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Interacting electrons, spin statistics, and information theory

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We consider a nearly (or quasi) uniform gas of interacting electrons for which spin statistics play a crucial role. A previously developed procedure, based on the extension of the Levy–Lieb constrained search principle and Monte Carlo sampling of electron configurations in space, allows us to approximate the form of the kinetic-energy functional. For a spinless electron gas, this procedure led to a correlation term, which had the form of the Shannon entropy, but the resulting kinetic-energy functional does not satisfy the Lieb–Thirring inequality, which is rigorous and one of the most general relations regarding the kinetic energy. In this paper, we show that when the fermionic character of the electrons is included via a statistical spin approach, our procedure leads to correlation terms, which also have the form of the Shannon entropy and the resulting kinetic-energy functional *does* satisfy the Lieb–Thirring inequality. In this way we further strengthen the connection between Shannon entropy and electron correlation and, more generally, between information theory and quantum mechanics. © 2010 American Institute of Physics. [doi:10.1063/1.3280953]

I. INTRODUCTION

In a series of previous publications,^{1–3} we developed an internally consistent variational procedure to approximate the kinetic-energy functional from a trial N -electron wave function. In brief, there are four essential steps: (1) the factorization of the $3N$ -dimensional wave function (squared) in terms of the standard (3-dimensional) electron density $\rho(\mathbf{r})$ and the $3(N-1)$ -dimensional conditional electron density; (2) the extension of the Levy–Lieb constrained search principle to this formalism; (3) the determination of the form of the $N-1$ conditional electron density; and (4) a Monte Carlo (MC) evaluation of the resulting multidimensional integrals. This procedure was applied to a nearly uniform spinless electron gas in which there are small fluctuations, due solely to Coulombic interactions, which average to zero. The results showed that the kinetic-energy functional could be written as the sum of two terms from information theory.⁴ One term resembles the Fisher information^{5,6} (analytical result), which is a measure of localization. The other term resembles the Shannon entropy⁷ (numerical result), which is a measure of delocalization. However, this kinetic-energy functional does not have the correct limiting behavior for the non interacting uniform electron gas. Also, it does not satisfy the Lieb–Thirring inequality $\langle \psi | \frac{1}{2} \nabla^2 | \psi \rangle \geq C_0 \int \rho^{5/3} d\mathbf{r}$,⁸ which is rigorous and one of the most general relations regarding the kinetic energy. In this paper we show that by introducing the fermionic character of the electrons via a statistical spin approach we obtain a kinetic-energy functional of the same form but which *does* satisfy the Lieb–Thirring inequality.

This kinetic-energy functional strengthens the connection between Shannon entropy and electron correlation, which has been explored in several recent publications.^{6,9–13} In the next sections, we report the main aspects of the procedure in order to introduce the reader to the new conceptual and numerical aspects and we then show results for the nearly uniform electron gas. Appendix A reports relevant technical aspects of the MC calculations.

II. LEVY–LIEB CONSTRAINED SEARCH PRINCIPLE

The *Levy–Lieb constrained search principle* can be used to determine the kinetic-energy functional for the ground state of a system of N electrons. Formally, the constrained minimum energy is¹⁴

$$E_0 = \min_{\rho} \left(\min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} | \Psi \rangle + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right), \quad (1)$$

where $v(\mathbf{r})$ is the external potential. In Eq. (1) the second term is manifestly not universal and our focus in this paper is on the first term [see Eq. (7) of Ref. 2].

Note that in Eq. (1), the inner minimization is restricted to all N -electron wave functions $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ leading to $\rho(\mathbf{r})$, while the outer minimization searches over all electron densities which integrate to N . In principle, the kinetic-energy functional is thereby determined as the expectation value of the kinetic energy for the optimum N -electron wave function in the inner minimization. However, the N -electron wave function is unknown and we must, in practice, develop a formulation which allows us to write Eq. (1) in terms of $\rho(\mathbf{r})$ only. This can be achieved by a formalism in which the N -electron wave function (squared) is expressed in terms of the one-electron (probability) density $p(\mathbf{r}) = p(\mathbf{r}_1) = \int |\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N$ [so that $\rho(\mathbf{r}) = Np(\mathbf{r})$] and the $N-1$ conditional electron density $f(\mathbf{r}_2, \dots, \mathbf{r}_N | \mathbf{r}_1)$ as Ψ^2

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$=p \cdot f$.¹⁵ Thus, for a fixed configuration of one of the electrons, $f(\mathbf{r}_2, \dots, \mathbf{r}_N | \mathbf{r}_1)$ is the probability of finding an $N-1$ electron configuration of the other electrons. Therefore, f changes as the configuration of electron 1 changes and the conditional electron density is a function of the coordinates of electrons 1 through N (not simply the coordinates of electrons 2 through N). Because the N -electron wave function is normalized, $\int_{\Omega_{N-1}} d\mathbf{r}_2 \dots d\mathbf{r}_N f(\mathbf{r}_2 \dots \mathbf{r}_N | \mathbf{r}_1) = 1, \forall \mathbf{r}_1$ and integration of f over the coordinates of all the electrons gives N . The conditional electron density must be symmetric with respect to the exchange of electron 1 and any of the other electrons and because the N -electron wave function must be antisymmetric with respect to the exchange of any two electrons, the conditional electron density must satisfy the following mathematical conditions:^{1,2,16}

$$(i) \quad f(\mathbf{r}_1 \dots \mathbf{r}_i \dots \mathbf{r}_{k-1} \mathbf{r}_{k+1} \dots \mathbf{r}_N | \mathbf{r}_k) = 0, \\ \text{for } \mathbf{r}_i = \mathbf{r}_k; \forall i, k. \\ (ii) \quad f(\mathbf{r}_1 \dots \mathbf{r}_i \dots \mathbf{r}_j \dots \mathbf{r}_{k-1} \mathbf{r}_{k+1} \dots \mathbf{r}_N | \mathbf{r}_k) = 0, \\ \text{for } \mathbf{r}_i = \mathbf{r}_j; \forall i, j \neq k. \quad (2)$$

