Grand-canonical-ensemble representability problem for the one-electron reduced density matrix

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We deal with many-electron systems having a noninteger number of electrons, which cannot be described properly by means of pure states or by canonical statistical ensemble states. The study of the one-electron reduced density matrix for these systems raises the problem of its representability in statistical ensembles of grand canonical type. We derive the necessary and sufficient conditions for the representability of the one-electron reduced density matrix of grand-canonical statistical ensembles.

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I. INTRODUCTION

The reduced density matrices (RDM's) [1–12] arise from an *average* over a subset of the variables of the N-electron density matrix (DM) corresponding to an N-electron system state, which is known as contraction mapping [9,13–15]. For all practical purposes, this average over $(N-p)$-electron variables, which leads to the p-RDM, does not imply any loss of the useful information. This is due to the fact that DM contains redundant information to compute the expectation values for p-electron observables and the $(N-p)$ variables averaged in the contraction mapping can be ignored [3,4,9]. Therefore, the RDM's may be regarded as statistical objects much simpler than the DM, depending on a lower number of variables.

The N-representability conditions are the constraints that a given pth-order density matrix must fulfill to be derivable from a DM corresponding to an N-electron system state [13–16]. These conditions have been completely established for the 1-RDM in systems with fixed integer number of electrons—i.e., systems described by means of pure states or canonical statistical ensembles. However, open systems in quantum chemistry, molecular physics, solid-state physics, embedding theories, etc., share the feature of possessing a noninteger (or variable) number of electrons [8,17–31]. Likewise, domains related to fragments within molecular systems such as Daudel's loges, "fuzzy" atoms, Bader's basins, etc., lead to a fractional electron number [32–35]. Therefore, such systems may not be described either by means of pure states or by canonical ensemble states. Thus, the necessity for such a description leads us to consider p-RDM's, and particularly the 1-RDM, within the scenario of *grand-canonical ensembles*. The aim of this paper is to establish the necessary and sufficient conditions for the representability of 1-RDM in this kind of ensembles, in order to provide a rigorous support to the interpretation of results in dealing with systems with a noninteger number of electrons.

The article is organized as follows. Section II reports the main features of the RDM's related to the representability problem. Section III deals with the mathematical derivation of the representability conditions for the 1-RDM in grand-canonical ensembles. Finally, Sec. IV summarizes the concluding remarks.

II. REDUCED DENSITY MATRICES: A BRIEF REVIEW

The most general description of a mixed quantum state of an N-electron system is given by the DM [2,3,36]. This matrix, which will be denoted as ${}^{N}D$, is defined as the weighted sum of the complete set of all accessible pure quantum states of the system, whose physical meaning is the statistical distribution of the states in the mixture given by

$$ {}^{N}D = \sum_{\mathcal{L}_N} w_{\mathcal{L}_N} |\mathcal{L}_N\rangle\langle\mathcal{L}_N|, \tag{1}$$

where $|\mathcal{L}_N\rangle$ stand for N-electron quantum state functions in the antisymmetric N-electron Hilbert space and $w_{\mathcal{L}_N}$ are the statistical weights or probability of occurrence of $|\mathcal{L}_N\rangle$ in the mixture. It is obvious that a single or pure state is represented as a particular case in which all weights vanish except only one:

$$ {}^{N}D = |\mathcal{L}_N\rangle\langle\mathcal{L}_N|. \tag{2}$$

The trace operation (full real-space integration) of ${}^{N}D$ is normalized to unity, so that $\mathrm{tr}({}^{N}D)=\Sigma_{\mathcal{L}_N} w_{\mathcal{L}_N}=1$. The matrix ${}^{N}D$ is Hermitian (self-adjoint), positive semidefinite (all its eigenvalues are non-negative), and bounded (the module of its elements has an upper bound).

