



# Energy dependence with the number of particles: Density and reduced density matrices functionals



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## ABSTRACT

The energy of a physical domain within a molecular system considered as a quantum open system is analyzed as a functional of the electron distribution dependence with the number of particles. Our attention is focused upon the constrained-search functionals of the electron density, the 1- and 2-reduced density matrices (1-, 2-RDMs) for grand-canonical states. It is shown that functionals of the 2-RDM depend on the number of particles if the ground state energy is not a convex function of them.

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## 1. Introduction

Chemical processes involve the rearrangement of electron distributions between fragments of the molecular structure. These units are physical domains likewise atoms, functional groups or moieties which exchange electrons between them and consequently possess a non-integer number of electrons, that may be interpreted as a time average in a given quantum state of an open system [1]. The accurate description of these domains inside a molecule [2] is of paramount importance to understand the relation function–structure, i.e., molecular structure and chemical reactivity. Chemical descriptors from the conceptual density functional theory (DFT) defined as derivatives of different magnitudes with respect to the number of electrons reflect the changes due to infinitesimal variations (electron exchange) [3,4]. The solution of the interacting many-electron problem rests on the search of an optimal of the energy including the correlation effects and posses a common feature for all type of approaches: it is a functional of the electron distribution completely described by the density matrix of the system  $D$  [5]. Namely, the ground state energy  $E$  of a system of  $N$  electrons ( $N$  being an integer number), may be obtained through the minimization of a functional  $E[D]$  over the set of  $D$ s (DM), subject to the constraint  $\int \rho(r)dr = N$  with  $\rho$  the electron density obtained from  $D$  and introduced by means of the  $\mu$  Lagrange multiplier in the form [6],

$$\delta \left\{ E[D] - \mu \left[ \int \rho(r)dr - N \right] \right\} = 0 \quad (1)$$

This constraint permits in principle to extend the energy functional to electron densities integrating to fractional electron numbers [1]. The different levels of approximation to this problem depends on

magnitude used to perform the description of the distributions, i.e.,  $\rho$  for the DFT [6], the one-particle reduced density matrix  ${}^1D$  (1-RDM) for the Reduced Density Matrix Functional Theory (RDMFT) [7], pair density functional theory (PDFT) [8–10] or the second-order reduced density matrix  ${}^2D$  (2-RDM) equivalent to the solution of the Schrödinger equation [11,12]. It is also of needs to mention some new ways as the path integral (PI) [13] and the chemical action functional formulation of chemical interactions which shares Eq. (1) to introduce electronic density and then any known or approximated density functional may be evaluated [14] which provides a suitable way to relate the reactivity descriptors within this framework [15]. Therefore, the search for the solutions of this problem can be treated on the same footing, i.e., the constrained search of an energy functional of the mentioned devices which provides the energy minimum. Also, the constrained search formalism has been used to derive functionals for systems with finite-temperature and for other state functions, most notably the grand potential [6,16–18].

Molecular open quantum systems, i.e., molecular fragments, with non-integer or fractional electron numbers have been described by the conjecture based on the convex combination of the  $N$  and  $N + 1$  electron states [1] within the DFT framework. Nevertheless, no intents have been reported out of it until recently, when a new approach to analyze open systems based on grand-canonical density matrices (DMs) was proposed [19]. This treatment, besides encompassing the DFT results for the energy of systems with non-integer electron numbers, allows to generalize it to arbitrary state functions [19]. The initial formulation of this method relies on the assumption that the energy of the system is a convex function of the number of particles. This property, empirically proven for isolated Coulomb systems (e.g. atoms and molecules) is not expected to hold for interacting reagents, i.e., species imbedded in some environment [3]. In a further study the contraction mappings (CM) for the grand-canonical description have been

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introduced for molecular systems and it was shown that when the energy is not a convex function of the number of particles some information is lost when connecting two RDMs of different order, i.e.,  $q$ - and  $p$ -RDM with  $q < p$ , by partial contractions [20].

