

Chemical Action Concept and Principle

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Abstract

Abstract. Since the nowadays growing interest in assessing specific chemical principles, the so called chemical action functional, $C_A = \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}$, its allied variational principle $\delta C_A = 0$ and of its consequences are employed in assessing chemical elemental periodicity, bonding and reactivity. As such, the role of chemical action concept and principle in chemical modeling is systematically summarized and exemplified at various levels of comprehension, e.g. in establishing the recent atomic scales of electronegativity, chemical hardness, ionization potential and electronic affinity, as well as by advancing the intriguing reformulation of the chemical bonding and of electronic pairing along the chemical bond within density functional and spinorial Dirac theories; equally, the role in entanglement and tunneling phenomena specific to chemical catalysis and complex ligand-receptor interaction are presented in an unitary manner allowing effective conceptual interpretation of chemical phenomena in analytical terms as well as providing the appropriate computational framework for their quantization.

1. Introduction

There is already recognized that since the discovery of the periodicity of elements Chemistry acquires its own status as “a great science” of Nature due to the power of prediction and synthesis of new compounds with general pre-established properties [1-4]. However, such milestone knowledge opens also the problem of whether Chemistry itself may have its own driving principles, i.e. if adds new natural laws to those already established by Physics, for instance. And indeed, the *aufbau principle* that underlies the Periodic System seems more and more as belonging to chemistry rather than to physics; more specifically, the quantum labeling according which many- electronic systems may be identified and classified as 1s, 2s, 2p, 3s, 3p, 3d, etc. obviously departs the physical principle according which electrons are indistinguishable particles – therefore, as far as such construction works, and already shown its reliability, this is not a physical principle [5-7]! It is therefore a chemical one [8-12]!

The next level in which Chemistry rather than Physics had advanced new principles of Nature comes from the celebrated Density Functional Theory (DFT) that is mainly based on the assumption according which a non-local interaction (as pairing of electrons for instance on orbitals and bonding) may be finely approximated (and eventually replaced) by a local (even with gradient extension) representation [13-24]. Again, such picture of chemical interaction clearly departed the custom physical many-body treatment, and since proved its power of truth was awarded with Nobel prize in Chemistry rather in Physics, although the prize was awarded to a physicists as Walter Kohn and a computational mathematician as John Pople, in 1998.

However, two main lessons may be drawn for further prospection of Chemical laws that complement the physical ones, namely:

- (i) the chemical phenomena are intriguing enough such that to require special framework and principles, specifically adapted for its range of (quantum) interaction that often lays in the semiclassical regime between the classical (macroscopic) and quantum (microscopic) levels of mater manifestation; this probably due to the peripheral or valence special electronic behavior of atoms-in-molecules, for instance, but also for atoms themselves due to the shielding effects [25];

- (ii) the density functional theory offers the actual appropriate conceptual and computational environment in order to quantify the chemical phenomena in such a way fulfilling both the quantum variational principles and the semiclassical specificity of chemical reactivity through the electronic density concept $\rho(\mathbf{r})$.

It is therefore the scope of this review presenting a new principle of chemistry, within DFT, and of its role in assessing the chemical description of elemental periodicity, atoms-in-molecules, electronic pairing, along with its role in elucidating the structure of atoms-in-molecules. This will be acquired through the link with other two main tools of conceptual DFT of chemistry, namely with electronegativity (χ) and with the chemical hardness (η) dully defined as the first and second derivatives of the total energy $E = E[N, V(\mathbf{r})]$ of a N -electronic V -representable system [26-34]:

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_{V(\mathbf{r})}, \quad (1)$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{V(\mathbf{r})} \quad (2)$$

Whorth noting these indices were consecrated as providing the main principles of chemical reactivity, namely the equalization and minimum of electronegativity (in bonding) [35-40]

$$d\chi \leq 0 \quad (3)$$

and hard-and-soft-acids-and-bases (HSAB) aka chemical hardness equalization [41-46], and maximum hardness (MH) [47-50] principles resumed under the chemical hardness inequality

$$d\eta \geq 0 \quad (4)$$

There still remain the open question whether these principles are of chemical nature or are they reducible to physical variational ones, in any conditions. Hopefully, in what next such question will be answer in positive in the chemical side along offering the framework in which a natural variational principle of the so called *chemical action functional* [21,34,51-60]

$$C_A = \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r} \quad (5)$$

convolutes the main ingredients of a chemical interaction, i.e. the electronic density and the external potential, is specific to chemical reactivity and bonding.

2. Chemical Reactivity and Chemical Action Principles

The variational principle of the chemical action density functional of Eq. (5)

$$\delta C_A = 0 \quad (6)$$

will be introduced, within DFT, this way proving its necessity in modern conceptual chemistry.

To this end one notes that in physical sciences the total energy variation

$$dE = 0 \quad (7)$$

fixes the equilibrium or the evolution towards equilibrium of natural systems. In conceptual DFT framework, however, if one expands the total energy $E = E[N, V(\mathbf{r})]$ such that to contain the electronegativity and chemical hardness appearance relating the number of electrons in first and second order variations in reactivity, respectively, as well as to contain the applied potential fluctuation, one has the working differential relationship

$$dE = -\chi dN + \eta (dN)^2 + \int \rho(\mathbf{r}) dV(\mathbf{r}) d\mathbf{r} \quad (8)$$

Yet, through combining eqs. (7) and (8), one has either that:

- there is no action on the system ($dN = dV = 0$) so that no chemical phenomena is recorded since the physical variational principle (7) is fulfilled for whatever electronegativity and chemical hardness values in (8);
- or there is no electronic system at all ($\chi = \eta = \rho(\mathbf{r}) = 0$).

