Properties of nonfreeness: an entropy measure of electron correlation

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Abstract

The "nonfreeness" of a many-fermion state ω is the entropy of ω relative to the free state that has the same 1-particle statistics as ω. The nonfreeness of a *pure* state is the same as its "particle-hole symmetric correlation entropy," a variant of an established measure of electron correlation. But nonfreeness is also defined for *mixed* states, and this allows one to compare the nonfreeness of subsystems to the nonfreeness of the whole. Nonfreeness of a part does not exceed that in the whole; nonfreeness is additive over independent subsystems; and nonfreeness is superadditive over subsystems that are independent on the 1-particle level.

1 Introduction

The word "correlation" in the context of many-electron systems is somewhat overcharged and ambiguous, except when used in the expression "correlation energy," where it refers to the difference between the energy of the true ground state of a many-electron system and the energy of the Hartree-Fock approximation. Usually, "correlation effects" refers to properties of a many-electron state that cannot be explained if its wavefunction is the single Slater determinant obtained by the Hartree-Fock method; but sometimes, even those classical statistical correlations rendered necessary by the very antisymmetry of fermion wavefunctions, as manifested, for example, in the phenomenon of the "Fermi hole," are also described as "Fermi

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correlations" [1]. Here we understand "correlation" in the former sense, and interest ourselves in measures of correlation that quantify the degree to which a given many-electron state can be distinguished from states pertaining to "free" (i.e., noninteracting) particles, e.g., states whose wavefunctions are Slater determinants. Such measures of electron correlation depend only on the given state, without reference to any extrinsic Hamiltonian, and therefore without reference to any prescribed "correlation energy." Several of these correlation measures are functions of the eigenvalues of the 1-particle density matrix (1PDM). This class includes the "nonidempotency" of the 1PDM [2, 3], the "degree of correlation" [4], and the "correlation entropy" [3, 5, 6, 7, 8]. Other correlation measures use the 1-particle and 2-particle position and momentum distributions, and quantify correlation in terms of the usual statistical correlation [1] or in terms of information [9, 10, 11].

In this article we prove that a version of the correlation entropy mentioned above, namely, the "particle-hole symmetric correlation entropy" of Ref. [12], is naturally extended to the domain of mixed states, so that the resulting measure of electron correlation, which we call "nonfreeness," behaves well when one considers subsystems of a given many-electron system. For example, given the electronic structure of a molecule, one may consider the electronic state of certain *parts* of the molecule, perhaps defined as regions of space that contain chemical bonds or functional groups of interest. Typically, the number of electrons in a subsystem is random, and the quantum state of the subsystem cannot be represented by any single wavefunction, i.e., it is not a "pure" state. Typically, the subsystem's state behaves as if it were a "mixture" of pure states, and is best represented by a density operator. Using nonfreeness allows one to speak of the amount of "correlation" in the state of a subsystem, and to compare it to the amount of correlation in the electronic state of the whole molecule. It will be seen that the nonfreeness of the state of a subsystem cannot exceed the nonfreeness of the state of the whole system. We will also show that nonfreeness is superadditive over disjoint subsystems, provided the states of the systems are independent on the 1-particle level. We feel that these properties of nonfreeness make it a natural and useful way to quantify electron correlation.

This article concentrates on finite systems of electrons, with a view toward applications in quantum chemistry. However, the concept of nonfreeness applies to any kind of fermionic particles, and the properties of nonfreeness proved here apply generally as well. Accordingly, though we discuss electrons in all our examples, we define nonfreeness and state our propositions for the general context where the Hilbert space for a single particle is denoted generically by $\mathcal{H}$ and the fermion Fock space over $\mathcal{H}$ is denoted by $\mathcal{F}_{\mathcal{H}}$.

In [13], we proposed to quantify electron correlation by comparing a given many-electron state to the free state that shares the same 1-particle statistics. In this article, we use relative entropy to compare the states, and define the nonfreeness of a many-fermion state to be the entropy of that state relative to the free state with the same 1-particle statistical operator. $\mathfrak{C}(\omega)$ denotes the nonfreeness of a state ω.

Proposition 1 gives a formula for the nonfreeness of a state of a finite system of fermions, represented by antisymmetric n-particle wavefunctions, or (more generally) by density operators the Fock space that feature finite expected particle number. Let $\mathcal{D}$ denote the set of all density operators Δ on $\mathcal{F}_{\mathcal{H}}$ such that

$$\Delta N = N\Delta \qquad \text{and} \qquad \mathrm{Tr}(\Delta N) < \infty \ , \tag{1}$$

where N is the number operator defined in formula (4) below. For $\Delta \in \mathcal{D}$, let γ_Δ denote the 1-particle statistical operator γ_Δ defined in formula (5) below, and let Γ_{γ_Δ} denote the density operator of the unique free state with 1-particle statistical operator γ_Δ. Proposition 1 states that the nonfreeness of Δ is the difference between the von Neumann entropy of Γ_{γ_Δ} and the von Neumann entropy of Δ, provided that the former entropy is finite, in which case it is a simple functional of the natural occupation probabilities.

