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REGULAR ARTICLE

On the non-integer number of particles in molecular system domains: treatment and description

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Abstract The energy of an atomic or molecular system undergoing Coulomb interactions is well known at the integer numbers of its neutral or ionic configurations. Nevertheless, the physical domains (atoms in molecules) inside the whole molecular system possess a non-integer number of particles due to the electron exchange with its surrounding. Hence, the dependence of the energy, the density matrix and their marginal distributions (reduced density matrices) with the number of particles become a problem of fundamental importance in the description of the electron distribution, its properties and transformations. In this work, we present a rigorous mathematical and physical basis for the treatment of this problem within the grand-canonical statistical distribution of few particles. In this context, the derivatives of the energy and the density referred as chemical descriptors (especially chemical potential and hardness) are analyzed in both cases, when the system is isolated and when it is subject to the interaction with an environment. The ground state energy convexity dependence with the number of particles of these systems simplifies the description.

Keywords Grand-canonical ensemble · Electronic structure · Density matrix · Descriptors

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1 Introduction

Generally, quantum chemical calculations of electronic structure take the number of electrons in the molecule as a fixed parameter which states for a closed system [1, 2], i.e., for its neutral state of N electrons or for any of their ionic configurations. This is usually the correct approach for a molecule in gas phase but not within the framework of a surrounding environment which may donate or accept electrons as for instance in the treatment of solvation phenomena, surface chemistry, or enzyme mechanisms, among others. Therefore, this scenario induces to describe these problems by means of fragments or physical domains as moieties like individual or group of atoms within the molecular structure. Thus, to associate non-integer charges to them is the main key to the understanding at atomic scale of complex processes of electron distributions undergoing charge flux transfer among subsystems of atoms and molecules under the influence of reactive interactions and/ or external perturbations, conformational changes or interactions, related to chemical reactivity [3–5]. For such a goal, the fundamental magnitudes to be described are the energy, the electron density and their derivatives [3, 4, 6]. Therefore, an accurate quantum treatment which attempts to reach a complete and rigorous description of the electron distribution and of ulterior way the determination of the physicochemical properties, needs a precise definition of the system, its energy and state. These problems merit the introduction of the Atoms in Molecules (AIM) concept and the energy and state dependence with the number of particles in the system.

It has been a common trend in the literature to assume under certain success that the quadratic electrostatic interactions constitute a suitable approach of the energy dependence on fractional charge and independent of the

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strength scale of the interaction [6–10]. Nevertheless, the inadequacy of this model has been noted, and a linear dependence within the density functional theory (DFT) and also for the state function approach was proposed as an attempt to obtain the right energy dependence for non-integral electron number $\mathcal{N}$ and its differentiability [4, 5, 11]. Recently, a general proof for that proposal going beyond the DFT and the pure state function approaches has been presented [12] under the hypothesis of the ground state energy convexity for atomic and molecular systems driven by Coulombic interactions [4, 5, 12, 13]. To understand the mechanism of charge transfer mentioned above, the fragments within the molecular structure or even a whole molecular system may be interpreted as open systems that exchange electrons and energy between them and/or with a reservoir [4, 14, 15]. Therefore, it follows that a non-integer electron number may arise as a time average caused by the fluctuating number of particles and thus the open system need to be described by a statistical mixture or ensemble of states with different number of particles [4, 6, 8, 12–14]. Regarding the dependence of each magnitude, i.e., energy and/or the density, with the number of particles, two kinds of descriptors arise from them. The zero-order descriptors are those which are integrated functions of the magnitudes itself such as those describing the electronic distribution from electron populations as atomic charges, covalent bond orders, valencies, free valencies among others [16, 17] or local indicators as those coming from the topological approach like critical points of the density, their ellipticity or the Laplacian functions of the density, among others [18, 19]. The other type are the so-called higher-order descriptors depending on the successive derivatives of these magnitudes as for instance, the chemical potential, the hardness, Fukui functions, etc. [3]. The behavior of the energy, density or other properties for ensemble [4, 12, 13] or even for pure states distributions [20, 21] is of fundamental importance for the latter type because of the discontinuities they undergo at integer numbers [4]. So that the system definition is supported on the AIM notion giving rise to atomistic models for molecules [18, 22, 23] which permits to determine the concept of net charge on an atom as the key variable for determining its energy [4, 9, 12]. The energy and the density matrices (DM) are piecewise-continuous linear functions of the number of particles $\mathcal{N}$ [4, 12], and consequently, its first derivatives are $\mathcal{N}$-staircase functions being undefined at the integers and constant in between [24]. So that, second derivatives vanish in between and are not defined at the integers. Hence, descriptors like hardness vanish [3]. This dependence has contradictory consequences as for instance, the violation of the electronegativity equalization principle [3, 6] closely related to reactivities and hardness [3].