Therefore, it seems that the variational physical principle of eq. (7) do not suffice in order the chemical principles of electronegativity and chemical hardness being encompassed, as above stipulated, see eqs. (3) and (4). As a consequence one is forced to perform the double variational procedure on the total energy, i.e. through applying the additional differentiation on physical energy expansion (8), within the so called “chemical variational mode” (and denoted as $\delta[\]$) where the total differentiation will be taken only over the scalar-global (extensive χ, η, dN) and local (intensive $\rho(\mathbf{r}), V(\mathbf{r})$) but not over the vectorial (physical – as the coordinate itself \mathbf{r}) quantities. This way, one has immediately

$$\delta[dE] = -\delta[\chi dN] + \delta[\eta (dN)^2] + \int \delta[\rho(\mathbf{r}) dV(\mathbf{r})] d\mathbf{r} \quad (9)$$

Now, the chemical variational principle applied to eq. (9) will look like

$$\delta[dE] \geq 0 \quad (10)$$

In conditions of chemical reactivity or binding certain amount of charge transfer and the system's potential fluctuations (departing from equilibrium) are involved

$$dN = |dN| = ct. \neq 0, \quad dV(\mathbf{r}) \neq 0 \quad (11)$$

When considering the chemical variation prescribed by eq. (9) in chemical transformation driven by the condition (10), a kind of reactivity towards equilibrium constraint or a sort of reverse Gibbs free energy condition, or a special kind of entropy variation within the second law of thermodynamics are in fact applied, while releasing with the individual reactivity principles:

- for electronegativity contribution we have the condition:

$$-\delta[\chi dN] \geq 0 \Leftrightarrow -|dN| \delta[\chi] \geq 0 \Rightarrow \delta[\chi] \leq 0 \quad (12)$$

recovering the electronegativity variational formulation (3) for chemical systems toward equilibrium.

- for chemical hardness contribution one gains directly the inequality of eq. (4)

$$\delta[\eta(dN)^2] \geq 0 \Leftrightarrow (dN)^2 \delta[\eta] \geq 0 \Rightarrow \delta[\eta] \geq 0 \quad (13)$$

- whereas for chemical action contribution there is now sufficient in having the exact equality

$$\delta \int \rho(\mathbf{r}) dV(\mathbf{r}) d\mathbf{r} = 0 \quad (14)$$

leaving with the successive equivalent forms

$$\begin{aligned} 0 &= \delta \int \rho(\mathbf{r}) \{V(\mathbf{r}) - V(\mathbf{r}_0)\} d\mathbf{r} \\ &= \delta \left\{ \int \rho(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} \right\} - \delta \left\{ V(\mathbf{r}_0) \int \rho(\mathbf{r}) d\mathbf{r} \right\} \end{aligned} \quad (15)$$

with $V(\mathbf{r}_0)$ being the constant potential at equilibrium. However, through employing the basic DFT relationship for electronic density

$$N = \int \rho(\mathbf{r}) d\mathbf{r} \quad (16)$$

and by recognizing the total number of electron constancy in the (atoms-in-molecules) system the eq. (14) produces the so called chemical action principle of eq. (6) that represents the chemical specialization for the physical variational principle of eq. (7).

Worth noting that the actual chemical action principle arises along the other chemical reactivity principles of electronegativity and chemical hardness in a natural

way, yet by performing special variation of the charge transfer and potential fluctuation around equilibrium rather than by the direct physical implementation of an “action” in searching for the system evolution’s “trajectory”. Therefore, the present analysis reveals two main features of chemical reactivity principles in general and of that of the chemical action in special:

- the chemical reactivity principles of electronegativity and chemical hardness belong to *chemical* variation principle rather to the physical optimization framework, this way inscribing themselves in the heritage of natural laws provided by Chemistry to complement those of Physics;
- the chemical action principle of eq. (6), apart representing as well a chemical principle since arising within the same conceptual DFT framework as those of electronegativity and chemical hardness, represents a variational principle that optimizes the relationship between the bijective main quantities of DFT, the electronic density and its driving bare potential, in a convoluted manner over the reactivity or binding space of interest; it may, eventually, produce the chemical global minima of equilibrium in reactivity or bonding.

However, the hierarchy of the electronegativity, chemical hardness and chemical action principles was recently advanced as describing the paradigmatic stages of bonding [34]; they may be resumed here through the sequence:

$$\delta\chi = 0 \rightarrow \delta C_A = 0 \rightarrow \Delta\chi < 0 \rightarrow \delta\eta = 0 \rightarrow \Delta\eta > 0 \quad (17)$$

as corresponding to the *encountering* (or the electronegativity equality) *stage*, followed by *chemical action minimum variation* (i.e. the global minimum of bonding interaction), then by *the charge fluctuation stage* (due to minimum or residual electronegativity), ending up with *the polarizability stage* (or HSAB) and with the *final steric* (due to maximum or residual hardness) *stage*. Nevertheless, from eq. (17) one observes the close laying chemical action with electronegativity influence in chemical reactivity and bonding principles.

3. Role of Chemical Action in Elemental Periodicity

In practical DFT implementation, the chemical reactivity indices that characterize the chemical systems and of their features are computed via the so called softness reactivity hierarchy [33, 61-69]

$$\frac{1}{2\eta} \equiv S = \int s(\mathbf{r})d\mathbf{r} = \iint s(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}' \quad (18)$$

in terms of the global, local, and kernel levels for the softness property, respectively [63,67]

$$S = - \left(\frac{\partial N}{\partial \chi} \right)_{V(\mathbf{r})}, \quad (19)$$

$$s(\mathbf{r}) = - \left(\frac{\partial \rho(\mathbf{r})}{\partial \chi} \right)_{V(\mathbf{r})}, \quad (20)$$

$$s(\mathbf{r}, \mathbf{r}') = - \left(\frac{\delta \rho(\mathbf{r})}{\delta V(\mathbf{r}')} \right)_N + \frac{s(\mathbf{r})s(\mathbf{r}')}{S} \quad (21)$$

where the fundamental DFT relationship (16) was employed for passing from the local to the global levels of softness. They can be eventually specialized for various DFT pictures, for instance when the local and non-local contributions are separated in certain factorial way, with the form (in atomic units) [61]

$$s(\mathbf{r}, \mathbf{r}') = L(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}') + \rho(\mathbf{r})\rho(\mathbf{r}') \quad (22)$$

with

$$L(\mathbf{r}) = \frac{\nabla \rho(\mathbf{r}) \cdot [-\nabla V(\mathbf{r})]}{[-\nabla V(\mathbf{r})]^2}, \quad (23)$$

being $\delta(\mathbf{r} - \mathbf{r}')$ the delta-Dirac function. In these conditions, under successive integration of (22) according with the recipe (18), the local and global softness become:

$$s(\mathbf{r}) = L(\mathbf{r}) + N\rho(\mathbf{r}), \quad (24)$$

$$S = a + N^2 \quad (25)$$

where the short-hand notation

$$a \equiv \int L(\mathbf{r})d\mathbf{r} \quad (26)$$

was considered.