Propositions 2 and 3 concern the way the nonfreeness of a many-electron system relates to the nonfreeness of its subsystems. Suppose that $\mathcal{H}_1$ is a closed subspace of the 1-particle Hilbert space $\mathcal{H}$, so that $\mathcal{H} \cong \mathcal{H}_1 \oplus \mathcal{H}_2$. The Hilbert space for the whole system is the Fock space over $\mathcal{H}$, and the Hilbert spaces for the subsystems under consideration are the Fock spaces over $\mathcal{H}_1$ and $\mathcal{H}_2$. A state ω of the whole system induces states ω_1 and ω_2 of the subsystems. Proposition 2 states that $\mathfrak{C}(\omega) \le \mathfrak{C}(\omega_1)$. Proposition 3 states that $\mathfrak{C}(\omega_1) + \mathfrak{C}(\omega_2) \le \mathfrak{C}(\omega)$ if the subsystems are "independent on the 1-particle level."

Propositions 2 and 3 are stated for finite systems, that is, for states represented by density operators in the class $\mathcal{D}$, but they hold true for infinite systems as well. Nonfreeness for infinite systems is discussed in Section 4.

2 Nonfreeness for finite systems

The nonfreeness of a pure n-electron state is an entropy-type function of the natural occupation probabilities. Given a normalized antisymmetric wavefunction $\psi(x_1, \ldots, x_n)$ representing an n-electron state, let γ_ψ denote the 1-particle "reduced density matrix," normalized to have trace

n: this is an operator with integral kernel

$$\gamma_\psi(x,y) \;=\; n\int dz_n \cdots \int dz_2\; \psi(x,z_2,\ldots,z_n)\overline{\psi(y,z_2,\ldots,z_n)}\;.$$

The eigenvalues of the operator γ_ψ lie between 0 and 1 and are known as "natural occupation probabilities." We define the *nonfreeness of* ψ by

$$\mathfrak{C}(\psi) \;=\; -\sum p_j \log p_j - \sum (1-p_j)\log(1-p_j) \tag{2}$$

where the p_j are the natural occupation probabilities for ψ. This is the entropy of the free state built from the spectral decomposition of γ (viz. Section 9.4.1 of [14]). $\mathfrak{C}(\psi)=0$ if and only if ψ is a Slater determinant. The first sum in (2) is known as the "correlation entropy" [3, 6, 7]. Formula (2) itself has been introduced and applied in Ref. [12], where it is called "particle-hole symmetric correlation entropy."

The nonfreeness functional $\mathfrak{C}$ extends to mixed states of variable particle number so that free states, and only such states, have 0 nonfreeness. To discuss such states, we need to recall the concept of fermion Fock space and the second quantization of operators. Let $\mathcal{H}$ denote the 1-particle Hilbert space, and let

$$\mathcal{F}_{\mathcal{H}} \;=\; \mathbb{C}\oplus\mathcal{H}\oplus(\mathcal{H}\wedge\mathcal{H})\oplus(\mathcal{H}\wedge\mathcal{H}\wedge\mathcal{H})\oplus\cdots$$

denote the fermion Fock space over $\mathcal{H}$. The first summand on the right hand side ($\mathbb{C}$) is spanned by the vacuum vector

$$\Omega \;\equiv\; \mathbf{1}_{\mathbb{C}}\oplus 0\oplus 0\oplus\cdots\;.$$

For any $h\in\mathcal{H}$, the corresponding creator $a_h^\dagger$ and annihilator a_h are represented by bounded operators on $\mathcal{F}_{\mathcal{H}}$. The creator is the adjoint of the corresponding annihilator; any two annihilators a_g and a_h anticommute; and

$$a_g^\dagger a_h + a_h a_g^\dagger \;=\; \langle h|g\rangle \mathrm{I}_{\mathcal{F}_{\mathcal{H}}}\;, \tag{3}$$

where $\langle h|g\rangle$ denotes the inner product of g and h. Let $f_1, f_2,\ldots$ be any ordered orthonormal basis of $\mathcal{H}$, and set $a_j\equiv a_{f_j}$. The number operator on $\mathcal{F}_{\mathcal{H}}$ is

$$N \;=\; \sum a_j^\dagger a_j \tag{4}$$

(the operator so defined does not really depend on the choice of ordered orthonormal basis). For any finite subset $\mathbf{s}$ of $\mathbb{N}=\{1,2,3,\ldots\}$, set

$$a_{\mathbf{s}} \;=\; a_{s_1}a_{s_2}\cdots a_{s_n} \qquad\text{and}\qquad a_{\mathbf{s}}^\dagger \;=\; a_{s_n}^\dagger\cdots a_{s_2}^\dagger a_{s_1}^\dagger\;,$$

where $s_1 < s_2 < \ldots < s_n$ are the elements of $\mathbf{s} = \{s_1, s_2, \ldots, s_n\}$, indexed in increasing order. When $\mathbf{s}$ is the empty subset of $\mathbb{N}$, let $a_{\mathbf{s}}$ and $a_{\mathbf{s}}^\dagger$ denote the identity operator on $\mathcal{F}_{\mathcal{H}}$. The set of all vectors $a_{\mathbf{s}}^\dagger\Omega$ in $\mathcal{F}_{\mathcal{H}}$, where $\mathbf{s}$ ranges over finite subsets of $\mathbb{N}$, including the empty set, is an orthonormal basis of the fermion Fock space. For any $\mathbf{s} \subset \mathbb{N}$, the operator $a_{\mathbf{s}}^\dagger a_{\mathbf{s}}$ is an orthogonal projector.

For any density operator Δ on the fermion Fock space, the 1-particle statistical operator γ_Δ is defined such that

$$\langle h|\gamma_\Delta g\rangle \;=\; \mathrm{Tr}(\Delta a_g^\dagger a_h) \tag{5}$$

for any $g, h \in \mathcal{H}$, where $a_x^\dagger$ denotes the creator of x on $\mathcal{F}_{\mathcal{H}}$. γ_Δ is a Hermitian operator whose spectrum is contained in the interval $[0,1]$. The average particle number is $\mathrm{Tr}(\Delta N) = \mathrm{Tr}(\gamma_\Delta)$, so γ_Δ has finite trace if and only if the average particle number is finite.

