

LEVELS OF A UNIFIED THEORY OF CHEMICAL INTERACTION

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ABSTRACT

New entanglement perspective on the nature of the chemical bond is reached by employment of the (sub)quantum Bohm potential with the chemical action at whatever level of chemical interaction, from atoms to molecules to macromolecules and biological activity; the classical influence is proved as an omnipresent counterpart to quantum events in bonding.

Keywords: quantum potential, electronic density, entangled chemical action, atoms-in-molecules.

1. INTRODUCTION

It was the quantum mechanics promise that the Chemistry is complete with the wave function description of the electronic structures. Unfortunately, the Dirac's prophecy was not yet completed since the most inherent concept and reality of chemical interaction seems to elude the quantification: the chemical bond. Although many extensions of the Schrödinger equation were made in order to assess the many electronic ground and interaction states throughout either the variational or perturbation or even variational-perturbation methods [1], there resulted that the chemical bonding is situated at the edge of the quantum and classical worlds so that no precise quantification neither a complete intuitive classical picture of it can be provided at a single level of interaction. However, after consuming the Hartree-Fock-Roothaan-Slater quantum chemical age [2], including the Pariser-Parr-Pople (PPP) molecular model [3], while arriving at the density functional theory of chemical bonding [4], the nature of chemical bond was unveiled with respect of many features of strength and localization however still leaving space in clarifying the legitimate connection (or correlation) between the structural distribution of electrons and their manifestation as global properties by means of reactivity indices for which the most preminent stands the electronegativity χ and chemical hardness η [5]. Moreover, the attempt to even treat the bio- or macro-molecular

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interaction, via quantum chemical paradigms of matter, or of its specializations and approximations, opened a real challenge among the physical chemists and chemical modelers. In this respect, we are sketching here the main directions that a proper unified theory of chemical interaction should include or be confronted with.

2. CHEMICAL ENTANGLEMENT

At the electronic level the generalized Schrödinger-de Broglie-Vigier-Bohm wave function [6]

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

is firstly employed in terms of its amplitude R and phase (action) S to lead with the quantum-classical conservation equation of forces:

$$\sum F_{classic} + \sum F_{quantum} = 0$$

with

$$F_{quantum} = -\left\langle \frac{\partial V_{qua}}{\partial x} \right\rangle,$$

while the (sub)quantum potential

$$V_{qua}(x) = -\frac{\hbar^2}{2m} \frac{\nabla^2 R}{R},$$

is responsible for the long-range or asymptotical (chemical) interaction since its non-vanishing structure in $R \sim \Psi$. Such a paradox reveals a hidden reality of interaction that should be responsible for the delocalization interaction in chemical systems, lighting on aromaticity concept [7], being however incompatible with the light velocity limitation of relativity theory [8]. Fortunately, such dichotomy was recently surpassed by reconsidering both the special relativity and quantum (algebraically) chemistry within the over-light velocity (or two steep light) mechanism when considering the wave package propagation in a real space-time framework [9]. Such ideas root in late de Broglie thoughts and may constitute the foreground of reconsidering the electronic wave-corpuseular manifestation in both its propagation and eigen-states [6b]. Eventually, it may lead with the closed loop quantification of charges [8]:

$$nh = \Lambda S = \oint dS = \oint \frac{\partial S}{\partial x} dx = \oint |\mathbf{V}_S| dx = \oint p dx$$

towards the *bonding stage* through the conservation of the exchanged electrons by the atoms-in-molecules Gaussian law respecting the bonding basin (with surface area Σ):

$$-\frac{\partial N}{\partial t} = \oint_{\Sigma} \mathbf{j} \cdot d\mathbf{s}$$

with the density of the charge current given by the hydrodynamic expression [8]:

$$\mathbf{j} = \frac{R^2}{m} \nabla S = \rho \frac{\mathbf{p}}{m} = \rho \mathbf{v}$$

where the total number of involved electrons N fulfills the consecrated density functional relationship [4, 5a-d]:

$$N = \int \rho d\tau .$$

In these conditions, the chemical *bond stage* can be unfolded by means of Stokes transformation of the loop charged quantification above to its open charge flux thus establishing the chemical interaction quantification:

$$nh = \frac{m}{\rho} \int_{\Sigma} (\nabla \times \mathbf{j}) d\mathbf{s} .$$

Nevertheless, this so called chemical entanglement can be further considered at the global level through employing the electronic density ρ and quantum potential $V_{quantum}$ in the so called entangled chemical action functional

$$C_A^{ent} = \int \rho(x) V_{qua}(x) d\tau = -\frac{\hbar^2}{2m} \int \rho^{1/2}(x) \nabla^2 \rho^{1/2}(x) dx$$

this way providing the second level for the chemical bonding comprehension: the density functionals realm emphasizing on the necessity of considering density gradient expansion in chemical bonding characterization. This is nothing less than the inclusion of the Heisenberg delocalization principle in bonding formation and stabilization. Again, the quantum paradox arises since the bonding stabilization involves the electronic delocalization.

