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Revisiting Lewis Dot Structures Weightings: a pair density perspective

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Abstract

A method based on a real space partitioning to measure the importance of Lewis structures is proposed in this work. A matrix containing diverse QTAIM atomic and diatomic properties endowed with significance within a Lewis structure framework is expanded in terms of what we call Lewis-structure matrices. Each of these matrices flawlessly describes an individual resonance structure and its associated linear expansion coefficient (Q-ALE coefficient) indicates the importance or convenience of the given Lewis structure. These coefficients were inspected looking at their evolution in a series of usual chemical issues. Among all the results, we find of interest that σ resonance structures in systems with π electrons are more important than normally expected, which justifies why the qualitative predictions arising from the application of the resonance model and the quantitative results based on QTAIM properties are sometimes discrepant. Likewise, we observe that the variation of the dielectric constant of the medium affects the π resonance in a greater extent than it does to the σ one. Other interesting results in this manuscript are connected to homolytic dissociation of diatomic molecules, periodic trends in hydrogen compounds, and polarization of aromatic systems as a consequence of their interaction with electric fields and with diverse ions.

Keywords: Resonance structures, QTAIM, Delocalization index, Q-ALE coefficients, Resonance form importance, Lewis model.

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1 Introduction

One of the most fruitful and fundamental concepts within Chemistry is that of “chemical bond”.[1] Paradoxically, as other fundamental concepts, it lacks a unique and precise definition and it has been the subject of a huge collection of studies, the seminal contribution being the cubical atom theory presented by Lewis in 1916.[2] Within the framework of this theory, a shared electron pair was the key step in the formation of a chemical bond. This point of view led to diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule. These diagrams, called Lewis dot structures (LDSs) and constructed according to a certain set of rules, allowed predicting geometry, polarity and reactivity of inorganic and organic compounds. Due to this obvious and immense impact on chemistry, Lewis theory became one of its most important milestones. So it is that, nowadays, LDSs define the language used in the description of chemical transformations. Thus, from the simplest chemical change to those routes designed to synthesize complex molecules of biological importance, Lewis structures have played (and still play) a crucial role in.

Indeed, most of the behaviors exhibited by any functional group are explained and understood in terms of its different LDSs. As an illustration of the predictability power associated to LDSs, the textbook example of the carbonyl group can be analyzed. In the basis of chemical intuition, it seems legitimate to propose this group as a combination of mainly two Lewis structures: the covalent C=O and the ionic $C^+{-}O^-$ (Figure 1a). Accordingly, two straightforward consequences emerge from this description: i) its bond strength should be greater than that of an alcohol group (from the C=O LDS) and ii) the carbonyl carbon should be prone to suffer a nucleophilic addition reaction due to its partial positive charge inherited from the $C^+{-}O^-$ LDS. Unquestionably, both properties of the carbonyl group are well-known experimental facts, which emphasizes the predictability potential of LDSs. Equally important would be the meaningful example of benzene, whose electronic structure is usually defined through the two famous Kekulé structures (Figure 1b). The consideration of only one of them would lead to a ring with two different kind of edges (C−C and C=C), precluding the actual D_{6h} symmetry of the system. Moreover, the consideration of different LDSs is hugely used to predict substituent effects on π conjugated systems such as benzene. A slew of excellent examples about the importance of Lewis structures to understand chemical reactivity and structure can be found in any general or advanced text of chemistry.[3–6]

Lewis ideas took root so much in the world of Chemistry that it was necessary to find ways of retaining them within the modern theories and conceptions about the molecular electronic structure. In fact, his ideas even survived the advent of quantum mechanics, whose fundamental wave equation was formulated in 1926.[7] Since that date, only two years were needed to develop the resonance theory,[8] where Linus Pauling combined the pair bonding ideas of Lewis together with the Heitler-London theory[9] and some concepts from the discussion presented by Werner Heisenberg about stationary states of the helium atom,[10] where the word "resonance" made its first appearance in the world of quantum mechanics. Within Pauling theory, and in analogy to Lewis ideas, the molecular electronic wave function, Ψ, is described as a superposition of ψ_i functions, each one describing a LDS:

$$\Psi = \sum_i c_i \psi_i \tag{1}$$

However, this direct connection between LDSs and quantum mechanics vanishes as soon as the Molecular Orbital (MO) philosophy is employed. In the framework of this theory, the first attempts to preserve Lewis point of view were based on localized molecular orbitals.[11–14] Although promising, they are, as any other MOs, mono-electronic functions and, consequently, they present no information about the physical role of electron pairs in chemical bonds. From a more general point of view, and regarding the total wave function instead of its components, other authors pointed that the proper connection between Lewis ideas and the quantum world would be better performed through the use of the pair density, the simplest quantity bearing information about the electron pairs.* Concretely, the first systematic analysis to the relation between the pair density and the chemical bond was performed by Bader,[15,16] who studied the fluctuation in the average population of regions defined within a molecule, expressed entirely in terms of the pair density. Actually, his well-known delocalization index (δ_{AB}) grants a measure of the electron sharing between Ω_A and Ω_B regions, whereas his localization index (λ_A) is related to the amount of electrons localized in Ω_A.[17] An important group of studies describes the connection between δ_{AB} values for a molecule and its standard Lewis structure, as those of Ponec and Fradera.[18–20]

Motivated by this train of thought, we considered of interest to analyze the pair density coming from a valence bond wave function in terms of these localization and delocalization

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*It is of importance to remember that Lewis model describes the electronic structure of a molecule in terms of electron pairs, being this the reason of why the pair density may play a crucial role.

indices.[21] The simplest case to confront was the H_2 molecule described by a combination of two individual ψ_i valence bond states (eq 1): one associated to H:H (ψ_{cov}) and another (ψ_{ion}) to the combination of ionic LDSs (:H H and H H:). Contrary to expectations, the evolution of both λ and δ for the individual Lewis states with the internuclear distance and for the total wave function with the relative ionic/covalent weighting did not follow the expected trends. Consequently, the association of an individual resonance state ψ_i with a given Lewis structure is actually inexact, unless in terms of the number of localized and delocalized pairs of electrons, magnitudes that seem to be the inexorable bridge between classical Lewis structures and the quantum world.

As a consequence of this shortcoming, it is necessary an alternative strategy to procure the importance of each LDS in a certain compound. In this work, we obtain LDS weightings that allow reproducing Bader's localization and delocalization indices and whose behavior is analyzed in different systems and processes, such as bond cleavages, application of an electric fields, π-ion interactions, or the variation of the bulk relative permittivity. We find that these weightings follow the expected trends and, with them, it will be possible to understand a chemical system as an actual combination of Lewis structures.

2 Theoretical details

2.1 A Lewis perspective for the fluctuation of the electron population

For a given Lewis structure, it seems straightforward to identify which electron pairs are delocalized between atoms and which pairs are localized in a single one. This trivial classification, together with the definition of the formal atomic charges of a Lewis structure, has a delightful implication: the formal amount of electrons associated to each atom of a molecule consists of two different contributions, one accounting for the pairs of electrons that are localized in each atom, the another indicating the number of pairs which fluctuates between a given atom and the rest of them.

