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Article

On the Nature of Chemical Bond: Space Enfoldings, Density Bond Matrices, Quantum Molecular Polyhedra, and a Collective Bond Description Proposal

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Abstract: The nature of the quantum mechanical LCAO-MO Mulliken-like description is analyzed in light of constructing basis function enfolded spaces. As a result, the concept of the chemical bond can transform into a collective functional structure, where one considers the whole set of molecular atoms plus enfolding centers as bearing the chemical bond in various collective forms. Such an endeavor permits the discussion of many collateral subjects like density bond matrices, polyatomic bonds, quantum molecular polyhedra, and bond comparisons.

Keywords: LCAO-MO; chemical bond; enfolded spaces; basis sets; collective chemical bonds; first order density function; density bond matrix; quantum molecular polyhedra; bond comparison

1. Foreword

The present study describes a *purely theoretical* point of view about the concepts created around the chemical bond via applying the principles of quantum mechanics.

The authors intend to advise future readers on the possible applications of the mathematical descriptions in this paper, but they do not perform any computational practical development here.

Such planning can be based on the authors' desire to show the pathways further quantum chemical development can follow, remaining neutral about choosing which one.

In some cases, they have intervened within [1] or promoted books [2] that try to present some trendy topics in 21st-century quantum chemistry.

Powerful available codes, adapted to many computational purposes, are present in the era of powerful electronic computational means at the dawn of quantum computing [3].

Then, what can be foreseen as a starting point providing new insight into the already typical quantum chemical molecular computation setup could be included and used systematically in the future.

Space *enfolding* is an essential concept for understanding the fundamentals and development of the present work [4]. Such a structure develops when Gaussian and similarly constructed functions containing positive definite norms between two variables are observed as an infinite set. That potential construct includes infinite functions in every possible infinite space location.

The organization of this text will be subject to a scheme as follows. First, an introduction including protohistory and history of the chemical bond will be resumed with notes on the essential role of quantum mechanics and density function. For evident reasons, such a section has to be extremely resumed, reflecting the picture the authors have about the chemical bond. Second, the concept of collective chemical bonds will be developed based on an idealized model of molecular orbital theory. Third, an analysis of the first-order density function expressible as a linear combination of related functions will be developed. Fourth, the structure of molecular orbital densities studied as a molecular polytope will be presented. Fifth, tools to compare two or more bonds are schematically discussed. Finally, a résumé and some conclusions will be proposed.

2. Introduction

2.1. Historical Remarks

Almost eight decades have passed since Pauling's "The Nature of the Chemical Bond" [5] in 1945. During this time, a vast amount of literature on the chemical bond subject was published, and a skyrocketing development of quantum mechanical tools applied to a deeper understanding of chemistry occurred. This development has been due to the extraordinary increase in computational power and the ease of use of sophisticated quantum chemical codes.

It is also interesting to note that, while Pauling has demonstrated how quantum mechanics could be applied to chemical problems in a previous 1935 volume [6], contemporary of a Born volume [7]: "Atomic Physics", pioneering atomic structure analysis from a physical perspective, in the 1945 Pauling's treatise: "The Nature of Chemical Bond" almost no mathematical development was present, offering the subject from an easy chemical perspective. Possibly, this was so because of Pauling's awareness that chemists of the post-WWII era were not very much acquainted, nor friendly enough, with the heavy mathematical burden associated with quantum mechanics applied to chemical structure.

However, a book by Eyring, Walter, and Kimball [8]: "Quantum Chemistry", contemporary to "The Nature of Chemical Bond", was published in 1944, but was written with a similar content and intention as the earlier Pauling's 1935 book on the same subject, but included an easy reading mathematical structure. Seven years later, a celebrated book by Coulson appeared, entitled "Valence" [9], that in some respects was an extension of "The Nature of Chemical Bond". Meanwhile, "Valence" has been celebrated by chemists along the time road, possibly because Coulson employed the same old chemical lore adaptation to present the chemical bond problem, just talking with the chemical valence slang in the title.

This archeological quantum chemical survey will not be complete without quoting the 1954 publication of Hirschfelder, Curtiss, and Bird: "Molecular Theory of Gases and Liquids" [10]. This was a heavy volume of more than a thousand pages presented within the formalism of the first half of the 20th century, nonetheless still valid, as well as other theoretical problems in many aspects related to physical chemistry and chemical physics. The theoretical issues that chemistry and physics face include the relationship between molecular interactions and the structure and properties of gases and liquids. Perhaps this shows that chemical bond is not a unique subject related to theoretical chemistry, which has to be studied to understand atomic and molecular behavior.

To finish this survey, it might be interesting to quote a nice booklet by Gray [11]: "Electrons and Chemical Bonding", published in (1964), that can be considered as a résumé of both "The Chemical Bond" and "Valence", providing more compact information additionally, and illustrated with a vivid graphical content. Gray's volume can be considered the connection, possibly the missing link, between the chemical ideas of Pauling and Coulson and the rise of modern quantum chemical knowledge schematized in Gray's book.

2.2. Advances up to Nowadays

As one could imagine, theoretical chemists have not forgotten the structure of chemical bonds in modern times. The continued interest in the subject proposed by Pauling has triggered many ideas related to the nature of the chemical bond. One was Mulliken's effort [12] to obtain information about atomic and bond densities from the first-order electronic density. Innumerable pieces of literature have followed Mulliken's pioneering work, for example, reference [13]. According to the recent literature, such initial efforts have not been forgotten, even though the early ideas of the atomic charges have been extended to some reference calculations, which might be as erroneous as the considered less accurate ones, as shown in reference [14].

A titanic effort after Mulliken's, developed as a scientific crusade by the author, corresponds to the theory of atoms in molecules of Bader [15]. Bader's theoretical development, mainly based on the properties of the density function gradient and Hessian, has been quite accepted by quantum chemists. Possibly because Bader's proposals allow the publication of nice images of molecular structures and visualizing molecular electronic density surroundings permits spare thousands of words. Anyhow, in Bader's theory, besides informing about atoms and bonds within a molecule provided by the topology of the density function and their first derivatives, resultant information can be visualized with nice graphical pictures to reveal where one can expect the appearance of a bond in a molecule.

However, a published counter-example [16] shows that some inaccurate or incomplete information might be issued from Bader's or similar analyses.

Yet, this is a general problem in many other theoretical chemistry subjects, where a seemingly general theoretical setup presents some instances that destroy the pretended general application.

Despite these problems, contemporary followers of Bader's ideas have also reported efforts to apply Bader's theory to QSPR and molecular design [17].

Other attempts to clarify the chemical ideas about bonds need to be mentioned. Mezey's concepts, with the description of density function shape analysis [18] and the holographic electron density theorem [19], constitute a clever effort to understand the role of atomic entities within molecular structures. Additionally, the account of the Cooper and Ponec electron-hole analysis [20] could offer insight into the chemical bond question, similar to how Bader provides adequate pictures to back up their findings.

Finally, a 2014 revision of the chemical bond subject by Causá, Savin, and Silvi (see reference [21]) not only contains a complete historical introduction to the chemical bond universe but is accompanied by an exhaustive bibliographic survey, which is so wide that there is no need to be repeated here, and the readers who want more bibliographic information might peruse that work. Besides, this general paper presents a very in-depth description of several modern chemical bond interpreting tools, so in this sense, it is highly recommended as a sound introduction to the present discussion.

New procedures to describe and study chemical bonds steadily appear in the literature, as can be seen by studying a recent reference [22], which can be considered in the present paper's track. Other notions around chemical bonding are constantly published on the same path, like the recent paper in reference [23] following the modern-day fashion of quantum entanglement and entropic aspects of the density function.

