

Chemical Notions from the Electron Density

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Abstract: The study of density and the role played by its atomic representation is proposed as a way for the rationalization of chemical behavior. As this behavior has been long rationalized in terms of the basic concepts of empirical structural chemistry, a direct link between both approaches is searched for by using the exact representation of the density provided by the deformed atoms in molecules method (Rico, J. F.; López, R.; Ema, I.; Ramírez, G.; Ludeña, E. *J. Comput. Chem.* **2004**, *25*, 1355–1363). Noting that the spherical terms of the pseudoatoms cannot be mainly responsible for the chemical behavior, we study the small nonspherical deformations and find that they reflect and support all basic concepts of empirical structural chemistry. Lone pairs; single, double, and triple bonds; different classes of atoms; functional groups; and so forth are paralleled by the density deformations in a neat manner. These facts are illustrated with several examples.

1. Introduction

Because one-electron density plays an increasingly central role^{1–9} in both the conceptual and practical developments of theoretical chemistry, the methods for its meaningful analysis are of paramount importance.^{10–26}

In the Born–Oppenheimer approximation (the paradigm in the study of molecular structure), the electronic energy including the nuclear repulsion is the potential energy for the movement of the nuclei, and as a consequence, the components of the force acting on a nucleus are determined by their derivatives with respect to its coordinates. The Hellmann–Feynman (electrostatic)²⁷ theorem states that these derivatives are equal to the components of the electrostatic force generated by the electron cloud plus the remaining nuclei. Thus, the forces can be obtained in two ways: from the electronic energy through its derivatives or from the electron density using classical electrostatics. The first way is expensive and hardly provides chemical insight. The second one is very cheap to apply and provides plenty of chemical insight.

Nonetheless, although the electrostatic theorem has been known for more than 60 years, the possibilities that it opens

up have been scarcely exploited, and today the theorem is mostly regarded as a scientific curiosity. There have been two main reasons for this. The first one is that the fulfillment of the theorem requires high quality densities. In particular, it leads to disastrous results for densities computed with commonly used poor basis sets, whereas energy is less sensitive to the quality of the basis set. The second reason comes from the fact that, for extracting chemical information from the theorem, one needs a representation of the density that brings insight to the chemist.

These reasons no longer hold. As it has been recently proved,²⁸ densities computed with good Slater basis sets, and with very high quality Gaussian basis sets too, fulfill the electrostatic theorem with an accuracy that is sufficient for most quantitative applications and, a fortiori, for the qualitative ones as well. Moreover, a representation of the density^{29–31} aimed to retain the identity of the atoms in a molecule as much as possible has also been reported, and that, in turn, facilitates the application of the electrostatic theorem.

This representation was originally intended as an aid for the calculation of several functionals of electron density such as the molecular electrostatic potential, molecular force field, forces on nuclei, and so forth, and the usefulness in those applications was proved.³² The method was also applied to the analysis of binding forces, to the calculation of bonding

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energies from density in diatomics,³³ and to the explanation of rotational barriers in terms of the density.³⁴

These studies render evidence that, when this representation of the density is combined with the electrostatic theorem, basic concepts of chemistry can be regarded from a novel perspective that may help to build a bridge between electron density and the classical notions of empirical structural chemistry. The exploration of this possibility is the aim of this work.

In Section 2, the electrostatic theorem is rederived in a way oriented to stress that chemical forces and energy variations are determined by the density alone. It follows that the relevant physical effects must be reflected in the density and must affect the forces and energies through density, a fact that, in turn, sets the study of density and its relationship with these forces as the central problem in the rationalization of chemical behavior. Section 3 deals with this relationship and with the role played by the atomic representation of the density in this regard.

It is noted there that the part of the density spherically distributed around the nuclei, although being largely dominant, is not responsible for the molecular stability. The chemical behavior of the molecules is mainly determined by small nonspherical deformations caused by the molecular environment on the density of the atoms.

On the other hand, chemical behavior has been largely rationalized by means of the concepts of empirical structural chemistry. As noted in Section 4, as much as they have been supported by many years of successful usage, these concepts must have some physical ground, and thus, the results of Section 2 imply that they must be somehow reflected in the density, and the arguments of Section 3 suggest that this should be searched for mainly in the density deformations.

Section 5 contains a summary of the results of this search, and some comments about the implications of these results are included in the final section.

2. Density, Chemical Forces, and Bonding

Because the bonding of atoms is usually explained in terms of electron pairing or exchange, while the electrostatic approach and its implications are often disregarded, a brief review on this subject is pertinent.

The electrostatic approach has its roots in the Hellmann–Feynman theorem,²⁷ which has been considered by Slater as *one of the most powerful theorems applicable to molecules*.³⁵ Herein, we will rederive the theorem in a way oriented to stress that chemical forces and bonding are related to either the whole electronic energy or the electron density through fundamental equations, whereas the relation with the components of energy is indirect.

Let $\hat{\mathcal{H}}$ be the electronic Hamiltonian of a molecule with a fixed number of electrons and an external potential $v(\mathbf{r})$, and let Ψ_I be its normalized eigenfunctions. Therefore

$$\langle \Psi_I | \hat{\mathcal{H}} | \Psi_I \rangle = E_I \quad (1)$$

and

$$\langle \Psi_J | \hat{\mathcal{H}} | \Psi_I \rangle = 0 \quad (2)$$

As it is well-known, these equations can be written as

$$E_I = \int d\mathbf{r} \rho^I(\mathbf{r}) v(\mathbf{r}) + \int d\mathbf{r} \left[-\frac{1}{2} \nabla^2 \hat{\rho}^I(\mathbf{r}, \mathbf{r}') \right]_{\mathbf{r}=\mathbf{r}'} + \int d\mathbf{r} \int d\mathbf{r}' \frac{\Gamma^I(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (3)$$

and

$$0 = \int d\mathbf{r} \rho^J(\mathbf{r}) v(\mathbf{r}) + \int d\mathbf{r} \left[-\frac{1}{2} \nabla^2 \hat{\rho}^J(\mathbf{r}, \mathbf{r}') \right]_{\mathbf{r}=\mathbf{r}'} + \int d\mathbf{r} \int d\mathbf{r}' \frac{\Gamma^J(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (4)$$

where $\hat{\rho}^I(\mathbf{r}, \mathbf{r}')$, $\rho^I(\mathbf{r})$, and $\Gamma^I(\mathbf{r}, \mathbf{r}')$ are, respectively, the density matrix, the density function, and the pair density function and $\hat{\rho}^J(\mathbf{r}, \mathbf{r}')$, $\rho^J(\mathbf{r})$, and $\Gamma^J(\mathbf{r}, \mathbf{r}')$ are the transition density matrix, transition density, and transition pair density functions, respectively.

Since a first-order change in the wave function Ψ_I can be expressed in terms of the Ψ_J :

$$\Psi' = \frac{\Psi_I + \sum_{J \neq I} \lambda_J \Psi_J}{(1 + \sum_{J \neq I} |\lambda_J|^2)^{1/2}} \quad (5)$$

Equation 2 implies

$$0 = \int d\mathbf{r} \delta\rho(\mathbf{r}) v(\mathbf{r}) + \int d\mathbf{r} \left[-\frac{1}{2} \nabla^2 \delta\hat{\rho}(\mathbf{r}, \mathbf{r}') \right]_{\mathbf{r}=\mathbf{r}'} + \int d\mathbf{r} \int d\mathbf{r}' \frac{\delta\Gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (6)$$

where $\delta\hat{\rho}(\mathbf{r}, \mathbf{r}')$, $\delta\rho(\mathbf{r})$, and $\delta\Gamma(\mathbf{r}, \mathbf{r}')$ are, respectively, the transition density matrix, density function, and pair density function associated with the wave function and its first-order change. Because this equation is valid for every electronic state, here and in subsequent equations, the indices referring to states will be suppressed for simplicity.