The purpose of this work is to establish the dependence of the energy functional of a molecular system with number of particles out of the energy convexity assumption, in terms of the electron density  $\rho$ , the 1-RDM and/or 2-RDM according to the level of description. Section 2 is devoted to the introduction of the constrained search method in a form that allows us to treat the energy functionals on the same footing and a brief introduction to the energy functionals for the canonical distribution case. The Section 3 introduces the grand-canonical energy functionals, showing their similarities and differences with respect to the canonical counterparts. Relevant to this part is the above mentioned loss of information within the contraction process which does not occur in the canonical case which allows to understand why the 2-RDM energy functionals of the grand-canonical distributions must depend on the number of particles. A final section is dedicated to the concluding remarks.

## 2. Theoretical aspects

### 2.1. Constrained search and energy functionals

The description of a quantum state based on density matrices  $D$  permits to introduce pure, canonical and grand-canonical ensembles in a unified manner [21,22]. Therefore, the application of variational principle techniques allows to determine the ground state energy of a system for an arbitrary number of electrons  $\mathcal{N}$ , i.e., integer or fractional,  $\mathcal{E}_0^{\mathcal{N}}$  as [6]

$$\mathcal{E}_0^{\mathcal{N}} = \min_D \text{Tr}(D \mathcal{H}) \quad (2)$$

where  $\mathcal{H}$  stands for the Hamiltonian of the system which will be expressed only by 1- and 2-particle terms as  $\mathcal{H} = \sum_i h(i) + \sum_{i < j} w(i, j)$  where  $h$  and  $w$  represent those terms, respectively. Hence the corresponding minimization process is carried out over  $D$ . Let us introduce the idea of constrained search methodology for systems with an arbitrary number of particles  $\mathcal{N}$ . Here we will deal with states with an integer number of particles  $N$ , while the grand-canonical treatment of systems, i.e., those with a fractional number of particles will be introduced in the next section to make evident the fundamental differences which this last one introduces. The key point in this strategy, known as constrained search, is the realization of Eq. (2) in two steps [6,23], i.e.,

$$\mathcal{E}_0^{\mathcal{N}} = \min_{\Lambda} (\min_{D \rightarrow \Lambda} \text{Tr}(D \mathcal{H})) \quad (3)$$

or equivalently,

$$E_{\Lambda}^{\mathcal{N}}[\Lambda] = \min_{D \rightarrow \Lambda} \text{Tr}(D \mathcal{H}) \quad (4a)$$

$$\mathcal{E}_0^{\mathcal{N}} = \min_{\Lambda} E_{\Lambda}^{\mathcal{N}}[\Lambda] \quad (4b)$$

The two steps in Eq. (3) expressed by Eqs. (4a) and (4b) may be interpreted as follows. The first step (Eq. (4a)) indicates the search for a set of  $D$ s which leads to the same device  $\Lambda$  obtained by a CM procedure on it, i.e.,  $D \rightarrow \Lambda$  with  $\Lambda$  a p-RDM or a density. This procedure is called 'internal' minimization [6,23] while the second step (Eq. (4b)) searches for the minimum within the set of representable  $\Lambda$ s, i.e., RDMs or electron densities derived from a  $D$  [5,24]. This is called 'external' minimization [6,23]. Both steps correspond to the search of the ground state  $D$  solution of Eq. (4b) for  $\Lambda = \Lambda_0$ ,  $\mathcal{E}_0^{\mathcal{N}} = E_{\Lambda_0}^{\mathcal{N}}[\Lambda_0]$ . The supraindex in  $E_{\Lambda}^{\mathcal{N}}[\Lambda]$  means that  $\mathcal{N}$  particle systems are considered, at the time of evaluating the expression  $\text{Tr}(D \mathcal{H})$ . Let us note that the constrained search provides a way to

determine  $\mathcal{E}_0^{\mathcal{N}}$  by means of the energy functionals  $E_{\Lambda}^{\mathcal{N}}[\Lambda]$  in a dramatically more efficient way than the one provided by Eq. (2) [6]. This methodology has been applied to  $\rho$  and 1-RDM energy functionals [25]. Of course, there are many differences between the energy functionals based on different choices of  $\Lambda$  [16,18,26–28]. However, Eqs.(4a) and (4b) admit to treat all them on an equal footing. Finally, it may be noted that within the GC framework it is possible to obtain the same  $\Lambda$  from different  $D$ s but many of them may correspond to systems with different number of particles. This feature indicates a possible dependence of the functional with the number of particles. Namely, energy functionals might depend on the number of particles of the system because not every  $D$  that originates a given  $\Lambda$  can be considered to evaluate the ground state energy. It will be discussed in detail in the following sections.

