# Contributions within Density Functional Theory with Applications in Chemical Reactivity Theory and Electronegativity

by
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*with Applications in Chemical Reactivity Theory and Electronegativity*

# Preface

The present English *Thesis* edition refines and enlarges the Romanian *Thesis* of the author, publicly defended in 15.03.2002 at West University of Timisoara, under the advisory of Prof. Dr. Eng. Adrian Chiriac. Since that date the author undertook an intensive Post-Doctorate research stage at University of Calabria under the advisory of Prof. Dr. Nino Russo. During this period the main results obtained in a theoretical fashion in author's *Thesis* were further extended and applied. For this reason, the present work likes also to emphasize, when opportunely, the fruitful prospective and aspects that emerged out from a certain author's original *Thesis* contribution, being no part of this work in conflict with other ventures currently under publishing considerations. However, by supplying the *Thesis* basic achievements with new ones will not affect the *Thesis* flavor but only enrich it.

Mihai V. Putz, Ph.D.

University of Calabria, Italy

Spring, 2003

Dedicated

to

Mama Kathy

and to

Papa Vio

My Steps, Yours Shines

*Abstract*

In the limits of the density functional theory there are introduced and deduced fundamental chemical descriptors as the chemical action concept, the chemical field, new electronegativity, rate reaction and chemical hardness formulations, the reduced total energy and the partial Hohenberg-Kohn functionals.

For electronic density computations the quantum statistic picture of the path integral Feynman-Kleinert formalism is employed to its markovian approximation, providing the framework in which the majority of the chemical reactions and the reactivity of the electronic systems can be treated together with the internal and environmental couplings.

Evaluation, representation and interpretation of the present analyzed chemical indices are performed for a prototype many-electronic system such that its electronic structure to display fundamental and excited anharmonic vibrations being in the thermal coupling with the medium.

The chemical descriptors introduced and computed shall contribute to the foundation of the chemical reactivity on the conceptual and analytical physical bases, being able to predict the chemical transformations and the characterization of the bonds formation.

*Key Words*:

Electronic Structure, Quantum Theory, Quantum Chemistry, Density Functionals, Reactivity Indices, Path Integrals, Feynman-Kleinert Formalism.

# *Acknowledgements*

# *Praise for Thesis*

## *Dr. Adrian Chiriac, Full Professor of Chemistry:*

… Mr. Mihai V. Putz comes with a consistent physical background in the modern quantum chemistry. Such formation fully qualify him to get inside into the Density Functional Theory, founded by the pioneeristic works of a physicist and a mathematician, Walter Kohn and John People, respectively, together awarded for this theory with the Nobel Prize in Chemistry on year 1998. …Mr. Putz's thesis gives a valuable contribution for conceptual ascribing of the electronegativity as the central measure of an electronic systems' reactivity. Throughout the new density functional electronegativity proposal by Mr. Putz's work, crucial reactivity indices like the chemical action, the chemical hardness as well as the energetic functionals are rigorously related and giving space to further developments. … For the computational methodology Mr. Putz had correctly used the path integral formalism in its Feynman-Kleinert picture that is a meaningful and a referentially solution of the electronic density implementation consistent with the density functional and the *V*-representability framework. This way, the Mr. Putz's thesis provides an elegant, conceptual and analytical tool allowing integrate multidisciplinary studies for a large class of many-electronic systems together with their internal and environmental markovian couplings. …

*West University of Timisoara, Romania*

*March, 2002*

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## *Dr. Nino Russo, Full Professor of Chemistry:*

The thesis of Mr. Mihai V. Putz deals with the fundamental problem of physical and chemical interactions in fermionic open thermodynamical systems. The thesis is original and deserves attention from the scientific community. The study approaches a theoretical direction in order to describe the chemical reactivity through chemical descriptors and reactivity indices inferred based on the description of quantum statistical electronic systems in the density functional theory. In this context, there are introduced and phenomenological evaluated the density functionals of electronic systems involved in interaction, exchange and transformation processes within the thermodynamical couplings with the environment. … The advantage of Mr. Putz approach is that within the path integral formulation he succeed to comprise all the main information for the electronic systems in the external applied potential. This way, the present study combines the path integral and density functional formulations in an unitary way consistent with the Hohenberg-Kohn theorems … and could significantly enlarge the reactivity indices theory and its applications.

