Universitat de Girona

DEVELOPMENT, IMPLEMENTATION AND APPLICATION OF ELECTRONIC STRUCTURAL DESCRIPTORS TO THE ANALYSIS OF THE CHEMICAL BONDING. AROMATICITY AND CHEMICAL REACTIVITY

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L’Eduard Matito i Gras, llicenciat en Química per la Universitat de Girona, ha realitzat sota la nostra direcció, a l’Institut de Química Computacional i al Departament de Química de la Facultat de Ciències de la Universitat de Girona, el treball d’investigació que porta per nom:

“*Development, Implementation and Electronic Structural Descriptors to the Analysis of Chemical Bonding, Aromaticity and Chemical Reactivity*”

que es presenta en aquesta memòria per optar al grau de Doctor en Química.

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Girona, 5 de Maig de 2006

Dr. Miquel Solà i Puig　　　　Dr. Miquel Duran i Portas

“And, when you want something, all the universe conspires in helping you to achieve it”

The Alchemist (Paulo Coelho)

Als meus pares
i a en Xevi,

a l’Anna.

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Preface. *Computational Chemistry and Theoretical Chemistry*

At the outset of the 21st century, theoretical and computational chemistry has arrived at a position of central importance in chemistry.[1] The algorithms of calculation are being improved, making calculations that were prohibitive feasible and with accuracies sometimes competing with experimental ones.

Roughly and generally speaking, theoretical chemistry may be defined as the use of non-experimental reasoning to explain or predict chemical phenomena. Therefore, a theoretical chemist uses chemical, physical, mathematical and computing skills to study chemical systems. In theoretical chemistry, chemists (or even physicists) develop theories, algorithms and computer programs for the prediction of atomic and molecular properties.

On its side, computational chemistry is regarded as a branch of theoretical chemistry, and focuses on the application of the results from theoretical chemistry to the analysis of interesting chemical problems. Although the term *computational chemistry* was originally regarded as an application of quantum mechanics to the study of chemical systems, nowadays it is understood in a wider sense, encompassing ab initio, semi-empirical and molecular mechanics methods. Hence, from computational chemistry, it is possible to address different problems such as benchmark calculations for small molecules, reaction simulations, studies of large biological systems, drug design or analyze protein folding, among others. The development of computers is opening a wide range of possibilities for computational and theoretical chemists to address larger and larger systems.

Nowadays, the specialization of quantum chemists, as either theoretical or computational ones, has widely separated the research fields. Some chemists essentially devote their research to the performance of computational experiments, in the same fashion an experimental chemist performs a laboratory task. While some chemists focus their research in a rather purely theoretical work, with scarce chemical applications and development and programming of theory instead. This thesis is neither one thing nor the other; or maybe both, as it takes a bit from each side.

In the following pages the reader will find the development, implementation and application of computational tools to the study of electronic structure of molecules, with special emphasis in the aromaticity and the electron sharing indexes, which help to grasp inside the nature of chemical bonding.

The main contents of this thesis are abridged in first chapters, where a brief review of the theory used throughout is given; whereas, chapters 4 and 5 are devoted to the applications and correspond to the works of the present thesis, as they were accepted or submitted to publication. Some of these projects came after and during the development and the calculation of density matrices for correlated calculations already presented in the Master Thesis. Therefore, for the details of these density matrices calculations, the algorithms and the formulas the reader is driven to ref. 2; although a brief review is given in next second section of the next chapter.

Chapter 4 collects all those works concerning electron sharing indexes and aromaticity (vide infra). They have been ordered so that the reader will first look into the concept of electron sharing index (ESI),[3] from partitions schemes; afterwards see its applicability to define quantitative aromaticity measures, which are finally analyzed and tested from different perspectives. The last section of chapter 4 comprises a brief review on the most recent applications of the Quantum theory of Atoms in Molecules (QTAIM)[4] to the study of aromaticity.

On its side, chapter 5 focuses on the analysis of the Electron Localization Function (ELF).[5] In the first section is given a review on the ELF for both monodeterminantal and many-body wave functions, whereas second section compares the description of the chemical bonding from the QTAIM-ESI and the ELF analyses to describe the electron structure of methyalkalimentals. The second section is about the ELF definition and calculations at correlated level, while 4.3 and 4.4 analyze the ELF as a tool to discern between two mechanistic approaches, the pericyclic and pseudopericyclic reactions.

1.- Quantum Mechanics

1.- Quantum Mechanics:

1.1.- A major breakthrough in physics and chemistry.

The advent of quantum mechanics supposed a Copernican turn not only for classical physicists, but also for the whole chemistry society. It meant a general breakdown of the understanding of rules that govern the matter behavior. Concepts like the Max Planck's quantization of energy, Erwin Schrödinger's Equation or Werner Heisenberg's Uncertainty Principle had a huge influence in physics, quickly moving towards chemistry.

In the framework of Quantum Mechanics concepts like chemical bonding, atomic charge or aromaticity are simply meaningless. Quantities which are not *observable* have no place in this theory. It was not until 1926, when Max Born gave his interpretation of the square wave function as the probability of the existence of a given state, that a statistical interpretation of the wave function was possible. It meant the end of determinism which had been ruling the physics so far. Therefore, although it was not possible to speak e.g. of an exact *amount* of electronic charge in a given region, one could assign a probability for that *amount* of electronic charge of being in a given region. This is to say, the square wave function plays the role of the probability density of occurrence. Namely, from the square wave function one can obtain the density and pair density, which are the one-particle and the two-particle electron distributions, respectively. From the density and the pair density the electron structure of given molecule can be *easily* depicted. Controversially, in spite of surrounding the pillars of classical physics -the determinism-, as we will see later on, Max Born's interpretation of the square wave function finally served to hold part of old conceptions of chemistry and physics.

Whereas the whole physicists' world dramatically changed in the 20th century, some hardly rooted conceptions in the chemistry remained. Chemists still used (and use) bonding strength, aromaticity or atomic charges as an explanation for a given chemical phenomena. In order to feed chemists hunger for old concepts, several research groups[3-52] have put considerable effort on reconciling quantum mechanics with these old chemical concepts. With the probabilistic interpretation of the square wave function as a starting point, the definition of atomic populations and charges,[51] bond orders of several kinds,[12, 23, 25, 45, 53] atomic decompositions of the molecular space, among others, helped bridging the classical chemistry with the quantum mechanics. Because of their computational cost, first works were devoted to rather approximated methods, covering only the most elementary quantum mechanics calculations.

With the development of computers, the calculation of more accurate structures was also brought together with the calculation of more sophisticated and reliable analysis of the electron distribution. Despite first calculations were based on atomic charges, currently no one bases a serious analysis of the electron distribution on atomic charges. Several charge schemes have been put forward, and for most calculations, it is difficult to reach an unanimous conclusion from different charge analyses (cf. chapter 4, section 1). This is so because populations and charges depend strongly on the model chosen to define an atom in a molecule.[54]

In the literature, several electronic descriptors based on the pair or the one-electron densities have been proposed[3, 6, 7, 12, 21-25, 27, 45, 48-50, 53, 55, 56] with more or less success in their practical applications. In order to be chemically meaningful the descriptor must give a definition of an "atom" in a molecule, or instead be able to identify some chemical interesting regions (such as lone pairs, bonding regions, among others). In this line, several molecular partition schemes have been put forward: the QTAIM,[4, 8, 9] the ELF,[5, 57] Voronoi cells, Hirshfeld atoms, Fuzzy-Atoms,[50, 58] etc.

The goal of this thesis is to explore the density descriptors based on the molecular partitions of AIM, ELF and Fuzzy-Atom, analyze the existing descriptors at several levels of theory, propose new aromaticity descriptors, and study its ability to discern between different mechanisms of reaction.

1.2.- Density Matrices

The wave function seems to be the angular stone of quantum chemistry. The wave quantum mechanics was introduced by Erwin Schrödinger, who explained the movement of the electron as a wave. At the same time, Werner Heisenberg set up a matricial treatment to explain the atom behavior, but his work was much harder to understand than wave mechanics used by Schrödinger and did not have much success. However, the most important scientist to contribute to mathematical foundations of quantum mechanics was not a physicist. The English mathematician John Von Neumann established the basis of quantum mechanics, and it was not done in terms of wave functions as such, but from density matrices. Let us put it into context.

A quantum state is any possible state in which a quantum mechanical system can be. If a quantum state is fully specified, it can be described by a state vector, a wave function, or a complete set of quantum numbers for a given system; such a state is said to be *pure*. On the other hand, a partially known quantum state, such as an ensemble with some quantum numbers fixed, can be uniquely described only by a density matrix; it is usually referred as a mixed quantum state, or an ensemble state as it represents a statistical distribution of pure states.

In 1927, Von Neumann introduced the formalism of the density matrices, or density operators, used in quantum theory to describe the statistical state of a quantum system. Its applicability, which covers a major range that the wave function itself, is discussed at some extent in ref 2.

A *N*-order density matrix, being *N* the number of electrons in our system, may be constructed in the following manner:

$$\rho_N\left(\vec{x}_1'...\vec{x}'_N \left|\vec{x}_1...\vec{x}_N\right.\right) = \Psi^*\left(\vec{x}_1'...\vec{x}'_N\right)\Psi\left(\vec{x}_1...\vec{x}_N\right) \qquad (1)$$

And thus, this matrix (for the sake of clarity, let us call so, even though tensor would be a more appropriate term to describe it), depends upon 2*N* variables. For most of proposes this dependence is beyond feasible computations with current computers, and that is the reason for reducing the number of variables of which it depends by integration. This way, one may construct the *m*-order reduced density matrices, by integration of *N-m* of its coordinates,

$$\gamma^{(m)}\left(\vec{x}_1'...\vec{x}'_m \left|\vec{x}_1...\vec{x}_m\right.\right) = \int \rho_N\left(\vec{x}_1'...\vec{x}'_N \left|\vec{x}_1...\vec{x}_N\right.\right)\Delta^N_{m+1} d\vec{x}_{m+1}...d\vec{x}_N \tag{2}$$

after setting $x_i = x'_i$ by means of a generalized Dirac delta:

$$\Delta^N_{m+1} \equiv \Delta\left(\vec{x}'_{m+1}...\vec{x}'_N \left|\vec{x}_{m+1}...\vec{x}_N\right.\right) = \prod_{i=m+1}^{N} \delta\left(\vec{x}'_i - \vec{x}_i\right) \tag{3}$$

In the case of a wave function expanded in terms of Slater determinants,

$$\Psi = \sum_K c_K \psi_K \tag{4}$$

with Ψ_K being the Slater determinant in Eq. (5). Without the loss of generalization, let us suppose that it is constructed from a set of orthonormalized spin orbitals:

$$\psi_K = \frac{1}{\sqrt{N!}}\left|\chi_1(\vec{x}_1)\chi_2(\vec{x}_2)...\chi_N(\vec{x}_N)\right| \tag{5}$$

In such a case, Equation (2) can be further simplified to read:

$$\gamma^{(m)}\left(\vec{x}_1'...\vec{x}'_m \left|\vec{x}_1...\vec{x}_m\right.\right) = \sum_{\substack{i_1 i_2 \cdots i_m \\ j_1 j_2 \cdots j_m}} \Gamma^{j_1 j_2 \cdots j_m}_{i_1 i_2 \cdots i_m} \chi^*_{i_1}\left(\vec{x}'_1\right)...\chi^*_{i_m}\left(\vec{x}'_m\right)\chi_{j_1}\left(\vec{x}_1\right)...\chi_{j_m}\left(\vec{x}_m\right) \tag{6}$$

As a result the *m*-order reduced density matrix (*m*-RDM) is calculated as an expansion of our basis set.

In our laboratory we have designed an algorithm for the calculation of these expansion coefficients, $\Gamma_{i_1 i_2 \cdots i_m}^{j_1 j_2 \cdots j_m}$ -which we call *m*-order density matrices (DM*m*)-, from the coefficients c_K given in Eq. (4).