The application of the contraction mapping to the DM leads to a general definition of the p-RDM's, which in the occupation number representation is given by

$$ {}^{p}D^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p} = \mathrm{tr}\left({}^{N}D \frac{c^{\dagger}_{i_1} c^{\dagger}_{i_2} \cdots c^{\dagger}_{i_p} c_{j_p} \cdots c_{j_2} c_{j_1}}{p!} \right) $$

$$ = \sum_{\mathcal{L}_N} w_{\mathcal{L}_N} {}^{p}D^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p}(\mathcal{L}_N), \tag{3}$$

where

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$$ {}^{p}D^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p}(\mathcal{L}_N) = \left\langle \mathcal{L}_N \left| \frac{c^{\dagger}_{i_1} c^{\dagger}_{i_2} \cdots c^{\dagger}_{i_p} c_{j_p} \cdots c_{j_2} c_{j_1}}{p!} \right| \mathcal{L}_N \right\rangle \tag{4} $$

stand for p-RDM's corresponding to all accessible pure quantum states of the system. The indices $i,j,\ldots$ denote a set of orthonormal one-electron functions (spin-orbitals), and $c^{\dagger}_i$ and c_j are the standard creation and annihilation fermion operators, respectively. The average process expressed throughout the trace symbol is performed over the remaining $(N-p)$ variables and hence for $p=1$ stands for the one-electron reduced density matrix, for $p=2$ the two-electron or pair reduced density matrix, and so forth. The p-RDM's are Hermitian, positive semidefinite, and bounded [4,13]. The normalization condition for these distributions is given by the binomial number of N electrons forming p-electron groups or p-ons, $\binom{N}{p}$.

The N-representability [13–16] plays a role of paramount importance in the performance of the p-RDM's. This feature ensures that a given pth-order density matrix derives from a pure state or from a canonical ensemble state of a fermion system with a fixed integer number of electrons, N, by contraction, as defined by Eq. (3). Hence, the fulfillment of the N-representability conditions may be established as a criterion to recognize whether a positive Hermitian matrix on the Hilbert space of p-electron functions admits a representation in the form of Eq. (3) or does not. Although the determination of the N-representability conditions remains open for two- and high-order RDM's, it has been solved completely in practice only for the 1-RDM [37]. Let us recall the N-representability conditions for this case reported by Coleman [13], in order to introduce our notation and the method that we will follow for working in the grand canonical ensemble.

Given a trial 1-RDM, its necessary and sufficient N-representability conditions are that its eigenvalues, one-electron occupation numbers $\{n_i\}$, must be bounded as

$$ 0 \leq n_i \leq 1, \quad i = 1, \ldots, r, \tag{5} $$

and must fulfill the conservation of the number of electrons throughout the trace operation as

$$ \sum_{i=1}^{r} n_i = N, \quad N \in \mathbb{N}, \tag{6} $$

where r stands for the dimension of the one-electron Hilbert space and $\mathbb{N}$ means the set of positive integer numbers.

While the necessity of these conditions arises from the properties of fermion operators, their sufficiency can be proved [13] taking into account that the set of DM's is convex and so is the set of allowable 1-RDM's. Hence, let us consider a bounded compact convex set $\mathbb{K}$ of the real field of dimension r, $\mathbf{R}^r$. An element x in $\mathbb{K}$ is said to be an *extreme element* of $\mathbb{K}$ if there are no two distinct elements x_1 and x_2 in $\mathbb{K}$ such that $x=\alpha x_1+(1-\alpha)x_2$ for some α, $0<\alpha<1$. According to the theory of convex sets any element $x \in \mathbb{K}$ may be written as a linear convex combination $x=\Sigma_i \alpha_i x_i$ where $\{x_i\}$ stands for the set of extreme elements of $\mathbb{K}$ and $\{\alpha_i \geq 0$ with $\Sigma_i \alpha_i = 1\}$ are the coefficients of the expansion. Therefore, to characterize the convex set of 1-RDM's we need to obtain its extreme elements. This task is successfully performed using the following theorems [38].

