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# Erratum: On Equilibrium Intensive Thermodynamic Properties of Composed $p$ -Particles in Many-Body Systems\*

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**ABSTRACT:** Equilibrium intensive thermodynamic properties of  $p$ -particles ( $p$ -ons), i.e., composed particles formed by few particles of the same nature such as fermion or boson pairs ( $p = 2$ ), trios ( $p = 3$ ), etc., are investigated. The relation of the  $p$ -particle correlation functions to its  $p$ -hole counterparts and an existing covariant structure in the hierarchy of the  $p$ -particle correlation functions allow these generalized intensive properties to be properly defined and characterized. The connection between these generalized properties of the composed objects and those of the components is also derived. An explicit derivation of the chemical potential for pairs and its generalization to  $p$ -particles is performed. Such results are further extended to any intensive property. Finally, the present development allows some previous results to be clearly interpreted thus yielding an important support for our theory. © 2002 John Wiley & Sons, Inc. Int J Quantum Chem 86: 313–321, 2002

**Key words:** propagators; correlation functions; quantum statistics;  $p$ -particle distributions

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## Introduction

Green's functions are widely used in various branches of mathematics and theoretical physics. Despite its rather long history, the method of the Green function continues to develop. This development concerns the application of this technique to statistical mechanics. This is probably the most significant area which the method of Green's functions has been applied to. The literature in this direction is too extensive to be cited here [1–4]. It is just the complexity of statistical mechanics that perpetually forces us to develop the method of Green's functions. Green's functions are a natural generalization of correlation functions [5, 6], some particular and important examples of which become the reduced density matrices [7–9] or distribution functions of many body systems that opened a new fundamental branch in many body physics. In fact, the dynamical behavior and properties of these systems (atoms, molecules, nuclei, and crystals, etc.) can be completely described in terms of Green's functions or propagators [10, 11]. All these possibilities are available because the method of two time quantum mechanical propagators combines the most effective techniques of quantum field theory [12] and therefore its close connection with the correlation functions admits us to introduce the description of composite particles like fermion pairs or trios and/or bosonic excitations like magnons, plasmons, etc., in both closed and open quantum systems [13]. The interest in such distributions becomes clear because of the growing field of application of such objects in a large variety of problems ranging from the quasiparticle excitation concept to Cooper pairs as particular examples that need to be described in terms of composed particles [14].

The present work deals with the application of the Green's function method to the concept of composite particles. This technique has been introduced some time ago by several authors in order to describe atomic systems composed by nucleons and electrons [15, 16]. However, not too much attention has been devoted to p-particles composed by the same kind of particles in a general manner. This goal has been central in our recent works concerned with many electron molecular systems showing that lower order densities (particle density) hides some information that enables us to understand some phenomena such as complex patterns of bonding [17, 18]. This difficulty can be overcome by using higher order densities such as

pair (two-particle), i.e., normal bonds in molecular systems or trios (three-particle) densities [17], i.e., nonclassical three center bonds in these kind of systems. In order to completely understand the many body system structure the hidden information must be recovered [18], a task that may be performed by means of the *correlation functions* as part of the propagators. When the p-particle distributions are considered, these functions are called *reduced density matrices* (RDM) [19].

In the present work we will exploit the relations between correlation functions associated to the particle distributions derived from the propagators. This provides the dynamical information of the system from which the meaning and nature of the intensive properties involved in the description of many body systems can be analyzed by means of composed p-particles.

The work is organized as follows: in the second section the notation and the basic relations are established. The third section is devoted to derive an expression for the chemical potential of a pair or two-particle and its generalization to a composite p-particle. The fourth section deals with the generalization of the previous idea to an arbitrary intensive property. Finally, a brief discussion about the physical meaning and comparison with other works in order to support the physical idea of the chemical potential is given in the last section.

## Basic Relations and Notation

The time-independent Hamiltonian of many body systems with an arbitrary interaction potential  $\mathbf{V}$  may be written as  $\mathbf{H} = \mathbf{H}_0 + \mathbf{V}$ , being  $\mathbf{H}_0$  an independent or a Hartree–Fock quasi-independent ensemble particle Hamiltonian defined by

$$\mathbf{H}_0 = \sum_k \varepsilon_k c_k^\dagger c_k \quad (1)$$

where  $\{\varepsilon_k, k = 1, 2, \dots\}$  the set of individual particle energies of the system.

The two time propagators of two arbitrary operators  $\mathbf{A}$  and  $\mathbf{B}$  are defined by [3]

$$\langle\langle \mathbf{A}(t); \mathbf{B}(t') \rangle\rangle = -i \hat{\tau} \{ \mathbf{A}(t) \mathbf{B}(t') \} \quad (2)$$

where the symbol  $\langle \dots \rangle$  indicates an ensemble average operation. Here,  $\hat{\tau}$  stands for the chronological or time-ordering superoperator whose action is defined by

$$\hat{\tau} \{ \mathbf{A}(t) \mathbf{B}(t') \} = \theta(\tau) \mathbf{A}(t) \mathbf{B}(t') + \eta \theta(-\tau) \mathbf{B}(t') \mathbf{A}(t) \quad (3)$$

with  $\tau = t - t'$  and  $\eta = \pm 1$  depending on the fermionic or bosonic character of the operators [3, 21] and  $\theta$  stands for the "step" function with values 0 or 1 if  $\tau < 0$  or  $\tau > 0$ , respectively.