It is of particular usefulness to further simplify Eq. (6) by only considering the diagonal terms of the *m*-RDM, which fulfill $x_i=x'_i$. When not taking into account the off-diagonal terms, we are left with the *m*-order density functions:

$$\gamma^{(m)}(\vec{x}_1 \ldots \vec{x}_m) = \sum_{\substack{i_1 i_2 \cdots i_m \\ j_1 j_2 \cdots j_m}} \Gamma_{i_1 i_2 \cdots i_m}^{j_1 j_2 \cdots j_m} \chi_{i_1}^{*}(\vec{x}_1) \ldots \chi_{i_m}^{*}(\vec{x}_m) \chi_{j_1}(\vec{x}_1) \ldots \chi_{j_m}(\vec{x}_m) \tag{7}$$

The most simple of these density functions is the one-electron density, or simply the density:

$$\gamma^{(1)}(\vec{x}_1) = \sum_{i,j} \chi_i^{*}(\vec{x}_1) \Gamma_i^j \chi_j(\vec{x}_1) \tag{8}$$

Also interesting is the definition of the pair density:

$$\gamma^{(2)}(\vec{x}_1, \vec{x}_2) = \sum_{\substack{i,j \\ k,l}} \chi_i^{*}(\vec{x}_1) \chi_j^{*}(\vec{x}_2) \Gamma_{ij}^{kl} \chi_k(\vec{x}_1) \chi_l(\vec{x}_2) \tag{9}$$

We can give to the pair density the significance of the probability density of finding a certain couple of electrons (*1*,*2*), regardless of the position of the remaining *N-2* electrons. The interpretation is analogous with the one given by Born in 1927 to the electron density in terms of the probability density of finding one electron, irrespective of the position of the others. In this line, all *m*-order density functions have a similar significance: they are related to the probability of finding *m* electrons independently of the positions of the other *N-m* electrons.

Maybe the reader is wondering why "*regardless* the position of the remaining *N*-2 electrons". Let us give a simple proof. Take Eq. (1), by setting $x_i=x'_i$ for all variables and integrating over the whole space, we would get 1 for a normalized wave function; which is to say, finding the *N* electrons over the whole space has probability of 100%, which is an obvious statement. If we take Eq. (2), and we consider it separately for any electron in the system, we would count separately the probability of finding 1, 2... over x_1. Summing up all terms we would have *N* times Eq. (2), as the probability of finding any electron by x_1. If now we integrate x_1 over the whole space, the result is 100*N*%. Unless we have one electron the probability is beyond 100%, as a consequence of summing repeated probabilities; therefore each separate one-electron distribution contains information regarding the positions of other electrons in the system. The following Venn diagram illustrates the phenomena for a three particle (A, B and C) system:

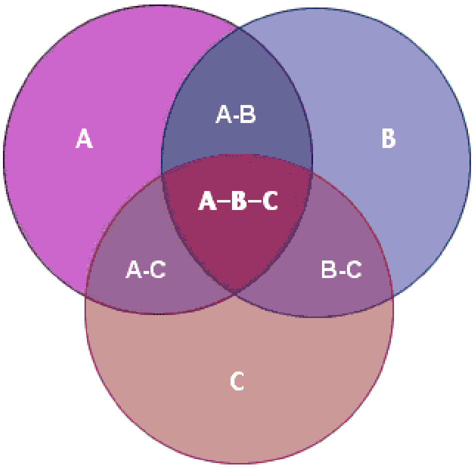

Figure1. Venn diagram for a three possibilities event.

Further details of the way of calculating probabilities of finding an electron (or some number of electrons) in certain position, while others are excluded from being in that region is also given in ref. 2.

It is of common practice to multiply Eq. (7) by either the number of unordered groups of size m taken from *N* elements, the binomial coefficient $C_m^N = \binom{N}{m}$, or all possible groups of size m, $P_m^N = \binom{N}{m} m!$. In this way, one obtains from the *m*-RDM the expected number of groups of *m* electrons.

The density matrices (DM) are intrinsically important in the work carried out in this thesis. For practical proposes DM are usually written in the basis of either atomic orbitals or molecular (spin) orbitals, and its construction from those wave functions formed as a linear combination of Slater determinants was performed through the aforementioned algorithm, which will be submitted elsewhere.[59] In particular, sections 4.2, 4.6, 4.7 and 4.8 benefit from this algorithm to calculate the Configuration Interaction with Simples and Doubles (CISD) second and first order reduced density matrices.

It is worth noticing these DM are not needed when dealing with monodeterminantal wave functions, since one can easily prove that they must be diagonal, regardless the order; the following relationship between *p*-RDM and *1*-RDM holds:

$$\gamma^{(p)}\left(\vec{x}_1'\ldots\vec{x}'_p\,\middle|\,\vec{x}_1\ldots\vec{x}_p\right)=\begin{vmatrix}\gamma^{(1)}\left(\vec{x}_1'\middle|\vec{x}_1\right) & \cdots & \gamma^{(1)}\left(\vec{x}_1'\middle|\vec{x}_p\right)\\ \vdots & \ddots & \vdots\\ \gamma^{(1)}\left(\vec{x}_p'\middle|\vec{x}_1\right) & \cdots & \gamma^{(1)}\left(\vec{x}_p'\middle|\vec{x}_p\right)\end{vmatrix} \tag{10}$$

and the analogous one for DM is as follows:

$$\Gamma^{l_1\cdots l_m}_{k_1\cdots k_m}=\begin{vmatrix}\Gamma^{l_1}_{k_1} & \cdots & \Gamma^{l_m}_{k_1}\\ \vdots & \ddots & \vdots\\ \Gamma^{l_1}_{k_m} & \cdots & \Gamma^{l_m}_{k_m}\end{vmatrix}=\begin{vmatrix}\delta^{l_1}_{k_1} & \cdots & \delta^{l_m}_{k_1}\\ \vdots & \ddots & \vdots\\ \delta^{l_1}_{k_m} & \cdots & \delta^{l_m}_{k_m}\end{vmatrix}=\delta^{l_1\cdots l_m}_{k_1\cdots k_m} \tag{11}$$

where deltas refer to well known Kronecker deltas.

Finally, in this context, it is worth to mention what are known as relaxed density matrices. The relaxed density matrices come from the non-fulfillment of the Hellmann-Feynman theorem. This theorem guarantees that any certain property reproduces the same value calculated from an expectation value or as an energy derivative. It holds for exact wave functions, and some approximate theoretical methods, such as the self-consistent field theory. However, Hellmann-Feynman theorem does not hold for perturbative, truncated configuration interaction, or coupled-cluster methods. Therefore, at such levels of theory one can calculate the corresponding DM as either the expected value of the corresponding Dirac delta, cf. Eq. (2), or as an energy derivative. The latter is known as response density matrix or relaxed density, since it includes effects due to orbital relaxation through the coupled-perturbed Hartree-Fock (CPHF) calculations; the other densities are called unrelaxed densities.

It is widely known that one-electron properties (which need of the DM1), such as dipole moments, produce more reliable results when computed as an energy derivative, since they represent the wave function response with respect to a perturbation. However, very little is said about the effect of relaxation in the electron distribution itself. In consequence, due to practical purposes, we have preferred to use the unrelaxed density, which is the one obtained with our algorithm. Since some computational packages provide the relaxed DM1 and DM2, we are considering the possibility of comparing these densities in a further study, especially their effects on the calculation of ESI which is our primary goal.

2.- Methodology

2.- Methods

2.1.- Electron Sharing Indexes

An extensive review of the concept of *sharing index* was done in prevision for the next Faraday discussion on Chemical Bonding (FD135) to be held in Manchester, and it is given in section 6 of chapter 4. Therefore, we do not review the concept of electron sharing index in great detail, but instead we comment on some aspects of the formulation not included in the next chapters.

The electron sharing indexes (ESI) account to some extent for the electron sharing of a given pair of atoms (or more generally of a pair of moieties). Hereafter the ESI computed are calculated from the exchange correlation density (XCD), which reads as follows:

$$\gamma_{xc}(\boldsymbol{x_1},\boldsymbol{x_2}) = \gamma^{(1)}(\boldsymbol{x_1})\gamma^{(1)}(\boldsymbol{x_2}) - \gamma^{(2)}(\boldsymbol{x_1},\boldsymbol{x_2}) \tag{12}$$

and measures the divergences of the pair density —a true electron pair distribution—, and a fictitious pair density constructed as the product of two independent one electron distributions. Therefore, the XCD integrates to *N*, since the density and the pair density integrate to $P^1_N=N$ and $P^2_N=N(N-1)$, respectively:

$$\iint \gamma_{xc}(\boldsymbol{x_1},\boldsymbol{x_2})d\boldsymbol{x_1}d\boldsymbol{x_2} = N \tag{13}$$

The XCD is an appealing function because it fulfills several interesting properties. First of all, it is non-negative definite; the number of fictitious pairs of electrons for a model of independent electrons is always greater than the actual number of pairs. A simple proof of this result for monodeterminantal wave function can be found in chapter 4.1. This proof also holds for wave functions constructed from several determinants. (See chapter 4.6) Secondly, by definition, in the case of non-interacting electrons the function is zero. And in third place, integrated over the whole space, it gives the number of electrons in the system, *N*.

In the literature several authors propose $\gamma_{xc}(\boldsymbol{x_1}, \boldsymbol{x_2})$ as a measure of electron sharing between points x_1 and x_2. The XCD ensures that a) every pair of points in the whole space is assigned a certain electron sharing (the decomposition is exhaustive), b) the sharing is always positive, c) for non-interacting points the sharing is equally zero. All these properties make the XCD a suitable candidate for the calculation of electron sharing between atoms; by integration of each coordinate in a given finite region (which we could somehow identify with an atom), we may get back to the classical concept of *bond*.

Some definitions of an atom in a molecule are explained in chapter 4.1, and the power of the ESI described from XCD is discussed in great detail in chapter 4.6.

Usually, in the literature people use Eq. (13) as it is written, however, providing most molecular calculations are closed-shell and monodeterminantal (either HF or DFT within the Kohn and Sham formalism), people sometimes prefer writing Eq. (13) further simplified and without spin dependence. Let us do this simple transformation, which will help us to realize about an important feature of the XCD.

For a monodeterminantal wave functions Eq. (10) indicates how to write the pair density from the 1-RDM:

$$\gamma^{(2)}(\vec{x}_1\vec{x}_2) = \begin{vmatrix} \gamma^{(1)}(\vec{x}_1|\vec{x}_1) & \gamma^{(1)}(\vec{x}_1|\vec{x}_2) \\ \gamma^{(1)}(\vec{x}_2|\vec{x}_1) & \gamma^{(1)}(\vec{x}_2|\vec{x}_2) \end{vmatrix} \tag{14}$$

Splitting the latter formula on its spin cases we get:

$$\begin{aligned} &\gamma^{(2)\alpha\alpha}(\boldsymbol{r_1}, \boldsymbol{r_2}) + \gamma^{(2)\beta\beta}(\boldsymbol{r_1}, \boldsymbol{r_2}) + \gamma^{(2)\alpha\beta}(\boldsymbol{r_1}, \boldsymbol{r_2}) + \gamma^{(2)\beta\alpha}(\boldsymbol{r_1}, \boldsymbol{r_2}) = \gamma^{(1)\alpha}(\boldsymbol{r_1})\gamma^{(1)\alpha}(\boldsymbol{r_2}) + \gamma^{(1)\beta}(\boldsymbol{r_1})\gamma^{(1)\beta}(\boldsymbol{r_2}) + \\ &\gamma^{(1)\alpha}(\boldsymbol{r_1})\gamma^{(1)\beta}(\boldsymbol{r_2}) + \gamma^{(1)\beta}(\boldsymbol{r_1})\gamma^{(1)\alpha}(\boldsymbol{r_2}) - \gamma^{(1)\alpha}(\boldsymbol{r_1} | \boldsymbol{r_2})\gamma^{(1)\alpha}(\boldsymbol{r_1} | \boldsymbol{r_2}) - \gamma^{(1)\beta}(\boldsymbol{r_1} | \boldsymbol{r_2})\gamma^{(1)\beta}(\boldsymbol{r_1} | \boldsymbol{r_2}) \end{aligned} \tag{15}$$

At this point we can realize about an interesting fact: the cross-spin terms at the r.h.s of the last equation come entirely from the density function. An important consequence is that the pair density calculated from Eq. (14) has its cross-spin contribution (also known as Coulomb correlation) calculated as a fictitious pair density constructed from two independent one electron densities.