Now, through expanding the electronegativity in the same manner as previously done for the total energy, i.e. within second order in charge – first order in potential variation- see eq. (8), one has in general the differential formulation [54]

$$d\chi = \left(\frac{\partial \chi}{\partial N} \right)_{V(\mathbf{r})} dN + \frac{1}{2} \left[\frac{\partial}{\partial N} \left(\frac{\partial \chi}{\partial N} \right)_{V(\mathbf{r})} \right]_{V(\mathbf{r})} dNdN + \int \left(\frac{\delta \chi}{\delta V(\mathbf{r})} \right)_N \delta V(\mathbf{r})d\mathbf{r} \quad (27)$$

that rewrites with the help of above softness local and global indices (19) and (20) as

$$d\chi = -\frac{1}{S} dN - \left[\frac{\partial}{\partial N} \left(\frac{1}{S} \right) \right] dNdN - \int \frac{s(\mathbf{r})}{S} \delta V(\mathbf{r}) d\mathbf{r} \quad (28)$$

and is finally rearranged within the actual softness kernel picture of eq. (22):

$$d\chi = -\frac{1}{a+N^2} dN + \frac{N}{(a+N^2)^2} dNdN - \int \frac{L(\mathbf{r}) + N\rho(\mathbf{r})}{a+N^2} \delta V(\mathbf{r}) d\mathbf{r} \quad (29)$$

Note that in turning eq. (27) into eq. (28) the Maxwell-DFT relationship was used, [15,16]

$$\left(\frac{\delta\chi}{\delta V(\mathbf{r})} \right)_N = - \left(\frac{\delta\rho(\mathbf{r})}{\delta N} \right)_{V(\mathbf{r})} \quad (30)$$

defining in fact the so called Fukui function [64], assuring therefore the correct frontier (or valence) framework in which the present analytical discourse is placed. This allows us computing the differential electronegativity by integrating eq. (30) up to the number of valence electrons in focus (N_v) with the result [54]

$$\chi = \int_0^{N_v} d\chi = -\frac{1}{\sqrt{a}} \arctan\left(\frac{N_v}{\sqrt{a}}\right) + \frac{N_v - \sqrt{a} \arctan(N_v/\sqrt{a})}{2a} - \frac{b + N_v C_d}{a + N_v^2} \quad (31)$$

where an additional notation was introduced, namely

$$b \equiv \int L(\mathbf{r})V(\mathbf{r})d\mathbf{r} \quad (32)$$

Next, also the related chemical reactivity indices may be evaluated with reference to the differential electronegativity (31). Firstly, through comparing eqs. (1) and (2) the chemical hardness may be evaluated under the so called absolute form [54]

$$\eta_{DFT} = -\frac{1}{2} \int_{N_v-1}^{N_v+1} d\chi = \frac{1}{4} \left\{ \frac{4[C_d(1+a-N_v^2) - 2bN_v]}{(1+a)^2 + 2(a-1)N_v^2 + N_v^4} + \frac{1}{\sqrt{a}} \left[\arctan\left(\frac{N_v-2}{\sqrt{a}}\right) + \arctan\left(\frac{N_v+2}{\sqrt{a}}\right) \right] - \frac{2}{\sqrt{a}} \left[\arctan\left(\frac{N_v-1}{\sqrt{a}}\right) + \arctan\left(\frac{N_v}{\sqrt{a}}\right) - \arctan\left(\frac{N_v+1}{\sqrt{a}}\right) \right] \right\} \quad (33)$$

Next, the total (valence) energy of eq. (8) explicitly becomes

$$dE = -\chi(N)dN - \frac{1}{2} \left(\frac{\partial \chi(N)}{\partial N} \right)_{V(\mathbf{r})} dN dN + \int \rho(\mathbf{r}) \delta V(\mathbf{r}) d\mathbf{r} \quad (34)$$

that allows in computing also the *absolute electronegativity* counterpart upon the specific integration [54]:

$$\begin{aligned} \chi_{DFT} &= -\frac{1}{2} \int_{N_v-1}^{N_v+1} dE \\ &= \frac{3}{16a} \left\{ \begin{aligned} &4N_v + 2\sqrt{a} \left[\begin{aligned} &(2b + 3N_v - 3) \arctan\left(\frac{N_v - 1}{\sqrt{a}}\right) \\ &-(2b + 3N_v + 3) \arctan\left(\frac{N_v + 1}{\sqrt{a}}\right) \end{aligned} \right] \\ &+ a(2C_A - 3) \ln \left[\frac{a + (N_v - 1)^2}{a + (N_v + 1)^2} \right] \end{aligned} \right\}, \quad (35) \end{aligned}$$

that nicely resembles, at the analytical level, the famous *Mulliken electronegativity* formulation viewed as the semi-sum of the ionization potential (IP) and electronic affinity (EA) [21,53,54]:

$$\chi_{M/ID} \equiv \frac{IP + EA}{2} = \frac{(E_{N_v-1} - E_{N_v}) + (E_{N_v} - E_{N_v+1})}{2} = \frac{E_{N_v-1} - E_{N_v+1}}{2} = -\frac{1}{2} \int_{N_v-1}^{N_v+1} dE \quad (36)$$

known also as the *finite-difference electronegativity*, when experimental IP and EA are implemented.

The form of eq. (36) gives the scheme in which the ionization potential and the electronic affinity themselves may be accordingly evaluated, having the respective expressions [54]

$$\begin{aligned} IP_{DFT} &= \int_{N_v}^{N_v-1} dE \\ &= \frac{3}{8a} \left\{ \begin{aligned} &2N_v - 1 + 2\sqrt{a} \left[\begin{aligned} &(2b + 3N_v - 3) \arctan\left(\frac{N_v - 1}{\sqrt{a}}\right) \\ &-(2b + 3N_v) \arctan\left(\frac{N_v}{\sqrt{a}}\right) \end{aligned} \right] \\ &+ a(2C_A - 3) \ln \left[\frac{a + (N_v - 1)^2}{a + N_v^2} \right] \end{aligned} \right\}, \quad (37) \end{aligned}$$

$$EA_{DFT} = \int_{N_v+1}^{N_v} dE = 2\chi_{DFT} - IP_{DFT} \quad (38)$$

There is obvious that in all these formulations the chemical action terms is present in linear relationships, while emphasizing on the $1/N_v$ and $1/N_v^2$ proportionality factors for differential electronegativity and absolute chemical hardness of eqs. (31) and (33), respectively. Their numerical representation is displayed in Figure 1 for the first four periods of elements. The plots of Figure 1 clearly suggest a smooth periodical trend acquired with the chemical action involvement as compared with the experimental counterpart. The correcting power is especially evident when comparing the actual trends as provided by DFT formulas given by eqs. (33)-(38) with the experimental electronic affinity and finite difference chemical hardness, being the latter one evaluated as

$$\eta_{FD} = \frac{IP_{EXP} - EA_{EXP}}{2} \quad (39)$$

Moreover, there is also apparent from Figure 1 that the experimental ionization and electronegativity trends resemble in general the periodicity provided by the present DFT formulation; worth noting that both χ_{DFT} and IP_{DFT} display by eqs. (35) and (37) linear dependencies with chemical action, C_A , however with different proportionality factors as 3/8 and 3/4, respectively. Such factors are however less relevant as far as the present DFT values (the right hand columns of Figure 1) may be fairly reduced to those recorded by experimental direct (for IP and EA) or indirect (χ & η) quantities by applying a factor of 1/10.

