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Communication: Reduced density matrices in molecular systems: Grand-canonical electron states

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Grand-canonical like descriptions of many electron atomic and molecular open systems which are characterized by a non-integer number of electrons are presented. Their associated reduced density matrices (RDMs) are obtained by introducing the contracting mapping for this type of distributions. It is shown that there is loss of information when connecting RDMs of different order by partial contractions. The energy convexity property of these systems simplifies the description. Consequently, this formulation opens the possibility to a new look for chemical descriptors such as chemical potential and reactivity among others. Examples are presented to discuss the theoretical aspects of this work. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4832495]

The rearrangement of electron distributions in molecular systems under the influence of external perturbations, internal conversions, conformational changes, or reactive interactions is closely related to chemical reactivity which is relevant to understand the molecular structure.1–3 The chemical reactions is closely related to chemical reactivity which is relevant to understand the molecular structure. The fundamental chemical concepts are the summary of the more general GC distribution. The density matrix describing the state of a system stands for a weighted sum of the complete set of all accessible electron molecular system which are characterized by a non-integer number of electrons are presented. Their associated reduced density matrices (RDMs) are obtained by introducing the contracting mapping for this type of distributions. It is shown that there is loss of information when connecting RDMs of different order by partial contractions. The energy convexity property of these systems simplifies the description. Consequently, this formulation opens the possibility to a new look for chemical descriptors such as chemical potential and reactivity among others. Examples are presented to discuss the theoretical aspects of this work. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4832495]

The density matrix \( D \) describing the state of a system stands for a weighted sum of the complete set of all accessible \( M \)-electron pure state density matrices \( M \mathcal{D}_p \mathcal{M} = |\Phi_k^M \rangle \langle \Phi_k^M | \) in the mixture, where \( |\Phi_k^M \rangle \) is the \( k \)th quantum state function in the antisymmetric \( M \)-electron Hilbert space \( \mathcal{F}_M \), being its carrier space the entire Fock space \( \mathcal{F} = \bigoplus_{M=0}^{\infty} \mathcal{F}_M \), where the \( \bigoplus \) symbol indicates direct sum. Therefore, \( D \) is expressed by

\[
D = \sum_M \sum_{\phi_p^M} \omega_{\phi_p^M} |\Phi_k^M \rangle \langle \Phi_k^M |
\]

(1)

where \( \omega_{\phi_p^M} \) stands for the statistical weight, i.e., probability of occurrence of the pure \( |\Phi_k^M \rangle \) state in the mixture. These states admit particle number fluctuation and hence the system may possess a non-integer number of particles. We will refer to it as the GC distribution. \( D \) is a Hermitian, positive semi-definite (its eigenvalues are null or non-negative), bounded (the module of its elements is bounded), and finite trace (full real space integration) matrix, and because of its probabilistic interpretation it may be normalized to unity, i.e.,

\[
tr(D) = \sum_M \sum_{\phi_p^M} w_{\phi_p^M} = 1
\]

Canonical distribution (C) (all states in the mixture possess the same number of particles \( N \)), expressed by

\[
N D = \sum_{\phi_p^N} \omega_{\phi_p^N} |\Phi_k^N \rangle \langle \Phi_k^N |
\]

and the microcanonical (MC) distribution (all weights vanish except one), i.e., pure states \( N D_{\phi_p^N} = |\Phi_k^N \rangle \langle \Phi_k^N | \) are particular cases of the more general GC distribution.

The fundamental chemical concepts are the summary of the physical information contained in the \( p \)-RDMs of an \( N \)-electron molecular system (\( p < N \)) which are derived from