These two mathematical conditions, resulting solely from Coulombic repulsion, ensure that the probability of any two electrons having the same position is zero. Equation (1) can now be rewritten as¹⁷

$$E_0 = \min_{\rho} \left(\frac{1}{8} \int \frac{|\nabla \rho(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)} d\mathbf{r}_1 + \min_f [\Gamma[f, \rho]] \right) \\ + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}, \quad (3)$$

where $\Gamma[f, \rho] = I_{\text{nonloc}}[f, \rho] + C_{ee}[f, \rho]$, with

$$I_{\text{nonloc}}[f, \rho] = \int \rho(\mathbf{r}_1) \left[\frac{1}{8} \int_{\Omega_{N-1}} \frac{|\nabla_{\mathbf{r}_1} f(\mathbf{r}_2, \dots, \mathbf{r}_N | \mathbf{r}_1)|^2}{f(\mathbf{r}_2, \dots, \mathbf{r}_N | \mathbf{r}_1)} \right. \\ \left. \times d\mathbf{r}_2 \dots d\mathbf{r}_N \right] d\mathbf{r}_1 \\ = \int \rho(\mathbf{r}_1) I[f, \rho(\mathbf{r}_1)] d\mathbf{r}_1 \quad (4)$$

and

$$C_{ee}[f, \rho] = \int \rho(\mathbf{r}_1) \left[\frac{(N-1)}{2} \int_{\Omega_{N-1}} \frac{f(\mathbf{r}_2, \dots, \mathbf{r}_N | \mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right. \\ \left. \times d\mathbf{r}_2 \dots d\mathbf{r}_N \right] d\mathbf{r}_1 \\ = \int \rho(\mathbf{r}_1) C[f, \rho(\mathbf{r}_1)] d\mathbf{r}_1. \quad (5)$$

Here I_{nonloc} is termed the Shannon integral (the reason for this choice will become clear when the link to information theory is discussed in Sec. VII) and C_{ee} is termed the Coulomb integral. The last equalities define the quantities $I[f, \rho(\mathbf{r}_1)]$ and $C[f, \rho(\mathbf{r}_1)]$, respectively.

In Eq. (3) the first and second terms are manifestly universal. The first is a kinetic energy term which, as discussed in Ref. 17, is identical to the well-known Weizsäcker term, T_W .¹⁸ For the second, one part, I_{nonloc} [see Eq. (4)], is a kinetic energy term while the other part, C_{ee} [see Eq. (5)], is a potential energy term. In Eq. (3) no kinetic energy term has been omitted and T_W and I_{nonloc} therefore comprise the (full) interacting kinetic energy (not the Kohn–Sham kinetic energy). Clearly, the first kinetic energy term is a functional of the electron density. Our focus in Secs. III–V is on the second kinetic energy term which is a functional of the $N-1$ conditional electron density and our goal is to express this quantity as a functional of the electron density.

III. SPINLESS ELECTRON GAS

The form of the $N-1$ conditional electron density is unknown but it can be built on the basis of physical arguments and the above mathematical conditions.^{1,2} The essence of the idea is that a gas of electrons does not display correlation effects, as long as there are no direct electron-electron interactions, except those of the basic Fermi distribution, or occupation of levels, for noninteracting electrons. However, when direct electron-electron interactions are switched on, each electron feels the presence of all the others in a non-trivial way. This means that the spatial distribution of the electrons is heavily governed by the fact that they optimize those correlations such that the spatial arrangement fulfills the minimum energy requirement. Thus, the conditional electron density is likely to be well described as a function of the electron-electron distance as $f = f(1/|\mathbf{r}_i - \mathbf{r}_j|)$. From this physical argument and the above mathematical conditions, the proposed conditional electron density f is

$$f = f(\mathbf{r}_2 \dots \mathbf{r}_N | \mathbf{r}_1) = e^{D_f(\mathbf{r}_1)} \cdot f', \quad (6)$$

where f' is the non-normalized conditional electron density, and e^{D_f} acts as the normalization factor. In detail,

$$f' = \prod_{n=2, N} e^{-\gamma E_H(\mathbf{r}_1, \mathbf{r}_n)} \prod_{i>j \neq 1} e^{-\beta E_H(\mathbf{r}_i, \mathbf{r}_j)}, \quad (7)$$

where

$$E_H(\mathbf{r}_1, \mathbf{r}_n) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_n|}, \quad E_H(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (8)$$

while

$$e^{-D_f(\mathbf{r}_1)} = \int d\mathbf{r}_2 \dots d\mathbf{r}_N \prod_{n=2, N} e^{-\gamma E_H(\mathbf{r}_1, \mathbf{r}_n)} \prod_{i>j \neq 1} e^{-\beta E_H(\mathbf{r}_i, \mathbf{r}_j)} \quad (9)$$

and we note that for $N=2$, $e^{-D_f(\mathbf{r}_1)} = \int d\mathbf{r}_2 e^{-\gamma E_H(\mathbf{r}_1, \mathbf{r}_2)}$ so that $f = e^{-\gamma E_H(\mathbf{r}_1, \mathbf{r}_2)} / \int d\mathbf{r}_2 e^{-\gamma E_H(\mathbf{r}_1, \mathbf{r}_2)}$.