Recall the class $\mathcal{D}$ of all density operators on $\mathcal{F}_{\mathcal{H}}$ that satisfy conditions (1) above. For any Hermitian operator ρ on $\mathcal{H}$ with finite trace and all eigenvalues in the interval $[0,1]$, there exists a unique free state, represented by a density operator $\Gamma_\rho \in \mathcal{D}$, whose 1-particle statistical operator is ρ, so that

$$\gamma_{\Gamma_\rho} = \rho \; . \tag{6}$$

Γ_ρ can be constructed explicitly as follows [14]. Let $p_1 \geq p_2 \geq \cdots$ be the list of positive eigenvalues of ρ, and let $f_1, f_2, \ldots$ be a list of corresponding eigenvectors. Set $a_j \equiv a_{f_j}$, and define the operators $a_{\mathbf{s}}^\dagger$ as above for finite subsets $\mathbf{s} = \{s_1, \ldots, s_n\} \subset \mathbb{N}$. Then

$$\Gamma_\rho \;=\; \sum_{\mathbf{s}} p(\mathbf{s}) \; |a_{\mathbf{s}}^\dagger\Omega\rangle\langle a_{\mathbf{s}}^\dagger\Omega| \tag{7}$$

with

$$p(\mathbf{s}) \;=\; \prod_{i\in\mathbf{s}} p_i \prod_{j\notin\mathbf{s}} (1-p_j) \; . \tag{8}$$

If $\Delta \in \mathcal{D}$, then γ_Δ has finite trace, and therefore Γ_{γ_Δ} can be constructed as above and is also in $\mathcal{D}$. Formula (6) shows that Γ_{γ_Δ} is the density operator of the free state with the same 1-particle statistics as Δ.

Let $S(X)$ denote the von Neumann entropy $-\mathrm{Tr}(X \log X)$ of a density operator X, and let $S(X|Y)$ denote the relative entropy $\mathrm{Tr}(X(\log X - \log Y))$ of two density operators X and Y [14, 15]. The von Neumann entropy and relative entropy of density operators are always nonnegative, but may equal $+\infty$. In particular, for density operators X and Y, $S(X|Y)$ is defined to equal $+\infty$ if the kernel of X is not contained in the kernel of Y.

For $\Delta \in \mathcal{D}$, we define the *nonfreeness of* Δ as

$$\mathfrak{C}(\Delta) \;=\; S(\Delta|\Gamma_{\gamma_\Delta}) \;. \tag{9}$$

This equals 0 if and only if $\Delta = \Gamma_{\gamma_\Delta}$, and it is never negative (though it may equal $+\infty$). In case the state is a pure state given by a n-electron wavefunction ψ, the corresponding density operator is

$$\Delta \;=\; 0 \oplus \cdots \oplus 0 \oplus \overset{n-particles}{|\psi\rangle\langle\psi|} \oplus 0 \oplus 0 \oplus \cdots$$

and it may be verified that $\mathfrak{C}(\Delta) = \mathfrak{C}(\psi)$.

Proposition 1 *Suppose* $\Delta \in \mathcal{D}$ *and*

$$-\sum p_j \log p_j - \sum (1-p_j)\log(1-p_j) \;<\; \infty \;, \tag{10}$$

where $p_1, p_2, \ldots$ *are the eigenvalues of* γ_Δ. *Then*

$$\mathfrak{C}(\Delta) \;\equiv\; S(\Delta|\Gamma_{\gamma_\Delta}) \;=\; -\sum p_j \log p_j - \sum (1-p_j)\log(1-p_j) - S(\Delta) \;. \tag{11}$$

The proof of Proposition 1 appears in Appendix A.

Proposition 1 means that the nonfreeness of a state represented by a density operator $\Delta \in \mathcal{D}$ is the amount that the von Neumann entropy of Δ falls short of the entropy of the corresponding free state Γ_{γ_Δ}, which is the largest von Neumann entropy possible for all states that have the same 1-particle operator γ_Δ.

Corollary 1 *Under the hypotheses of Proposition 1, the von Neumann entropy of a state satisfies*

$$S(\Delta) \;\leq\; -\sum p_j \log p_j - \sum (1-p_j)\log(1-p_j) \;,$$

with equality if and only $\Delta = \Gamma_{\gamma_\Delta}$.

Proof: This follows from equation (11) and the observation that $S(\Delta|\Gamma_{\gamma_\Delta})$ equals 0 if $\Delta = \Gamma_{\gamma_\Delta}$, otherwise $S(\Delta|\Gamma_{\gamma_\Delta})$ is strictly positive. □

Corollary 2 *Suppose* $\Delta \in \mathcal{D}$ *and* $\mathrm{rank}(\gamma_\Delta) = k$. *Then* $\mathfrak{C}(\Delta) \leq k$.