A similar division scheme can be obtained in the quantum world, as Bader indicated in his quantum theory of atoms in molecules (QTAIM).[17] Specifically, the fluctuation in the average number of electrons for a region Ω, $\Lambda(\Omega)$, is defined as:

$$\Lambda(\Omega) = \Lambda_\Omega = \overline{N^2}(\Omega) - \left[\overline{N}(\Omega)\right]^2 \tag{2}$$

and it can be expressed entirely in terms of the pair density. This function, denoted by $\rho(\mathbf{r}_1, \mathbf{r}_2)$, is defined as:[†]

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \int d\sigma_1 \int d\sigma_2 \int d\boldsymbol{\tau}_3 ... \int d\boldsymbol{\tau}_N \Psi^* \Psi \tag{3}$$

which allows writing $\overline{N^2}(\Omega)$ as:[22]

$$\overline{N^2}(\Omega) = 2 \int_\Omega d\mathbf{r}_1 \int_\Omega d\mathbf{r}_2 \rho(\mathbf{r}_1, \mathbf{r}_2) + \int_\Omega d\mathbf{r}_1 \rho(\mathbf{r}_1) \tag{4}$$

while $\overline{N}(\Omega)$, which defines the average number of electrons in the region Ω, takes the form:

$$\overline{N}_\Omega = \overline{N}(\Omega) = \int_\Omega d\mathbf{r}_1 \rho(\mathbf{r}_1) \tag{5}$$

where the electronic charge density $\rho(\mathbf{r}_1)$ is:

$$\rho(\mathbf{r}_1) = \frac{2}{N-1} \int d\mathbf{r}_2 \rho(\mathbf{r}_1, \mathbf{r}_2) \tag{6}$$

In order to simplify the expression for the fluctuation, it is convenient to define the quantity $F_{\Omega\Omega}$:

$$F_{\Omega\Omega} = 2 \int_\Omega d\mathbf{r}_1 \int_\Omega d\mathbf{r}_2 \rho(\mathbf{r}_1, \mathbf{r}_2) - \left[\overline{N}_\Omega\right]^2 \tag{7}$$

In this manner, eq 2 can be rewritten as:

$$-F_{\Omega\Omega} = \overline{N}_\Omega - \Lambda(\Omega) \tag{8}$$

Bearing in mind the localized/delocalized ideas from the Lewis model, it is tempting to identify the quantity $-F_{\Omega\Omega}$ to the amount of electrons localized within the region Ω, due to the fact that it is the difference between the average number of electrons belonging to Ω and its fluctuation. Consequently, this magnitude is commonly known as the localization index for the region Ω, $\lambda_\Omega = -F_{\Omega\Omega}$. As an illustration, we can consider the whole space as our region of interest ($\Omega = \mathbb{R}^3$). Undoubtedly, the fluctuation of the average electronic population is zero and, consequently, all the electrons contained in Ω are completely localized, as is also indicated by $\lambda_\Omega = \overline{N}_\Omega$. Conversely, when the region Ω defines an atom in a molecule which is bonded to other atoms, its localized electron population will be smaller than its average population. To measure of the number of electron pairs involved in a given bond, we can consider an isolated A$-$B bond. As a consequence of the isolation, the fluctuation in $\Omega_A + \Omega_B$ is zero but, as indicated, $\Lambda(\Omega_A)$ and $\Lambda(\Omega_B)$ would

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[†] $\boldsymbol{\tau}_i$ denotes a product of spin (σ_i) and space ($\mathbf{r}_i$) coordinates and $d\boldsymbol{\tau}_i = d\sigma_i d\mathbf{r}_i$

differ from such a value, inasmuch as electrons fluctuate between both atoms. In fact, it can be written:

$$\Lambda(\Omega_A+\Omega_B) = N_A + N_B + F_{AA} + F_{BB} + 2F_{AB} = \Lambda(\Omega_A) + \Lambda(\Omega_B) + 2F_{AB} \tag{9}$$

with:

$$F_{AB} = 2\int_{\Omega_A} d\mathbf{r}_1 \int_{\Omega_B} d\mathbf{r}_2 \rho(\mathbf{r}_1,\mathbf{r}_2) - \overline{N}_A\overline{N}_B \tag{10}$$

As the fluctuation for the whole system is zero, the individual atomic fluctuations are collected in $-2F_{AB}$. For this reason, this quantity is called delocalization index, $\delta_{AB} = -2F_{AB}$, and measures the amount of electrons fluctuating between Ω_A and Ω_B.

In this manner, through the definition of the fluctuation around $\overline{N}(\Omega)$ for a given region Ω and the localized/delocalized classification of the electron pairs based on the Lewis model, the magnitudes λ_A and δ_{AB} can be endowed with chemical meaning.

The argumentation described above can be easily generalized to an arbitrary number of atoms.

2.2 Mathematical representation of Lewis dot structures

In a Lewis structure, a covalent bond between two atoms is normally depicted as a straight line connecting the corresponding atoms. In this manner, the bonding structure of a given LDS is equivalent to an undirected multigraph, $g = (V, E)$, with V being the nonempty set of atoms and E being a multiset of unordered pairs of bonded atoms. Consequently, the covalent bond skeleton of a given Lewis structure can be described unequivocally by its corresponding adjacency matrix (some examples are depicted in Figure 2a). As this matrix describes the covalent bonds in the LDS, we will refer it as the bonding matrix or $\mathbf{B}$.

However, the covalent skeleton is not the only feature of a given LDS. It is also characterized by its intrinsic distribution of formal charges. Consequently, to completely describe a LDS, we also need a (diagonal) matrix which accounts for such a distribution. We could use, indistinctly, atomic electron populations or atomic charges ($q_\Omega = Z_\Omega - N_\Omega$, with Z_Ω being the atomic number of the nucleus contained in Ω) for defining this matrix (given rise to the population matrix, $\mathbf{N}$, and to the charge matrix, $\mathbf{Q}$, respectively). These two matrices are interrelated through the diagonal matrix of the corresponding atomic numbers $\mathbf{Z}$, which remains invariant in all the Lewis structures of a given system ($\mathbf{Z} = \mathbf{Q}+\mathbf{N}$). For the sake of simplicity, we will consider, in most of the cases, the $\mathbf{Q}$ matrix for describing the electronic distribution of a given LDS.

It is important to notice that self-loops lack of sense in the graph representation of a Lewis structure. Hence, the diagonal elements of $\mathbf{B}$ are always zeros. Consequently, the information enclosed in both $\mathbf{B}$ and $\mathbf{Q}$ matrices can be compacted in a single matrix $\mathbf{L} = \mathbf{B} + \mathbf{Q}$. Each "Lewis-structure matrix" $\mathbf{L}$ defines flawlessly each Lewis dot structure for a given system (some examples in Figures 2b and 2c).

2.3 QTAIM-adapted Lewis coefficients

In the previous section we defined the "Lewis-structure matrix" of a given LDS. Whereas atomic charges define the diagonal elements, the number of electron pairs involved in the bond between each pair of atoms is collected in the corresponding off-diagonal element. In terms of QTAIM, a Lewis-structure matrix for the system ($\mathbf{L_s} = \mathbf{Q_s} + \mathbf{B_s}$) can be also defined if we consider QTAIM atomic charges ($\mathbf{Q_s}$) and delocalization indices ($\mathbf{B_s}$). As our goal is to understand, whenever possible, the most important features of the molecular electronic structure in terms of LDS's, it is chemically appealing to assume (although not rigorously found) that this Lewis-structure matrix for the system can be expressed as a linear combination of structure matrices associated to individual LDS's. This is:

$$\mathbf{L_s} = \sum_j w_j \mathbf{L_j} \tag{11}$$

with w_j being a coefficient which measures the importance of the j-th Lewis dot structure.