By putting together those spin parts that depend upon the density or the pair density we arrive at:

$$\gamma^{(2)}(\boldsymbol{r_1},\boldsymbol{r_2}) = \gamma^{(1)}(\boldsymbol{r_1})\gamma^{(1)}(\boldsymbol{r_2}) - \gamma^{(1)\alpha}(\boldsymbol{r_1}\,|\,\boldsymbol{r_2})\gamma^{(1)\alpha}(\boldsymbol{r_1}\,|\,\boldsymbol{r_2}) - \gamma^{(1)\beta}(\boldsymbol{r_1}\,|\,\boldsymbol{r_2})\gamma^{(1)\beta}(\boldsymbol{r_1}\,|\,\boldsymbol{r_2}) \qquad (16)$$

Notice in Eq. (15) we cannot join the out-of-diagonal terms of the 1-RDM, excepting in a closed-shell system where we would write:

$$\gamma^{(2)}(\boldsymbol{r_1},\boldsymbol{r_2}) = \gamma^{(1)}(\boldsymbol{r_1})\gamma^{(1)}(\boldsymbol{r_2}) - \frac{1}{2}\gamma^{(1)}(\boldsymbol{r_1},\boldsymbol{r_2})\gamma^{(1)}(\boldsymbol{r_1},\boldsymbol{r_2}) \qquad (17)$$

From Eq. (14) one may write the XCD for a monodeterminantal closed-shell wave function:

$$\gamma_{xc}(\boldsymbol{x_1},\boldsymbol{x_2}) = \left|\gamma^{(1)}(\boldsymbol{x_1},\boldsymbol{x_2})\right|^2 \qquad (18)$$

and by analogy with Eq. (12), we can give the spinless version of the XCD for a monodeterminantal closed-shell wave function:

$$\gamma_{xc}(\boldsymbol{r_1},\boldsymbol{r_2}) = \frac{1}{2}\left|\gamma^{(1)}(\boldsymbol{r_1},\boldsymbol{r_2})\right|^2 \qquad (19)$$

Therefore, it is important noticing the factor of one half, due to the fact that actually $\gamma_{xc}^{\alpha\beta}(\boldsymbol{r_1},\boldsymbol{r_2}) = 0$ within a monodeterminantal wave function. Further consequences of this fact, encountered when comparing monodeterminantal and many-body wave functions, are commented in chapter 4.6.

2.2.- Aromaticity from ESI analyses

In 1825 an English chemist, Michael Faraday, synthesized a colorless and flammable liquid with a pleasant, sweet smell which he gave it the name *bicarburet of hydrogen*. Few years after that, a German scientist, Eilhard Mitscherlich produced the same compound via distillation of benzoic acid and lime; Mitscherlich gave the compound the German name *benzin*.

Synthesized by Faraday from the decomposition of oil by heat, benzene turned out the first of a large series of compounds with a characteristic smell. Indeed, the term *aromaticity* was named after the Greek term aroma (αρωμα), meaning “pleasant odour”. Organic textbooks are full of references to aromatic compounds, the organic chemistry –actually the whole chemistry- is strongly ruled by aromaticity criteria to assess the failure or the success of reactions.

Not even the advent of quantum mechanics, which consigned to oblivion a wide range of classical chemical concepts, could make chemists forget about the tenet of aromaticity. Widely used for both experimentalists and computational chemists, despite lacking a clear and unambiguous definition, it has remained as natural tool to explain several chemical phenomena. Since it is not an observable property, aromaticity is regarded to be measured from its manifestations, which are many. Among the most common characteristics of an aromatic compound, one can include: bond length equalization, abnormal chemical shifts and magnetic anisotropies, energetic stabilization and high electron delocalization. Such a wide range of manifestations makes aromaticity quantification rather cumbersome. One must take into account several aromaticity characteristics before stating a molecule as aromatic. Moreover, some authors[60] suggest abandoning the term *aromaticity*, to use instead specific nomenclature such as energetic-aromaticity, or magnetic-aromaticity, and so forth.

A statistical study of aromaticity indexes by means of a principal component analysis served Katritzky et al.[61] to show magnetic-aromaticity is orthogonal to other aromaticity measures as energetic-aromaticity or geometrical-aromaticity. Indeed, nowadays aromaticity is considered a multifold property, and most of researchers involved in this field suggest several aromaticity indexes to be calculated prior to any judgement about the actual aromaticity of a given compound. In our group we have focused our efforts in the development of electronic aromaticity indexes, gathered the former experience in the field of electronic structure characterization.

In this thesis we will essentially focus on the aromaticity measured from electron delocalization. Since the study of ESI could account for the extent of electron sharing, we thought a good idea to apply our knowledge in the field of ESI to the study of aromaticity (cf. chapter 4.7). The first work in our group in this line was carried out by Poater et al.[62] when defining the PDI (the para delocalization index), which measures the electron sharing between atoms in *para* position, in a given ring. The idea came from the work of Bader et al,[13] who investigated the electron sharing between carbons in para and meta positions for benzene, with the finding of a higher electron sharing in the former case, despite the larger distance. It is worth to mention Fulton[29] observed previously this feature of benzene. The main shortcoming of PDI is the need for para-related atoms, which only exist for six-membered rings. Therefore, aromaticity in rings of other sizes cannot be recovered with PDI.

In this line, we tried to devise a new aromaticity index whose applicability was extended to any given size of a ring. The aromatic fluctuation index (FLU)[39] was constructed by comparing electron sharing between bonded pairs of atoms in a ring, with respect to a typical aromatic molecule. It is fair to say, the HOMA index[63] of aromaticity, defined beforehand, was our inspiration to construct an index which measures, not divergences in bond length with respect to aromatic molecules, but divergences in the electron sharing with that of aromatic molecules. A detailed definition of FLU and its motivation is extensively given in chapter 4.3.

Since different ESI have already been considered, a natural extension of the work on aromaticity indexes was testing different ESI for the calculation of aromaticity measures.[44] In chapter 4.5 we discuss the applicability of the Fuzzy-Atom ESI to the study of PDI, FLU and FLU_{π} measures. Similarly, chapter 4.6 collects PDI, FLU values at CISD level of theory to analyze the effect of the inclusion of electron correlation in these indexes, calculated from ESI defined from both partitions, QTAIM and Fuzzy-Atom.

But it is not a matter of defining aromaticity indexes to simply broaden the number of aromaticity measures in the literature. Although chemistry community accepts aromaticity as a manifold property, it would be a rather awkward task to calculate all existing indexes of aromaticity in order to evaluate such property. Some aromaticity indexes, such as HOMA, are computationally inexpensive, while others, as NICS, have a remarkable computational cost. On the other hand, some aromaticity indexes may fail on giving the answer expected from most elementary chemical grounds. Therefore, the utility of aromaticity indexes needs to be tested; a continued revision of aromaticity and their adequacy for each chemical situation must be also a major goal for aromaticity researchers. Since aromaticity is hardly rooted in the chemistry community, chemists have certain preconceived ideas about aromaticity. In chapter 4.4 we address this issue, and we examine the simplest Diels-Alder reaction (whose transition state is said to be most aromatic point along the reaction path) with HOMA, NICS and FLU indexes. Since SCI was not considered when the work of chapter 4.4 was published we also re-examinate the performance of this index for this reaction in chapter 4.6. Chapter 4.3 includes a false-positive test on FLU index –there defined- which is shown not to be fulfilled by all indexes of aromaticity; for instance, NICS index of aromaticity fails to reproduce it.

2.3.- The Electron Localization Function

The pair density and the density can be split according to the next spin cases:

$$\gamma^{(2)}(\vec{r}_1,\vec{r}_2)=\gamma^{(2)\alpha\alpha}(\vec{r}_1,\vec{r}_2)+\gamma^{(2)\beta\beta}(\vec{r}_1,\vec{r}_2)+\gamma^{(2)\alpha\beta}(\vec{r}_1,\vec{r}_2)+\gamma^{(2)\beta\alpha}(\vec{r}_1,\vec{r}_2) \tag{20}$$

$$\rho(\vec{r}_1)=\rho^{\alpha}(\vec{r}_1)+\rho^{\beta}(\vec{r}_1) \tag{21}$$

The pair density contains the information about the position of electron pairs, and thus the correlation between pairs of electrons. The pair density of electrons of the same spin contains not only the information about the so-called Coulomb correlation, but also the information of correlation due to the presence of electrons with the same spin, the Fermi correlation. Whereas Coulomb correlation is mainly introduced by many-body methods (vide supra), Fermi correlation is already present in monodeterminantal wave functions.

We have commented in the last chapter the probabilistic interpretation of the density functions. Playing with probabilities we can construct the *conditional probability* (CP) of finding electron 2 nearby $\mathbf{r}_2$ when electron 1 is at $\mathbf{r}_1$:

$$P(\vec{r}_1,\vec{r}_2)=\frac{\gamma^{(2)}(\vec{r}_1,\vec{r}_2)}{\rho(\vec{r}_1)} \tag{22}$$

Both the pair density and the CP contain all necessary information about the correlation of electrons. The main advantage of the CP function is that it is actually discounting irrelevant information concerning the position of the reference electron. This is the function Becke and Edgecombe[5] used to define the electron localization function (ELF); namely the spherical average of the Fermi contribution to this function, $P^{\sigma\sigma}(\vec{r}_1,\vec{r}_2)$:

$$\left\langle e^{\vec{s}\cdot\vec{\nabla}} P^{\sigma\sigma}\left(\vec{r},\vec{r}+\vec{s}\right)\right\rangle = \frac{\sinh\left(s\nabla\right)}{s\nabla} P^{\sigma\sigma}\left(\vec{r},\vec{r}+\vec{s}\right)\Big|_{\vec{s}=\vec{0}}, \tag{23}$$

whose series of Taylor around the reference electron (s=0) reads:

$$\left\langle e^{\vec{s}\cdot\vec{\nabla}} P^{\sigma\sigma}\left(\vec{r},\vec{r}+\vec{s}\right)\right\rangle = \left(1+\frac{1}{6}s^2\nabla_s^2+\ldots\right) P^{\sigma\sigma}\left(\vec{r},\vec{r}+\vec{s}\right)\Big|_{\vec{s}=0} \approx \frac{1}{6}s^2\nabla_s^2 P^{\sigma\sigma}\left(\vec{r},\vec{r}+\vec{s}\right)\Big|_{\vec{s}=\vec{0}}. \tag{24}$$

Becke and Edgecombe used the relative ratio of Eq. (24) with respect to the same quantity for the homogenous electron gas (HEG) assuming a monodeterminant situation (use Eq. (17) in Eq. (22) for the HEG[64]):

$$D_\sigma^0 = \frac{3}{5}\left(6\pi^2\right)^{2/3}\left(\rho^\sigma\right)^{5/3} = \frac{3}{10}\left(3\pi^2\right)^{2/3}\rho^{5/3} = c_F\,\rho^{5/3}, \tag{25}$$

where $c_F = \frac{3}{10}\left(3\pi^2\right)^{2/3}$ is the Fermi constant. Hence the relative ratio reads:

$$\frac{D_\sigma}{D_\sigma^0} = \frac{\nabla_s^2\gamma^{(2)\sigma\sigma}\left(\vec{r},\vec{r}+\vec{s}\right)\Big|_{\vec{s}=\vec{0}}}{c_F\left[2\rho^\sigma\left(\vec{r}\right)\right]^{8/3}} \tag{26}$$

Becke and Edgecombe chose the following scaling to define the ELF:[5]

$$ELF = \frac{1}{1+\left(D_\sigma / D_\sigma^0\right)^2}. \tag{27}$$

Since the probability of finding an electron with spin σ when there is another electron with the same spin nearby is lower when the former is localized, Eq. (27) is larger for localized systems. It is straightforward noticing the ELF ranges in the interval [0,1].

