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Quantum perspectives on the nature of the chemical bond

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Abstract

In the history of chemistry, the revolutionary concepts of quantum mechanics lead with both conceptual and innovative understanding and designing of molecular structures. In this review, we would like to survey the main references in this rich and fascinating field of bonding knowledge. In this respect, the intensive level of chemical bonding such as the Schrödinger many-electronic-poly-nuclei problem is firstly approached under the consecrated Hartree-Fock (HF), Roothaan and Kohn-Sham Self-Consistent Field (SCF) quantum frames. The localization problem is considered as the next level, in which context both the orbital and density localization functions are discussed. Finally, the chemical reactivity is indexed

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through the global density functionals of electronegativity and chemical hardness and of the associate principles. A study case of the particular series of acidic halogens in reactions with hydrogen peroxide is undertaken at each level of chemical bond characterization. It is found that the quantitative structure-property (activity) multi-linear relationships - QSP(A)Rs - may be faithfully employed aiming to unify the levels of chemical bonding in single equation.

1. Introduction

Quoting Roald Hoffmann: “There is nothing more fundamental to chemistry than the chemical bond” and still, according with Charles A. Coulson: “It does not exist. No one has ever seen one. No one ever can. It is a figment of our own imagination”. Just like the millenary search for the Holy Grail, the revelation of the engines that promote, hold and activate a molecular structure remains a permanent challenge for the human intelligence. Shortly, it is worth noting the seminal contributions of the *dualist theory* of Berzelius (1819) advancing for the first time the idea of electrostatic interaction between two opposite charged atoms in defining chemical bonding. However, without taking into account the causes of the charges involved, the theory fails to explain the bonding between two identical atoms, as well as the plethora or organic compounds. It was the *unitary theory* of Dumas (1834) that solves the dichotomy by assuming the bonding forces to be of the same kind whatever the component atoms considered may be. Nevertheless, each of these theories assesses, in fact, a specific type of the chemical bond, the ionic and covalent ones, respectively. Still, Pandora’s Box was opened when the very connection between these two extremes was hidden under the inorganic and organic roughly classification of the chemical compounds. Despite the efforts of star chemist as Kekulé [1], Couper [2], Butlerov [3], van’t Hoff [4], Le Bel [5] or Werner [6] in the second part of the XIX century to elucidate the structural constitution of molecules on conceptual grounds, the history of chemical bonding remains with the concept of valence as another mysterious benchmark of the nature’s mode of action.

Then, while the first half of the XX century brings to light the *quantum theory* of matter, the subsequent searches of accommodating the valence concepts with the quantum principles dominate the conceptual chemistry through the cornerstone works of Lewis [7], Kossel, Heitler and London [8,9], Pauling [10,11], Mulliken [12], Hund [13], Hückel [14,15], Herzberg [16], Schrödinger [17], Dirac [18] and Slater [19]. It follows that the chemical bond widescreen can be summarized as the inter-connections between the four fundamental types of bonds: covalent, ionic, metallic, and van der Waals, see Figure 1. At this point, it is worth noting the seminal contribution of Lewis (1916) through his “The Atom and the Molecule” work [7], where the chemical intuition overwhelms the

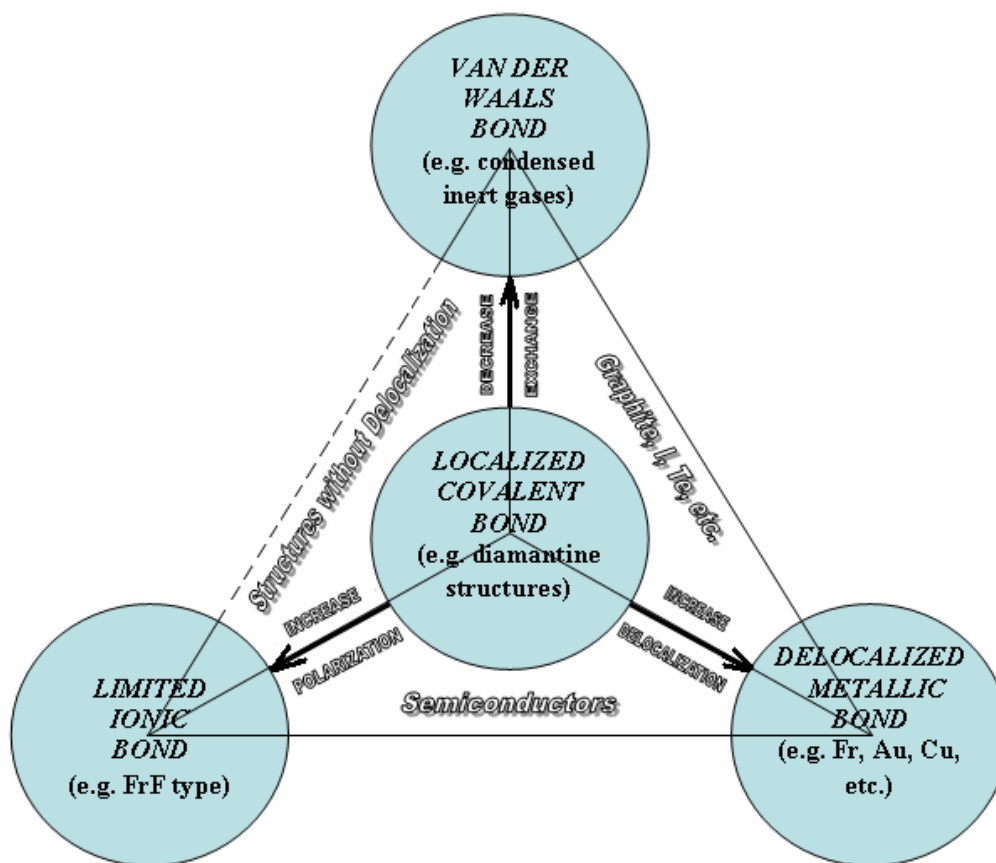


Figure 1. Sketch of the conceptual unity of the covalent, ionic, metallic and van der Waals chemical bonds throughout the quantum concepts of localization, polarization, delocalization, and exchange interactions, respectively.

already three-year old Bohr Theory of hydrogenic atoms [20, 21] by introducing the surreal concept of “cubical atom”. Although, at first sight, such a paradigm may seem strange now, there it was the first affirmation of the necessity that the atom itself has to be assumed with an inherent structure, viz. orbitals, of symmetry types different even circumvented by the spherical one. Such intuition was, more than ten years later, confirmed when the Schrödinger equation was analytically solved for the hydrogenic atoms and recovering the Bohr’s energy in addition to the celebrated orbital functions [17].

Moreover Lewis’ lone and bond pair or electrons, abstracted from its “cubical atomic” combinations through connecting of their edges with electronic occupancy between 0 and 2, becomes the main “lingua franca” of chemical bonding analysis leading to the disputed concepts of bonding localizations both at the orbital (intensive) and functional (global) approaching levels. However, the atomic structure was afterwards found as the key of both explaining the atomic periodicities, i.e. recovering and definitely certifying the Mendeleyev systematic arrangement of the elements in its table, and providing

the quantitative tools, i.e. atomic orbitals, with the help of which the entire molecular panorama seems to be on the way of unfolding. The fundamental works of Hartree [22], Fock [23], Roothaan [24], again Slater [25], and Kohn [26,27] further enlightened the quantum nature of the chemical bond at the intensive level of electronic spin-orbitals.

Consequently, from the second part of the XX century nowadays the first rate scientifically research has been focused mainly on the synergistic quantum approaches to the structure and properties of the natural complex systems, i.e. the polyatomic and biomolecular ones [28].

While pure physics struggled on the great unification paradigm through the fundamental forces in nature, "being subject, in the last decade, to a continuous reform, a similar attitude is now emerging in chemistry, at the quantum level of representation, related to the existing natural chemical bonds. However, because the types of the chemical bonds coexist in various degrees and combinations in the organization of the matter, only a unitary quantum treatment, based on the first physical-chemical principles, can release an estimation of the structure-properties correlations across the complex natural nano-systems: metals, clusters, fullerenes, liquid crystals, polymers, ceramics, biomaterials, metalloenzymes [29-36].

This way, a unitary picture to link and flexibly adapt the quantum mechanical formalisms at the chemical bonding problem was intensively studied [28]. Still, with the belief that the unification of the chemical bonds can be achieved through a single equation or force [37] we advance in this work the iterative link between the intensive, local and global levels of chemical bond in a unitary presentation.

2. Intensive level of quantum chemical bond

Very often, the famous words of Dirac, i.e. "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known", are quoted by theorists in physics when they like to underline that chemistry is in principle solved by the basics of quantum mechanics so that some more interesting problems should be solved. Despite this, from 1929 nowadays, quantum physics of atoms and molecules largely turns into quantum chemistry, an interdisciplinary discipline that still struggles with the elucidation of the actual behaviour of electrons in nano- and bio- systems. While the total success is still not in sight, the achievements in the arsenal of concepts, principles, and implementation was considerable and already enters goes into the arsenal of humankind hall-of-fame giving thus hope for a shining dawn in the poly-electronic interaction arena [38-82]. However, when questing for the underlying principles of the chemical bond, the first compulsory level of expertise may be called as the intensive level of analysis in which the main ingredients of a many-electronic-many-nuclear problem has to be clarified. These are subjected in the below following sections.

2.1. Molecular orbital approach

The basic starting point is the consecrated time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (1)$$

with non-relativistic Hamiltonian

$$\begin{aligned} \hat{H} &= \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn} \\ &= -\frac{1}{2} \sum_i \nabla_i^2 - \frac{1}{2} \sum_A \frac{\nabla_A^2}{M_A} - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} \end{aligned} \quad (2)$$

$i, j = \overline{1, N}; A, B = \overline{1, M}$

accounting for the electron kinetic, nuclear kinetic, electron-electron repulsion, electron-nuclear attraction and nuclear-nuclear repulsion energetic terms, respectively.

Of course, as it is, equation (1) cannot be solved exactly, in its most general way. The approximations have to be implemented in such a way as to include the specific reality of the dynamic electronic-nuclear system. In this respect, considering an approximation is not viewed as a limitation here, but rather as a sort of rescaling of the concerned issue. Epistemologically, it is equivalent with Descartes' scholastic methodology of reducing a problem to smaller problems through the method of analysis. Such a procedure has been long verified in mathematical-physics with impressive practical applications, e.g. the integral-differential recipes, and will be thus safely implemented also here without loss in generality of the basic problem.