Proof: Since γ_Δ has rank k, the von Neumann entropy of $S(\Gamma_{\gamma_\Delta}) \le k < \infty$, and Proposition 1 implies that $\mathfrak{C}(\Delta) \le S(\Gamma_{\gamma_\Delta}) \le k$. □

The upper bound in Corollary 2 is not always attained. Indeed, $\mathfrak{C}(\Delta) = 0$ if $\mathrm{rank}(\gamma_\Delta) = 1$. Also, $\mathfrak{C}(\Delta) \le 1$ if $\mathrm{rank}(\gamma_\Delta) = 2$ (this can be shown using formula (23) of Appendix C). However, if $2m > 2$ is an even number, then there do exist states Δ such that $\mathrm{rank}(\gamma_\Delta) = 2m$ and $\mathfrak{C}(\Delta) = 2m$. For example, let $\{\phi_1, \ldots, \phi_m, \psi_1, \ldots, \psi_m\}$ be an orthonormal set in $\mathcal{H}$, and let Φ and Ψ denote Slater determinants in $\phi_1, \ldots, \phi_m$ and $\psi_1, \ldots, \psi_m$, respectively. Then

$$\mathfrak{C}\big(\tfrac{1}{\sqrt{2}}\Phi + \tfrac{1}{\sqrt{2}}\Psi\big) \;=\; 2m \;,$$

that is, the nonfreeness of $\frac{1}{\sqrt{2}}(\Phi + \Psi)$ attains the maximum possible for states of rank $2m$.

3 Nonfreeness of subsystems' states

The electronic state of a molecule determines the properties of any "subsystem" of the molecule's electrons. In this section we will consider subsystems of a special form, including those consisting of precisely those electrons that occupy a given region of space or a given bond orbital. If the electronic state of the molecule is given by a Slater determinant, then any subsystem is in a free state. But if the molecule is in a "correlated" state, the subsystem will typically be in a correlated state too. One would expect there to be less "correlation" in the subsystem than there is in the whole molecule, and indeed, nonfreeness behaves this way: it is monotone with respect to consideration of subsystems. The "monotonicity" of nonfreeness is a consequence of the monotonicity of quantum relative entropy, a very important and rather deep property of quantum entropy [16]. The monotonicity of quantum relative entropy was first established for density operators by Lindblad [17, 18] and later for general states on von Neumann algebras by Uhlmann [15, 19].

The kind of subsystem we consider here has the following general form. Let $\mathcal{H}_1$ be a (closed) subspace of the 1-particle space $\mathcal{H}$, and let $\mathcal{H}_2$ be the complementary subspace, so that $\mathcal{H} \cong \mathcal{H}_1 \oplus \mathcal{H}_2$. For example, if we want to consider the electronic subsystem associated to a region R of space, then $\mathcal{H}_1$ will be the space of spin-orbitals ψ such that $\psi(r, \sigma) = 0$ unless r lies in the region R. Let $\mathcal{F}_1$ and $\mathcal{F}_2$ denote the Fock spaces $\mathcal{F}_{\mathcal{H}_1}$ and $\mathcal{F}_{\mathcal{H}_2}$, respectively. The Fock spaces $\mathcal{F}_1$ and $\mathcal{F}_2$ may be regarded as subspaces of $\mathcal{F}_{\mathcal{H}}$: for example, $\mathcal{F}_1$ is isomorphic to the subspace of $\mathcal{F}_{\mathcal{H}}$ that is spanned by Slater determinants in spin-orbitals taken from $\mathcal{H}_1$. The whole Fock space $\mathcal{F}_{\mathcal{H}}$ is isomorphic to $\mathcal{F}_1 \otimes \mathcal{F}_2$ as follows [14]. Let $\{h_j\}$ be an orthonormal basis of $\mathcal{H}$ such that each h_j is either in $\mathcal{H}_1$ or in $\mathcal{H}_2$, and set $S = \{j \in \mathbb{N} : h_j \in \mathcal{H}_1\}$ and $S' = \mathbb{N} \setminus S$. The map

$$a^\dagger_{\mathbf{s}\cup\mathbf{s}'}\Omega \longleftrightarrow a^\dagger_{\mathbf{s}}\Omega \otimes a^\dagger_{\mathbf{s}'}\Omega \tag{12}$$

defined for $\mathbf{s} \subset S, \mathbf{s}' \subset S'$ extends to an isomorphism. If Δ is a density operator on $\mathcal{F}$, let

$$\Delta_1 \; = \; \mathrm{Tr}_{\mathcal{F}_2}(\Delta)$$

denote the partial trace of Δ over $\mathcal{F}_2$. This is a density operator on $\mathcal{F}_1$ that we will call the "restriction of Δ over $\mathcal{H}_1$."

From definition (5) of the 1-particle statistical operator, it follows that γ_{Δ_1} is the compression to $\mathcal{H}_1$ of the 1-particle statistical operator for Δ, i.e.,

$$\gamma_{\Delta_1} \; = \; P_1 \circ \gamma_\Delta \,\big|_{\mathcal{H}_1} \;, \tag{13}$$

where P_1 denotes the orthogonal projector on $\mathcal{H}$ whose range is $\mathcal{H}_1$.

We return to the subject of nonfreeness. For the rest of this section, all density operators are implicitly assumed to lie in the class $\mathcal{D}$, for we have only defined nonfreeness for density operators in this class. However, as we will discuss in Section 4, the definition of nonfreeness can be generalized to apply to *all* many-fermion states and the results of this section remain true in the greatest generality.