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the DM and represent marginal distributions.\textsuperscript{8} Most of the attempts to describe the electron distribution in molecular systems have been concentrated on the 1-RDM ($D^1$) and 2-RDM ($D^2$), which determine electron densities and the energy of the system and provide intuitive interpretations of chemical data.\textsuperscript{1,3,12-14} Let us first sketch the contracting mapping (CM) for C and MC distributions as the basis to introduce this operation for the GC case. The CM, $\hat{L}_p$, applied to $^N D$\textsuperscript{8,9} gives rise to the $p$-RDM, i.e., $^p D$, for both canonical and pure states. It stands for an averaging process over the remaining $N-p$ variables\textsuperscript{15} defined by

$$ p D_{j_1j_2...j_p} = \frac{\langle N \rangle}{p} \hat{L}_p [^N D] $$

$$ = \sum_{\Phi_k^p} \omega_{\Phi_k^p} p D_{j_1j_2...j_p} (\Phi_k^p) $$

where $p D_{j_1j_2...j_p}$ represents the $p$-RDM corresponding to the $|\Phi_k^N \rangle$ accessible pure state of the system and from $p$ the combinatorial number for the Coleman normalization to the number of $p$-ons, i.e., number of composite p-fermion particles,\textsuperscript{8} i.e., $p = 1, 2, ...$ stand for the one-electron reduced density matrix \(1D\), the two-electron reduced density matrix \(2D\), and so forth. The indices $i, j, ...$ denote a set of orthonormal one-electron functions (spin-orbitals) which represent the basis set. The $p$-RDMs are hermitian, positive semi-definite, and bounded.\textsuperscript{6-8} Other essential property is its representability defined as the constraints that a given $p$-RDM must fulfill to be derivable from a DM corresponding to GC, C, or MC system state (cf. Eq. (1)).\textsuperscript{8,9}

Let us remark that consequently for C and MC distributions in which the number of particles is fixed for all states in the distribution $^q D$ and $^q D (q < p)$ are connected by a contraction operation.\textsuperscript{8,9}

The physical domains within the molecular structure mentioned above possessing a non-integer number of particles $N = N + v$ with $N \in \mathbb{N}$ and $v \in \mathbb{R}$ in the interval $v \in (0, 1)$ (\(N \in \mathbb{N}\) and \(v \in \mathbb{R}\) fields of positive integer and real numbers, respectively) cannot be described either by a C or by a MC. Therefore, the appropriate scenario for that goal is the GC states (Eq. (1)), where the number of particles $M (M \in \mathbb{N})$ is not fixed\textsuperscript{1,5} and then $N$ may be considered as an average.\textsuperscript{2} This distribution is expressed by the DM in Fock space,\textsuperscript{5,11} $D \in \mathcal{F}$ defined as $D = \bigoplus_{\Phi_k^p} \omega_{\Phi_k^p} M_{\Phi_k^p}$, where $M_{\Phi_k^p} \in \mathcal{F}_M$, $\omega_{\Phi_k^p} \geq 0$, and $\sum_{\Phi_k^p} \omega_{\Phi_k^p} = 1$. The introduction of the CM for GC states to obtain the $p$-RDMs is performed by the application of the CM to $D$ given by Eq. (1) on the Fock space, hence it involves several states $|\Phi_k^M \rangle (|\Phi_k^M \rangle)$, whose number of particles fulfill the condition that $M \geq p$, i.e., the order of contraction $p$ must be less than or equal to $M$. Thus, several states in the mixture may contribute to a $p$-RDM derived from a GC $D$, and all other states, whose $M < p$, will not contribute to this distribution. Namely, the states with $M < p$ do not contribute because they are not able to support $p$-distributions due to the number of particles they contain are less than the required to form the composed $p$-particles in the distribution, for instance, no pairs ($p = 2$) may be formed from one particle systems, or 3-ons from two-particle systems, and so on. Therefore, the $p$-RDMs for this ensemble may be defined by introducing the GC CM $\hat{L}_p$ by

$$ p D = \hat{L}_p [D] = \bigoplus_{\Phi_k^p} \omega_{\Phi_k^p} (M) \hat{L}_p [^M D_{\Phi_k^p}] $$

where it was assumed that $\hat{L}_p [^M D_{\Phi_k^p}] = \mathbf{I}$ for $M < p$, and $\hat{L}_p [^p D_{\Phi_k^p}] = \mathbf{I}$ with $I$ and $\mathbf{O}$, the identity and null superoperators, respectively.\textsuperscript{16} These requirements complete the definition for the CM in Fock space. Therefore, the $p$-RDM is expressed by