In Ref. [24], it is clearly noted that the formal $\mathcal{N}$ piecewise-continuous linear dependence of the physical magnitudes with the number of particles contains the essence of the model for non-integer electron systems [4, 12]. Thus, admitting the onset of a more accurate reactivity theory going beyond the mentioned inconsistencies, it must be recognized that reactivity descriptors are chemical environment dependent and may not be defined for isolated species without considering a fragment and/or reservoir interaction, i.e., generally, system–reservoir (S–R) interactions from which the species exchanges or transfers electrons [24]. A formal approach which addresses the problem and proposed a formal solution at an ensemble level can found in Ref. [25].

The objective of this work is to introduce some recent rigorous developments about the structure of the density matrices (DM), i.e., the state of the system as an ensemble of pure states of different number of fixed particles M commonly called grand-canonical ensemble (GC), the calculation of the energy under the hypothesis of its convexity for ground state isolated molecular systems and their extensions to systems under the influence of an environment interaction, i.e., a fragment or a reservoir [14]. In this way, we attempt to obtain a solution based on the interaction between the subsystems (S–R) inducing a coherent DM distribution which overcomes the inconsistencies mentioned above. Hence, the solution lies within the formal structure of reactivity theory, and the second-type chemical descriptors (second derivatives) are obtained in the natural scenario of the GC [12, 13] and the chemical context in which the species exchanges or transfers electrons.

Finally, the marginal distributions of the GC DMs, i.e., p-RDMs of the non-coherent (isolated systems) [13] distributions of the molecular open systems, are calculated by means of the contraction mappings [13, 26] in order to evaluate the properties as averages of the associated quantum observable. As an example, an explicit derivation and generalization of the Fukui functions are shown as a first-order descriptor of the density from this formalism without using the finite difference methods. The article is organized as follows. Section 2 presents the theoretical aspects introducing the definition, characterization and features of the systems, the energy determination, their states (DM) and marginal distributions, i.e., the reduced density matrices p-RDMs in the GC ensemble. Also in this section, some important properties for the open systems are sketched. In Sect. 3, the chemical descriptors of interest and the solution for the quantum state of the system in the framework of the S–R interaction are presented to show the machinery in action. A final Section is dedicated to the concluding remarks.

2 Theoretical background

2.1 The system

The dissociation process of a molecule leads to separated atoms, i.e., physically isolated, which are neutral. This is an experimentally very well-supported result because the greatest electron affinity (EA) of all the neutral atoms is smaller than the least ionization potential (IP) [5, 6]. The inverse process of the dissociation is the formation of a stable structure by bonding interactions where their densities distort from the isolated ones and then polarize to produce a charge transfer as is also very well known by experimentalists [27]. Consequently, they become fractionally charged to form covalent, ionic or any other type of distribution [18, 19] regarding the linked atoms as open systems free to exchange electrons between them [4, 5] and no longer as isolated. Therefore, the notion of an atom in a molecule (AIM) as a physical domain within the physical space is needed for a theoretical determination of the transferred fraction of charge. For practical implementations, each physical magnitude may be decomposed for atoms or a group of them like moieties that can be for instance a functional group or a simple atom. Two equivalent methods but of different nature may be considered, the topological ones based on the physical partition of the real space by means of a rigorous methodology like the Bader's AIM [16–18, 28–30] or those supported by empirical parameters as the "fuzzy" atoms [22, 31, 32] while others, the fragment methods (FM) which are not of topological nature [23]. These ideas introduce the concept we will have in mind when we invoke the treatment of a non-integer domain population, i.e., they house a number of particles $\mathcal{N}$ with $\mathcal{N} \in \mathbb{R}$. In general, these systems can be considered a subsystem within a molecular framework or a whole molecule in contact with an electron reservoir so that both schemes admit the electron exchange [15].