In quantum chemistry the specific method was consecrated as Born-Oppenheimer approximation that separates the electronic-nuclear system and problem in two smaller parametrically linked subsystems associated with an electronic motion, defined by equations

$$\begin{cases} \hat{H}_e \Psi_e = E_e \Psi_e \\ \hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} \end{cases} \Rightarrow \Psi_e(\{r_i\}, \{R_A\}); E_e(\{R_A\}) \quad (3)$$

and the corresponding nuclear motion

$$\begin{cases} \hat{H}_n \Psi_n = E \Psi_n \\ \hat{H}_n = \hat{T}_n + E_e(\{R_A\}) + \hat{V}_{nn} \end{cases} \quad (4)$$

It is worth noting that this phenomenological separation of electronic and nuclear problems may be possible due to the impressive difference in their mass that practically fixes the nuclei as the reference system in which the electronic system evolves. This is, nevertheless, only the first and most straight (however appropriate) approximation considered upon a many-body (electrons and nuclei) problem [55-82].

As a consequence, two stages of the overall solution can be given. One is obtained when solving the electronic problem only, therefore producing the so called *single-point* calculation, i.e. the clamped nuclei remaining in a single inter-position.

The next stage is when replacing the electronic coordinates by their average values, since they move much faster than the nuclei, solving the nuclear Schrödinger equation (4) thus furnishing the vibration, rotation and translation solutions of a molecule. This way, the so called *potential-energy surface* solution has been provided since $E_e(\{R_A\}) + \hat{V}_{nn}$ constitutes the potential for the nuclear motion as a whole.

While, molecular mechanics methods fairly provides nuclear solution of motion the electronic problem remains as the main, first cut, challenge to be addressed also because its elucidation leaves the sign also on the electronic pairing problem, the cornerstone concept in chemical bonding nature.

Thus, focusing only on the electronic Schrödinger equation (3), it can further be seen as a composite Hamiltonian, namely

$$\hat{H}_e = \hat{H}_e^I + \hat{H}_e^{II} \quad (5)$$

in terms of the electron solely and external electron energies

$$\hat{H}_e^I = \hat{T}_e + \hat{V}_{en} \quad (6)$$

for the kinetic and nuclear potential, respectively, on the one hand, and

$$\hat{H}_e^{II} = \hat{V}_{ee} \quad (7)$$

separating the electron-electron contribution, that already feel that has to have a specific behaviour, both at classical and quantum levels of manifestations, at other hand.

Now, moving on to the specific electronic wave functions, let us consider the spin-orbitals

$$\chi_i^\sigma(1) = \phi_i(1)\sigma(1), \quad (8)$$

with their intrinsic ortho-normalized conditions fulfilled,

$$\langle \chi_i^\sigma | \chi_j^\rho \rangle = \int \chi_i^{\sigma*}(\mathbf{1}) \chi_j^\rho(\mathbf{1}) d\tau_1 = \delta_{ij} \delta_{\sigma\rho}, \quad (9)$$

as being *one-electron functions* or *molecular orbitals* MO, each as a product of a spatial orbital $\phi_i(\mathbf{1})$ and a spin function $\sigma(\mathbf{1}) = \alpha, \beta$.

In these conditions, for a system with N electrons, the trial wave function (equivalent with the so called Slater determinant) takes the so called *trial Hartree-Fock (HF) form*:

$$\Psi_e^{HF} = \sqrt{N!} \hat{\wp} \Psi_e^H \quad (10)$$

with the Hartree wave function as simple product of spin-orbitals (the so called *orbital approximation*)

$$\Psi_e^H = \prod_{\substack{i=1 \\ \sigma=\alpha,\beta}}^N \chi_i^\sigma(\mathbf{1}) \quad (11)$$

and the antisymmetrisation operator

$$\hat{\wp} = \frac{1}{N!} \sum_P (-1)^P P \quad (12)$$

having Hermitian and commutation properties:

$$\hat{\wp}^2 = \hat{\wp}, \quad (13)$$

$$\left[\hat{H}_e^I, \hat{\wp} \right] = \left[\hat{H}_e^{II}, \hat{\wp} \right] = 0, \quad (14)$$

respectively.

This way, we formally succeed to further separate the many-electronic problem in as many one-electronic problems as electrons are considered in the molecular system.

From now on, basically, one can solve the many-electronic equation by manipulating the one-electronic properties of the system. How this can best be performed, at what cost and under what conditions, will be in next addressed.

2.2. Hartree-Fock approach

Skipping the reference to the electronic (e) subscripts throughout equations (5)-(14), the Hartree-Fock trial functional can firstly be arranged as

$$E_0 \leq E_{trial}^{HF}[\Psi^{HF}] = \langle \Psi^{HF} | \hat{H} | \Psi^{HF} \rangle = \langle \Psi^{HF} | \hat{H}^I | \Psi^{HF} \rangle + \langle \Psi^{HF} | \hat{H}^{II} | \Psi^{HF} \rangle. \quad (15)$$

The one-electron (core) energetic component of (15) may be successively unfolded as:

$$\begin{aligned} & \langle \Psi^{HF} | \hat{H}^I | \Psi^{HF} \rangle \\ &= N! \langle \Psi^H | \hat{\wp} \hat{H}^I \hat{\wp} | \Psi^H \rangle \\ &= N! \langle \Psi^H | \hat{H}^I \hat{\wp}^2 | \Psi^H \rangle \\ &= N! \langle \Psi^H | \hat{H}^I \hat{\wp} | \Psi^H \rangle \\ &= \sum_{i=1}^N \sum_P (-1)^P \langle \Psi^H | \left[-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \right] \hat{\wp} | \Psi^H \rangle \\ &\equiv \sum_{i=1}^N \sum_P (-1)^P \langle \Psi^H | \hat{h}_i(1) \hat{\wp} | \Psi^H \rangle \\ &= \sum_{i=1}^N \langle \Psi^H | \hat{h}_i(1) | \Psi^H \rangle \\ &= \sum_{i=1}^N \langle \chi_i^\sigma(1) | \hat{h}_i(1) | \chi_i^\sigma(1) \rangle \\ &= \sum_{i=1}^N \int \chi_i^{\sigma*}(1) \hat{h}_i(1) \chi_i^\sigma(1) d\tau_1 \\ &\equiv \sum_{i=1}^N h_{ii} \\ &\equiv H_{ii}. \end{aligned} \quad (16)$$

where it was considered that the introduced one-electron effective operator $\hat{h}_i(1)$ selects from the Hartree wave function (11) the associate spin-orbital, for each electron, accordingly.

Similarly, the two-electron energetic component of (15) may be successively transformed as:

$$\begin{aligned}
& \langle \Psi^{HF} | \hat{H}^{II} | \Psi^{HF} \rangle \\
&= N! \langle \Psi^H | \hat{\wp} \hat{H}^{II} \hat{\wp} | \Psi^H \rangle \\
&= N! \langle \Psi^H | \hat{H}^{II} \hat{\wp}^2 | \Psi^H \rangle \\
&= N! \langle \Psi^H | \hat{H}^{II} \hat{\wp} | \Psi^H \rangle \\
&= \sum_{\substack{i,j=1 \\ i < j}}^N \sum_P (-1)^P \langle \Psi^H | \frac{1}{r_{ij}} \hat{\wp} | \Psi^H \rangle \\
&= \sum_{\substack{i,j=1 \\ i < j}}^N \langle \Psi^H | \frac{1}{r_{ij}} (1 - P_{ij}) | \Psi^H \rangle \\
&= \sum_{\substack{i,j=1 \\ i < j}}^N \langle \Psi^H | \frac{1}{r_{ij}} | \Psi^H \rangle - \sum_{\substack{i,j=1 \\ i < j}}^N \langle \Psi^H | \frac{1}{r_{ij}} P_{ij} | \Psi^H \rangle \\
&= \sum_{\substack{i,j=1 \\ i < j}}^N \langle \chi_i^\sigma(1) \chi_j^\sigma(2) | \frac{1}{r_{12}} | \chi_i^\sigma(1) \chi_j^\sigma(2) \rangle - \sum_{\substack{i,j=1 \\ i < j}}^N \langle \chi_i^\sigma(1) \chi_j^\sigma(2) | \frac{1}{r_{12}} | \chi_j^\sigma(1) \chi_i^\sigma(2) \rangle \\
&\equiv \sum_{\substack{i,j=1 \\ i < j}}^N \langle \chi_i^\sigma(1) | \hat{J}_j(1) | \chi_i^\sigma(1) \rangle - \sum_{\substack{i,j=1 \\ i < j}}^N \langle \chi_i^\sigma(1) | \hat{K}_j(1) | \chi_i^\sigma(1) \rangle \\
&= \sum_{\substack{i,j=1 \\ i < j}}^N \iint \chi_i^{\sigma*}(1) \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_i^\sigma(1) \chi_j^\sigma(2) d\tau_1 d\tau_2 - \sum_{\substack{i,j=1 \\ i < j}}^N \iint \chi_i^{\sigma*}(1) \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_j^\sigma(1) \chi_i^\sigma(2) d\tau_1 d\tau_2 \\
&\equiv \sum_{\substack{i,j=1 \\ i < j}}^N J_{ij} - \sum_{\substack{i,j=1 \\ i < j}}^N K_{ij} \\
&= \frac{1}{2} \sum_{i,j=1}^N [J_{ij} - K_{ij}] \\
&\equiv U_{ee}
\end{aligned} \tag{17}$$

resulting in the effective electron-electron repulsion energy once the quantum exchange terms K_{ij} are subtracted from the classical Coulombic ones J_{ij} . Here we recognize the combined classical (Coulombic) – quantum (exchange) effects that appear in the inter-electronic repulsion Hamiltonian term (7).

All together, with the results (16) and (17) back in (15), we get for the trial Hartree-Fock functional the expression:

$$E_{trial}^{HF}[\Psi^{HF}] = \sum_{i=1}^N h_{ii} + \frac{1}{2} \sum_{i,j=1}^N [J_{ij} - K_{ij}]. \quad (18)$$

In next, we are going to apply the variational principle respecting the variations of the spin-orbitals in terms of Lagrange multipliers ε_{ij} that widely demands that:

$$\delta \left\{ E_{trial}^{HF}[\Psi^{HF}] - \sum_{i,j=1}^N \varepsilon_{ij}^{HF} \left(\langle \chi_i^\sigma(1) | \chi_j^\sigma(1) \rangle - 1 \right) \right\} = 0. \quad (19)$$

However, by employing the canonical transformation, i.e. the N^2 parameters may be considered as the elements of a Hermitian matrix which through a unitary transformation become a diagonal matrix, the outset form of the variational principle (19) now reads:

$$\delta \left\{ E_{trial}^{HF}[\Psi^{HF}] - \sum_{i=1}^N \varepsilon_i^{HF} \left(\langle \chi_i^\sigma(1) | \chi_i^\sigma(1) \rangle - 1 \right) \right\} = 0. \quad (20)$$

Note that performing a unitary transformation will not affect the average of the electronic Hamiltonian but only the *HF* wave function by a phase factor of unity modulus.