Proposition 2 *Let Δ be a density operator on the fermion Fock space over $\mathcal{H}$ and let $\mathcal{H}_1$ be a subspace of $\mathcal{H}$. Then $\mathfrak{C}(\Delta_1) \leq \mathfrak{C}(\Delta)$.*

Proof: If Γ_γ is the density operator of a free state, then its restriction over $\mathcal{H}_1$ is also a free state. In fact

$$(\Gamma_\gamma)_1 \; = \; \Gamma_{P_1\gamma|_{\mathcal{H}_1}} \;. \tag{14}$$

By (14) and (13), $(\Gamma_{\gamma_\Delta})_1 = \Gamma_{\gamma_{\Delta_1}}$. Thus, the inequality

$$\mathfrak{C}(\Delta) \; = \; S(\Delta|\Gamma_{\gamma_\Delta}) \; \geq \; S\big(\mathrm{Tr}_{\mathcal{F}_2}(\Delta)|\mathrm{Tr}_{\mathcal{F}_2}(\Gamma_{\gamma_\Delta})\big) \; = \; S\big(\Delta_1|(\Gamma_{\gamma_\Delta})_1\big) \; = \; S\big(\Delta_1|\Gamma_{\gamma_{\Delta_1}}\big) \; = \; \mathfrak{C}(\Delta_1)$$

follows from the monotonicity of relative entropy (viz. Lemma 2 of [18]). $\square$

Let Δ be a density operator on the Fock space over a Hilbert space $\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2$ and let Δ_1 and Δ_2 denote the restrictions of Δ over $\mathcal{H}_1$ and $\mathcal{H}_2$. We say that the two subsystems corresponding to $\mathcal{H}_1$ and $\mathcal{H}_2$ are "independent" if $\Delta \cong \Delta_1 \otimes \Delta_2$. We say they are "independent on the 1-particle level" if Δ and $\Delta_1 \otimes \Delta_2$ have the same 1-particle statistical operator, or (equivalently) if $\gamma_\Delta = \gamma_{\Delta_1} \oplus \gamma_{\Delta_2}$ with respect to the decomposition $\mathcal{H}_1 \oplus \mathcal{H}_2$ of $\mathcal{H}$. The nonfreeness of independent subsystems is additive, i.e.,

$$\mathfrak{C}(\Delta_1 \otimes \Delta_2) = \mathfrak{C}(\Delta_1) + \mathfrak{C}(\Delta_2) \ .$$

The next proposition states that the nonfreeness is *superadditive* if the subsystems are independent on the 1-particle level. This follows from the superadditivity of entropy and the fact that, for free states, independence on the 1-particle level implies independence, i.e., $\Gamma_{\gamma_1 \oplus \gamma_2} = \Gamma_{\gamma_1} \otimes \Gamma_{\gamma_2}$.

Proposition 3 *Let Δ be a density operator on the Fock space over a Hilbert space $\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2$ and let Δ_1 and Δ_2 denote the restrictions of Δ over $\mathcal{H}_1$ and $\mathcal{H}_2$. If $\gamma_\Delta = \gamma_{\Delta_1} \oplus \gamma_{\Delta_2}$ then*

$$\mathfrak{C}(\Delta) \ \geq \ \mathfrak{C}(\Delta_1) + \mathfrak{C}(\Delta_2) \ . \tag{15}$$

If $\mathfrak{C}(\Delta) < \infty$, then equality holds in (15) if and only if $\Delta \cong \Delta_1 \otimes \Delta_2$.

Proof: If $\gamma_\Delta = \gamma_{\Delta_1} \oplus \gamma_{\Delta_2}$ then $\Gamma_{\gamma_\Delta} \cong \Gamma_{\gamma_{\Delta_1}} \otimes \Gamma_{\gamma_{\Delta_2}}$. Superadditivity of relative entropy implies the inequality

$$\mathfrak{C}(\Delta) \ = \ S(\Delta | \Gamma_{\gamma_\Delta}) \ = \ S(\Delta \mid \Gamma_{\gamma_{\Delta_1}} \otimes \Gamma_{\gamma_{\Delta_2}}) \ \geq \ S(\Delta_1 | \Gamma_{\gamma_{\Delta_1}}) + S(\Delta_1 | \Gamma_{\gamma_{\Delta_2}}) \ = \ \mathfrak{C}(\Delta_1) + \mathfrak{C}(\Delta_2) \ ,$$

with the stated conditions for equality (see Corollary 5.21 of [15]). □

For example, consider a many-electron state in which there is a precise number of electrons in some region R_1 of space. The two subsystems consisting of (i) the electrons in R_1, and (ii) the electrons in the complementary region R_2, are independent on the 1-particle level. Therefore the nonfreeness of the state is greater than (or equal to) the nonfreeness of the restriction of the state over R_1 plus the nonfreeness of the restriction of the state over R_2.

More generally, Proposition 3 has the following consequence, whose proof appears in Appendix B.

Corollary 3 *Let $\mathcal{F}_\mathcal{H}$ denote the Fock space over a Hilbert space $\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2$ and let N_1 denote the number operator for the subspace $\mathcal{H}_1$. If Δ is a density operator on $\mathcal{F}_\mathcal{H}$ such that $N_1 \Delta = \Delta N_1 = n\Delta$ for some integer n, then*

$$\mathfrak{C}(\Delta) \ \geq \ \mathfrak{C}(\Delta_1) + \mathfrak{C}(\Delta_2)$$

where Δ_1 and Δ_2 denote the restrictions of Δ over $\mathcal{H}_1$ and $\mathcal{H}_2$.