2.2 Energy and states

To describe these systems, the physical extension of the ground energy level $\mathcal{E}_0^{\mathcal{N}}$ where $\mathcal{N}$ is the number of particles with $\mathcal{N} \in \mathbb{R}$, as well as their states as a function of a continuous number of particles is needed. The most general description of the state of a quantum system is the density matrix D [26, 33]. It describes the state of an isolated system as a non-coherent convex sum of the complete set of all accessible M-electron pure state density matrices [26, 33, 34]

$$^M D_{\Phi_k^M} = |\Phi_k^M\rangle\langle\Phi_k^M| \tag{1}$$

in the mixture, where $|\Phi_k^M>$ is the kth quantum state function in the antisymmetric M-electron Hilbert space $\mathfrak{F}_M$ (Hamiltonian eigenstates) [34, 35]. Therefore, D is expressed by [34, 35]

$$D = \sum_M \sum_{\Phi_k^M} \omega_{\Phi_k^M} |\Phi_k^M\rangle\langle\Phi_k^M|;$$
$$\sum_M \sum_{\Phi_k^M} \omega_{\Phi_k^M} = 1; \quad \omega_{\Phi_k^M} \geq 0 \tag{2}$$

where $\omega_{\Phi_k^M}$ are the statistical weights, i.e., the probability of occurrence of the pure state $|\Phi_k^M\rangle$ in the mixture. The carrier space for this type of description is the entire Fock space $\mathfrak{F} = \bigoplus_{M=0}^{\infty} \mathfrak{F}_M$, where the symbol $\bigoplus$ indicates direct sum [35]. These states admit particle number fluctuation, and the number of particles is an average so that the system may posses a non-integer number of particles. We will refer to this state as the *grand-canonical* distribution (GC). The background of the GC formalism ideas to be used for systems with a few number of particles, like a molecule or an atom, is supported by the statistical interpretation of the DM and the existence of some physical criteria to determine the weights for the distribution, i.e., maximum entropy in statistical physics [6] or minimum energy in ground states of systems with a non-integer number of particles as shown in Ref. [12] on the mathematical basis of a finite subspace of the Fock space [36]. Hence, this representation admits the different number of particles M of the system, and therefore, their populations $\omega_{\Phi_k^M}$ are the variables defining any state DM [12, 13]. Note that it stands for a generalization of the PPLB [4] conjecture. D is an Hermitian, positive semi-definite (all eigenvalues are nonnegative or vanishing), bounded (the module of its elements are bounded) and finite trace (sum of the diagonal elements) matrix, and because of its probabilistic interpretation it may be normalized to unity, i.e., $\mathrm{Tr}(D) = \sum_M \sum_{\Phi_k^M} w_{\Phi_k^M} = 1$ [33, 34]. Let us mention that the well-known *canonical distribution* (C, all states in the mixture posses the same number of particles N), expressed by $^N D = \sum_{\Phi_k^N} \omega_{\Phi_k^N} |\Phi_k^N\rangle\langle\Phi_k^N|$, and the *microcanonical distribution* (MC, all weights vanish except one), i.e., pure states $^N D_{\Phi_k^N} = |\Phi_k^N\rangle\langle\Phi_k^N|$, are particular cases of the GC distribution.

The energy $\mathcal{E}$ is the average of the Hamiltonian over the distribution D and is defined by [33, 34]

$$\mathcal{E} = \mathrm{Tr}(D\,\mathcal{H}) = \sum_M \sum_{\Phi_k^M} \omega_{\Phi_k^M} \mathrm{Tr}\left(^M D_{\Phi_k^M} \mathcal{H}\right) \tag{3}$$

where $\mathcal{H}$ is the system Hamiltonian operator, and Tr means the mathematical trace operation. Let $^M D_0$ be a non-degenerate or removable degenerate ground pure state DM [37, 38] of the M-particle system and its associated energy given by

$$\mathcal{E}_0^M = \text{Tr}\left(^M D_0 \, \mathcal{H}\right) \tag{4}$$

Introducing the notation, $\Delta^M = \mathcal{E}_0^{M-1} - \mathcal{E}_0^M$ as the energy difference convenient interval, i.e., the first ionization potential of the system, and the assumption that for $M > 1$, the $\Delta^M > \Delta^{M+1} > 0$ inequality holds [4–6, 24], then it results that the sequence $\left\{\mathcal{E}_0^M\right\}_{M \in \mathbb{N}}$ verifies the above inequality for arbitrary $N, M \in \mathbb{N}$ numbers, such that for $M \neq N, N+1$, it follows

$$\mathcal{E}_0^M \geq (N+1-M)\mathcal{E}_0^N + (M-N)\mathcal{E}_0^{N+1} \tag{5}$$

and the equality holds only for $M = N, N+1$ [12]. Equation (5) stands for the mathematical expression of the energy convexity for the ground state energies with respect to the number of particles. Let us introduce explicitly the non-integer number of electrons in the systems, $\mathcal{N} = N + \nu$ with $N \in \mathbb{N}$ and $\nu \in (0, 1)$, i.e., between the consecutive integer numbers, N and $N + 1$, to extend the dependence of the energy between these numbers. The use of the variational principle for the energy in Eq. (3) with the statistical weights $\{\omega_{\Phi_k^M}\}$ as variational parameters and the constrain of the number of particles $\mathcal{N}$ leads to the solution for this problem in which D is unique and expressed by [12]