Looking toward numerical evaluation, $I[f, \rho]$ and $C[f, \rho]$ can be expressed as³

$$I[f, \rho(\mathbf{r}_1)] = \left[\frac{1}{8} \int_{\Omega_{N-1}} d\mathbf{r}^{N-1} \frac{|\vec{\nabla}_{\mathbf{r}} f|^2}{f} \right]_{\rho(\mathbf{r}_1)} \quad (10)$$

and

$$C[f, \rho(\mathbf{r}_1)] = \left[\frac{1}{N} \sum_{i=1, N} \sum_{j>i} \int_{\Omega_{N-1}} d\mathbf{r}^{N-1} \frac{f}{|\mathbf{r}_i - \mathbf{r}_j|} \right]_{\rho(\mathbf{r}_1)} \quad (11)$$

so that

$$\begin{aligned} \Gamma[f, \rho] &= \int \rho(\mathbf{r}_1) [I[f, \rho(\mathbf{r}_1)] + C[f, \rho(\mathbf{r}_1)]] d\mathbf{r}_1 \\ &= \int \rho(\mathbf{r}_1) \Xi[f, \rho(\mathbf{r}_1)] d\mathbf{r}_1, \end{aligned} \quad (12)$$

where the last equality defines $\Xi[f, \rho(\mathbf{r}_1)]$ (we keep the explicit dependence on f because in Sec. IV we will introduce a new conditional electron density).

Because of the way f is constructed, the minimization with respect to f is reduced to a minimization with respect to the parameters γ and β

$$E[\rho] = \min_f (\Gamma[f, \rho]) = \min_{\gamma, \beta} (\Gamma[f_{\gamma, \beta}, \rho]). \quad (13)$$

We now consider the minimization of $\Gamma[f_{\gamma, \beta}, \rho]$ with respect to γ and β . This gives a functional of $\rho(\mathbf{r}_1)$ after integration over all $N-1$ variables except \mathbf{r}_1 . The relevant question is how to solve the $3(N-1)$ -dimensional integrals in order to evaluate $\Xi[f, \rho(\mathbf{r}_1)] = I[f, \rho(\mathbf{r}_1)] + C[f, \rho(\mathbf{r}_1)]$. It turns out that this expression can be efficiently evaluated via MC sampling¹⁹ (see Appendix A, Section A 1 for details regarding this procedure). We choose $\beta = \gamma$ because, at least at this stage, each exponential term of f expresses the same physics. The resulting expressions for $I[f, \rho]$ and $C[f, \rho]$ are²⁰

$$I[f, \rho(\mathbf{r}_1)] = -\frac{\gamma^2}{8} \langle \tilde{Q} \rangle_f^2 + \frac{\gamma^2}{8} \langle P \rangle_f \quad (14)$$

and

$$C[f, \rho(\mathbf{r}_1)] = \langle R \rangle_f, \quad (15)$$

where $\langle \cdot \rangle_f$ is the ensemble average obtained by sampling the conditional electron density and, with $\tilde{q}_n \doteq \tilde{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_n)$,

$$\tilde{Q} \doteq \sum_{n=2, N} \tilde{q}_n, \quad (16)$$

$$P \doteq \sum_{i \neq 1} \sum_{j \neq 1} [\tilde{q}_i \cdot \tilde{q}_j], \quad (17)$$

$$R \doteq \frac{1}{N} \sum_{i=1, N} \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (18)$$

Application of the MC procedure led to numerical evidence for the existence of a minimum for $\Xi[f, \rho(\mathbf{r}_1)]$ as a function of γ .³ This corroborated the conjecture that the problem is variational and allowed us to find the optimal γ . Having the optimal γ for the different densities, we could fit the numerical results to a convenient functional form, and the result was that $I[f, \rho]$ was well fit by a logarithmic expression. In this way we obtained the kinetic-energy functional for the spinless electron gas

$$K_{\text{spinless}}[\rho] = T_W + \int \rho(\mathbf{r}_1) (A + B \ln \rho(\mathbf{r}_1)) d\mathbf{r}_1. \quad (19)$$

Unfortunately, $K_{\text{spinless}}[\rho]$ does not satisfy the Lieb–Thirring inequality $\langle \psi | \frac{1}{2} \nabla^2 | \psi \rangle \geq C_0 \int \rho^{5/3} d\mathbf{r}$,⁸ which is rigorous and one of the most general relations regarding the kinetic energy and, more evidently, $K_{\text{spinless}}[\rho]$ does not have the correct limiting behavior for the uniform electron gas. The problem lies in the fact that the conditions on $f(\mathbf{r}_2, \dots, \mathbf{r}_N | \mathbf{r}_1)$ in Eq. (2) are only necessary and not sufficient if the particles are fermions. In fact, the conditional electron density must satisfy the same conditions even if the particles are bosons because the Coulomb interaction would lead to a singularity for any $r_i = r_j$ (for any $i \neq j; i, j = 1, N$). Thus, in practice, the term $(A + B \ln \rho(\mathbf{r}_1))$ only expresses correlations among electrons due to their Coulomb interactions. In order to overcome this problem we must include the fermionic character of the electrons in the conditional electron density via the Pauli principle.

IV. STATISTICAL SPIN APPROACH: PAULI WEIGHTING FUNCTION

In order to include the fermionic character of the electrons we modify the form of the conditional electron density, taking care that the properties of Eq. (2) are preserved. Thus the two mathematical conditions of Eq. (3), resulting solely from Coulombic repulsion, are strengthened to ensure that, in accord with the Pauli exclusion principle, the probability of any two same-spin electrons having the same position is zero (even if the Coulomb interaction is switched off).

The proposed new conditional electron density, renamed g , is

$$g = g(\mathbf{r}_2 \dots \mathbf{r}_N | \mathbf{r}_1) = e^{D_g(\mathbf{r}_1)} \cdot p \cdot f', \quad (20)$$

where f' is the same non-normalized conditional electron density introduced above [see Eq. (7)]. Here p is termed the Pauli weighting function and e^{D_g} acts as the new normalization factor to ensure that $\int_{\Omega_{N-1}} d\mathbf{r}_2 \dots d\mathbf{r}_N g(\mathbf{r}_2 \dots \mathbf{r}_N | \mathbf{r}_1) = 1, \forall \mathbf{r}_1$ and that integration of g over the coordinates of all the electrons gives N . In detail,

$$p = \prod_{\text{Pauli pairs}} e^{-\alpha |\mathbf{r}_i - \mathbf{r}_{pp(i)}|}, \quad (21)$$