3.1 Illustration: a highly correlated state of lattice fermions

Consider a system of $2L$ electrons, half of them of spin up and half of spin down, on a lattice of $2L$ sites, subject to the Hubbard Hamiltonian with an on-site repulsion of strength U and with nearest neighbor hopping of strength t. In the "atomic" limit, where t tends to 0 while U remains constant, the on-site repulsion forces there to be one electron at each lattice site. Let $\mathcal{H}_0$ denote the subspace of states for which there is only one electron per site. The compression of the Hubbard Hamiltonian to $\mathcal{H}_0$ is the zero operator to first order in t, but to *second* order in t, it is the Hamiltonian of the antiferromagnetic Heisenberg model. This second order effect, called "superexchange" by P. W. Anderson [20], can be justified rigorously [21] using degenerate perturbation theory [22, 23].

Thus, in the atomic limit, the ground state of the Hubbard model tends toward the ground state of the antiferromagnetic Heisenberg model, *considered as a state of the system of lattice fermions*. In this state there is one electron per site, and therefore the 1-electron density matrix is diagonal; moreover, every eigenvalue of the 1-electron density matrix is equal to $1/2$ thanks to spin symmetry. By Proposition 1, the nonfreeness of this state equals $4L$, which is the maximum possible for any many-electron state on a lattice of $2L$ sites, by Corollary 2.

The nonfreeness of the restriction of the ground state over one site is also as large as possible: it equals 1. If there were no correlation between sites, then the total nonfreeness would be $2L \times 1 = 2L$ by Proposition 3, but in fact the nonfreeness is $4L$, not $2L$. This means that half of the nonfreeness of the state is due to correlations between different sites.

4 Concluding remarks

The common message of this article and our Letter [13] is that the "correlation" intrinsic to a many-fermion state with density operator Δ may be quantified by comparing Δ to Γ_{γ_Δ}, the unique free state with 1-particle statistical operator γ_Δ.

In this article, we have used relative entropy to compare Δ to Γ_{γ_Δ}, but in [13] we used "fidelity" instead. There we defined

$$\mathrm{Corr}(\Delta) = -2\ \log\left(\mathrm{Tr}(\Delta^{1/2}\Gamma_{\gamma_\Delta}\Delta^{1/2})^{1/2}\right)\ . \tag{16}$$

That is a very reasonable choice, because "fidelity" has some nice technical properties, thanks to which Corr is monotone and additive just as $\mathfrak{C}$ is, $\mathrm{Corr}(\Delta)$ is always finite, and Corr is a continuous functional when restricted to the domain of n-electron states. In contrast, $\mathfrak{C}$ is not continuous, and sometimes equals $+\infty$. Nonetheless, we prefer $\mathfrak{C}$ to Corr because $\mathfrak{C}$ enjoys the superadditivity property expressed in Proposition 3, and because the nonfreeness of a pure state equals its "particle-hole symmetric correlation entropy" as defined in [12].

Although our discussion here and in [13] is limited to density operators in the class $\mathcal{D}$, nonfreeness and similar measures of fermion correlation can be extended to *infinite* systems as well. It is just a question of comparing two states. States of an infinite system are represented by positive linear functionals on the CAR algebra over the 1-particle Hilbert space $\mathcal{H}$. If ω is a state of the CAR algebra over $\mathcal{H}$, then there exists a unique generalized free state γ_ω such that $\omega(a_g^\dagger a_h) = \gamma_\omega(a_g^\dagger a_h)$ for all $g, h \in \mathcal{H}$, and $\mathfrak{C}(\omega)$ may be defined as the entropy of ω relative to γ_ω in the sense of Umegaki and Araki [15]. Similarly, $\mathrm{Corr}(\omega)$ may be defined as the negative logarithm of Uhlmann's transition probability [24, 25] connecting these states, which equals (16) if $\omega(X) = \mathrm{Tr}(\Delta X)$.

The functionals $\mathfrak{C}$ and Corr share a couple of remarkable properties. Both are invariant under Bogoliubov automorphisms of the CAR algebra, and both enjoy the following general monotonicity property, of which Proposition 2 is a special case. Suppose $\phi : \mathfrak{B} \longrightarrow \mathfrak{A}$ is a "quasifree completely positive map" between CAR algebras [14, Chapter 8.5]. If ω is a state on a CAR algebra $\mathfrak{B}$, and $\phi_*(\omega)$ denotes the state on $\mathfrak{A}$ induced by ϕ, then $\mathfrak{C}(\phi_*(\omega)) \leq \mathfrak{C}(\omega)$ and $\mathrm{Corr}(\phi_*(\omega)) \leq \mathrm{Corr}(\omega)$.

The invariance of nonfreeness under Bogoliubov transformations explains why the formula for $\mathfrak{C}(\Delta)$ is symmetric in p_j and $1 - p_j$. It must be so, for particle-hole duality is implemented by a Bogoliubov transformation.

Finally, we remark that a BCS ground state, which models the condensed state in the theory of conventional superconductivity, is also a kind of free state. According to our point of view that "electron correlation" means "nonfreeness," conventional superconductivity is *not* an example of a correlation phenomenon.

Appendix A

Here is the proof of Proposition 1.