In the study of the electronic structure of molecules, the external potential is a continuous function $v(\mathbf{r}, \lambda)$ of a set of parameters, $\lambda = (\lambda_1, \lambda_2, \dots, \lambda_n)$ (the nuclear charges and the degrees of freedom associated with the coordinates of the nuclei), so that all of the terms of eq 3 are functions of these parameters.

Derivation with respect to λ_p yields

$$\frac{\partial E(\lambda)}{\partial \lambda_p} = \int d\mathbf{r} \rho(\mathbf{r}, \lambda) \frac{\partial v(\mathbf{r}, \lambda)}{\partial \lambda_p} + \int d\mathbf{r} v(\mathbf{r}, \lambda) \frac{\partial \rho(\mathbf{r}, \lambda)}{\partial \lambda_p} + \int d\mathbf{r} \left[-\frac{1}{2} \nabla^2 \frac{\partial \hat{\rho}(\mathbf{r}, \mathbf{r}', \lambda)}{\partial \lambda_p} \right]_{\mathbf{r}=\mathbf{r}'} + \int d\mathbf{r} \int d\mathbf{r}' \frac{\partial}{\partial \lambda_p} \frac{\Gamma(\mathbf{r}, \mathbf{r}', \lambda)}{|\mathbf{r} - \mathbf{r}'|} \quad (7)$$

and since eq 6 holds for every λ , the three last terms must cancel out. Thus

$$\frac{\partial E(\lambda)}{\partial \lambda_p} = \int d\mathbf{r} \rho(\mathbf{r}, \lambda) \frac{\partial v(\mathbf{r}, \lambda)}{\partial \lambda_p} \quad (8)$$

which is the Hellmann–Feynman theorem.

In the study of a particular molecule, the nuclear charges, z_A , are fixed, and the external potential only depends on the

nuclear coordinates, that is, $\lambda = \lambda(\mathbf{R}_1, \mathbf{R}_2, \dots)$. Furthermore, the electronic energy plus the nuclear repulsion plays the role of potential energy, $E_T(\lambda)$, for the movement of the nuclei, and hence, the force acting upon every nucleus is determined by its gradient. Therefore, one has

$$\mathbf{F}_A = -\vec{\nabla}_A E_T = \zeta_A \left[\int d\mathbf{r} \rho(\mathbf{r}, \lambda) \frac{\mathbf{r} - \mathbf{R}_A}{|\mathbf{r} - \mathbf{R}_A|^3} - \sum_{B \neq A} \zeta_B \frac{\mathbf{R}_B - \mathbf{R}_A}{|\mathbf{R}_B - \mathbf{R}_A|^3} \right] \quad (9)$$

where

$$\vec{\nabla}_A = \mathbf{i} \frac{\partial}{\partial X_A} + \mathbf{j} \frac{\partial}{\partial Y_A} + \mathbf{k} \frac{\partial}{\partial Z_A} \quad (10)$$

which is the electrostatic theorem.

In response to a previous criticism by Coulson and Bell³⁶ on the Hellmann–Feynman theorem, Berlin noted³⁷ that the nuclear attraction term

$$V(\lambda) = \int d\mathbf{r} \rho(\mathbf{r}, \lambda) v(\mathbf{r}, \lambda) \quad (11)$$

can be considered as the sum of two different components: such that

$$V(\lambda) = V_1(\lambda) + V_2(\lambda) \quad (12)$$

$$\frac{\partial V_1(\lambda)}{\partial \lambda_p} = \int d\mathbf{r} \rho(\mathbf{r}, \lambda) \frac{\partial v(\mathbf{r}, \lambda)}{\partial \lambda_p} \quad \forall p \quad (13)$$

and

$$\frac{\partial V_2(\lambda)}{\partial \lambda_p} = \int d\mathbf{r} v(\mathbf{r}, \lambda) \frac{\partial \rho(\mathbf{r}, \lambda)}{\partial \lambda_p} \quad \forall p \quad (14)$$

Thus, if $T(\lambda)$ and $G(\lambda)$ are, respectively, the kinetic energy and the two-electron repulsion, and eq 6 is taken into account, one has

$$\frac{\partial E(\lambda)}{\partial \lambda_p} = \frac{\partial V_1(\lambda)}{\partial \lambda_p} \quad (15)$$

$$\frac{\partial}{\partial \lambda_p} [V_2(\lambda) + T(\lambda) + G(\lambda)] = 0 \quad (16)$$

Berlin used these equations to invalidate Coulson and Bell's objection to the electrostatic theorem, but one can go beyond this point analyzing their implications. Thus, eqs 15 and 16 imply

$$E(\lambda_2) - E(\lambda_1) = V_1(\lambda_2) - V_1(\lambda_1) = \int_{\lambda_1}^{\lambda_2} \int d\mathbf{r} \rho(\mathbf{r}, \lambda) dv_{\lambda}(\mathbf{r}, \lambda) \quad (17)$$

where

$$dv_{\lambda}(\mathbf{r}, \lambda) = \sum_p \frac{\partial v(\mathbf{r}, \lambda)}{\partial \lambda_p} d\lambda_p \quad (18)$$

and

$$V_2(\lambda) + T(\lambda) + G(\lambda) = \text{const} \quad (19)$$

Equation 17 is the integrated Hellmann–Feynman theorem,^{5,38} which establishes an explicit relationship between density and energy.

Equation 19 is the extremum condition of eq 6 written in a different way and implies that throughout a chemical process, the changes in kinetic energy, $T(\lambda)$, and in electron repulsion, $G(\lambda)$, are just canceled by changes in $V_2(\lambda)$.

Berlin's partition of eq 12 is not the only way to look at chemical bonding. Since energy and its components are scalars, instead of dividing the nuclear attraction term into two parts, one could divide the kinetic energy, or the electron repulsion, or some combination of both, and define constants involving parts of these quantities, as it has been implicitly done in studies of the chemical bond based on the kinetic energy density^{39–46} or in conventional explanations based on the electron pair density.

Nonetheless, it seems that Berlin's partition of $V(\lambda)$ is the most natural choice and, probably, the most simple and useful. This partition is grounded in two fundamental equations: the extremum condition—eq 6—and the Hellmann–Feynman theorem—eq 8. It introduces two functions endowed with very clear insight: $V_1(\lambda)$ is associated with the total electron energy, and $V_2(\lambda)$ is associated with the universal functional⁴⁷ $F = T + G$ of the density functional theory.^{1–4} Note, in this respect, that

$$-dV_2(\lambda) = dT(\lambda) + dG(\lambda) = dF(\lambda) \quad (20)$$

$$V_2(\lambda) = \text{const} - F(\lambda) \quad (21)$$

Finally, it provides relations for linking these functions with the basic physical variables: electron density and external potential,^{48–52} which are exact, simple, and easy to apply in practice.

Bearing in mind these arguments, our search for the relationship between the classical notions of chemistry and electron density will be based on this approach.

It is noteworthy that, from this point of view, kinetic energy and electron repulsion only appear in the extremum condition, eq 6, which fixes the density for every conformation, and therefore, they influence the energy through density.

In this context, the physical effects appearing in the kinetic energy or in the two-electron term cannot be directly related to bond energies, because these quantities are part of the constant in eq 19. One must consider, instead, using eq 6, how they affect the density and, next, through eq 17, whether or not the induced changes favor the decrease in energy. In summary, from this perspective, one must be aware that every physical effect must put its mark in the density, and it is through this mark that it affects the energy.

3. Density Partition and Forces: A Way For Rationalizing Chemistry

The arguments of the previous section prove that the rationalization of chemical behavior must deal with the study of density and its evolution along the chemical process. This study provides us a complete theoretical description because, from density, it is possible not only to follow the changes of the electronic energy but also to analyze the forces acting

upon the several parts of the system and to know how they contribute to changing the energy.