$$D = (1 - \nu) \, ^N D_0 + \nu \, ^{N+1} D_0 \tag{6}$$

Consequently, the energy of the system with non-integer number of particles reads as [12]

$$\mathcal{E}_0^{N+\nu} = (1 - \nu)\mathcal{E}_0^N + \nu \mathcal{E}_0^{N+1}. \tag{7}$$

which is the rigorous derivation of the PPLB proposal [4] and consequently for the corresponding DM structure of Eq. (6). Therefore, it follows that Eqs. (6) and (7) are valid for any type of state function, i.e., particle independent or correlated models [39]. At this stage, it is important to mention that all results are also valid for $N - \nu$, so we only refer to the $N + \nu$ case unless necessary for a clarifying need.

The fundamental chemical concepts derived from the physical properties and the chemical descriptors of a system are the summary of the physical information contained in the p-particle reduced density matrices $^p D$ (p-RDM) of an M-electron molecular system ($p < M$) which are derived by contraction operations from the DM and represent its marginal distributions [26]. Any property associated with a physical magnitude $\mathcal{A}$ is the average of the corresponding quantum observable A expressed by

$$\langle A \rangle = Tr(DA) \tag{8}$$

In general, the operators A are not a function of the coordinates of all particles in the system but only of a few of

them, a subset p. They connect p-particles and are called p-particle operators noted by $^p A$, as for instance kinetic, nucleus–electron interaction potential or dipolar moment are 1-particle operators, $^1 A$; electron–electron interaction potential are 2-particle operators, $^2 A$ and so on [26, 40]. So that, the averages become [26, 40]

$$\langle ^p A \rangle = Tr(^p D \, ^p A) \tag{9}$$

As said above, $^p D$ are the marginal distributions of the whole distribution D. To obtain them, the contraction mapping (CM) operation may be performed on D in order to reduce the number of variables from a fixed M number of particles to p, i.e., the order of contraction [26, 41]. In order to define this operation for the GC distribution which has no fixed number of particles, let us first sketch it for the MC and C distributions. For this goal, we introduce the p-RDMs in terms of the p-order replacement operators $^p E$ [42] in the second quantization formalism [43]

$$^p E_{j_1, j_2, \ldots, j_p}^{i_1, i_2, \ldots, i_p} = c_{i_1}^+ c_{i_2}^+ \ldots c_{i_p}^+ c_{j_p} \ldots c_{j_2} c_{j_1} \tag{10}$$

in which $i, j, k, l, \ldots$ indices denote spin orbitals of an orthogonal basis set, and c^+, c stand for the usual creation and annihilation fermion operators, respectively [43]. For a pure state $^M D$, the CM becomes defined by Eq. (11) as [26, 38]

$$^p D_{j_1, j_2, \ldots, j_p}^{i_1, i_2, \ldots, i_p} = Tr(^M D \, ^p E_{j_1, j_2, \ldots, j_p}^{i_1, i_2, \ldots, i_p}) \tag{11}$$

The p-RDMs are hermitian, positive semi-definite and bounded [26] and obey the essential property of representability which states for the constraints that a given p-RDM must fulfill to be derivable from a DM [26, 44]. For both C and MC distributions in which the number of particles is fixed for all states in the distribution, any two of the reduced density matrices, say $^q D$ and $^p D$ ($q < p$), are related by a contraction operation [26, 41]. Equation (11) can be expressed in a more compact equivalent form by

$$^p D = \binom{M}{p} \hat{L}_p^M \{^M D\} \tag{12}$$

where CM denoted by the symbol $\hat{L}_p^M$ is applied to $^M D$ and thus the p-RDM arise for both C or MC states [26, 41]. The binomial symbol $\binom{M}{p}$ is the Coleman's normalization factor or the number of the composed p-particles or p-ons [26]; $p = 1, 2, \ldots$ stand for the one-electron reduced density matrix $^1 D$ of M particles; the two-electron reduced density matrix $^2 D$ of $\binom{M}{2}$ pairs, and so on. More explicitly, it reads,

$$^p D_{j_1, j_2, \ldots, j_p}^{i_1, i_2, \ldots, i_p} = \sum_{\Phi_k^M} \omega_{\Phi_k^M} \, ^p D_{j_1, j_2, \ldots, j_p}^{i_1, i_2, \ldots, i_p}(\Phi_k^M) \tag{13}$$

where $^pD_{j_1,j_2,...,j_p}^{i_1,i_2,...,i_p}(\Phi_k^M) = \binom{M}{p}\hat{L}_p^M\{^MD_{\Phi_k^M}\}$ stands for the p-RDM associated with the $|\Phi_k^M\rangle$ kth accessible M-particle pure state of the system. The physical meaning of this operation is nothing but an *averaging* process over the remaining $M - p$ variables [45].