Under these circumstances, the famous Hartree-Fock equation results from the successive equivalent forms:

$$\begin{aligned} \sum_{i=1}^N \frac{\delta}{\delta \chi_i^{\sigma*}(1)} \left\{ -\frac{1}{2} \int \chi_i^{\sigma*}(1) \nabla_i^2 \chi_i^\sigma(1) d\tau_1 - \sum_A Z_A \int \chi_i^{\sigma*}(1) \frac{1}{r_{iA}} \chi_i^\sigma(1) d\tau_1 \right. \\ \left. + \frac{1}{2} \sum_{j=1}^N \iint \chi_i^{\sigma*}(1) \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_i^\sigma(1) \chi_j^\sigma(2) d\tau_1 d\tau_2 \right. \\ \left. - \frac{1}{2} \sum_{j=1}^N \iint \chi_i^{\sigma*}(1) \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_j^\sigma(1) \chi_i^\sigma(2) d\tau_1 d\tau_2 - \varepsilon_i^{HF} \int \chi_i^{\sigma*}(1) \chi_i^\sigma(1) d\tau_1 \right\} = 0 \\ \Leftrightarrow \left[-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \right] \chi_i^\sigma(1) + \left[\sum_{j=1}^N \int \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_j^\sigma(2) d\tau_2 \right] \chi_i^\sigma(1) \\ - \left[\sum_{j=1}^N \int \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_i^\sigma(2) d\tau_2 \right] \chi_j^\sigma(1) = \varepsilon_i^{HF} \chi_i^\sigma(1) \end{aligned} \quad (21)$$

Still, a more compact form of *HF* equation (21) may be achieved since specific potential notations are introduced. For instance, the electrostatic repulsion potential (i.e. the Coulombic interaction) can be shortened as:

$$V_j^{ee}(1) = \int \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} \chi_j^\sigma(2) d\tau_2 \quad (22)$$

while for the exchange potential (i.e. non-local interaction) we can define it as satisfying the relation:

$$V_j^{ex}(1)f(1) = \left[\int \chi_j^{\sigma*}(2) \frac{1}{r_{ij}} f(2) d\tau_2 \right] \chi_j^\sigma(1). \quad (23)$$

With these the above *HF* equation (21) reduces to its most simple form:

$$\hat{F}(1)\chi_i^\sigma(1) = \varepsilon_i^{HF} \chi_i^\sigma(1) \quad (24)$$

where the one-electronic Fock operator

$$\hat{F}(1) = -\frac{1}{2}\nabla_i^2 + V_i^{HFeff}(1) \quad (25)$$

was introduced in terms of the effective-one potential

$$V_i^{HFeff}(1) = -\sum_A \frac{Z_A}{r_{iA}} + \sum_{j=1}^N V_j^{ee}(1) - \sum_{j=1}^N V_j^{ex}(1). \quad (26)$$

Now, since the spin-orbitals satisfies the normalization condition

$$\int |\chi_i^\sigma(1)|^2 d\tau_1 = 1 \quad (27)$$

the orbital energies look like:

$$\varepsilon_i^{HF} = \int \chi_i^{\sigma*}(1) \hat{F}(1) \chi_i^\sigma(1) d\tau_1 = h_{ii} + \sum_{j=1}^N [J_{ij} - K_{ij}] \quad (28)$$

while the total HF energy will take the form:

$$E^{HF}[\Psi^{HF}] = \sum_{i=1}^N \varepsilon_i^{HF} - U_{ee} \quad (29)$$

where

$$\sum_{i=1}^N \varepsilon_i^{HF} = \sum_{i=1}^N h_{ii} + \sum_{i,j=1}^N [J_{ij} - K_{ij}]. \quad (30)$$

Remarkably, one can clearly see that the predicted *HF* energy (29) differs from the simple sum over the *HF* orbital energies (30) by the effective electron-electron interaction energy U_{ee} .

2.3. Roothaan approach

Usually, the *HF* method becomes computationally expensive if not almost impossible to apply for the most macro-molecules. At this point the great achievement of computational chemistry was to consider the finite expansion of the one-electron spin-orbitals of the *HF* equation (24), in terms of some set of fixed one-electron basis function or *basis set*:

$$\chi_i^\sigma(\mathbf{l}) = \sum_{\nu} C_{\nu i}^\sigma \phi_{\nu}(\mathbf{l}). \quad (31)$$

Since the basis set may be chosen as being composed of hydrogenic-like functions centered in one atom one can say that the molecular orbitals have been expanded in terms of *linear combination of atomic orbitals* (LCAO).

In these conditions, submitting the LCAO-MO in the above *HF* equation (24), multiplying at left by ϕ_{μ}^* and integrating one finds the so called *Roothaan equations*:

$$\sum_{\nu} C_{\nu i} \int \phi_{\mu}^*(\mathbf{l}) \hat{F}(\mathbf{l}) \phi_{\nu}(\mathbf{l}) d\tau_1 = \varepsilon_i \sum_{\nu} C_{\nu i} \int \phi_{\mu}^*(\mathbf{l}) \phi_{\nu}(\mathbf{l}) d\tau_1 \quad (32)$$

which can be arranged in a matrix form, as

$$\mathbf{FC} = \mathbf{SC}\varepsilon \quad (33)$$

with the Fock matrix elements

$$\mathbf{F}_{\mu\nu} = \int \phi_{\mu}^*(\mathbf{l}) \hat{F}(\mathbf{l}) \phi_{\nu}(\mathbf{l}) d\tau_1 \quad (34)$$

together with the *overlap matrix* ones

$$\mathbf{S}_{\mu\nu} = \int \phi_{\mu}^*(\mathbf{l}) \phi_{\nu}(\mathbf{l}) d\tau_1. \quad (35)$$

The new one-electronic type equations (32) made the history of the computational chemistry in the last century since they can be computed either from first principles (in which case one says that an *ab initio* approach was

undertaken) or by resorting to experimental data (in which case the *semiempirical* approach was chosen).

It is worth noting that the particularization of Roothaan equations to spin up (alpha state) or spin down (beta state) through considering different spatial parts of the spin-orbitals generates the so called *unrestricted Hartree-Fock* (UHF) frame of analysis. However, it describes the homolytic dissociation products or reactions in which the change in spin pairing is allowed. Otherwise, the so called *restricted Hartree-Fock* (RHF) method can be employed whenever one would prefer to use orbital energy diagrams with two electrons rather than one electron per orbital.

Computationally, the procedure for solving the *HF* or Roothaan equations is *self-consistent* in the sense that the involved Fock operator depends implicitly upon the solutions. This feature is derived from the assumed one-electron picture in which a single electron would feel the potential influence coming from the fixed (or clamped) collection of nuclei and the average effects of all other $N-1$ electrons.

Therefore, the basic algorithm solves the one-electron problems iteratively: guess the position for each electron (i.e. guess **C**), then guess the average potential that an electron feels from the rest of electrons in the system (i.e. guess **F**), solve the matrix equation (i.e. diagonalize to a new **C**), form a new **F**, repeat the procedure until the one-electronic wave function becomes consistent with the field produced by it and other electrons.

Regarding the *ab initio* methods, they are very effective since an arbitrary basis set of LCAO-MO produces accurate results without imposing additional approximations.

Unfortunately, this method was criticized for this arbitrary degree of freedom, arguing that it produces a recipe in which “anything computes everything”.

While this endeavour was made in the efforts to discredit the MO approach and the orbital concept in general, we believe that atomic orbitals and their linear combination provide the set of “elementary properties” of matter on which base the whole chemistry can be rationalized based on a single (i.e. the eigen value problem) principle, either in Schrödinger, Hartree-Fock, Roothaan or Kohn-Sham (see below) approaches.

2.4. About correlation

The post self-consistent era was mainly dedicated to the implementation of the so nominated *correlation energy* in the computation.

Firstly, it was noticed that a single Slater determinant (on which base the current *HF* analysis was exposed) can never account for a complete description of the many-electronic interaction. That is, the correlation energy can be introduced as the difference between the exact eigen-value and the Hartree-Fock energy of the same Hamiltonian for the concerning state:

$$E_{corr} = E - E^{HF} . \quad (36)$$

The next step was sustained by the assumption that the correlation energy can be seen as the perturbation of the self-consistent-field energy which is associated with a wave function derived for a single electronic configuration. At this point the basic methods of approximation used in quantum chemistry, namely the *perturbation* and *variational*, can be considered.

In the case that perturbation method is employed, assuming the unperturbed wave function and energy as the HF solutions the exact eigenfunctions and eigen-values can be written as expanded series

$$\Psi_e = \Psi_e^{HF} + \ell \Psi_e^{(1)} + \ell^2 \Psi_e^{(2)} + \dots , \quad (37a)$$

$$E_e = E^{HF} + \ell E_e^{(1)} + \ell^2 E_e^{(2)} + \dots \quad (37b)$$

by introducing the ordering parameter ℓ . Through truncating the series in the second, third or fourth order generates the so called Møller-Plesset MP2, MP3, and MP4 perturbative approximations, respectively.

On the other side, the linear variational method can be practiced within the *configuration interaction (CI)* approach of the many-electronic wave-function:

$$\Psi_e^{CI} = c_0 \Psi_e^{HF} + \sum_s c_a^s \Psi_a^s + c_{ab}^{sd} \Psi_{ab}^{sd} + c_{abc}^{sdt} \Psi_{abc}^{sdt} + \dots \quad (38)$$

where the Ψ_0 , Ψ_a^s , Ψ_{ab}^{sd} , Ψ_{abc}^{sdt} stands for the ground, single excited, double excited, and triple excited N -electron trial wave functions, respectively, for a given spin state.