In particular, it must be noted that the direct relation between density and forces ensures that fragments with similar densities in different molecules will contribute in a similar way to the driving forces of their chemical processes and that this fact sets the description of the molecular electron densities as the key for the comparative study of their chemical properties.

As it is well-known, the electron density of a molecule in its ground state is highly peaked and strongly concentrated around the nuclear positions for every conformation. Thus, it is convenient to partition the electronic density of a molecule into fragments centered at the nuclei and such that every fragment accompanies its nucleus in the displacement to the largest possible extent.

Denoting the fragments as $\rho^A(\mathbf{r}_A)$, one can write

$$\rho(\mathbf{r}) = \sum_A \rho^A(\mathbf{r}) \quad (22)$$

and following the usual convention, one can consider the fragments $\rho^A(\mathbf{r})$ as atoms in molecules (or pseudo-atoms), though being aware that atoms in molecules are no longer quantum mechanical observables and, therefore, that this denomination is just a mere resort to endow them with chemical insight.

There are several ways to carry out the decomposition of eq 22, but irrespective of their merits or limitations, all of them can be combined with the electrostatic theorem to yield a model of forces in the system. Thus, all of them imply a separation of the force on each nucleus into two distinct contributions. Combining eq 22 with eq 9, one has

$$\mathbf{F}_A = \zeta_A \int d\mathbf{r} \rho^A(\mathbf{r}_A) \frac{\mathbf{r}_A}{r_A^3} + \zeta_A \sum_{B \neq A} \left[\int d\mathbf{r} \rho^B(\mathbf{r}_B) \frac{\mathbf{r}_A}{r_A^3} - \zeta_B \frac{\mathbf{R}_B - \mathbf{R}_A}{|\mathbf{R}_B - \mathbf{R}_A|^3} \right] \quad (23)$$

where ζ_i denotes the nuclear charges and \mathbf{R}_i denotes the nuclei positions.

The first contribution on the right-hand side of eq 23 is the internal or *self-pulling* force, namely, the force exerted on nucleus A by its own electronic cloud. The second one is the *external force* exerted on A by the clouds and nuclei of the remaining atoms.

As it has been remarked above, the electron density of a molecule is strongly concentrated around its nuclei and, for every reasonable partition, the spherical averages of the atomic densities:

$$f_{00}^A(r_A) = \frac{1}{4\pi} \int_0^{2\pi} d\phi_A \int_0^\pi d\theta_A \sin \theta_A \rho^A(\mathbf{r}_A) \quad (24)$$

are, by far, the largest components of the density. Therefore, it is convenient to distinguish this dominant part from the small remaining parts:

$$\Delta^A(\mathbf{r}_A) = \rho^A(\mathbf{r}_A) - f_{00}^A(r_A) \quad (25)$$

and to analyze separately the roles of the spherical components and the rest in the force model of eq 23. For this purpose, one can write

$$\mathbf{F}_A = \zeta_A \int d\mathbf{r} f_{00}^A(r_A) \frac{\mathbf{r}_A}{r_A^3} + \zeta_A \sum_{B \neq A} \left[\int d\mathbf{r} f_{00}^B(r_B) \frac{\mathbf{r}_A}{r_A^3} - \zeta_B \frac{\mathbf{R}_B - \mathbf{R}_A}{|\mathbf{R}_B - \mathbf{R}_A|^3} \right] + \zeta_A \sum_B \int d\mathbf{r} \Delta^B(r_B) \frac{\mathbf{r}_A}{r_A^3} \quad (26)$$

Symmetry considerations are sufficient to see that the first term on the right-hand side is null. Moreover, the second term can be written in terms of the effective charges, ζ_B^{eff} , given by the Gauss theorem

$$\zeta_B^{\text{eff}} = \zeta_B - 4\pi \int_0^{|\mathbf{R}_B - \mathbf{R}_A|} dr_B r_B^2 f_{00}^B(r_B) \quad (27)$$

so that the expression (eq 26) of the force can be rewritten as

$$\mathbf{F}_A = -\zeta_A \zeta_B^{\text{eff}} \frac{\mathbf{R}_B - \mathbf{R}_A}{|\mathbf{R}_B - \mathbf{R}_A|^3} + \zeta_A \sum_B \int d\mathbf{r} \Delta^B(r_B) \frac{\mathbf{r}_A}{r_A^3} \quad (28)$$

As one could expect, *the spherical terms yield no contribution to the internal forces and only participate in the external forces through the partial screening of the nuclear charges*. It should be noted, in this respect, that the electronic charge of an atom is given by

$$Q_{00}^B = 4\pi \int_0^\infty dr_B r_B^2 f_{00}^B(r_B) \quad (29)$$

and, hence, in atoms with positive density, the second term of eq 27 will be smaller than the electronic charge. As a consequence, neutral atoms or cations have a positive ζ_B^{eff} and give a net repulsive force on A at all distances. For anions, ζ_B^{eff} is negative at long distances but it turns to positive at short distances. Thus, the forces exerted by negative ions on nucleus A will be attractive when they are far away from A, but they will repel it at short distances.

In view of this, it is very illustrative to consider what the forces between a pair of atoms or ions with positive defined and strictly spherical densities would be. In this case, the self-pulling forces are obviously zero and only external forces remain. As proved before, these forces are repulsive for couples of neutral atoms, an atom and a cation, or pairs of cations. In the case of a system consisting of a cation (or a neutral atom) and an anion, the force on the anion nucleus will be repulsive at all distances whereas the force on the cation nucleus will be attractive at long distances and repulsive at short ones. Finally, for a couple of negative ions, the forces on both nuclei will be attractive at sufficiently long distances and will become repulsive when the separation decreases. Moreover, the forces on both nuclei will be, in general, different, and the reversions will occur at different distances.

Certainly, the absence of interactions between the clouds in the context of the electrostatic theorem makes these forces very different from the ones expected when electrostatics is applied to spherical ions in the usual way, and this leads to an evident conclusion: *none of these couples can conform a stable system*. To form a stable system, densities cannot have spherical symmetry or, in other words, *density deformations are essential for the appearance of stable systems*.

Let us complete this analysis by considering the contribution of the atomic deformations to the forces. To do this, atomic densities can be expanded in spherical harmonics centered at the nuclei:

$$\rho^A(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l z_l^m(\mathbf{r}_A) f_{lm}^A(r_A) \quad (30)$$

where $f_{lm}^A(r_A)$ are atomic radial factors:

$$f_{lm}^A(r_A) = \frac{2l+1}{2(1+\delta_{m0})\pi r^l} \frac{(l-|m|)!}{(l+|m|)!} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta z_l^m(\mathbf{r}/r) \rho^A(\mathbf{r}) \quad (31)$$

and $z_l^m(\mathbf{r})$ are the regular harmonics:

$$\begin{aligned} z_l^m(\mathbf{r}) &= r^l (-1)^m P_l^m(\cos\theta) \cos(m\phi) & \text{for } m \geq 0 \\ z_l^m(\mathbf{r}) &= r^l (-1)^{|m|} P_l^{|m|}(\cos\theta) \sin(|m|\phi) & \text{for } m < 0 \end{aligned} \quad (32)$$

$P_l^{|m|}$ being the associated Legendre functions.⁵³

The terms with $l=0$ are just the spherical averages whose roles were discussed above. The remaining terms ($l>0$) are the atomic deformations:

$$\Delta^A(\mathbf{r}) = \rho^A(\mathbf{r}) - f_{00}^A(r_A) = \sum_{l=1}^{\infty} \sum_{m=-l}^l z_l^m(\mathbf{r}_A) f_{lm}^A(r_A) \quad (33)$$

but decomposed so that one can identify dipole-type contributions ($l=1$), quadrupole ($l=2$), octapole ($l=3$), and so on.

