CHEMICAL REACTIVITY AND ELECTROMAGNETIC FIELD

Mihai V. Putz[*]

Laboratory of Computational and Structural Physical Chemistry,
Chemistry Department, West University of Timisoara,
Pestalozzi Street No.16, Timisoara, RO-300115, Romania

ABSTRACT

The Maxwell relation of total energy of a chemical N-electronic system is combined with Maxwell electromagnetic equations to provide new chemical reactivity framework in terms of electronegativity, chemical hardness and chemical action structural descriptors. The reliability of the present approach is suggested by providing a generalized equation of the density functional electronegativity.

Keywords: density functional theory, chemical reactivity indices, chemical action, electromagnetic equations.

1. INTRODUCTION

The modern birth of Chemistry starts while introducing the heuristic electronegativity concept through Berzelius works; since then it achieves continuous qualitative (energy, force, potential) and quantitative (by Pauling, Mulliken, Gordy, Iczkowski-Margrave, Parr, and – more recently by Putz – just to name a few) forms of comprehension [1]. Nevertheless, electronegativity still resists from being measured as an observable perhaps because quantifying a smooth combination of the inherent chemical propensity to either attach or donate electrons, although in different degrees, thus manifesting a dual nature recalling the quantum and electro-magnetic duality of manifestations. From other point of view, being merely an abstract concept, the electronegativity "reality" is involved in almost all fundamental chemical phenomenology equally at the structure and reactivity levels. However, as originated on the particle (nuclear and electric) fields, while acting on particle charges, the electronegativity concept is yet susceptible to be assumed like a sort of a *chemical filed* with a

[*] E-mails: mv_putz@yahoo.com or mvputz@cbg.uvt.ro; Tel: +40-0256-592-633; Fax:+40-0256-592-620; Web: http://www.cbg.uvt.ro/mvputz

close counterpart in Maxwell electromagnetic fields and equations. The present work unfolds such chemical field perspective through making the appropriate correspondences between chemical reactivity indices and the electromagnetic field quantities. The result eventually produces the related chemical field equation of reactivity.

2. CHEMICAL COUNTERPART OF ELECTROMAGNETIC FIELD

The starting point for establishing a chemical field theory is provided by the *density functional theory* applied on chemical systems [1e] of whose the main tools are given by three "generations" of descriptors, namely: (i) the electronic density $\rho(\mathbf{r})$, the applied (Coulomb and/or external) potential $V(\mathbf{r})$, and the total energy of a given N-electronic system E_N; (ii) the density functionals of the total number of electrons $N = \int \rho(\mathbf{r})d\mathbf{r}$ and of the chemical action $C_A = \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}$ [2]; (iii) the reactivity indices of electronegativity $\chi = -(\partial E/\partial N)_{V(\mathbf{r})}$ and of chemical hardness $\eta = -0.5(\partial \chi/\partial N)_{V(\mathbf{r})} = 0.5(\partial^2 E/\partial N^2)_{V(\mathbf{r})}$; they are based and combined on behalf of fundamental quantum principles to yield the main chemical reactivity principles with descriptive value for chemical dynamics. For instance, they assure in writing of the total differential expression for the total energy $E_N = [N, V(\mathbf{r})]$ as [3]:

$$dE_N = -\chi dN + \int \rho(\mathbf{r})dV(\mathbf{r})d\mathbf{r} \qquad (1)$$

from where the Cauchy condition is extracted as the Maxwell chemical reactivity relation:

$$-\frac{\delta \chi}{\delta V(\mathbf{r})} = \frac{\partial \rho(\mathbf{r})}{\partial N} \qquad (2)$$

Remarkably, when comparing equation (2) with the electromagnetic continuity equation of charges (ρ) and currents ($\mathbf{j}$), $\partial \rho/\partial t + \mathbf{div\,j} = 0$, one gets the formal correspondences:

$$\partial/\partial t \to \partial/\partial N; \ (\mathbf{div}\,or)\nabla \cdot \to \delta/\delta V; \ \mathbf{j} \to \chi \qquad (3)$$

In first, such transformations offer a heuristically interpretation of time and space transformation - in *physics* as being equivalent with total number of particle and the total applied potential variations - in *chemistry*, respectively, while the electronegativity plays the "role" of the physical current density in/out of the concerned chemical system!

