New measure of electron correlation

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Abstract

We propose to quantify the "correlation" inherent in a many-electron (or many-fermion) wavefunction ψ by comparing it to the unique uncorrelated state that has the same 1-particle density operator as does $|\psi\rangle\langle\psi|$.

Electron correlation is of fundamental importance in quantum chemistry and magnetism, but as yet there is no definitive way to quantify it: given the wavefunction $\psi(x_1, x_2, \ldots, x_N)$ representing the state of a system of N electrons, how much "correlation" is there in that N-electron state? By definition, a wavefunction that has the form of a Slater determinant represents an "uncorrelated" state, but how much "correlation" should be attributed to states that are *not* represented by a Slater determinant wavefunction? Some measures of "correlation" have already been advanced in the literature: the "degree of correlation" [1, 2] and the "correlation entropy" [3, 4, 5, 6, 7], for example. These correlation measures depend completely upon the eigenvalues of the 1-particle statistical operator γ, i.e., the operator with the integral kernel

$$\gamma(x,y) = N \int \psi(x, z_2, \ldots, z_N)\overline{\psi(y, z_2, \ldots, z_N)}\; dz_2 dz_3 \cdots dz_N \tag{1}$$

(supposing that the wavefunction ψ has norm 1, so that the trace of γ equals the number of electrons). The "degree of correlation" is inversely proportional to the sum of the squares of the eigenvalues of γ, and the "correlation entropy" is the Shannon entropy of those eigenvalues. Such measures ascribe the same amount of "correlation" to all wavefunctions that have the same 1-particle statistical operator. We feel it imposes a severe conceptual limitation to have to say that all wavefunctions having the same 1-particle operator (or the same 2-particle operator, for that matter) contain the same amount of correlation. Here we propose a new measure of correlation which does not suffer that limitation.

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States represented by Slater determinant wavefunctions are the only *pure* states are deemed "uncorrelated"; but certain *mixed states* should also be regarded as "uncorrelated", namely, the mixed "quasifree states." These have random particle number and must be represented by density operators (i.e., statistical operators of trace 1) on the fermion Fock space. Let $\mathcal{H}$ be the 1-electron Hilbert space, and let $a_f^\dagger$ and a_f denote the electron creation and annihilation operators for $f \in \mathcal{H}$. A density operator Γ on the fermion Fock space over $\mathcal{H}$ represents a "quasifree state" [8] if

$$\mathrm{Tr}\big(\Gamma a_{f_1}^\dagger a_{f_2}^\dagger \cdots a_{f_m}^\dagger a_{g_n} \cdots a_{g_2} a_{g_1}\big) \;=\; \delta_{mn}\ \det\big(\mathrm{Tr}(\Gamma a_{f_i}^\dagger a_{g_j})\big)_{i,j=1}^{n} \tag{2}$$

for all n and all $f_1, \ldots, f_m, g_1, \ldots, g_n \in \mathcal{H}$ (δ_{mn} denotes Kronecker's delta). The two-point correlations $\mathrm{Tr}(\Gamma a_f^\dagger a_g)$ determine all higher correlations under the quasifree state Γ, and in this sense a density operator satisfying (2) may be called "uncorrelated." The 1-particle operator γ defined by

$$\langle g, \gamma f\rangle \;=\; \mathrm{Tr}(\Gamma a_f^\dagger a_g) \tag{3}$$

has trace equal to the average particle number under Γ, i.e., $\mathrm{Tr}(\gamma) = \mathrm{Tr}(\Gamma \mathrm{N})$ where N denotes the number operator.