From this expansion, one easily finds that

$$\begin{aligned} \mathbf{F}_{\text{int}}^A &= \zeta_A \int d\mathbf{r} \Delta^A(\mathbf{r}) \frac{\mathbf{r}_A}{r_A^3} \\ &= -\mathbf{i}q_{11}^A - \mathbf{j}q_{1-1}^A - \mathbf{k}q_{10}^A \end{aligned} \quad (34)$$

where

$$q_{lm}^A = \frac{4\pi}{3} \zeta_A \int_0^\infty dr r f_{lm}^A(r) \quad m = -1, 0, 1 \quad (35)$$

It is clear that *the self-pulling force on an atom is only determined by the dipole-type deformation of its own density*. Moreover,

$$\begin{aligned} \mathbf{F}_{\text{ext}}^A &= \zeta_A \sum_{B \neq A} \left[\int d\mathbf{r} \rho^B(\mathbf{r}) \frac{\mathbf{r}_A}{r_A^3} - \zeta_B \frac{\mathbf{R}_B - \mathbf{R}_A}{|\mathbf{R}_B - \mathbf{R}_A|^3} \right] \\ &= \zeta_A \left[\zeta_B^{\text{eff}} \frac{\mathbf{R}_B - \mathbf{R}_A}{|\mathbf{R}_B - \mathbf{R}_A|^3} + \bar{\nabla}_A \sum_{B \neq A} \sum_{l=1}^{\infty} \sum_{m=-l}^l \frac{z_l^m(\mathbf{R}_B - \mathbf{R}_A)}{|\mathbf{R}_B - \mathbf{R}_A|^{2l+1}} V_{lm}^B(|\mathbf{R}_B - \mathbf{R}_A|) \right] \end{aligned} \quad (36)$$

where

$$V_{lm}^B(\mathbf{r}) = \frac{4\pi}{2l+1} \left[\int_0^r dr' r'^{2l+2} f_{lm}^B(r') + r^{2l+1} \int_r^\infty dr' r' f_{lm}^B(r') \right] \quad (37)$$

so that the external force contains the forces associated with the density deformation beside the contribution of the screened nuclear charges.

We stress that the atomic deformations caused by the molecular environment play a basic role in the study of chemical behavior supported by the electrostatic theorem. As proved above, they completely determine the self-pulling forces and a part of the external forces, being essential for the existence of stable systems.

We finally note that, though these conclusions are valid for every *exact* partition of the density, the detailed form of both the spherical averages and the atomic deformations depend on the definition of the atomic fragments, $\rho^A(\mathbf{r})$, and thus, one is faced with the choice of the partition criterion. We will return to this point in the following section.

4. Empirical Structural Chemistry: The Conventional Rationalization Of Chemistry

Let us consider, now, the main ideas employed by experimentalists in the description of chemical behavior. As it is well-known, they need neither to determine or analyze the density nor to invoke the electrostatic theorem. Instead of it, they use some simple concepts that have their roots in empirical structural chemistry, mostly developed before the advent of quantum mechanics, from the rationalization of empirical data.

In this thought, a structural hypothesis is basic, according to which molecules are composed by bonded atoms that are distributed in space adopting characteristic conformations. Moreover, there are groups of atoms (functional groups) that share conformations and properties in distinct molecules.

Atoms are bonded by their valence electrons, whose structures can be described by Lewis' rules⁵⁴ in terms of lone pairs (owned by individual atoms), bond pairs (shared by pairs of atoms), and eventually by lone electrons, all of them lying around the ionic core formed by the nuclei and their core electrons.

Bonds can be single, double, or triple according to the number of the bond pairs shared by a couple of atoms. The set of bonds conforms the skeleton of the molecule, and chemical reactions are regarded as reorganizations of the skeleton in which some bonds are broken and others are formed.

These basic assumptions are too simple to embrace all chemical behavior, but complemented with some ideas extracted from valence theory (resonance, hyperconjugation, etc.), they compose a powerful tool that allows experimentalists to describe macroscopic substances and chemical processes at the molecular level and to carry out temtable predictions, in summary, to rationalize most of the chemical behavior.

One has, thus, two different approaches to the rationalization of chemistry: the one based on the study of electron density and, in particular, on its small deformations and that of empirical structural chemistry, mainly based on Lewis' structures.

The first one is firmly grounded in theory. The second is supported by many years of successful usage. In view of this, it seems licit to ask ourselves whether they are as different as they appear at first sight or, on the contrary, they are simply two different comprehensions of the same objects. Note, in this respect, that according to the discussion in Section 2, *as far as Lewis structures and the remaining concepts of empirical structural chemistry have some physical basis, they must be somehow reflected in electron density.*

To analyze whether, and eventually how, they are reflected, we have carried out a systematic study of density oriented to analyze its relationship with Lewis' structures and other basic concepts of empirical structural chemistry.

In the analysis, we have used *atomic deformations*, which are defined as the atomic densities minus their spherical averages, that is, the Δ^A functions introduced in eq 25; *group deformations*, which are the sum of the atomic deformations of a given group of atoms:

$$\Delta^G(\mathbf{r}) = \sum_A^{\text{group}} \Delta^A(\mathbf{r}_A) \quad (38)$$

and, finally, *molecular deformations*, in which the sum extends over all the atoms of a given molecule:

$$\Delta(\mathbf{r}) = \sum_A^{\text{molec}} \Delta^A(\mathbf{r}_A) \quad (39)$$

Molecular deformations have an antecedent in (but should not be confused with) the so-called charge density difference functions,⁵⁵ which are the differences between the molecular density and the density of a hypothetical molecule built with the isolated atoms, in suitable valence states, and placed in the corresponding sites with appropriate orientations.

Note, in this respect, that the spherical averages defined in eq 24 are obtained from the very molecular density itself, without invoking the existence of reference atoms in ad hoc valence states.

Thus, conceptual distinctions apart, the density difference functions, $D(\mathbf{r})$, contain terms dependent on the angular moments of the reference atoms, which do not appear in the molecular deformations as defined above. In fact, the density of an isolated atom in a state with angular moment L has the expansion

$$\rho^A(\mathbf{r}_A) = \sum_{l=0}^L \sum_{m=-2l}^{2l} z_{2l}^m(\mathbf{r}_A) f_{2lm}^A(r_A) \quad (40)$$

If the molecular density is partitioned and expanded—according to eqs 22, 30, and 31—and the densities of the isolated atoms are subtracted, one has

$$D(\mathbf{r}) = \Delta(\mathbf{r}) + \sum_A [f_{00}^A(r_A) - \sum_{l=0}^L \sum_{m=-2l}^{2l} z_{2l}^m(\mathbf{r}_A) f_{2lm}^A(r_A)] \quad (41)$$

If, as usual, the reference atoms are spherical, the $D(\mathbf{r})$ function will contain spherical contributions, $f_{00}^A(r_A) - f_{00}^A(r_A)$, that are not present in molecular deformations. If they are in a P state, a further contamination with quadrupole-type terms appear, and so on.

Atomic and group deformations do not have, to our knowledge, direct antecedents, yet Hirshfeld and Rzotkiewicz⁵⁶ have researched this type of information on diatomics in the context of the charge density difference functions.