Chapter 5.1 contains the full development of the formulas of the ELF for monodeterminantal and many-body methods, with special emphasis in the meaning and the features of the ELF. Besides, chapter 5.2 examines a chemical system where ELF and AIM lead to divergence concerning the character of bonding. Interestingly, ELF seems to provide the correct answer. Chapter 5.3 and 4.4 are devoted to explain how ELF can give inside into the mechanistic differences between pericyclic and pseudopericyclic reactions.

3.- Goals of the present thesis

3.- Goals of the present thesis.

The present thesis is devoted to the study of electron sharing indexes (ESI) and the electron localization function (ELF). The main goal of this thesis is to grasp inside the concepts of ESI and the ELF as a tools to describe the electronic distribution in molecules.

The potential of the ESI has been widely documented in the literature for monodeterminantal methods, but at the post-Hartree-Fock level of theory the studies are scarce. Since aromaticity is said to be tightly connected with the electron delocalization in molecules, the exploration of the ESI to account for the aromaticity of the system will be the subject of our study.

On the other hand, the ELF is a novel method for the analysis of the electron structure. So far, most ELF analyses have been performed at HF or DFT (within the Kohn-Sham formalism) levels of theory and thus, the analysis of the ELF for correlated calculations is of considerable interest. Indeed, some molecular systems need of highly correlated calculations to be properly described, and thus the correlated ELF counterpart is needed for a good description of its electronic structure. The definition, implementation and application to interesting chemical systems will be the goal of our studies.

To these aims, correlated first- and second-order density matrices will be needed, for which, the development done in the Master Thesis will be crucial.[2] Nonetheless, an improvement of this algorithm will be needed to deal with large systems.

4.- Applications I: Electron Sharing Indexes and Aromaticity

4.1.- Comparison of AIM Delocalization Index and the Mayer and Fuzzy Atom Bond Orders.

Eduard Matito, Jordi Poater, Miquel Solà, Miquel Duran, and Pedro Salvador. “Comparison of the AIM Delocalization Index and the Mayer and Fuzzy Atom Bond Orders”. *Journal of Physical Chemistry A*. Vol. 109, no. 43 (November 2005) : p. 9904-9910

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Abstract:

In this paper the behavior of three well-known electron-sharing indexes, namely, the AIM delocalization index and the Mayer and fuzzy atom bond orders are studied at the Hartree-Fock level. A large number of five-membered ring molecules, containing several types of bonding, constitute the training set chosen for such purpose. A detailed analysis of the results obtained shows that the three indexes studied exhibit strong correlations, especially for homonuclear bonds. The correlation is somewhat poorer but still significant for polar bonds. In this case, the bond orders obtained with the Mayer and fuzzy atom approaches are normally closer to the formally predicted bond orders than those given by the AIM delocalization indexes, which are usually smaller than those expected from chemical intuition. In some particular cases, the use of diffuse functions in the calculation of Mayer bond orders leads to unrealistic results. In particular, noticeable trends are found for C-C bonds, encouraging the substitution of the delocalization index by the cheaper fuzzy atom or even the Mayer bond orders in the calculation of aromaticity indexes based on the delocalization index such as the para-delocalization index and the aromatic fluctuation index.

4.2.- Exploring the Hartree-Fock Dissociation Problem in the Hydrogen Molecule by Means of Electron Localization Measures.

Eduard Matito, Miquel Duran, and Miquel Solà. “A Novel Exploration of the Hartree–Fock Homolytic Bond Dissociation Problem in the Hydrogen Molecule by Means of Electron Localization Measures”. *Journal of Chemical Education*. Vol. 83, no. 8 (August 2006) : p. 1243

http://www.jce.divched.org/Journal/Issues/2006/Aug/abs1243.html

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ABSTRACT

Most introductory quantum chemistry textbooks discuss the well-known problem of the inappropriate description given by the restricted Hartree–Fock (HF) method of the homolytic bond dissociation. This weakness of the restricted HF method is generally addressed by analyzing the difference between the energies at long internuclear distances obtained with the configuration interaction (CI) and HF methods, which requires an exhaustive understanding of the methodology. In this article we provide a new insight into this subject using localization and delocalization indices defined in the framework of the atoms-in-molecules theory to analyze the homolytic bond dissociation in the hydrogen molecule. It is shown that the restricted HF requirement of molecular orbitals to be occupied simultaneously by a couple of electrons with different spin is responsible for localization to hold on the same value while dissociation is happening, thus reflecting the well-known deficiency of the HF method to deal with bond dissociation. On the other hand, when the CI method is used, the localizability of the electrons in the system turns into the intuitive scheme expected for homolytic bond dissociation.

KEYWORDS

Computational Chemistry; Computer-Based Learning; Graduate Education / Research; Learning Theories; Lewis Structures; Molecular Properties / Structure; Physical Chemistry; Quantum Chemistry; Textbooks / Reference Books; Theoretical Chemistry; Upper-Division Undergraduate

4.3.- The Aromatic Fluctuation Index. (FLU): A New Aromaticity Index Based on Electron Delocalization.

Eduard Matito, Miquel Duran, and Miquel Solà. “The aromatic fluctuation index (FLU): A new aromaticity index based on electron delocalization”. *The Journal of chemical physics*. Vol. 122 (1 January 2005) 014109

http://scitation.aip.org/journals/doc/JCPSA6-ft/vol_122/iss_1/014109_1-div0.html
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Abstract:

In this work, the aromatic fluctuation index (FLU) that describes the fluctuation of electronic charge between adjacent atoms in a given ring is introduced as a new aromaticity measure. This new electronic criterion of aromaticity is based on the fact that aromaticity is related to the cyclic delocalized circulation of π electrons. It is defined not only considering the amount of electron sharing between contiguous atoms, which should be substantial in aromatic molecules, but also taking into account the similarity of electron sharing between adjacent atoms. For a series of rings in 15 planar polycyclic aromatic hydrocarbons, we have found that, in general, FLU is strongly correlated with other widely used indicators of local aromaticity, such as the harmonic-oscillator model of aromaticity, the nucleus independent chemical shift, and the para-delocalization index (PDI). In contrast to PDI, the FLU index can be applied to study the aromaticity of rings with any number of members and it can be used to analyze both the local and global aromatic character of rings and molecules.

Keywords:

molecular electronic states; organic compounds

See Also

- Erratum: "The aromatic fluctuation index (FLU): A new aromaticity index based on electron delocalization" [J. Chem Phys. **122**, 014109 (2005)]
  Eduard Matito *et al.*
  J. Chem. Phys. **125**, 059901 (E) (2006)

4.4.- An Analysis of the Changes in Aromaticity and Planarity Along the Reaction Path of the Simplest Diels-Alder Reaction. Exploring the Validity of Different Indicators of Aromaticity.

Eduard Matito, Jordi Poater, Miquel Duran and Miquel Solà. “An analysis of the changes in aromaticity and planarity along the reaction path of the simplest Diels–Alder reaction. Exploring the validity of different indicators of aromaticity”. *Journal of molecular structure: Theochem*. Vol. 727, no. 1-3 (16 August, 2005) : p. 165-171

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Abstract:

In this work, we analyze the changes in aromaticity and planarity along the reaction path of the Diels–Alder reaction between ethene and 1,3-butadiene. To this end, a new index that quantifies the planarity of a given ring is defined. As expected, the planarity of the ring being formed in the Diels–Alder cycloaddition increases along the reaction path from reactants to product. On the other hand, the aromaticity of the ring formed is measured using several well-established indices of aromaticity such as the nucleus independent chemical shift (NICS), the harmonic oscillator model of aromaticity (HOMA), and the *para*-delocalization index (PDI), as well as a recently defined descriptor of aromaticity: the aromatic fluctuation index (FLU). The results given by the NICS and PDI indices, at variance with those obtained by means of the HOMA and FLU indicators of aromaticity, confirm the existence of an aromatic transition state for this reaction. The reasons for the failure of some of the descriptors of aromaticity employed are discussed. The results support the multidimensional character of aromaticity.

Keywords:

Aromaticity; Nucleus independent chemical shift (NICS); *Para*-delocalization index (PDI); Harmonic oscillator model of aromaticity (HOMA); Aromatic fluctuation index (FLU); Planarity; Atoms in Molecules theory (AIM); Diels–Alder reaction

4.5.- Aromaticity Measures from Fuzzy-Atom Bond Orders (FBO). The Aromatic Fluctuation (FLU) and the para-Delocalization (PDI) indexes.

Eduard Matito, Pedro Salvador, Miquel Duran, and Miquel Solà. “Aromaticity Measures from Fuzzy-Atom Bond Orders (FBO). The Aromatic Fluctuation (FLU) and the para-Delocalization (PDI) Indexes”. *Journal of Physical Chemistry A*. Vol. 110, no. 15 (April 20, 2006) : p. 5108-5113

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Abstract:

In the past few years, there has been a growing interest for aromaticity measures based on electron density descriptors, the para-delocalization (PDI) and the aromatic fluctuation (FLU) indexes being two recent examples. These aromaticity indexes have been applied successfully to describe the aromaticity of carbon skeleton molecules. Although the results obtained are encouraging, because they follow the trends of other existing aromaticity measures, their calculation is rather expensive because they are based on electron delocalization indexes (DI) that involve cumbersome atomic integrations. However, cheaper electron-sharing indexes (ESIs), which in principle could play the same role as the DI in such aromaticity calculations, can be found in the literature. In this letter we show that PDI and FLU can be calculated using fuzzy-atom bond order (FBO) measures instead of DIs with an important saving of computing time. In addition, a basis-set-dependence study is performed to assess the reliability of these measures. FLU and PDI based on FBO are shown to be both good aromaticity indexes and almost basis-set-independent measures. This result opens up a wide range of possibilities for PDI and FLU to also be calculated on large organic systems. As an example, the DI and FBO-based FLU and PDI indexes have also been calculated and compared for the C_{60} molecule.

Available Supporting Information

- pdf files:
  jp057387isi20060204_054422.pdf (17 K)

4.6.- Electron Sharing Indexes at Correlated Level. Application to Aromaticity Calculations.

Electron sharing indexes at the correlated level.

Application to aromaticity calculations.

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Electron sharing indexes (ESI) have been applied to numerous bonding situations to grasp inside in the nature of the molecular electronic structures. Some of the most popular ESI given in the literature, namely the delocalization index (DI), defined in the context of the quantum theory of atoms in molecules (QTAIM), and the Fuzzy-Atom bond order (FBO), are here calculated at correlated level for a wide set of molecules. Both approaches are based on the same quantity, the exchange-correlation density, to recover the electron sharing extent, and their differences lay on the definition of an atom in a molecule. In addition, while FBO atomic regions enable accurate and fast integrations, QTAIM definition of an atom leads to atomic domains that occasionally make the integration over these ones rather cumbersome. Besides, when working with a many-body wavefunction one can decide whether to calculate the ESI from first-order density matrices, or from second-order ones. The former way is usually preferred, since it avoids the calculation of the second-order density matrix, which is difficult to handle. Results from both definitions are discussed.

Although these indexes are quite similar in their definition and give similar descriptions, when analyzed in greater detail, they reproduce different features of the bonding. In this manuscript DI is shown to explain certain bonding situations that FBO fail to cope with.

Finally, these indexes are applied to the description of the aromaticity, through the aromatic fluctuation (FLU) and the para-DI (PDI) indexes. While FLU and PDI indexes have been successfully applied using the DI measures, other ESI based on other partition such as Fuzzy-Atom can be used. The results provided in this manuscript for carbon skeleton molecules encourage the use of FBO within FLU and PDI indexes even at correlated level.

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4.7.- Aromaticity Analyses by Means of the Quantum Theory of Atoms in Molecules.