The important fact is that chemical action concept and functional has the power of regulation of the elemental trends across the periods of the Periodic Table, beside it linearly correlates with electronegativity as the basic chemical reactivity index that is responsible for the encountering stage in bonding and reactivity.

Being this observation doubled by the previous section remarked similarity in electronegativity equalization and chemical action principle in the first stages of bonding and reactivity, see eq. (17), one can practically assume that the chemical action has the “power” of electronegativity and can be even replaced by it in certain circumstances of bonding,

$$C_A \sim \chi, \quad (40)$$

for instance when the electronegativity represents the global electronegativity of the system or the electronegativity of atoms in molecules.

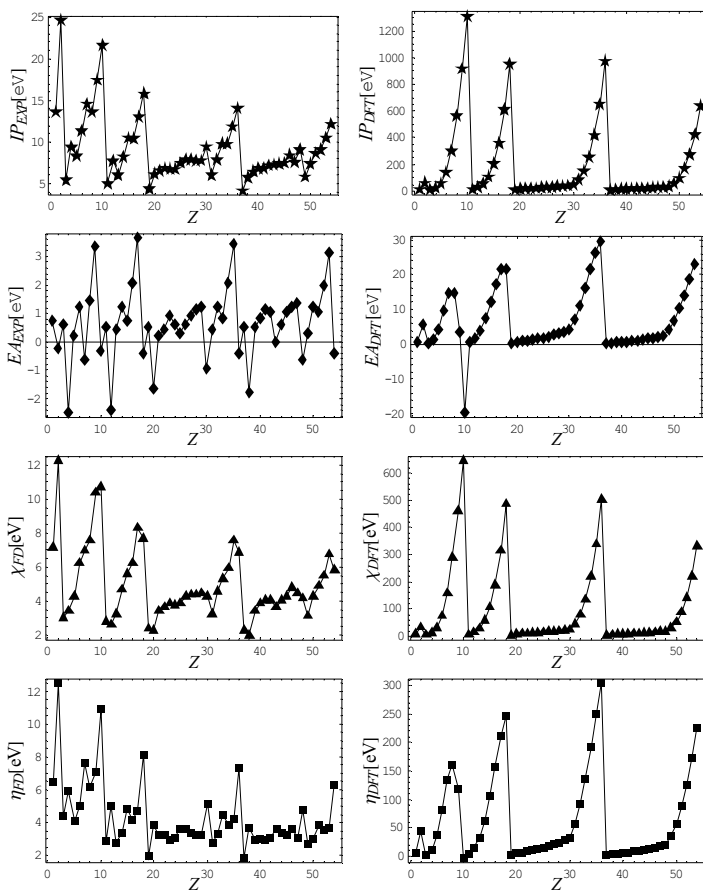


Figure 1. Comparative representation of the periodic behavior for the first four periods of elements for the ionization potential (IP), electron affinity (EA), electronegativity (χ), and chemical hardness (η) as provided by experiment (EXP), the present Density Functional Theory (DFT), and by finite-difference (FD) approaches, respectively [54].

Such ansatz is supported also by earlier (simplified) potential definition of electronegativity that, before being fully identified with the minus of the chemical potential ($\chi = -\mu$) through DFT definition of eq. (1), was associated with the convoluted Coulomb potential with the electronic density of the system [70]

$$\chi(N) = -\left\langle \frac{1}{|\mathbf{r}|} \right\rangle = -\int \rho(N, \mathbf{r}) \frac{1}{|\mathbf{r}|} d\mathbf{r} = \int \rho(N, \mathbf{r}) V_{COULOMB}(\mathbf{r}) d\mathbf{r} = C_A^{COULOMB} \quad (41)$$

The chemical action functional will be in next fully employed when the chemical action principle of eq. (6) will be used to describe the chemical bonding within the DFT and softness kernel framework.

4. Chemical Action in DFT Kernel Forms

Once the chemical action principle of eq. (6) is explicitly unfolded with the help of chemical action concept of eq. (5)

$$0 = \int \delta\rho(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r}) \delta V(\mathbf{r}) d\mathbf{r} \quad (42)$$

one recognizes it reduces to the working expression

$$0 = \int \delta\rho(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} \quad (43)$$

since cancelling the second term in (42) due to the Hellmann-Feynman theorem [71,72]; note that the resulted eq. (43) stays as a sort of physical specialization for the chemical variational form of eq. (14). However, when performing first order expansion in total number of electrons (eventually restricted to those participating in bonding) and of the potential for the electronic density $\rho = \rho[N, V(\mathbf{r})]$ one yields from eq. (43) the density solution form [57]

$$\rho(\mathbf{r}) = -\int \kappa(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') d\mathbf{r}' \quad (44)$$

in terms of the bilocal response function [62]

$$\kappa(\mathbf{r}, \mathbf{r}') = \left(\frac{\delta\rho(\mathbf{r})}{\delta V(\mathbf{r}')} \right)_N \quad (45)$$

that already appeared under the softness kernel of eq. (21). With the density-kernel dependencies of eqs. (44) and (45) back in chemical action definition (5) the *kernel density functional of chemical action* shapes as

$$C_A = -\iint V(\mathbf{r}) \kappa(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (46)$$

