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Inverse atomic densities and inequalities among density functionals

J. C. Angulo, E. Romera, and J. S. Dehesa
Departamento de Física Moderna and Instituto Carlos I de Física Teórica y Computacional, Universidad de Granada, 18071-Granada, Spain

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Rigorous relationships among physically relevant quantities of atomic systems (e.g., kinetic, exchange, and electron–nucleus attraction energies, information entropy) are obtained and numerically analyzed. They are based on the properties of inverse functions associated to the one-particle density of the system. Some of the new inequalities are of great accuracy and/or improve similar ones previously known, and their validity extends to other many-fermion systems and to arbitrary dimensionality. © *2000 American Institute of Physics.* [S0022-2488(00)01512-7]

I. INTRODUCTION

The interest in the description of many properties of D-dimensional N-fermion systems in terms of the one-particle density

$$\rho(\mathbf{r})\equiv\sum_{\sigma_i=-1/2}^{+1/2}\int|\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N;\sigma_1,\sigma_2,\ldots,\sigma_N)|^2 d^D r_2\cdots d^D r_N$$

has increased in the last years, mainly due to the relevant role which plays in a density functional theory framework.[1] Much attention has been paid to the study of some observables, such as the radial expectation values,[2,3]

$$\langle r^n\rangle\equiv\int r^n\rho(\mathbf{r})d^D r \quad (n>-D)$$

and the mean logarithmic radius,[4–6]

$$\langle\ln r\rangle\equiv\int(\ln r)\rho(\mathbf{r})d^D r$$

which is the logarithm of the geometric mean of the variable,[7] and it is related to the quantities $\langle r^n\rangle$ as

$$\langle\ln r\rangle=\left[\frac{d\langle r^n\rangle}{dn}\right]_{n=0}. \tag{1}$$

The expectation values $\langle r^n\rangle$ are proportional to the moments

$$\mu_n\equiv\int_0^\infty r^n\rho(r)dr \tag{2}$$

of the spherically-averaged one-particle density

$$\rho(r)=\frac{1}{\Omega_D}\int\rho(\mathbf{r})d\Omega_D,$$

where $\Omega_D = 2\pi^{D/2}/\Gamma(D/2)$ is the D-dimensional solid angle, and $d^D r = r^{D-1} dr d\Omega_D$. More precisely, $\langle r^n \rangle = \Omega_D \mu_{n+D-1}$, and the normalization is given by $\langle r^0 \rangle = 1$.

For atomic systems, the expectation values $\langle r^n \rangle$ and $\langle \ln r \rangle$ have been extensively used to bound and/or estimate other global quantities[6,8,9] and the density itself.[10–12] Among those quantities, let us remark the so-called frequency moments of both $\rho(\mathbf{r})$ and $\rho(r)$,

$$\omega_n \equiv \int \rho^n(\mathbf{r}) d^D r, \tag{3}$$

$$\hat{\omega}_n \equiv \int \rho^n(r) d^D r = \Omega_D \int_0^\infty r^{D-1} \rho^n(r) dr. \tag{4}$$

It can be proved that $\omega_n \geqslant \hat{\omega}_n$ for any $n \geqslant 1$, and $\omega_n \leqslant \hat{\omega}_n$ for $0 < n \leqslant 1$. To do that, it is sufficient to expand the function $F[\rho(\mathbf{r})] = \rho^n(\mathbf{r})$ around $\rho^n(r)$ as

$$\rho^n(\mathbf{r}) = \rho^n(r) + [\rho(\mathbf{r}) - \rho(r)] n \rho^{n-1}(r) + [\rho(\mathbf{r}) - \rho(r)]^2 n(n-1) g^{n-1}(\mathbf{r})$$

with $g(\mathbf{r}) \geqslant 0$ being a function between $\rho(\mathbf{r})$ and $\rho(r)$ for each $\mathbf{r}$. The last term of the above equation is non-negative for $n \geqslant 1$, and then

$$\rho^n(\mathbf{r}) \geqslant \rho^n(r) + [\rho(\mathbf{r}) - \rho(r)] n \rho^{n-1}(r)$$

which, after integrating on $d^D r$ and taking into account that $\int \rho(\mathbf{r}) \rho^{n-1}(r) d^D r = \int \rho^n(r) d^D r$, provides the desired inequality $\omega_n \geqslant \hat{\omega}_n$ for $n \geqslant 1$. Similarly, the relationship $\omega_n \leqslant \hat{\omega}_n$ for $0 < n \leqslant 1$ is obtained.