In case the average particle number is finite, we can reconstruct Γ from the 1-particle operator γ as follows. Let $\{\phi_i\}_{i=1}^{\infty}$ be a complete system of eigenvectors of γ with

$$\gamma(\phi_i) \;=\; \lambda_i \phi_i\ . \tag{4}$$

The eigenvalues λ_i are all between 0 and 1; we will interpret them as "occupation probabilities." Let $\mathcal{S}$ denote the class of all finite sets of positive integers, including the empty set. We can choose a random member of $\mathcal{S}$, that is, we can form a random set $\mathbf{s}$ of positive integers, by including i in $\mathbf{s}$ with probability λ_i (and excluding it with probability $1-\lambda_i$) independently of all other positive integers which may or may not be included in $\mathbf{s}$. This procedure produces the set $\mathbf{s}$ with probability

$$p(\mathbf{s}) \;=\; \prod_{i\in\mathbf{s}} \lambda_i \prod_{i\notin\mathbf{s}} (1-\lambda_i)\ . \tag{5}$$

For any nonempty $\mathbf{s} = \{i_1, \ldots, i_n\} \in \mathcal{S}$, let $\Psi_{\mathbf{s}}$ denote a normalized Slater determinant in the natural orbitals $\phi_{i_1}, \ldots, \phi_{i_n}$ (the phase of $\Psi_{\mathbf{s}}$ is arbitrary) and define

$$\mathrm{P}_{\mathbf{s}} \;=\; 0 \oplus \cdots \oplus 0 \oplus \overset{n-particle\ space}{|\Psi_{\mathbf{s}}\rangle\langle\Psi_{\mathbf{s}}|} \oplus 0 \oplus 0 \oplus \cdots$$

— a projector on the Fock space; in case $\mathbf{s}$ is the empty set, let $\mathrm{P}_{\mathbf{s}}$ denote projection onto the vacuum space. It can be shown [9] that

$$\Gamma \;=\; \sum_{\mathbf{s}\in\mathcal{S}} p(\mathbf{s}) \mathrm{P}_{\mathbf{s}} \tag{6}$$

satisfies (2) and (3). Slater determinants are special cases of quasifree states: if Ψ is a Slater determinant in the 1-electron orbitals $\psi_1, \ldots, \psi_N$ then the projector

$$\mathrm{P}_{\mathbf{s}} \;=\; 0 \oplus \cdots \oplus 0 \oplus \overset{N-particle\ space}{|\Psi\rangle\langle\Psi|} \oplus 0 \oplus 0 \oplus \cdots$$

represents a quasifree state whose 1-particle statistical operator is the projector onto the span of $\{\psi_1, \ldots, \psi_N\}$.

Our idea is to quantify the "correlation" in a many-electron wavefunction ψ by comparing it to the unique uncorrelated (quasifree) state Γ having the same 1-particle statistical operator γ as does $|\psi\rangle\langle\psi|$. The more $|\psi\rangle\langle\psi|$ resembles Γ, the less "correlated" we consider ψ to be: we would like to quantify the correlation inherent in ψ by some measure of the dissimilarity of $|\psi\rangle\langle\psi|$ and Γ. There are several ways one might measure this "dissimilarity" and thereby quantify electron correlation; our choice is the following one: we identify ψ with an N-particle vector in the Fock space and define

$$\mathrm{Corr}(\psi) \;=\; -\log\, \langle \psi, \Gamma\psi \rangle \;, \tag{7}$$

where Γ is the quasifree density (6) determined by the 1-particle statistical operator (1) for ψ. This quantity is nonnegative, and it equals 0 if and only if ψ is a Slater determinant. It can be seen from the discussion in the following paragraph that $\mathrm{Corr}(\psi) < \infty$.

It is easy to calculate $\mathrm{Corr}(\psi)$ if the expansion of ψ in Slater determinants in the eigenvectors of the 1-particle statistical operator (1) is available. The eigenvectors of γ are called natural orbitals and the corresponding eigenvalues lie between 0 and 1 [10]. Here, "natural orbitals" will refer only to eigenvectors of γ with *nonzero* eigenvalues. Recalling the notation in formulas (4) and (5) above, let $\mathcal{S}_N$ consist of all sets of N positive integers, each of which is the index of a natural orbital. The wavefunction ψ is a superposition of Slater determinants in the natural orbitals, even when the natural orbitals don't span the whole 1-particle space [11]. Thus $\psi = \sum_{\mathbf{s}\in\mathcal{S}_N} c(\mathbf{s})\Psi_{\mathbf{s}}$, where $\Psi_{\mathbf{s}}$ denotes a Slater determinant in the orbitals indexed by $\mathbf{s}$, and we have