*University of Calabria, Italy*

*March, 2002*

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*Dr. Onuc Cozar, Full Professor of Applied Physics:*

…Mr. Mihai V. Putz's work is situated as contents in the framework of molecular quantum mechanics and quantum chemistry. … Starting from the general equations for changing in energy and chemical potential for an open electronic system the author inferred new density functionals within the density functional theory limits: the chemical action, the chemical field and its period, an original electronegativity density functional formulation. … As a note, it can be said that, a more emphasis for the own results would be welcome. … There is remarked the very careful attention paid to presentation that turns the whole work into a substantial thesis but not harmful overcrowded. … The stile of discourse is clear and concise with a structure that leads with a coherent comprehensibility of the main literature concepts in the field as well as the author's rigorously integrated and applied contributions. …

*Babes-Bolyai University of Cluj - Napoca, Romania*

*December, 2001*

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*Dr. Branko Dragovich, Research Professor of Physics:*

…According to my positive experience with the path integral method in foundation of quantum theory (quantum mechanics, quantum field theory and string theory) I think that this method should be applied to any particular physical and chemical quantum system. Theoretical foundations of open molecular electronic systems just start from Feynman's path integral method in this Ph.D. thesis of Mihai V. Putz. I find such approach well founded, very attractive and promising. Mr. Putz's thesis presents significant contribution to the theory of open electronic systems, exhibits author's inventivety and contains sufficient number of original results. …

*Belgrade Institute of Physics, Serbia*

*December, 2001*

# *List of Main Symbols*

| Symbol(s) | Meaning(s) |
|---|---|
| $g$ | anharmonic coupling parameter |
| $j$ | charge current |
| $W[j]$, $W(j)$ | charge field: functional, function |
| $C_A$ | chemical action |
| $\omega_C$; $\omega$, $\Omega$ | chemical field; frequency: proper, trial |
| $\eta(x)$, $\eta_S$, $\eta_\chi$ | chemical hardness: local, global from softness and global from electronegativity |
| $s(x,x')$, $s(x)$, $S$ | chemical softness: kernel, local, global |
| $A$ | classical action |
| $\rho$, $\rho(x)$ | electronic densities |
| $\chi$, $\chi_M$, $\chi_P$, $\chi'$, $\chi^{\sqrt{}}$ | electronegativity: absolute, Mulliken, universal Parr, mean arithmetic and mean geometric |
| $E$, $E[\rho]$, $\Delta E$ | energy: total, functional, transferred |
| $x_0$ | Feynman-centroid |
| $a^2$ | Feynman-Kleinert smeared out width |
| $\overline{F}$, $F$ | Feynman-Vernon functional, free energy |
| $f(x)$ | Fukui function |
| $F_{HK}[\rho]$, $F_{HK}^P[\rho]$ | Hohenberg-Kohn functional: universal, partial |
| $\beta$ | inverse thermal energy |
| $L(x)$, $L(x,\dot{x},t)$ | local linear response function, the Langranjean |
| $Z^*$ | nuclear charge |
| $N$, $N[\rho]$, $\Delta N$ | number of electrons: total, functional, transferred |
| $\hat{H}$, $\hat{W}(t)$ | operator: Hamiltonian, density |
| $\gamma$, $\xi$ | parameter: scaling, orbital zeta |
| $Z$, $Z_1$ | partition function: standard, first order approximation |
| $Dx(\ )$ | path integral measure |
| $V(x)$, $V_{eff}(x)$, $W_1(x)$ | potential: external, effective, first order approximation |
| $\Gamma[\rho]$; $\Gamma[]$ | rate reaction functional; gamma Euler function |
| $t$, $\tau$ | time: real, imaginary |
| $x$; $p$ | spatial vector position; impulse coordinate |
| $m_0$, $\hbar$, $k_B$ | standard constants: electronic mass, Planck, Boltzmann |
| $a$, $b$ | symbolic integrals |
| $T$; $T_C$ | thermodynamical temperature; chemical period |
| $k$ | wave vector modulus, force constant |