2.3. The Nature of Chemical Thought: The Aromaticity Concept as an Ill-defined Example in Modern Times

Someone has already commented about how mainstream chemists work and proceeded to envisage their thinking about the future of chemistry and how the structure of molecules and their properties shall be described. Then, perhaps the ideas we try to develop are repeated, most probably in our way, but possibly imaging previously dispersed discussions of which we are unaware. If these notions are pristine, much better; if not, we assume that they can be added to some previous ones to enrich, in any case, the ways of the usual chemical endeavor.

When one seeks to grasp the essence of the development of thoughts in old and new papers, what can surprise readers of chemical lore at any level is the *lack of generalizing power* of both the initial purposes and the conclusions of chemical bond studies. Many broad-looking papers rely on the study of very narrow problems, usually born from anomalies that can perhaps be attributed to some initial theoretical setup or deeply depend on the algorithms used to solve Schrödinger's equation.

One of the well-known theories about the chemical bond can be used as an example. One can refer to the so-called QTAIM or quantum theory of atoms in molecules [15]. It constitutes a general way to study the role of atoms in molecular structures, the appearance of bonds, and other cherished chemical ideas, such as electron lone pairs, … However, as already mentioned, some doubts about the general apparent picture of QTAIM have been described; see reference [24] for more details, showing that even an intended general theoretical structure in chemistry cannot be fully considered void of particular incongruences, logical traps, and paradoxes.

A recent publication on a subject that has generated an unfathomable amount of printed paper, *aromaticity*, is a good example of how good chemists, devoted for a long time to publishing informative results about a specific topic, are behaving. We cannot say if the choral publication [25] we are referring to has had a whole consensus of all authors, as the final published result lacks some information, for example, reference [26], and a simple perusal leads the readers to some contradictory conclusions or vicious circles. The author chorus possibly ignores printed ideas that do not fit into theirs.

One can choose the paper mentioned earlier [25] as a clear example of how a chemical concept can be, with time, the subject of an enormous amount of literature, becoming a widespread, fuzzy set of studied molecular structures and remaining an obscure problem from its birth; while remaining in darkness through a new path of theoretical lore. It looks like the well-documented authors try not to solve the conundrum of the discussed subject by any means, despite the warnings of some clearly-minded publications, like Hoffmann's study on the aromaticity subject [27].

Such a panorama allows one to think that chemistry needs to adhere to some quantum chemical descriptions that can be inconsistent with the chemical way of describing molecular behavior and properties. Aromaticity, on the contrary, is among many other accepted ways to study molecules that are not completely attached to the quantum mechanical way to obtain the molecular properties; see, for example [28].

The main reason for this well-accepted but fuzzy chemical thought is the oblivion of the basic quantum mechanical rule when studying any submicroscopic system: only a molecular property attached to a well-defined Hermitian operator as an observable can be adequate and admitted.

This document aims to set a general, purely theoretical framework for studying molecular structures that do not rely on fuzzy chemical concepts and lack a basic and well-defined theoretical background and mathematical description.

In this sense, one can accept new developments that might not be attached to some "physical" object but can be employed as a variational addition to the well-known ones. Linear, like the LCAO-MO coefficients, and nonlinear, like the Gaussian-type orbitals (GTO) or the frozen atomic positions in the Born-Oppenheimer approximation [29].

2.4. The Quantum Mechanical Framework

The present study pretends to look at an aspect of molecular structure that, while intrinsic to the usual quantum-mechanical ideas, is not completely associated with local chemical bond concepts nurtured by chemists fond of the old 20th-century chemical lore.

A quantum mechanical submicroscopic object, like a molecule, according to quantum mechanics, has to be observed as a *unique* system without separation of the whole set of particles or parts that constitute the entity. This fact is not in complete accordance with the opinions about molecular behavior cherished by chemists at all times, much less with the usual models with which molecules are represented when this paper is written.

Thus, the usual discussion about the chemical bond does not need to appear under the theoretical wave function description associated with a quantum-mechanical perspective. The chemical bond concept is still a lively subject because any chemists, experimental or theoretical, when discussing the nature of the chemical bond, visualize some mental image, essentially made by two (sometimes three or four, in case the actors are ambitious) interacting atoms located at some distance(s), and involving from one [30] to several electrons as if they were isolated from the bulk molecular structure.

Now, it is obvious that a molecular system is usually a stable or unstable set of many interacting atoms, which can be associated with a quantum mechanical wave function describing the whole molecule without the possibility of separating their elements, except in some well-defined approximate cases, processes, or simplifying circumstances.

One of the most important of these situations, which permits the separation of the nuclear wave function from the electronic one, was proposed in a 1927 paper describing the so-called Born-Oppenheimer theorem [29]. This almost centennial paper demonstrates that the wave function of an entire molecular particle structure, electrons, and nuclei could be separated into the nuclear and the electronic parts without significant loss of accuracy. However, the resultant wave function and all the attached observables must be considered an approximation depending on the atomic coordinates. These shall be considered embedded parametric constants contained in the system's wave function and the correct observables.

The Born-Oppenheimer theorem might be explained briefly by admitting that the nuclear masses are measured as being around three or more orders of magnitude larger than the electron mass. Consequently, the nuclear kinetic energies are almost negligible in front of the electronic kinetic energy values. This is the usual way molecular electronic wave functions and energies are obtained nowadays, considering the nuclear frame frozen in the three-dimensional Euclidian space. In such a nuclear framework, the immobile nuclear charges generate the electrostatic potential where the electronic cloud interacts and yields what can be called the molecular structure.

Since Born and Oppenheimer's 1927 paper, almost all the molecular structure computations one can find in the literature or obtain with available computer codes are performed under such a simplification. Therefore, the Born-Oppenheimer approximation is supposed to hold in the present study. The nuclei are considered frozen in space positions, occupying well-defined coordinates in three-dimensional Euclidean space. Accepting such a condition does not interfere with or impair the development of the main objective of the present discussion.

Given these considerations, one might talk about the chemical bond's collective nature rather than its usual diatomic individual form. This is the essence and purpose of the present study.

3. On the Description of Collective Chemical Bonds

The present paper delves into the ideas first developed by one of us in a previous publication [31], trying to present a well-defined background just sketched in this previous study.

Several things might be considered when adopting the Born-Oppenheimer approximation and assuming it is applicable in the present discussion.

From a radical theoretical point of view, it is basic to continue this writing development with the following facts and considerations, expressed in the present paragraph as subsections and further developed in forthcoming sections.

3.1. About Basis Functions Centering

Basis functions have been an active branch of quantum chemistry research, requiring much effort to evolve to its current status. A nice paper studies modern aspects of this interesting auxiliary quantum chemical information; see reference [32] for a modern example of the basis set development.

The basis function centers need not be atomic sites but can, in principle, be located at any point in the space surrounding a molecule. This point of view does not correspond to the protocol that the most popular and available quantum chemical codes adopt. The usual standard procedure is assigning simple up to highly sophisticated sets of basis functions to atomic centers only.

This broader point of view, even outside the actual mainstream molecular structure calculations, has a well-defined mathematical background, as several previous papers [4,33–38] have established.

In these studies, the so-called space enfoldment has been described, their properties set up, and some examples developed. The idea of a space enfoldment is simple: an enfolded space is considered a computational Euclidean space of three dimensions, $\mathbb{Q}^3$ say, where at each point, a function or a set of functions might be centered. Studies on Gaussian enfoldments, such as references [4] and [33], have been the starting point of such a modified classical space.

In the present description, though, one can imagine that the enfolding functions can be centered on the nodes of some network associated with molecular symmetry or, in principle, to any network arrangement.