As stated above, any physical system featured by a non-integer number of particles $\mathcal{N}$ cannot be described by any other state than the GC. Therefore, a CM to take into account properly the M-particle different states in D defined by Eq. (2) in Fock space to calculate the p-RDMs marginal distributions may be introduced. This expression has been obtained recently [13] as

$$^pD = \hat{L}_p\{D\} = \sum_{\{\Phi_k^M, M \geq p\}} \omega_{\Phi_k^M}\binom{M}{p}\hat{L}_p^M\{^MD_{\Phi_k^M}\} \quad (14)$$

Equation (14) is the definition for the GC CM $\hat{L}_p$ and permits to note that it involves several pure states $^MD_{\Phi_k^M}$ with the condition that the number of particles was $M \geq p$, i.e., the order of contraction p must be less than or equal to M and all states in the mixture not lying in this interval, i.e., $M < p$, will not contribute to the GC distribution, while for $M = p$, no action is needed [13]. These mathematical conditions are expressed by

$$\hat{L}_p^M\{^MD_{\Phi_k^M}\} = \mathbf{O} \quad M < p$$

and

$$\hat{L}_p^p\{^pD_{\Phi_k^p}\} = \mathcal{I}\ ^pD_{\Phi_k^p} = {}^pD_{\Phi_k^p}$$

with $\mathcal{I}$ and $\mathbf{O}$, the identity and null superoperators, respectively [13]. These requirements complete the definition for the CM in Fock space, and the *p-RDM*s may be expressed by the expansion,

$$^pD = \sum_{\{\Phi_k^M, M \geq p\}} \omega_{\Phi_k^M}\ ^pD_{\Phi_k^M} \quad (15)$$

It is worthy to note that the trace operation calculated by $\mathrm{Tr}(^pD) = \sum_{\{\Phi_k^M, M \geq p\}} \omega_{\Phi_k^M}\binom{M}{p} = \langle\binom{M}{p}\rangle$ is the number of p-ons number in the system as an average which is noted by the symbol $\langle\ldots\rangle$. In particular, for $p = 1$, $\mathrm{Tr}(^1D) = \sum_{\{\Phi_k^M, M \geq 1\}} \omega_{\Phi_k^M} M = \langle M \rangle$, is the number of particles expressed by the non-integer number $\langle M \rangle = N + \nu$ mentioned above.

To finish this section, let us mention some important consequences coming from the marginal distributions in the GC structure of the density matrices which we will not treat in this work. As noted in this section, within the C and MC states, any ^qD may be obtained from other matrix ^pD with $q < p$ by a contraction operation [26]. The same

is not true within the GC distribution [cf. Eq. (2)] without losing some information and hence any matrix may be only obtained directly by contraction of D [13]. Nevertheless, for the case of our interest in which the energy has a convex structure [cf. Eq. (6)], no information is lost, except for the case in which $q = N$ and $p = N + 1$ [13]. The other consequence we want to mention is that for a closed atomic and molecular systems, the energy is a functional of the second-order reduced density matrix as $\mathcal{E}_0^N = \mathrm{Tr}(^2D_o^N{}^2\mathcal{K}_N)$, where $^2\mathcal{K}_N$ stands for the Coleman reduced Hamiltonian, $^2D_o^N$ the ground state second-order reduced density matrix with a supra-index N which indicates that the 2-RDM comes from contraction of a N-particle DM [26, 38]. In contrast, for an open atomic or molecular system, the energy cannot be expressed similarly as a functional of the corresponding $^2D_o^{N+\nu}$ but as $\mathcal{E}_0^{N+\nu} = \nu\mathrm{Tr}(^2D_o^{N+1}\ {}^2\mathcal{K}_{N+1}) + (1 - \nu)\ \mathrm{Tr}(^2D_o^N\ {}^2\mathcal{K}_N)$, namely the energy is a functional $\mathbf{F}$ of $^2D_o^N, {}^2D_o^{N+1}$ and the fractional population number ν, i.e., $\mathcal{E}_0^{N+\nu} = \mathbf{F}(^2D_o^{N+1}, {}^2D_o^N, \nu)$ [13, 46].