For many-fermion systems, it is well-known[1] that the frequency moments $\omega_{4/3}$ and $\omega_{5/3}$ are related to the local density approximations to the exchange and kinetic energies K_0 and T_0, respectively, as

$$K_0 = \frac{(3N)^{4/3}}{4\pi^{1/3}} \omega_{4/3}, \quad T_0 = \frac{(3N)^{5/3} \pi^{4/3}}{10} \omega_{5/3}$$

and that $\omega_2 = \langle \rho \rangle$ is the average density. Concerning the radial expectation values $\langle r^n \rangle$, specially relevant are those corresponding to $n = -1$ and $n = 2$ in atomic systems. They are proportional to the electron–nucleus attraction energy (which absolute value will be denoted by E_{eN}) and the diamagnetic susceptibility, respectively. In this sense, it is worthy to mention that

$$E_{eN} = ZN \langle r^{-1} \rangle, \tag{5}$$

Z being the nuclear charge of the N-electron atom.

Another physically meaningful quantity is the information entropy of the density and its spherical average, S_ρ and $\hat{S}_\rho$ respectively, defined as[13]

$$S_\rho = -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d^D r, \tag{6}$$

$$\hat{S}_\rho = -\int \rho(r) \ln \rho(r) \, d^D r, \tag{7}$$

which play a relevant role in an information-theoretic framework as a measure of the delocalization of the density. They are related to the frequency moments as

$$S_\rho = -\left[\frac{d\omega_n}{dn} \right]_{n=1},$$

$$\hat{S}_\rho = -\left[\frac{d\hat{\omega}_n}{dn}\right]_{n=1}.$$

Consequently with the relationship between ω_n and $\hat{\omega}_n$, it is easily shown that $S_\rho \leqslant \hat{S}_\rho$.

Different upper and lower bounds on the frequency moments ω_n (Ref. 8) and the information entropy S_ρ (Ref. 6) have been variationally obtained, in terms of radial expectation values and/or the mean logarithmic radius.

The aim of this work is to obtain a new set of rigorous relationships among the aforementioned quantities (i.e., radial expectation values, mean logarithmic radius, frequency moments, and information entropy) starting from several known inequalities among them. In doing so, we will study the global properties of a new function $z(t)$, which is the inverse function of $[\rho(r^{1/D})]^{1/D}$, as described in Sec. II. The new general inequalities are obtained and numerically analyzed in Sec. III, and some monotonicity properties of $z(t)$ are studied in Sec. IV. Finally, some concluding remarks are given.

II. METHOD

Let us consider a rescaling $f(r) \equiv \rho^\alpha(r^\beta)$ of a monotonically decreasing function $\rho(r) > 0$, for arbitrary $\alpha, \beta > 0$. The decreasing character of $\rho(r)$ induces the same property on the function $f(r)$. Consequently, $f(r)$ reaches its maximum value $f_{\max} = \rho^\alpha(0)$ at $r=0$, decreasing to zero as r goes to infinity. Such a monotonic behavior allows one to consider the well-defined inverse function $f^{-1}(t)$, which is also decreasing, and its domain being the interval $[0, \rho^\alpha(0)]$. Then, the function $z(t) \equiv f^{-1}(t)$ assigns the value r to the abscissa $t = \rho^\alpha(r^\beta)$. More clearly,

$$z[\rho^\alpha(r^\beta)] = r$$

or, equivalently,

$$z[\rho^\alpha(r)] = r^{1/\beta}.$$

Let us show now that, for specific values of the parameters α and β, there exists a strong relationship between different global properties of $\rho(r)$ and $z(t)$, such as moments, frequency moments, mean logarithmic radius, and information entropy. We consider the general case of D-dimensional systems, but the three-dimensional one (i.e., $D=3$) will be emphasized.