Theorem 1. Let $Ax \leq b$ be a linear system of inequalities and their solutions $\mathbb{K}=\{x \in \mathbf{R}^r / Ax \leq b\}$. If $\mathbb{K}$ is bounded, it holds that (i) $\mathbb{K}$ is a compact convex set, (ii) the number of extreme elements of this set is *finite*, and (iii) the extreme elements in $\mathbb{K}$ are those that at least verify r equalities associated to the linear system. It must be noted that the general case in which a part of the linear system is expressed by $Ax \geq b$ is easily solved by only transforming $A \rightarrow -A$.

Theorem 2. Regarding identical hypotheses than in theorem 1, the extreme elements may be determined by the following procedure: (i) Choose r inequalities from the linear system $Ax \leq b$. (ii) Replace the inequalities of i by equalities. (iii) If the linear system of r equalities defined in (ii) has a *unique* solution satisfying all the original inequalities, it defines an *extreme* element in $\mathbb{K}$. (iv) If the system defined in (ii) has not a *unique* solution, its solutions are discarded. (v) As there are, in general, more than r conditions defining the system, it is necessary to consider all possible sets of r inequalities and to repeat the above steps.

The above described procedure allows us to find all extreme elements of the convex set of 1-RDM's defined by Eqs. (5) and (6) and therefore to characterize any element in the convex set as a linear convex expansion of these extreme elements. Thus, let x be a vector whose components are the sequence of one- electron spin-function natural occupation numbers $\{n_i,\ i=1,\ldots,r\}$. The first step is to consider r equalities with $n_i=0$ or $n_i=1$. By virtue of theorem 2 the solutions of the linear system must also fulfill the trace relation that fix the sum of the components $\{n_i\}$ to the total number of electrons (trace constraint). Thus, the feasible solutions—i.e., extreme points—are vectors composed of N components equal to 1 and the remaining $r-N$ ones equal to zero. The other family of solutions arises from choosing $r-1$ equalities with $n_i=0$ or $n_i=1$ for all indices i except one which is determined by the trace constraint. However, this family of solutions turns out to be identical to the previous one. Hence, the complete set of extreme points is composed of vectors having N components equal to 1 and the remaining $r-N$ ones equal to zero. From now on we will call these extreme points as *binary states* or *binary points* of level N. Therefore, as the components of these vectors are one-electron states (or spin-orbital) occupation numbers, it follows that they stand for 1-RDM's arising from N-electron state functions of Slater type (Slater determinants) [13]. Hence, any other 1-RDM fulfilling Eqs. (5) and (6) may be written as a linear convex combination of these extreme 1-RDM's and consequently admits a representation in the form of Eq. (3). These results stand for the necessary and sufficient conditions for a 1-RDM to be N-representable. This set of N-representability conditions has been widely analyzed and discussed by several authors from different points of view [3,13–16,39–46].

III. REDUCED DENSITY MATRICES FOR GRAND-CANONICAL ENSEMBLES

In the previous section we have introduced RDM's in Hilbert spaces with a fixed integer number of electrons. How-

ever, a noninteger number of electrons appears in several systems which have been reported in the literature [17] which cannot be interpreted within the above-mentioned ensembles. Therefore, the description of these systems must be performed within the *grand-canonical ensemble* formulation that admits such situations. For such a goal we may use DM's within this ensemble in which the number of electrons is not fixed. These matrices are expressed by

$$D = \sum_{M\geq 0} \sum_{\mathcal{L}_M} w_{\mathcal{L}_M} |\mathcal{L}_M\rangle\langle\mathcal{L}_M|, \tag{7}$$

where $|\mathcal{L}_M\rangle$ and $w_{\mathcal{L}_M}$ stand for M-electron state functions and their corresponding statistical weights or probability of occurrence in the statistical mixture, respectively. The trace operation (full real-space integration) of D remains normalized, and thus $\Sigma_{M\geq 0}\Sigma_{\mathcal{L}_M} w_{\mathcal{L}_M}=1$. The mathematical properties of D are identical to those mentioned for the canonical ensemble.