while

$$\begin{aligned} e^{-D_g(\mathbf{r}_1)} &= \int d\mathbf{r}_2 \dots d\mathbf{r}_N \prod_{N/2 \text{ Pauli pairs}} e^{-\alpha |\mathbf{r}_i - \mathbf{r}_{pp(i)}|} \\ &\times \prod_{n=2, N} e^{-\gamma E_H(\mathbf{r}_1, \mathbf{r}_n)} \prod_{i>j \neq 1} e^{-\beta E_H(\mathbf{r}_i, \mathbf{r}_j)}, \end{aligned} \quad (22)$$

where ‘‘Pauli pairs’’ are defined unambiguously in the following way: All $N(N-1)/2$ possible pairs of electrons are listed and ordered from nearest to farthest. The nearest pair of electrons is the first Pauli pair and both these electrons are eliminated from every instance in the list. This procedure is repeated in the refreshed list until $N/2$ Pauli pairs are obtained. Inclusion of the Pauli weighting function ensures that the new conditional electron density captures much of the fermionic character of the N -electron wave function. How-

ever, the Pauli weighting function is not rigorous and thereby constitutes the primary approximation of our approach.

In Eq. (21), the modulus $|\mathbf{r}_i - \mathbf{r}_{pp(i)}|$ relates electron i , one of $N/2$ electrons, to $pp(i)$, its *unique* “Pauli paired” electron. A set of Pauli pairs with even one pair of electrons that are far from each other have weight exponentially less than a set with all pairs of electrons that are close to each other. Thus the exponent $\alpha|\mathbf{r}_i - \mathbf{r}_{pp(i)}|$ assumes the meaning of an effective “spin interaction.” Basically, this process sorts out the closest pairs and implicitly assumes that they are of opposite spin. This approximation should be valid for the high density regime where statistically one can always find a particle with opposite spin within the nearest neighborhood. We have therefore named this the statistical spin approach. If the Coulomb interaction is switched off, each pair collapses at a point, but the average density is unaffected and the Fermi limit of the kinetic-energy functional is obtained when the proper value of α is used (see below). Alternately, one could assign an explicit spin σ_i to each particle and specifically sort out nearest pairs of opposite spin with the closure condition $\sum_i \sigma_i = 0$. However this requires a larger computational effort (as one must also sample in position and for dense systems) and test runs with explicit spin show essentially no difference from the current results.

V. MC EVALUATION

For the MC evaluation, we write

$$\begin{aligned} I[g, \rho(\mathbf{r}_1)] &= \left[\frac{1}{8} \int_{\Omega_{N-1}} d\mathbf{r}^{N-1} g \left| \frac{\vec{\nabla}_1 g}{g} \right|^2 \right]_{\rho(\mathbf{r}_1)} \\ &= \left\langle \frac{1}{8} \left| \frac{\vec{\nabla}_1 g}{g} \right|^2 \right\rangle_{g, \rho(\mathbf{r}_1) = \text{const}}. \end{aligned} \quad (23)$$

The acceptance rule for the importance sampling is

$$a(\text{old} \rightarrow \text{new}) = \min\left(1, \frac{g_{\text{new}}}{g_{\text{old}}}\right), \quad (24)$$

$$\begin{aligned} \frac{g_{\text{new}}}{g_{\text{old}}} &= \frac{p_{\text{new}}}{p_{\text{old}}} e^{-\gamma(E_H(\mathbf{r}_1, \mathbf{r}_k^{\text{new}}) - E_H(\mathbf{r}_1, \mathbf{r}_k^{\text{old}}))} \\ &\times \prod_{i \neq 1, k} e^{-\beta(E_H(\mathbf{r}_i, \mathbf{r}_k^{\text{new}}) - E_H(\mathbf{r}_i, \mathbf{r}_k^{\text{old}}))}, \end{aligned} \quad (25)$$

where k labels the attempted electron move. If the moved electron does not change its Pauli paired, then the $p^{\text{new}}/p^{\text{old}}$ term is simply

$$\frac{p_{\text{new}}}{p_{\text{old}}} = e^{-\alpha(|\mathbf{r}_k^{\text{new}} - \mathbf{r}_{pp(k)}^{\text{new}}| - |\mathbf{r}_k^{\text{old}} - \mathbf{r}_{pp(k)}^{\text{old}}|)}. \quad (26)$$

If the moved electron changes its Pauli paired, all pairs may change and one must consider all new pairs and distances in the acceptance rule.

Working out Eq. (23),

$$\begin{aligned} \left| \frac{\vec{\nabla}_1 g}{g} \right|^2 &= \left| \vec{\nabla}_1 D_g(\mathbf{r}_1) - \gamma \sum_{i=2, N} \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i) \right. \\ &\quad \left. - \alpha \vec{\nabla}_1 |\mathbf{r}_1 - \mathbf{r}_{pp(1)}| \right|^2. \end{aligned} \quad (27)$$

It holds

$$\vec{\nabla}_1 |\mathbf{r}_1 - \mathbf{r}_{pp(1)}| = \mathbf{u}_p, \quad (28)$$

$$\vec{\nabla}_1 D_g(\mathbf{r}_1) = \alpha \langle \mathbf{u}_p \rangle_g + \gamma \left\langle \sum_{i=2, N} \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i) \right\rangle_g, \quad (29)$$

where \mathbf{u}_p is the unit vector along the direction defined by the vector $\mathbf{r}_1 - \mathbf{r}_{pp(1)}$. Thus,

$$\begin{aligned} \left| \frac{\vec{\nabla}_1 g}{g} \right|^2 &= \gamma^2 \sum_{i=2, N} \sum_{j=2, N} [\vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i) \cdot \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_j)] \\ &\quad + 2\alpha\gamma \mathbf{u}_p \cdot \sum_{i=2, N} \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i) + \alpha^2 + |\vec{\nabla}_1 D_g(\mathbf{r}_1)|^2 \\ &\quad - \vec{\nabla}_1 D_g(\mathbf{r}_1) \cdot \sum_{i=2, N} \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i) \\ &\quad - \alpha \vec{\nabla}_1 D_g(\mathbf{r}_1) \cdot \mathbf{u}_p. \end{aligned} \quad (30)$$