As $\mathbf{L_s}$ is the sum of two matrices, we can split the previous equation into two, one associated to the bonding matrix:

$$\mathbf{B_s} = \sum_j w_j \mathbf{B_j} \tag{12}$$

an another associated to the charge matrix:

$$\mathbf{Q_s} = \sum_j w_j \mathbf{Q_j} \tag{13}$$

We note that an equivalent equation would be obtained if we used the population matrix instead of the charge matrix:

$$\mathbf{N_s} = \sum_j w_j \mathbf{N_j} \tag{14}$$

If the description in terms of the **Q** matrix is equivalent to that of **N**, the w_j coefficients should remain invariant whatever representation is chosen. Consequently, if we sum both equations 13 and 14, we obtain a normalization-like condition for the w_j coefficients:

$$\mathbf{Z} = \mathbf{Q_s} + \mathbf{N_s} = \sum_j w_j \underbrace{(\mathbf{Q_j} + \mathbf{N_j})}_{\mathbf{Z}} \rightarrow \sum_j w_j = 1 \tag{15}$$

where we leveraged the fact that the sum of the two matrices generates the diagonal matrix **Z**, which is obviously the same in each individual LDS. As these coefficients are obtained in terms of QTAIM quantities, we will refer to them as QTAIM-Adapted Lewis coefficients, or just Q-ALE coefficients.

In general, we are not interested in reproducing the whole $\mathbf{L_s}$ matrix, but only some QTAIM properties of it. According to eq 11, each chosen QTAIM descriptor involved in $\mathbf{L_s}$ is given by:

$$(\mathbf{L_s})_{ik} = \sum_j w_j (\mathbf{L_j})_{ik} \tag{16}$$

The consideration of as many equations (including the normalization condition) as Lewis structures gives rise to a system of linear equations, which can be expressed all together through matrix notation as:

$$\mathbf{A} = \mathbf{D} \cdot \mathbf{w} \tag{17}$$

where **A** is the column vector formed by the $\mathbf{L_s}$ chosen elements, the corresponding $(\mathbf{L_j})_{ik}$ elements are collected in the **D** square matrix, and **w** is the column vector of Q-ALE coefficients. Therefore, the latter is obtained through:

$$\mathbf{w} = \mathbf{D}^{-1} \cdot \mathbf{A} \tag{18}$$

2.4 On the negative value of Q-ALE coefficients

Let us image a neutral diatomic molecule, AB, with B bearing higher electronegativity. In this case, we would instinctively describe its $\mathbf{L_s}$ matrix through two Lewis-structure matrices: $\mathbf{L_{cov}}$, associated to A−B, and $\mathbf{L_{\pm}}$, identified with A^+B^- (Figure 2b):

$$\mathbf{L_s} = w_{cov}\mathbf{L_{cov}} + w_{\pm}\mathbf{L_{\pm}} \tag{19}$$

The resolution of this equation yields $w_{cov} = \delta_{AB}$ and $w_{\pm} = q_A$ and, bearing in mind the normalization condition (eq 15), a restriction is imposed on $q_A + \delta_{AB}$: it has to be equal to 1. However, real systems do not fulfill this condition generally and, consequently, the other ionic resonance structure (A^-B^+) has to be explicitly considered[‡] in order to avoid this constraint on the system. Positive coefficients for this LDS can be used to reduce the charge of A without affecting δ_{AB} and, consequently, situations where $q_A + \delta_{AB} < 1$ would be described. On the contrary, negative $w_\mp$ values are needed to mimic systems where $q_A + \delta_{AB} > 1$.

More specifically, if we consider now the three resonance structures to reconstruct $\mathbf{L_s}$, it can be found that the w_j coefficients are given by:

$$w_{cov} = \delta_{AB} \tag{20a}$$

$$w_\pm = \frac{(1-\delta_{AB}) + q_A}{2} \tag{20b}$$

$$w_\mp = \frac{(1-\delta_{AB}) - q_A}{2} \tag{20c}$$

Different regions can be defined depending on the values of the coefficients:

a) All the coefficients are positive ($w_i > 0\ \forall i$). Systems in this region verify $\delta_{AB} + q_A < 1$. Setting the perfect sharing with no electron transfer as a reference ($\delta^0_{AB} = 1$, $q^0_A = 0$), reductions in the delocalization index in this region are greater than the charge transference to the electronegative atom ($\delta^0_{AB} - \delta_{AB} > q_A - q^0_A$). Figure 3a presents, in terms of a curved arrow formalism, an example for this situation. In it, the electron density withdrawn in a partial cleavage of the perfectly shared bond is distributed between the two atoms, being the most electronegative the one receiving more amount. The total homolytic cleavage of a A–B bond is an extreme situation in this region, where the pair of electrons is equally distributed between the two atoms.

b) $w_{cov}, w_\pm > 0$ whereas $w_\mp = 0$. In this situation, the reduction in the delocalization index matches with the charge transference to B ($1 - \delta_{AB} = q_A$). It corresponds to the archetypical situation of a perfect heterolytical cleavage, where the amount of electron density withdrawn from the bond goes entirely towards the more electronegative atom (Figure 3b). The perfectly shared bond, with $\delta_{AB} = 1$ and no charge transference, is also placed in this region.

c) $w_{cov}, w_\pm > 0$ but $w_\mp < 0$. Here, the reduction in the delocalization index ($1 - \delta_{AB}$) is bounded to the $[0, q_A)$ interval. An example of this situation is depicted in Figure

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[‡] Actually, it is implicitly considered due to the fact that the matrices for the two ionic structures are not linearly independent($\mathbf{L}_\pm = -1 \cdot \mathbf{L}_\mp$, where ± refers to A^+B^- and ∓ alludes to A^-B^+; see Figure 2b).

3c, where the transference to the electronegative atom does not come exclusively from the electron density withdrawn from the perfectly shared bond, but also from the other atom.

d) $w_{cov} > 1$ and $w_{\mp} < 0$. In this situation, $\delta_{AB} > 1$ and $w_{\pm}$ can be either positive ($\delta_{AB} < 1+q_A$) or negative ($\delta_{AB} > 1+q_A$). The values of Q-ALE coefficients indicate that resonance structures involving more than one bond should be considered.

Thus, although the Q-ALE coefficients present a normalization condition (eq 15), their individual values can be either positive or negative and, hence, they should not be interpreted as relative probabilities. However, whereas there is no logistic problem with positive values, negative ones could be considered preposterous from a chemical point of view. From our perspective, they are just an indication of the obvious limitations associated to the chosen LDS's to properly describe the system (as previously exemplified in the description of the different regions). In this manner, negative values are an indication about the inadequacy associated to the set of LDS's normally employed to characterize a molecule. Concretely, a change in the LDS basis can solve this problem, as we will shown in a subsequent section.

3 Results

We will present here some results in a series of selected prototypical systems and processes. In general, all the concepts explored in this article are appropriately described at the Hartree-Fock level. We only use the Full Configuration Interaction (FCI) methodology to properly describe the bond dissociation in HF and LiH molecules. Whereas Hartree-Fock wave functions are obtained with Gaussian 09[23] and analyzed using the AIMPAC package of programs,[24,25] calculations associated to the FCI methodology were performed using MOLCAS[26] and the associated localization and delocalization indices were obtained using the PROMOLDEN code.[27]

3.1 LiH and FH bond cleavage

Among the tests that Q-ALE coefficients should overcome, one of them is the proper description of a bond cleavage. For that, we will analyze two cases: LiH and FH. The first is considered basically an ionic molecule typically described by the Li^+ H^- LDS, while the second is considered a polarized covalent molecule, being both F$-$H and F$^-$ H$^+$ of great importance. In both cases, the homolytic dissociation should lead to the $\cdot$A H$\cdot$ (with A being Li or F) LDS or, equivalently, to both A$^-$ H$^+$ and A$^+$ H$^-$ LDSs contributing equally to the molecule, as the sum of their Lewis-structure matrices is equivalent to that associated to $\cdot$A H$\cdot$. It is important to note that, using Lewis structures, it is not possible to discriminate between the dissociated ground state and an excited state coming from the appropriate combination of ionic structures.