Before concluding this section we would like to briefly discuss a critical issue related to  $\rho$ , p-RDM and their associated energy functionals which is central to our work: N-representability problem. A given device  $\Lambda$  is said to be N-representable if it can be obtained from a DM corresponding to a fermionic system through a CM procedure [5]. As mentioned earlier, when finding the minimum of the energy functional  $E_{\Lambda}^{\mathcal{N}}[\Lambda]$  (cf. Eq. (4b)), only N-representable  $\Lambda$ s are allowed as trial functions. This condition can not be relaxed; otherwise, it would lead to solutions with lower energy than the ground state, which of course have no physical meaning. A great amount of work oriented towards the derivation of necessary and sufficient conditions for the N-representability, has been performed mainly for the electron density, 1-RDM and 2-RDM [12]. Therefore, as mentioned before, imposing necessary and sufficient N-representability conditions is mandatory when working with sets of arbitrary  $\Lambda$ s, to obtain meaningful results, but however as in this work we will consider only sets of N-representable  $\Lambda$ s, consequently all the minimization procedures will give us the exact ground state energy. From now on, each time we refer to an electron density, 1-RDM or 2-RDM it must be assumed that they are N-representable. Closely related to the N-representability of the  $\rho$  and the p-RDMs is the corresponding problem for their energy functionals which introduces several restrictions for them [29,30]. Nonetheless, because as stated above, the set of  $\Lambda$ s used in the searching process are N-representable we will restrict ourselves to the set of N-representable functionals in due course of the present work.

### 2.2. Canonical states: DMs, RDMs and energy functionals

In the above subsection, we have imposed no restrictions to the type of the number of particles, however this is a non-trivial issue. Let us introduce the canonical states (C) to treat closed systems which possess a fixed integer  $M \in \mathbb{N}$  number of particles ( $\mathbb{N}$ , set of natural numbers) for all the contributing states as the starting point before considering the GC functionals for open quantum domains. The general form of  $D$  for a canonical state of the system is

$${}^M D = \sum_{\{\Phi_k^M\}} \omega_{\Phi_k^M} |\Phi_k^M\rangle \langle \Phi_k^M|; \sum_{\{\Phi_k^M\}} \omega_{\Phi_k^M} = 1; \omega_{\Phi_k^M} \geq 0 \quad (5)$$

where  $\{|\Phi_k^M\rangle, k = 1, \dots\}$  stands for the set of  $M$ -electron quantum state functions belonging to the antisymmetric  $M$ -electron Hilbert space  $\mathcal{F}_M$  and  $\{\omega_{\Phi_k^M}, k = 1, \dots\}$  the corresponding associated statistical weights. The particular case in which all the weights but one are zero corresponds to a microcanonical state, i.e., pure state

$${}^M D_{\Phi_k^M} = |\Phi_k^M\rangle \langle \Phi_k^M| \quad (6)$$

The differences between these systems will not be important in the following, then we will only refer in the future to canonical states, keeping in mind that the results and discussions concerning these

states will be also valid for micro-canonical states. Contraction mappings for canonical states are well known [5,12]. The p-RDMs,  ${}^pD$ , are obtained after averaging  $M - p$  variables of the canonical  ${}^M D$ , by application of the contraction mapping  $\hat{L}_p^M$ , defined as [5]