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*Cards suffuse, display abound,*

*How can they be turned to swans?*

Robert G. Parr – Density Functional Theory

# CHAPTER 1.

## MOTIVATION

*Don't be afraid, I will go away like an echo…*


*Garcia Lorca – Song without flowering*

During the time, the nature sciences evolved under different theoretical shapes in order to causatively describe the objective-experimental reality, the evolution and interaction of species. [1-10]

Physics and Chemistry were in turn, but also correlated, in state to discover in a proper way the innovating kind of evolution which characterizes the natural systems. Anyway, they set up the relative different ways of exploring, at various levels of interaction, the reality of manifestation of the same objects. The important thing is that the two approaches have always lend one to the other the major concepts (electron, atom, molecule, time dependence) in order to cooperate for the elucidation of the phenomenology of interaction and of the emergence of the natural (atomic, molecular, chemical, and biological) species in a self consistent organization. [5-11]

Since the appearance of the quantum mechanics, the (theoretical) methods of Chemistry and Physics used for describing the atoms and molecules made up an unit. [1, 2]

For instance, the description of the atomic and molecular systems through *the wave function*, beyond its abstract, mathematical and philosophical representation, that is still in the middle of enmities and interpretations, [2, 12] is like a bridge between the physical and chemical descriptions applied to the microscopic world. [13, 14]

However, besides the wave function (of atomic and molecular orbitals), other complementary (or alternative) models have been developed aiming to describe the multi-electronic systems. [15-23]

Such an example is the *density functional theory* (*DFT*), which has on the foreground the *electronic density* associated to a system in its fundamental quantum state. [18-20]

Certainly, also the quantum statistical models, based on *the partition function*, or the synergetic models, based on the *structure information*, have been developed, [7-9] but all of them can be reduced directly or indirectly to a correlation with the density or with the density of probability of the analyzed electronic system. Nevertheless, the big advantage of treating the multi-electronic systems through the associates density functionals consists in the *observable* character these functionals receive, once they are expressed as functions of electronic density. Moreover, the calculus of the electronic density can also be made on the base of the partition functions which, at their turn, can be calculated throughout an alternative formalism of solving the Schrödinger equation for the electronic systems. [15]

Such an alternative method is made up by the path integral(s)-*PI* formalism, presented both in its general quantum mechanical (*QM*) manner as well as in the quantum statistical (*QS*) realization within Feynman-Kleinert approach, [24] in the Chapter 2.

Unlike solving the Schrödinger equation, that assumes between two quantum events the quantum evolution gap, the calculus based on the path

integrals takes into account, in principle-precisely, the amount of all possibilities of filling the quantum gap separating two arbitrary quantum events. Although these models are different, they coincide with a precision of under 1% for the electronic systems governed by the polynomial potentials (like the electronic molecular ones). [25]