$$ p D = \bigoplus_{\Phi_k^p} \omega_{\Phi_k^p} p D_{\Phi_k^p} $$

The trace operation is calculated by $\text{Tr}(p D) = \sum_{\Phi_k^p} \omega_{\Phi_k^p} (M) = \langle M \rangle_p$, where $\langle ... \rangle$ indicates the average number of $p$-ons. For instance, for $p = 1$, $\text{Tr}(1 D) = \sum_{\Phi_k^p} \omega_{\Phi_k^p} M = \langle M \rangle = N + v$, as stated above.

Some consequences arising from the reduced distributions in the GC framework are particularly interesting. In contrast with the C and MC states, in the GC distribution it is not possible to obtain $^q D$ by contraction of a previously obtained $^p D$ for $q < p$\textsuperscript{8} without losing some information, hence such contraction may be performed only directly from $D$. It may be noted by expressing $^q D$ as

$$ q D = \bigoplus_{\Phi_k^p, M \{q,p\}} \omega_{\Phi_k^p} ^q D_{\Phi_k^p} + \bigoplus_{\Phi_k^p, M \{q,p\}} \omega_{\Phi_k^p} ^q D_{\Phi_k^p} $$

where the expression for $^q D$ has been split into two contributions. The first term in Eq. (5) means that the number of particles of the $|\Phi_k^N \rangle$ states belong to the half-open interval $q \leq M < p$, i.e., $M \{q,p\}$, and the second term, the contributions from those states with $M \geq p$. This process represents symbolically the direct contraction operation $D \rightarrow ^q D$. Let us consider a contraction process performed in two steps with this previous one for comparison, i.e., to obtain $^p D$ from $D$ and then to obtain $^q D$ by $^p D$ contraction, in symbols, $D \rightarrow ^p D \rightarrow ^q D$. It is clear that the difference between both contraction procedures to obtain $^q D$ is described by the first term in Eq. (5). It is due to the fact that this term would not be present in $^p D$ after contraction. Hence, it shows that the lost information distribution $I_{q\rho}$, in performing the two step process, is $I_{p \rho} = \bigoplus_{\Phi_k^p, M \{q,p\}} \omega_{\Phi_k^p} ^p D_{\Phi_k^p}$ which indicates that the right marginal distributions within the GC distribution must be obtained applying the CM on $D$ matrix in a one step process. Nevertheless, for an interacting electron atomic or open molecular system driven by a 2-particle Coulombic potential with Hamiltonian, $\mathcal{H} = \sum_{i,j} h_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{i,k,l} (ij[k]c_i^\dagger c_j c_k^\dagger c_l)$ with $\beta_i$ and $c_j$ the standard creation/annihilation fermion operators, respectively, $h_{ij}$ the matrix elements of the mono-electronic terms $h$, and $(ij[k])$ those of the Coulomb bi-electronic terms of the Hamiltonian,\textsuperscript{17} the GC ground state DM possesses a convex structure\textsuperscript{10} expressed by

$$ D = (1-v) ND_0 + v N^+ D_0 $$
where $N_{D_0}$ and $N_{+}1D_0$ stand for the $N$ and $N + 1$ particle system DMs of a non-degenerate or removable degenerate ground state, respectively. Therefore, it is straightforward to see from Eqs. (5) and (6) that for this case there is no information loss, except for $q = N$ and $p = N + 1$, i.e., for $q < N$, the $qD_0$ distribution can be equivalently obtained from $D$ or $pD_0$ ($p < q$). Let us see some interesting consequences from these results. The energy for a $M$-particle system may be expressed by

$$\varepsilon_0^M = \text{Tr}(1D_0^M h) + \text{Tr}(2D_0^M v) = \text{Tr}(2D_0^M \mathcal{K}_M), \quad (7)$$