In these cases, eq 18 takes the form:

$$\begin{pmatrix} 1 \\ q_H \\ \delta \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 \\ 0 & 1 & -1 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} w_{cov} \\ w_{\pm} \\ w_{\mp} \end{pmatrix} \tag{21}$$

where the first row of $\mathbf{D}$ accounts for the normalization condition. The solution of this system of linear equations is actually shown in eq 20, with q_A and δ_{AB} being q_{Li} and δ_{LiH} for LiH and q_H and δ_{HF} for HF. The evolution of the three Q-ALE coefficients is plotted in Figures 4a and 5a. It can be seen how at short bond distances, as chemically expected, the LiH is basically described by the ionic Li$^+$ H$^-$ LDS whereas, for FH, both F$-$H and F$^-$ H$^+$ structures contribute with similar importance. In the dissociation limit, the contribution of the covalent A$-$H structure tends to zero, whereas both ionic Q-ALEs equate to represent the homolytic cleavage.

In both cases, we observe that the A$^-$B$^+$ resonance structure (Li$^-$H$^+$ and H$^-$F$^+$) is endowed with a negative Q-ALE coefficient at short nuclear distances. However, its absolute value is not very large (< 0.10) and, consequently, the picture given by the triplet A$-$B, A$^+$B$^-$, and A$^-$B$^+$ could be considered chemically acceptable. Nevertheless, this picture could be improved. If we consider a dative-like structure at short distances, where a bond exists and the two atoms are still characterized by an atomic charge (A$^+$ $\leftarrow$B$^-$), in lieu of the A$^-$B$^+$ LDS, we find that the three Q-ALE coefficients present a positive value (Figures 4b and 5b).

3.2 The effect of the electronegativity difference

In a previous work,[28] we corroborated the impact that the electronegativity difference between bonded atoms has on the topological distribution of their bond electron density. Actually, the result agrees with a well-known statement in chemistry: the larger the difference in electronegativity between two atoms involved in a chemical bond, the more ionic (or polar) the bond is.[29] Hence, if Q-ALE coefficients really own the ability of bringing the Lewis picture of the molecular structure close to the world of the quantum mechanics, they should behave according to this rule. In order to test such a skill, we analyze the bond of elements of the second to the fourth period (excluding noble gases and transition metals) to H, concretely in closed-shell hydrogen compounds (AH_n).

For the sake of simplicity, we only contemplate the covalent ($H{-}AH_{n-1}$) and the two ionic ($H^+ \; {}^-AH_{n-1}$ and $H^- \; {}^+AH_{n-1}$) Lewis structures associated exclusively to one of the A−H bonds. Evidently, these LDSs describe the population of the H atom and of the AH_{n-1} moiety, likewise the delocalization index between H and the AH_{n-1} fragment. Results are illustrated in Figure 6, where it is clear the the ionic coefficients present periodic trends: the $H^- \; {}^+AH_{n-1}$ participation seems to decreases across a period from left to right and while going down a group. The opposite behavior along a period is found for the $H^+ \; {}^-AH_{n-1}$ LDE. We also notice that the ionic structures have almost no contribution in the case of CH_4. This property can be undoubtedly ascribed to the small electronegativity difference between C and H atoms.

Moreover, the importance of each Lewis structure presents a clear connection to the electronegativity difference between A and H, as indicated in Figure 7, where Q-ALE coefficients are represented against the Allred-Rochow electronegativity.[§] Therefore, these coefficients based on the pair density function seem to behave, once again, according to the rules governing chemistry.

Finally, we want to remark that the objective of this section is to corroborate that periodic trends are fulfilled by the Q-ALE coefficients. Consequently, we were not concerned about the problems associated to negative values, which were discussed in previous sections.

3.3 The π-resonance in the allyl cation

The Lewis structures associated to π-resonance are widely used in chemistry and they are one of the cornerstones to understand chemical reactivity and molecular stability of diverse systems. For example, the allyl cation is known by its relative stability and by its reactivity through the terminal C atoms. Both facts are explained in terms of the two

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[§] This electronegativity scale has been chosen in accordance with one of our previous studies,[28] where we found that this scale, among the standard ones, provides the best reproduction of the bond electron density distribution.

resonance forms represented in Figure 8.

The QTAIM population analysis of this system at the HF/6-311++(2d,2p) 6d level of theory provides interesting results: although the terminal CH_2 groups own a positive charge of +0.366 au, the inner CH moiety is also characterized by a large group charge (+0.267 au). This distribution of the positive charge is not contemplated in the previously considered resonance structures and could be understood as a mismatch between the resonant conception of the allyl cation and the vision provided by the QTAIM. On the basis of these results, one could expect no reliability for the QTAIM-ALE coefficients, as QTAIM seems not to represent the chemistry of the system. However, if we consider both σ and π electronic structures separately, we find agreement between both resonance model and QTAIM results.

At HF level, we observe that the electronic structure associated to the π contribution can be perfectly reconstructed through the two classical structures for the allyl cation (bottom of Figure 9). In this manner, the resonance forms usually proposed to describe the π structure are in agreement with the Q-ALE coefficients. In contrast, the positive charge on the CH moiety is inherited from the resonance in the σ structure. We highlight, firstly, that the set of standard resonance structures presents negative Q-ALE coefficients, which indicates that the proposed resonance structures are not totally reliable to describe the σ skeleton. Secondly, it is obvious that the deviations with regard to the expected result stem from the σ structure. Thus, it can be stated that the resonance of the σ electronic skeleton is more important than normally expected and should not be ignored.

In our opinion, this example can be the foundation to break a long controversy between widespread qualitative chemical interpretations based on the resonance model (RM) and quantitative studies carried out with the QTAIM for π-systems. The origins of discrepancies hitherto reported can be traced back to the arbitrary and capricious way the RM is usually applied, neglecting the importance of the σ resonance structures in systems with π electrons.

3.4 Influence of the environment

Sometimes, a certain behavior of a molecule, such as a particular reaction, can be mainly ascribed to the features presented in one of its LDSs. In these situations, having information about how contributions of Lewis structures vary can be crucial to, for example, favor one reaction path over another. Actually, the modification in the polarity of the reaction medium is a frequently used technique in chemistry.

In this section, we will analyze the influence of the relative permittivity of the medium (ε_r) in the Q-ALE coefficients for two simple molecules, hydrogen fluoride and formaldehyde. To carry out such an undertaking, we will use the polarizable continuum model (PCM),[30,31] implemented in the Gaussian 09 code.

In the case of hydrogen fluoride, we consider the three Lewis structures ascribed to a single bond (see previous sections). We observe that the Q-ALE coefficients for F^+ H^- does not change significantly with ε_r and, moreover, its value is also negligible (absolute value *ca.* 0.083). With regard to the significant ionic structure, F^- H^+, Figure 10 illustrates how its contribution is even more significant as ε_r enlarges. This result is consistent with the observed increase in the molecular dipole moment.

Concerning formaldehyde, we also performed a σ/π division, as previously done for the allyl cation. Results for the different contributions in gas phase show that the Q-ALE coefficients are in line with the characteristic polarity of the CO bond (Figure 11). It is interesting to note that the resonance structure associated to the CO cleavage where the oxygen withdraws the bond pair presents a larger relative Q-ALE coefficient (with regard with the correspondent perfectly shared bond) in the σ distribution than in the π one. Therefore, the σ skeleton is more prone to suffer the effects of the electronegativity difference between the bonded atoms.