Suppose that $\Delta \in \mathcal{D}$ and (10) holds. We want to show that

$$S(\Delta|\Gamma_{\gamma_\Delta}) \;=\; -\sum p_j \log p_j - \sum (1-p_j)\log(1-p_j) - S(\Delta) \;.$$

To do this we will use the following formula for the relative entropy of two density operators D and G, which is valid if $\mathrm{Ker}(G) \subset \mathrm{Ker}(D)$ or, equivalently, if $\overline{\mathrm{Range}(D)} \subset \overline{\mathrm{Range}(G)}$. In such cases the entropy of D relative to G is given by

$$S(D|G) \;=\; \sum_{j,k} |\langle \phi_j, \psi_k\rangle|^2 (d_j \log d_j - d_j \log g_k + g_k - d_j) \;, \tag{17}$$

where $\{\phi_j\}$ and $\{\psi_k\}$ are two orthonormal bases of $\overline{\mathrm{Range}(G)}$ consisting of eigenvectors of D and G, respectively, and d_j and g_k denote the respective eigenvalues [26]. The terms in the sum on the right hand side of (17) are all nonnegative, so $S(D|G)$ is a finite nonnegative number or $+\infty$. Formula (17) implies that

$$0 \;\leq\; S(D) + S(D|G) \;=\; -\mathrm{Tr}(D \log G) \tag{18}$$

if $-\mathrm{Tr}(D\log G) < \infty$. In the next paragraph we show that $\mathrm{Ker}(\Gamma_{\gamma_\Delta}) \subset \mathrm{Ker}(\Delta)$, so we may use formula (18) with Δ for D and Γ_{γ_Δ} for G. It follows that

$$S(\Delta|\Gamma_{\gamma_\Delta}) = -\mathrm{Tr}(\Delta \log \Gamma_{\gamma_\Delta}) - S(\Delta)$$

if $-\mathrm{Tr}(\Delta \log \Gamma_{\gamma_\Delta}) < \infty$. In the last paragraph of this proof, we show that $-\mathrm{Tr}(\Delta \log \Gamma_{\gamma_\Delta}) = -\sum p_j \log p_j - \sum (1-p_j)\log(1-p_j)$. That will prove statement (11).

First we establish that $\mathrm{Ker}(\Gamma_{\gamma_\Delta}) \subset \mathrm{Ker}(\Delta)$. Let $\{g_j\}_{j\in\mathbb{N}}$ be an orthonormal basis of $\mathcal{H}$ such that each g_j lies either in $\mathrm{Ker}(\gamma_\Delta)$ or in $\overline{\mathrm{Range}(\gamma_\Delta)}$, and let

$$\begin{aligned} K &= \{j \in \mathbb{N} : g_j \in \mathrm{Ker}(\gamma_\Delta)\} \\ R &= \{j \in \mathbb{N} : g_j \in \overline{\mathrm{Range}(\gamma_\Delta)}\} \;. \end{aligned} \tag{19}$$

Set $a_j \equiv a_{g_j}$, and define the operators $a^\dagger_{\mathbf{s}}$ as above for finite subsets $\mathbf{s} = \{s_1, \ldots, s_n\} \subset \mathbb{N}$. It is clear from the construction of Γ_{γ_Δ} by (7) and (8) that

$$\mathrm{Ker}(\Gamma_{\gamma_\Delta}) \;=\; \overline{\mathrm{span}}\{a^\dagger_{\mathbf{s}}\Omega : \mathbf{s} \cap K \neq \emptyset\} \;. \tag{20}$$

But the following argument shows that each $a^\dagger_{\mathbf{s}}\Omega$ such that $\mathbf{s}\cap K \neq \oslash$ is also in the kernel of Δ, whence we may conclude $\mathrm{Ker}(\Gamma_{\gamma_\Delta}) \subset \mathrm{Ker}(\Delta)$. Given $\mathbf{s}$ such that $\mathbf{s}\cap K \neq \oslash$, take $k \in \mathbf{s}\cap K$, and note that $a^\dagger_{\mathbf{s}}a_{\mathbf{s}} < a^\dagger_k a_k$ holds for the Hermitian projectors $a^\dagger_{\mathbf{s}}a_{\mathbf{s}}$ and $a^\dagger_k a_k$ because $k \in \mathbf{s}$. It follows that

$$0 \;\leq\; \langle a^\dagger_{\mathbf{s}}\Omega|\Delta a^\dagger_{\mathbf{s}}\Omega\rangle \;\leq\; \mathrm{Tr}(a_{\mathbf{s}}\Delta a^\dagger_{\mathbf{s}}) \;=\; \mathrm{Tr}(\Delta a^\dagger_{\mathbf{s}}a_{\mathbf{s}}) \;\leq\; \mathrm{Tr}(\Delta a^\dagger_k a_k) \;=\; \langle g_k|\gamma_\Delta g_k\rangle \;=\; 0\;.$$

This proves that $a^\dagger_{\mathbf{s}}\Omega \in \mathrm{Ker}(\Delta)$ since Δ is a positive semidefinite operator.

Finally, we verify that $-\mathrm{Tr}(\Delta\log\Gamma_{\gamma_\Delta}) = -\sum p_j\log p_j - \sum(1-p_j)\log(1-p_j)$. The operator $\log\Gamma_{\gamma_\Delta}$ restricted to $\mathrm{Ker}(\Gamma_{\gamma_\Delta})$ is supposed to be the zero operator. Accordingly, we may calculate $\mathrm{Tr}(\Delta\log\Gamma_{\gamma_\Delta})$ with respect to any orthonormal basis of $\overline{\mathrm{Range}(\Gamma_{\gamma_\Delta})}$. We use the basis $\{a^\dagger_{\mathbf{s}}\Omega : \mathbf{s}\subset R\}$, where R is defined in (19), the basis $\{g_j\}$ of $\mathcal{H}$ having been chosen so that $\gamma_\Delta(g_j) = p_j g_j$. For a finite subset $\mathbf{s}\subset\mathbb{N}$, define $p(\mathbf{s})$ by formula (8) and express