The advantage of applying the path integrals formalism presents, at least, two correlated aspects. First of all, the partition function can be calculated for the (thermodynamically) open electronic systems, and moreover, this calculation (although presumes in most of the cases the effective potential approximation) doesn't imply a perturbation method, as is the case of the Schrödinger-Rayleigh standard approach. [14, 26-31]
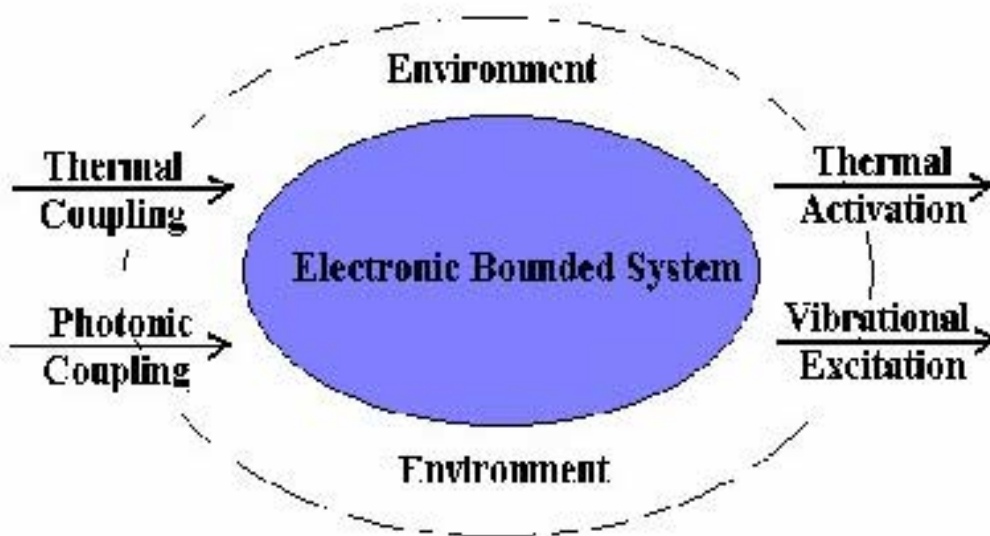


**Figure 1.1.** *The paradigm of the chemical-physical processes for an open electronic system.*

Being *DFT* a manifestly *structure* theory, due its bases on the stationary principles of the ground-state, its combination with *PI* quantum statistical scheme seems more adequate than with those of wave function. This because, the *QM* wave function does not provide directly the structure (electronic density) information, being in a multi-coordinate many-particle space dependence, while *QS* directly associates with the electronic density throughout the partition function, a global energetic measure of the structure.

In these conditions, to take into account the interactions, the changes and the couplings with the external environment it appears more accessible (for theoretical analysis) through the using of the path integrals method in solving the quantum statistic partition function – and then, the density associated to the open electronic systems. [32-38]

The idealization of the real systems is generally admitted, Figure 1.1. In fact, the evolution of natural systems (or species) cannot take place in the absence of the couplings, interactions, and exchanges between these systems

and the external environment (seen as a collection of other open systems). Without emphasizing here on the physical and philosophical side of this statement - the Mach's principle, the principle of non-separability, and so on, [2, 4, 12] - one shall limit upon the importance of studying the open electronic systems, and of their exchanges and couplings with the external environment .

This work will analyze the potency of an termodyanamically (from here implicitly) open atomic and molecular electronic system to enter in a reaction channel. Beside the coupling with the nuclear system and/or with an external (photonic) electromagnetic field, the entire electronic ensemble is placed within a thermal bath allowing so far the thermal exchange, being the springing effect the excitation on the anharmonic vibrational states. [39-42]

The present work is structured in two main parts.

In Chapter 2 there are introduced and analytically deduced, within the limits of *DFT*, the chemical descriptors – as density functionals – with validity (also) for the open electronic systems: *the chemical action, the chemical field, the chemical field period, electronegativity (also with its Mulliken version and the atomic path integral sketched scale), new reaction rate, the reduced total energy and the partial Hohenberg-Kohn functionals.* All these descriptors are directly or indirectly related, by means of conceptual quantum chemistry, with the driving electronegativity as the systems' electronic potency to enter into a (virtual) reaction channel. [43-56]

In Chapter 3 are calculated, represented and analytically interpreted the chemical descriptors introduced in Chapter 2 for a prototype molecular electronic system, governed by a generalized anharmonic potential, employing the Markovian approximation of the ultra-short correlations with the environment. The calculus of the associated electronic densities emerges out from the method of the Feynman-Kleinert variational algorithm in *QS* path integrals. [57-63]

The chemical descriptors introduced in the present work show, through their density functional structure associable also to the open systems, a general character for the capacity of an electronic system to participate at a reaction. By their definition and the manner in which they were inferred, the considered chemical descriptors allow a wide range of density implementations, associated to the aimed electronic states, leading as well a coherent phenomenology of the reactivity.