The principal components of the quadrupole moment tensor can also define a set of ellipsoidal surfaces that can define a network of points located at the surface of several sheets where the enfolding function set can be located.

Enfolding functions might not be associated with the molecular atomic centers, where the basis functions are compulsively centered in the available program codes. They can even be chosen and disposed of on arbitrary constellation sites. Also, their positions can be associated with a constant set of coordinates or subject to non-linear variational procedures. Enfolding functions can be used together with the usual basis functions, providing an unending possibility of variationally improving the accuracy of the solutions of the Schrödinger equation.

Nevertheless, the pictures of enfolded spaces can be imagined in the following way. To begin, according to the usual procedures, one can admit that at the points where some atoms form the nuclear structure of a known molecule, the usual atomic basis sets are centered.

Such is the customary geometrical structure from which the molecular orbitals (MOs) were later constructed by linear combinations of atomic-centered functions named atomic orbitals (AO) in the old times. Constructing the basic LCAO MO methodology in this way.

In this habitual picture, if nothing else is prepared, the space enfolding might continue to be supposedly constructed in some simplistic way, assuming that at every point $\mathbf{R} \in \mathbb{Q}^3$, located in the space other than the atomic sites, there are centered just zero-type functions, $\theta(\mathbf{r}-\mathbf{R})$ namely, easily defined as:

$$\forall \mathbf{r} \in \mathbb{Q}^3 : \theta(\mathbf{r}-\mathbf{R}) = 0$$

In the same way, one can also suppose a practical enfolded space where some function is located in point $\mathbf{R}_\varepsilon$, just writing:

$$\exists\left(\mathbf{r} \wedge \mathbf{R}_\varepsilon \notin \left\{\mathbf{R}_A \middle| A = 1, \mathrm{R}_{Atoms}\right\}\right) \subset \mathbb{Q}^3 \rightarrow \exists\chi(\mathbf{r}-\mathbf{R}_\varepsilon)$$

and R_{Atoms} is the number of atomic centers of the studied molecular structure.

In this sense, such a definition admits that some enfoldment points possess a function different from the zero one.

These functions can be used as additional basis functions and, therefore, can also be associated with calculating the molecular wave function in the same manner as the usual atomic basis sets centered at the molecular atomic sites.

As described earlier, several criteria can be used to choose the enfoldment points; even the set of the enfoldment could be subject to variational procedures.

3.2. On the Set of Basis Functions Cardinality

The set of M MOs, obtained after solving the Schrödinger equation for some molecule in some specific state and conformation in the present work, will be considered complete. That is, the space generated by the MOs has or might have the same dimension as the space generated by the atomic and enfolded function basis set, which, if named by N, then one will accept that $M = N$, hold without exceptions.

This is the same as supposing that one will not have to deal with or use the so-called virtual orbitals, that is, the MOs, which appear as a consequence of the solution of the Schrödinger equation and are not occupied by electrons in the studied molecular state.

Virtual orbitals might be observed as a subproduct of the usual quantum mechanical calculations on molecular structures but, for simplification purposes, become non-existent in the present framework. Such a situation might appear weird in the usual computational lore. Still, it can be made possible when the complete set of occupied and virtual MOs, obtained in a primary computation, is used as a whole in a posterior complete multiconfigurational structure involving all the obtained MOs.

One must remember that current quantum chemical calculations rely on an $M \ll N$ arrangement, and the presence of virtual MOs orbitals is always true. Virtual orbitals might be considered a collateral subproduct of the solution of the Schrödinger equation, produced by the excess of atomic basis functions connected with the usual wave function computational procedures.

Therefore, virtual MOs will be accepted as nonexistent to have an ideal setup in the present development. This is the same as considering that every MO orbital is occupied by a fraction of the total electronic cloud, as it occurs when multiconfigurational wave function calculations are performed.

3.3. Enfolding Spaces, Basis Sets, and Large Molecules

Basis sets in the general case that one might supposedly use here to construct MOs can be associated with a number R of several enfolding loci: $\left\{\mathbf{R}_A | A=1,\mathrm{R}\right\}$, say. At each point $\mathbf{R}_A$, a set of β_A basis functions is supposedly centered:

$$\left\{\chi_{A\mu}\left(\mathbf{r}-\mathbf{R}_A\right) | \mu=1,\beta_A | A=1,\mathrm{R}\right\}$$

thus, in this setup, the total number of basis set functions, *N*, becomes:

$$N=\sum_{A=1}^{\mathrm{R}}\beta_A$$

and to do not make still more complex the present construction, one does not consider that every function $\chi_{A\mu}$ can also be constructed as a linear combination of atomic-optimized functions.

Here, R represents now the *total* number of centers where basis set functions are sitting. Thus, one can suppose that this number of centers is a sum of the atomic plus the enfolding centers.

Then, through this picture, every MO can be built by a precise linear combination of the chosen basis set, that is:

$$\forall I=1,M : |I\rangle=\sum_{A=1}^{\mathrm{R}}\sum_{\mu=1}^{\beta_A}C_{I;A\mu}\chi_{A\mu}\left(\mathbf{r}-\mathbf{R}_A\right) \qquad (1)$$

where the coefficient set $\left\{C_{I;A\mu} | I=1,M | A=1,\mathrm{R} : \mu=1,\beta_A\right\}$ is a variational set of parameters that must be computed in each case of study.

Again, one must remember that the basis functions can now be centered at a set of points: $\left\{\mathbf{R}_A | A=1,\mathrm{R}\right\}$, some of which might not necessarily coincide with the atomic centers.

Still, in large molecular structures like proteins, polymers, liquids, or crystals, the basis set atomic centers acquire the characteristic of very dense partial enfoldments because of the large number of atomic centers involved.

Due to the atomic center density, enfolding might not appear necessary in these cases, but it can be as relevant as in simpler molecular structures. For instance, one can choose a systematic enfolding, where the centers of charge or mass between every pair of atoms can be used as enfolding sites.

For example, one can think about a globular protein to imagine the basis set of atomic centers as a space enfoldment. However, this basis set display can be transformed into an even denser enfolding using basis functions located at the middle points between every two atoms or denser, centering more basis functions at the centroid of every triangle made by every three atoms, and so on...

3.4. The Charge Distribution in Enfolding Spaces

Such freedom of choosing the locations, where the basis sets are centered in the $\mathbb{Q}^3$ Euclidian space, also transforms the problem of the atomic charge density location into a completely different one. As one can imagine, the total molecular number of electrons will become dispersed within the molecular and atomic centers, as the space enfoldment will be non-coincident with atomic positions.

The enfolding possibility generates a general situation that does not correspond to the usual chemical ideas about where atomic charges might be located. It adds more controversial elements to the long-lasting discussion about how atomic charges can be calculated and measured in quantum chemistry.