The contraction mapping of Eq. (3) in the grand-canonical ensemble has contributions arising from each of the M-electron Hilbert subspaces and, in a formal way, the p-RDM's may be written as

$${}^pD^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p} = \sum_{M\geq 0} \sum_{\mathcal{L}_M} w_{\mathcal{L}_M} {}^pD^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p}(\mathcal{L}_M) \tag{8}$$

where ${}^pD^{i_1,i_2,\ldots,i_p}_{j_1,j_2,\ldots,j_p}(\mathcal{L}_M)$ stands for p-RDM's corresponding to quantum-state functions $|\mathcal{L}_M\rangle$ in the M-electron subspace. Note that subspaces with $M<p$ do not contribute to that sum.

One of the central hypotheses when solving the N-representability problem for canonical ensembles is that the number of electrons is fixed and integer. However, in the grand-canonical case this is not a consistent hypothesis. Hence, hereafter we will use the term *representability* instead of N-representability in dealing with grand-canonical ensembles. The set of necessary and sufficient representability conditions should be determined anew. Thus, since the fermion properties are still valid, the necessary conditions for the representability of the 1-RDM in this scenario are given by

$$0 \leq n_i \leq 1, \quad i = 1, \ldots, r,$$

$$\sum_{i=1}^{r} n_i = N + \eta, \quad N \in \mathbb{N}_0, \quad \eta \in \mathbb{R}, \quad 0 < \eta < 1, \tag{9}$$

where $\mathbb{N}_0$ and $\mathbb{R}$ mean the set of non-negative integer numbers and the set of real numbers, respectively. The last equation indicates that the trace of the matrix is now a noninteger number. The set of conditions expressed by Eq. (9) stands for the generalization of the canonical ensemble representability conditions (where $\eta=0$ or $\eta=1$) as has been solved in Ref. [13] and reviewed in the previous section. Its sufficiency can be proved following a similar procedure to that used in the canonical ensemble case, taking into account that the set of grand-canonical 1-RDM's defined by Eq. (9) also presents a convex structure. Hence, we state the following theorem.

Theorem 3. A vector $(n_1, n_2, \ldots, n_r)$ such that its components are bounded as $\{0\leq n_i\leq 1,\ i=1,\ldots,r\}$ and fulfill the constraint $\Sigma_{i=1}^{r} n_i = N+\eta$, with $0<\eta<1$, may be written as a linear convex combination of binary points of levels N and $N+1$.

Proof. Let us apply the algorithm given by theorem 2. The first step is to consider only the conditions leading to identical solutions to that of the canonical ensemble case: that is, $\{n_i=0$ or $n_i=1, i=1,\ldots,r\}$—i.e., binary points. However, these solutions are not compatible with the constraint. Hence, the other family of solutions arises from choosing $r-1$ equalities with $n_i=0$ or $n_i=1$ for all indices i except one which will be determined by the constraint. Let j be this distinct index, and let us write the constraint as

$$n_j + \sum_{i\neq j}^{r} n_i = N + \eta \tag{10}$$

or, equivalently,

$$n_j - \eta = N - \sum_{i\neq j}^{r} n_i. \tag{11}$$

The numerical value of the left-hand side of this equation lies in $-1<(n_j-\eta)<1$ while the value of its right-hand side is an integer number. Therefore, the only feasible solution for this equation is that both members are zero. Hence, $n_j=\eta$ and the remaining components of the vector must be equal to 0 and 1, summing N. Thus, the vector structure of the extreme points is given by $(1,\ldots,1,\eta,0,\ldots,0)$ or any other arbitrary permutation of the occupation numbers. We will call these elements, or extreme points, *η-binary* points. Hence, by virtue of the convex set definition and theorems 1 and 2, any arbitrary vector of the type defined within the hypothesis of theorem 3 may be written as a linear combination of these extreme *η-binary* points. The second step to complete the proof of this theorem is to show that these *η*-binary points may also be expressed as a linear convex combination of *binary* points. For this goal, let us choose a point v_η of this *η*-binary point set such that $n_j=\eta$ and any other $n_{i\neq j}$ is 0 or 1. Let us define v_0 as the point with $n_j=0$, while the others $n_{i\neq j}$ remain identical to those of v_η; then, v_0 is a binary point of level N—i.e., the sum of its components is N. In the same way, we define a point v_1 that only differs from v_η in that its jth component is $n_j=1$, so that this is a $(N+1)$-level binary point. Then we may write that