Aromaticity Analyses by Means of the Quantum Theory of Atoms in Molecules

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An overview of recent aromaticity indicators defined in the framework of the Quantum Theory of Atoms in Molecules (QTAIM) is presented. Two new indexes based on the calculation of the QTAIM delocalization indexes have been defined: the *para*-delocalization index (PDI) and the aromatic fluctuation index (FLU). We give a short review of recent calculations of local aromaticity in a series of polycyclic aromatic hydrocarbons employing these new defined indexes with special emphasis on the strengths and weaknesses of these novel as well as previously defined descriptors of aromaticity.

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5.- Applications II: The Electron Localization Function

5.1.- The Electron Localization Function at Correlated Level.

Electron Localization Function at the Correlated Level

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Abstract

The electron localization function (ELF) has been proved so far a valuable tool to determine the location of electron pairs. Because of that, the ELF has been widely used to understand the nature of the chemical bonding and to discuss the mechanism of chemical reactions. Up to now, most applications of the ELF have been performed with monodeterminantal methods and only few attempts to calculate this function for correlated wavefunctions have been carried out. Here, a formulation of ELF valid for mono- and multiconfigurational wavefunctions is given and compared with previous recently reported approaches. The method described does not require the use of the homogeneous electron gas to define the ELF, at variance with the ELF definition given by Becke. The effect of the electron correlation in the ELF, introduced by means of CISD calculations, is discussed in the light of the results derived from a set of atomic and molecular systems.

Keywords: ELF (Electron Localization Function), correlated methods, second-order density.

5.2.- Bonding in Methylalkalimetal $(CH_3M)_n$ (M = Li – K; n = 1, 4). Agreement and Divergences between AIM and ELF Analyses.

Eduard Matito, Jordi Poater, F. Matthias Bickelhaupt, and Miquel Solà. "Bonding in Methylalkalimetals $(CH_3M)_n$ (M = Li, Na, K; n = 1, 4). Agreement and Divergences between AIM and ELF Analyses". *Journal of Physical Chemistry B*. Vol. 110, no. 14 (April 13, 2006) : p. 7189-7198

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Abstract:

The chemical bonding in methylalkalimetals $(CH_3M)_n$ (M = Li-K; n = 1, 4) has been investigated by making use of topological analyses grounded in the theory of atoms in molecules (AIM) and in the electron localization function (ELF). Both analyses describe the C-M bond as an ionic interaction. However, while AIM diagnoses a decrease of ionicity with tetramerization, ELF considers tetramers more ionic. Divergences emerge also when dealing with the bonding topology given by each technique. For the methylalkalimetal tetramers, the ELF analysis shows that each methyl carbon atom interacts through a bond pair with each of the three hydrogen atoms belonging to the same methyl group and through an ionic bond with the triangular face of the tetrahedral metal cluster in front of which the methyl group is located. On the other hand, the AIM topological description escapes from the traditional bonding schemes, presenting hypervalent carbon and alkalimetal atoms. Our results illustrate that fundamental concepts, such as that of the chemical bond, have a different, even colliding meaning in AIM and ELF theories.

Available Supporting Information

- pdf files: jp057517nsi20051226_020928.pdf (51 K)

5.3.- Comment on the “Nature of Bonding in the Thermal Cyclization of (Z)-1,2,4,6-Heptatetraene and Its Heterosubstituted Analogues”.

Eduard Matito, Miquel Solà, Miquel Duran, and Jordi Poater. "Comment on the "Nature of Bonding in the Thermal Cyclization of (*Z*)-1,2,4,6-Heptatetraene and Its Heterosubstituted Analogues" ". *Journal of Physical Chemistry B*. Vol. 109, no. 15 (April 21, 2005) : p. 7591-7593

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Available Supporting Information

- pdf files:
  jp048033e_s.pdf (0 K)
  jp048033e_s.pdf (19 K)

5.4.- Electron fluctuation in Pericyclic and Pseudopericyclic Reactions.

Eduard Matito, Jordi Poater, Dr., Miquel Duran, Prof. Dr., Miquel Solà, Prof. Dr.
“Electron fluctuation in pericyclic and pseudopericiclyc reactions”.
ChemPhysChem. Vol. 7, no. 1 (January 16, 2006) : p. 111-113

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Keywords

Electrocyclic reactions . Electron localization function . Pericyclic reactions . Transition states

Abstract

No abstract

6.- *Results and Discussion*

6.- Results and Discussion

The results of the present thesis can be divided into three parts: the calculation of the ESI, the aromaticity studies and the analyses of the ELF.

Electron Sharing Indexes

All the ESI reviewed in this manuscript are based on the XCD. The adequacy of this function to recover the extent of electron sharing has been discussed in the introduction. Its ability to explain the electron distribution of molecules has been extensively discussed in the literature. Particularly it is interesting noticing the pedagogic potential of this ESI to explain some difficulties arising in the computational chemistry, as it is the case of the homolytic dissociation of the hydrogen molecule in the framework of a restricted calculation with a single determinant. Chapter 4.2 discusses how the impossibility of occupying two different orbitals with one electron each, because of the restricted formalism, leads to a hydrogen-hydrogen electron sharing of one electron all along the dissociation process; likewise the energy of the dissociation process is overestimated within the same formalism. The usage of two Slater determinants enables the description of the process as an average between two configurations: the ground state one (with two electrons occupying the σ bonding orbital), and the excited state (were the two electrons have been promoted to the σ^* antibonding orbital). This way the dissociation energy decreases, similarly the electron sharing between the hydrogen atoms decreases with the bond distance to reach zero for two non-interacting hydrogen atoms; see the picture and the table below:

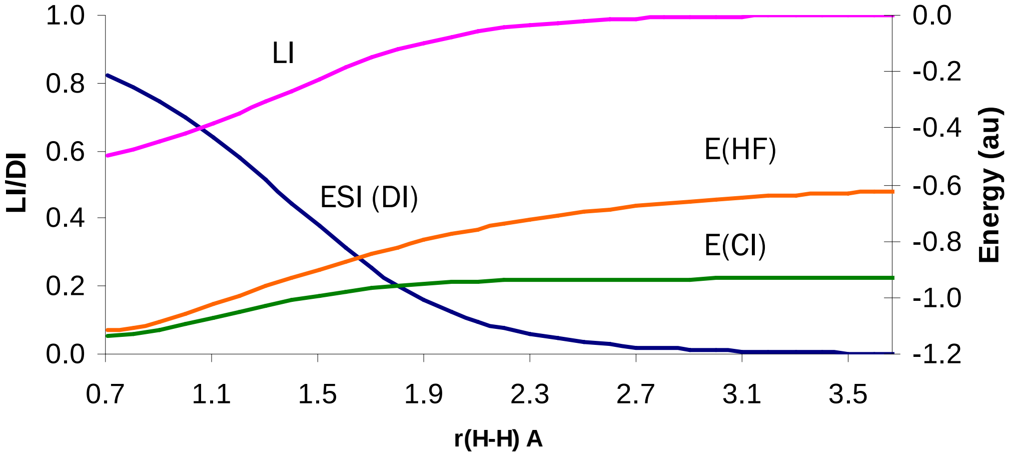

Figure2. The LI and the ESI(DI), the CI and HF energies for H_2 dissociation.

Table1. The ESI (DI), the CI and HF energies for H_2 dissociation.

r(H-H)Å	E. CI(au)	E. HF(au)	δ(H-H) CI
0.7351	-1.1373	-1.1170	0.8237
1.0350	-1.0936	-1.0561	0.6955
1.4350	-1.0091	-0.9306	0.4444
1.8350	-0.9590	-0.8204	0.2033
2.2350	-0.9403	-0.7406	0.0753
2.4350	-0.9368	-0.7112	0.0449
3.0350	-0.9336	-0.6537	0.0096
3.6350	-0.9332	-0.6250	0.0021
4.2350	-0.9332	-0.6100	0.0004
...	...	...	...
∞	E(H)	$E(H)+K_{12}/2$	0

Another interesting property of this system, is that the symmetry itself gives the only non-penetrating molecular space decomposition into atomic fragments, thus these results holds for some other partitions of the molecular space such as Voronoi cells.

In this sense, it has also been analyzed how the partition of the molecular space enables different ESI with different features but a common background. In chapter 4.1 the differences between the Mulliken, Fuzzy-Atom and the QTAIM partitions have been compared, to show the same qualitative trends, especially concerning carbon-carbon bonds. It is of special importance the agreement between QTAIM and Fuzzy-Atom partitions, since the former are widely used in the literature, but its computational expense sometimes prevents its usage. The following graphic shows how for bonded pairs of atoms both partitions agree, with the exception of certain pairs, as those containing Be, B or Al, or the for P-O bonds:

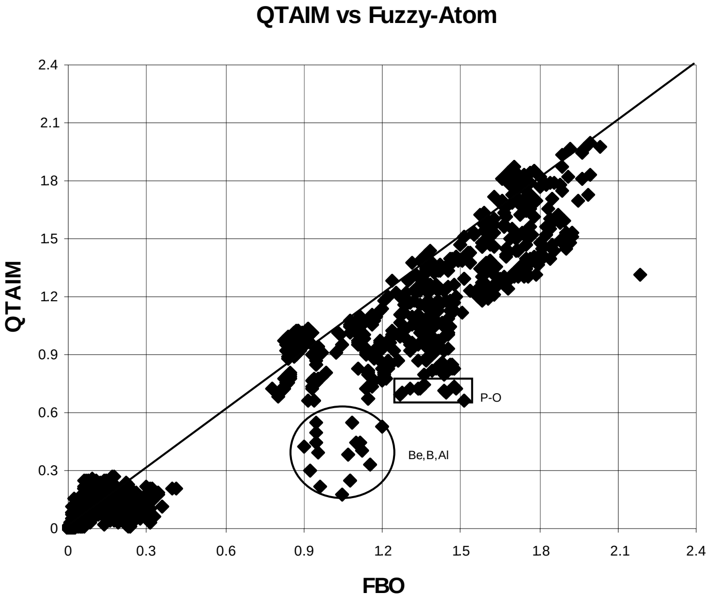

Figure3. Correlation betweem QTAIM-ESI and Fuzzy-Atom ESI.

On the other hand, the QTAIM partition has been demonstrated as a very suitable one, since –unlike Fuzzy-Atom approach- it enables the description of the dissociation of an ionic species into neutral atoms, where a maximum of electron sharing is expected at a certain distance (see Figure4).

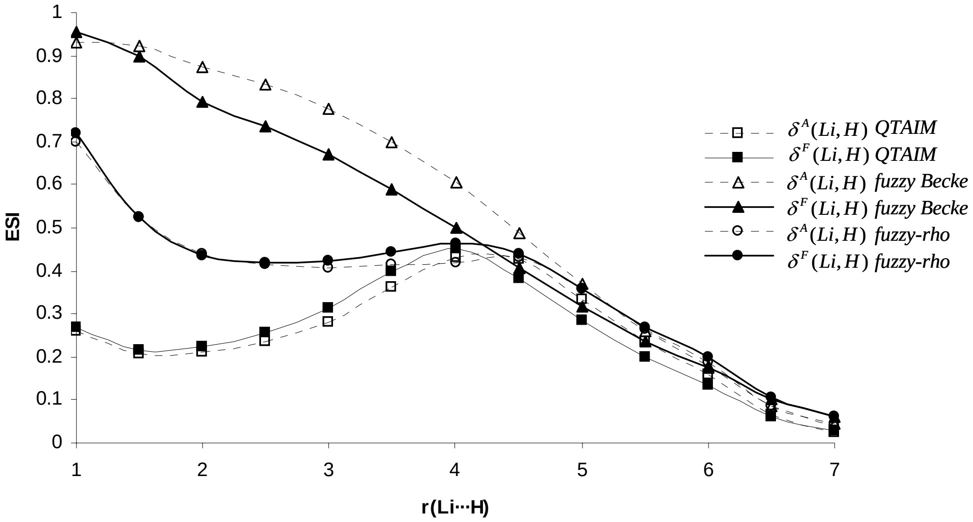

Figure4. LiH dissociation in neutral species; Angyan and Fulton ESI for QTAIM, Becke's Fuzzy-Atom and density based Fuzzy-Atom partitions.