In order to deal with p-particle distributions it is necessary to identify the operators involved in Eq. (2) with the p-particle annihilation and creation operators as

$$\begin{aligned} \mathbf{A}(t) &= \psi(\mathbf{x}_1, t)\psi(\mathbf{x}_2, t)\cdots\psi(\mathbf{x}_p, t) \\ \mathbf{B}(t') &= \psi^\dagger(\mathbf{x}'_p, t')\cdots\psi^\dagger(\mathbf{x}'_2, t')\psi^\dagger(\mathbf{x}'_1, t') \end{aligned}$$

where  $\psi$  and  $\psi^\dagger$  represent the annihilation and creation field operators of individual particles, respectively, and the variables  $\mathbf{x}_i$  stand for the set of spatial  $\mathbf{r}_i$  and spin  $\mathbf{s}_i$  coordinates of the  $i$ th particle. Therefore the hierarchy of particle distributions in terms of the 1-, 2-, ..., p-particle propagators reads as follows [22]:

$$\begin{aligned} \langle\langle\psi(\mathbf{x}, t); \psi^\dagger(\mathbf{x}', t')\rangle\rangle & \quad \text{one-particle propagator} \\ \langle\langle\psi(\mathbf{x}_1, t)\psi(\mathbf{x}_2, t); \psi^\dagger(\mathbf{x}'_1, t')\psi^\dagger(\mathbf{x}'_2, t')\rangle\rangle & \quad \text{two-particle propagator} \\ \langle\langle\psi(\mathbf{x}_1, t)\psi(\mathbf{x}_2, t)\cdots\psi(\mathbf{x}_p, t); \psi^\dagger(\mathbf{x}'_1, t')\psi^\dagger(\mathbf{x}'_2, t')\cdots\psi^\dagger(\mathbf{x}'_p, t')\rangle\rangle & \quad \text{p-particle propagator.} \end{aligned}$$

Equation (2) has two terms both of which exhibit the well-known *correlation functions* defined by

$$F_{AB}(t, t') = \langle\mathbf{A}(t)\mathbf{B}(t')\rangle \quad (4)$$

and

$$F_{AB}(t, t') = \langle\mathbf{B}(t')\mathbf{A}(t)\rangle \quad (5)$$

representing the propagator for  $t > t'$  and for  $t' > t$ , respectively.

Making use of a simple property expressed as [22, 24]

$$\psi\mathbf{N} = (\mathbf{N} + \mathbf{I})\psi \quad (6)$$

where  $\mathbf{N}$  is the particle number operator defined by

$$\mathbf{N} = \int \psi^\dagger(u)\psi(u) du$$

and  $\mathbf{I}$  is the identity operator, and taking into account the Heisenberg picture for the operators and the grand canonical ensemble for the distribution, a master relation for the correlation functions of field operators [22] can be written as

$$F_{\psi^\dagger\psi}(0, \tau) = zF_{\psi\psi^\dagger}(-i\beta, \tau). \quad (7)$$

Here,  $i\beta$  stands for an imaginary time (Wicks rotation) [22] with  $\beta = (kT)^{-1}$ ,  $k$  is the Boltzmann constant, and  $T$  the absolute temperature. It may be noted that the fugacity  $z$  of the system defined as

$\exp(\beta\mu)$  with  $\mu$  the chemical potential, relates the one-particle correlation functions  $F_{\psi^\dagger\psi}$  to its associated one-hole counterpart  $F_{\psi\psi^\dagger}$  [19, 24].

## Chemical Potential for Two-Particle (Pairs) and Generalization

In order to obtain the chemical potential of pairs of particles, let us now inspect the case of two-particle distributions. The central idea is to prove a similar relation to that of Eq. (7) for the present distributions.

The pair correlation functions are defined by ( ${}^1\mathbf{C}_{\psi\psi^\dagger}(t, t') \equiv F_{\psi\psi^\dagger}$ )

$$\begin{aligned} {}^2\mathbf{C}_{\psi\psi^\dagger}(t, t') & \equiv F_{\psi\psi\psi^\dagger\psi^\dagger}(t, t') \\ & = \langle\psi(\mathbf{x}_1, t)\psi(\mathbf{x}_2, t)\psi^\dagger(\mathbf{x}'_2, t')\psi^\dagger(\mathbf{x}'_1, t')\rangle \quad (8) \end{aligned}$$

$$\begin{aligned} {}^2\mathbf{C}_{\psi^\dagger\psi}(t, t') & \equiv F_{\psi^\dagger\psi^\dagger\psi\psi}(t, t') \\ & = \langle\psi^\dagger(\mathbf{x}'_1, t')\psi^\dagger(\mathbf{x}'_2, t')\psi(\mathbf{x}_2, t)\psi(\mathbf{x}_1, t)\rangle. \quad (9) \end{aligned}$$