Then, by taking into account the Amperé-Maxwell local relationship in absolute units ($\mathbf{j} = \alpha\,\mathbf{curl\,H}$), further chemical reactivity-electromagnetic field correspondences are released, namely:

$$(\mathbf{curl}\,or)\nabla\times \to \partial/\partial N; \mathbf{H} \to E_N; \alpha \to -1. \qquad (4)$$

Worth noting that the last physical-to-chemical reactivity conversion rules reveal two crucial ideas; one is about the time meaning in *chemistry*, that throughout the above relations (3) and (4) achieves the "circularity" feature in particle exchanges; this is indeed important since in ordinary quantum mechanics *the time* has neither any known operator nor the associate eigen-values and equation, while the total number of particle in a system not only has a viable operator and an observable character but may be written within an up-and-down operators, in close agreement with the "circular time" chemical processes' present picture [1g]!

The second consequence regards the gauge chemical reactivity value $\alpha = -1$, sensible different by its physical counterpart ($\alpha = 1$ in International System or $\alpha = c$ – the speed of light – in Gauss System) in a manner that consecrates chemical reactivity as a distinct, albeit related, reality!

Next, there is immediate to show that when magnetic induction field fulfills the chemical electronegativity assignment:

$$\mathbf{B} \to -0.5\chi \,, \tag{5}$$

the consecrated density functional chemical hardness is regained as the magnetic variation:

$$\tilde{\eta} = \frac{\partial \mathbf{B}}{\partial t} \tag{6}$$

With relation (6) we may advance the chemical reactivity field theory as based on the introduced *chemical hardness field* $\tilde{\eta}$. Now, the double electronegativity association with current density and magnetic field of relations (3) and (5) is solved out by the Biot-Savart law ($\alpha \,\mathbf{curl}\,\mathbf{B} = \mu_0 \mathbf{j}$) consistently with the correspondences (3), (4) and (5) when the vacuum magnetic permeability in chemical space becomes

$$\mu_0 \approx 2N \,. \tag{7}$$

By a similar procedure, using the electrical field-current density relationship intermediated by the conductibility parameter σ ($\mathbf{j} = \sigma\mathbf{E}$), the electrostatic Gauss law ($\varepsilon_0 \,\mathbf{div}\,\mathbf{j} = \sigma\rho$) provides for the vacuum electric permittivity the value as

$$\varepsilon_0 \approx -\sigma N \tag{8}$$

when the finite right-hand-side of the Maxwell chemical relation (2) is considered. However, for further determination of the conductibility "chemical value" the Faraday-Lenz induction law ($\alpha \,\mathbf{curl}\,\mathbf{j} = -\sigma \,\partial\mathbf{B}/\partial t$) is substituted with the present chemical correspondences to yield

$$\sigma = -2 \tag{9}$$

that leaves with the chemical form for electric permittivity in vacuum:

$$\varepsilon_0 \approx 2N .$$

(10)

Worth noted that having the same chemical values (in atomic units) for magnetic and electric vacuum conducting (field) properties, see relations (8) and (10), respectively, strengthen the idea that the electric and magnetic fields collapse into electronegativity-chemical hardness reactivity space [2a] thus affirming these indices as of fundamental relevance in description of chemical structure and dynamics.

3. CHEMICAL REACTIVITY FIELD EQUATION

Once introduced the chemical reactivity-electromagnetic field main correspondences the chemical reactivity field equation should be delivered. This way, when an isolated, however composed, polyatomic system is concerned the Maxwell magneto-static law ($\mathbf{div\,B} = 0$) resembles the chemical reactivity principle of *electronegativity equalization* [2, 3]:

$$-\frac{1}{2}\frac{\delta\chi}{\delta V(\mathbf{r})} = 0 \Rightarrow \chi = ct\big|_{V=ct}$$

(11)

while, when further combined with the above chemical reactivity Maxwell equality (2) the *generalized Bader flux condition* is achieved [4]:

$$\nabla_N \rho(\mathbf{r}) = 0$$

(12)

with the basins defined over the charge circulation merely than on the spatial partitions. As such, the earlier limitations of Laplacean based approaches in explaining the molecular structure and reactivity may be eventually removed once the explicit N- and V- dependencies of density and electronegativity [1f] are achieved and employed, in accordance with the basic N- and V- representability prerequisites of density functional theory itself [2].