3 Chemical descriptors: system–environment interactions and derivative discontinuities

The higher chemical descriptors are derivatives of the energy or of the electron density with respect of the number of particles $\mathcal{N}$ [3]. They are related to the concept of reactivity interpreted as a response function to proper chemical interactions [24]. Joint together with the zero-order descriptors, i.e., energy and functions of the density itself, provides the complete and detailed description of a molecular system and its intra- (with a solvent, a reservoir, etc.) and inner-interactions (between different fragments in the molecule). So that it imposes the knowledge of these magnitudes, $\mathcal{E}_0^{\mathcal{N}}$ and $\rho^{\mathcal{N}}$ (or more generally the associated DM from which $\rho^{\mathcal{N}}$ is obtained), dependence with $\mathcal{N}$ [5, 12, 13]. The common use of the method of finite differences with respect to integer number of the particles of isolated species to evaluate the derivatives [3] neglects their values at non-integer numbers [24] and consequently the true electron exchange between molecular subsystems which constitutes the onset of chemical behavior.

For ground states, the dependence of the energy $\mathcal{E}_0^{\mathcal{N}}$ and the DMs is a piecewise-continuous linear functions of $\mathcal{N}$ and only the closed systems with integers N and $N \pm 1$ enter in this ensemble as stated by Eqs. (6) and (7), respectively [12]. Hence, all ground state properties then have similar dependence, and the first derivatives of the energy and the density are staircase functions of $\mathcal{N}$, undefined at the integers and constant in between [24] leading to the second derivatives to vanish in between integers [4, 24]. The consequences of this dependence are nonphysical,

for example, the electronegativity equalization principle and the electronic principles based on hardness are sense-less because they lose their foundations [3, 4, 24]. Let us show such dependence and make explicit the inconsistencies. The chemical potential is defined at constant external potential υ by [3, 6]

$$\mu = \left(\frac{\partial \mathcal{E}_o^{\mathcal{N}}}{\partial \mathcal{N}} \right)_\upsilon \tag{16}$$

which by explicit use of the ground state energy expression for open systems for both signs, i.e., $\pm\upsilon$ in Eq. (7) [4, 12]

$$\mathcal{E}_0^{N\pm\upsilon} = (1-\upsilon)\mathcal{E}_0^N + \upsilon\mathcal{E}_0^{N\pm1}. \tag{17}$$

with $\mathcal{E}_0^{N\pm\upsilon}, \mathcal{E}_0^N$ and $\mathcal{E}_0^{N\pm1}$ the energy of the systems with non-integer $N\pm\upsilon$, N and $N\pm1$ number of electrons, respectively; then regarding $\partial\mathcal{N} = \pm\partial\upsilon(N = $ constant), the derivative is

$$\mu^\pm = \pm\left(\frac{\partial \mathcal{E}_o^{\mathcal{N}}}{\partial \upsilon} \right)_\upsilon = \pm\left(\mathcal{E}_0^{N\pm1} - \mathcal{E}_0^N \right) \tag{18}$$

yielding the two branches [4]

$$\mu^+ = \mathcal{E}_0^{N+1} - \mathcal{E}_0^N = -EA, \quad \mu^- = \mathcal{E}_0^N - \mathcal{E}_0^{N-1} = -IP \tag{19}$$

with EA and IP the electron affinity and ionization potential energies, respectively [1, 2]. Hence, since both energies are different, the discontinuity becomes explicit. The other important first derivative is that of the electron density $\rho(\mathbf{r})$ at point $\mathbf{r}$ in space, at constant external field υ which is also expressed into two branches by

$$f^\pm(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial\mathcal{N}} \right)_\upsilon^\pm = \pm\left(\frac{\partial\rho(\mathbf{r})}{\partial\upsilon} \right)_\upsilon^\pm \tag{20}$$

which stand for the well-known Fukui functions [3, 6, 47, 48]. The two derivatives appear by considering the cases in which $\mathcal{N}$ increases/decreases from N to $N\pm\upsilon$, respectively. This expression may be generalized to matrix form taking into account that $\rho(\mathbf{r})$ is the diagonal element of ^1D in the coordinate representation [26]. Therefore, application of the CM of Eq. (14) to D matrix of Eq. (6) and introducing the expression for $^1D^{N\pm\upsilon}$, where the supra-index indicates the matrix comes from the state of $N\pm\upsilon$ electrons, it results

$$F^\pm(\mathbf{r}|\mathbf{r}') = \pm\left({}^1D^{N\pm1}(\mathbf{r}|\mathbf{r}') - {}^1D^N(\mathbf{r}|\mathbf{r}') \right) \tag{21}$$

It establishes a rigorous justification to the forms used to deal with accurate Fukui functions [3]. It is worthy to note

Ref. [49] as a previous GC DFT formulation of the problem coincident with the determination performed by finite differences. For a complete description and properties of a matrix formulation of these magnitudes, see Refs. [50, 51]. Nevertheless, this magnitude has a different physical meaning than those coming from the energy, and it will not be subject of the present work.