$$v_\eta = \eta v_1 + (1-\eta) v_0, \tag{12}$$

which is also a linear convex combination of two binary points v_1 and v_0. Consequently, we may conclude that any vector under the hypothesis of theorem 3 may be written as linear convex combinations of *η-binary* points. Moreover, each of these *η*-binary points may be written by means of a linear convex combination of *binary* points of levels N and $N+1$, which proves the theorem.

According to theorem 3, any first-order density matrix fulfilling Eq. (9) may be written by means of linear convex combinations of *binary* points of levels N and $N+1$. As each of these binary points stands for a 1-RDM arising from Slater-type N- and $(N+1)$-electron-state functions, it follows that this matrix admits a representation in the form of Eq.

(8). This result allows us to enunciate that *the necessary and sufficient representability conditions for a given 1-RDM to be representable within the grand-canonical ensemble are that its eigenvalues must be bounded between 0 and 1*—i.e., $\{0 \leq n_i \leq 1, i=1,\ldots,r\}$, r being the dimension of the one-electron Hilbert space.

The mathematical proof we have given above states that any 1-RDM with noninteger number of electrons, $N+\eta$, ${}^1D^{(N+\eta)}$, may be written as a convex combination of only two canonical-ensemble-state binary points of levels N and $N+1$. Thus, it is worthwhile to interpret this result within the statistical framework because of the nature of the 1-RDM. For such a goal we may recall that

$$ {}^1D^{(N+\eta)} = \sum_{M\geq 0} c_M {}^1D^{(M)}, \tag{13}$$

where c_M and ${}^1D^{(M)}$ stand for the convex coefficients and for the canonical ensemble 1-RDM's corresponding to mixtures of Slater determinant 1-RDM's (extreme elements) with trace equal to M, respectively. Equation (13) represents the fact that neither pure states nor canonical ensemble states are able to describe a 1-RDM with a noninteger number of electrons. The calculation of the trace of expression (13) leads to

$$ N+\eta = \sum_{M\geq 0} c_M \mathrm{tr}({}^1D^{(M)}) = \sum_{M\geq 0} c_M M, \tag{14}$$

which, regarding the meaning of the coefficients, shows that the noninteger number of electrons *is an average of the number of electrons* of the systems involved in the expansion. Furthermore, because of Eqs. (12) and (14), expression (13) may be written as

$$ {}^1D^{(N+\eta)} = c_{N+1} {}^1D^{(N+1)} + c_N {}^1D^{(N)}, \tag{15}$$

which after an elementary algebra leads to $c_{N+1}=\eta$ and $c_N=1-\eta$, in complete agreement with theorem 3. This result establishes a rigorous justification of using Eq. (15) as an ansatz to built up accurate functionals within the framework of density matrix and density functional theories previously reported by several authors [20,25,27,29].

It is worthwhile to note that expression (15) is not the only expansion that fulfills the necessary and sufficient conditions derived in this section. Other expansions containing canonical ensembles with a number of particles other than N and $N+1$ are also compatible with these conditions. However, theorem 3, which used to come to the expansion (15), does not assure the coefficients of such other expansions different from Eq. (15) are nonzero.

IV. CONCLUDING REMARKS

In this work we have dealt with systems possessing a noninteger number of electrons which need be described within the grand-canonical-ensemble formulation. Our treatment has set out the representability problem for reduced density matrices corresponding to this kind of systems. We have characterized the necessary and sufficient conditions that a first-order density matrix must fulfill to ascertain that it derives from a grand-canonical-ensemble state. An important achievement arising from our work is that a 1-RDM corresponding to an electronic system with *noninteger* number of electrons may be described by means of *only two* statistical ensemble states of N and $N+1$ electrons.

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