3.5. The First-Order Density Function

Thus when $M=N$, this is the same as considering that the first-order density function is defined as the result of a multiconfigurational expression involving *all* the MOs functions issued from a preliminary computational procedure. Then, one can write the first-order density function as:

$$\rho(\mathbf{r})=\sum_{I=1}^{M}\sum_{J=1}^{M}\Gamma_{IJ}\,|I_o\rangle\langle J_o|$$

the MO set $\{|I_o\rangle|I=1,M\}$ might correspond to an initial set obtained from the solution of the Schrödinger equation for the system in study. In case the $(M\times M)$ symmetric coefficient matrix: $\mathbf{\Gamma}=\{\Gamma_{IJ}\,|I,J=1,M\}$, is expressed via its canonical decomposition:

$$\Gamma_{IJ}=\sum_{K=1}^{M}\gamma_K U_{KI}U_{JK}$$

where the matrix: $\mathbf{U}=\{U_{IJ}\,|I,J=1,M\}$ is orthogonal to the vast majority of cases and $\{\gamma_K\,|K=1,M\}$ corresponds to the eigenvalues of the matrix $\mathbf{\Gamma}$. Note that even if complex coefficients can play a role in defining MOs as in the equation (1), a real representation has been chosen here to simplify the writing of formulae in this discussion. Therefore, the matrix **U** can be chosen as orthogonal, not unitary. Then, one can write:

$$\begin{aligned}\rho(\mathbf{r})&=\sum_{I=1}^{M}\sum_{J=1}^{M}\left(\sum_{K=1}^{M}\gamma_K U_{KI}U_{JK}\right)|I_o\rangle\langle J_o|\\&=\sum_{K=1}^{M}\gamma_K\left(\sum_{I=1}^{M}U_{KI}\,|I_o\rangle\right)\left(\sum_{J=1}^{M}\langle J_o|U_{JK}\right)\\&=\sum_{I=1}^{M}\gamma_I\,|I\rangle\langle I|=\sum_{I=1}^{M}\gamma_I\rho_I(\mathbf{r})\end{aligned}$$

One must also be aware that what can be named as the *occupation numbers* set: $\{\gamma_I\,|I=1,M\}\subset\mathbb{Q}^+$ has to be a rational, positive set, not a natural number set, as is usual in a monoconfigurational framework calculation. The reason for this numerical characteristic of the occupation numbers corresponds to the fact that these quantities shall be obtained via a computational procedure. Then, from the point of view of practical proceedings, the results of these calculations must be considered rational, not real.

3.6. The Minkowski Norm of the Density Function

Moreover, the Minkowski norm of the first-order density function yields the number of electrons of the studied molecular system:

$$\langle\rho\rangle=\sum_{I=1}^{M}\gamma_I\langle\rho_I\rangle=\sum_{I=1}^{M}\gamma_I=N_e$$

this is so because the MOs set is considered normalized without loss of generality:

$$\forall I=1,M:\langle\rho_I\rangle=\int_D\rho_I(\mathbf{r})\,d\mathbf{r}=\langle I|I\rangle=1 \qquad (2)$$

and then one can supposedly admit that the whole MOs set is orthonormalized, that is:

$$\forall I,J=1,M:\langle I|J\rangle=\delta_{IJ}$$

4. First-Order Density Function as a Linear Combination

These previous definitions and deductions are analogous to constructing the (first-order) density function as a linear combination of a set of MOs density functions. A linearly independent basis set of M functions, which can be easily defined as:

$$I = 1, M : \rho_I(\mathbf{r}) = |I\rangle\langle I| \tag{3}$$

Because the MOs density set: $\mathrm{P} = \left\{\rho_I(\mathbf{r}) \middle| I = 1, M\right\}$ constitutes a linearly independent function set generating an M-dimensional semispace [38]. The set P can be considered as linearly independent because of the equation:

$$\sum_{I=1}^{M} \alpha_I \, |I\rangle\langle I| = \sum_{I=1}^{M} \alpha_I \rho_I(\mathbf{r}) = \theta(\mathbf{r}) \rightarrow \forall I = 1, M : \alpha_I = 0$$

where $\theta(\mathbf{r})$ is the zero-function centered at the origin:

$$\forall \mathbf{r} \in \mathbb{Q}^3 : \theta(\mathbf{r}) = 0$$

Whenever some coefficient is non-zero, say:

$$\exists \alpha_J \neq 0 \rightarrow \rho_J(\mathbf{r}) = \alpha_J^{-1} \sum_{I \neq J}^{M} \alpha_I \rho_I(\mathbf{r})$$

then the set P will be linearly dependent, contradicting the initial linear independence hypothesis.

Thus, the set P of MOs density functions is entitled to be a basis for constructing the first-order density function.

4.1. The Role of the Basis Set Centers

When considering the equation (1) in the expression (3) one can write:

$$\forall I = 1, M : \rho_I(\mathbf{r}) = |I\rangle\langle I| = \sum_{A=1}^{\mathrm{R}} \sum_{B=1}^{\mathrm{R}} \sum_{\mu=1}^{\beta_A} \sum_{\nu=1}^{\beta_B} C_{I;A\mu} C_{I;B\nu} \left| \chi_{A\mu}(\mathbf{r} - \mathbf{R}_A) \right\rangle \left\langle \chi_{B\nu}(\mathbf{r} - \mathbf{R}_B) \right| \tag{4}$$

and using the compact notation for the linear combinations to simplify the above expression:

$$\forall I = 1, M \wedge \forall A = 1, \mathrm{R} : \left| \varphi_{IA}(\mathbf{r} - \mathbf{R}_A) \right\rangle = \sum_{\mu=1}^{\beta_A} C_{I;A\mu} \left| \chi_{A\mu}(\mathbf{r} - \mathbf{R}_A) \right\rangle$$

it is obtained for each MO density:

$$\forall I = 1, M : \rho_I(\mathbf{r}) = \sum_{A=1}^{\mathrm{R}} \sum_{B=1}^{\mathrm{R}} |\varphi_{IA}\rangle\langle\varphi_{IB}|$$

thus, the dependency of *all* the basis set centers in the expression of each MO density is evident.

In the same way, the total density might be expressed in terms of the enfolding centers, writing:

$$\rho(\mathbf{r}) = \sum_{I=1}^{M} \gamma_I \sum_{A=1}^{\mathrm{R}} \sum_{B=1}^{\mathrm{R}} |\varphi_{IA}\rangle\langle\varphi_{IB}| = \sum_{A=1}^{\mathrm{R}} \sum_{B=1}^{\mathrm{R}} \sum_{I=1}^{M} \gamma_I \, |\varphi_{IA}\rangle\langle\varphi_{IB}| = \sum_{A=1}^{\mathrm{R}} \sum_{B=1}^{\mathrm{R}} \rho_{AB}(\mathbf{r})$$

while the set $\left\{\rho_{AB}(\mathbf{r}) \middle| A, B = 1, \mathrm{R}\right\}$ of enfolding center densities is defined now by:

$$\forall A, B = 1, \mathrm{R} : \rho_{AB}(\mathbf{r}) = \sum_{I=1}^{M} \gamma_I \, |\varphi_{IA}\rangle\langle\varphi_{IB}| \tag{5}$$

4.2. The Enfolding Centers Density Bond Matrix

Arriving at this point, one can admit that the equation (5) defines a symmetric $(\mathrm{R} \times \mathrm{R})$ matrix, which can be easily described by:

$$\mathbf{\Delta} = \left\{ \Delta_{AB} = \rho_{AB}(\mathbf{r}) | A, B = 1, \mathrm{R} \right\}$$

One can call such a matricial function structure a *density bond matrix*.

It is interesting to note that the complete sum of the elements of the matrix $\mathbf{\Delta}$ yields the first-order density matrix that has been discussed so far; therefore, it can be set as:

$$\langle \mathbf{\Delta} \rangle = \sum_{A=1}^{\mathrm{R}} \sum_{B=1}^{\mathrm{R}} \Delta_{AB} = \rho(\mathbf{r})$$

Noting that the elements of the matrix $\mathbf{\Delta}$ are functions of the electron position vector $\mathbf{r}$, which, if needed, one can explicitly write as: $\mathbf{\Delta}(\mathbf{r})$, thus one can also obtain:

$$\langle\langle \mathbf{\Delta} \rangle\rangle = \int_D \langle \mathbf{\Delta}(\mathbf{r}) \rangle \, d\mathbf{r} = \left\langle \int_D \mathbf{\Delta}(\mathbf{r}) \, d\mathbf{r} \right\rangle = N_e$$

The matrix $\mathbf{\Delta}$ construction becomes similar to the density partitions, already mentioned, due to Mulliken [12] and the point of view of Roby [39].