Therefore, explicitly writing the average in Eqs. (8) and (9), making use of the grand canonical ensemble for which our central property, the chemical potential, plays a fundamental role, and taking into account Eq. (6) for an arbitrary function defined as a power series of  $\mathbf{N}$ , it follows that [24]

$${}^2\mathbf{C}_{\psi^\dagger\psi}(0, \tau) = \exp(2\beta\mu){}^2\mathbf{C}_{\psi\psi^\dagger}(-i\beta, \tau). \quad (10)$$

Furthermore, a similar and simple expression for the associated p-particle distributions

$$\begin{aligned} {}^p\mathbf{C}_{\psi^\dagger\psi}(t, t') & = \langle\psi^\dagger(\mathbf{x}'_1, t')\psi^\dagger(\mathbf{x}'_2, t')\cdots \\ & \quad \psi^\dagger(\mathbf{x}'_p, t')\psi(\mathbf{x}_p, t)\cdots\psi(\mathbf{x}_2, t)\psi(\mathbf{x}_1, t)\rangle \end{aligned}$$

is obtained as

$${}^p\mathbf{C}_{\psi^\dagger\psi}(0, \tau) = \exp(\beta p\mu){}^p\mathbf{C}_{\psi\psi^\dagger}(-i\beta, \tau) \quad (11)$$

which relates both p-particle and p-hole correlation functions [6].

Let us interpret the new results given by Eqs. (10) and (11). We have remarked that Eq. (7) can be written by means of the fugacity  $z = \exp(\beta\mu)$  as

$${}^1\mathbf{C}_{\psi^\dagger\psi}(0, \tau) = z{}^1\mathbf{C}_{\psi\psi^\dagger}(-i\beta, \tau)$$

and also it may be noted from Eq. (10) that

$${}^2\mathbf{C}_{\psi^\dagger\psi}(0, \tau) = z^2{}^2\mathbf{C}_{\psi\psi^\dagger}(-i\beta, \tau)$$

holds for pairs, where  $z^2 = \exp(2\beta\mu)$ . Thus from Eq. (11), it can be written as

$${}^p\mathbf{C}_{\psi^\dagger\psi}(0, \tau) = z^p{}^p\mathbf{C}_{\psi\psi^\dagger}(-i\beta, \tau).$$

Therefore the p-particle distribution representing the correlation functions allows one to identify the proportionality  $p_z$  factor as

$$p_z \equiv \exp(\beta p \mu) = z^p; \quad {}^1z \equiv z \quad (12)$$

and may be interpreted as the fugacity of the p-particle distribution. Thus, Eq. (11) in conjunction with the definition in Eq. (12) lead to

$$z^p = \exp(\beta p \mu) = {}^1z(p \mu) \quad (13)$$

where  ${}^1z(p \mu)$  indicates the fugacity of the one-particle distribution as a function of the argument  $p \mu$ . On the other hand, from the definition of fugacity it follows that

$$p_z = \exp(\beta {}^p \mu) \quad (14)$$

where  ${}^p \mu$  indicates the chemical potential of the p-particle distribution, i.e., for  $p = 1$ ,  ${}^1 \mu$  means  ${}^1 \mu = \mu$ ; thus, a direct comparison of Eqs. (13) and (14) yields the simple relation

$${}^p \mu = p \mu \quad (15)$$

which is completely valid within the nonrelativistic quantum statistical physics. It means that the p-particle distribution possess a p-chemical potential that is p-times that of the 1-particle distribution. We will return to this result in order to give it a more realistic basis from its physical meaning.

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### Intensive Properties: Generalization

Let us consider an effective Hamiltonian  $\mathcal{H}$  of the type usually used in statistical physics such that it can be written as

$$\mathcal{H} = \mathbf{H} - \lambda \odot \mathbf{A} \quad (16)$$

where  $\mathbf{H}$  is composed of the kinetic energy and the particle interaction and the second term on the rhs of Eq. (16) is the coupling between an operator  $\mathbf{A}$  associated to an extensive thermodynamic magnitude and its associated response magnitude  $\lambda$  (intensive thermodynamic property). Here, the symbol  $\odot$  indicates a generalized product; i.e., a  $c$ -number in the case that the product is between  $\lambda$  as pressure and volume as the extensive magnitude; scalar product in the case of electric field and electric dipole moment associated with polarizability of the system; etc. For the sake of simplicity, this symbol will be dropped from the equations from now on.

In order to generalize the previous results to any intensive property let us follow a procedure closely related to that used to derive the chemical potential.