With regard to the change in the solvent permittivity, we notice that the contribution of the π ionic structure with a negatively charged oxygen rises (Figure 12). Similarly, those LDSs characterized by the ionic H^+ C^- cleavage increase their participation. Again, the growing importance of these structures agrees to the fact that the dipolar moment of the molecule increases with ε_r. The evolution of the Q-ALE coefficients with increased solvent permittivity also reveals another interesting trend: the contribution of the π structures are more affected by the solvent dielectric constant than the σ ones. This can be related to the fact that whereas σ electron density is more confined among the nuclei, the π one can be distorted by external fields in a more efficient way.

3.5 The influence of an electric field

In recent works, N. Ramos-Berdullas *et al*, inspired by advances in the field of molecular electronics, have considered different aromatic chains connected differently to metal structures,[32] confirming interesting experimental trends: when the contact took place through a methylene linker, the conductance of the molecular junction increased;[33] if the phenyl rings were in direct contact to the metal structure, it decreased.[34] Wisely, they explained this finding using models based on resonance Kekulé structures polarized at the contacts, contributing with a more chemical and deep comprehension to the field of molecular electronics. Their new and clear study exemplifies the importance of Lewis structures in modern scientific fields.

In this section, we will consider the benzene molecule subjected to an electric field, in order to ascertain that Q-ALE coefficients for the π-LDSs behave according to expectations. This electric field, ranging from 0.00 to 0.02 au, is applied in the direction defined by one of the C_2 axis of rotation of benzene which contains no atoms. In order to analyze the evolution of the Q-ALE coefficients, we will consider, exclusively, the π contribution to the delocalization indices between the following pairs of CH moieties: 2-3, 5-6, 1-4, 2-5, and 3-6 (see Figure 1 for numbering). According to that, it can be written:

$$\begin{pmatrix} \delta^{\pi}_{2,3} \\ \delta^{\pi}_{5,6} \\ \delta^{\pi}_{1,4} \\ \delta^{\pi}_{2,5} \\ \delta^{\pi}_{3,6} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} w_{K1} \\ w_{K2} \\ w_{D1} \\ w_{D2} \\ w_{D3} \end{pmatrix} \tag{22}$$

with w_{K1} and w_{K2} accounting for Kekulé LDSs, whereas w_{D1} to w_{D3} refer to Dewar ones.

We observe that Q-ALE coefficients reproduce an important well-known chemical fact (Figure 13): the preeminence of Kekulé resonance structures with regard to Dewar ones. Actually, in absence of electric field, each Dewar structure contribute to the system with a coefficient of *ca* 0.10, whereas individual Kekulé forms are endowed with a Q-ALE coefficient of *ca* 0.35. With regard to the electric field, as it increases, the electron density flows to the left side (see Figure 13). Consequently, the Kekulé resonance form which allows the accumulation of π electron density in the left side of the molecule increases its Q-ALE coefficient, whereas the one locating it at the right side, decreases. Moreover, we notice that none of the Dewar resonance structures favors C2−C3 over C5−C6 (in terms of double bond) or vice versa. This justifies why the Q-ALE coefficients for Dewar forms vary in a lesser degree than Kekulé ones.

3.6 Interaction of an aromatic system with an ion

In this section we examine another type of perturbation over the aromatic benzene ring: its interaction with a cation and with an anion. Similarly to the previous section, we will consider the two Kekulé and the three Dewar structures, also through the same QTAIM properties. Concretely, we will analyze how the description of the benzene varies when the ion is situated along the line defined by a C_2 axis of rotation containing no atoms, as indicated in Figure 14.

In both situations (cation and anion), we observe that Kekulé structures are those subjected to more changes, as happened when an electric field was applied. Moreover, the overall behavior of each Q-ALE coefficient does not seem to depend on the nature of the ion, although the origin in its evolution is certainly different. For the cation, represented by Li^+, the attraction generated by the positive charge polarizes the benzene π electron cloud towards the cation. Consequently, the resonance form displaying the double bond in the best location for this charge transference decreases. Oppositely, when an anion (modeled by F^-) interacts with the benzene ring, the deformation has its origin in repulsive interactions. Thus, resonance structures presenting an accumulation of electron density near the anion decrease their Q-ALE coefficient.

4 Conclusions

In this work, we have presented an approach to ponder the importance of Lewis resonance structures from real space analyses based on the Quantum Theory of Atoms in Molecules. For this purpose, we have defined a matrix containing a set of QTAIM accessible properties with a well defined intuitive value for each Lewis dot structure (such as atomic charges and delocalization indices). Intuitively, we have assumed that this matrix can be obtained as a linear combination of equivalent matrices, each one defining an individual Lewis structure. The coefficients involved in such a linear expansion, Q-ALE coefficients, point to the importance of each Lewis structure.

In order to analyze the performance of these Q-ALE coefficients, we have tested them in different systems. Firstly, the analysis of these coefficients in diatomic systems allowed us to interpret their negative values, which could be considered preposterous *a priori*. Actually, negative coefficients indicate that the chosen Lewis basis is not really able to describe the system from a chemical perspective, although it does so from a mathematical point of view. In this manner, we observed that the A–B, A^+B^- and A^-B^+ basis to describe both LiH and HF molecules fails at shorts distances and that another basis of Lewis structures needs to be invoked, where a dative-like bond between charged atoms is needed.

The evolution of the Q-ALE coefficients shows the expected tendency along the homolytic cleavage of HF and LiH and we have also observed periodic trends in the ionic Q-ALE coefficients associated to diverse hydrogen compounds. Moreover, the allyl cation was used to analyze both σ and π contributions to the resonance of the electronic structure. This system allows concluding that controversies between qualitative conclusions based on the resonance model (RM) and quantitative results obtained within the QTAIM framework can be probably associated to the resonance in the σ skeleton, whose effects are normally ignored when the RM is invoked. The effect of the dielectric constant of the solvent has been also analyzed through FH and formaldehyde molecules. Once again, the behavior of the Q-ALE coefficients behaves according to chemical expectations, rising the contribution of the ionic form when the permittivity increases. Moreover, we have also observed that the solvent permittivity affects the resonance of the π structure more than the σ one. Finally, polarization effects were also examined considering the distortion of the benzene electron distribution by an external electric field or by the approach of an ion (Li^+ or F^-). The evolution of Q-ALE coefficients mimics the expected polarization trends also in these cases.

We think that this work brings concepts of two worlds of chemistry together (Lewis structures and real space partitioning) through the formulation of a practical scheme to evaluate the importance of the different composing Lewis structures in a molecule.

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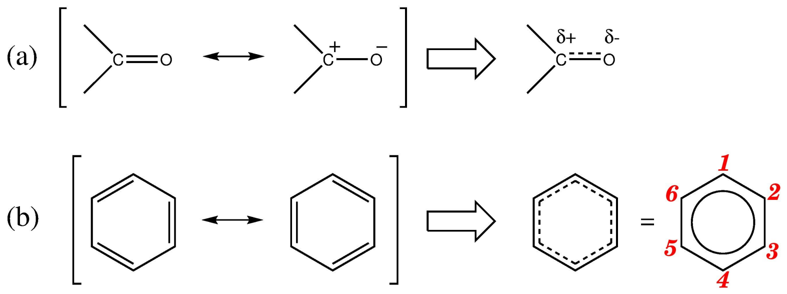

Figure 1: Most important Lewis structures and the corresponding composite resonance hybrid for (a) the carbonyl group and (b) the benzene molecule.