However, the differences correspond to the structure we admitted in the MOs formalism and, more importantly, apart from the presence of atomic centers, where basis sets are usually centered, allowing the inclusion of general enfolding centers.

4.3. Mulliken Populations in Atomic and Enfolding Centers

Thus, one can use Mulliken-like ideas and describe center densities as complete sums of the columns or rows of the $\mathbf{\Delta}$ matrix. That is, constructing the columns of the enfolding centers' matrix as a column vector:

$$\forall A = 1, \mathrm{R} : |\boldsymbol{\rho}_A\rangle = \left\{ \rho_{AB}(\mathbf{r}) | B = 1, \mathrm{R} \right\} \leftrightarrow \mathbf{\Delta} = \left(|\boldsymbol{\rho}_A\rangle | A = 1, \mathrm{R} \right)$$

then, the complete sum of each of these rows can be interpreted as the enfolding centers' density functions:

$$\forall A = 1, \mathrm{R} : \rho_A(\mathbf{r}) = \langle |\boldsymbol{\rho}_A\rangle \rangle = \sum_{B=1}^{\mathrm{R}} \rho_{AB}(\mathbf{r})$$

and recovering Mulliken's definition, the integral:

$$\forall A = 1, \mathrm{R} : Q_A = \langle\langle \rho_A \rangle\rangle = \int_D \langle \boldsymbol{\rho}_A(\mathbf{r}) \rangle \, d\mathbf{r}$$

describes the enfolding center population set $\left\{ Q_A | A = 1, \mathrm{R} \right\}$, which, summed up, provides again the number of electrons:

$$\sum_{A=1}^{\mathrm{R}} Q_A = N_e$$

Contrary to the usual quantum chemical lore, the populations of the enfolding centers include atomic and out-of-atom enfolding centers.

If this is the case, the sum of *atomic* populations will never be equal to the total number of electrons but a *fraction* of it. The remaining population segment can be ascribed to the pure enfolding electronic charge distribution. This can be written like:

$$\sum_{I=1}^{\mathrm{R}_{Atoms}} Q_I = N_{Atoms} < N_e$$

to stress the role of non-atomic enfolding centers.

One can now propose that all the discussions about the descriptions of molecular electronic populations in the current literature so far lack the possible dilution of electron density in the atomic neighborhood constituting the molecular enfolding chosen.

In this sense, the atomic populations provided as an output of popular quantum chemical codes are calculated, no matter how, as if *a priori* the electronic density is *completely localized* in the atomic centers, which might appear as a false statement when allowing the extension of basis functions in an extra enfolding structure.

Without a deep and honest discussion about the nature of molecular electronic clouds, one can ask if such a general situation will be accepted without further research.

4.4. The Nature of the Molecular Bonds

This previous discussion in the company of the density bond matrix $\mathbf{\Delta}$ opens the way to consider, no matter whether to face small or large molecular systems if it is impossible to systematically speak of three or more center bonds, up to consider a molecule as a *collective* bond involving all the molecular atoms and electrons. Even including the surrounding enfolding space where some basis set functions might be centered.

Such a point of view looks far from the chemical lore adopted from the early birth and posterior evolution of quantum chemistry. However, in many aspects, the initial and modern quantum chemical points of view have not tried to show new descriptions of molecular landscapes but have adapted theoretical computational results to chemical tradition.

Even in recent papers, chemical descriptions based on experimental data use theoretical and computational results to back up the bond figures encountered. Reference [30], where a one-electron chemical bond between two carbon atoms has been announced, might be an example of the unmoving trend in chemical bonds, even if an iconoclastic novelty flavor emanates from the paper. Using the number of electrons to define a diatomic bond is not correct in an absolute mode because a chemical bond can occur, like one has been commenting, involving three atoms or more, even at the scale of the whole molecular structure atomic cluster.

For instance, the density bond matrix $\mathbf{\Delta}$ can be employed to consider the electronic cloud around all the atomic (involving enfolding centers, if needed) dyads, triads, or groups of several atoms in a given molecular structure.

Choosing the center triads, as a dyad is usually taken to define classical diatomic bonds, the submatrices of the matrix $\mathbf{\Delta}$ define a set of triads with the form:

$$\forall \{I < J < K = 1, R\} : \mathbf{\Delta}_{IJK} = \begin{pmatrix} \rho_{II} & \rho_{IJ} & \rho_{IK} \\ \rho_{JI} & \rho_{JJ} & \rho_{JK} \\ \rho_{KI} & \rho_{KJ} & \rho_{KK} \end{pmatrix} \qquad (6)$$

considering that these matrices are symmetric, so: $\rho_{IJ} = \rho_{JI}$, and so on... Also, for application purposes, the three subindices provide matrices equally descriptive upon subindex permutations, that is:

$$\mathbf{\Delta}_{IJK} = \mathbf{\Delta}_{KIJ} = \mathbf{\Delta}_{KJI} = \ldots$$

Thus, any of these submatrices permit the study of the three-atom bonding systematic description, which has not been used in this manner in the literature as far as we know.

This is because it doesn't conform to the simplified chemical reasoning of two-atom bonding. As defined in the equation (6) above, the whole set of three-center submatrices: $\{\mathbf{\Delta}_{IJK} | I < J < K = 1, R\}$ can be manipulated like the whole-density bond matrix and might provide interesting information about local electronic density.

In the same way, such partition of the density bond matrix can be used to define higher intramolecular matrix structures, even involving both atoms and enfolding centers.

However, continuing in this way, the discussion will become reiterative, and then it can be stopped here to be further extended in forthcoming research.

4.5. The Perron-Frobenius Theorem (PFT)

The theorem mentioned in this section states that square positive matrices, with real positive definite entries, possess a maximal simple positive-definite eigenvalue and an attached eigenvector with positive coefficients; see references [40–42] for example.

One can use the PFT for the recently defined bond density matrix, which is symmetric, that is:

$$\mathbf{\Delta}^T = \mathbf{\Delta} \leftrightarrow \forall A, B = 1, R : \Delta_{BA} = \Delta_{AB}$$

Suppose one can be certain that $\mathbf{\Delta}$ it is a positive matrix. In that case, one can be sure that a positive definite eigenvalue, as a function of the electron position, certainly exists and is associated with a positive definite eigenvector.

Note that, by construction, the elements of the matrix $\mathbf{\Delta}$ depend on the electron coordinates; therefore, its eigenvalues will also be dependent on them.

4.5.1. Diatomic Molecules

It is easy to study the case of a diatomic molecule with a void enfolding space. The matrix $\mathbf{\Delta}$ and its polynomial will be in this simplified case:

$$\mathbf{\Delta} = \begin{pmatrix} \rho_{AA} & \rho_{AB} \\ \rho_{BA} & \rho_{BB} \end{pmatrix} \to (\rho_{AA} - \lambda)(\rho_{BB} - \lambda) - (\rho_{AB})^2 = 0$$

using the fact that: $\rho_{AB} = \rho_{BA}$. Therefore, one can write:

$$\begin{aligned} &\lambda^2 - (\rho_{AA} + \rho_{BB})\lambda + Det|\mathbf{\Delta}| = 0 \to \\ &\lambda = \frac{1}{2}\left((\rho_{AA} + \rho_{BB}) \pm \sqrt{(\rho_{AA} + \rho_{BB})^2 - 4Det|\mathbf{\Delta}|}\right) \to \\ &\lambda = \frac{1}{2}\left((\rho_{AA} + \rho_{BB}) \pm \sqrt{(\rho_{AA} - \rho_{BB})^2 + (2\rho_{AB})^2}\right) \end{aligned} \quad (7)$$

where only the plus sign can yield the maximal root.