The correlation function for the one-particle distribution at  $t = 0$  in the Gibbs distribution is defined by

$${}^1C_{\psi^\dagger \psi}(0, t') = Z^{-1} \text{Tr}[\psi(\mathbf{x}, 0) \times \exp(-\beta(\mathbf{H} - \lambda \mathbf{A}))\psi^\dagger(\mathbf{x}', t')] \quad (17)$$

where the cyclic property of the trace has been used. Introducing the identity  $\exp(-\beta(\mathbf{H} - \lambda \mathbf{A})) \exp(\beta(\mathbf{H} - \lambda \mathbf{A}))$ , we get

$${}^1C_{\psi^\dagger \psi}(0, t') = \langle \exp(\beta(\mathbf{H} - \lambda \mathbf{A}))\psi(\mathbf{x}, 0) \times \exp(-\beta(\mathbf{H} - \lambda \mathbf{A}))\psi^\dagger(\mathbf{x}', t') \rangle. \quad (18)$$

To proceed further we consider the general case in which  $[\mathbf{H}; \mathbf{A}]_- \neq 0$ . Therefore, regarding that the exponential of noncommuting operators may be written as shown in Appendix B, it follows that the correlation function may be expressed as

$${}^1C_{\psi^\dagger \psi}(0, t') = \langle \mathbf{F}_{-\beta \lambda \mathbf{A}}(\mathbf{H}) \exp(-\beta \lambda \mathbf{A})\psi(\mathbf{x}, 0) \times \exp(\beta \lambda \mathbf{A})\bar{\mathbf{F}}_{\beta \lambda \mathbf{A}}(-\mathbf{H})\psi^\dagger(\mathbf{x}', t') \rangle \quad (19)$$

where all commutator effects are recasted into the  $\mathbf{F}_{-\beta \lambda \mathbf{A}}(\mathbf{H})$  and  $\bar{\mathbf{F}}_{\beta \lambda \mathbf{A}}(-\mathbf{H})$  functionals.

Now we will go further by considering that the operator  $\mathbf{A}$  can be split into diagonal and off diagonal parts as

$$\mathbf{A} = \mathbf{A}_d + \mathbf{A}_{od}$$

where  $[\mathbf{A}_d; \mathbf{A}_{od}]_- \neq 0$  is assumed; thus by application of the noncommutative expression for the exponentials containing  $\mathbf{A}$  in Eq. (19) as

$$\begin{aligned} \exp(\pm \beta \lambda \mathbf{A}) &= \exp(\pm \beta \lambda \mathbf{A}_d \pm \beta \lambda \mathbf{A}_{od}) \\ &= \exp(\pm \beta \lambda \mathbf{A}_d)\bar{\mathbf{F}}_{\pm \beta \lambda \mathbf{A}_d}(\pm \beta \lambda \mathbf{A}_{od}) \\ &= \mathbf{F}_{\pm \beta \lambda \mathbf{A}_d}(\pm \beta \lambda \mathbf{A}_{od}) \exp(\pm \beta \lambda \mathbf{A}_d) \end{aligned}$$

and by inserting such expression into Eq. (19) yields the rather complex expression

$$\begin{aligned} {}^1C_{\psi^\dagger \psi}(0, t') &= \langle \mathbf{F}_{-\beta \lambda \mathbf{A}}(\mathbf{H}) \exp(-\beta \lambda \mathbf{A}_d)\psi(\mathbf{x}, 0) \\ &\quad \times \exp(\beta \lambda \mathbf{A}_d)\bar{\mathbf{F}}_{\beta \lambda \mathbf{A}}(-\mathbf{H})\psi^\dagger(\mathbf{x}', t') \rangle \\ &+ \langle \mathbf{F}_{-\beta \lambda \mathbf{A}}(\mathbf{H}) \exp(-\beta \lambda \mathbf{A}_d)\psi(\mathbf{x}, 0) \exp(\beta \lambda \mathbf{A}_d) \\ &\quad \times \delta \bar{\mathbf{F}}_{\beta \lambda \mathbf{A}_d}(\beta \lambda \mathbf{A}_{od})\bar{\mathbf{F}}_{\beta \lambda \mathbf{A}}(-\mathbf{H})\psi^\dagger(\mathbf{x}', t') \rangle \\ &+ \langle \mathbf{F}_{-\beta \lambda \mathbf{A}}(\mathbf{H})\delta \mathbf{F}_{\beta \lambda \mathbf{A}_d}(\beta \lambda \mathbf{A}_{od}) \exp(-\beta \lambda \mathbf{A}_d)\psi(\mathbf{x}, 0) \\ &\quad \times \exp(\beta \lambda \mathbf{A}_d)\bar{\mathbf{F}}_{\beta \lambda \mathbf{A}}(-\mathbf{H})\psi^\dagger(\mathbf{x}', t') \rangle \\ &+ \langle \mathbf{F}_{-\beta \lambda \mathbf{A}}(\mathbf{H})\delta \mathbf{F}_{\beta \lambda \mathbf{A}_d}(\beta \lambda \mathbf{A}_{od}) \exp(-\beta \lambda \mathbf{A}_d)\psi(\mathbf{x}, 0) \\ &\quad \times \exp(\beta \lambda \mathbf{A}_d)\delta \bar{\mathbf{F}}_{\beta \lambda \mathbf{A}_d}(\beta \lambda \mathbf{A}_{od}) \\ &\quad \times \bar{\mathbf{F}}_{\beta \lambda \mathbf{A}}(-\mathbf{H})\psi^\dagger(\mathbf{x}', t') \rangle. \quad (20) \end{aligned}$$