Equation (46) may be further refined in terms of softness kernel and chemical hardness, since recognizing their connection with electronic density goes like

$$\rho(\mathbf{r}) = 2N \int s(\mathbf{r}, \mathbf{r}') \eta(\mathbf{r}') d\mathbf{r}' \quad (47)$$

due to the basic softness-hardness kernel integration rule [67]

$$2 \int s(\mathbf{r}, \mathbf{r}') \eta(\mathbf{r}', \mathbf{r}'') d\mathbf{r}' = \delta(\mathbf{r}'' - \mathbf{r}) \quad (48)$$

actually fulfilled by the respective working kernels

$$\eta(\mathbf{r}, \mathbf{r}') = -\frac{1}{2} \frac{\delta V(\mathbf{r})}{\delta \rho(\mathbf{r}')},$$

$$s(\mathbf{r}, \mathbf{r}') = -\frac{\delta \rho(\mathbf{r})}{\delta V(\mathbf{r}')} \quad (49)$$

through recognizing the local chemical hardness with the form

$$\eta(\mathbf{r}) = \frac{1}{N} \int \eta(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r}' \quad (50)$$

Now, a close comparison between eqs. (44) and (47) leaves with the “reactivity” related bilocal response function

$$\kappa(\mathbf{r}, \mathbf{r}') = -2N \frac{\eta(\mathbf{r}') s(\mathbf{r}, \mathbf{r}')}{V(\mathbf{r}')} \quad (51)$$

that finally provides in eq. (47) the softness-hardness form of the chemical action functional

$$C_A^{s-h} = 2N \iint V(\mathbf{r}) s(\mathbf{r}, \mathbf{r}') \eta(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (52)$$

These are the forms of chemical action functional as derived from chemical variational principle to be further specialized once local or non-local versions of the involved kernel functions are considered.

For instance, when eq. (49) is restrained to its local form

$$s(\mathbf{r}, \mathbf{r}')^{local} = -\frac{\delta \rho(\mathbf{r}')}{\delta V(\mathbf{r}')} \delta(\mathbf{r} - \mathbf{r}') \quad (53)$$

the associate kernel of eq. (51) writes as [57]:

$$\kappa(\mathbf{r}, \mathbf{r}')^{local} = -\frac{1}{V(\mathbf{r}')} \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\nabla_r \rho(\mathbf{r})|} \delta(\mathbf{r} - \mathbf{r}') \quad (54)$$

and the chemical action casts accordingly from eq. (46)

$$C_A^{local} = \int V(\mathbf{r}) \rho(\mathbf{r}) \frac{\rho(\mathbf{r})}{|\nabla_r \rho(\mathbf{r})|} d\mathbf{r} \quad (55)$$

Note that when comparing the equation (55) with the chemical action basic definition of eq. (5) one gets the so called *local equation of bonding*:

$$|\nabla_r \rho(\mathbf{r})| = \rho(\mathbf{r}) \quad (56)$$

in accordance with the Bader zero flux condition [73-75]

$$\rho(\mathbf{r}) = \nabla_r \rho \cdot \mathbf{n} = 0 \quad (57)$$

for the asymptotic densities

$$\rho(r)^{local} = \frac{N}{8\pi} \exp(-r) \quad (58)$$

On the other side, when considering also the non-local effects, the softness kernel may write as

$$s(\mathbf{r}, \mathbf{r}')^{non-local} = s(\mathbf{r}, \mathbf{r}')^{local} + \rho(\mathbf{r})\rho(\mathbf{r}') \quad (59)$$

producing the associate non-local response function kernel with the form [57]

$$\kappa(\mathbf{r}, \mathbf{r}')^{non-local} = \kappa(\mathbf{r}, \mathbf{r}')^{local} - \frac{\rho(\mathbf{r}')}{V(\mathbf{r})} C_A \quad (60)$$

where the Poisson finite difference or long range approximations, the re-application of the Hellman-Feynman theorem, and the saddle point approximation for transforming an integral term to a local one were considered. In these conditions, the non-local chemical action equation for or delocalized bonding description raises as a generalization of eq. (55) and looks like

$$C_A^{non-local} = C_A \frac{\rho(\mathbf{r})}{|\nabla_r \rho(\mathbf{r})|} + C_A^2 \Delta r \quad (61)$$

where the explicit bonding displacement Δr modulates the chemical action amplitude; worth remarking that as Δr vanishes as the previous local case of bonding is formally recovered, see eq. (55). Remarkably, both local and non-local instants of chemical action produce the present chemical bonding picture in a complete non-orbital way, as we will see next.

5. Chemical Bonding By Chemical Action

The nonlocal equation of chemical action, eq. (61), may be regarded as the starting point in revealing the binding forces in a molecule; it firstly rewrites as a sort of *adapted Heisenberg relation* for chemical bonding:

$$C_A \Delta r = 1 - \frac{\rho(\mathbf{r})}{|\nabla_r \rho(\mathbf{r})|} \quad (\text{in a. u.}) \quad (62)$$

Then, it may be rearranged in a working equation with separate variables

$$\frac{d\rho}{\rho} = \frac{1}{1 - \Delta r C_A} dr \quad (63)$$

Next, the integration of eq. (63) is made under assumption that for initial condition of integration we have $r_0 = 0$ & $\rho_0 = \rho^{local}$ of Eq. (58), with two distinct cases, namely:

- for constant delocalization ($\Delta r \sim R = \text{bonding length}$), with the solution

$$\rho(r)^{bonding-I} = \rho_0 \exp\left(\frac{r}{1 - RC_A}\right) \quad (64)$$

- for variable delocalization ($\Delta r \sim r$), with the solution

$$\rho(r)^{bonding-II} = \rho_0 \exp\left(-\frac{1}{C_A} \ln(1 - rC_A)\right) \quad (65)$$

both having the remarkable property yielding the same values $\{\rho_0, N/8\pi, \infty\}$ for the chemical action limits $C_A \rightarrow \{\infty, 0, 1/R\}$, respectively. Such behavior allows equating the two density forms of eqs. (64) and (65), jointly with turning the *delocalization* towards *localization*, i.e. performing the limit $r \rightarrow R = \lambda$ in the first order expansion of the chemical action, $C_A \rightarrow 0$, i.e. within the second entry in above set of limits, corresponding with the finite number of electrons in bonding region, considerate in pairs and within a spherical bonding locus of radius λ centered on CM of bonding.

5.1. General Description of Bonding

From above discussion, appears that chemical bonding may be described as the balance between two kind of binding influences, conveniently denoted as *anti-bonding and bonding functions*

$$f_\alpha(\lambda, C_A) = 1 - \Omega \lambda C_A = \begin{cases} 1, & \lambda \rightarrow 0 \\ -\infty, & \lambda \rightarrow \infty \end{cases}, \quad (66)$$

$$f_\beta(\lambda, C_A) = \exp(-\Omega \lambda C_A) = \begin{cases} 1, & \lambda \rightarrow 0 \\ 0, & \lambda \rightarrow \infty \end{cases} \quad (67)$$

for the reason grounded on their specific asymptotical behavior, respectively; the introduced Ω -factor accounts for assumed dimensionless nature of the binding

measures of eqs. (66) and (67) being adequately set in fundamental units as $\Omega = 1/\hbar c = 0.506773 \cdot 10^{-3} J^{-1} m^{-1}$.