$$\mathrm{Corr}(\psi) \;=\; -\log \sum_{\mathbf{s}\in\mathcal{S}_N} p(\mathbf{s})|c(\mathbf{s})|^2 \;, \tag{8}$$

where $p(\mathbf{s})$ is as defined in (5).

Remark 1: a formula for $\mathrm{Corr}(\psi)$ in 2-particle systems.

When $\psi(x,y) = -\psi(y,x)$ is a 2-electron wavefunction $\mathrm{Corr}(\psi)$ is a functional of the eigenvalues of the 1-particle statistical operator. In this case, it is known [12] that there exist an orthonormal system $\{f_1,\ g_1,\ f_2,\ g_2,\ \ldots\ \}$ of 1-electron orbitals and nonnegative numbers $p_1, p_2, \ldots$ such that

$$\psi(x,y) \;=\; \sum_{j=1,2,\ldots} \sqrt{p_j}\,\tfrac{1}{\sqrt{2}}\big(f_j(x)g_j(y) - g_j(x)f_j(y)\big) \;. \tag{9}$$

The wavefunctions f_i and g_i are natural orbitals with occupation probabilities p_i, for

$$\gamma \;=\; \sum_i p_i \big(|f_i\rangle\langle f_i| + |g_i\rangle\langle g_i| \big) \ .$$

In this case, one can calculate that

$$\mathrm{Corr}(\psi) \;=\; -\log \sum_i p_i \Big\{ p_i \prod_{j:j\neq i} (1-p_j) \Big\}^2 \tag{10}$$

using formula (8). Formula (10) shows that $\mathrm{Corr}(\psi)$ can be arbitrarily large, for the 2-electron wavefunction (9) can have arbitrarily small coefficients p_j [13].

It is interesting to apply formula (10) to an exactly solvable model: the "two-site Hubbard model" that was investigated in [6] as a study of "correlation entropy." This simple model can be used to illustrate the "kinetic exchange" correction to the Heitler-London theory of diatomic hydrogen [14]. There are two fixed spatial orbitals, labelled 1 and 2, whose span must accomodate two electrons, and the Hamiltonian is

$$H \;=\; -t \left(a^\dagger_{1\uparrow} a_{2\uparrow} + a^\dagger_{2\uparrow} a_{1\uparrow} + a^\dagger_{1\downarrow} a_{2\downarrow} + a^\dagger_{2\downarrow} a_{1\downarrow} \right) \;+\; U \left(a^\dagger_{1\uparrow} a_{1\uparrow} a^\dagger_{1\downarrow} a_{1\downarrow} + a^\dagger_{2\uparrow} a_{2\uparrow} a^\dagger_{2\downarrow} a_{2\downarrow} \right) \ ,$$

where U is the on-site repulsion energy (or attraction energy if $U < 0$). The 2-electron ground state of H depends only upon the dimensionless interaction parameter $u = U/t$. Denote this ground state by ψ_u. The ground state ψ_0 for $u = 0$ is a Slater determinant, and ψ_u tends towards the maximally correlated Heitler-London state $\frac{1}{\sqrt{2}}\big(a^\dagger_{1\uparrow} a^\dagger_{2\downarrow} + a^\dagger_{2\uparrow} a^\dagger_{1\downarrow}\big)|\ \rangle$ as u tends to $+\infty$. The correlation entropy (i.e., the Shannon entropy of the spectrum of the 1-particle operator) of ψ_u was found [6] to be strictly increasing in $|u|$, approaching its maximum possible value as $|u| \longrightarrow \infty$. The same is true of $\mathrm{Corr}(\psi_u)$. However, $\mathrm{Corr}(\psi_u)$ seems better behaved than the correlation entropy $S(\psi_u)$ for small values of $|u|$: the former is infinitely differentiable at $u = 0$ but the latter is only differentiable once there, and $\lim\limits_{u\to 0} S(\psi_u)/\mathrm{Corr}(\psi_u) = \infty$. If $S(\psi_u)$ is normalized so that $\lim\limits_{u\to\infty} S(\psi_u)/\mathrm{Corr}(\psi_u) = 1$, then $S(\psi_u)$ is larger than $\mathrm{Corr}(\psi_u)$ for all $|u| > 0$.