Finally, it may be noted that the action of the field operator  $\psi$  on  $\mathbf{A}_d$  in the exponential functionals in Eq. (20) furnishes a factor  $\Delta_1(\lambda)$  which is common to all terms of the correlation functions, i.e.,

$${}^1C_{\psi^\dagger\psi}(0, t') = \Delta_1(\lambda) \{ {}^1C_{\psi\psi^\dagger}(0, t') + {}^1P_{\psi\psi^\dagger}^{corr}(\lambda\mathbf{A}, \mathbf{H}, t') \} \quad (21)$$

with

$$\Delta_1(\lambda) = \exp(\beta\lambda a(x))$$

where  $a(x)$  stands for the diagonal part or density of the operator  $\mathbf{A}$  and  ${}^1P_{\psi\psi^\dagger}^{corr}(\lambda\mathbf{A}, \mathbf{H}, t')$  the term collecting all commutators between the operators  $\mathbf{H}$  and  $\mathbf{A}$  and nondiagonal effects of the operator  $\mathbf{A}$  as shown above.

Such a result allows us to find an explicit way of defining the generalized  ${}^p\lambda$  property in the same way we associated the chemical potential to a p-on particle. By looking at the successive action of the field operators on the operator  $\mathbf{A}$ , it follows that the p-particle correlation function may be written as

$${}^pC_{\psi^\dagger\psi}(0, t') = \Delta_p(\lambda) \{ {}^pC_{\psi\psi^\dagger}(0, t') + {}^1P_{\psi\psi^\dagger}^{corr}(\lambda\mathbf{A}, \mathbf{H}, t') \} \quad (22)$$

which is a *covariant* expression of Eq. (21). Here,  $\Delta_p(\lambda)$  is the proportionality factor common to all functionals which relates the correlation functions and which becomes defined [cf. Eq. (22)] by

$$\Delta_p(\lambda) = \Delta_1(p\lambda) \equiv \Delta_1({}^p\lambda)$$

with

$${}^p\lambda = p\lambda.$$

Analogously to the chemical potential we define the  $\lambda$  – *fugacity*,  ${}^pZ(p\lambda)$  as

$${}^pZ(p\lambda) = {}^1Z(p\lambda) \quad (23)$$

which generalizes the previous result on the chemical potential. Therefore we have found a simple and powerful relation between the correlation functions which is valid to any time. It appears to be very striking because of its possible application of statistical distribution of p-particles for the elucidation of the role of compound particles in the onset of superphenomena in physics [25].

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## Discussion and Final Remarks

The result on the chemical potential is central to determine the correlation functions and, because

of its validity to any order in the statistical description of the system and also for any interaction potential, it seems to be very interesting for its application in statistical physics of p-particles such as electron pairs and trios in condensed matter in order to understand the onset of superphenomena in physics [25, 26] from the behavior of compound particles. The generalization of the chemical potential appears to be the most adequate tool to interpret prior results about pair distributions. In order to add some further understanding on this topic let us now discuss the pair chemical potential concept; i.e., the chemical potential of a fermion pair within the statistical distribution of such two-particles and compare our present approach with early results. The physical meaning of the chemical potential suggests that there exists some limit for the occupied levels described by the p-state functions that house the p-particles (p = 1, orbitals; p = 2, geminals; ...; p-ons). At zero temperature ( $T = 0$ ) we know from the ideal Fermi gas that the particles occupy the N lowest energy levels in which the Fermi level is coincident with the chemical potential  $\mu$ . In the case of fermion pairs we expect this formalism to provide a similar physical interpretation. Let us consider the particular case of an ideal pair gas, i.e., a gas of noninteracting fermions ( $\mathbf{V} = \mathbf{0}$ ; interaction potential between the individual fermions) described in terms of pair distributions. It is well known that the pair population as a function of the pair energy defined as the sum of the individual energies of both particles in a given configuration represented by a *geminal* state function (two-particle state function)  $|\lambda\rangle = |\lambda_i\lambda_j\rangle$  with  $\lambda_i > \lambda_j$  [27, 28]

$$E_\lambda = \varepsilon_{\lambda_i} + \varepsilon_{\lambda_j} \quad (24)$$

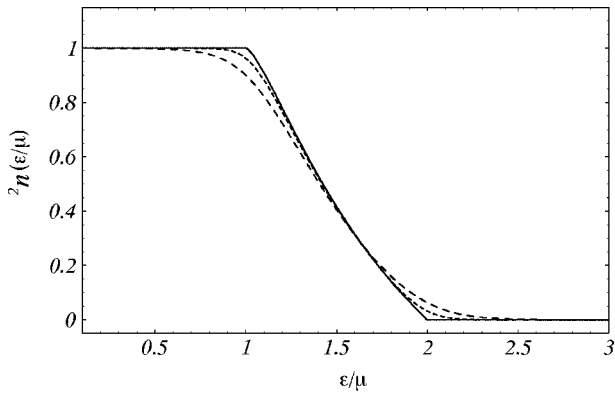
can be obtained from propagator's methods [29]. Thus, the pair occupancies  ${}^2n(\varepsilon)$  in terms of the two-reduced density matrices (diagonal elements of the correlation functions of the field operators) may be defined as

$${}^2n(\varepsilon) = \sum_{\lambda_i\lambda_j(\varepsilon_{\lambda_i} + \varepsilon_{\lambda_j} = E_\lambda)} {}^2D_{\lambda\lambda}. \quad (25)$$