While the *CI* wave function is the subject of the eigen-problem:

$$\hat{H}_e \Psi_e^{CI} = \tilde{E}_0 \Psi_e^{CI} \quad (39)$$

the correlation correction to *HF* energy can be achieved through subtracting the *HF* energy from last equation

$$\left(\hat{H}_e - E^{HF} \right) \Psi_e^{CI} = \left(\tilde{E}_0 - E^{HF} \right) \Psi_e^{CI} = E_{corr} \Psi_e^{CI} . \quad (40)$$

However, although, starting from this point, many sophisticated methods for wave function expansion, e.g. the coupled cluster approach, multi-configuration self-consistent-field method or multi-reference *CI* methods, have been developed [52, 68, 73, 76], the correlation problem faced many computational limitation,

some of them almost insurmountable, due to the immense number of integrals to be evaluated.

2.5. Density functional approach

Fortunately, a completely different approach was invented to overcome from a single shot both the *exchange and correlation* terms to the total electronic energy. That was possible, however with the price of revisiting the wave function concept, in fact to contract it into the electronic density:

$$\rho(r) = \sum_i n_i \sum_{\sigma=\alpha,\beta} |\chi_i^\sigma(r)|^2 \quad (41)$$

written in general terms of the fractional occupancy numbers $n_i \in [0,1]$ so that [26]

$$N[\rho] = \int \rho(r) dr = \sum_i n_i. \quad (42)$$

Note that from the beginning since the introducing of the fractional occupation numbers both the concepts of one-orbitals as well as exact N -one-orbitals have been generalized to fractionally occupied orbitals and to an arbitrary number of orbitals, hereafter called as *Kohn-Sham orbitals*. This way the distinction respecting the Hartree-Fock approach is made in clear.

More transparently, within the density functional formalism the trial *HF* energy is replaced by the so called *Kohn-Sham (KS) trial functional* [27]:

$$E_{trial}^{KS}[\rho] = T_J[\rho] + C_A[\rho] + \frac{1}{2}J[\rho] + E_{xc}[\rho] \quad (43)$$

where

$$T_J[\rho] = \min \left[\sum_i n_i \int \chi_i^{\sigma*}(r) \left(-\frac{1}{2} \nabla^2 \right) \chi_i^\sigma(r) dr \right], \quad (44)$$

$$C_A[\rho] = \int V_{ext}(r) \rho(r) dr \quad (45)$$

$$J[\rho] = \iint \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 \quad (46)$$

stands for the generalized (Janak) kinetic energy [54], chemical action only not restricted to the bare potential of the nuclei, and classical Coulombic energy functionals, respectively [53].

The exchange-correlation energy functional $E_{xc}[\rho]$ replaces in *KS* trial energy both the *HF* exchange $(-1/2)(\sum_{ij} K_{ij})$ and the missing correlation terms.

As previously presented *HF* formalism the optimized *KS* energy is achieved through minimizing the trial *KS* energy respecting the set of spin-orbitals χ_i^σ :

$$\frac{\delta}{\delta \chi_i^{\sigma*}} \left\{ E_{trial}^{KS}[\rho] - \sum_i \varepsilon_i'^{KS} \left(\int |\chi_i^\sigma(r)|^2 dr - 1 \right) \right\} = 0 \quad (47)$$

for a fixed set of occupancy numbers n_i .

The intermediate result of the above functional derivation furnishes the explicit expression:

$$-\frac{1}{2} n_i \nabla^2 \chi_i^\sigma(r) + n_i \chi_i^\sigma(r) \frac{\delta J[\rho]}{\delta \rho(r)} + n_i \chi_i^\sigma(r) \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} + n_i \chi_i^\sigma(r) V_{ext}(r) = \varepsilon_i'^{KS} \chi_i^\sigma(r) \quad (48)$$

since the density-wave function link is employed.

While for $n_i \neq 0$ one can set $\varepsilon_i^{KS} = \varepsilon_i'^{KS} / n_i$ it is now clear that the last expression can be rearranged under the form:

$$\left[-\frac{1}{2} \nabla^2 + \left(V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|} dr' + V_{xc}(r) \right) \right] \chi_i^\sigma(r) = \varepsilon_i^{KS} \chi_i^\sigma(r), \quad (49)$$

or, more compactly, under the celebrated Kohn-Sham equation

$$\left[-\frac{1}{2} \nabla^2 + V^{KS_{eff}}(r) \right] \chi_i^\sigma(r) = \varepsilon_i^{KS} \chi_i^\sigma(r), \quad (50)$$

where the Kohn-Sham effective potential

$$V^{KS_{eff}}(r) = V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|} dr' + V_{xc}(r) \quad (51)$$

was introduced in terms of the *exchange-correlation potential*:

$$V_{xc}(r) = \frac{\partial E_{xc}[\rho]}{\partial \rho(r)}. \quad (52)$$

Finally, performing the sum over the *KS* orbital energies ε_i^{KS} :

$$\begin{aligned}\sum_i n_i \varepsilon_i^{KS} &= \sum_i n_i \left\langle \chi_i^\sigma \left| -\frac{1}{2} \nabla^2 + V^{KS_{eff}}(r) \right| \chi_i^\sigma \right\rangle \\ &= T_J[\rho] + \int V^{KS_{eff}}(r) \rho(r) dr \\ &= T_J[\rho] + C_A[\rho] + J[\rho] + \int V_{xc}(r) \rho(r) dr,\end{aligned}\quad (53)$$

by submitting it in the trial *KS* energy above the *KS* total energy can be determined:

$$E^{KS}[\rho] = \sum_i n_i \varepsilon_i^{KS} - \frac{1}{2} J[\rho] + E_{xc}[\rho] - \int V_{xc}(r) \rho(r) dr \quad (54)$$

obtaining that, just as in the *HF* case, the total electronic energy is not the simple sum of orbital energies.

It is worth mentioning that the major difference between orbital *HF* and density functional *KS* methods relies in missing and including of the correlation interaction among the electrons in a many-electronic system, respectively. In other terms, while in the *HF* case the Slater determinantal (wave function) is shared between interacting and non-interacting versions of a many-electronic system, within the *KS* case the total electronic energy is shared between the correlated and non-correlated electrons of the molecule. It is therefore the case to state on the conceptual supremacy of the density functional theory inspiring the further use of the electronic density as the main tool in quantifying of chemical bonding.

3. Localization level of quantum chemical bond

Despite the fact that Hartree-Fock or Kohn-Sham self-consistent field (*SCF*) equations provide in principle the complete set of electronic orbitals that describe the multi-electronic-poly-centre bonds, their main drawback is that of providing the delocalized description over an entire molecular space. Such an analysis has to be accomplished with special techniques through which the localized orbitals and localized chemical bond are to be recovered [83-152]. Only this way can quantum mechanics provide a viable rationale, i.e. quantum chemistry, in chemical bond characterization. Nevertheless, such a rationale can be achieved in two ways: one of them involves the orbital transformation producing the localized set of orbitals and indices [83-120]; the other one, based on electronic density, includes the electronic density, to a certain degree, into an *electronic localization (super) function* - ELF so as to generate a local, analytical indication of the electronic pair of the chemical bond [121-152]. In what follows, we are going to outline both these major approaches.

3.1. Orbital localization

Let's assume that, for instance, after the *HF-SCF* computation is undertaken the set of *canonical molecular one-electronic orbitals* are determined so that the Slater determinantal wave function for $2N$ electrons with N doubly occupied orthonormal real orbitals $\chi_1, \chi_2, \dots, \chi_N$ is laid down [83]:

$$X = \frac{1}{\sqrt{2N!}} \left| (\chi_1 \alpha)^{(1)} (\chi_1 \beta)^{(2)} \dots (\chi_N \alpha)^{(2N-1)} (\chi_N \beta)^{(2N)} \right|. \quad (55a)$$

It has to be transformed into the corresponding localization wave function

$$\Lambda = \frac{1}{\sqrt{2N!}} \left| (\lambda_1 \alpha)^{(1)} (\lambda_1 \beta)^{(2)} \dots (\lambda_N \alpha)^{(2N-1)} (\lambda_N \beta)^{(2N)} \right| \quad (55b)$$

on the basis of the *strictly localized orbitals* $\lambda_1, \lambda_2, \dots, \lambda_N$.

Fortunately, such orbital transformation is allowed by the flexibility carried by the determinantal wave function respecting a unitary transformation that takes the canonical into localized orbitals through the matrix (**T**)

$$\lambda_i = \chi_j T_{ij}. \quad (56)$$

In order to complete the localization picture some "physical" criterion has to be assumed in order that matrix (**T**) to be determined. Such constraints may refer to the maximization of the distance between the electrons of the same *spatially non-localized* orbitals, i.e. the so called Boys condition [86]:

$$SL = \sum_i \langle \chi_i | r | \chi_i \rangle^2 \rightarrow \max \quad (57)$$

in terms of χ_i or, reversely, asking that the energy interaction that equally appears in Coulomb and exchange terms be minimized in localized orbitals, i.e. the Edmiston-Reudenberg, or *orbital localization*, condition [95]

$$OL = \sum_i \langle \chi_i^2 | r^{-1} | \chi_i^2 \rangle \rightarrow \min \quad (58)$$

for orbitals χ_i^2 , where we have least localization.

When employing the last condition one firstly gets:

$$0 = \delta OL = 4 \sum_i \langle \chi_i^2 | r^{-1} | \chi_i \delta \chi_i \rangle. \quad (59)$$

Next, remembering that a change in delocalized towards localized orbitals follows the orthogonal transformation rules:

$$\chi_n + \delta\chi_n = \sum_i \chi_i T_{in} \quad (60)$$

$$\sum_n T_{in} T_{jn} = \delta_{ij} . \quad (61)$$

Then, assuming that

$$T_{ij} = \delta_{ij} + t_{ij} \quad (62)$$

the relations (60) and (61) lead to the first order connections:

$$\delta\chi_n = \sum_i \chi_i t_{in} , \quad (63)$$

$$t_{in} + t_{ni} = 0 , \quad (64)$$

respectively.

It is worth noting that the condition (64) accounts for the anti-symmetries of the spatial orbitals in fulfilling Pauli principle. With these, the least localization principle (59) can be successively written as:

$$\begin{aligned} 0 = \delta OL &= 4 \sum_{ni} \langle \chi_i^2 | r^{-1} | \chi_i \chi_n \rangle t_{ni} \\ &= 4 \sum_{n>m} \left\{ \langle \chi_n^2 | r^{-1} | \chi_m \chi_n \rangle - \langle \chi_m^2 | r^{-1} | \chi_m \chi_n \rangle \right\} t_{mn} \end{aligned} \quad (65)$$

leaving with the delocalization orbital condition:

$$\langle \chi_n^2 | r^{-1} | \chi_m \chi_n \rangle = \langle \chi_m^2 | r^{-1} | \chi_m \chi_n \rangle \quad (66)$$

that, nevertheless is identical in nature to that associated with the localized orbitals:

$$\langle \lambda_n^2 | r^{-1} | \lambda_m \lambda_n \rangle = \langle \lambda_m^2 | r^{-1} | \lambda_m \lambda_n \rangle \quad (67)$$

due to the fact that the optimum condition $\delta OL = 0$ do not distinguish between the minimal and maximum constraints, respectively.