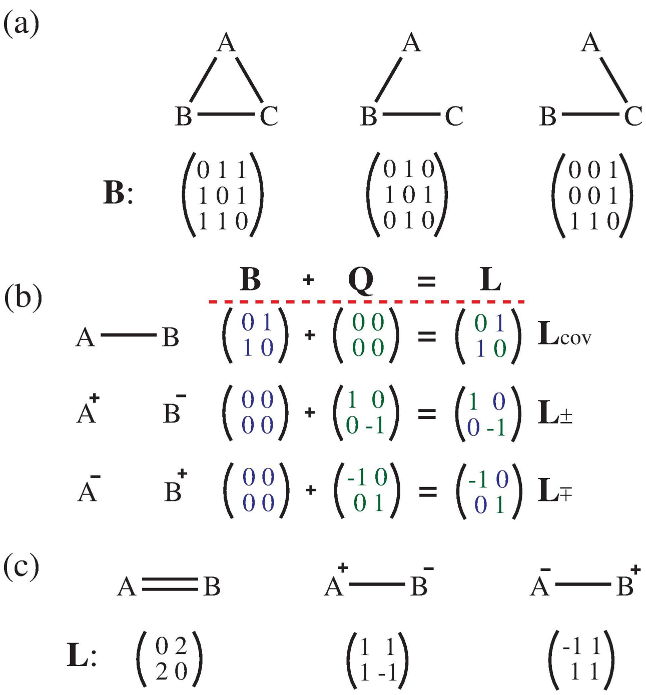

Figure 2: Some Lewis structures and the corresponding matrices: (a) examples of bonding matrices, (b) generation of the structure matrix from the bonding and the charge matrices, and (c) structure matrices for the Lewis resonance forms associated to a double bond.

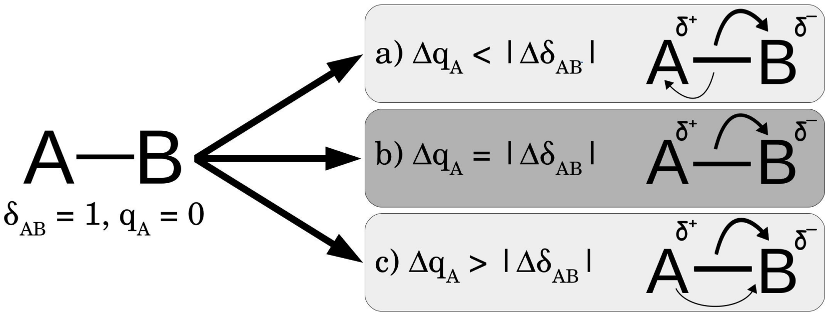

Figure 3: Different regions that can be defined in accordance to the values of w_{cov}, $w_{\pm}$ and $w_{\mp}$ for $\delta_{AB} \leqslant 1$ au.

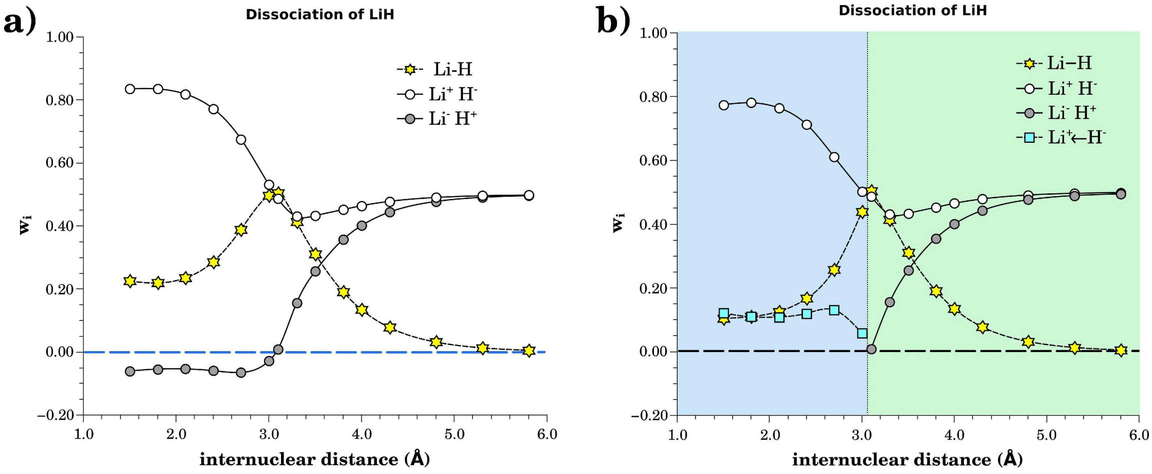

Figure 4: Evolution of the Q-ALE coefficients for LiH along its homolytic cleavage: a) using the Li−H, Li^+H^- and Li^-H^+ LDS's, b) changing the basis of LDS's in order to get all w_i coefficients positively defined. The values were calculated at the FCI/6-31G** level of theory.

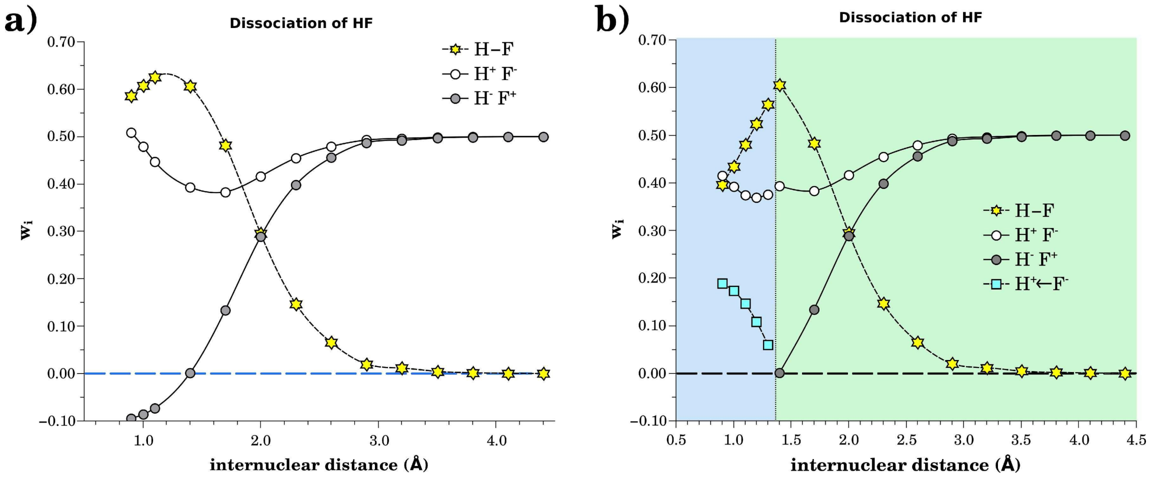

Figure 5: Evolution of the Q-ALE coefficients for HF along its homolytic cleavage: a) using the H−F, H^+F^- and H^-F^+ LDS's, b) changing the basis of LDS's in order to get all w_i coefficients positively defined. Atomic populations and delocalization indices were obtained from the FCI/6-31G wave function.

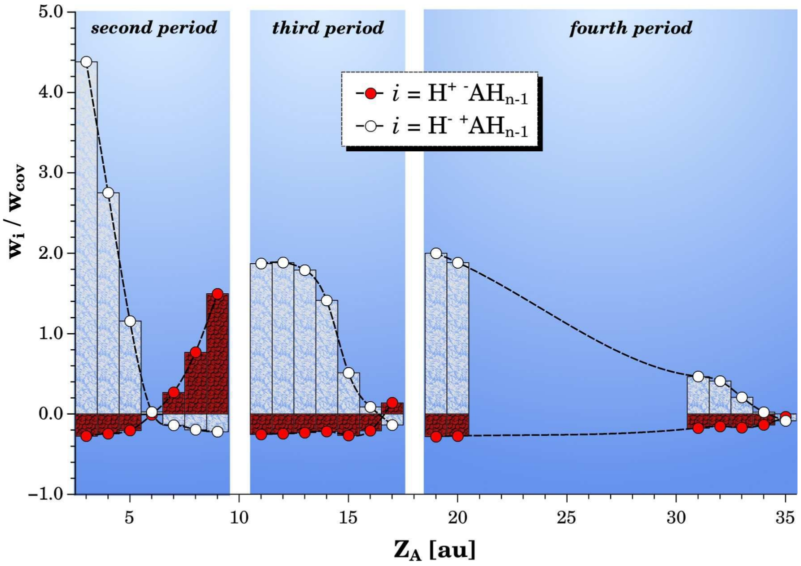

Figure 6: Relevance of the ionic Lewis structures in closed-shell hydrogen compounds (with regard to the covalent structure) across the Periodic Table. Data are derived from HF/6-311++G** approximate wave functions.