However, when using the information given by the topology of the electron density to define a Fuzzy-Atom, a better description of this dissociation may be gathered, as it also shown in the picture above (fuzzy-rho). The conclusions hold for the CAS(4,4) calculation of LiH with two approximations to the true QTAIM-ESI, the Angyan (A) and the Fulton (F) ones (see chapter 4.6 for further details).

Therefore, one concludes that the QTAIM partition may be replaced by the less computationally expensive Fuzzy-Atom partition, to reproduce the same qualitative trends. Nonetheless, it is specially recommendable to use the information regarding the topology of the density (whose calculation is computationally inexpensive) to better approach the QTAIM partition, and maybe achieve quantitative results. In our laboratory we are currently exploring such possibility for the set of molecules given in chapter 4.1.

Aromaticity and its Quantification

Aromaticity is a cornerstone of current chemistry, and it quantification turns out to be one of the challenges of the present researchers in the field. Since aromaticity it is not an observable, several aromaticity descriptors may be put forward, and thus any proposal of a new aromaticity quantitative descriptor should be also followed by a proper testing of its ability to reproduce some trends of aromaticity known from chemical grounds.

In the present thesis we have defined a new aromaticity index, FLU (the short form of fluctuation aromaticity index), which uses the electron sharing between adjacent atoms along the ring on its definition; the formula is as follows:

$$FLU = \frac{1}{n}\sum_{A-B}^{RING}\left[\left(\frac{V(B)}{V(A)}\right)^{\alpha}\left(\frac{\delta(A,B)-\delta_{ref}(A,B)}{\delta_{ref}(A,B)}\right)\right]^{2} \quad , \tag{28}$$

where *n* stands for the number of members in a given ring, $\delta(A,B)$ and $\delta_{ref}(A,B)$ are the ESI of the corresponding pair and the ESI of the corresponding atoms A-B in a typical aromatic molecule chosen as a reference respectively; V(A) is the valence of atom A and reads:

$$V(A) = \sum_{B \neq A}\delta(A,B) = 2\left[N(A) - \lambda(A)\right] \quad , \tag{29}$$

and finally α is set so that the ratio of valences in Eq. (28) is greater than 1, penalizing those cases with highly localized electrons:

$$\alpha = \begin{cases} 1 & V(B) > V(A) \\ -1 & V(B) \leq V(A) \end{cases} \quad . \tag{30}$$

The FLU aromaticity index has been show to give good correlations with other indexes. In particular, the correlations of FLU with the PDI and HOMA are excellent, and even though NICS correlation with FLU, PDI or HOMA is not so good (see figures in chapter 4.3), one can easily attribute it to the multidimensional character of aromaticity.

Although FLU needs a reference value taken from aromatic molecules with the bond pairs of the molecule we want to take into study; this is not a big deal because most organic aromatic molecules are composed of carbon-carbon bonds, and thus benzene can serve as a reference. However, a striking shortcoming of the FLU index, as it is the case of HOMA index, is its inadequacy to study chemical reactivity. This is shown in chapter 4.4 by analyzing the value of different aromaticity indexes along the reaction path of the simplest Diels-Alder reaction; this graphic illustrates the phenomena:

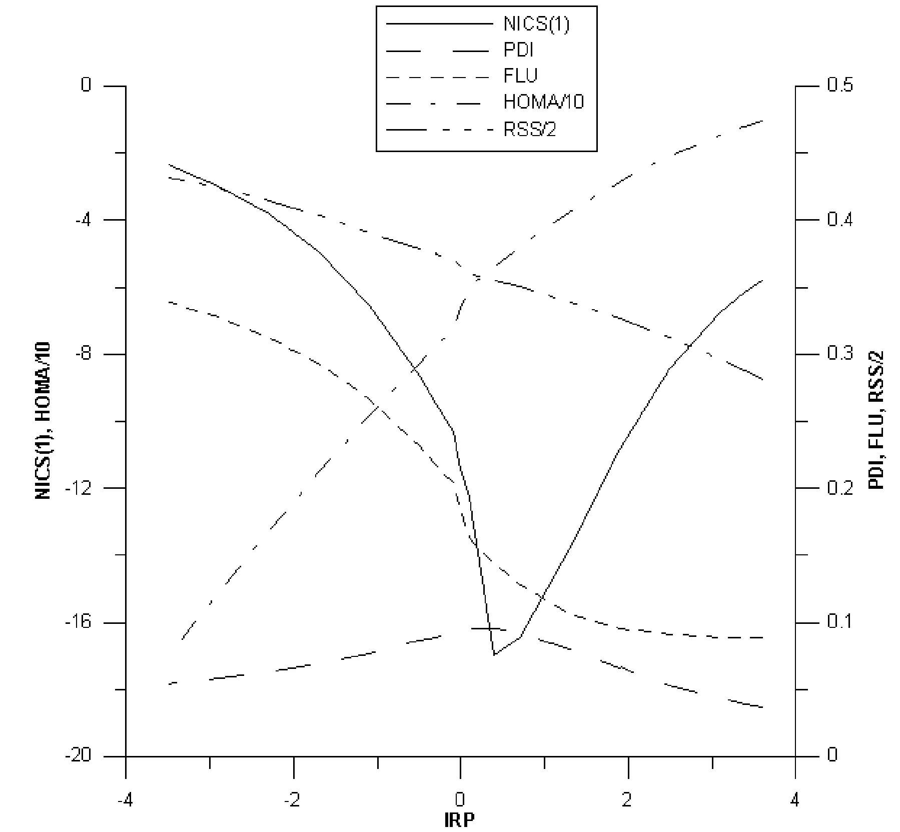

Figure5. NICS, PDI, FLU, HOMA, and Root Sum Square (RSS) of the distances of the atoms to the best fitted plane for the Diels-Alder reaction path.

Here we can see how the most aromatic point in the reaction path (the transition state) is only stated as such by PDI and NICS values, whereas FLU or HOMA give the cyclohexene as the most aromatic species. It is due to the fact that the structure and electron sharing of the reference molecule (benzene) is more similar to the cyclohexene rather than the transition state, where the bond lengths are unusually larger and therefore yield lower electron sharing between the corresponding atoms. As a consequence one may conclude that when aromaticity is enhanced by larger bond lengthening, HOMA or FLU indexes may fail to reproduce the expected trends. It is not that these indexes are completely useless for reactivity studies, but at least it is clear by results of chapter 4.4 that for such analysis one must apply these indexes with care.

Another aromaticity index, which uses π-electron sharing and avoids references, is the FLU$_\pi$. It has been defined as:

$$FLU_\pi = \frac{1}{n}\sum_{A-B}^{RING}\left[\left(\frac{V_\pi(B)}{V_\pi(A)}\right)^\alpha \left(\frac{\delta_\pi(A,B)-\delta_{av}}{\delta_{av}}\right)\right]^2 \quad , \tag{31}$$

where all quantities correspond to the π counterpart of those given in Eq. (30), and δ_{av} is the average of all bonded ESI in a given ring. This index needs not for reference parameters, but it can be only exactly calculated for planar molecules, where the exact orbital decomposition of the ESI into its σ and π parts is possible. Usually aromatic molecules are also planar, but if we were about to estimate the aromaticity of a non-planar species with FLU$_\pi$ we would need the implementation of localization scheme to compute it. FLU$_\pi$ has been shown to reproduce the same trends of FLU for the series of molecules studied in chapter 4.3.

Finally it is worth noticing that the ESI used in Eqs. (30) and (31) use the XCD function but with a QTAIM partition. However, there is no reason why we should limit ourselves to ESI calculated from this partition. In this line, in chapter 4.5 FLU, PDI and FLU$_\pi$ have been shown to yield quantitative the same results for QTAIM partition than for Fuzzy-Atom one (see Figures 1-3 in chapter 4.5). Besides, the basis set dependence of these indexes for the Fuzzy-Atom partition has been tested in the same chapter, with the finding of strong independence of the basis set employed.

The Electron Localization Function

Defined by Becke and Edgecombe by 1990, the ELF has been one the most successful approaches to the study of electron localization. While the ELF has been extensively used for single determinant wave functions (HF or DFT within the Kohn-Sham formalism), there has been few attempts to address this issue for wave functions composed of several determinants. In chapter 5.1 we have reviewed the definitions given in the literature for the ELF to show their equivalence, and that indeed there is no need of the arbitrary factor originally used by Becke and Edgecombe to define the ELF. The expression of the ELF at correlated level for both closed- and open-shell systems reads:

$$ELF = \left[1 + \left(\frac{ \nabla_s^2 \gamma^{(2)\beta\beta}\left(\vec{r}, \vec{r} + \vec{s}\right)\Big|_{\vec{s}=0} + \nabla_s^2 \gamma^{(2)\alpha\alpha}\left(\vec{r}, \vec{r} + \vec{s}\right)\Big|_{\vec{s}=0} }{ 2c_F \left[\rho(\vec{r})\right]^{8/3} } \right)^2 \right]^{-1} . \qquad (32)$$

In the same chapter the ELF is shown to recover the shell structure for atoms Li to Kr, and to partially reproduce the shell numbers, with lesser accuracy as the atomic number increases. Finally, chapter 5.1 includes the values for the integration of certain interesting functions over the ELF basins (the regions of molecular space which are surrounded by a zero flux surface of a certain function or by infinity; for ELF basins the function corresponds to the ELF function, whereas for QTAIM basins, the function is simply the density). For instance, the density and the pair density lead to the population and pair populations, whose combination enable the calculation of the covariance and the variance of the basin populations. Unlike QTAIM, whose basins are uniquely related with an atom in a molecule, the ELF partition leads to a molecular space partition which is more connected to Lewis concepts, such as bonding regions, lone pairs or core basins.

The literature is full of examples which show the way to obtain chemically interesting information from the ELF; we also address this point in chapters 5.2-5.4. The first of these chapters is devoted to analyze a special case, where two of the most widely used tools to elucidate the electronic structure of molecules, QTAIM and ELF, differ on their explanation of the electronic structure of $(CH_3Li)_4$ species.

For this system the QTAIM reports nine bond paths connecting carbon with the three closest hydrogen atoms, the other three carbon atoms, and the three closest lithium atoms, as in the QTAIM picture shown below:

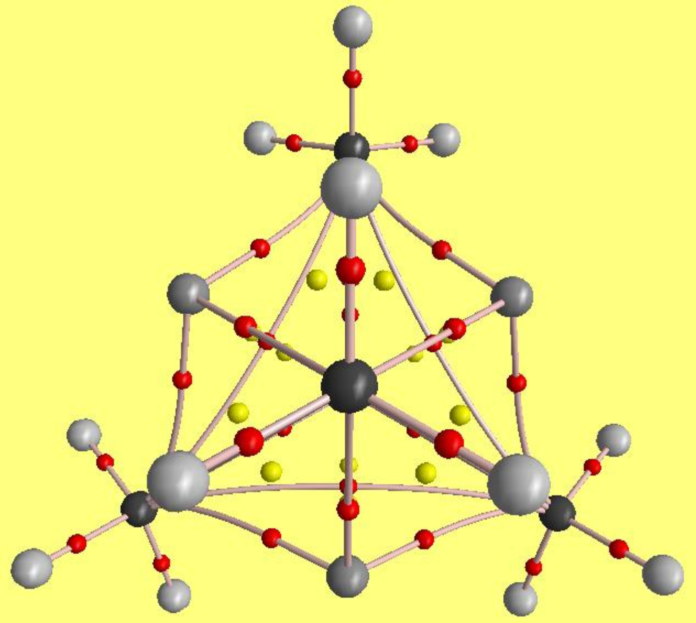

Figure6. Electron-density topology of $(CH_3Li)_4$ on its eclipsed conformation; the bond critical points are in red and the ring critical

Following Bader,[65] each bond path must be associated with a *bond*, and therefore from a QTAIM perspective the carbons in this cluster should be nonavalent. On its side, the ELF picture of the same molecule looks:

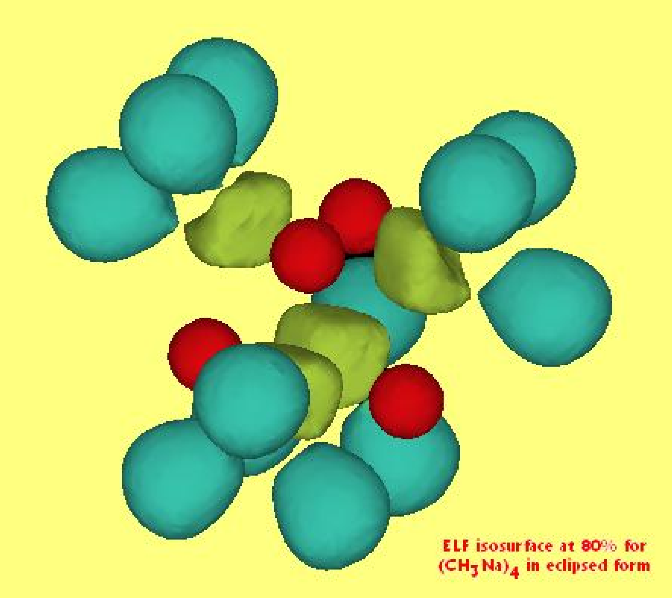

Figure7. The ELF topology of $(CH_3Li)_4$ eclipsed conformation; the lithium basins are red, the carbon ones are yellow and the hydrogen ones are blue. Isosurface ELF=0.80.

where each carbon basin (in yellow) points towards the plane consisting of three lithium atoms, as if the bonding interactions were four: three covalent ones with the hydrogen atoms, plus one polar bond with the center of the three lithium plane.