Yet, such dual behaviour of localization measure OL represents the quantum mechanical basis for *hybridization* and *bonding*. For instance, one can check that while the simple set of $\{\chi_A, \chi_B\}$ orbitals provide the interaction measure

$$OL_I = \langle \chi_A^2 | r^{-1} | \chi_A^2 \rangle + \langle \chi_B^2 | r^{-1} | \chi_B^2 \rangle, \quad (68)$$

once the linear combination between them is considered, namely $\{(\chi_A + \chi_B)/\sqrt{2}$ and $(\chi_A - \chi_B)/\sqrt{2}\}$, they provide the interaction augmented measure

$$OL_{II} = \frac{1}{2}OL_I + \langle \chi_A^2 | r^{-1} | \chi_B^2 \rangle + 2 \langle \chi_A \chi_B | r^{-1} | \chi_A \chi_B \rangle. \quad (69)$$

Now, the difference between the terms OL_I and OL_{II} can be easily visualized since the pure covalent homo-orbitals case is consider giving:

$$OL_{II}^{\text{cov}} = 2OL_I^{\text{cov}} = 4 \langle \chi_A^2 | r^{-1} | \chi_A^2 \rangle. \quad (70)$$

The lesson is clear: the hybridized orbitals have provided the maximum localization measure whereas the simple pair of orbitals associates with minimum localization measure-maximum delocalization behaviour. This way, the old concept of Pauling regarding hybridization is quantum mechanically restored through localization recipe. As well the bonding and anti-bonding concepts of Coulson find here their full power of interpretation in the light of symmetrical/anti-symmetrical spatial orbitals that contribute to localization of chemical bonding.

The exposed localization aspects were refined over the last 60 years through all available quantum mechanical scheme of computation: from joining with semiempirical schemes [87-94], unitary transformations of operators and bases [95-120] until the most accurate population analyses [92,106,114,119,121].

In this respect it is worth mentioning that the Mulliken population analysis produces an alternative way of looking at chemical bond in terms of charge localization by means of the sum of partial populations that participate in the i -th bond, core, or lone pair,

$$P = \sum_i P_i \quad (71)$$

with

$$P_i = \sum_{(v,\mu) \in \Gamma_i} C_{iv} C_{i\mu} S_{v\mu}, \quad (72)$$

when the bonds are recognized (by chemical intuition or by preliminary simplified quantum analysis, e.g. Hückel analysis) from the beginning in order to define the sets Γ_i of bonding atomic orbitals.

Finally, we need to briefly discuss the way the cornerstone chemical concept of *valence* can be equally recovered by means of localization

procedure. At this point the developed theory stands as the *pseudo-potential formalism* [124] since its main purpose is to provide the *valence-only* theory for atoms and molecules. In fact, the pseudo-potential techniques aim to substitute the Pauli Exclusion Principle with specific operators and potentials. The main advantage relies on the reduced number of orthogonal conditions, namely those related with valence (say χ^{val}) and core orbitals (say $\{\chi_i^{core}\}$) through the pseudo-potential wave function or pseudo-orbital (*PO*) \mathcal{G} :

$$\mathcal{G} = \chi^{val} + \sum_i \alpha_i \chi_i^{core} \quad (73a)$$

with

$$\alpha_i = \langle \chi_i^{core} | \mathcal{G} \rangle, \quad (73b)$$

which is widely recognized as being of Gram-Schmidt orthogonalization type [98].

Formally, it appears that the valence orbital is localized respecting the rest of core orbitals, and one can assume the basic Schrödinger equation exclusively for it, so that as all other core orbitals would not exist, i.e. dividing the intrinsic eigen-problem into two, possible disjoint, regions associated with valence:

$$\hat{H} \chi^{val} = \varepsilon^{val} \chi^{val} \quad (74)$$

and core

$$\hat{H} \chi_i^{core} = \varepsilon_i \chi_i^{core} \quad (75)$$

orbitals.

However, this localization is achieved through the pseudo-orbitals of above type. This way the valence orbitals are localized once the pseudo-orbital is determined and the core orbitals are properly subtracted from it. That is, the pseudo-orbital eigen-equation has to be solved, namely:

$$\left(\hat{H} + \hat{V}_{PP} \right) \mathcal{G} = \varepsilon^{val} \mathcal{G} \quad (76)$$

where the so called Phillips-Kleinman (*PK*) pseudo-potential (*PP*) [125]

$$\hat{V}_{PP} = \sum_i \alpha_i \frac{(\varepsilon^{val} - \varepsilon_i) \chi_i^{core}}{\mathcal{G}} \quad (77)$$

results from combining of equations (73)-(76).

More, generally, since the *PK* pseudo-potential is rewritten in its linear form:

$$\hat{V}_{PP} = \sum_i (\varepsilon^{val} - \varepsilon_i) |\chi_i^{core}\rangle \langle \chi_i^{core}| \quad (78)$$

it follows that any transformation of the *PO*

$$\tilde{\mathcal{G}} = \mathcal{G} + \sum_i a_i \chi_i^{core}, \quad (79)$$

with a_i 's are arbitrary constants, leads to solutions of *PP* equation (76) with the same eigen-value:

$$\begin{aligned} \left(\hat{H} + \hat{V}_{PP} \right) \tilde{\mathcal{G}} &= \left(\hat{H} + \hat{V}_{PP} \right) \mathcal{G} + \left(\hat{H} + \hat{V}_{PP} \right) \sum_j a_j |\chi_j^{core}\rangle \\ &= \varepsilon^{val} \mathcal{G} + \sum_j a_j \hat{H} |\chi_j^{core}\rangle + \sum_{i,j} a_j (\varepsilon^{val} - \varepsilon_i) |\chi_i^{core}\rangle \langle \chi_i^{core} | \chi_j^{core}\rangle \\ &= \varepsilon^{val} \mathcal{G} + \sum_j a_j \varepsilon_j \chi_j^{core} + \sum_j a_j (\varepsilon^{val} - \varepsilon_j) \chi_j^{core} \\ &= \varepsilon^{val} \left(\mathcal{G} + \sum_j a_j \chi_j^{core} \right) \\ &= \varepsilon^{val} \tilde{\mathcal{G}}. \end{aligned} \quad (80)$$

Such a feature of equivalent pseudo-orbitals in establishing the localization of the valence orbital and eigen-value consecrates the reality of the valence reality, on the one hand, and corresponds to those involving localization measures through unitary orthogonal transformations, described before, on the other hand.

3.2. Density localization

With the advent of the density functional theory, i.e. with the growing recognition of the role that electronic density plays in describing quantum states of atoms and molecules, there also appears the possibility of visualizing bonds and electronic localization through procedures applied on electronic densities.

Basically, the theory of atoms in molecules (*AIM*) was born with the Hellmann-Feynman theorem formulation [104],

$$\frac{dE}{dQ} = \langle \Psi | \frac{d\hat{H}}{dQ} | \Psi \rangle, \quad (81)$$

prescribing the variation of the total energy E respecting an arbitrary parameter Q of the system, e.g. the inter-nuclear distance, from its quantum-mechanically average. Since $Q=R$, the resulted force on particular nucleus, dE/dR , yields, in fact, the electronic localization measure in that molecular region; it can be

easily visualized by further connection between the force and density by means of Poisson equation:

$$\vec{F}(r) = -\nabla V(r) = 4\pi \frac{r}{r} \int_{+\infty}^r \rho(\tau) d\tau. \quad (82)$$

This way the chemical bond is classically partitioned into binding and anti-binding regions.

However, other approaches have also been formulated, aiming to more accurately exploit the electronic bond by using electronic density directly, so as to include the Pauli Exclusion Principle – the vital ingredient when it comes to electronic pairs. In this respect, the next quoted contribution comes from the Daudel's lodges [98], resulting in the difference density between the actual molecular density ρ_{mol} and the so called *reference density* ρ_{ref} , a hypothetical entity associated with the obtained molecular density when at each nuclear position neutral spherical ground states atoms are placed:

$$\Delta\rho(r) = \rho_{mol}(r) - \rho_{ref}(r). \quad (83)$$

Although useful among crystallographers, where it is known as the *standard deformation density concept* [97-99], the Daudel localization measure of bonding seems to disagree with Pauli Exclusion Principle due to the reference density concept that allows atomic charges to overlap unchanged.

A step forward is made with considering the topological issues associated with electron density. In this context, the bond finds both an in-depth and geometrical interpretations once the so called *critical points* of bonds are employed to describe the wild variety of chemical compounds, especially those categorised as electron deficient or posing hypervalences [127-137]. This way, Bader developed a theory according which atoms in molecules are seen now as open systems forming basins of attractors and repellers, bounded by a surface $\Sigma(r_\Sigma)$ of local zero flux in the gradient vector field defined by the so called *zero-flux partitioning condition of electron densities* [137]:

$$\nabla\rho(r) \cdot \vec{n} = 0, \forall r \in \Sigma(r_\Sigma). \quad (84)$$

A close consequence of this condition is assuming the Laplacian of the electron density $\nabla^2\rho(r)$ as the associate localization measure of bonds, obtained by functional integration of the last condition:

$$\delta \int_{\Omega(\Sigma)} d\tau \nabla^2\rho(r) = 0 \quad (85)$$

locally, on the domain $\Omega(\Sigma)$.

However, despite the physical background of Bader's approach, its local zero flux has been found with some limitation in defining bonding [138-146]. For instance, it was established that a bond path between two nearby helium atoms in forming He_2 exists quite analogue to that appeared in forming H_2 , although the He-He bond has been spectroscopically detected only at very low temperature.

Fortunately, another route for defining a localization measure with the help of electronic density was explicated in the context of Thom's theory of catastrophe combined with quantum theory. It leads to the so called *electronic localization functions (ELFs)* [147-152]. Nevertheless, it was recently showed that a suitable *ELF* should be shaped as

$$ELF(r) = \frac{1}{f \left[\frac{g(r)}{h(r)} \right]} \quad (86)$$

with the limiting constrains

$$\lim ELF(r) = \begin{cases} 0, \nabla \rho(r) \gg \rho(r) \\ 1, \nabla \rho(r) \ll \rho(r) \end{cases} \quad (87)$$

ensuring the fulfilment of the Heisenberg and Pauli principles. In this context the *ELF* is defined as the error in localization of electrons within traps. Such meaning is true when the inverse of difference in local kinetic terms is involved in *ELF* definition as bellow considered.