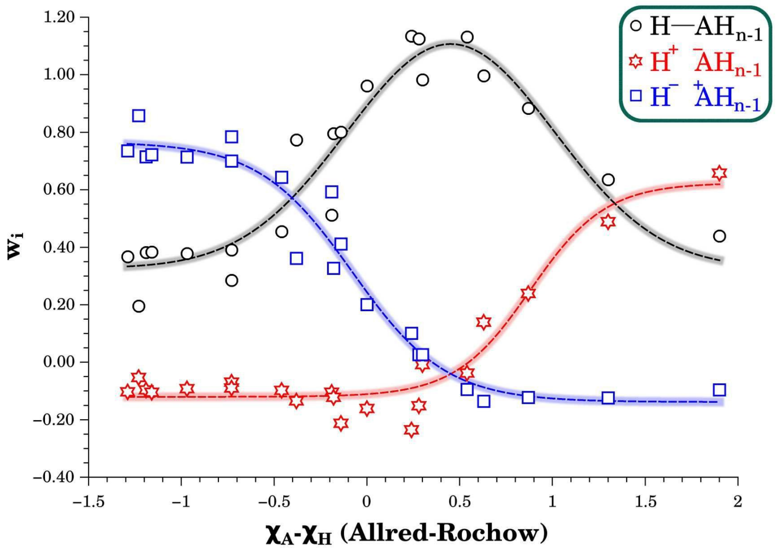

Figure 7: Dependence of Q-ALE coefficients for AH_n compounds with the Allred-Rochow electronegativity difference. While the covalent coefficient seems to follow a gaussian trend, ionic contributions better fit a sigmoid evolution.

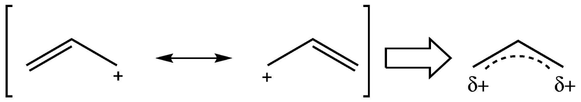

Figure 8: Most important π-resonance forms for allyl cation.

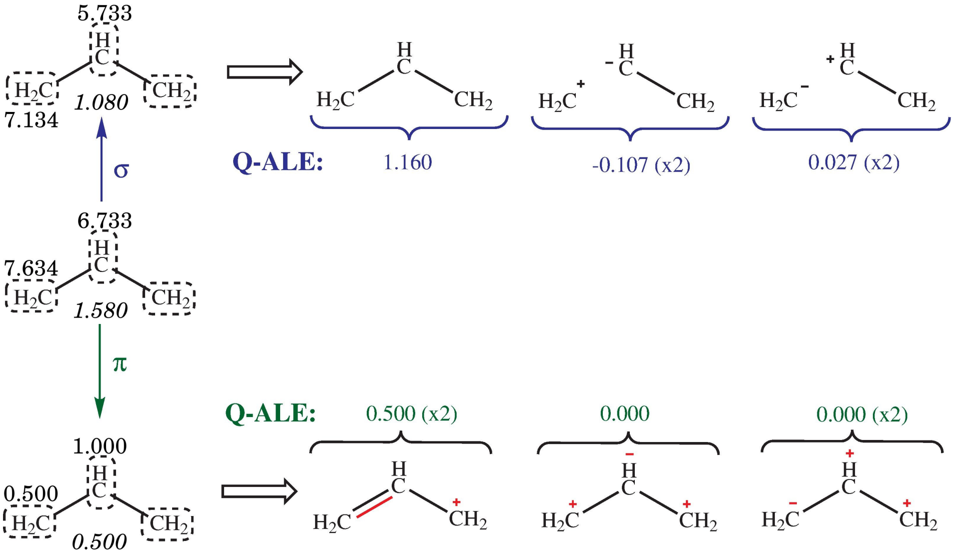

Figure 9: Q-ALE coefficients associated to σ and π resonance structures. Numbers in italic correspond to the delocalization index between the moieties CH_2 and CH, whereas electron populations are printed above each moiety. Data obtained from HF/6-311++(2d,2p) 6d calculations. The existence of two equivalent LDS structures with the same Q-ALE coefficient is indicated as (x2).

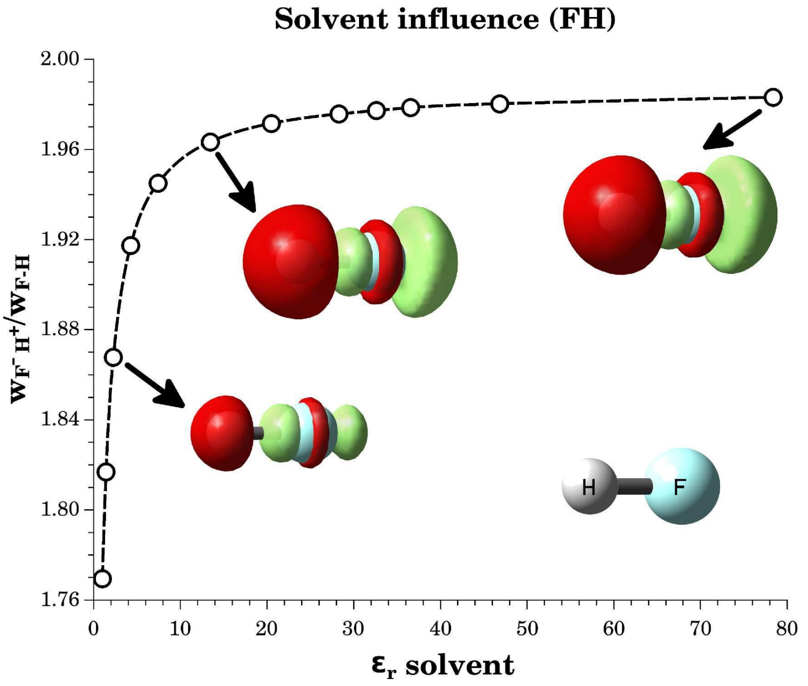

Figure 10: Evolution of the F^- H^+ importance with regard to the relative permittivity of the medium. Isosurfaces of 0.001 au (green) and -0.001 au (red) for $\rho(\epsilon_r) - \rho(\epsilon_r = 1)$ confirm the rise in the contribution of the ionic structure. Data obtained from HF/cc-pVTZ calculations.

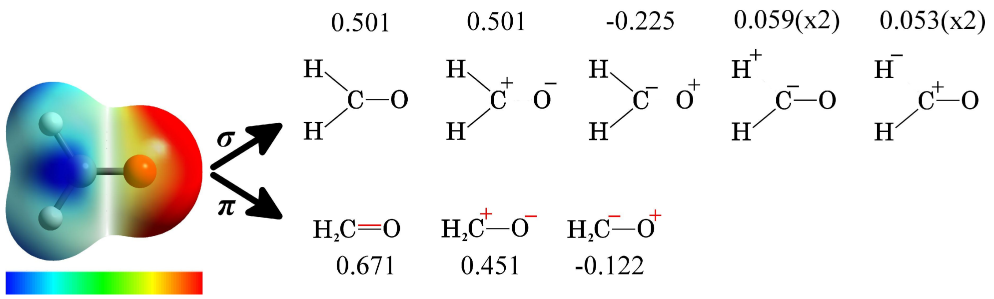

Figure 11: Importance of different Lewis dot structures for formaldehyde in gas phase. A mapped surface of the total electrostatic potential (at $\rho = 0.01$ au isosurface) is also shown. Data obtained from HF/cc-pVTZ calculations. The existence of two equivalent LDS structures with the same Q-ALE coefficient is indicated as (x2).