It was remarked in Section 3 that the detailed form of the atomic deformations depends on the particular partition adopted to define the atomic fragments, which, as it is well-known, fall into two categories. In space-partition schemes,^{10,12–17} the molecular density is separated into pieces, each one contained in an atomic domain Ω_A (satisfying $\cup_{A=1}^M \Omega_A = R^3$ and $\Omega_A \cap \Omega_B = \phi$, $\forall A \neq B$) so that

$$\rho(\mathbf{r} \in R^3) = \sum_{A=1}^M \rho(\mathbf{r} \in \Omega_A) \quad (42)$$

Alternatively, the density can be decomposed in overlapping fragments centered at the nuclei, each one extending over the whole space R^3 :^{11,18,19,21,29–31,57}

$$\rho(\mathbf{r} \in R^3) = \sum_{A=1}^M \rho(\mathbf{r}_A \in R^3) \quad (43)$$

Though the general features of the forces model discussed above are valid for every decomposition in which the fragments add up exactly to the whole density (note that this only excludes approximations based on spherical atoms and the like^{18,57}), not all of the partition schemes are equally useful in this context. It must be recalled, in this regard, that conventional studies of density are aimed at analyzing the dependence of $\rho(\mathbf{r}, \lambda)$ with respect to \mathbf{r} for fixed λ , while for the study of forces and energy, the essential point is how the density evolves when λ varies.

From a practical standpoint, the methods of the second category are much more suitable in this respect. Among them, the method of *deformed atoms in molecules* (DAM)^{29–31} offers clear advantages because it allows for the direct application of the approach discussed in Section 3, and therefore, we will use it in this study. In the DAM method, the partition of the density is intended to retain, as much as possible, the identity of the atoms within the molecule at every conformation. Basically, in this method, the minimal distortion of each atomic density is achieved by assigning to it the one-center charge distributions centered at its nucleus as well as the parts of the two-center distributions nearest to

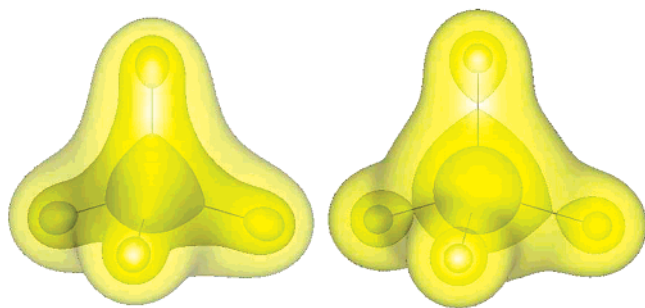


Figure 1. Electron density surfaces in methane. Total density (left) and summation of the spherical atomic contributions (right). Contour values: 0.3 (innermost), 0.2, and 0.1 (outermost) au.

it. With such a partition, the densities of all the fragments exactly retrieve (on summation) the whole density and, furthermore, can be accurately expanded when regular harmonics are multiplied by analytical radial factors, a fact that greatly facilitates the application of the electrostatic theorem. Though this method has been described in detail in previous works,^{29–31} a short review is given in the Appendix for the sake of completeness.

5. Results

We have studied the density deformations in a sizable sample consisting of several tens of molecules at their equilibrium geometries. For all of them, the densities were computed at the Hartree–Fock (HF) level using the reasonably good VB1 Slater basis set⁵⁸ (composition: [5,3,1] for B to Ne and [3,1] for H). The calculation of integrals and HF optimization were carried out with the SMILES program.^{59–63} The atomic expansions were carried out with the DAM method using the DAM program.^{29–31} For testing the effects of the basis set on the results, some calculations were repeated using the CVB2 Slater basis set⁵⁸ and Dunning’s cc-pVTZ and cc-pVQZ Gaussian basis sets⁶⁴ with the Gaussian version of DAM (G-DAM⁶⁵). The effect of correlation was also examined by performing configuration interaction with single and double excitation (CISD) calculations with MOLPRO.⁶⁶ No qualitative changes were observed in the test samples (see below), and quantitative changes were so small that HF calculations with the VB1 basis sets were considered sufficiently good for our purposes.

The density, the atomic and accumulated spherical terms, and its deformations were visualized by depicting their constant value surfaces with gOpenMol.⁶⁷ As an example, we consider the methane molecule, whose density varies from more than 100 au (e/b^3), in the nearness of the C nucleus, to 0 au, far away from the molecular region, while its deformation varies only from 0.08 to -0.03 au.

Because of the smallness of the density deformation, the contour surfaces of the whole density of this molecule and those of the accumulated spherical terms are very similar, as it is illustrated in Figure 1, so that the details of the difference are difficult to appreciate. On the contrary, the structure of these differences is evident in the contour surfaces of the density deformations depicted in Figure 2. This figure shows the density deformations obtained at

Roothaan–Hartree–Fock (RHF) and CISD levels using Slater VB1⁵⁸ and Gaussian pVTZ⁶⁴ basis sets and illustrates the changes in the density deformations produced by changes in the computational method or the basis set.

Because the deformations bear no net charge (they integrate to zero), physical space is partitioned into regions where the electronic charge is accumulated (positive deformation) and into others in which it is depleted (negative). In every region, surfaces of a given absolute value are enclosed by surfaces of lower absolute value.

For methane, the contours corresponding to positive deformations (red surfaces in Figure 2) show four electron charge accumulations with nearly cylindrical symmetry between the carbon and hydrogens, just giving a clear image of the four σ bonds of this molecule. The pictures of negative deformations (blue surfaces in Figure 2) complete the description of the charge redistribution, showing the regions where the electronic charge is drawn from.

Looking at these type of pictures for several molecules, one finds that the concepts of empirical chemistry appear in a beautiful and neat, though somewhat unexpected, manner. Lone pairs and bonds are paralleled by charge accumulations placed where one would expect them to be; single, double, and triple bonds are clearly distinguished; concepts such as aromaticity and delocalization can be directly visualized. The different chemical classes of a given atom can be identified by glancing at their atomic density deformations. At the same time, the individuality of each atom can be recognized from the features of the dominant spherical term. Functional groups are identified as a common group of atoms of given classes that retain their structure and density in different molecules, and so on.

For obvious reasons, the literally hundreds of pictures that have been drawn cannot be included in this paper. We present a minimal selection of them in order to support and clarify our previous comments. Further pictures can be found at <http://www.uam.es/departamentos/ciencias/qfa/DAM>.

5.1. Lone Pairs. Because the notion of a localized electron pair is essential in Lewis’⁵⁴ and other^{68,69} successful models for geometry and reactivity, its physical support has been extensively researched in the context of the pair density function⁷⁰ and associated⁶ with the maxima of the density Laplacian, $\nabla_i^2 \rho(\mathbf{r}, \lambda)$.

Certainly, the interactions between electrons should be studied in terms of pair density, but as stressed in Section 2, its chemical relevance is determined by its effect on the density, which, according to Section 3, can be searched for in the density itself through the density deformations.

Lone pairs compose a nice example of the close relationship between chemical notions and density deformations. Figure 3 shows the atomic deformations of nitrogen in ammonia (left plate) and the full molecular deformations (right plate). In ammonia, besides the three charge accumulations along the N–H bonds, there is a large, and nearly spherical, charge accumulation in the vicinity of the N atom, just as it would be expected from the presence of a single lone pair there ($:\text{NH}_3$).