Using Eq. (29) to reformulate the last three terms,

$$\begin{aligned} \left| \frac{\vec{\nabla}_1 g}{g} \right|^2 &= \gamma^2 \sum_{i=2, N} \sum_{j=2, N} [\vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i) \cdot \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_j)] \\ &\quad + 2\alpha\gamma \mathbf{u}_p \cdot \sum_{i=2, N} \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i) + \alpha^2 - \alpha^2 \langle \mathbf{u}_p \rangle^2 \\ &\quad - \gamma^2 \left\langle \sum_{i=2, N} \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i) \right\rangle^2 \\ &\quad - 2\alpha\gamma \langle \mathbf{u}_p \rangle \cdot \left\langle \sum_{i=2, N} \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i) \right\rangle. \end{aligned} \quad (31)$$

In Eq. (31), the last three terms [coming from $\vec{\nabla}_1 D_g(\mathbf{r}_1)$] must vanish for a uniform (in particular, isotropic) distribution and, indeed, they do vanish in our numerical evaluations. The third term, α^2 , is the only one surviving for a uniform electron gas. We therefore choose $\alpha = \sqrt{C_F} r_0$, where C_F is the Thomas–Fermi constant $C_F = (3/10)(3\pi^2)^{2/3}$ (and r_0 is the average distance between electrons uniformly distributed at density ρ ; $r_0 = \rho^{1/3}$) and this term is then identical to the well-known Thomas–Fermi term, T_{TF} .^{21,22} There is no simple formulation of the first and second terms but it turns out that they can be evaluated via a MC procedure (see Appendix A, Section A 2) as shown in Sec. VI.

VI. RESULTS

We name the first term in Eq. (31)

$$I_C \doteq \bar{\gamma}^2 \sum_{i=2, N} \sum_{j=2, N} [\vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i) \cdot \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_j)] \quad (32)$$

the “kinetic coulomb correlation term” and the second term in Eq. (31)

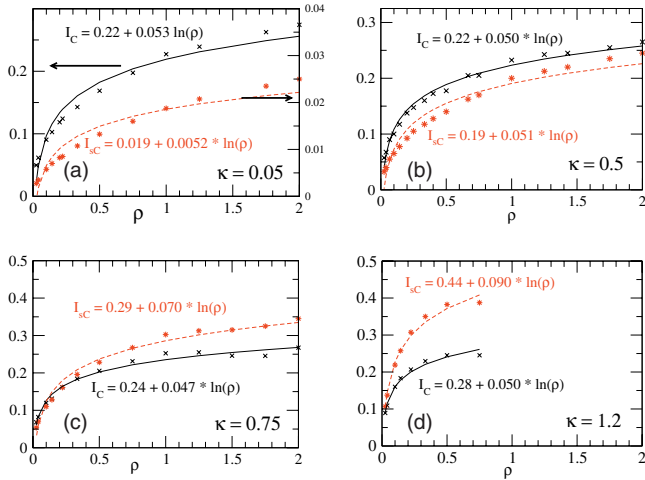


FIG. 1. Calculated and fitted values for I_C [Eq. (32), solid line] and I_{sC} [Eq. (33), dashed line] at increasing values of κ . For $\kappa=0.05$ the scale on the right is for the kinetic Coulomb correlation term, while the left scale is for the kinetic cross term (as indicated by the arrows). At $\kappa=1.2$ the data stops at the highest density at which a minimum for $\Xi[g_{\bar{\gamma}}, \rho(\mathbf{r}_1)]$ was visible.

$$I_{sC} \doteq 2\alpha\bar{\gamma}u_p \cdot \sum_{i=2,N} \vec{\nabla}_i E_H(\mathbf{r}_1, \mathbf{r}_i) \quad (33)$$

the “kinetic spin-coulomb cross correlation term,” or simply “kinetic cross term”(see Appendix B for details regarding this term), and we refer to them collectively as the kinetic correlation terms. Here, $\bar{\gamma}$ is the optimal value of γ at a particular density (i.e., the value of $\bar{\gamma}$ that minimizes the functional $\Xi[g_{\bar{\gamma}}, \rho(\mathbf{r}_1)]$). Appendix A, Section 2 gives crucial details regarding the MC procedure for the full spin case and, in particular, the need to sample a softened spin interaction, by means of a scaling factor κ , which has the value $\kappa=0$ in the spinless case $\kappa=2$ in the full spin case. The physically meaningful value of the kinetic correlation terms at “full spin” must be obtained by extrapolating the value of these terms at softened values of the spin interaction.

In Fig. 1 we show that for four different κ values, the kinetic correlation terms are well fit by logarithmic expressions. In view of the discussion in Sec. VII, we underline that these logarithmic expressions are good fits to both I_C and I_{sC} for any κ value. In this way we obtain the kinetic energy functional for the electron gas with spin

$$K_{\text{spin}}[\rho] = T_W + T_{\text{TF}} + \int \rho(\mathbf{r}_1)(A_C + B_C \ln \rho(\mathbf{r}_1))d\mathbf{r}_1 + \int \rho(\mathbf{r}_1)(A_{sC} + B_{sC} \ln \rho(\mathbf{r}_1))d\mathbf{r}_1, \quad (34)$$

which has correct limiting behavior.