where $1D_0^M$ and $2D_0^M$ are the ground state 1- and 2-RDMs of the $M$-particle system as indicated by the supraindex $M$, or equivalently, by virtue of the reduced Hamiltonian $2\mathcal{K}_M$. Therefore, the generalization of ground states $M$ of the ensemble (cf. Eq.(4)) 2

$$|\Phi_M^t\rangle\rightarrow\sum_{M} \langle\Phi_M^t|\mathcal{N}|\Phi_M^t\rangle = \mathcal{K}_M\langle\Phi_M^t|\mathcal{N}|\Phi_M^t\rangle \nonumber$$

or equivalently $\varepsilon_0^N = \text{Tr}(\mathcal{D}_0^{N+1} 2\mathcal{K}_N)$ which means that the energy is a functional $\mathcal{F}$ of $2\mathcal{D}_0^M$, $2\mathcal{D}_0^{M+1}$, and the fractional population number $v$, i.e., $\varepsilon_0^{N+\nu} = \mathcal{F}(\mathcal{D}_0^{N+1}, 2\mathcal{D}_0^N, v)$. We will present at this point some descriptive examples to illustrate the potentialities of the above theory. Let us begin at first considering a system in its ground state described at the Hartree-Fock level of approximation, whose GC DM (cf. Eq. (6)) reads

$$D = (1 - v) |\chi_1 \cdots \chi_N\rangle\langle \chi_1 \cdots \chi_N| + v |\chi_1 \cdots \chi_N \chi_{N+1}\rangle\langle \chi_1 \cdots \chi_N \chi_{N+1}|, \quad (9)$$

where $\{|\chi_i\rangle, i = 1, 2, \ldots\}$ stands for the set of spin-orbitals in the Slater determinant states $|\chi_1 \mathcal{K}_2 \cdots\rangle$ of the $N$ and $N + 1$ electron systems assuming the frozen approximation. Then, performing the CM operation for $p = 1$ (Eqs. (3) and (6)), it yields

$$\varepsilon_0^{N+\nu} = \sum_{M=N}^{N+1} \omega_2^M \text{Tr}(2D_0^M \mathcal{K}_M) $$

$$+ (1 - v) \text{Tr}(2D_0^N \mathcal{K}_N) \quad (8)$$

or equivalently $\varepsilon_0^{N+\nu} = \text{Tr}(2\mathcal{D}_0^{N+1} 2\mathcal{K}_N)$ which means that the energy is a functional $\mathcal{F}$ of $2\mathcal{D}_0^M$, $2\mathcal{D}_0^{M+1}$, and the fractional population number $v$, i.e., $\varepsilon_0^{N+\nu} = \mathcal{F}(\mathcal{D}_0^{N+1}, 2\mathcal{D}_0^N, v)$. We will present at this point some descriptive examples to illustrate the potentialities of the above theory. Let us begin at first considering a system in its ground state described at the Hartree-Fock level of approximation, whose GC DM (cf. Eq. (6)) reads

$$D = (1 - v) |\chi_1 \cdots \chi_N\rangle\langle \chi_1 \cdots \chi_N| + v |\chi_1 \cdots \chi_N \chi_{N+1}\rangle\langle \chi_1 \cdots \chi_N \chi_{N+1}|, \quad (9)$$

where $\{|\chi_i\rangle, i = 1, 2, \ldots\}$ stands for the set of spin-orbitals in the Slater determinant states $|\chi_1 \mathcal{K}_2 \cdots\rangle$ of the $N$ and $N + 1$ electron systems assuming the frozen approximation. Then, performing the CM operation for $p = 1$ (Eqs. (3) and (6)), it yields

$$1D_0^{N+\nu} = L_1[D] = v \left( \begin{array}{c} N+1 \\ 1 \end{array} \right) L_1^{N+1}(N+1D_0) + (1 - v) \left( \begin{array}{c} N \\ 1 \end{array} \right) L_1^N(ND_0), \quad (10)$$

where $\langle N^+1\rangle L_1^{N+1}(N+1D_0) = 1D_0^{N+1}$ and $\langle N\rangle L_1^N(ND_0) = 1D_0^N$. Hence, $1D_0^{N+\nu} = v 1D_0^{N+1} + (1 - v) 1D_0^N$ stands for the 1-RDM of the $N + \nu$ particles system and introducing the structure of each $1D_0^M$ in Eq. (10) it follows