The last two chapters of this thesis discuss the utility of the ELF to discern between two mechanisms of reaction which may lead to confusion, the pericyclic and pseudopericyclic reactions. Pericyclic reactions are widely known and characterized by the Woodward and Hoffmann rules, whereas the pseudopericyclic ones were discovered by 1976, when Ross et al.[66] put forward reactions which broke the rules given by Woodward and Hoffmann. Pseudopericyclic reactions are low or non-existing barrier reactions, with planar transition state and cyclic overlap disconnections. Since other researchers documented pericyclic reactions with low barriers or with quite planar transition states, these features of the pseudopericyclic reactions are sometimes arbitrary, and it is hard to say whether the reaction occurs through a pericyclic or pseupericyclic mechanism.

We propose the analysis of the transition state of the electrocyclic processes by means of the ELF, to investigate the electron localizability, in order to assess whether exists connectivity between the adjacent bonds which are about to be broken/formed in the concerted reaction. In a pericyclic reaction the electron charge is spread among the bonds involved in the rearrangement, whereas pseudopericyclic reactions are characteristic for electron accumulations and depletions on different atoms, and thus the electron distribution is far from being uniform for the bonds involved in the rearrangement. Since the ELF accounts for the electron distribution we expect connected (delocalized) pictures of bonds in pericyclic reactions, while pseudopericyclic reactions will give rise to disconnected (localized) pictures. The magnitude of fluctuation between adjacent bonds can be also used to assess the localized/delocalized character of the transition states.

This way one can help elucidating the mechanisms of reaction for controversial cases. In Figure8, the ELF picture of the transition state for a series of electrocyclic processes is depicted, together with the fluctuation diagrams. From ELF analysis one may conclude that reactions C, F and G occur through a pericyclic mechanism, while the others are pseudopericyclic reactions.

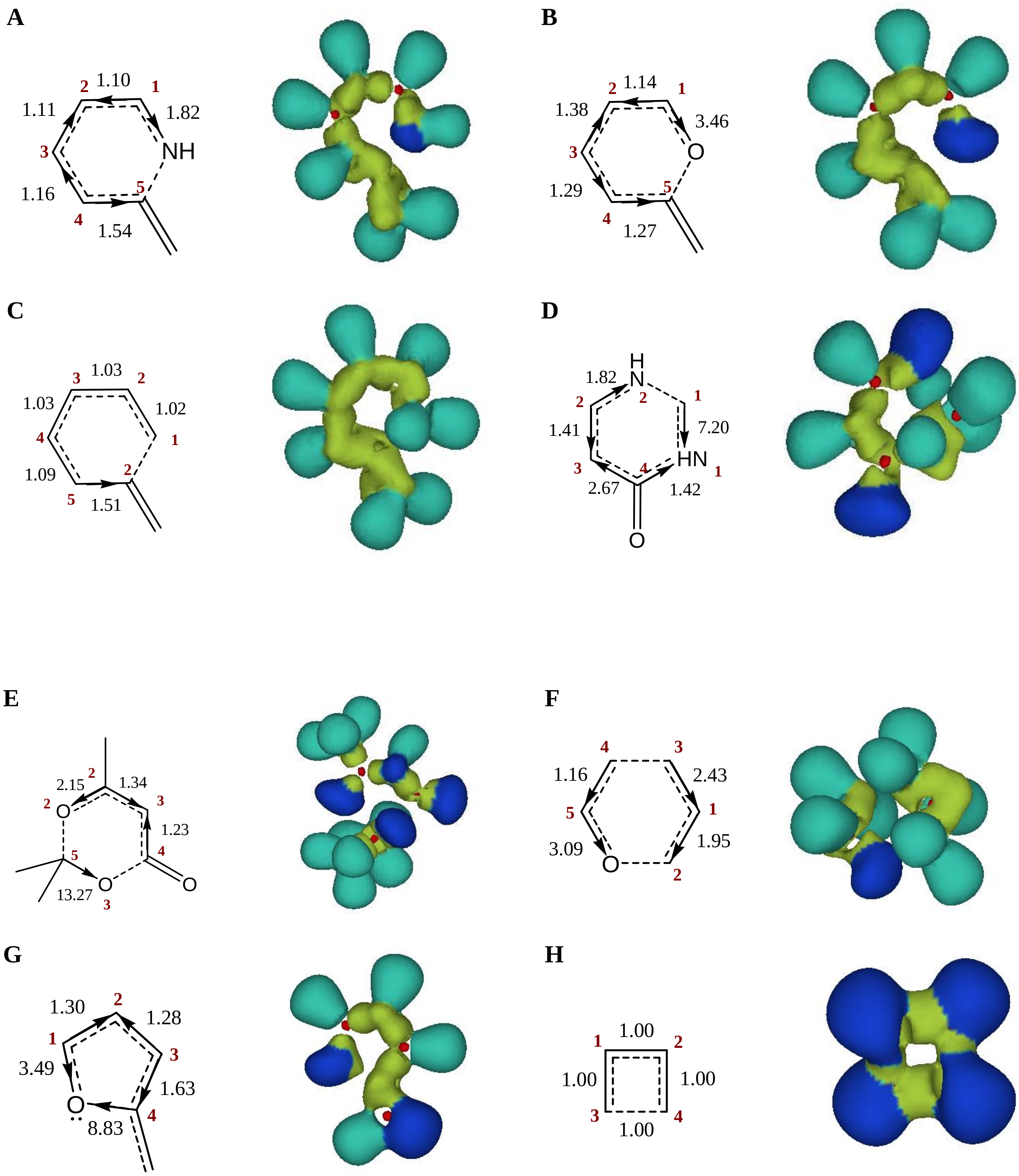

Figure8. The ELF=0.60 isosurfaces of the transition state of electrocyclic reactions A-H. The fluctuation diagrams with arrows pointing towards the preferred direction of fluctuation, and its magnitude are also given. Two arrows with significant magnitude pointing towards the same atoms is an indication of electron accumulation, two arrows pointing outwards means electron depletion.

7.- Conclusions

7.- Conclusions

Applications I: Electron Sharing Indexes and Aromaticity.

1.- The ESI based on QTAIM and Fuzzy-Atom partitions, and the Mayer Bond Order (MBO), mainly reproduce the same trends in the bonding. This does not necessarily mean that the three ESI have the same value. The exceptions to this are mainly due to systems containing aluminum, boron and beryllium. Specially striking is the relationship found for carbon-carbon bonds; this result suggests hydrocarbons and other carbon skeleton species, may reproduce the same bonding patterns from the three ESI, whose computational cost ranges from extremely cheap (MBO) to considerable expensive (QTAIM).

2.- The localizability of electrons in the hydrogen molecule may be presented to an undergraduate student to get a deeper understanding of the homolytic bond dissociation problem in the restricted HF method. The necessity of molecular spin orbitals to be doubly occupied is the responsible for localization to hold on the same value while dissociation is happening. To avoid this shortcoming one must use correlated methods, such as configuration interaction. The QTAIM ESI enables an easy explanation of this phenomena: for monodeterminantal wave functions the ESI is equally 1 for the whole reaction path, whereas for CI the atomic electron localizability increases with interatomic distance until one electron localizes in each atom, while mutual shared electrons decrease to reach no sharing in the limit of non-interacting fragments.

3.- We have defined in this thesis the aromatic fluctuation index (FLU), which analyzes the amount of electron sharing between contiguous atoms, which should be substantial in aromatic molecules, but it also takes into account the similarity of electron sharing between adjacent atoms. We have demonstrated that the FLU index and its π analog, the FLU_π descriptor, are simple and efficient probes for aromaticity. We have shown that, for a series of planar PAHs, FLU and FLU_π correlate well, with few exceptions, with other already existing independent local aromaticity parameters, like the geometry-based descriptor, HOMA, the magnetic-based criterion, NICS, and the electronic-based PDI index, which are of common use nowadays.

4.- The paradigmatic Diels-Alder reaction between 1,3-butadiene and ethene, presenting an aromatic TS, has been analyzed to show that some aromaticity indices may fail to describe aromaticity in chemical reactions. The NICS and PDI indicators of aromaticity correctly predict that a structure close to the TS is the most aromatic species along the reaction path. On the contrary, we have found that HOMA and FLU indices are unsuccessful to account for the aromaticity of the TS. These indexes show that the most planar species along the reaction path of the DA reaction between 1,3-butadiene and ethene is cyclohexene, the final product. The failure of some indexes to detect the aromaticity of the TS in the simplest DA cycloaddition reinforces the idea of the multidimensional character of aromaticity and the need for several criteria to quantify the aromatic character of a given species.

5.- PDI, FLU and FLU_{π}, measures have been calculated for a series of aromatic and non-aromatic molecules replacing the QTAIM ESI by the Fuzzy-Atom one. The corresponding values for each aromaticity index are in excellent agreement, particularly for the molecules containing only C-C bonds. The correlation for the PDI index is surprisingly good, taking into account that it is based on the electron sharing between non-bonded atoms. The slight deviations between the FBO and DI between C-C and C-N bonded atoms are translated into some differences between the FLU and FLU_{π} indexes, as the corresponding electron sharing reference and average values change, respectively. Nevertheless, the correlation between the FBO- and DI-based FLU and FLU_{π} is still excellent. It has been proved that these indexes are strongly insensitive to the basis set, even for the modest STO-3G basis set.

6.- The effect of the inclusion of correlation has been analyzed for the ESI from different partition schemes (QTAIM and Fuzzy-Atom), based on both the first- and the second-order density matrices. It has been shown that for weakly bonded molecules most indexes coincide and the effect of the electron correlation is minor; whereas for covalent and polar covalent molecules the electron correlation effects are notorious, and ESI based on first-order density matrices do not wholly reproduce the trends shown by the ESI based on second-order one. Fuzzy-Atom approach for the set of radii determined by Koga has been shown to not reproduce a maximum of electron sharing in the dissociation of LiH species in neutral atoms. Nevertheless, an improvement in the description is gathered if the radius corresponding to the distance from the attractor to the bond critical point is used. Finally, aromaticity indexes have been studied for first time for correlated calculations, leading to a general trend similar to that already reported for monodeterminantal methods. Nevertheless, is worth to mention these indexes are more dependent on the methodology employed rather than the basis set used.

Applications II: The Electron Localization Function (ELF)

7.- We have reviewed the ELF definition for correlated wave functions, showing the equivalence of the most recently proposed definitions of the ELF, and how its monodeterminantal version reproduces Becke and Edgecombe's definition. We have computed the ELF for CISD level of theory, providing populations and variance analysis for a correlated partitioning according to the ELF function. These results have been discussed with respect to results derived from the loge theory.