Such occupancies are shown in Figure 1 from which it follows that

$$\begin{aligned} {}^2n(\varepsilon) &= 1 & 0 < \varepsilon < \mu \\ 0 < {}^2n(\varepsilon) &< 1 & \mu < \varepsilon < 2\mu \\ {}^2n(\varepsilon) &= 0 & 2\mu \leq \varepsilon. \end{aligned}$$

We may note from this figure that such occupancies or populations indicate that the distribution



**FIGURE 1.** Populations (occupation) of free fermion pairs for  $T = 0$  (solid line) and  $T \neq 0$  (dashed lines).

exhibits a *cutoff* at  $\varepsilon = 2\mu$  for  $T = 0$ . This result is in complete agreement with the interpretation of the chemical potential, an independent result that supports our conjecture. It is worthwhile to make some comments on the fermion pair population curve in order to interpret its behavior and to note the meaning of the chemical potential within this context. The first characteristic to be noted is that its shape does not seem to represent a typical Fermi system. However, if we accept the so-called *Bopp's conjecture* [30] which asserts the existence of an *abrupt cutoff* which ensures the correct pair normalization (the sum over states gives the number of pairs  $\binom{N}{2}$  while retaining the Fermi shape for free particle fermions), i.e., uniform pair population, it implies the existence of a chemical potential for pairs whose value is  $\zeta\mu$  with  $1 < \zeta < 2$ . Thus, the results provided by this conjecture are wrong because the fermion pairs are not fermions [25, 26] as is imposed by Bopp's approach. An other way to understand such failure is that there are several two-particle configurations with the same energy and therefore all of them contribute to the population in Eq. (25). Therefore, such condition ( $E_\lambda = \varepsilon$ ) introduces an additional physical consequence: the contributing pairs come from different configurations ranging from those composed by a particle of very low energy and other of high energy [27] to those formed by similar individual energies in order to keep the pair energy level fixed. Thus, the probability that the outer energy levels ( $\varepsilon > \mu$ ) become appreciably populated is rather low because of the energy constraint, i.e., lower number two-particle fermion configurations are available for a given energy as it approaches the cutoff, and therefore the pairon occupation begins to decrease to zero as  $\varepsilon$

reaches  $\mu$ . It means that there are low configurations with the same energy that contribute to the population until  $\varepsilon = 2\mu$ , from which no compatible pair configurations are possible. Thus, the population for this energy, i.e., the cutoff, vanishes and therefore, the chemical potential concept is retained. We have used the same methodology to derive the free fermion trios distribution and a similar result has been found leading to an energy cutoff equal to  $3\mu$  at  $T = 0$  as expected from the above considerations.

From previous results [31], we may say that no concrete evaluations of pair populations associated to the RDM concept are easily found, except that of Coleman [26]. This author gets a similar curve to Figure 1 but which has been obtained from a different point of view. In this work the fermion pair chemical potential appears naturally as a consequence of the convoluted individual energies of the pair and which turns out to be a particular case of (25). Therefore we conclude that this result is a strong support for our example and the interpretation of this curve is a convincing argument for a future generalization to other intensive properties. Atomic condensate systems are nowadays the most striking field connected with these results because of the condensation phenomena and therefore experimental evidence on chemical potential of composed p-particles is expected from it. However no fermion pair condensation but ordinary boson like is considered for explanation of the related phenomena [31–33].

Finally we want to remark an important point about the validity of our results. Thus far the relation of the chemical potential of a p-particle to that of their components is also valid for any interacting system in a stationary state, which is strongly supported by few examples in the literature [34]. The extension of our conjecture to any other intensive property is based on the evaluation of operators of nondiagonal character leading to nonlocal (nondiagonal) contributions to the action of the p-field operators on the associated extensive magnitude. However, the definitions of the so-called generalized  $\lambda$ -fugacity is supported by the covariance structure of the correlation function relations to any order  $p$  in the reduced description. We may also note that the intensive properties mainly depend on the diagonal or density of the operator describing the extensive property. Lines along this direction are being explored in our laboratory.

## Appendix A: Master Relation for the Correlation Functions of Field Operators

The correlation functions defined in the text are explicitly written as

$$F_{\psi^\dagger\psi}(t, t') = \mathcal{Z}^{-1} \text{Tr}[\exp(-\beta(\mathbf{H} - \mu\mathbf{N})) \exp(i\mathbf{H}t')\psi^\dagger(\mathbf{x}', 0) \times \exp(-i\mathbf{H}(t' - t))\psi(\mathbf{x}, 0) \exp(-i\mathbf{H}t)] \quad (\text{A1})$$

where  $\mathcal{Z}$  stands for the partition function in the grand canonical ensemble.