Remark 2: $\mathrm{Corr}(\psi)$ **is not a function of the** 1**-particle operator.**

We have seen that $\mathrm{Corr}(\psi)$ is a function of the spectrum of the 1-particle statistical operator in case ψ is a 2-electron wavefunction. In general, however, $\mathrm{Corr}(\psi)$ is not a function of the 1-particle statistical operator. To show this, we exhibit two 3-particle wavefunctions that have the same 1-particle statistical operator but contain different amounts of correlation. Let $e_1, e_2, \ldots, e_6$ be six orthonormal 1-electron orbitals, and let us denote 3-particle Slater determinants in these orbitals by listing the three indices involved (in increasing order) in between vertical lines, so that, for example,

$$|245| \;=\; \frac{1}{\sqrt{6}} \big(|e_2 e_4 e_5\rangle + |e_5 e_2 e_4\rangle + |e_4 e_5 e_2\rangle - |e_4 e_2 e_5\rangle - |e_2 e_5 e_4\rangle - |e_5 e_4 e_2\rangle \big) \ .$$

Consider the two 3-particle wavefunctions

$$\begin{aligned} \Psi &= \sqrt{\tfrac{2}{3}}\,|135| \;+\; \sqrt{\tfrac{1}{3}}\,|246| \\ \Phi &= \sqrt{\tfrac{1}{3}}\,\Big(|123| + |345| + |156|\Big)\ . \end{aligned}$$

These have the same 1-particle statistical operator

$$\begin{bmatrix} 2/3 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2/3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2/3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/3 \end{bmatrix}$$

but $\mathrm{Corr}(\Psi) \approx 4.08$ and $\mathrm{Corr}(\Phi) \approx 5.51$, taking logarithms to the base 2 in formula (8). (The matrix above displays only the matrix elements $\langle e_i | \gamma e_j \rangle$; outside this finite block all matrix elements are 0.)

Similar examples can be contrived to show that Corr is not a function of the m-particle statistical operator for any $m > 1$ either [15].

Remark 3: Corr **for mixed states.**

The measure (7) of fermion correlation can be extended to from pure states (given by wavefunctions) to mixed states (given by density operators). If D is a density operator, we would require "the correlation in D" to equal 0 if and only if D is a quasifree density, and of course "the correlation in D" must equal $\mathrm{Corr}(\psi)$ in case $D = |\psi\rangle\langle\psi|$. These requirements are met by

$$Corr(D) = -2\ \log\big(\mathrm{Tr}(D^{1/2}\Gamma D^{1/2})^{1/2}\big)\ , \tag{11}$$

where Γ is the quasifree density (2) corresponding to the 1-particle statistical operator γ defined by $\langle g, \gamma f\rangle = \mathrm{Tr}(D a_f^\dagger a_g)$ [16]. Formula (11) uses the generalized "transition probability" [17] or "fidelity" [18] between D and Γ:

$$\mathrm{Tr}(D^{1/2}\Gamma D^{1/2})^{1/2} \;=\; \big\| D^{1/2}\Gamma^{1/2}\, \big\|_{trace} \;=\; \mathrm{Tr}(\Gamma^{1/2} D \Gamma^{1/2})^{1/2}\ ,$$

This generalized transition probability recommends itself as a measure of the closeness of any two density operators — D and Γ in this case — because it enjoys several properties that distinguish it as a useful quantity in quantum information geometry [19, 17, 20, 21].