The example of the chemical potential shows the nature of the discontinuities caused by the lack of terms depending on the charge transferred coupling the states of different number of particles. Hence, it does not enable the onset of nonvanishing higher-order derivatives. Let us deal with this lacking information and relate it to the interaction of the subsystem (fragment) within a molecular frame and/or the interaction of the whole molecule with an environment (reservoir) which permits electron exchange and so charge transfer. Some attempts based in the treatment of the energy dependence from the point of view of the state function approach have been reported in order to overcome these discontinuities and thus incorporate the information into the descriptors [5, 15, 52]. Nevertheless, as the theory indicates, a general statistical formulation is needed at the GC level of description to consider the interaction of the system with the environment, i.e., other subsystem and/or reservoir (S–R) interactions. Early attempts to implement such formulation within the DFT can be found in Ref. [25].

The remaining part of this report will be devoted to this topic in order to introduce such interactions within the DM structure [4, 12, 13] and thus calculate the expressions for the descriptors to shed some light into the essence of these reactivity indices.

In the previous section, it has been shown that the convex structure of D and the energy for ground states evolve into two branches, each one as a two-state level model of N and $N\pm1$ Hilbert spaces as expressed in Eqs. (6) and (7) [4, 12, 13]. The corresponding pure ground state DMs in Dirac notation reads,

$${}^ND_0 = |\Phi_0^N\rangle\langle\Phi_0^N|$$

and

$${}^{N\pm1}D_0 = |\Phi_0^{N\pm1}\rangle\langle\Phi_0^{N\pm1}|,$$

respectively. The interaction of the system (subsystem) with the environment may be described by means of a potential $\mathbf{U}_\upsilon$ which may have diverse nature regarding the type of interaction we are dealing with and depends on the electron fraction υ as indicated by the subscript. For instance, such potential may be considered as describing the interaction between subsystem fragments within the Atoms in Molecules (AIM) framework [11] or fragment methods [53], reservoir interactions effects [34], the influence of a solvent field on molecular systems (liquid phase)

[54, 55] or environmental effects [55] among others. Therefore, the Hamiltonian in the adiabatic approximation [56] for each of the two branches,

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{U}_\nu \tag{22}$$

can be expressed in matrix form as

$$
\begin{aligned}
\mathcal{H} = {} & \mathcal{E}_0^N |\Phi_0^N\rangle\langle\Phi_0^N| \; + \; \mathcal{E}_0^{N\pm1} |\Phi_0^{N\pm1}\rangle\langle\Phi_0^{N\pm1}| \\
& + \; \mathcal{U}_\nu^\pm |\Phi_0^N\rangle\langle\Phi_0^{N\pm1}| \; + \; \mathcal{U}_\nu^{\pm*} |\Phi_0^{N\pm1}\rangle\langle\Phi_0^N|
\end{aligned}
\tag{23}
$$

where $\mathbf{H}_0$ represents the isolated system Hamiltonian whose spectra and eigenstates are noted in Eq. (23) by the energies $\mathcal{E}_0^N$ and $\mathcal{E}_0^{N\pm1}$, and $|\Phi_0^N\rangle$ and $|\Phi_0^{N\pm1}\rangle$ for the neutral and the ionic states, respectively. $\mathbf{H}_0$ is diagonal at the basis set of its eigenstates as well as its density matrix D. The action of the interaction potential induces a new distribution $\tilde{D}$ which may describe the open system and reflects the coupling between both states, that of N with those of $N \pm 1$ [57, 58]. This equilibrium state may reach a permanent regime of electron exchange, i.e., the rate of electron exchange is constant in time. Therefore, the density matrix $\tilde{D}$ may exhibit a coherent structure (nondiagonal elements or coherences are no vanishing) due to the action of the interaction potential $\mathbf{U}_\nu$ [34], so that it will be expressed by

$$\tilde{D} = D + \Delta_\nu^\pm |\Phi_0^N\rangle\langle\Phi_0^{N\pm1}| + \Delta_\nu^{\pm*} |\Phi_0^{N\pm1}\rangle\langle\Phi_0^N| \tag{24}$$