Figure 2 shows our linear extrapolation for the coefficients of the logarithmic expressions for $\kappa=2$, i.e., full spin case. The estimated kinetic correlation coefficients in Eq. (34) are $A_C=0.31$, $B_C=0.043$, $A_{sC}=0.71$, and $B_{sC}=0.12$. Note that in Fig. 2 we also included the values of A and B resulting from the spinless case ($\kappa=0$). Here, the computational need of switching on smoothly the spin interaction is a happy accident. It allows us to show that a smooth and robust “adiabatic connection” links the spinless and full spin

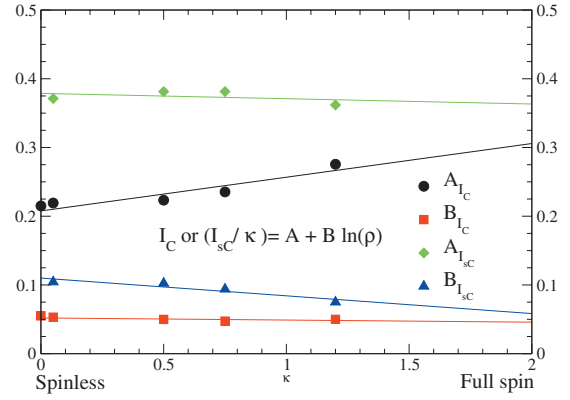


FIG. 2. Linear extrapolation of the coefficients of the logarithmic expressions for the kinetic Coulomb correlation term I_C and the kinetic cross term I_{sC} , up to the full spin value $\kappa=2$. The coefficient for I_{sC} are represented divided by κ , given the explicit linear dependence of I_{sC} on this factor [see Eq. (33)]. For I_C , we have also included the values resulting from the spinless case.

cases. Nonetheless, the results obtained in this way should only be interpreted as indicative. We are working on the design of a biased MC move (i.e., not isotropic and uniformly distributed as now implemented) in order to improve the “Pauli pairs exchange” statistics and calculate the relevant quantities directly.

VII. FISHER INFORMATION AND SHANNON ENTROPY

We have shown¹⁷ that the two kinetic energy terms in Eq. (3) are purely quantum and that the first arises from local quantum fluctuations, while the second arises from nonlocal ones. Nelson²³ proposed a quantization procedure whereby quantum fluctuations are added to the classical momentum to obtain the quantum momentum. We recently^{24,25} proposed a dequantization procedure whereby quantum fluctuations are stripped from the quantum momentum to obtain the classical momentum. The quantum fluctuation term is the same for the quantization and dequantization processes and leads to these kinetic energy terms. We now consider the relationship of each kinetic energy term to information theoretic quantities.

The Fisher information,^{5,6} which is a cornerstone of information theory, is

$$\mathcal{I}_F = \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d^3\mathbf{r}. \quad (35)$$

Thus \mathcal{I}_F is a functional of the electron density, and the greater the *localization* of $\rho(\mathbf{r})$, the greater the value of the Fisher information. Comparison of the first kinetic energy term [the first term of Eq. (3)] and Eq. (35) shows that the Weizsäcker term is proportional to the Fisher information (with $T_W = N\hbar^2/8m\mathcal{I}_F$).

The Shannon entropy,⁷ which is another cornerstone of information theory, is

$$\mathcal{E}_S = - \int \rho(\mathbf{r}) \ln(\rho(\mathbf{r})) d^3\mathbf{r}. \quad (36)$$

Thus \mathcal{E}_S is a functional of the electron density and the greater

the *delocalization* of $\rho(\mathbf{r})$, the greater the value of the Shannon entropy. The second kinetic energy term [Eq. (4)] is a functional of the $N-1$ conditional electron density, not the electron density. However, via a statistically rigorous MC procedure we expressed this quantity as the integral of $I(\rho(\mathbf{r}))=A+B \ln(\rho(\mathbf{r}))$ for the spinless electron gas and as the Thomas–Fermi term plus the integrals of $I_C(\rho(\mathbf{r}))=A_C+B_C \ln(\rho(\mathbf{r}))$ and $I_{sC}(\rho(\mathbf{r}))=A_{sC}+B_{sC} \ln(\rho(\mathbf{r}))$ for the electron gas with spin. Clearly, the integrals of I , I_C , and I_{sC} are proportional to the Shannon entropy.

Our expression for the kinetic-energy functional of the nearly uniform electron gas contains the Weizsäcker term and (for the electron gas with spin) the Thomas–Fermi term. These are both well-known kinetic-energy functionals which are exact for the limiting cases of the hydrogen atom and the uniform electron gas, respectively. Also, our expression for the kinetic-energy functional of the nearly uniform electron gas contains additional terms which have a Shannon entropy form. The Shannon entropy expression is a good fit to the integral of I for the spinless electron gas and to the integrals of both I_C and I_{sC} for the electron gas with spin. This is an indication of a rather strong connection between the statistical theory of information and the physics of electron correlations. Furthermore, it was recently shown by one of us¹² that the numerical results obtained via the MC procedure (which results in the Shannon entropy expression) are consistent with the behavior of the kinetic-energy functional under linear scaling of the spatial coordinates. It was also shown that this *numerical* functional is the first order term in an expansion of a kinetic-energy functional with exact scaling behavior which involves an exponential of the Shannon entropy.

VIII. CONCLUSIONS

We have presented a combined theoretical-numerical approach to designing kinetic-energy functionals based on the ansatz of writing the square of the N -electron wave function as a product of the electron density and the $N-1$ conditional electron density. An analytic form for the latter quantity, incorporating the effect of electron spin, was proposed and, via a reformulation of the Levy–Lieb constrained search principle, a variational expression for the kinetic-energy functional was obtained. This expression involves integrations in a high dimensional space which cannot be done analytically; however, the form of this expression is optimal for integration via a MC procedure. This numerical evaluation led to an expression for the kinetic-energy functional as the Thomas–Fermi functional and functionals proportional to the Fisher information and the Shannon entropy. Although, to date, this connection with information theoretic quantities has been made only for the nearly uniform electron gas, these results are intriguing since there has recently been an ongoing effort to link information theory and density functional theory. Starting from a general statistical approach we have, for the first time, established this connection without imposing any *a priori* conditions.

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APPENDIX A: DETAILS OF MC PROCEDURE FOR THE NEARLY UNIFORM ELECTRON GAS

1. Spinless case

For numerical evaluation, the number of electrons in a simulation must be finite, but care must be taken either to obtain a size independent result or to design a strategy for extrapolating the finite sized result to the infinite limit. We modeled a nearly uniform distribution of electrons by means of a system of N electrons, with N ranging from 10 to 500, in a cubic box.