Assuming that the Hamiltonian of the system,  $\mathbf{H}$ , commutes with the particle number operator  $\mathbf{N}$ , i.e., particle conserving Hamiltonian, and supposing absolute convergence on the argument of the trace operation in Eq. (A1) in order to use the cyclic property of the trace, it is obtained that

$$F_{\psi^\dagger\psi}(t, t') = \mathcal{Z}^{-1} \text{Tr}[\exp(-\beta(\mathbf{H} - \mu\mathbf{N})) \times \exp(i\mathbf{H}(t' - t))\psi^\dagger(\mathbf{x}', 0) \times \exp(-i\mathbf{H}(t' - t)) \times \psi(\mathbf{x}, 0)] \quad (\text{A2})$$

and thus particularly ( $t' \equiv \tau$ )

$$F_{\psi^\dagger\psi}(0, \tau) = \mathcal{Z}^{-1} \text{Tr}[\exp(-\beta(\mathbf{H} - \mu\mathbf{N})) \times \psi^\dagger(\mathbf{x}', \tau)\psi(\mathbf{x}, 0)]. \quad (\text{A3})$$

Applying the cyclic property again and introducing the identity operator expressed as the product  $\exp(-\beta(\mathbf{H} - \mu\mathbf{N}))\exp(\beta(\mathbf{H} - \mu\mathbf{N}))$ , it may be followed that

$$F_{\psi^\dagger\psi}(0, \tau) = \mathcal{Z}^{-1} \text{Tr}[\exp(-\beta(\mathbf{H} - \mu\mathbf{N})) \times [\exp(\beta(\mathbf{H} - \mu\mathbf{N}))\psi(\mathbf{x}, 0) \times \exp(-\beta(\mathbf{H} - \mu\mathbf{N}))\psi^\dagger(\mathbf{x}', \tau)]] \quad (\text{A4})$$

or

$$F_{\psi^\dagger\psi}(0, \tau) = \langle \exp(\beta(\mathbf{H} - \mu\mathbf{N}))\psi(\mathbf{x}, 0) \times \exp(-\beta(\mathbf{H} - \mu\mathbf{N}))\psi^\dagger(\mathbf{x}', \tau) \rangle. \quad (\text{A5})$$

Application of the property expressed as  $\psi(\mathbf{x})f(\mathbf{N}) = f(\mathbf{N} + \mathbf{I})\psi(\mathbf{x})$  leads to

$$F_{\psi^\dagger\psi}(0, \tau) = \exp(\beta\mu) \langle \exp(\beta\mathbf{H})\psi(\mathbf{x}, 0) \times \exp(-\beta\mathbf{H})\psi^\dagger(\mathbf{x}', \tau) \rangle. \quad (\text{A6})$$

Therefore, the master property for the one-particle distribution or correlation function is

$$F_{\psi^\dagger\psi}(0, \tau) = \exp(\beta\mu)F_{\psi\psi^\dagger}(-i\beta, \tau). \quad (\text{A7})$$

The same procedure may be followed on the two-particle correlation functions. It will lead us to obtain a similar relation for these objects which may be written as

$${}^2\mathbf{C}_{\psi^\dagger\psi}(t, t') = \mathcal{Z}^{-1} \text{Tr}[\exp(-\beta(\mathbf{H} - \mu\mathbf{N})) \times \exp(i\mathbf{H}t')\psi^\dagger(\mathbf{x}'_1, 0)\psi^\dagger(\mathbf{x}'_2, 0) \times \exp(-i\mathbf{H}(t' - t)) \times \psi(\mathbf{x}_2, 0)\psi(\mathbf{x}_1, 0) \exp(-i\mathbf{H}t)]. \quad (\text{A8})$$

Assuming the conditions imposed on the one-particle correlation function for the present case, it may be obtained that

$${}^2\mathbf{C}_{\psi^\dagger\psi}(t, t') = \mathcal{Z}^{-1} \text{Tr}[\exp(-\beta(\mathbf{H} - \mu\mathbf{N})) \times \exp(i\mathbf{H}(t' - t))\psi^\dagger(\mathbf{x}'_1, 0)\psi^\dagger(\mathbf{x}'_2, 0) \times \exp(i\mathbf{H}(t' - t))\psi(\mathbf{x}_2, 0)\psi(\mathbf{x}_1, 0)] \quad (\text{A9})$$

and particularly,

$${}^2\mathbf{C}_{\psi^\dagger\psi}(0, \tau) = \mathcal{Z}^{-1} \text{Tr}[\exp(-\beta(\mathbf{H} - \mu\mathbf{N}))\psi^\dagger(\mathbf{x}'_1, \tau) \times \psi^\dagger(\mathbf{x}'_2, \tau)\psi(\mathbf{x}_2, 0)\psi(\mathbf{x}_1, 0)]. \quad (\text{A10})$$

