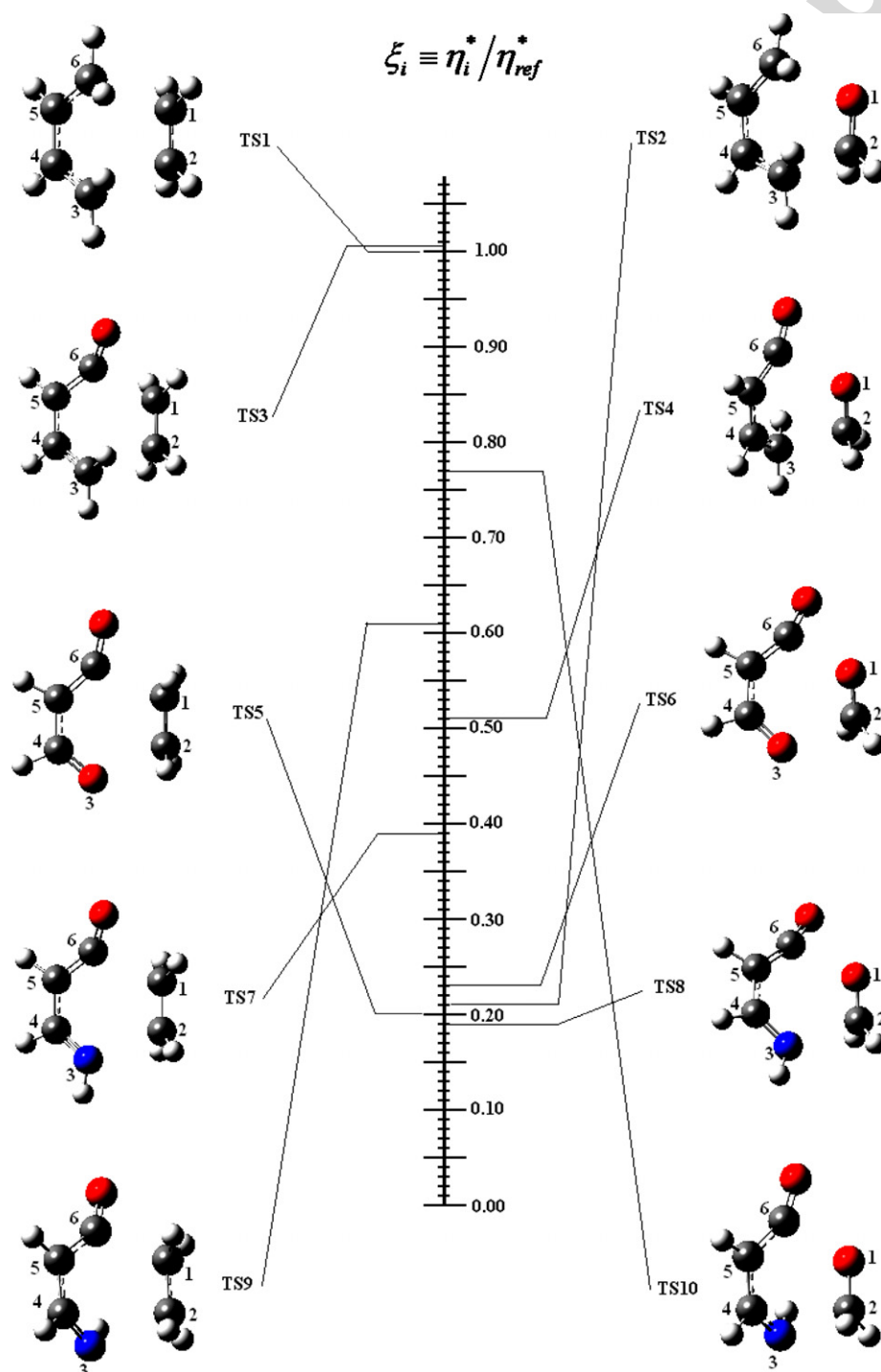


Fig. 2. A theoretical scale for pericyclic and pseudopericyclic reactions based on the analysis of the electron localization function (ELF).



$0.25 < \xi_i < 0.40$ , while values of  $\xi_i > 0.40$  will define proper pericyclic transition states. Hence, such an ELF-based scale allow us to properly classify reactions 1 ( $\xi = 1.00$ ), 3 ( $\xi = 1.08$ ), 4 ( $\xi = 0.51$ ), 9 ( $\xi = 0.61$ ) and 10 ( $\xi = 0.77$ ) as pericyclic, in complete agreement with energetic, geometric and magnetic observations, recently discussed [33]. In the same context, reactions 5 ( $\xi = 0.20$ ), 6 ( $\xi = 0.23$ ), and 8 ( $\xi = 0.19$ ) can be described as pseudopericyclic processes, whereas reaction 7 ( $\xi = 0.39$ ) can be classified as a borderline case. On the other hand, transition state for reaction 2 exhibits however a low value of relative delocalization,  $\xi = 0.21$ . The nature of bonding of transition state 2, as described through the  $\xi_i$  index, and in contradiction to previous conclusions [33], belongs here to the pseudopericyclic side of such a scale. The NBO analysis shows a degree of participation of the oxygen lone pairs in the formation of the new bond, although a non-planar geometry as well as magnetic properties for this reaction preserve characteristic properties of pericyclic reactions (as for instance the enhanced magnetic susceptibility, negative NICS values and the presence of a ring current revealed by the ACID methodology) [33]. It seems that within the  $\xi_i$  ELF-based scale, a pseudopericyclic nature (mechanism) of bonding could become over emphasized as lone pairs participate effectively in bonding interactions [2,3,16,17]. A careful examination of this issue remains open to further analysis [17,23,24,26,29].

Note also that within such a framework, the degree of delocalization can only be indirectly established by examining the critical isosurface value (CIV) at which the ACID topology changes from a cyclic to an open structure. It is also known that CIV values provide information about the induced current, but not about the aromaticity of the structure (e.g., a highly antiaromatic system also exhibit a high CIV value). In practice, the current density vectors have to be plotted onto an isosurface of ACID, in order to allow us a diagnosis about the aromaticity of the system [6,15,16]. Thus, within such a magnetic-based tool, pericyclic topologies have been associated to CIV values higher than 0.030 while pseudopericyclic ones to CIV values lower than 0.020. In contrast to the proposed ELF-based scale, such distinction using CIV values leaves a narrow interval for borderline cases. Thus, as compared to CIV values study of Ref. [33], our scale defines a broader range for such considerations.

### 3. Concluding remarks and perspectives

A theoretical and absolute scale based on the relative delocalization index  $\xi_i$  may be successfully used to rationalize (and to predict) the pericyclic/pseudopericyclic nature of these transition states, in general agreement with results based on energetic, structure, orbital interactions and magnetic evidence [33]. ELF analysis, as compared to other tools, also becomes computationally affordable, and its usefulness is widely known, as being a reliable measure of local Pauli repulsion. The continuous character observed

in ELF scale is a consequence of the choice of parameters defining the degree of pericyclicity (i.e.,  $\eta_i^*$  and  $\xi_i$ ). The range on this scale associated to a proper pericyclic or pseudopericyclic transition state should be consistently chosen in comparison to structural, theoretical and experimental available evidence for the studied systems. This ongoing study opens the possibility to build up new theoretical general (and relative) scales that contribute helping us in the general goal of validation, categorization, and rationalization of the character of the nature of bonding at the transition state of concerted reactions [17,23,24,26,29]. Work devoted to the extension of these scales is now in progress.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2007.06.025](https://doi.org/10.1016/j.cplett.2007.06.025).

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