$$\begin{aligned} {}^p D_{j_1 j_2 \dots j_p}^{i_1 i_2 \dots i_p} &= \binom{M}{p} \hat{L}_p^M \{ {}^M D \} = \text{Tr} \left( {}^M D \frac{c_{i_1}^\dagger c_{i_2}^\dagger \dots c_{i_p}^\dagger c_{j_1} \dots c_{j_2} c_{j_1}}{p!} \right) \\ &= \sum_{\Phi_k^M} w_{\Phi_k^M} {}^p D_{j_1 j_2 \dots j_p}^{i_1 i_2 \dots i_p} (\Phi_k^M) \end{aligned} \quad (7)$$

where the indices  $i, j, \dots$  make reference to an orthonormal set of spin-orbitals basis for the representation of the p-RDM;  $c_i^\dagger$  and  $c_j$  are the standard second quantization creation/annihilation fermion operators, respectively [31],  $\text{Tr}$  indicate the mathematical trace operation or physical sum over states,  $\binom{M}{p}$  is the normalization factor (Coleman's normalization convention) [5] and

$$\begin{aligned} {}^p D_{j_1 j_2 \dots j_p}^{i_1 i_2 \dots i_p} (\Phi_k^M) &= \binom{M}{p} \hat{L}_p^M \{ {}^M D_{\Phi_k^M} \} \\ &= \left\langle \Phi_k^M \left| \frac{c_{i_1}^\dagger c_{i_2}^\dagger \dots c_{i_p}^\dagger c_{j_1} \dots c_{j_2} c_{j_1}}{p!} \right| \Phi_k^M \right\rangle \end{aligned} \quad (8)$$

stands the p-RDM matrix elements corresponding to the  $\Phi_k^M$  pure state [32]. Here we will be mainly concerned with the cases  $p = 1$  and  $p = 2$ , i.e., 1- and 2-RDM respectively. Besides, we will consider the electron density  $\rho$ , which can be obtained from the diagonal elements of the 1-RDM.

The constrained search equation for the energy functionals of 2-RDM for C states (cf. Eqs. (3) and (4)) reads

$$\mathcal{E}_0^M = \min_{{}^M D \rightarrow {}^2 D} E_{2D}^M [{}^2 D] \quad (9)$$

where the search condition  ${}^M D \rightarrow {}^2 D$  points out the fact that the process only admits those 2-RDMs obtained by CM of DMs corresponding to a system of  $M$  particles and the solution is reached for  ${}^2 D_0$ . The  $M$  supraindex is redundant in C states and thus can be omitted because the number of particles is univocally defined from the 2-RDM, throughout the normalization condition  $\text{Tr}({}^2 D) = \frac{M(M-1)}{2}$ . Namely, for closed systems there is no need to mention the number of particles in the 2-RDM energy functional. For this case the functional is completely known and defined by  $E_{2p}[{}^2 D] = \text{Tr}({}^1 D h) + \text{Tr}({}^2 D w)$  [33], where  ${}^1 D$  is obtained by CM of  ${}^2 D$ , i.e.,  ${}^1 D_j^i = \frac{2}{M-1} \sum_k {}^2 D_{jk}^{ik}$ . This is a particular property of RDMs which ensures that for a system with a fixed number of particles any q-RDM can be obtained from a p-RDM by a simple partial contraction, with the only condition that  $p > q$  [5]. Therefore, this case is equivalent to solve the Schrödinger equation. It is worthy to note once again that in this work we are only considering both N-representable 2-RDMs and energy functionals and that the normalization condition is not sufficient to guarantee the N-representability of an arbitrary 2-RDM. However, we have shown that the normalization condition suffices to separate the set of N-representable 2-RDMs into disjoint domains, each of them associated with an unique particle number  $M$  and hence the index  $M$  appearing in some expressions above must not be confused with the M-representability of the involved RDMs and energy functionals and it only points out the number of particles of the system. Consequently, it is redundant and must be understood of such way than that  ${}^M D \rightarrow {}^2 D$  can be simply expressed by  $D \rightarrow {}^2 D$ , namely, that for a given a N-representable  ${}^2 D$ , the number of particles of all the fermionic DMs that can originate it is the same and is determined from the normalization of  ${}^2 D$ .