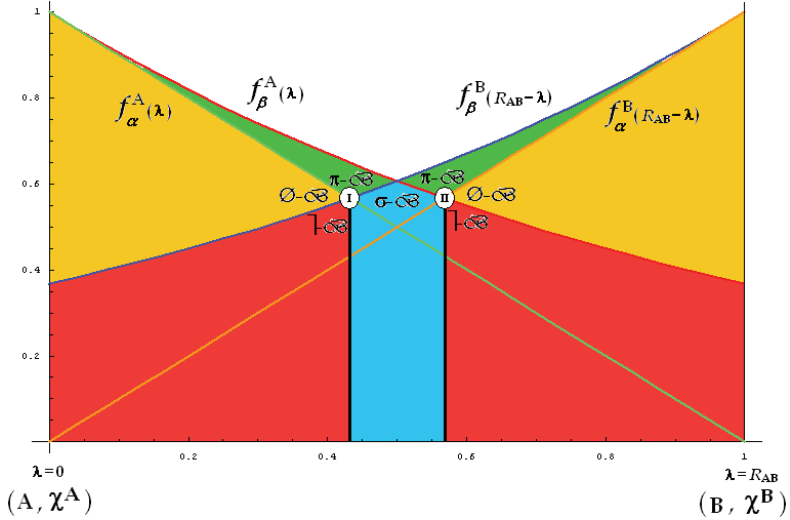


Figure 2. Geometrical loci of the sigma-bonding (σ -B in blue), anti-bonding ($\bar{\sigma}$ -B in red), no-bonding (\emptyset -B in orange), and pi-bonding (π -B in green) for chemical bonding from equal (electronegativity) influences of two systems **A** and **B**. Here the atomic electronegativities χ^A & χ^B stay for chemical actions for each individual atom or system involved in bonding, C_A^A & C_A^B respectively, as eq. (40) prescribes [57].

For a paradigmatic chemical bonding made by two atoms (say **A** and **B**) in a molecule (**AB**), with the bond length R_{AB} , the electronic pair-localization region is given by equating bonding and anti-bonding functions (66) and (67) in a reciprocal manner, such that assuring the full charge transfer between the two atomic regions of the molecule, by building the system

$$(I) : f_\alpha^A(\lambda_I, C_A^A) = f_\beta^B(R_{AB} - \lambda_I, C_A^B) \quad (68)$$

$$(II) : f_\alpha^B(R_{AB} - \lambda_{II}, C_A^B) = f_\beta^A(\lambda_{II}, C_A^A) \quad (69)$$

whose solutions (**I** & **II**) give the common region length (if $\lambda_{\text{II}} \neq \lambda_{\text{I}}$) or point ($\lambda_{\text{II}} = \lambda_{\text{I}}$), i.e. for hetero- and homo- bonding systems, shared by the two atoms-in-molecule due to their chemical action influences C_A^A and C_A^B across the bonding length R_{AB} . The general depiction of chemical bonding for a diatomic molecule is displayed in Figure 2, with the note the respective chemical actions were replaced by the associate electronegativities, according with the prescription of eq. (40).

The actual modeling of chemical bonding of Figure 2 reveals four main region of interaction that corresponds with consecrated types of bonding, yet personalized here as follows [57]:

- the *sigma-bonding* region (**σ -B**) is delimited by the area under bonding functions f_{β}^A and f_{β}^B along the pairing interval $(\lambda_{\text{I}}, \lambda_{\text{II}})$ on the bond length; it is uniquely defined and has no “nodes” or discontinuities, while corresponding to the consecrated bonding wave-function density $|\Psi_A + \Psi_B|^2$ in the conventional molecular orbital (MO) theory;
- the *anti-bonding* region (**$\bar{\sigma}$ -B**) also defined by the area under bonding functions f_{β}^A and f_{β}^B but outside of the interval $(\lambda_{\text{I}}, \lambda_{\text{II}})$ on the bond length, being thus corresponding with the anti-bonding state density $|\Psi_A - \Psi_B|^2$ with separated parallel spin-electronic pair in MO theory;
- the *non-bonding* region (**\emptyset -B**) is formed by the area delimited by all the binding functions of eqs. (68) and (69) around the binding points **I** and **II**, outside of the interval $(\lambda_{\text{I}}, \lambda_{\text{II}})$ and not crossing the bond length, being composed by two parts, one in each binding side respecting sigma-bonding.
- the *pi-bonding* region (**π -B**) is resulted by the area defined by all the binding functions of eqs. (68) and (69) around the binding points **I** and **II**, partially outside and partially inside (with a node) of the interval $(\lambda_{\text{I}}, \lambda_{\text{II}})$, while spanning the bond length entirely, making this way it compatible with the consecrated pi-bond type of the MO theory.

However, since the present approach does not discriminate among each of two electrons in bonding, such feature may be obtained through advancing more

information about electrons and their spins, as available by spinorial Dirac description, for instance. Such endeavor is in the sequel unfolded.

5.2. Spinorial Description of Bonding

When the Dirac *binding spinor* is employed with the form [60]

$$[\Psi] = \begin{bmatrix} (1 - \lambda\Omega C_A) \exp\left(-\frac{i}{\hbar}|E| \cdot t\right) \\ \exp(-\lambda\Omega C_A) \exp\left(+\frac{i}{\hbar}|E| \cdot t\right) \end{bmatrix} \quad (70)$$

one has to replace the binding functions (66) and (67) with the actual working *Dirac binding functions*, namely:

- The Dirac anti-bonding function remains the same as given within the density kernel approach by eq. (66):

$$f_{\alpha}^{Dir}(\lambda, \chi) = 1 - \Omega\lambda C_A; \quad (71)$$

- and the *Dirac positive and negative* bonding functions modified respecting the previous one given by eq. (67) such that to enrich the bonding analysis with two-folded spin related way of couplings:

$$f_{\beta(\pm)}^{Dir}(\lambda, \chi) = \pm \exp(-2\Omega\lambda C_A) \quad (72)$$