The MC scheme works as follows: one electron is selected randomly and a trial move is attempted. A trial move is a uniformly distributed (isotropic) displacement of a randomly selected electron. When possible, the maximum displacement is chosen such that around 50% of the moves are accepted. In fact, when the density is very low, almost all moves are accepted whatever the maximum displacement.

On the other hand, when the density is very high we encounter a more subtle problem. The higher the density the smaller the value of $\bar{\gamma}$, and (since γ weights the exponent of the acceptance rule) a smaller value of γ implies a smaller value of the exponent and thus an exponential closer to 1, i.e., the acceptance is increased. More clearly, the same sequence of configurations along the Markov chain is more likely to be accepted when γ is small. This is counterbalanced, as noted above, by increasing the maximum displacement but, although this remedy can bring the acceptance into the desired range, there can be an undesirable level of numerical noise due to the “compression” of the exponent. At very small values of γ , i.e., where at higher densities $\bar{\gamma}$ would be found, the numerical noise hinders the location of the minimum of $\Xi[f_\gamma, \rho(\mathbf{r}_1)]$. In the spirit of biased MC techniques,¹⁹ we solved this problem by multiplying the exponent by a fixed factor $\epsilon > 1$. The biased acceptance rule is then

$$\frac{f_{\text{new}}}{f_{\text{old}}} = e^{-\epsilon\gamma(E_H(\mathbf{r}_1, \mathbf{r}_k^{\text{new}}) - E_H(\mathbf{r}_1, \mathbf{r}_k^{\text{old}}))} \times \prod_{i \neq 1, k} e^{-\epsilon\beta(E_H(\mathbf{r}_i, \mathbf{r}_k^{\text{new}}) - E_H(\mathbf{r}_i, \mathbf{r}_k^{\text{old}}))}. \quad (\text{A1})$$

Keeping in mind that we imposed $\gamma=\beta$, we note that the change in the acceptance rule artificially alters the value of γ in the sampling but the correct value of the integral $\Xi[f_\gamma, \rho(\mathbf{r}_1)]$ is recovered because, since the integral $I[f_\gamma, \rho(\mathbf{r}_1)]$ is proportional to γ^2 , the biased acceptance rule makes it proportional to $\epsilon^2 \gamma^2$. When the integral $C[f_\gamma, \rho(\mathbf{r}_1)]$ is also multiplied by ϵ^2 , the two integrals are again consistent and the minimum $\Xi[f_\gamma, \rho(\mathbf{r}_1)]$ as a function of γ recovers the original meaning. In principle, one can apply a different (more convenient) value of ϵ at each sampled density; consistency is kept when $\Xi[f_\gamma, \rho(\mathbf{r}_1)]$ is “normalized” upon multiplication by ϵ^2 . In practice, we found that with $\epsilon=2$, we had

a clear minimum at all sampled densities. Also, with the choice $\epsilon=2$, one can alternately decrease the acceptance by taking the square root of the random number to be compared to the ratio $f_{\text{new}}/f_{\text{old}}$ in the Metropolis algorithm (and keep the exponent of the original formulation). It should be noted that, because the Pauli weighting function is not rigorous, the minimum of $\Xi[f_\gamma, \rho(\mathbf{r}_1)]$ is not necessarily an upper bound to the true value.

Returning to the implemented MC move, we kept the electron at position \mathbf{r}_1 fixed, so that the evaluation of $I[f_\gamma, \rho(\mathbf{r}_1)]$ is referred to the position of this electron. In the case considered here, i.e., (quasi) uniform density, the acceptance rule given in Eq. (A1) automatically samples configurations at quasiuniform density. Here we stress that the “quasi” specification we add to “uniform,” means that with a finite number of electrons the uniformity is conserved only in an average sense, i.e., taking few configurations along the chain, the average distribution of the particles is indeed uniformly distributed in the simulation box. Obviously, every displacement from a lattice-wise rigorously uniform distribution of the electrons is a “wobble” in the uniformity of the distribution itself. It is actually in these wiggles that the correlation information we are sampling is hidden. In case of nonuniform density (where an external field is present, e.g., atomic-like distributions generated by the nuclear electric field), a more complicated acceptance rule must explicitly fix (on average) the imposed density.

In order to tackle finite size effects, the standard strategy of imposing periodic boundary conditions and the minimum image convention was adopted.¹⁹ In practice, each displaced electron was, in turn, the center of the box and only one instance per particle was used in evaluating the quantities. Periodic replicas of the system would be necessary for the evaluation of the slowly decaying “Coulomb” integral [Eq. (15)]; in contrast, for the evaluation of $I[f_\gamma, \rho(\mathbf{r}_1)]$, it would be physically wrong to count correlations of periodic replicas (therein including spurious self-correlations between the displaced electron and its images): each electron should contribute to the integral only once. This choice leads to a strong finite size effect for $C[f_\gamma, \rho(\mathbf{r}_1)]$.

Concerning the minimization with respect to f [Eq. (3)], we perform the search numerically at each density. We evaluated the minimum of $\Xi[f_\gamma, \rho(\mathbf{r}_1)]$ by calculating its value at different values of γ . The estimate for the minimum comes from a parabolic fit to these values around the visual minimum of the curve. As emphasized in Ref. 3, the value of γ that minimizes the functional at each density is independent of the size of the system (the number of electrons). Likewise (within numerical accuracy), the value of $I[f_\gamma, \rho(\mathbf{r}_1)]$ at each density does not depend on the number of electrons. This *a posteriori* size independence is a robust property of our numerical scheme.