8.- The AIM and ELF topological approaches partially agree but also show significant divergences in the description of the bonding in methylalkalimetals $(CH_3M)_n$ with M = Li – K, n = 1, 4. They coincide in indicating that C-M bonds for these compounds are highly polar. However, whereas AIM indicates that tetramerization of CH_3M slightly reduces the polarity, ELF suggests the opposite. More importantly, and also more strikingly, AIM yields nonavalent carbons in tetramethyllithium. According to AIM, the carbon atoms in this methylalkalimetal have three individual bonds to the three closest hydrogen atoms, three individual bonds to the three closest metal atoms, and three individual bonds to the three closest carbon atoms. At variance, ELF yields tetravalent carbon atoms that form three covalent bonds with their hydrogens plus one polar bond with a triangular face of the central metal cluster.

9.- We have shown that a recent work by Chamorro and Notario[67] has incorrectly assigned a pericyclic nature to reactions **A** and **B** in chapter 5.3. Our conclusion is achieved by means of a covariance analysis based on contributions arising from the same basin, and by comparison to the reaction of cyclization of 5-oxo-2,4-pentadienal to pyran-2-one, with an already assigned pseudopericyclic nature.

10.- We have reported that the electron distribution of TS studied by means of the ELF provides a clear picture of the electron rearrangement, which reveals the mechanism of the reaction for several electrocyclic processes with the only need of the TS structure. This way, a reliable manner to distinguish between pericyclic and pseudopericyclic mechanisms have been put forward.

8.- Complete List of Publications

8.- *Complete list of publications:*

1.- Matito E., Solà M., Duran M., and Poater J.; Comment on *"Nature of Bonding in the Thermal Cyclization of (Z)-1,2,4,6-Heptatetraene and its Heterosubstituted Analogues"*; *J. Phys. Chem. B* 109, 7591-7593 (2005)

2.- Matito E., Duran M., and Solà M.; *The aromatic fluctuation index (FLU): A new aromaticity index based on electron delocalization*; *J. Chem. Phys.* 122, 014109 (2005)

3.- Matito E., Poater J., Duran M., Solà M.; *An analysis of the changes in aromaticity and planarity along the reaction path of the simplest Diels-Alder reaction. Exploring the validity of different indicators of aromaticity*; *J. Mol. Struct. (THEOCHEM)* 727, 165-171 (2005)

4.- Matito E., Poater J., Solà M., Duran M., and Salvador P.; *Comparison of the AIM Delocalization Index and the Mayer and Fuzzy Atom Bond Orders; J. Phys. Chem. A* 109, 9904-9910 (2005)

5.- Matito E., Poater J., Duran M., and Solà M.; *Electron fluctuation in pericyclic and pseudopericyclic reactions*; *ChemPhysChem* 7, 111-113 (2006)

6.- Matito E., Kobus J., and Styszyński J.; *Bond centred functions in relativistic and non-relativistic calculations for diatomics; Chem. Phys.* 321, 277-284 (2006)

7.- Matito E., Poater J., Bickelhaupt F.M., and Solà M.; *Bonding in Methylalkalimetal* $(CH_3M)_n$ *(M = Li – K; n = 1, 4). Agreement and Divergences between AIM and ELF Analyses*; *J. Phys. Chem. B* 110, 7189-7198 (2006)

8.- Matito E., Salvador P., Duran M., and Solà M.; *Aromaticity measures from Fuzzy-Atom Bond Orders. The aromatic fluctuation (FLU) and the Para-Delocalization (PDI) indexes*; *J. Phys. Chem.* A 110, 5108-5113 (2006)

9.- Jiménez-Halla J.O.C., Matito E., Robles J., and Solà M.; *Nucleus-independent chemical shift (NICS) profiles in a series of monocyclic planar inorganic compounds*; *J. Organometallic Chem.* (ASAP)

10.- Matito E., Duran M., and Solà M.; *Exploring the Hartree-Fock Dissociation Problem in the Hydrogen Molecule by means of Electron Localization Measures*; *J.* Chem. *Educ.* (in press, to appear issue July2006)

11.- Matito E., Silvi B., Duran M., and Solà M.; *Electron Localization Function at Correlated Level*; *J. Chem. Phys.* (accepted)

12.- Matito E., Poater J. and Solà M.; *Aromaticity Analyses by Means of the Quantum Theory of Atoms in Molecules. Recent Advances in the Quantum Theory of Atoms in Molecules; R. J. Boyd and C. F. Matta, Eds., Wiley-VCH, New York, 2006,* (accepted)

13.- Matito E., Salvador P., Duran M., and Solà M; *Electron sharing indexes at correlated level. Application to aromaticity calculations. Faraday Discussions* (accepted)

14- Jiménez-Halla J.O.C., Matito E., Robles J., Solà M.; *Interaction of* Na^+ *with cyclo*-$[Mg_3]^{2-}$ *triggers an unprecedented change of* σ- *to* π-*aromaticity.* (submitted)

15.- Güell M., Matito E., Luis J.M., Poater J., and Solà M.; *Analysis of Electron Delocalization in Aromatic Systems: Individual Molecular Orbital Contributions to Para-Delocalization Indexes (PDI). PCCP* (submitted)

16.- Matxain J. M., Eriksson L. A., Mercero J. M., Lopez X., Ugalde J. M., Poater J., Matito E., Solà M.; *Stability and Aromaticity of* $B_{12}N_{12}$ *Fullerene Dimer. JCTC* (submitted)

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APENDIX: Technical details

Gaussian Package

For the geometry optimization and single point calculations of the systems given in this thesis we have only used the commercial software Gaussian, in the two last versions, Gaussian98[68] and Gaussian03.[69] Let us give some details about the calculations performed with Gaussian.

- The wave function

In most works the analysis of the wave function is crucial for the understanding of the chemical problem. In this sense, PROAIM and ToPMoD computational packages need the wave function given in specific format, thus the Gaussian keyword *out=wfn* will be used in most calculations. This keyword is used in combination with the keyword density=current to obtain the wave function at the current level of theory. Otherwise, by default, Gaussian prints the HF wave function for all post-HF methods (CISD, CASSCF, CCSD, etc.). Furthermore, one must change the threshold used in link 9999 (l9999) of Gaussian in order to print occupancies for CISD which are above 10^{-7}. By default an own modified version of l9999 of Guassian (both 98 and 03) set all occupancies lower than 10^{-7} to 10^{-7}, this way we make sure PROAIM program considers also this orbitals to compute the AOM.

In a HF calculation if we want Gaussian to print the virtual orbitals the keyword we must use is the Iop(99/18=-1), it is needed for the modified version of ToPMoD program used in chapter 5.1.

- Density Matrices

The calculation of the DM1 and DM2 goes through a program designed in our laboratory,[59] which takes the coefficients of the CI expansion, as indicated before. The program creates the DM1 and DM2 from these coefficients, in terms of molecular spin orbitals. However, most programs work either with natural spin orbitals or with atomic orbitals; our case is the former. Thus, we need to transform all those quantities (in practice the so-called atomic overlap matrices in a given partition) from natural spin orbitals to molecular spin orbitals. To this aim, we diagonalize the DM1 to obtain the natural orbitals.

The diagonalization of a given symmetric matrix, as it is the case of DM1, goes through a unitary transformation. Such a transformation is unique excepting for a multiplicative factor in each eigenvector given. The only case of the unitary transformation being undetermined by more than a multiplicative factor is when the eigenvalues are degenerated; for degenerated eigenvalues any combination of the corresponding eigenvectors can be used in the unitary transformation. The reason is simple: any combination of degenerated eigenvectors is also an eigenvector of the system with the same eigenvalue. It occurs on molecules with degenerated levels, which is a common situation. Therefore, unless we are dealing with a molecule with no degenerated levels, for the diagonalization of the DM1 one needs to read from Gaussian (or any other software used) the specific unitary transformation used by this program.

By default all gradient calculations for correlated calculation are performed within link 913. This link computes the *relaxed* first-order reduced density matrix, as one checks by simple inspection of natural occupancies (which are above one or below zero). In order to obtain the *unrelaxed* first-order reduced density matrix. It is necessary to force Gaussian to use old link 916, by setting use=l916. Likewise, one must set density=current to also write the unrelaxed density in the wave function file. In general it is better optimizing the geometry with the usual link (916) and, once converged, using the link 913 to obtain the unrelaxed density. Finally it is also worth noticing that sometimes one needs to set off the symmetry (keyword nosymm) to achieve the wave function convergence with link 916.

- Input example:

Here the example of NH_3 molecule for the calculation of the unrelaxed density (relaxed density is also obtained) for CISD with 6-311++G(2d,2p) basis set, with Cartesian *d* and *f* functions. The wave function and the formatted checkpoint (fchk) files are also obtained; gfinput is included to print the basis set.

```
%subst l9999 /users/eduard/g03
%chk=NH3.chk
%rwf=/tmp/eduard/1.scr,2000mb,/tmp/eduard/2.scr,2000mb,/tmp/eduard/3.scr
,2000mb,/tmp/eduard/4.scr,2000mb,/tmp/eduard/5.scr,-1
#CISD/6-311++G(2d,2p) 6d 10f opt out=wfn density=current

HF

0 1
 n
 h   1 hc
 h   1 hc       2 hch
 h   1 hc       3 hch         2 dih

 hc=1.00964742
 hch=107.08384316
 dih=114.57936516

NH3rel.wfn

–Link1–
%subst l9999 /users/eduard/g03
%chk=NH3.chk
%rwf=/tmp/eduard/1.scr,2000mb,/tmp/eduard/2.scr,2000mb,/tmp/eduard/3.scr
,2000mb,/tmp/eduard/4.scr,2000mb,/tmp/eduard/5.scr,-1
#CISD/6-311++G(2d,2p) 6d 10f scf=tight geom=check out=wfn Iop(9/40=7)
Iop(9/28=-1) density=rhoci fchk use=l916 nosymm gfinput


0 1

NH3unrel.wfn
```

30/04/2006

I semblava que aquest dia tardaria en arribar... I el cert és que aquests quatre anys m'han passat sense quasi adonar-me'n. Aquesta tesi representa el meu esforç de quatre anys i conté gran part dels treballs que he realitzat a l'Institut. Al contrari que la tesina, que contenia principalment els treballs sobre la teoria i l'algoritme de càlcul de matrius de densitat, aquesta tesi versa sobre els treballs més pràctics, amb l'excepció potser d'algun capítol.

Arribats aquí toca agrair a tots aquells que m'han ajudat en aquests quatre anys. Primer de tot estan els meus directors de tesi, en Miquel Solà i en Miquel Duran (Quel). Gràcies Miquel pel teu recolzament i per la teva paciència al llarg d'aquests quatre anys, els teus consells i la teva ajuda han fet d'aquesta tesi el que avui presento. Hem començat tantes coses que crec que necessitaria dues tesis per donar cabuda a tot plegat. A tu Quel, et dono les gràcies per la teva visió crítica, la teva capacitat d'estructurar els treballs, que ha donat més rigor als projectes que ocupen aquestes pàgines. I sobretot per les xerrades i discussions, sobre Hellmann-Feynman, matrius de densitat d'ordre *n*, etc. No dubtis pas que acabarem trobant "a Catalan molecule". A tots dos us dec també l'oportunitat de col·laborar amb vària gent de l'estranger, així com poder assistir i participar en una colla de congressos.

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I am also endebted to the people from Poland, to the ones in Torun: Jacek Kobus and Jacek Karwowski for their kind hospitality. And of course to the ones in Szczecin, Marcin, Kasia, Jacek and Jerzy; they helped to make my stay in Szczecin a nice

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També vull dedicar unes línies als meus amics. Als de Girona, en Marc, en Gerard, l'Albert, l'Ernest, l'Inma i l'Òlbia; als de la Universitat, en Sebes, l'Hèctor, en Bernat, l'Eva, l'Ester, en Carles, l'Amadeu i la Núria; i als SASA: l'Albert, la Marta, en Pere i la Gemma.

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A tots plegats, i a tu que tens la paciència de llegir-me,

Moltes gràcies.