For homonuclear diatomic molecules, the equation (7) above transforms into the simpler expression:

$$\lambda_{\pm} = \rho_{AA} \pm \rho_{AA'} \quad (8)$$

However, as in this last case, the first-order density can be written as:

$$\rho(\mathbf{r}) = 2(\rho_{AA} + \rho_{AA'}) \to \rho(\mathbf{r}) = 2\lambda_{+}$$

then, observing which kind of Perron-Frobenius eigenvalue one can obtain in slightly complicated cases seems interesting.

4.5.2. Triatomic Molecules

Suppose three equal atomic centers appear in the structure of an equilateral triangle. In that case, the matrix $\mathbf{\Delta}$ can be written in the following form since one can expect that the equality $\rho_{A'A} = \rho_{AA'}$, holds:

$$\mathbf{\Delta} = \begin{pmatrix} \rho_{AA} & \rho_{AA'} & \rho_{AA'} \\ \rho_{AA'} & \rho_{AA} & \rho_{AA'} \\ \rho_{AA'} & \rho_{AA'} & \rho_{AA} \end{pmatrix} = \rho_{AA}\mathbf{I} + \rho_{AA'}\mathbf{T}$$

where $\mathbf{I} + \mathbf{T} = \mathbf{1}$. The unity matrix: $\mathbf{1} = \{1_{IJ} = 1 | \forall I, J\}$, has been used to have a well-defined description of the two Hückel matrices: $\mathbf{I} = \{\mathrm{I}_{IJ} = \delta_{IJ} | \forall I, J\}$ the diagonal unit matrix and, then: $\mathbf{T} = \mathbf{1} - \mathbf{I} = \{\mathrm{T}_{IJ} = 1 - \delta_{IJ} | \forall I, J\}$.

Therefore, the eigenvalues of the matrix $\mathbf{\Delta}$ can be written as:

$$\mathbf{\Delta x} = \lambda \mathbf{x} \to \mathbf{Tx} = \left[\left(\rho_{AA'} \right)^{-1} \left(\lambda - \rho_{AA} \right) \right] \mathbf{x} = \mu \mathbf{x}$$

thus, the Perron-Frobenius eigenvalue can also be associated with $\mu_{\max}$, the maximal eigenvalue of the matrix $\mathbf{T}$, and so:

$$\lambda = \rho_{AA} + \mu_{\max} \rho_{AA'}$$

but in this case, one can use the Hückel result of $\mu_{\max} = 2$; thus, the Perron-Frobenius eigenvalue could be written as:

$$\lambda = \rho_{AA} + 2\rho_{AA'}$$

therefore, the total first-order density function can be expressed as:

$$\rho(\mathbf{r}) = 3\rho_{AA} + 6\rho_{AA'} = 3\lambda$$

However, as the number of atomic centers in this case is $\mathrm{R}=3$, one can see that the conjecture for atomic clusters of simplex type geometry without enfolding:

$$\rho(\mathbf{r}) = \mathrm{R}\lambda$$

seems plausible.

Perhaps the most interesting feature in this section is the relationship between the bond density matrix, Hückel's theory, and the Perrin-Frobenius eigenvalue via the PFT. En passant, we note that in our density mathematical structure, the density and its partition in two-center form can result from a sophisticated computational procedure, which paradoxically seems related to the simplistic Hückel theoretical framework via the PFT.

4.5.3. Diatomic Molecules with an Enfolding Center

In this case, one can consider a homonuclear diatomic molecule with an enfolding point situated symmetrically at the same distance of both atoms. The density bond matrix $\mathbf{\Delta}$ can be written as:

$$\mathbf{\Delta} = \begin{pmatrix} \rho_{AA} & \rho_{AA'} & \rho_{AO} \\ \rho_{AA'} & \rho_{AA} & \rho_{AO} \\ \rho_{AO} & \rho_{AO} & \rho_{OO} \end{pmatrix}$$

with the additional enfolding center identified with the subindex O.

Thus, the roots of the secular determinant in this case can be written as:

$$\begin{aligned} \lambda_0 &= \rho_{AA} - \rho_{AA'} \\ \lambda_\pm &= \frac{1}{2}\left[\left(\rho_{AA} + \rho_{AA'} + \rho_{OO} \right) \pm \sqrt{\left(\rho_{AA} + \rho_{AA'} - \rho_{OO} \right)^2 + 8\rho_{AO}^2} \right] \end{aligned} \tag{9}$$

This result clearly shows the enfolding point's influence on a diatomic molecule's electron distribution. The eigenvalues in the equation (9) can be compared with those provided in the equation (8). The lower diatomic eigenvalue remains invariant, but the Perron-Frobenius eigenvalue becomes perturbed by the enfolding center densities.

Note that the eigenvalues $\lambda_\pm$, when the enfolding center is absent, transform into the Perron-Frobenius eigenvalue for the homonuclear molecule plus a null remnant value.

Also, one can see that when the enfolding point is such that one can consider the bond density element as the zero function, that is:

$$\rho_{AO}^2 \left(\mathbf{r} - \mathbf{R}_O \right) \approx \theta \left(\mathbf{r} - \mathbf{R}_O \right)$$

then one can write the eigenvalues $\lambda_\pm$ as:

$$\lambda_{\pm} \Rightarrow \begin{cases} \lambda_{+} = \rho_{AA} + \rho_{AA'} \\ \lambda_{-} = \rho_{OO} \end{cases}$$

so, the enfolding point does not influence the Perrin-Frobenius eigenvalue.

5. MOs Densities as a Quantum Polyhedron: Density Centroid

The set of MOs densities: $\mathrm{P} = \{\rho_I(\mathbf{r}) | I = 1, M\}$ might now be observed as a *quantum MOs polyhedron* located in an infinite-dimensional semispace; see reference [43] for more details.

Such a polyhedron made of infinite-dimensional functions as vertices might be called a *polytope*, and the generated semispace, a vector space where no negative scalars are used, is an *orthant*. However, the present authors decided to keep this initial notation because it was employed in so many previous publications (see, for example, references [43–51]) that it would be confusing to change it.

The quantum MOs polyhedron P vertices are the MOs density functions themselves. With them, the MOs polyhedron centroid can be constructed by a uniform linear combination of the MOs density functions as:

$$\rho_C(\mathbf{r}) = M^{-1} \sum_{I=1}^{M} \rho_I(\mathbf{r})$$

Thus, the centroid function might be considered as nothing else than an arithmetic mean of the quantum polyhedron vertices.

Remembering the unit Minkowski norm of the MOs density functions as shown in the equation (2), then the Minkowski norm of the quantum MOs polyhedron centroid function yields:

$$\langle \rho_C \rangle = \int_D \rho_C(\mathbf{r})\, d\mathbf{r} = M^{-1} \sum_{I=1}^{M} \langle \rho_I \rangle = M^{-1} M = 1$$

In the sense of this last property, the centroid function is a probability density function constructed so that all the MOs density basis set has the same coefficient, coinciding with the inverse of the number of vertices of the quantum MOs polyhedron.