This way, the present study proposes itself to contribute to fundament the chemical reactivity on physical bases.

# CHAPTER 2.

# THE PHYSICAL BASES OF THE CHEMICAL REACTIVITY

*Prometheus: Release me, Zeus, I've already suffered enough…*


*Luciano di Samosata-Dialogs of Gods,*

*Prometheus and Zeus, 1*

## 2.1 INTRODUCTION

The present chapter likes to formulate some chemical descriptors in a unitary way in the frame of the density functional theory (*DFT*) allowing so far a high level of generality which should include the case of open electronic systems too.

For instance, there have been formulated different manners of determination and measurement for electronegativity. [64-80] Although this descriptor is a fundamental one in characterization of charge exchange for forming and transforming of atoms and molecules, an analytical general expression of it, as density functional, hasn't yet been formulated. Based on the density functional theory, in this chapter, will be deduced an electronegativity density functional and its Mulliken version.

Equally, are defined and deduced other basic functionals, like is the case of Hohenberg-Kohn universal functional, presented here in its partial venture.

Considering the equations for the transformation of electronic ground states, within the density functional theory framework, new reactivity indices – as quantitative density functional descriptors of reactivity potency – will be introduced: the chemical action, the chemical field and its period, new rate reaction and chemical hardness functionals.

In the literature study, there is also presented  the quantum mechanical and the quantum statistical respectively descriptions for the electronic systems' evolutions by means the path integrals perspective.

The quantum statistical path integral formulation is chosen as the main tool for the analytical calculus of the electronic densities, and will be fully employed in Chapter 3 for a prototype anharmonic molecular system, to compute the reactivity descriptors introduced in the present chapter.

All these considerations, formulations and deductions for defining and introducing of the reactivity density functionals – all from the direct or indirect electronegativity perspective – like to contribute for the characterization of an electronic system's reactivity through the adequate descriptors, displaying therefore a general predicting character, with the goal in providing an unitary view regarding the capacity of the electronic systems to enter in chemical reactions.

## 2.2 LITERATURE STUDY

### 2.2.1 The Electronegativity Concept

Historically, the electronegativity ($\chi$) accounts for the tendency of the atoms to build up molecular systems. It was firstly proposed by J. J. Berzelius in 1811.

Linus Pauling in 1932, [64] by an ingenious mixture of quantum mechanical and thermodynamical arguments correlates electronegativity with the bond energy $D$ of an arbitrarily species $AB$, $A_2$ and $B_2$ as:

$$\chi_A = \chi_B + 0.208 \left\{ D(AB) - \frac{1}{2}\left[D(A_2) + D(B_2)\right] \right\}^{1/2} \, [Energy]^{1/2}.$$

(2.1)

This way, it was introduced so far the referential electronegativity scale: once being fixed the $\chi$ of a chosen atom the other atomic values will depend of this choice according with relation 2.1.

Immediately after, Mulliken, during the years 1934-35, had proposed the electronegativity as the average of the binding energy of the outer electrons between the neutral atom (A) and its corresponding negative ion (A⁻): [65]

$$\chi_M(A) = \frac{IP(A) + IP(A^-)}{2} \, [Energy]$$

(2.2)

being $IP$ the respective ionization potentials. After many years, it have been proved the deeply quantum nature of the Mulliken proposed $\chi$ formulation, [18] since the ionization potential was quantified by the integral of the highest occupied (molecular) orbital ($HOMO$) energy, $\varepsilon_{HOMO}$, respecting to the electronic population $n$ of a given $N$-electronic system, $N = \sum\limits_{orbitals} n_{orbitals}$ :

$$-IP = E_N - E_{N-1} = \int_0^1 \varepsilon_{HOMO}(n)\,dn$$

(2.3)

being $E_N$ and $E_{N-1}$ the total energies of the $N$ and $N$–1 electronic systems, respectively.

Afterwards, Gordy in 1946 finds a correlation of electronegativity with the effective nuclear charge $Z_{eff}$ acting on the outermost electrons: [66]