Note that (11) assigns positive correlation to most mixtures of uncorrelated states. For example, if ϕ_1 and ϕ_2 are orthogonal 1-particle wavefunctions, then

$$Corr\big(\tfrac{1}{2}|\phi_1\rangle\langle\phi_1| + \tfrac{1}{2}|\phi_2\rangle\langle\phi_2|\big) \;=\; 1$$

(taking logarithms to the base 2). It may seem odd to assign positive correlation to a 1-particle state, but it is due to our identification of "uncorrelated" with "quasifree." This means that a state is deemed "uncorrelated" only if the occupations of its natural orbitals are statistically independent. In the example, the natural orbitals ϕ_1 and ϕ_2 are each occupied with probability $1/2$, but the probability that *both* natural orbitals are occupied (at the same time) is not $1/2 \times 1/2$. We consider the state to be "correlated" because the occupation numbers of its natural orbitals are correlated random variables.

Conclusion

We have proposed a new way to measure the "correlation" in states of many-electron (or other many-fermion) systems. The idea is to compare the state to its unique reference state: the quasifree state with the same 1-particle statistical operator. To quantify the agreement between the many-electron state and its reference state, we have chosen the negative logarithm of the overlap, viz. formulas (7) and (11).

Our correlation measure, as formulated above, applies only to *finite* systems (atoms and molecules) but not infinite systems (solids). Other interesting measures of correlation are available for (infinite) uniform electron gases [3, 22, 23]. Can a serviceable formulation of our correlation measure be found for infinite systems as well?

The most intriguing property of the measure $\mathrm{Corr}(\psi)$ is the fact that it is not a function of the 1-particle statistical operator: wavefunctions with the same 1-particle statistical operator may have different amounts of "correlation." For wavefunctions of 2-electron systems, however, $\mathrm{Corr}(\psi)$ is a function of the eigenvalues of the 1-particle operator, viz. formula (10). Further investigation of the comportment of $\mathrm{Corr}(\psi)$ is underway, to see whether it conforms to what we would intuitively expect from a measure of electron correlation.

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[8] We adopt the terminology of Section 6.2.3 of Reference [26]. States satisfying (2) would be described more precisely as normal “gauge-invariant quasi-free” states, as in Example 5.2.20 of *Operator Algebras and Quantum Statistical Mechanics 2* by O. Bratteli and D. W. Robinson, Springer-Verlag, Berlin, 1997.

[9] See Example 6.5 of Reference [26].

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[11] See Lemma 1.2 of Reference [27].

[12] See Theorem 4.2 of Reference [27]. Perhaps the earliest reference to this fact is P.-O. Löwdin and H. Shull, *Natural orbitals in the quantum theory of two-electron systems*, Physical Review 101 (6) (1956) 1730 - 1739.

[13] Note that this argument does not work for fermions with a finite-dimensional 1-particle space: in such cases the correlation of a 2-fermion wavefunction has a finite upper bound.

[14] P. Fazekas. *Lecture Notes on Electron Correlation and Magnetism.* World Scientific, Singapore, 1999. See Section 2.5.2.

[15] However, in view of C. N. Yang's conjecture that the superconducting state is characterized by the existence of an eigenvalue of the 2-particle statistical operator of order N in the thermodynamic limit $N \longrightarrow \infty$, we conjecture that there might be lower bounds on Corr

when N is large and the 2-particle operator has an eigenvalue of order N. See *Concept of Off-Diagonal Long-Range Order and the quantum phases of liquid He and of superconductors*, by C. N. Yang, Reviews of Modern Physics 34 (4) (1962) 694 - 704. Yang's conjecture is persuasively promoted in Reference [27].

[16] Here $Corr(D)$ is only defined for D such that $\mathrm{Tr}(D\mathrm{N}) < \infty$, i.e., for mixed states with finite average particle number, because we want Γ in (11) to be a density operator.

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