In a similar manner, for energy functionals of the electron density or  ${}^1 D$ , there is also no need to indicate the number of particles because for both devices, this number is univocally determined by

the conditions  $\int \rho(\mathbf{r}) d\mathbf{r} = N$  or  $\text{Tr}({}^1 D) = N$ , respectively. For  ${}^1 D$  the corresponding energy functionals are expressed by

$$\mathcal{E}_0^M = \min_{{}^1 D} E_{1D} [{}^1 D] \quad (10a)$$

$$E_{1D} [{}^1 D] = F_{1D} [{}^1 D] + \text{Tr}({}^1 D h) \quad (10b)$$

where  $F_{1D} [{}^1 D]$  is the correlation-exchange functional of  ${}^1 D$  [25] and  $\mathcal{E}_0^M = E_{1D} [{}^1 D_0]$  the solution of the search process. Analogously, for the electron density

$$\mathcal{E}_0^M = \min_{D \rightarrow \rho} E_\rho [\rho] \quad (11a)$$

$$E_\rho [\rho] = F_\rho [\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \quad (11b)$$

where  $F_\rho [\rho] = \min_{D \rightarrow \rho} \text{Tr}(D(T + V_{ee}))$  where  $T$  and  $V_{ee}$  stand for the kinetic and electron-electron repulsion energy operators, respectively. Eq. (11a) means that the search is performed over the set of  $\rho$  derived from a  $D$ .

Let us note finally that as we have pointed out early, the particles number constraint must be imposed for each minimization processes in Eqs. (9), (10a) or (11a) to obtain  $\mathcal{E}_0^M$ . Therefore, a more general form for this constraint is

$$\delta \{ E_\Lambda [\Lambda] - \mu N[\Lambda] \} = 0 \quad (12)$$

where  $E_\Lambda [\Lambda]$  stands for the functional of  $\Lambda$ , i.e.,  ${}^2 D$ ,  ${}^1 D$  or  $\rho$  and  $N[\Lambda]$  expresses the number of particles univocally determined by  $\Lambda$ . Consequently, Eq. (12) allow us in principle to extend the domain of definition of the energy functionals to deal with systems of non-integer (or fractional) number of particles as we will explore in the next section.

### 3. Grand-canonical distributions: DMs, RDMs and energy functionals

As introduced before the physical domains within a molecule or molecules interacting with their environment can be considered as quantum open systems and possess fractional number of particles. Then, to study these systems we must extend the notion of canonical  ${}^M D$ s and begin considering grand-canonical  $D$ s. The expression for a grand-canonical  $D$  of a system with  $\mathcal{N} = N + \nu$  particles, with  $N \in \mathbb{N}$  and  $\nu \in \mathbb{R}$  in the interval  $\nu \in (0, 1)$  (with  $\mathbb{R}$  the field of real numbers) is [21,22,34]

$$D = \bigoplus_{\{\Phi_k^M\}} \omega_{\Phi_k^M} {}^M D_{\Phi_k^M}, \quad \sum_{M \geq 0} \omega_{\Phi_k^M} = 1, \quad \omega_{\Phi_k^M} \geq 0 \quad (13)$$

where the carrier space is the complete Fock space  $\mathcal{F} = \bigoplus_{M=0}^{\infty} \mathcal{F}_M$  and  $\bigoplus$  represents the direct sum. Then, p-RDMs for the GC states in molecular systems can be expressed as [20]

$${}^p D = \bigoplus_{\{\Phi_k^M, M \geq p\}} \omega_{\Phi_k^M} {}^p D_{\Phi_k^M} \quad (14)$$

Then, the number of particles of the system is not fixed, and can only be determined as an average  $\mathcal{N} = \sum_{\{\Phi_k^M, M \geq 0\}} \omega_{\Phi_k^M} M$  [20,24].