where the first term stands for the isolated distribution of Eq. (6), i.e., corresponding to $\mathbf{H}_0$ [4, 12, 13], while the last two terms describe the coupling interaction of the $|\Phi_0^N\rangle$ and $|\Phi_0^{N\pm1}\rangle$ states. The coherences must obey the inequality related to its diagonal elements (or populations), $|\tilde{D}_{nm}|^2 \leq \tilde{D}_{nn}\tilde{D}_{mm}$ whose physical meaning is that there can be coherences only between states whose populations are not zero; in this case, $\left|\Delta_\nu^\pm\right|^2 \leq (1-\nu)\nu$ and if $\nu = 1, 0$, i.e., one of the states, that of N or $N \pm 1$ respectively, has no populations. Thus, the coherence between them vanishes, so that $\Delta_0^\pm = 0$ [59]. Then, the energy for the system interacting with the environment using Eq. (3) with $\tilde{D}$ distribution is expressed by

$$\tilde{\mathcal{E}}_0^{N\pm\nu} = Tr(\mathcal{H}\tilde{D}) = \mathcal{E}_0^{N\pm\nu} + 2\mathbb{R}e(\mathcal{U}_\nu^{\pm*}\Delta_\nu^\pm) \tag{25}$$

where the symbol $\mathbb{R}e$ indicates the real part of the complex number $\mathcal{U}_\nu^{\pm*}\Delta_\nu^\pm$. This term determines the interaction with the environment, and because the interaction potential must depend on the fraction ν to ensure the electron transfer, it introduces a ν-nonlinearity dependence for the energy and the DM. Thus, it enable us to perform the calculation of the chemical descriptors of arbitrary order avoiding the discontinuity problem. To show the machinery in action, let us write the descriptors defined above in order to clarify these ideas. The chemical potential of Eq. (16) becomes

$$\tilde{\mu}^\pm = \left(\frac{\partial\tilde{\mathcal{E}}_0^\mathcal{N}}{\partial\mathcal{N}}\right)_\nu = \pm\left(\frac{\partial\tilde{\mathcal{E}}_0^{N\pm\nu}}{\partial\nu}\right)_\nu \tag{26}$$

and then it results

$$\tilde{\mu}^\pm = \mu^\pm \pm 2\mathbb{R}e\left(\frac{\partial(\mathcal{U}_\nu^{\pm*}\Delta_\nu^\pm)}{\partial\nu}\right)_\nu \tag{27}$$

The second term of the r.h.s of Eq. (27) permits to avoid the chemical potential discontinuity [4, 24], and thus the equalization principle can be fulfilled [3]. To understand it, let us consider two fragments Ω_A and Ω_B within a molecular framework which at equilibrium must obey the condition $\tilde{\mu}_{\Omega_A}^+ = \tilde{\mu}_{\Omega_B}^-$, i.e., the chemical potential of the donor fragment must be equal to that of the acceptor fragment; it is the second term of the r.h.s. of Eq. (27) which enables this condition. Hence, the hardness which vanishes identically because of the chemical potential discontinuity for an isolated system, i.e., without interaction with an environment [24], becomes non-null due to the interaction and reads

$$\tilde{\eta}^\pm = \frac{1}{2}\left(\frac{\partial^2\tilde{\mathcal{E}}_0^\mathcal{N}}{\partial^2\mathcal{N}}\right)_\nu = \pm\mathbb{R}e\left(\frac{\partial^2(\mathcal{U}_\nu^{\pm*}\Delta_\nu^\pm)}{\partial^2\nu}\right)_\nu \tag{28}$$

showing the two signs as in the case of the chemical potential because of the openness of the systems.

4 Discussion and concluding remarks

The GC distribution has been used here avoiding the concept of temperature but explicitly based on the electronic information. This description has been recognized adequate to introduce the S–R interactions on the descriptors and permits by the means of a charge-dependent interaction potential to overcome the problem of the discontinuities in the derivatives of the energy. This treatment recovers the piecewise dependence when the interaction vanishes, i.e., $\mathbf{U}_\nu \to 0$, as expected. This formulation, as has been pointed out, is more realistic than evaluating the descriptors in isolated systems by finite difference methods. In conclusion, the GC distribution for open molecular domains enables to introduce statistical concepts to describe electron distributions in the molecular structure even they are few body systems.

It may be noted that for the present developments, the general structure of the DMs has been used, and hence, the results are valid at any level of approximation of the state functions, i.e., particle independent or correlated ones. Furthermore, it depends only of the model used for system–environment interaction.

Several topics deserve our attention as natural continuation of the present work to continue the understanding of the reactivity phenomena from a rigorous point of view and are being considered in our laboratory. Some of them are related to obtain an equation that preserves the constant rate of electron transfer between the open domains in the molecular structure and provides DM evolution within this context, the modeling of the interaction potential of different nature and the contraction mappings in Fock space for coherent density matrices, among others.

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