5.1. MOs Densities Origin Shift

The set P of MOs densities, the quantum MOs polyhedron, can be *origin-shifted* so that the new quantum polyhedron, obtained from the original MOs polyhedron, has a centroid equal to zero. This origin shift is easily made in the following way shown below, with the result about the shifted centroid as:

$$\begin{aligned} \forall I = 1, M : \tau_I(\mathbf{r}) = \rho_I(\mathbf{r}) - \rho_C(\mathbf{r}) \Rightarrow \tau_C(\mathbf{r}) &= M^{-1} \sum_{I=1}^{M} \tau_I(\mathbf{r}) \\ &= M^{-1} \sum_{I=1}^{M} \rho_I(\mathbf{r}) - M^{-1} \sum_{I=1}^{M} \rho_C(\mathbf{r}) \\ &= \rho_C(\mathbf{r}) - M^{-1} M \rho_C(\mathbf{r}) = \theta(\mathbf{r}) \end{aligned}$$

where $\theta(\mathbf{r})$ is the zero function. Thus, one can write: $\tau_C(\mathbf{r}) = \theta(\mathbf{r})$, and the set of shifted functions or origin shifted quantum MOs polyhedron will be described by the function set: $\mathrm{T} = \{\tau_I(\mathbf{r}) | I = 1, M\}$.

5.2. Origin Shifted MOs Densities

Therefore, the set T of origin-shifted functions corresponds to a quantum polyhedron with vertices, which are no longer positive definite nor constituting an independent set of M functions but a linearly dependent set generating a subspace of dimension $M-1$.

This can be easily seen because one can write the equation below, showing the linear dependence of the set T:

$$\sum_{I=1}^{M}\alpha_I\tau_I(\mathbf{r})=\theta(\mathbf{r})\Rightarrow\exists\alpha_K\neq 0$$

but if the set is linearly independent, then:

$$\theta(\mathbf{r})=\sum_{I=1}^{M}\alpha_I\tau_I(\mathbf{r})\Rightarrow\forall I=1,M:\alpha_I=0$$

however, using the vector of the coefficients and the complete sum of these, defined like: $\boldsymbol{\alpha}=\{\alpha_I\,|I=1,M\}\wedge\langle\boldsymbol{\alpha}\rangle=\sum_{I=1}^{M}\alpha_I$, one obtains in this case:

$$\begin{aligned}\theta(\mathbf{r})&=\sum_{I=1}^{M}\alpha_I\tau_I(\mathbf{r})=\sum_{I}^{M}\alpha_I\rho_I(\mathbf{r})-\left(\sum_{I}^{M}\alpha_I\right)\rho_C(\mathbf{r})\\&=\sum_{I}^{M}\alpha_I\rho_I(\mathbf{r})-\langle\boldsymbol{\alpha}\rangle\rho_C(\mathbf{r})\\&=\sum_{I}^{M}\alpha_I\rho_I(\mathbf{r})-\langle\boldsymbol{\alpha}\rangle M^{-1}\sum_{I}^{M}\rho_I(\mathbf{r})\\&=\sum_{I=1}^{M}\left(\alpha_I-\langle\boldsymbol{\alpha}\rangle M^{-1}\right)\rho_I(\mathbf{r})\end{aligned}$$

therefore, being the MOs density set linearly independent, then it must necessarily hold that:

$$\begin{aligned}&\forall I=1,M:\alpha_I-\langle\boldsymbol{\alpha}\rangle M^{-1}=0\rightarrow\alpha_I=\langle\boldsymbol{\alpha}\rangle M^{-1}\\&\rightarrow\alpha_I=M^{-1}\sum_{J=1}^{M}\alpha_J=M^{-1}\langle\boldsymbol{\alpha}\rangle\Rightarrow\forall I:\alpha_I=M^{-1}\langle\boldsymbol{\alpha}\rangle\end{aligned}$$

and this means that it will only hold in case that all the coefficients are equal, for example:

$$\forall I=1,M:\alpha_I=a\Rightarrow\langle\boldsymbol{\alpha}\rangle=Ma$$

The coefficients will be equal to a constant value a, and the mean arithmetic value of the same coefficients if the linear combination is the zero function. So, if some coefficient is non-zero:

$$\exists\alpha_K\neq 0\rightarrow\alpha_K-\langle\boldsymbol{\alpha}\rangle M^{-1}=\alpha_K-a\neq 0$$

this result contradicts the hypothesis; thus, the set T of origin-shifted MOs density functions must be linearly dependent.

5.3. The Geometrical Implication of Origin Shifted MOs Densities

From the geometrical point of view, the set T resumes any given molecular structure whose MOs density function set is known and transformed into a quantum polyhedron. In this manner, a molecule can be easily compared with another different structure or with states and conformers of itself [51].

Of course, the set T will depend on the type of molecule studied but will also be attached to the structure of the basis set used and where these functions are centered in three-dimensional space. Therefore, these conditions will influence the structure of the calculated MOs and, thus, the quantum MOs polyhedron.

The origin shifted set T constructed as described will be perfectly comparable to MOs results computed with different basis sets in any other or the same molecule.

6. How nearby is a Chemical Bond from another?

6.1. Quantum Similarity

Now that the definition of the density bond matrix and the origin-shifted densities have been discussed, one can devote some words to comparing the chemical bonds of molecular structures.

Such a prospect has to be schematically given because details about it might produce an excessive enlargement of this report.

The possible comparison quantum system involving two density functions was already described in an initial 1980 paper [52], where ideas from the still-infant AI were borrowed. This line of work is known as *quantum similarity*. The technique has evolved with time to include comparisons of an undefined number of molecules, leading to the development of collective distances theoretical background and algorithms in 2015 [53]. Many quantum similarity advances, generalizations, algorithms, and applications have been published in this time interval. Readers interested in this research can peruse the web under 'quantum similarity' identification words.

Resuming the main idea, though, of quantum similarity since 1980 corresponds to that, once known the density functions of two quantum systems written as: $\{\rho_A(\mathbf{r}),\rho_B(\mathbf{r})\}$, then the *similarity integral*, Z_{AB}, can be computed as the measure integral involving a positive definite Hermitian operator $\Omega(\mathbf{r}_1,\mathbf{r}_2)$:

$$Z_{AB}=\int_{D_1}\int_{D_2}\rho_A(\mathbf{r}_1)\Omega(\mathbf{r}_1,\mathbf{r}_2)\rho_B(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2 \qquad (10)$$

When the chosen operator is Dirac's delta function $\delta(\mathbf{r}_1-\mathbf{r}_2)$, then one can write:

$$Z_{AB}=\int_{D_1}\int_{D_2}\rho_A(\mathbf{r}_1)\delta(\mathbf{r}_1-\mathbf{r}_2)\rho_B(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2=\int_D\rho_A(\mathbf{r})\rho_B(\mathbf{r})\,d\mathbf{r} \qquad (11)$$

which is the result also used in reference [22]. Curiously enough, the authors of the mentioned publication ignore the extensive previous background to which his basic tool and discussion have to be related. This shows a similar characteristic of the already mentioned obliviousness also revealed by the authors of the aromaticity choral work [25] concerning a quantum similarity point of view.

The integral (11) can grasp how two electronic densities are related quantitatively. For example, defining the squared Euclidian distance:

$$\begin{aligned}D_{AB}^2&=\int_D\left|\rho_A(\mathbf{r})-\rho_B(\mathbf{r})\right|^2 d\mathbf{r}=\\&\int_D(\rho_A(\mathbf{r}))^2 d\mathbf{r}+\int_D(\rho_b(\mathbf{r}))^2 d\mathbf{r}-2\int_D\rho_A(\mathbf{r})\rho_B(\mathbf{r})\,d\mathbf{r}=\\&\mathrm{Z}_{AA}+Z_{BB}-2Z_{AB}\end{aligned} \qquad (12)$$

where the integrals involving the same density function $\{\mathrm{Z}_{AA},Z_{BB}\}$ are called *selfsimilarity* integrals. The distance in the equation (12) corresponds to a quantum dissimilarity measure in the wording of this AI-related context.