$$1D_0^{N+\nu} = \sum_{i=1}^{\nu} |\chi_i\rangle\langle \chi_i| + \nu |\chi_{N+1}\rangle\langle \chi_{N+1}|, \quad (11)$$

where the first term of the r.h.s. stands for the $1D_0^N$ and the remaining term, $\nu |\chi_{N+1}\rangle\langle \chi_{N+1}|$, is the single occupied spin-orbital contribution from state of the $N + 1$ system which is the fraction of the density difference between the states of $N + 1$ and $N$ systems. Hence, it is immediate to obtain the energy for this system from Eq. (7) as

$$E_{N}^{N+\nu} = E_0^N + v \varepsilon_{N+1}, \quad (12)$$

where $E_0^N$ and $E_0^{N+\nu}$ are the Hartree-Fock energies of the $N + \nu$- and $N$-particle systems, respectively, and $\varepsilon_{N+1}$ stands for $(N+1)$th orbital energy. The same procedure may be followed for the case $N - \nu$ which yields $E_0^{N-\nu} = E_0^N - v \varepsilon_{N+1}$. Thus, the energy is that of the $N$-particle system plus the $\nu$ fraction of the single occupied spin-orbital.

Other applications of importance are the determination of the first derivatives of the energy and the electron density with respect to the number of particles $N$ at fixed external field $v$. These magnitudes are at the basis of the definitions of two fundamental chemical descriptors defined from the conceptual density functional theory:13 the chemical potential and the Fukui functions (reactivity indices), respectively.1,3

The chemical potential becomes defined by

$$\mu = \left( \frac{\partial \varepsilon_0^N}{\partial N} \right)_v \quad (13)$$

regarding that the ground state energy of these open systems may be expressed by

$$\varepsilon_0^{N \pm \nu} = (1 - v) \varepsilon_0^N + v \varepsilon_0^{N \mp \nu}, \quad (14)$$

with $\varepsilon_0^{N \pm \nu}$, $\varepsilon_0^N$, and $\varepsilon_0^{N \pm \nu}$ the energy of the systems with $N \pm \nu$, $N$, and $N \pm 1$ electrons, respectively, and because $\partial N = \pm \partial v$ ($N$ constant), this derivative becomes

$$\mu_\pm = \pm \left( \frac{\partial \varepsilon_0^N}{\partial v} \right)_v = \pm (\varepsilon_0^{N \pm 1} - \varepsilon_0^N) \quad (15)$$

showing its discontinuity2 which yields

$$\mu_+ = \varepsilon_0^{N+1} - \varepsilon_0^N = -\varepsilon A, \quad (16)$$

$$\mu_- = \varepsilon_0^N - \varepsilon_0^{N-1} = -\varepsilon P,$$

where $EA$ and $IP$ stand for the electron affinity and the ionization potential, respectively. Therefore, the generalization
of these formulae using Eq. (16) is obtained as $(\mathcal{E}_o^{N+v} - \mathcal{E}_o^{N}) + (\mathcal{E}_o^{N-v} - \mathcal{E}_o^{N}) = IP^{N+v} - EAN^{v+} = v(IP - EA)$. Furthermore, the form of the Hartree-Fock energy (Eq. (12)) tempt to equate

$$IP^v = v IP \text{ and } EAN^v = v EA$$

where their physical meaning is based on the idea that on average $v$ electrons are removed or attached to the system, respectively.

The other important example is the first derivative of the electron density $\rho(r)$ at point $r$ in space with respect to the number of particles at constant external field $\nu$. Defined by $f^{\pm}(r) = \left( \frac{\partial \rho(r)}{\partial N} \right)^{\pm}$. They are known as Fukui functions or reactivities. Following the same arguments as those applied in Ref. 21, it is possible to obtain representations of $D$ with more than two terms but these are not states of minimal energy.\(^{16}\)

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