Figure 4 shows the atomic density deformations of oxygen (left plates) and the full molecular deformations (right plates)

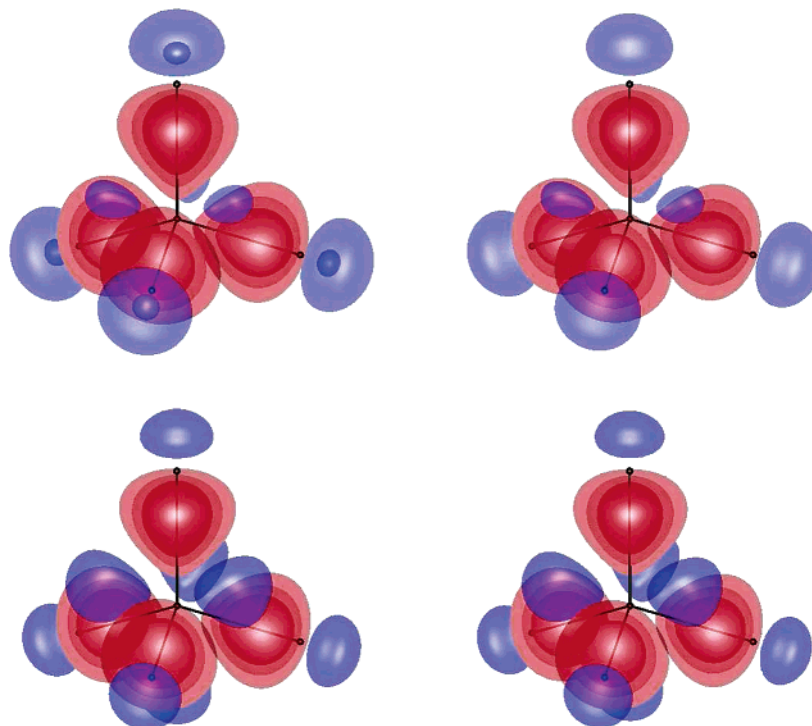


Figure 2. Molecular deformation of methane. Red: positive deformation. Blue: negative deformation. Contour values: 0.045 (innermost), 0.030, 0.015 (outermost), -0.030 , and -0.015 au. Upper: Slater VB1 basis set. Lower: Gaussian pVTZ basis set. Left: RHF density. Right: CISD density.

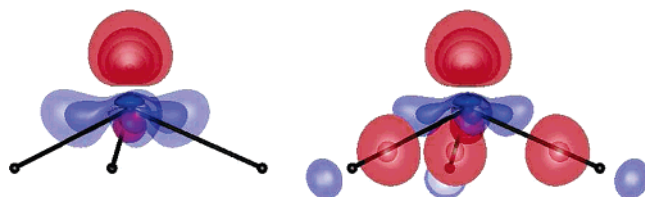


Figure 3. Atomic density deformations of nitrogen (left) and the molecular deformation (right) in ammonia. Contour values in au: 0.150, 0.125, 0.100, 0.075, 0.050 (red); -0.075 , -0.050 (blue).

in water ($:\ddot{\text{O}}\text{H}_2$), formaldehyde ($:\ddot{\text{O}}=\text{CH}_2$), and carbon monoxide ($:\text{O}\equiv\text{C}:$). In water, the charge accumulations associated with the two lone pairs of oxygen extend above and below the molecular plane, whereas in formaldehyde, they are placed in the molecular plane. Finally, in carbon monoxide, the two charge accumulations placed outside the bond region show the existence of a lone pair on each atom. Moreover, the characteristic deformations of the lone pairs appear in the atomic density, supporting the idea that they are owned by atoms.

It is noteworthy that these structures appear almost unchanged everywhere the empirical chemistry evinces this class of atom. Thus, the distortion of nitrogen in ammonia is reproduced practically unchanged in amines; that of oxygen in water appears in alcohols, ethers, carboxylic acids, esters, and so forth. The distortion of oxygen in formaldehyde is typical of the keto oxygen, and it can be observed in aldehydes, ketones, carboxylic acids, and so on.

As an example, we present in Figure 5 the density deformations of the oxygen atom and the full molecular deformations in methanol, dimethyl ether, and phenol, where

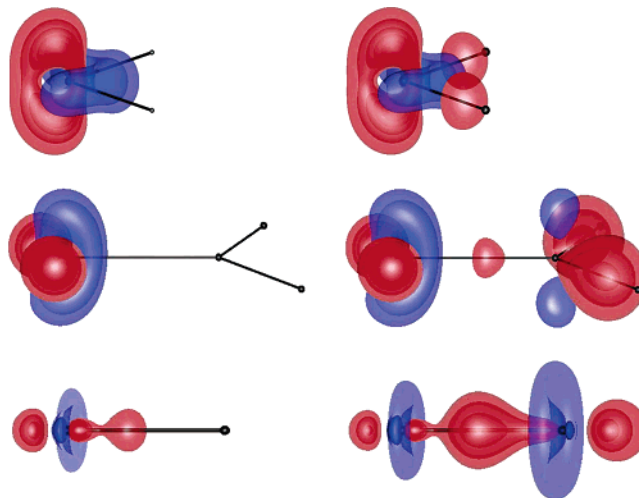


Figure 4. Oxygen deformation (left plates) and molecular deformation (right plates) in water (upper), formaldehyde (middle), and carbon monoxide (lower). Contour values in au: 0.150, 0.125, 0.100, 0.075, 0.050 (red); -0.075 , -0.050 (blue).

the presence of two lone pairs such as those of water is clear, despite the strongly different molecular environments. Certainly, the presence of a charge accumulation, everywhere lone pairs are predicted to be, shows that this notion has an actual support in the density.

5.2. Single, Double, and Triple Bonds. Figure 6 illustrates how the density deformations reflect the chemical notions of single, double, and triple bonds. It shows several contour surfaces corresponding to ethane (first plate), ethylene (second plate), and acetylene (third plate). In ethane, the σ -bond skeleton is clearly reflected by charge accumulations

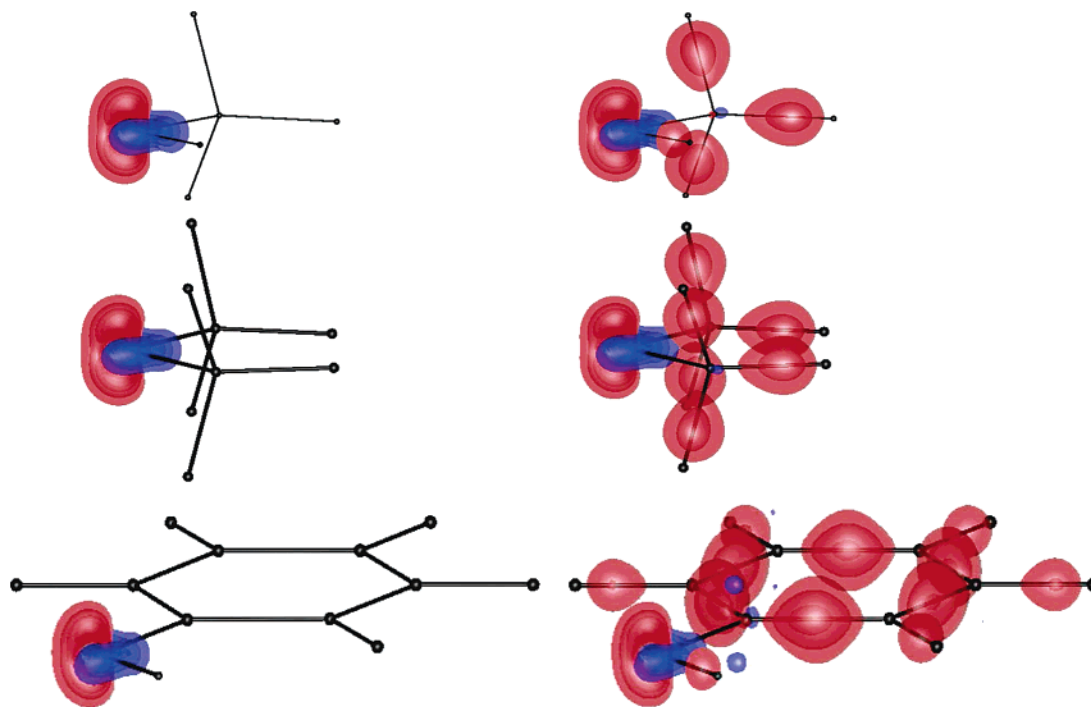


Figure 5. Atomic deformation of oxygen (left plates) and molecular deformation (right plates) in methanol (upper), dimethyl ether (middle), and phenol (lower). Contour values: ± 0.150 , ± 0.125 , ± 0.100 , ± 0.075 , ± 0.050 au (red: positive. blue: negative).