Other related similarity indices can be used once the similarity and selfsimilarity integrals are known; for example, references [54,55] provide more details.

6.2. Measuring the Differences in Triatomic Chemical Bonds

Suppose the density bond submatrix involving three arbitrary centers, as defined in the form of the equation (6): $\mathbf{\Delta}_{IJK}$. Choose another one arbitrarily involving a set of three alternative centers: $\mathbf{\Delta}_{ABC}$.

One can try to describe an algorithm for comparing both density submatrices that allows one to enlarge both the number of bond sets and the implied centers.

The first step is to obtain a new matrix that permits the calculation of the corresponding quantum similarity integrals associated with the chosen bond density functions.

A possible construction is to perform the *inward product* [56] of both submatrices. Inward products are also called matrix diagonal products and can be used in matrix algebra to transform vector and matrix sets into structures resembling scalars. In the present example, one can write:

$$\mathbf{\Theta}=\mathbf{\Delta}_{IJK} * \mathbf{\Delta}_{ABC}=\begin{pmatrix} \rho_{II}\rho_{AA} & \rho_{IJ}\rho_{AB} & \rho_{IK}\rho_{AC} \\ \rho_{JI}\rho_{BA} & \rho_{JJ}\rho_{BB} & \rho_{JK}\rho_{BC} \\ \rho_{KI}\rho_{CA} & \rho_{KJ}\rho_{CB} & \rho_{KK}\rho_{CC} \end{pmatrix}$$

and then one can compute the similarity integral of the resultant submatrix, taking into account that the first two subindices are symmetric and the same for the last two:

$$\mathbf{Z}_{IJK;ABC}=\int_D \mathbf{\Theta} d\mathbf{r}=\begin{pmatrix} Z_{IIAA} & Z_{IJAB} & Z_{IKAC} \\ Z_{IJAB} & Z_{JJBB} & Z_{JKBC} \\ Z_{IKAC} & Z_{JKBC} & Z_{KKCC} \end{pmatrix} \quad (13)$$

with the convention that:

$$Z_{PQRS}=\int_D \rho_{PQ}(\mathbf{r})\rho_{RS}(\mathbf{r})d\mathbf{r}$$

Finally, one can use a generic collective squared distance through the matrix (13):

$$D^2_{IJk;ABC}=Z_{IIAA}+Z_{JJBB}+Z_{KKCC}-2\left(Z_{IJAB}+Z_{IKAC}+Z_{JKBC}\right)$$

that might provide a way to compare three-center bonding between two such bonds within the same molecular structure or between two different molecular frames.

6.3. *The Measure of Intra- and Intermolecular Substructure Differences*

The previous paragraphs sufficiently describe the flexible and numerous ways that one can set up to compare subsets of enfolding centers within a molecule or between two or more molecular frames.

Using these calculations to discover the role of amino acid moieties in proteins seems an immediate application. How large the difference of the same set of atomic centers in diverse molecular frames can be another one that can shed light on the role of reactive environments in a set of different molecules bearing the same group of atoms. Applications appear to be almost without end.

Therefore, one can consider how a simple theoretical framework can become a large toolkit for tackling chemical problems without adhering to the frozen frame of the classical diatomic bond structure.

7. Resuming and Concluding

7.1. *Resuming*

Due to the general description described so far, the nature of molecular bonds is already depicted as a slightly ambiguous concept. This is so because even the simplest case of a diatomic molecule can be associated with some functions, which might not be centered at one of the two constituent atoms but anywhere in the Euclidian space surrounding the atomic centers.

One can consider an enfolded space [34] with appropriate enfolding functions and the molecular atomic centers in the appropriate space positions. One can contemplate calculating a simple diatomic molecule where the dimension M has been chosen extensively or is quite large compared with the nature of the molecular structure.

For instance, in addition to the usual basic sets of functions centered in the atoms along the diatomic molecular axis, a set of functions could be arranged following some *a priori* criterion arbitrarily chosen. This axial disposition can even be enlarged with functions belonging to a set of spheric, cylindrical, or conic surfaces surrounding the molecular axis or around the molecular atoms.

So, the conventional atomic basis function picture can be completely superseded by this kind of extra basis set function enfolding arrangements centered at some points of an arbitrary subjective, even random, chosen grid.

A slightly complicated computational structure in which the enfolding center coordinates are taken as extra variational parameters can enrich such arbitrariness.

7.2. On the Collective Nature of the Chemical Bond

If this can be imagined for a diatomic molecule, it can be set similarly, even in a more sophisticated way, around the pairs of atomic centers in larger molecules, no matter how large the number of atoms composing the molecular structure appears.

Therefore, seeking classical molecular bonds in the usual picture chemists have fabricated around molecular structures when quantum chemical calculations can be set up in enfolded spaces is a bit out of the question.

As the authors know, two examples of spherical functions are employed to perform molecular calculations. One is the old technique, FSGO by Frost, where only spherical Gaussian functions are employed to obtain molecular structures that optimize the coordinates as variational parameters [57]. More recently, a spherical DFT proposal where only spherical Gaussians are used [58]. Therefore, spherical functions can even be centered on the enfolding surroundings of the atomic centers without additional problems in quantum chemical calculations.

Employing enfolding functions, in addition to typical atomic-centered basis set functions, seems to be no problem given the minimal computational times nowadays reached and the possibility of introducing the whole structure in future quantum computing machines.

The best policy for building a quantum mechanical picture of a given molecular entity would be to consider the whole molecule as an intricate building of diatomic bonds, perhaps even involving atom pairs not classically considered to be bonded.

However, further on, nothing opposes considering triplets or a higher number of atomic sets, where to center basis functions to construct the MO set finally.

For molecular energy optimization, the quantum mechanical variational theorem (see, for instance, references [6,8,10]) states that the larger the number of basis functions and variational parameters, the lower the energy of singlet closed-shell ground states.

Generally speaking, chemists consider the feature of chemical bonds essential to study atomic pairs in a molecule appearing to be a given distance apart. Additionally, non-neighboring atomic pairs are considered irrelevant or not bonded. Pauling adopted this idea in "The Nature of Chemical Bond" and Coulson in "Valence."

To discover this chemical idea, one only has to examine chapter V of "The Nature of Chemical Bond," which informs about interatomic distances, and peruse the first chapter table on page 161, dealing with the single bond C-C distances. Immediately, one has the sensation of redundancy, as all distances in the table appear to have an arithmetic mean of 1.54 Å, with fluctuations of ±0.01 Å.

Thus, shall one admit that there is a chemical bond if the distances between two neighboring atoms fall within some experimentally determined distance interval? It could not be better to consider also bonded atoms, all the pairs, triplets, and so on, of atoms? Then, if this last idea is acceptable, why not consider the whole atomic set bonded? Why do we not consider the collection of *all* interacting atoms in a molecule as the *real nature of the chemical bond*? in agreement with the quantum mechanical idea of considering submicroscopic systems as a set of non-separable particles.

7.3. Concluding

Such a situation can be easily studied using the elements of the density bond matrix.

Agreeing to consider all or several atoms implied simultaneously into the chemical bonding, then the quantum MOs polyhedra, originally made of MOs density functions or origin shifted, the sets P and T respectively, can be used to provide additional and original information depending on the molecular structure and the basis set used about the collective molecular bonding, according to Mezey's ideas about the role of molecular electronic density functions.

Moreover, the possibility of using the elements of the bond density matrix to compute generalized quantum similarity measures and, thus, allowing to measure the dissimilarity between atomic or enfolding subsets allows us to foresee an extra dimension in studying the molecular bonding role and applying it to chemistry to open new unwalked research paths.

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