Using the cyclic property of the trace and introducing the identity as  $\exp(-\beta(\mathbf{H} - \mu\mathbf{N}))\exp(\beta(\mathbf{H} - \mu\mathbf{N}))$  the correlation function may be rewritten in terms of the average

$${}^2\mathbf{C}_{\psi^\dagger\psi}(0, \tau) = \langle \exp(\beta(\mathbf{H} - \mu\mathbf{N}))\psi(\mathbf{x}_1, 0)\psi(\mathbf{x}_2, 0) \times \exp(-\beta(\mathbf{H} - \mu\mathbf{N}))\psi^\dagger(\mathbf{x}'_2, \tau)\psi^\dagger(\mathbf{x}'_1, \tau) \rangle \quad (\text{A11})$$

and thus

$${}^2\mathbf{C}_{\psi^\dagger\psi}(0, \tau) = \exp(2\beta\mu) \langle \exp(\beta\mathbf{H})\psi(\mathbf{x}_1, 0)\psi(\mathbf{x}_2, 0) \times \exp(-\beta\mathbf{H})\psi^\dagger(\mathbf{x}'_2, \tau)\psi^\dagger(\mathbf{x}'_1, \tau) \rangle \quad (\text{A12})$$

or

$${}^2\mathbf{C}_{\psi^\dagger\psi}(0, \tau) = \exp(2\beta\mu) \langle \psi(\mathbf{x}_1, -i\beta)\psi(\mathbf{x}_2, -i\beta) \times \psi^\dagger(\mathbf{x}'_2, \tau)\psi^\dagger(\mathbf{x}'_1, \tau) \rangle \quad (\text{A13})$$

where successive application of the property  $\psi(\mathbf{x})f(\mathbf{N}) = f(\mathbf{N} + \mathbf{I})\psi(\mathbf{x})$  has been used.

Finally we obtain the master relation

$${}^2\mathbf{C}_{\psi^\dagger\psi}(0, \tau) = \exp(2\beta\mu) {}^2\mathbf{C}_{\psi\psi^\dagger}(-i\beta, \tau). \quad (\text{A14})$$

## Appendix B: Structure of Exponential of Noncommuting Operators

In most of the problems of theoretical quantum physics it is necessary to evaluate a function like  $f(\mathbf{A} + \mathbf{B})$  when the form of  $f$  is given, the spectra of the operator  $\mathbf{A}$  is known and the commutator  $[\mathbf{A}, \mathbf{B}]$  is not null.

This paragraph is devoted to write out briefly the formulas for the expansions of a function of this type as a Taylor series as was done in Ref. [35].

Let  $\mathbf{A}$  and  $\mathbf{B}$  as described above, then

$$\begin{aligned} f(\mathbf{A} + \mathbf{B}) &= \sum_{n=0}^{\infty} \frac{C^{(n)}(\mathbf{A}, \mathbf{B})}{n!} f^{(n)}(\mathbf{A}) \\ &= \sum_{n=0}^{\infty} f^{(n)}(\mathbf{A}) \frac{\bar{C}^{(n)}(\mathbf{A}, \mathbf{B})}{n!} \end{aligned} \quad (\text{B1})$$

where  $C^{(n)}(\mathbf{A}, \mathbf{B})$  and  $\bar{C}^{(n)}(\mathbf{A}, \mathbf{B})$  become defined through the recursion relations

$$C^{(n)} = (\mathbf{A} + \mathbf{B})C^{(n-1)} - C^{(n-1)}\mathbf{A} \quad (\text{B2})$$

and

$$\bar{C}^{(n)} = \bar{C}^{(n-1)}(\mathbf{A} + \mathbf{B}) - \mathbf{A}\bar{C}^{(n-1)} \quad (\text{B3})$$

with special values  $C^{(0)} = \mathbf{I}$ ,  $\bar{C}^{(0)} = \mathbf{I}$ , and  $f^{(0)}(\mathbf{A}) \equiv f(\mathbf{A})$ , where  $\mathbf{I}$  stands for the identity operator.

In our particular case we deal with exponential functions whose argument is the sum of operators as  $\exp(\mathbf{A} + \mathbf{B})$  and therefore the relation (B2) and (B3) leads to express these functions as

$$\exp(\mathbf{A} + \mathbf{B}) = \left\{ \sum_{n=0}^{\infty} \frac{C^{(n)}(\mathbf{A}, \mathbf{B})}{n!} \right\} \exp(\mathbf{A})$$

or

$$\exp(\mathbf{A} + \mathbf{B}) = \mathbf{F}_A(\mathbf{B}) \exp(\mathbf{A}) \quad (\text{B4})$$

and similarly we also may write

$$\exp(\mathbf{A} + \mathbf{B}) = \exp(\mathbf{A}) \left\{ \sum_{n=0}^{\infty} \frac{\bar{C}^{(n)}(\mathbf{A}, \mathbf{B})}{n!} \right\}$$

or

$$\exp(\mathbf{A} + \mathbf{B}) = \exp(\mathbf{A}) \bar{\mathbf{F}}_A(\mathbf{B}) \quad (\text{B5})$$

and viceversa.

Note that all commutator effects between  $\mathbf{A}$  and  $\mathbf{B}$  are recasted into the functionals  $\mathbf{F}_A(\mathbf{B})$  and  $\bar{\mathbf{F}}_A(\mathbf{B})$  which are different from one another. Furthermore it is straightforward to note that both functionals may be split into

$$\mathbf{F}_X(\mathbf{Y}) = \mathbf{I} + \delta\bar{\mathbf{F}}_X(\mathbf{Y}) \quad \bar{\mathbf{F}}_X(\mathbf{Y}) = \mathbf{I} + \delta\mathbf{F}_X(\mathbf{Y}) \quad (\text{B6})$$

which is used in the central part of the work.

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