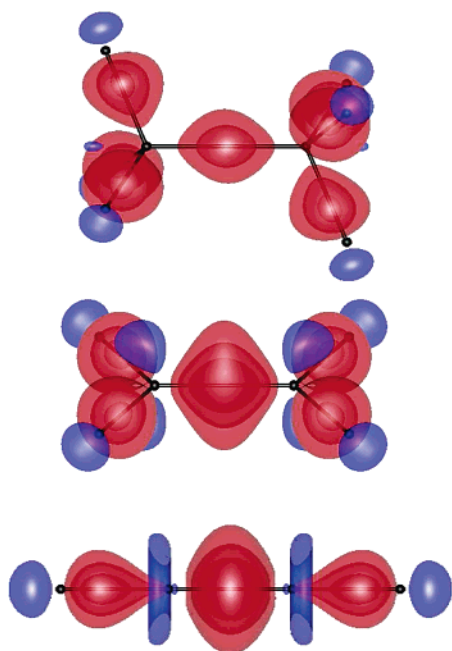


Figure 6. Density deformation of ethane (upper), ethylene (middle), and acetylene (lower). Contour values: 0.075 , 0.050 , ± 0.025 au (red: positive. blue: negative).

with nearly cylindrical symmetry placed where the C–H and C–C bonds are expected to be. Moreover, a comparison between Figures 2 and 6 renders evident the close similarity of the C–H σ -type charge deformation in methane and ethane.

In ethylene, besides the σ -type deformation characteristic of the C–H bonds, there is a strong charge accumulation, with upward and downward distortions, in the middle of the C–C line as well as charge depletions above and below the

molecular plane near the carbons. Again, the density deformation parallels known properties. The π character is evident from the asymmetry (ellipticity⁶) of the charge distribution, and the large rotational barrier around the C–C bond can be attributed both to this distortion and to the charge depletions, which must generate forces that hinder the movements of the hydrogens out of the plane.

The density deformation of acetylene shows the two C–H σ bonds and a strong charge accumulation of cylindrical symmetry in the C–C line, accompanied by two perpendicular rings of charge depletions centered in the carbons. This structure is characteristic of the C \equiv C triple bond, but it also appears (with quantitative but not qualitative changes) in triple bonds involving other atoms, as it can be seen, for instance, in case of carbon monoxide, Figure 4.

5.3. Aromaticity. The chemical notions of a delocalized cloud and aromaticity are also reflected in the density deformations. For high deformation values, contour surfaces of aromatic molecules show only the charge concentrations associated with the skeleton of conjugated double bonds (intermediate between single and double), as well as those of their σ bonds. If that contour value is lowered in order to follow the corresponding evolution of the charge accumulation, one observes the growth of upward and downward protuberances in the middle of the double bond. Additional lowering shows that the protuberances tend to acquire a shape like two mushrooms placed at opposite sides. In aromatic compounds, the tops of adjacent mushrooms tend to join each other, forming a sandwich cloud that encloses the deformations of the internal skeleton. On the contrary, in nonaromatic compounds, this joint does not occur.

Figure 7 shows the contour surfaces of values ± 0.001 for the deformations of benzene, anthracene, and diphenylene

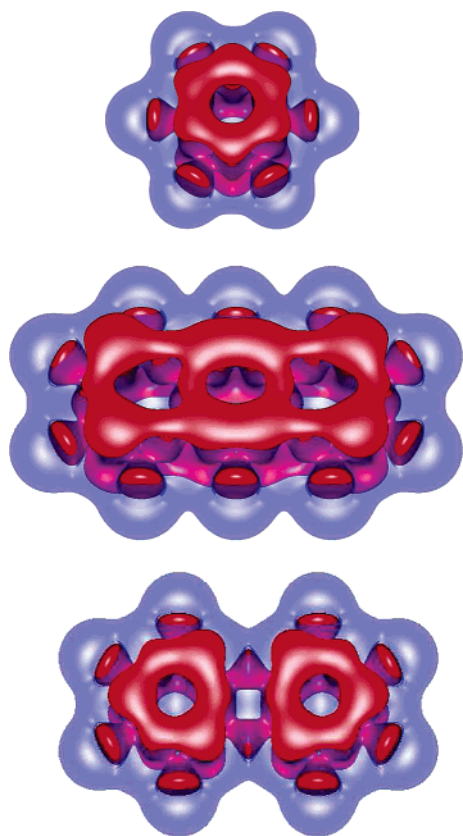


Figure 7. Molecular density deformations in benzene (upper), anthracene (middle), and diphenylene (lower). Contour values ± 0.001 au.

(note that this contour value is much lower than those previously chosen). It can be seen that the external cloud in benzene and anthracene is delocalized over all the molecule, while in diphenylene, it extends separately over each benzene ring. Clearly, the density deformations allow us to visualize this chemical notion in a neat manner.

5.4. Atoms in Molecules. The strong differences between the shapes of the density deformations associated with the different *classes* of a given atom may induce (see Figure 4, for instance) one to think that atoms, in the usual meaning of the term, cannot be distinguished in molecules, contradicting the intuitive notion of molecules as composed by slightly deformed atoms. The point to be stressed here is that the values of density deformations (typically about 10^{-2} au or less) are several orders of magnitude smaller than those of the spherical terms and that it is in these latter where the *identity* of the atoms resides. To illustrate this fact, we depict, in Figure 8a, the spherical radial factors, $f_{00}(r_O)$, of oxygen in a set of molecules covering the different classes of oxygen discussed above together with the radial factor of the isolated atom in its ground state. Note that the differences are so small in the scale of the figure that all the oxygen atoms seem to have the same spherical radial factor. To make perceptible these differences, we also present, in Figure 8b, the usual radial distributions, $4\pi r_O^2 f_{00}(r_O)$, that enhance the resolution in the valence zone.

Now, one can observe that all of the atomic radial distributions of oxygen are greater than that corresponding

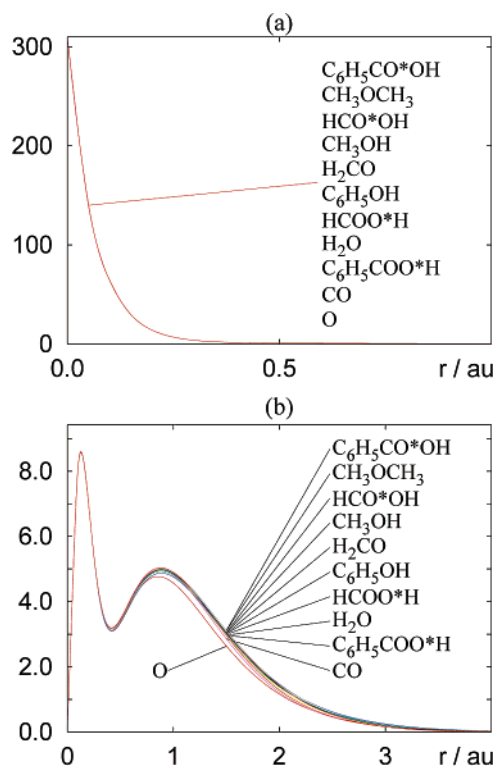


Figure 8. Comparison of the radial factors of spherical terms of oxygen in different molecules. (a) $f_{00}(r)$, (b) radial charge densities, $4\pi r^2 f_{00}(r)$.

to the isolated atom (evincing the charge transfer toward the O), but the differences among them are still very small.