Analytically, based on typical Thom functions of the universally unfolded potential, a particular Markovian-based *ELF* was formulated as [152]

$$ELF(r) = \exp \left\{ - \frac{3}{2} \left[\frac{g(r)}{h(r)} \right]^2 \right\} \quad (88)$$

where the components:

$$g(r) = \frac{1}{2} \sum_i \left[\nabla_r \chi_i(r) \right]^2 - \frac{1}{8} \frac{[\nabla_r \rho(r)]^2}{\rho(r)}, \quad (89)$$

$$h(r) = \frac{3}{10} (3\pi^2)^{2/3} [\rho(r)]^{5/3} \quad (90)$$

are responsible for the gradient (*g*) and the homogenous (*h*) electronic distributions, respectively. With this definition, the closer *ELF* is to zero, the better electronic localization will be provided, according with the above limits.

4. Reactivity level of quantum chemical bond

Starting from the dictum that “A chemical reaction is a change in bonding” [153], we arrive at the third level of chemical bonding characterization through chemical reactivity concepts. They are, however, classified as reactivity indices that span the local and global indicators responsible for chemical affinity and bonding, and reactivity principles that consecrate the rules upon which the reactions can be rationalized when reactivity indices are employed [154-162]. Here we survey upon both these reactivity sides.

4.1. Reactivity indices

For an N -electronic system placed into an external potential $V(r)$ the general (first order) equation of the change in the total energy for the electronic system, $E = E[N, V(r)]$, can be written as [53,159,160]:

$$dE = \mu dN + \int \rho(r) dV(r) dr \quad (91)$$

where the chemical potential and the electronic density, $\rho(r)$, are defined as:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{V(r)}, \quad (92)$$

$$\rho(r) = \left(\frac{\delta E}{\delta V(r)} \right)_N. \quad (93)$$

It is worth noting that by applying on its negative value the finite difference approximation around the referential number of electrons N_0 of the total energy change

$$-\left(\frac{\partial E_N}{\partial N} \right)_{V(r)} \cong -\frac{E_{N_0+1} - E_{N_0-1}}{2} = \frac{(E_{N_0-1} - E_{N_0}) + (E_{N_0} - E_{N_0+1})}{2} = \frac{IP + EA}{2} = \chi \quad (94)$$

we obtain the spectroscopic Mulliken formula for electronegativity, in terms of ionization potential (IP) and electron affinity (EA).

Just as electronegativity, that is a minus chemical *potential*, accounts for the first order effects of the total energy change, the second order effect should be explored for recovering the *force* contribution to the bonding change. For achieving that, in the same manner in which equation (91) was drawn, the change of chemical potential, $\mu = \mu[N, V(r)]$, can be encoded as [53,159,160]:

$$d\mu = 2\eta dN + \int f(r) dV(r) dx, \quad (95)$$

in which the variation of the chemical potential μ (or the electronegativity in the Parr definition $\mu = -\chi$) for an electronic state correlates with the charge and potential variation through the introduced chemical hardness (η):

$$2\eta = \left(\frac{\partial \mu}{\partial N} \right)_{V(r)} = \left(\frac{\partial^2 E}{\partial N^2} \right)_{V(r)} \quad (96)$$

and the Fukui function (f):

$$f(r) \equiv \left(\frac{\delta \mu}{\delta V(r)} \right)_N \quad (97)$$

In other words, the chemical potential (or the electronegativity) of an electronic state depends on the associated chemical hardness and on the spatial integrated frontier function.

Remarkable, since from the equation (91) one can recognize the Maxwell identities:

$$\left(\frac{\delta \mu}{\delta V(r)} \right)_N = \left(\frac{\partial \rho(r)}{\partial N} \right)_{V(r)}, \quad (98)$$

the Fukui index can be rewritten in terms of the density and the number of electrons as:

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{V(r)} \quad (99)$$

thus providing the reactive measure of the chemical bond localization. Moreover, it can be arranged as the ratio

$$f(r) = \frac{s(r)}{S} \quad (100)$$

with the newly introduced reactivity local and global measures:

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu} \right)_{V(r)}, \quad (101)$$

$$S = \left(\frac{\partial N}{\partial \mu} \right)_{V(r)} \quad (102)$$

being the so called local and global softness indices, respectively.

Considering of global and local softness contributions, the link between them can be immediately checked to be of additive type

$$S = \int s(r)dr \quad (103)$$

on the basic constraint of the density functional theory, see also equation (42):

$$N = \int \rho(r)dr \quad (104)$$

This softness' additive feature allows the formulation of a molecular chemical hardness η_M from the atomic chemical hardnesses η_A ones. The procedure is followed by combining the local level associated with atoms-in-molecule (*AIM*) with the global one where the molecule is considered as a whole entity. In these conditions the algorithm undergoes three simple steps. Firstly, one can write

$$S_A = f_A S_M = f_A \sum_A S_A \quad (105)$$

from where the atomic Fukui functions can be obtained:

$$f_A = \frac{S_A}{\sum_A S_A} \quad (106)$$

Then, through employing the chain rule of derivation,

$$\eta = \eta \left(\frac{\partial N}{\partial N} \right)_{V(r)} = \int \eta \left(\frac{\partial \rho(r)}{\partial N} \right)_{V(r)} dr = \int \eta f(r) dr, \quad (107)$$

one can consider the additive atom-in-molecule level of chemical hardness:

$$\eta_M = \sum_A f_A \eta_A \quad (108)$$

Finally, the replacement of atomic Fukui functions (106) is carried out along the particularization of the observed hardness-softness relationship:

$$\eta = \frac{1}{2S} \quad (109)$$

leading to the working formula

$$\eta_M = \frac{n^{AIM}}{\sum_A \frac{n^A}{\eta_A}} \quad (110)$$

under the constraint that the sum over the atom types in molecules equals the total number of atoms-in-molecule:

$$\sum_A n^A = n^{AIM} . \quad (111)$$

Quite remarkably, a similar atoms-in-molecule recipe can be formulated for atomic and molecular electronegativity once it is assumed that between electronegativity and hardness a sort of universal inter-conversion factor θ exists at whatever level of electronic organization:

$$\chi = \theta\eta . \quad (112)$$

Therefore, for the neutral molecules, it looks like:

$$\chi_M = \frac{n^{AIM}}{\sum_A \frac{n^A}{\chi_A}} . \quad (113)$$

However, aiming to closely connect electronegativity and chemical hardness in a single conceptual and computational vision, they can be unitarily related with the change in total energy of the molecular system throughout the second order truncated expansion:

$$\Delta E \cong -\chi\Delta N + \eta(\Delta N)^2 \quad (114)$$

known as the parabolic charge-dependence of chemical reactivity. While this expression seems to naturally follow from the electronegativity and chemical hardness definitions (94) and (96), respectively, its universal viability or even realistic character in bonding is still disputed. It will be the subject of the present study case as well, in a moment. Nevertheless, it is worth noting that electronegativity and chemical hardness, viewed as minus chemical potential and force, respectively, may be considered as a sufficient minimal set of descriptors to be considered for establishing the driving principles of chemical reactivity.

4.2. Reactivity principles

The key concepts that underlie chemical reactivity are electronegativity and chemical hardness [157]. This is because they are the chemical correspondent of the potential and force based on which the entirely (point) charge transfer can be formulated in similar way the electrostatic laws are applied with potential and force fields.

Regarding electronegativity, since it can be seen as the minus of the chemical potential, it drives the course of charge transfer until the equilibrium, i.e. overall equality, between all involved parts of bonding is attained. The resulting principle stands as the *electronegativity equalization principle (EE)* and consecrates that “the electronegativities of all the constituent atoms in a molecule have the same value” [159,160]. Remarkably, this electronegativity principle combined with the previous parabolic dependence of the total energy on the transferred charge lead with the equilibrium electronegativity formula that can be generalized with the one derived from the atom-in-molecule reactivity indices in previous section.

Moving on to the next stage in reactivity, i.e. the second order effects of charge transfer, the chemical hardness comes into play in the same manner as electronegativity did before. This time, the equalization of chemical harnesses is transposed in the so called *hard-and-soft-acids-and-base principle (HSAB)* that simply states that:”hard likes hard and soft likes soft”. Nevertheless, this step in reaction accounts more for the covalent refinement of the bonding while the difference in electronegativities among the bond constituents corresponds with the ionic character and stage of bonding.

However, both *EE* and *HSAB* principles may lead to departures from the demanded equality rules when applied on certain reactions. Such discrepancies are not a weakness of the principles themselves, but rather natural effects of quantum fluctuations when the chemical bonding is envisaged through association and dissociation phenomena.

Therefore the electronegativity and chemical hardness equality principles have to be accompanied with the corresponding inequality principles thus generating the inequality electronegativity (*IE*) and maximum hardness (*MH*) principles, respectively. Their most general form may be comprised in the variational equations [162]:

$$\delta\chi \geq 0, \quad (115a)$$

$$\delta\eta \geq 0. \quad (115b)$$

However, the resulted $\Delta\chi$ and $\Delta\eta$ has to correlate with the mismatching energy ΔE between the products and reactants throughout chemical reactions, in accordance with the prescription (114). The way in which such correlations are or not of the above parabolic nature is still subject to controversies of which a general theoretical demonstration is still absent.

Nevertheless, we may check the analytical correlations of electronegativity and chemical hardness differences respecting the reactions energies for certain paradigmatic chemical reactions, an endeavour that is undertaken in what follows.

5. A case study of quantum chemical bonding and reactivity

It is largely recognized that the covalent bond is the most widespread type of bond in chemical combinations. This is because it attains of the localization of electrons in the most direct way by pairing in bonding, see also Figure 1. Therefore, even though simple at the first glance the ionic compounds may be chosen as the basic test in bonding localization and reactivity principles. From the classical electrostatic point of view it is reasonable that as the ionic volume is increased together with the decrease of their charge the reciprocal force of attraction diminishes and their dissociation is more favourable. Based on this empirical consideration it follows that the small series of hydracids (HF, HCl, HBr, and HI) may be arranged by means of their increasing in acidic dissociation constants at ordinary temperature:



Let us analyze the quantum chemical characters of this series by means of the previously described localization and reactivity concepts.