$$\Gamma_{\gamma_\Delta} = \sum_{\mathbf{s}\subset R} p(\mathbf{s})\;|a^\dagger_{\mathbf{s}}\Omega\rangle\langle a^\dagger_{\mathbf{s}}\Omega|$$

as a sum over finite subsets of R (cf. formula (7)). With this notation, we calculate

$$\begin{aligned}\mathrm{Tr}(\Delta\log\Gamma_{\gamma_\Delta}) &= \sum_{\mathbf{s}\subset R}\log p(\mathbf{s})\langle a^\dagger_{\mathbf{s}}\Omega|\Delta a^\dagger_{\mathbf{s}}\Omega\rangle \\ &= \sum_{j\in R}\log p_j \sum_{\mathbf{s}\subset R: j\in\mathbf{s}}\langle a^\dagger_{\mathbf{s}}\Omega|\Delta a^\dagger_{\mathbf{s}}\Omega\rangle \;+\; \sum_{j\in R}\log(1-p_j)\sum_{\mathbf{s}\subset R: j\notin\mathbf{s}}\langle a^\dagger_{\mathbf{s}}\Omega|\Delta a^\dagger_{\mathbf{s}}\Omega\rangle\;. \end{aligned} \tag{21}$$

By (5), $\mathrm{Tr}(\Delta a^\dagger_j a_j) = \langle g_j|\gamma_\Delta g_j\rangle = p_j$, and therefore, if $j\in R$, then

$$\begin{aligned}\sum_{\mathbf{s}\subset R: j\in\mathbf{s}}\langle a^\dagger_{\mathbf{s}}\Omega|\Delta a^\dagger_{\mathbf{s}}\Omega\rangle &= \sum_{\mathbf{s}\subset R: j\notin\mathbf{s}}\langle a^\dagger_{\mathbf{s}}\Omega|a_j\Delta a^\dagger_j a^\dagger_{\mathbf{s}}\Omega\rangle \;=\; \sum_{\mathbf{s}\subset R}\langle a^\dagger_{\mathbf{s}}\Omega|a_j\Delta a^\dagger_j a^\dagger_{\mathbf{s}}\Omega\rangle \\ &= \mathrm{Tr}(a_j\Delta a^\dagger_j) \;=\; \mathrm{Tr}(\Delta a^\dagger_j a_j) \;=\; p_j\;. \end{aligned} \tag{22}$$

Equations (21) and (22) imply that $\mathrm{Tr}(\Delta\log\Gamma_{\gamma_\Delta}) = \sum_{j\in R} p_j\log p_j \;+\; \sum_{j\in R}(1-p_j)\log(1-p_j)$.

Appendix B

Here is the proof of Corollary 3.

Let g and h be any vectors in $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively. With respect to the isomorphism (12), the operator $a^\dagger_g$ is identified with $a^\dagger_g\otimes I_2$, where I_2 denotes the identity operator on $\mathcal{F}_2$ and $a^\dagger_g$ denotes the creator of g on the Fock space $\mathcal{F}_1$ (with a slight abuse of notation). Similarly, a_h

is identified with $I_1 \otimes a_h$. Thus, the operator $\Delta a_g^\dagger a_h$ is identified with the operator $\Delta(a_g^\dagger \otimes a_h)$ on $\mathcal{F}_1 \otimes \mathcal{F}_2$. Let $P : \mathcal{F}_1 \longrightarrow \mathcal{F}_1$ denote the projector onto the n-particle subspace of $\mathcal{F}_1$. The hypothesis of the corollary means that $\Delta = (P \otimes I_2)\Delta(P \otimes I_2)$, where P denotes the projector onto the n-electron space in $\mathcal{F}_1$. Thus, $\mathrm{Tr}(\Delta a_g^\dagger a_h)$ equals

$$\mathrm{Tr}\big((P \otimes I_2)\Delta(P \otimes I_2)(a_g^\dagger \otimes a_h)\big) \;=\; \mathrm{Tr}\big(\Delta(P \otimes I_2)(a_g^\dagger \otimes a_h)(P \otimes I_2)\big) \;=\; \mathrm{Tr}\big(\Delta(P a_g^\dagger P \otimes a_h)\big) \;.$$

But this implies that $\mathrm{Tr}(\Delta a_g^\dagger a_h) = 0$, since $P a_g^\dagger P$ is the zero operator on $\mathcal{F}_1$. From the definition (5) of γ_Δ, we see that $\langle h | \gamma_\Delta g \rangle = 0$ when $g \in \mathcal{H}_1$ and $h \in \mathcal{H}_2$. This proves that γ_Δ has a direct sum decomposition with respect to the subspaces $\mathcal{H}_1$ and $\mathcal{H}_2$, and the corollary now follows from Proposition 3.

Appendix C

Suppose $\mathcal{H}$ is a two-dimensional Hilbert space and Δ is a density operator on $\mathcal{F}(\mathcal{H})$ that commutes with the number operator. Let p_1 and p_2 be the natural occupation probabilities and let q be the probability that there are two particles. Then

$$\begin{aligned}\mathfrak{C}(\Delta) \;=\; & -p_1 \log p_1 - (1-p_1)\log(1-p_1) - p_2 \log p_2 - (1-p_2)\log(1-p_2) \\ & + q \log q + (p_1 - q)\log(p_1 - q) + (p_2 - q)\log(p_2 - q) \\ & + (1 - p_1 - p_2 + q)\log(1 - p_1 - p_2 + q) \;. \end{aligned} \tag{23}$$

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