Nevertheless, the above quantum-classical force balance in chemical interaction at the level of forces can be further specialized at the level of chemical action functional which is nothing else than the observable of the potential involved; it provides the entangled equation of the electronic density:

$$|\nabla \rho^{ent}(x)| = \frac{\nabla^2 [C_A^{class}(x) + C_A^{ent}(x)]}{V_{class}(x) + V_{qua}(x)},$$

were the adequate Laplacian-type chemical action

$$C_A^{class/ent}(x) = \int \rho(x) V_{class/qua}(x) d\tau$$

preserves the wave nature of the electronic movements throughout the Laplacian character of both equation and chemical actions. It nevertheless can be regarded as the chemical bonding electronic density equation.

3. BIOACTIVITY ENTANGLEMENT

Going to the next level of chemical bonding the ligand-receptor (L-R) or substrate-enzyme (S-E) interactions are treated is such that the quantum (fluctuating) nature of the biomolecular reactions can be visualised by combining the relationship between the catalytic rate (k_{cat}) and temperature (T) with that between the reaction rate and the turnover number or the effective time of reaction (Δt) via Heisenberg relation,

$$\frac{1}{k_{cat}} \propto \Delta t \cong \frac{\hbar}{\Delta E_{tunnelling}^{ent}} = \frac{\hbar}{k_B T},$$

while considering entangled tunnelling energy as

$$\Delta E_{tunnelling}^{ent} = \sum C_A^{class} - \sum C_A^{ent} = \int \rho(x) [\sum V_{class}(x) - \sum V_{qua}(x)] d\tau$$

with k_B the Boltzmann constant. Of course, in last relation, the equivalence between quantum statistics and quantum mechanics was physically assumed when equating the thermal and quantum (tunnelling) energies, $k_B T$ and ΔE , respectively. Nevertheless, it is this point the basis of start rethinking upon the static character of the energetic barrier, recalling the so called steady state approximation, usually assumed in modeling enzyme catalysis [10], within the transition state theory (TST):

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

with

$$|\nabla \rho_{L-R}^{ent}(x,t)| = \frac{\nabla^2 \left[\sum_{L,R} C_A^{class(L,R)}(x,t) + \sum_{L,R} C_A^{ent(L,R)}(x,t) \right]}{\sum_{L,R} V_{class(L,R)}(x,t) + \sum_{L,R} V_{qua(L,R)}(x,t)}$$

delivering the ligand-receptor equation for its (macroscopic) concentration [L - R] in terms of the stationary flux quantum-classical electronic density.

Finally, various chemical reactivity pathways may be combined to eventually produce the biological activity with which to (statistically) correlate specific structural (quantum or topological) descriptors. Each such correlation should correspond to a certain molecular mechanism towards biological actions and can macroscopically be quantified through a norm $\|\bullet\|$ and a statistical factor r , while for a given or measured activity the chemical-biological interaction is associated with the least path principle fulfilled, i.e. the variational optimum ergodic condition across different possible or potentially active molecular mechanisms [11]

$$\delta \left[A_{(\|\bullet\|,r)}, B_{(\|\bullet\|,r)} \right] = 0, \text{ A \& B: biological endpoints;}$$

it stands as a macroscopic reflection of the quantum tunneling or entanglement structural (thus intimate and somehow hidden) interaction. However, also the least path principle can be further rewritten in terms of above entangled electronic density as the generalized Bader zero-flux condition of atoms-in-molecules [12] applied on biomolecular bonding maps:

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

yielding the chemical action classical conservation relation for the bioactivity entanglement

$$\sum_{L,R} \nabla^2 C_A^{class(L,R)}(x) + \sum_{L,R} \nabla^2 C_A^{ent(L,R)}(x) = 0$$

as a natural chemical (inter)action counterpart of the above classical-quantum force balance in electronic structures.

4. CONCLUSION

There was proved that at any level of chemical interaction the classical and quantum facets of reality interfere in a unique manner such that to either assure the wave nature of the grounding electronic structure as well the corpuscular manifestation of it through observable (measurable) quantities. There results that such classical-quantum combination makes so much fascination on the chemical bonding world whereas hindering with the same degree the mysteries of life and of its creation.

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