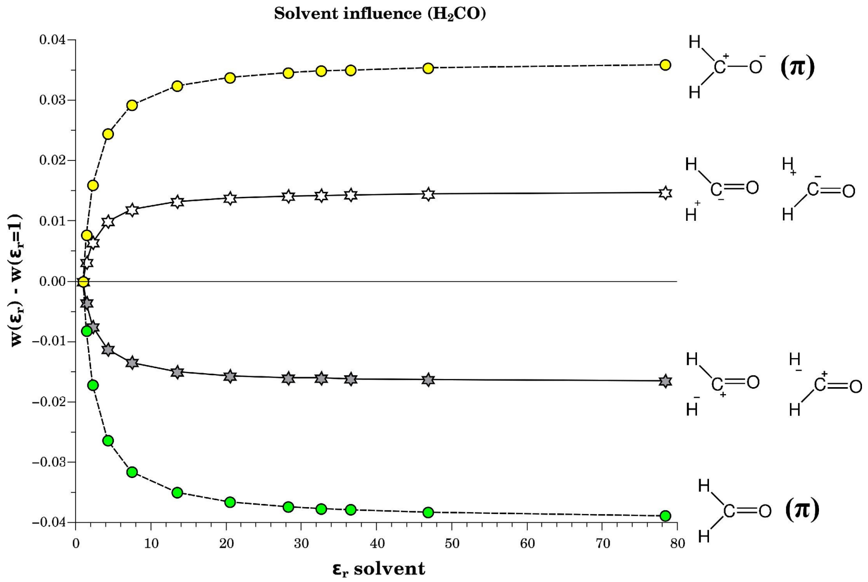

Figure 12: Influence of ε_r in the Q-ALE coefficients associated to formaldehyde Lewis structures. Only those structures whose Q-ALE coefficients vary, in absolute value, more than 0.005 are shown. Data obtained from HF/cc-pVTZ calculations.

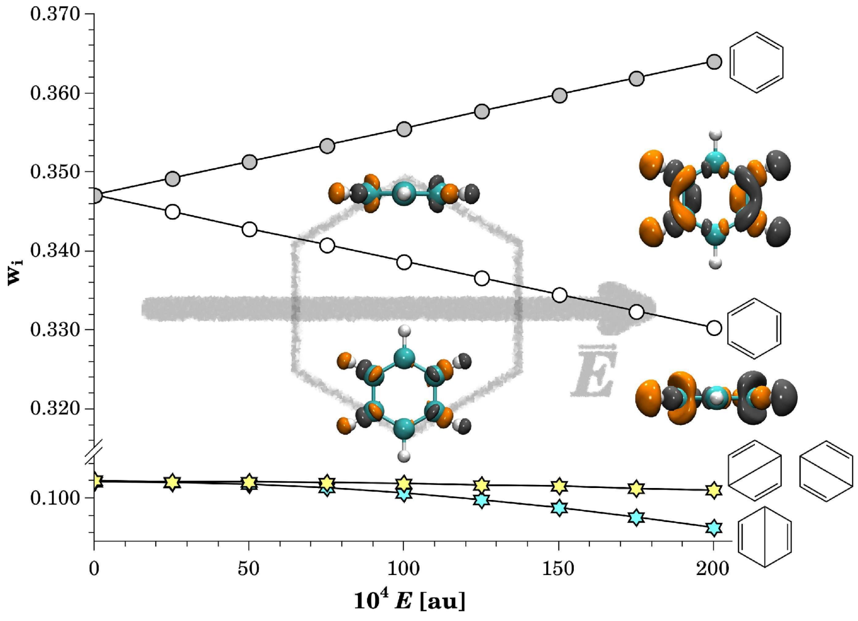

Figure 13: Influence of the electric field in Kekulé and Dewar Q-ALE coefficients for benzene. Isosurfaces of 0.002 au (orange) and -0.002 au (gray) for the variation of the electron density with regard to the benzene molecule in absence of electric field are also shown. Data obtained from HF/cc-pVTZ wave funtions.

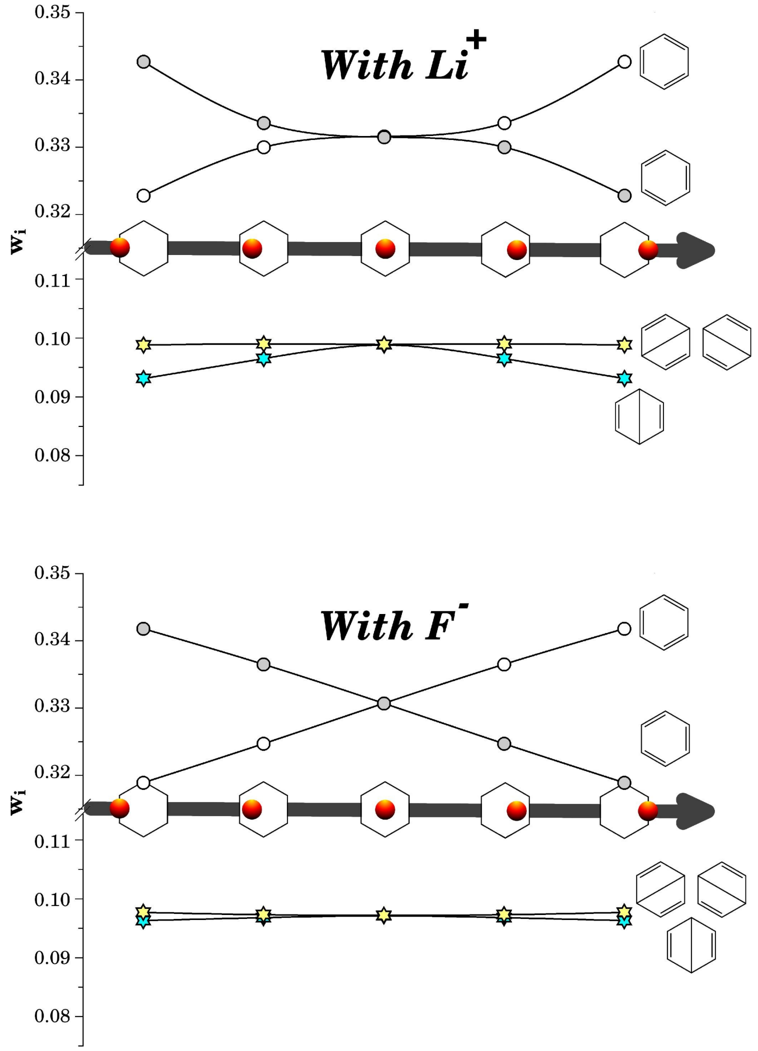

Figure 14: Variation of the Q-ALE coefficients for the interaction of Li^+ (top) and F^- (bottom) with benzene. Both the benzene geometry and the distance between ion and the benzene plane (1.881 Å for Li^+ and 3.094 Å for F^-) are frozen in the values obtained for the C_{6v} optimized structure of $[AC_6H_6]^+$ (A being the corresponding ion) at the HF/cc-pVTZ level of calculation.