Note that in eqs. (71) and (72) the chemical action-electronegativity equivalency of eq. (40) may be implemented at any time for making the bonding functions “ready” for atoms-in-molecules treatment. Nevertheless, the bonding geometric loci for a molecule AB are determined by the system of equations:

$$(I) : f_{\alpha}^A(\lambda_I, C_A^A) = f_{\beta(+)}^{Dir-B}(R_{AB} - \lambda_I, C_A^B), \quad (73)$$

$$(II) : f_{\alpha}^B(R_{AB} - \lambda_{II}, C_A^B) = f_{\beta(+)}^{Dir-A}(\lambda_{II}, C_A^A), \quad (74)$$

$$(III) : f_{\alpha}^A(\lambda_{III}, C_A^A) = f_{\beta(-)}^{Dir-A}(\lambda_{III}, C_A^A), \quad (75)$$

$$(IV) : f_{\alpha}^B(R_{AB} - \lambda_{IV}, C_A^B) = f_{\beta(-)}^{Dir-B}(R_{AB} - \lambda_{IV}, C_A^B) \quad (76)$$

One observes that now, while eqs. (73) and (74) are of previous general types of eqs. (68) and (69), there appear two new equations of bonding, namely the last two equations (75) and (76) that may be regarded as quantifying the “interference” effect of the anti-bonding with the negative bonding functions belonging to the same atom in the molecule.

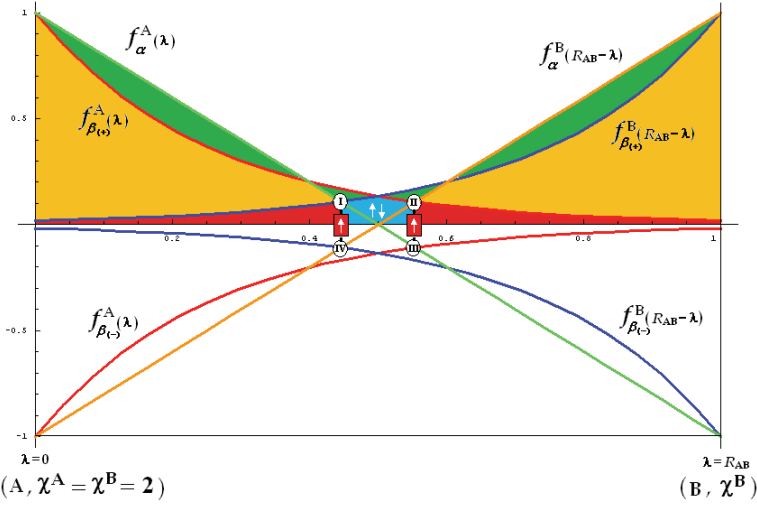


Figure 3. Geometrical loci of the bonding regions as in Figure 2 for chemical binding from equal chemical actions or electronegativity influences of two systems **A** and **B** throughout equations (73)-(76) with Dirac binding functions (71) and (72) through constants and parametric settings as $\hbar = c = 1$, $C_A^A = C_A^B = 2$, $R_{AB} = 1$. Here the atomic electronegativities χ^A & χ^B stay for chemical actions for each individual atom or system involved in bonding, C_A^A & C_A^B respectively, as eq. (40) prescribes [60].

Going to special points of bonding, worth discussing the case of the equal chemical actions $C_A^A = C_A^B = C_A$ providing the so called *critical regime*; as such, from the particular form of eq. (75) one has

$$f_{\alpha}^A\left(\frac{R_{AB}}{2}, C_A\right) = f_{\beta(-)}^{Dir-A}\left(\frac{R_{AB}}{2}, C_A\right), \quad (77)$$

which give the information on localization of pairing of anti-parallel electronic spins at the half of the bond length. More precisely, employing the half of the bonding length distance for all length (λ) parameters in eqs. (73)-(76) for equal two fold chemical actions in bonding (in atomic units), $C_A^A = C_A^B = 2$, for instance, one gets the bonding and anti-bonding spinning picture of Figure 3, with the critical bonding (Dirac) points having the hierarchy

$$IV \stackrel{\uparrow}{=} I < II \stackrel{\uparrow}{=} III \quad (78)$$

along the *critical distances* on bonding scale

$$\lambda_I = \lambda_{III} = 0.445571 [R_{AB}], \quad (79)$$

$$\lambda_{II} = \lambda_{IV} = 0.554429 [R_{AB}]. \quad (80)$$

The actual Dirac formulation of chemical bonding, actually, through its specialization in localization of pairing anti-parallel spins at the mid length of bonding, may be easily generalized and applied for whatever particular place within chemical bonding, furnishing therefore important practical tools and results, for example, when one likes to control the magnetic properties of quantum material composed by two aggregates.

5. Role of Chemical Action in Quantum Entanglement

Once exploring the Dirac version of chemical bonding with chemical action as the main driving force, one would like questing upon other fundamental quantum phenomena, as are the quantum tunneling, entanglement, or even bio-chemical interaction.

To this end, one starts remembering that when the generalized Schrödinger-de Broglie-Vigier-Bohm wave function is considered for bonding/tunneling/interaction with the form [76-78]

$$\Psi(\mathbf{r}, t) = R(\mathbf{r}, t) \exp\left(i \frac{S}{\hbar}\right) = \rho(\mathbf{r}, t)^{1/2} \exp\left[\frac{i}{\hbar}(\mathbf{p} \cdot \mathbf{x} - Et)\right] \quad (81)$$

in terms of its amplitude $R(\mathbf{r}, t)$ and phase (action) S , it modifies the conservation equation of quantum-classical forces:

$$\sum F_{classic} + \sum F_{quantum} = 0 \quad (82)$$

in the sense that the quantum force

$$F_{quantum} = -\langle \nabla V_{qua} \rangle \quad (83)$$

depends on the (sub)quantum potential

$$V_{qua}(\mathbf{r}) = -\frac{\hbar^2}{2m} \frac{\nabla^2 R(\mathbf{r}, t)}{R(\mathbf{r}, t)} \quad (84)$$

that is responsible for the long-range or asymptotical non-vanishing interaction.