When it comes to localization, the basic density contours of the molecules of (116) are considered, see Figure 2, from the *DFT-ab initio* computation within Hyper7 environment leading with the series of equilibrium inter-atomic distances:

$$R_{\text{HF}} = 0.908378 \text{ \AA} < R_{\text{HCl}} = 1.69244 \text{ \AA} < R_{\text{HBr}} = 1.78848 \text{ \AA} < R_{\text{HI}} = 1.88766 \text{ \AA} \quad (117)$$

In the bonding region, i.e. in the space between the hydrogen and halogen atomic centres in H-X molecules of (116), there are represented both the electron densities [163] and the associate *ELFs* of eqs. (88)-(90) are represented for the involved *AIM*, see Figure 2.

From Figure 2 one can clearly see that while the crossing of hydrogen and halogen radial densities does not provide the right bonding region, the corresponding *ELFs* cross-lines of *AIMs* finely indicate the frontier of atomic basins in hydracids thus confirming their refined way of identifying chemical bonds and bonding. One can equally say that in the crossing vicinity of *AIM-ELFs* the electrons are at the same time completely localized (with $ELF \rightarrow 0$) and completely delocalized (with $ELF \rightarrow 1$), according to the *ELF* definition in section 2.2. This can be viewed as the *ELF definition of the chemical bond that identifies the molecular region in which the electrons undergo the transition from the complete delocalization to complete localization behaviour*. Such a feature gives, nevertheless, an in-depth understanding of the quantum nature of the chemical bond by associating the mysterious pairing of electrons, despite their classical electrostatic inter-repulsion, with an intrinsic order of their spins, orbitals and thus densities, at those narrow regions of molecular space where

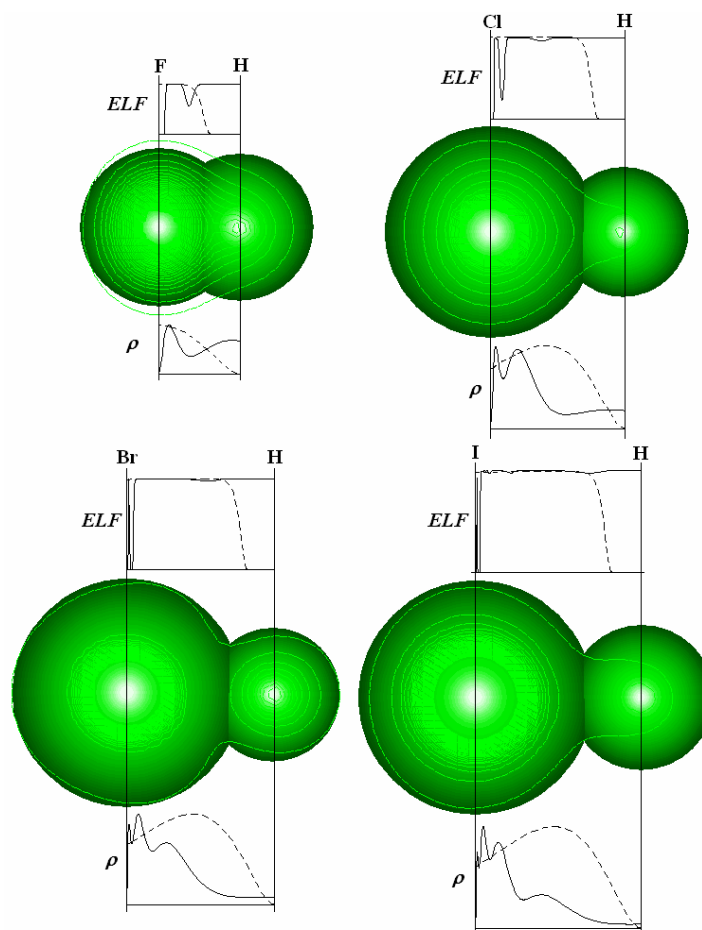
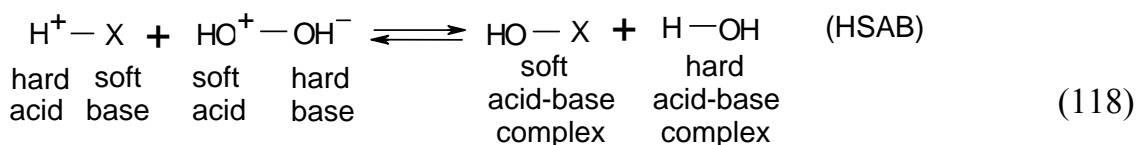


Figure 2. Comparative analysis of the charge density contours, electronic localization functions (ELFs), and radial densities for the H (dashed lines), F, Cl, Br, and I (full lines) atoms in molecular combinations HF, HCl, HBr, and HI, respectively.

the Heisenberg and Pauli principles are jointly satisfied through *AIM-ELF*'s extreme values. Moreover, since the chemical bond can be modelled by *AIM-ELF* values jumping between 0 and 1 the way of further interpreting of bonding in the frame of quantum information theory is hereafter open.

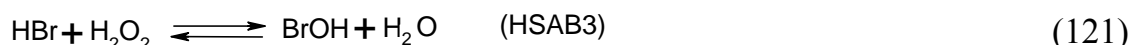
Therefore, it has been proved that localization issues indeed link the classical classification of bond as ionic or covalent, or partly ionic or covalent, in a continuous quantum reality.

As we go into the analysis of the reactivity principles it is worth involving the molecules of (116) in the paradigmatic scheme of HSAB [161, 162],



by which a hard acid substitutes a hard base from a soft acid so that the hard-hard and soft-soft acid-bases complexes are formed.

Particularization of the scheme (117) on the molecules of the (116) series lead with the associate *HSAB* reactions:



Now, we would like to derive the change in total energy, electronegativity and chemical hardness values among the reactants of (HSAB1)-(HSAB4) reactions of (119)-(122), and of their inter-correlations, employing different theoretical and computational methods.

As such, for total energy the semiempirical AM1 (Austin Model 1) and PM3 (re-parameterized AM1 with less repulsive nonbonding interactions) were considered among the *ab initio* HF and DFT methods. The results are presented in Tables 1 and 2.

Table 1. Values of the total energies for the molecules considered through chemical reactions (HSAB1)-(HSAB4) of equations (119)-(122) computed with semi-empirical (AM1 and MP3) and self-consistent field (HF and DFT) environments. The computations were performed using HyperChem Release 7" [164]. All values are expressed in MJ/mol, where 1MJ/mole \approx 10.4eV/atom.

Method Molecule	$-\text{E}_{\text{AM1}}$	$-\text{E}_{\text{PM3}}$	$-\text{E}_{\text{HF}}$	$-\text{E}_{\text{DFT}}$
HF	48.2	43.99	262.33	234.66
HCl	37.42	32.07	1206.75	1134.5
HBr	35.43	35.55	6716.48*	6465.96*
HI	34.83	29.26	18068.2*	17612.6*
FOH	78.7	71.99	458.33	402.71
ClOH	68.13	60.27	1402.9	1278.71
BrOH	65.72	63.26	6911.32*	6575.28*
IOH	65.69	57.6	18263.4*	17709.3*
H₂O₂	64.22	59.41	395.483	334.87
H₂O	33.6	31.32	199.41	171.9

* computed with small 3-21G orbital base

Table 2. Values of the variation of the total energies for the molecules considered through chemical reactions (HSAB1)-(HSAB4) in the computational cases of the Table 1. All values are expressed in MJ/mol.

Reaction \ Method	ΔE_{AMI}	ΔE_{PM3}	ΔE_{HF}	ΔE_{DFT}
HSAB1	-30.5	0.09	0.073	-5.08
HSAB2	-0.09	-0.11	-0.077	18.76
HSAB3	0.33	0.38	1.233	53.65
HSAB4	-0.24	-0.25	0.873	66.27

Table 3. Values of the structural indices electronegativity (χ), chemical hardness (η), in finite-difference [165], density functional [155], and semiclassical [156] modes for the atoms of the reactants of chemical reactions (HSAB1)-(HSAB4). All values are expressed in MJ/mol.

Level \ Atom	<i>Finite-Difference</i>		<i>Functional</i>		<i>Semiclassical</i>	
	χ_{FD}	η_{FD}	χ_{DFT}	η_{DFT}	χ_{SC}	η_{SC}
H	0.69	0.62	0.69	0.62	0.69	0.62
O	0.73	0.59	27.87	15.48	$1.07 \cdot 10^{-1}$	$0.21 \cdot 10^{-1}$
F	1.00	0.68	44.25	11.45	$1.34 \cdot 10^{-1}$	$0.22 \cdot 10^{-1}$
Cl	0.80	0.45	30.29	20.33	$0.19 \cdot 10^{-2}$	$0.32 \cdot 10^{-3}$
Br	0.73	0.41	32.58	24.02	$0.32 \cdot 10^{-4}$	$0.44 \cdot 10^{-5}$
I	0.65	0.36	21.26	16.56	$0.35 \cdot 10^{-6}$	$0.5 \cdot 10^{-7}$

Different models were assessed for the electronegativity and chemical hardness as well, namely the experimental based finite-difference (*FD*) [165], conceptually based *DFT* [155], and path-integral based semiclassical (*SC*) [156] ones. The atomic values for atoms involved in reactions (119)-(122) are displayed in Table 3, while the molecular results, based on equations (110) and (113), are presented in Table 4 for electronegativity and chemical hardness, respectively.

It is worth noting that from Table 4 the experimental based finite difference and path integral based semi-classical hardness hierarchy is neatly prescribed as:

$$\eta_{\text{HF}} > \eta_{\text{HCl}} > \eta_{\text{HBr}} > \eta_{\text{HI}} \quad (123)$$

while the OH-X complexes are in general softer than H-OH one, excepting FOH. This situation clearly reverses the empirical order of (116) thus proving that the quantum mechanical calculation can overcome the empirical judgements, a situation often met in connection with quantum phenomena. However, the conceptual based *DFT* analysis suggest that while the order (116) is somehow observed, the complex H-OH appears harder than all

products OH–X in Table 5, according to reactions (119)-(122). At this point, it is clear that another cutting criterion has to be checked in order to decide which of these approaches should be chosen as most appropriate for the molecular series (116) involved in the (117) *HSAB* type reaction.