Finally, one may employ the general case of the Biot-Savart law ($\alpha\,\mathbf{curl\,H} = \mathbf{j} + \partial\mathbf{D}/\partial t$) combined with the material law of polarization ($\mathbf{D} = \varepsilon_0\mathbf{j}/\sigma + \mathbf{P}$), among the actual chemical reactivity-electromagnetic field correspondences, to produce the general equation of the chemical transformations:

$$-\frac{\partial E_N}{\partial N} = -N\frac{\partial\chi}{\partial N} + \frac{\partial C_A}{\partial N} ;$$

(13a)

$$-\chi = 2N\eta + \frac{\partial C'_A}{\partial N} ,$$

(13b)

while the physical polarization vector was associated with chemical action [2c],

$$\mathbf{P} \to C_A = \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}.$$
(14)

Observe that the equation (13b) decays on the no reactivity condition $\chi = 0$ when the chemical action variation per particle equals the double negative of the chemical hardness ($-2N\eta = \partial C_A / \partial N$).

With these, equations (13) provide the most general analytical forms of reactivity so far: the change in the total energy of the system due to the particle transfer is equivalent with the electronegativity field having the chemical hardness and the variation of the chemical action components related with the exchanged or the valence electrons N. However, equations (13) may be solved either for total energy, electronegativity, chemical hardness, or chemical action as particular chemical problems demand.

CONCLUSION

The main density functional chemical reactivity concepts as electronegativity, chemical hardness and chemical action were analyzed in relation with the electromagnetic field laws. Such endeavor leads with both fundamental and advanced ideas about the chemical space and reactivity; for instance, it was inferred that the physical space-time transformation counterparts for the N- and V- representability of the chemical structures and reactions, while the electric and magnetic fields collapse into the electronegativity-chemical hardness bi-dimensional space of reactivity; as well, the electronegativity equalization principle and the N- variant of the zero flux Bader condition for atoms-in-molecules were raised as a natural consequence of the present field treatment of reactivity. Moreover, since the chemical action was corresponded with the polarization field in electrodynamics, new chemical reactivity equation was revealed paving the way for further formulation of the chemical fields, forces and currents. There is therefore hope that the chemical bond description may soon be achieved in terms of quantum chemical operators and associated eigenvalues.

REFERENCES

[1]   (a) Pauling L. The nature of the chemical bond IV. The energy of single bonds and the relative electronegativity of atoms, *J. Am. Chem. Soc.* 1932, 54, 3570-3582; (b) Mulliken R.S. A new electroaffinity scale: together with data on valence states and an ionization potential and electron affinities, *J. Chem. Phys.* 1934, 2, 782-793; (c) Gordy W. A new method of determining electronegativity from other atomic properties, *Phys. Rev.* 1946, 69, 604-607; (d) Iczkowski R.P., Margrave J.L. Electronegativity, *J. Am. Chem. Soc.* 1961, 83, 3547-3551; (e) Kohn W., Becke A.D., Parr R.G. Density functional theory of electronic structure, *J. Phys. Chem.* 1996, 100, 12974-12980; (f) Putz M.V. Systematic Formulation for Electronegativity and Hardness and Their Atomic Scales within Density Functional Softness Theory, *Int. J. Quantum Chem.* 2006, 106, 361-386; (g) Putz M.V. Electronegativity: Quantum Observable, *Int. J. Quantum Chem.* 2009, 109, 733-738.

[2] (a) Putz M.V. Unifying Absolute and Chemical Electronegativity and Hardness Density Functional Formulations through the Chemical Action Concept, in *Progress in Quantum Chemistry Research*, Erik O. Hoffman (Ed.), Nova Science Publishers Inc., New York, 2007, Chapter 2, pp. 59-121; (b) Putz M.V. Levels of a Unified Theory of Chemical Interaction, *Int. J. Chem. Model.* 2009, 1(2), 000-000; (c) Putz M.V. Chemical Action and Chemical Bonding, *J. Mol. Struct. (THEOCHEM)* 2009, doi:10.1016/j.theochem.2008.12.026.

[3] (a) Parr R.G., Yang W. *Density Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989; (b) Putz, M.V. *Contributions within Density Functional Theory with Applications to Chemical Reactivity Theory and Electronegativity*, Disertation.Com, Parkland, Florida, 2003, http://www.dissertation.com/book.php?method=ISBNandbook=1581121849.

[4] Bader R.F.W. *Atoms in Molecules - A Quantum Theory*, Oxford University Press, Oxford, 1990.