Now, once the quantum potential (84) is replaced in chemical action (5) the so called *entangled chemical action* functional can be further constructed

$$C_A^{ent} = \int \rho(\mathbf{r}) V_{qua}(\mathbf{r}) d\mathbf{r} = -\frac{\hbar^2}{2m} \int \rho^{1/2}(\mathbf{r}) \nabla^2 \rho^{1/2}(\mathbf{r}) d\mathbf{r} \quad (85)$$

Yet, when the electronic density is viewed as being bijective with both classical and quantum potentials, it can be computed through transforming the equilibrium equation (82) into the entanglement self-consistent equation [58]

$$\nabla \rho^{ent}(\mathbf{r}) = \frac{\nabla^2 [C_A^{class}(\mathbf{r}) + C_A^{ent}(\mathbf{r})]}{V_{class}(\mathbf{r}) + V_{qua}(\mathbf{r})} \quad (86)$$

with the adequate *chemical actions*

$$C_A^{class/ent}(\mathbf{r}) = \int_0^{\mathbf{r}} \rho(\mathbf{s}) V_{class/qua}(\mathbf{s}) d\mathbf{s} \quad (87)$$

rewritten to fulfill the Laplacian-type equations

$$\nabla C_A^{class/ent}(\mathbf{r}) = \rho(\mathbf{r}) V_{class/qua}(\mathbf{r}) \quad (88)$$

However, the solutions or even the approximate solution of integral-differential equation (86) for entangled density would certainly open new perspectives in characterizing the localization/non-localization phenomena in quantum chemistry, having aromaticity as the first preeminent application.

On the other side, when the difference in classical and entangled chemical actions is advanced as the *entangled tunnelling energy*

$$\Delta E_{tunnelling}^{ent} = \sum C_A^{class} - \sum C_A^{ent} = \int \rho(\mathbf{r}) [\sum V_{class}(\mathbf{r}) - \sum V_{qua}(\mathbf{r})] d\mathbf{r} \quad (89)$$

it eventually drives, via the Heisenberg type relationship, the reaction rate and the turnover number or the effective time of reaction (Δt) for the ligand-receptor ($L-R$) or substrate-enzyme ($S-E$) interactions (catalysis) [79,80]

$$\frac{1}{k_{cat}} \propto \Delta t \cong \frac{\hbar}{\Delta E_{tunnelling}^{ent}} \quad (90)$$

At this point one may rethink upon the celebrated steady state approximation in enzyme or ligand-receptor kinetics, within the transition state theory (TST) [59]

$$\frac{d}{dt}[L-R] \cong 0 \rightarrow \frac{d}{dt} \nabla[L-R] = 0 \rightarrow \frac{d}{dt} \nabla \rho_{L-R}^{ent} = 0 \quad (91)$$

that has the realization

$$0 = \frac{d}{dt} \left\{ \frac{\nabla^2 \left[\sum_{L,R} C_A^{class(L,R)}(\mathbf{r}, t) + \sum_{L,R} C_A^{ent(L,R)}(\mathbf{r}, t) \right]}{\sum_{L,R} V_{class(L,R)}(\mathbf{r}, t) + \sum_{L,R} V_{qua(L,R)}(\mathbf{r}, t)} \right\} \quad (92)$$

through eq. (86) this way delivering the ligand-receptor equation for its (macroscopic) concentration $[L - R]$ in terms of the stationary flux of quantum-classical electronic density for concerned bio-chemical interaction.

Finally, one shall recall that the vanishing of the density gradient itself across the chemical bonding recovers the Bader zero-flux condition of atoms-in-molecules [73-75]

$$\nabla \rho_{L-R}^{ent}(\mathbf{r}, t) \cdot \mathbf{n} = 0 \quad (93)$$

that in entangled (or quantum-classical) version of eq. (86) cast as

$$\sum_{L,R} \nabla^2 C_A^{class(L,R)}(\mathbf{r}) + \sum_{L,R} \nabla^2 C_A^{ent(L,R)}(\mathbf{r}) = 0 \quad (94)$$

In any case, the actual classical-quantum combination in describing entangled electronic density is particularly appropriate for modeling electronic density involved in chemical phenomena due to the peculiar features the many-electronic systems display at the quantum-classical (or semiclassical) interface of many-body dynamics (interaction) with equilibrium (bonding). This is a fruitful and challenging approach towards nonlocal chemical bonding characterization in long or complex nanostructures by means of the chemical action and will be approached and applied in future communications.

6. Conclusion

Assessing reactivity and bonding stand as ones of the main issues of Chemistry. Yet, although with the advent of quantum mechanics many important features of the structure of atoms and molecules were elucidated in gas phase and usually by 0K ab initio computations, the appropriate framework in which the chemical interaction appears with specific forces was achieved only within the density functional theory and of its formulation for the so called chemical reactivity indices.

There turns out that the electronegativity viewed as the minus of the chemical potential, chemical hardness defined as the electronegativity variation respecting the number of exchanged electrons in a chemical interaction, and the chemical action that

bijectionally links the electronic density and applied potential in which chemical system evolves appear to be the natural indices for modeling chemical phenomena in an unitary functional way.

However, the so called double-variation of the total energy functional of a system instead of the simple first order variation is required in order the chemical reactivity principles to be properly captured for these indices. In this regard the Chemistry may be seen as the next order of the reality after the physical encountering, being thus more specific in semi-classical causes and effects. In fact, the chemical realm, being situated as the quantum-classical interface of observability clearly demands such “second order” approach of variations. Thus the principles of reactivity are formulated as being specific to chemistry rather as being reduced to a physical recipe.

The next step regards the hierarchy of chemical reactivity principles; at this point, the chemical action functional lays in between electronegativity equalization and of its residual quantum fluctuation behavior, see eq. (17), being this way closely related with the electronegativity itself that it often represents in practical applications. However, chemical action role in periodicity across elements of Periodic Table was shown to be essential, especially in regularizing the intra-periodic trends. Equally, the chemical action influence in chemical bonding was shown to be crucial since its basic definition relating the average of the bare potential; remarkably, chemical action is present in chemical bonding at whatever level of modeling, from nonlocal kernel formulation of the linear response softness until the bonding and antibonding spin localization along the bonding length within the Dirac spinorial approach.

Not less relevant is the chemical action involvement in the so called entanglement effects that appear when both classical and quantum potentials are considered in many-electronic analysis.

The versatility of chemical action in modeling various levels of chemical manifestation of matter, from elemental periodicity and bonding to entangled electronic density formulation, tunneling and ligand-receptor interaction in biocatalyzed reactions offers confidence in considering chemical action as one of the major conceptual tool in theoretical and computational chemistry in general and in chemical reactivity and bonding in special.

Future applications and realizations of this concept and of allied variational principle are expected to further strengthen its reliability in characterizing the stability, aromaticity and reactivity of available or newly designed compounds.

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