As mentioned above, a  ${}^q D$  cannot be obtained by CM of any  ${}^p D$  for  $q < p$  without information loss within the GC framework unless the energy were a convex function of the number of particles [20]. In this work, we will not restrict ourselves to the convexity assumption in order to validate the results to incorporate the description of molecular systems of interacting reagents, species imbedded in some environment or atoms and functional groups in a molecule [3]. The number of particles in this distribution  $\mathcal{N}$  and related to the density by  $\int \rho(\mathbf{r}) d\mathbf{r} = \mathcal{N}$  permits to consider the constrain Eq. (12) given a  $\rho$  or  ${}^1 D$  and univocally determine the number of particles of the system. Therefore this implies, similarly

to MC and C distributions, that the GC energy functionals of  $\rho$  or  ${}^1D$  do not depend on the number of particles of the system and then we can define functionals in an analogous form as those in Eqs. (10) and (11). Nevertheless, notably differences between the closed and open systems arise when considering the description based on the  ${}^2D$ . Unlike in C distributions where the energy depends on both,  ${}^1D$  and  ${}^2D$  which are connected via CM, this is not longer valid for GC distributions because  ${}^1D$  can not be obtained from  ${}^2D$  via a CM [20] and consequently a similar equation as Eq. (9) is no longer valid for the GC one.

This distinction rests on the dependence of  ${}^2D$  energy functional with  $N$ . Hence, as it has been stated above, the main point is to respond the question if it is possible to univocally determine the number of particles from a GC  ${}^2D$ . The number of particles of a molecular open system,  $\mathcal{N}$  is determined by the coefficients  $\{\omega_{\Phi_k^M}, M, k = 0, 1, \dots, \infty\}$ . Therefore, it may be argued that for determining the number of particles of the system it is not necessary to know all the coefficients, i.e., indeed, if we do not know the coefficient  $\omega_{\Phi_0^0}$  we can calculate the number of particles noting that

$$\mathcal{N} = \sum_{M=0}^{\infty} \sum_{\{\Phi_k^M\}} \omega_{\Phi_k^M} M = 0 \omega_{\Phi_0^0} + \sum_{M=1}^{\infty} \sum_{\{\Phi_k^M\}} \omega_{\Phi_k^M} M \quad (15)$$

then, the coefficients needed are only  $\{\omega_{\Phi_k^M}, M, k = 1, \dots, \infty\}$ . Besides, if coefficient  $\omega_{\Phi_0^0}$  is unknown and  $\omega_{\Phi_0^1}$  is known, the former can be calculated from the normalization condition  $\sum_{M=0}^{\infty} \sum_{\{\Phi_k^M\}} \omega_{\Phi_k^M} = 1$ . The problem arises when contracting a DM GC state to obtain the corresponding  ${}^2D$  and consequently the information from  $\omega_{\Phi_0^0}$  and  $\omega_{\Phi_0^1}$  coefficients is lost. Then, it is not possible to univocally determine the number of particles of a GC system like distribution from  ${}^2D$ . Let us clarify this point by means of a simple example. Let two GC DMs be

$$D_a = \omega_{\Phi_0^0}^a |\Phi^0\rangle\langle\Phi^0| + \omega_{\Phi_0^1}^a |\Phi^1\rangle\langle\Phi^1| + \sum_{\{\Phi^M\}, M>1} \omega_{\Phi^M} |\Phi^M\rangle\langle\Phi^M| \quad (16a)$$

$$D_b = \omega_{\Phi_0^0}^b |\Phi^0\rangle\langle\Phi^0| + \omega_{\Phi_0^1}^b |\Phi^1\rangle\langle\Phi^1| + \sum_{\{\Phi^M\}, M>1} \omega_{\Phi^M} |\Phi^M\rangle\langle\Phi^M| \quad (16b)$$

such that  $\omega_{\Phi_0^0}^a \neq \omega_{\Phi_0^0}^b$  and  $\omega_{\Phi_0^1}^a \neq \omega_{\Phi_0^1}^b$ . It is evident that

$$\hat{L}_2\{D_a\} = \hat{L}_2\{D_b\} \equiv {}^2D \quad (17)$$

where  ${}^pD = \hat{L}_p\{D\} = \bigoplus_{\{\Phi_k^M, M \geq p\}} \omega_{\Phi_k^M} \binom{M}{p} \hat{L}_p^M\{D_{\Phi_k^M}\}$  and it was assumed that  $\hat{L}_p^M\{D_{\Phi_k^M}\} = \mathbf{O}$  for  $M < p$ , and  $\hat{L}_p^p\{D_{\Phi_k^p}\} = \mathcal{I}$  with  $\mathcal{I}$  and  $\mathbf{O}$ , the identity and null superoperators, respectively [20]. Therefore, it holds