5.5. Functional Groups. A notion related to the *class* and *identity* of an atom is that of the *functional group*. As remarked above, atoms of the same class can be identified from the resemblance of both their spherical averages and atomic deformations. In functional groups, this resemblance extends to the whole set of atoms forming the group, thus giving fragments with similar densities in different molecules. According to Sections 2 and 3, these fragments will contribute in almost the same way to the chemical behavior of the molecules. Figure 9 illustrates the density deformation of the carboxylic group of formic and benzoic acids. These pictures render evident the resemblance of the group deformations of $-\text{COOH}$ in these significantly different environments, the very small differences between both pictures being illustrative of the smallness of the environmental effects.

Once again, another basic notion of empirical chemistry is supported by the density structure in a nice manner.

6 Final Comments

When the total one-electron density distribution of a molecule is examined, nothing about classic chemical notions is apparent.^{6,7} There are no lone pairs, no distinct chemical bonds, no π clouds, and so forth. This occurs because the molecular density is so largely dominated by the spherical terms of its constituent atoms that the chemically relevant structure is completely masked. However, when the spherical terms are removed, the fine structure of the molecular density becomes evident and, from its analysis, there emerges a

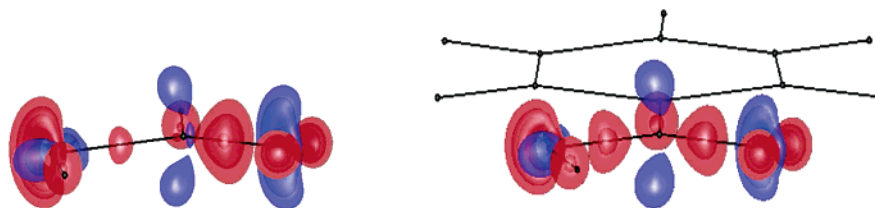


Figure 9. Accumulated density deformations of the $-\text{COOH}$ group in formic acid (left) and benzoic acid (right). Contour values in au: 0.150, 0.125, 0.100, 0.075, 0.050 (red); -0.075 , -0.050 (blue).

picture that reflects and supports all the intuitive notions of the empirical chemistry.

The reason for this is clear from the standpoint of the Hellmann–Feynman (electrostatic) theorem: chemical forces only depend on electron density, and the physical effects determine the chemical behavior through their influence on the density. Moreover, the spherical parts of the atomic density, along with the nuclei charges, cannot lead to stable systems, and consequently, these cannot play the main role in the explanation of the chemical behavior. This behavior is determined by the small nonspherical deformations of the density at the same time that it is described by the empirical notions of chemistry. Chemical notions and nonspherical density deformations must be related to each other, and they actually are.

In this work, a systematic study of the density deformations of several tens of molecules has been summarized. This study has been aimed at analyzing whether, and eventually how, these deformations reflect Lewis' structures and other basic concepts of empirical structural chemistry.

The theoretical support of this analysis lies on the extremum condition and the Hellmann–Feynman theorem. It has been remarked that the explicit relationship between density, force, and energy, previously reported in the framework of the DAM method, can be extended in a straightforward manner to almost any other method for the analysis of density. In particular, we note that, for every molecular partition of the electron density into atomic contributions, the spherical averages can be separated from the rest. In this way, atomic, group, and molecular deformations can be defined without invoking any external reference such as the density of isolated atoms. Moreover, it was also noted that this separation facilitates both the description of the energy changes in terms of forces and the forces in terms of density. Bearing all this in mind, we have carried out a detailed discussion on the interatomic forces, in the context of the electrostatic theorem, that evinces the basic role played by small density deformations in chemical behavior, and which supports the idea that these deformations are related to the basic notions of chemistry.

For the practical determination of these relationships, reasonably good densities were computed for a number of representative molecules, using Slater basis sets⁵⁸ with SMILES,⁶³ and these densities were analyzed with the DAM package.³¹

As illustrated in Section 5, molecules were classified according to their conventional structures (having lone pairs; single, double, or triple bonds; etc.), and their density deformations were depicted and compared. The density

deformations thus obtained show clear and characteristic structures associated with every classical notion, the correspondence being so tight that it seems possible to accurately predict (with a suitable parametrization of the deformations) the density of molecules from their conventional chemical formulas.

The appearance of such a close relationship between chemical notions and density deformations gives us sensible grounds to regard the traditional chemical language as a symbolic representation of the density deformations responsible for chemical behavior. From this perspective, it is both gratifying and amazing to confirm that chemists, on the basis of macroscopic data alone and being guided just by their intuition, were able to create this symbolic language almost a century before these deformations were studied.

This work has been circumscribed to the study of density at the equilibrium conformation, but as remarked above, even more important is how to characterize the evolution of density along conformational and reactive changes. We are, at present, carrying out an analysis of the derivatives of density with respect to nuclear coordinates and exploring the fit of multidimensional energy surfaces and forces in terms of the density, with practical applications in molecular dynamics, spectroscopy, and molecular mechanics. The preliminary results are encouraging and will soon be reported.

A beta version of the DAM codes used in this work is available upon request at rafael.lopez@uam.es.

Appendix

In the linear combination of atomic orbitals context, one-electron density has the expression

$$\rho(\mathbf{r}) = \sum_A \sum_a \sum_{a'} \rho_{aa'} \chi_a(\mathbf{r}_A) \chi_{a'}(\mathbf{r}_A) + \sum_A \sum_{B \neq A} \sum_a \sum_b \rho_{ab} \chi_a(\mathbf{r}_A) \chi_b(\mathbf{r}_B) \quad (44)$$

where A , B , and so forth label the nuclei, centered respectively at \mathbf{R}_A , \mathbf{R}_B , and so forth; a , a' , b , and b' label the subsets of the basis functions, $\chi_a(\mathbf{r}_A)$, $\chi_b(\mathbf{r}_B)$, and so forth; and $\mathbf{r}_A = \mathbf{r} - \mathbf{R}_A$, $\mathbf{r}_B = \mathbf{r} - \mathbf{R}_B$.

In the DAM method, the atomic fragments are defined by

$$\rho^A(\mathbf{r}_A) = \sum_a \sum_{a'} \rho_{aa'} \chi_a(\mathbf{r}_A) \chi_{a'}(\mathbf{r}_A) + 2 \sum_{B \neq A} \sum_a \sum_b \rho_{ab} d_{ab}^A(\mathbf{r}_A) \quad (45)$$

The first contribution contains the one-center distributions placed at \mathbf{R}_A . The second one is obtained by partitioning the

two-center distributions into minimally deformed components assigned, respectively, to *A* and *B*:

$$\chi_a(\mathbf{r}_A) \chi_b(\mathbf{r}_B) = d_{ab}^A(\mathbf{r}_A) + d_{ab}^B(\mathbf{r}_B) \quad (46)$$

The minimal deformation criterion used in this partition and its practical implementation have been detailed elsewhere.^{29–31}

Finally, each atomic fragment of eq 45 is expanded in regular harmonics centered in its nucleus, so that the whole density becomes

$$\rho(\mathbf{r}) = \sum_A \sum_{l=0}^{\infty} \sum_{m=-l}^l z_l^m(\mathbf{r}_A) f_{lm}^A(r_A) \quad (47)$$

If one regards these fragments as (pseudo-) atoms, it is clear that the terms with $l = 0$ can be associated with the spherical parts of the atomic clouds and the remaining ones with the deformations caused by the environment. The spherical parts contain the whole electronic charge of the molecule and are largely dominant. The remaining terms determine the atomic dipoles ($l = 1$), quadrupoles ($l = 2$), octapoles ($l = 3$), and so on. As proved in our previous works,^{29–31} these terms are small and quickly decreasing with l .

From these equations, it is evident that the DAM method is basis-set-dependent, and in fact, it will lead to meaningless results for highly unbalanced basis sets, such as strictly one-center ones. Nevertheless, when reasonably good basis sets are used, the results are qualitatively independent of the particular basis set chosen, the quantitative changes in density deformations being rather small, as it was illustrated in Figure 2.

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