Therefore, the electronegativity and chemical hardness excesses ($\Delta\chi, \Delta\eta$) for reactions (119)-(122) are reported in Table 5 and are finally correlated with total energy differences (ΔE) of Table 2 by employing the (spectral) quantitative structure-property relationships (QSPR) analysis [166], here of the form:

$$E = a + b\chi + c\eta \quad (124)$$

The QSPR results through all energy and electronegativity and chemical hardness combined methods are presented in Table 6, emphasising both the

Table 4. Values of the structural indices electronegativity (χ), chemical hardness (η), in finite-difference, density functional and semiclassical modes for the reactants of chemical reactions (HSAB1)-(HSAB4). All values are expressed in MJ/mol.

Molecule	Finite-Difference		Functional		Semiclassical	
	χ_{FD}	η_{FD}	χ_{DFT}	η_{DFT}	χ_{SC}	η_{SC}
HF	0.82	0.65	1.36	1.18	0.22	0.04
HCl	0.74	0.52	1.35	1.2	$0.38 \cdot 10^{-2}$	$0.06 \cdot 10^{-2}$
HBr	0.71	0.49	1.35	1.21	$0.06 \cdot 10^{-3}$	$0.88 \cdot 10^{-5}$
HI	0.67	0.46	1.34	1.2	$0.7 \cdot 10^{-6}$	$0.1 \cdot 10^{-6}$
FOH	0.79	0.63	1.99	1.70	0.16	0.03
ClOH	0.74	0.54	1.98	1.74	$0.56 \cdot 10^{-2}$	$0.09 \cdot 10^{-2}$
BrOH	0.72	0.52	1.98	1.75	$0.1 \cdot 10^{-3}$	$0.01 \cdot 10^{-3}$
IOH	0.69	0.49	1.96	1.73	$1.05 \cdot 10^{-6}$	$1.5 \cdot 10^{-7}$
H₂O₂	0.71	0.6	1.35	1.19	0.19	0.04
H₂O	0.70	0.61	1.02	0.91	0.25	0.06

Table 5. Variations of the electronegativity (χ) and chemical hardness (η) by employing the finite-difference, density functional, and semiclassical methods for chemical reactions (HSAB1)-(HSAB4) of equations (119)-(122). All values are in MJ/mol.

Reaction	Finite-Difference		Functional		Semiclassical	
	$\Delta\chi_{FD}$	$\Delta\eta_{FD}$	$\Delta\chi_{DFT}$	$\Delta\eta_{DFT}$	$\Delta\chi_{SC}$	$\Delta\eta_{SC}$
HSAB1	-0.04	-0.01	0.3	0.24	0.00	0.01
HSAB2	-0.01	0.03	0.3	0.26	0.062	0.02
HSAB3	0.00	0.04	0.3	0.26	0.06	0.02
HSAB4	0.01	0.04	0.29	0.25	0.06	0.02

Table 6. Coefficients of the correlation of the variation of the total energies of the Table 2 with the electronegativity and hardness variations of the Table 5 in finite-difference, density functional, and semiclassical models of chemical reactions (HSAB1)-(HSAB4), respectively. The deviation from the parabolic expansion $E=a+b\chi+c\eta$ in terms of the ratio c/b^2 as well as the correlation factor of the QSAR model (r) are also indicated.

Method of		QSAR results				
χ & η	Energy	a	b	c	c/b^2	r
FD	AM1	-35.58	-381.92	965.46	0.007	0.989014
	PM3	-0.93	-30.81	26.15	0.028	0.576147
	HF	1.08	30.35	-9.92	-0.011	0.682117
	DFT	81.55	2451.31	-945.31	-0.0002	0.967383
DFT	AM1	50.56	-1495.0	1531.0	0.0007	0.999937
	PM3	-11.325	36.25	2.25	0.0017	0.681353
	HF	10.438	-54.75	25.25	0.0084	0.527625
	DFT	1020.72	-5070.75	2064.25	0.00008	0.899406
SC	AM1	-65.095	-67.5	3459.5	0.7593	0.999884
	PM3	-5.135	-87.5	522.5	0.068	0.33817
	HF	-34.807	-565.0	3488.0	0.011	0.97237
	DFT	-1306.12	-20600.0	130104	0.00031	0.987422

degree of parabolic dependence of (123), i.e. how closely $c/b^2 \rightarrow 1$, and the consecrated statistical correlation coefficient (r).

From Table 6 there it is now clear that a parabolic form of total energy respecting electronegativity and chemical hardness is possible, it is attained within SC-AM1 approach, and when this is the case the associated correlation coefficient goes asymptotically to unity.

With these, other lessons about bonding and reactivity can be learned. One is that the chemical intuition should be never abandoned as far semiempirical models can provide reliable results. Another may state that no quantum method should be excluded from the outset but tested through all reactivity principles. For instance, in this particular problem analyzed the semiclassical approaches appear to better respond to the bonding demands, at the edge between the classical and quantum effects. Nevertheless, for each envisaged problem the whole available arsenal of quantum methods should be explored and depending on the results, the problem should be classified as involving more or less intensive, localized or reactive effects.

6. Conclusion

“When you’re a quantum chemist, it’s like you’re sitting at the top of the mountain. The distinction between biochemistry, inorganic, and organic chemistry are less important, as all of chemistry revolves around what the electrons are doing in molecules, and that domain can be best <<seen>> by

applying theory” says Rodney J. Bartlett, on receiving the 2007 American Chemical Society award in theoretical chemistry.

Indeed, the impact of the quantum view upon the nature of the chemical bond was considerable, as it offered both qualitatively and quantitatively a scheme of structure analysis together with the chemical-physical transformations, being accurately confirmed by both the computational and the experimental expertise in all branches of chemistry, and whenever the electronic structure is about. As a consequence, the chapters of the structural physical chemistry should be classified within an *intensive, localization, and reactivity levels* of chemical bonding assessment [167-189].

At the intensive level it was established that, for an adequate treatment in the quantum space of the polyatomic combinations, the electronic density $\rho(r)$ rather than the already historical wave function $\psi(r_1, \dots, r_N)$ stays as the main variable for a system with N electrons. This is because, contrary to the wave function, the electronic density is an experimental detectable quantity, defined in the real three dimensional space, and not within a $3N$ Hilbert abstract one, being also directly related to the total number of electrons in the concerned system through the functional relation $N = \int \rho$.

However, since the quantum existence of the atoms in molecules represents the key to chemical bonding description depending on how much of the individuality of an atom is preserved and how much of it is transferred to the bond, the localization level appears as a compulsory next stage in chemical bond characterization. In this context the idea of molecular partitioning in terms of the domains of stability of molecular electronic density was advanced.

The results consist in the emergence of the so called *atomic basins* that include all the atomic nuclei but also their interspaces until the surface delimited by fulfilment of the zero flux condition of electronic density ($\nabla \rho(r) \cdot \vec{n} = 0$) according with Bader and co-workers’ atoms-in-molecules approaches.

Nevertheless, the electronic localization complements, at the local level, the quantum information comprised in the reactivity indices, being ultimately described through the so called *localization functions*. These should express the balance between the local stability and the delocalization tendency of the involved electrons in the chemical bond in the view of the forthcoming transformations.

So, the localization functions indicate the ratio of the non-uniformly localized electronic distribution to the uniform delocalization of the electronic gas, accordingly with the Heisenberg quantum principle of delocalization and that of the Pauli indiscernability. It was however proved, through a series of hydracids molecules that the atoms-in-molecule electronic localization function in its exponential form and with error interpretation, as recently recommended by one of the authors’ recipe [152], stands as a viable quantum tool for identifying bonds within the bonding space.

On the other way, at the global level, the reactivity indices' studies are essential for indicating the propensity of a multielectronic system to participate into a chemical reaction. At the molecular level, these indices are defined so as to quantitatively measure the chemical reactivity, while at the biomolecular level they are associated with the biological activity, being the best candidates to be correlated in the context of quantitative structure activity (property) relationships, QSA(P)Rs.

Thus, since the reactivity indices are placed at the informational interface between the electronic systems' stability and their tendency to transform and combine they are mathematically introduced as the integral functions of the electronic density function, releasing the so called *electronic density functionals* as the efficient tool for the global prediction of the electronic properties of the investigated nanosystems.

In this respect the electronegativity and chemical hardness seems to provide the minimal set of descriptors to be considered for characterizing the bond involvements in chemical reactions [37, 155, 156, 160, and 162]. Such an analysis was also performed on specific hard-and-soft-acids-and-bases reactions characteristic for the hydric acids considered.

However, all above phenomenologically identified levels of quantum nature of the chemical bond can be analytically or computationally inter-related as well through particular QSA(P)R models, see Figure 3. This way the inner circle of quantum chemistry is opened to include application to biological interaction in a unitary manner.

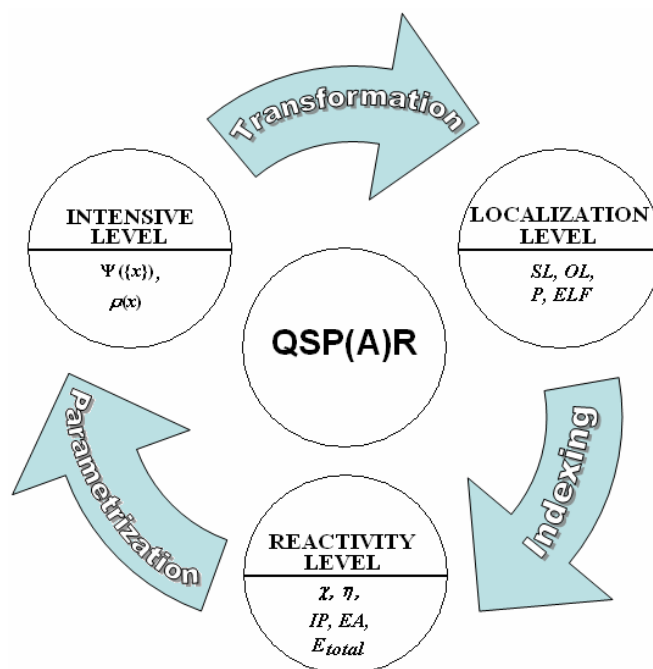


Figure 3. Synopsis of the intensive, local, and global levels of quantum chemistry and their inter-relation respecting the chemical bond characterization.

Overall, searching for the unity of the manifestation forms of the chemical bonding at various levels of matter organization has become a very active interdisciplinary field in the last years, being one of the main goals in the frame of the nanosciences. The quantum paradigm of bonding unification through the formulation of a minimal set of concepts and quantities having as much universal multielectronic relevance as possible represents a real challenge for the conceptualization and prescription of the viable applicative directions of the nanosystems, from atoms to biomolecules in the years to come.

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