$$\mathcal{N}_a - \mathcal{N}_b = \omega_{\Phi_0^1}^a - \omega_{\Phi_0^1}^b \neq 0 \quad (18)$$

where  $\mathcal{N}_a$  and  $\mathcal{N}_b$  represent the number of particles from  $D_a$  and  $D_b$ , respectively. It means that two GC  $D$  corresponding to systems with different number of particles can originate the same  ${}^2D$ . Therefore, it is not possible to determine  $\mathcal{N}$  for a molecular open system from the associated  ${}^2D$  and consequently it implies that the energy functional for a GC  ${}^2D$  depends on  $\mathcal{N}$ . Finally, let us argue about these results from another point of view. As pointed out above,  ${}^2D$  can be obtained from different DMs, giving rise to  $\mathcal{N}_a$  and  $\mathcal{N}_b$  particles, respectively. Suppose  $D_a$  is chosen as a trial when determining the ground state energy for the GC state of systems with  $\mathcal{N}_a$  particles. Hence, to determine the value of the energy functional for  ${}^2D$  from the minimum of the expression  $\text{Tr}(D\mathcal{H})$ , we must consider  $D_a$  and not  $D_b$ . Conversely, for systems with  $\mathcal{N}_b$  particles,  $D_b$  must be considered and not  $D_a$ . Nevertheless, despite in both cases we can use the same  ${}^2D$ , the energy functionals will be different. Namely, the searching space in both situations for the minimum of the expression  $\text{Tr}(D\mathcal{H})$  is defined over different domains and

then, the corresponding energy functionals will be necessarily different

$$E_{2D}^{\mathcal{N}_a}[{}^2D] \neq E_{2D}^{\mathcal{N}_b}[{}^2D] \quad (19)$$

This result has important consequences. It forbids us to formulate the GC case of Eq. (9) in terms of the constraint given by Eq. (12). On one side, the energy functional unlike that of the C case cannot be extended to arbitrary numbers of electrons due to the non-universality of the energy functional of  ${}^2D$  with respect to the number of particles, i.e., there are different energy functionals for different particle number; on the other side, there is no expression for  $\mathcal{N}[{}^2D]$  since it is not possible to univocally determine the number of particles of the DMs that originate a given  ${}^2D$ .

#### 4. Concluding remarks

Energy functionals for molecular quantum open systems have been analyzed in comparison with closed ones within the formulation of density matrices. As we are mainly concerned with 2-particle Hamiltonians, attention was focused on  $\rho$ ,  ${}^1D$  and  ${}^2D$  energy functionals. The corresponding CM for canonical and grand-canonical states of the systems were reviewed with emphasis in the loss of information present in the grand-canonical case. This feature, which is absent in closed systems, is of paramount importance for understanding the energy functionals of  $\rho$ ,  ${}^1D$  and  ${}^2D$ . Nonetheless, open systems for which the ground state energy is a convex function of the number of electrons are closely related to their canonical counterparts. The main differences between these systems, besides of the number of particles, arise when the convexity of the energy is not valid. Although the canonical and grand-canonical descriptions in terms of  $\rho$  and  ${}^1D$  are very similar, the formulation for  ${}^2D$  highly differs. The reason is that while the number of particles of a grand-canonical systems can be univocally determined from  $\rho$  and  ${}^1D$ , this is not the case for the  ${}^2D$  and consequently the energy functional for  ${}^2D$  within the GC distributions depends on the number of particles of the system, unlike its canonical analog. Thus, it is not possible to formulate the variational principle for the ground state energy in terms of the  ${}^2D$  for GC distributions using particle number constraints. Energy convexity are not expected to follow for interacting molecules as reagents in a chemical reaction or for species imbedded in solvents because of the different nature of intermolecular forces, thus to study the properties of grand-canonical distributions without recurring to the convexity assumption will help to understand these phenomena and are among our interests.

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