2. Full spin case

We modeled a nearly uniform distribution of electrons with a system of $N=64$ electrons. We did not carry out an extensive study for different values of N because we have shown that there is no N dependence of $I[f_\gamma, \rho(\mathbf{r}_1)]$ for the

spinless case and, since the spin interactions are very short ranged, there is no reason to think that there would be a significant N dependence for the full spin case. We have nonetheless carried out some tests with other values of N and, indeed, they confirm the expected N independence. Following the above argument on the introduction of the scaling factor ϵ , in the case of the Pauli weighting, the consistency with $\epsilon=2$ holds if the spin interaction is also multiplied by 2. In fact, all the terms [Eq. (31)] are proportional to γ^2 , $\alpha\gamma$, or α^2 . Thus, by substituting α in Eq. (31) with an effective $\alpha' = \kappa\alpha$, consistency is recovered when $\epsilon=2$ and $\kappa=2$. In this way, though, we encounter another problem related to poor sampling. For a correct sampling of the phase space, it is necessary that the Pauli pairs change with a non-negligible rate; more clearly, when an attempted move is such that some (at least two!) Pauli pairs change, the acceptance of this move should not be too low. Otherwise the sampling will be nonergodic. We find that, at almost all densities [except the smaller ones, viz. $\rho < 0.15$], the incomplete sampling due to poor exchange between Pauli pairs leads to the disappearance of the minimum in the functional $\Xi[g_\gamma, \rho(\mathbf{r}_1)]$. Identifying the problem in the spin interaction that appears to be too strong for the sake of numerical evaluation, we softened the spin interaction by weighting α' with a factor smaller than 1; this is the same as weighting the physically meaningful quantity α with a factor κ smaller than 2. In this case, we find that, for $\kappa \leq 1$, $\Xi[g_\gamma, \rho(\mathbf{r}_1)]$ shows a minimum, but we can no longer reach a closed consistency, i.e., we cannot simply scale other integrals in order to obtain the correct result (in order to reach consistency we should lower ϵ , but this would also lead to poor sampling for reasons noted above). The route we followed was to calculate the integrals at increasing values of κ , where the integral $\Xi[g_\gamma, \rho(\mathbf{r}_1)]$ showed a minimum at most of the sampled densities, and then to (linearly) extrapolate to $\kappa=2$. Figure 2 shows the calculated values of the fitting coefficients to $I_C[g, \rho(\mathbf{r}_1)]$ and $I_{SC}[g, \rho(\mathbf{r}_1)]$ at various values of κ together with the linear extrapolation to $\kappa=2$. The values of the coefficients come from the values of the integral at all densities. It might seem that extrapolating to $\kappa=2$ using data evaluated in the interval $[0,1,2]$ is rather brave, but one has first to note the mild dependence of the coefficients as a function of κ . As a consistency test, at lower densities minima of the functional $\Xi[g_\gamma, \rho(\mathbf{r}_1)]$ were found directly at $\kappa=2$ and we determined (see Fig. 3) that the extrapolated values of $I_C[g, \rho(\mathbf{r}_1)]$ and $I_{SC}[g, \rho(\mathbf{r}_1)]$ were in reasonable agreement.

APPENDIX B: COMMENT ON THE SIGN OF THE KINETIC CROSS TERM

Our calculations show that the kinetic cross term I_{SC} is always positive. This can be understood with the following argument: when interactions are absent, only T_{TF} (i.e., α^2) survives and electrons occupy the energy levels in pairs (order two degeneracy). When (Coulomb) interactions are “switched on,” electron pairs can no longer be in the same state (i.e., the same position) and the kinetic energy increases due to repulsive interactions. When these interactions are small (i.e., γ is small), it is necessary that the kinetic cross

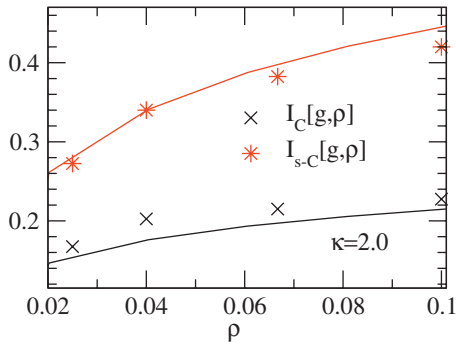


FIG. 3. Check of the extrapolated fitted kinetic correlation terms I_C and I_{sC} at $\kappa=2$. The symbols are the data at the only densities we could see a minimum for $\Xi[g, \gamma, \rho(\mathbf{r}_1)]$. The continuous lines are the fits [see Eq. (34) and related discussion].

term is positive because for small γ the kinetic Coulomb correlation term, which goes as γ^2 , will be smaller than the kinetic cross term, which goes as γ . If the kinetic cross term could be negative, then it would no longer be assured that the kinetic energy of a (repulsively) interacting uniform electron gas would be greater than that of a noninteracting one. From a configuration point of view, one should consider that the unit vectors \mathbf{u}_p always point from the particle at position $\mathbf{r}_{pp(1)}$ toward the particle at position \mathbf{r}_1 , i.e., its Pauli paired, and that the $\vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i)$ term always points from the particle at position \mathbf{r}_1 toward the particle at position \mathbf{r}_i . The fact that the dot product of the unit vector \mathbf{u}_p and the vector $\sum_{i=2,N} \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i)$ is positive suggests that these vectors “point in the same direction.” This can be visualized, considering that particle $pp(1)$ is, by construction, near particle 1; these two particles attract each other, but repel all the others (and also repel themselves at short distances). Looking from particle 1, the presence of $pp(1)$ will cause a relative depletion (semi)cone along the $pp(1)$ –1 line. On average, the closest particles to 1 [those contributing with greater $\vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i)$] will be more likely on the semisphere other than $pp(1)$, causing $\sum_{i=2,N} \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i)$ to point away from

$pp(1)$. Thus \mathbf{u}_p and $\sum_{i=2,N} \vec{\nabla}_1 E_H(\mathbf{r}_1, \mathbf{r}_i)$ will, on average, point in the same direction. This argument also explains why we find a finite value for I_{sC}/κ , for $\kappa \rightarrow 0$ (see Fig. 2); in fact, there will always be the above noted depletion around any pair of first neighbors, even with vanishing “Pauli attraction.”

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