The moment μ_n of order $n > -1$ of the density $\rho(r)$ is given by Eq. (2), and it is related to the corresponding radial expectation value as $\langle r^n \rangle = \Omega_D \mu_{n+D-1}$. For $D=3$, $\Omega_3 = 4\pi$. Concerning the inverse function $z(t)$, the moments

$$\nu_n \equiv \int_0^{\rho^\alpha(0)} t^n z(t) dt \tag{8}$$

are proportional to its radial expectation values as $\langle t^n \rangle = \Omega_D \nu_{n+D-1}$, similarly to the case of $\rho(r)$.

We now define the frequency moments of $z(t)$ by

$$\Theta_n \equiv \Omega_D \int_0^{\rho^\alpha(0)} t^{D-1} z^n(t) dt, \tag{9}$$

and its information entropy as

$$S_z \equiv -\int z(t) \ln z(t) d^D t = -\left[\frac{d\Theta_n}{dn}\right]_{n=1}. \tag{10}$$

Let us prove that, for $\alpha = \beta = 1/D$, the moments and the frequency moments of $z(t)$ are related to those of $\rho(r)$ as

$$\nu_n = \frac{D}{(n+1)\Omega_D} \hat{\omega}_{\frac{n+1}{D}} \quad (n > -1), \tag{11}$$

and

$$\Theta_n = n\Omega_D \mu_{Dn-1} = n\langle r^{D(n-1)} \rangle \quad (n > 0). \tag{12}$$

To do that, we perform the change of variable $t = \rho^{\alpha}(r)$ in Eq. (8), what gives rise to

$$\nu_n = -\alpha \int_0^{\infty} r^{1/\beta} \rho^{\alpha(n+1)-1}(r) \rho'(r) dr.$$

Integrating by parts this equation, one straightforwardly obtains the expression

$$\nu_n = \frac{1}{\beta(n+1)} \int_0^{\infty} r^{(1/\beta)-1} \rho^{\alpha(n+1)}(r) dr,$$

which provides the desired relationship (11) between ν_n and $\hat{\omega}_{\frac{n+1}{D}}$ by choosing $\alpha = \beta = 1/D$ and taking into account Eq. (3). Carrying out a similar procedure starting from Eq. (9), the corresponding relationship (12) between Θ_n and μ_{Dn-1} is also obtained.

From Eq. (12), it is observed that the radial expectation values of the charge density are proportional to the frequency moments of $z(t)$ in the three-dimensional case as

$$\langle r^n \rangle = \frac{3}{n+3} \Theta_{1+(n/3)}.$$

Concerning the information entropy and the geometric mean of $z(t)$, we only need to remember Eqs. (6) and (10)–(12) to obtain the following relationships involving the same functionals of $\rho(r)$:

$$\langle \ln t \rangle = -\frac{1}{D}(1 + \hat{S}_{\rho}), \tag{13}$$

$$S_z = -1 - D\langle \ln r \rangle. \tag{14}$$

To have an idea of the functional form of $z(t)$, let us consider the three-dimensional case corresponding to the charge density of hydrogen-like atoms with nuclear charge Z in the ground state, namely,

$$\rho(r) = \frac{Z^3}{\pi} e^{-2Zr}. \tag{15}$$

With the change $t \equiv \rho^{1/3}(r^{1/3})$, this equation transforms into

$$z(t) = \left[\frac{3}{2Z} \ln \frac{Z}{\pi^{1/3} t} \right]^3, \quad t \in [0, Z/\pi^{1/3}]. \tag{16}$$

Then, the functional form of $z(t)$ (at least for hydrogenlike atoms) is $(a - b \ln t)^3$.

It is worthy to mention that Eqs. (11) and (13) are also valid for nonmonotonic densities, while Eqs. (12) and (14) transform into inequalities as

$$\Theta_n \leqslant n\Omega_D \mu_{Dn-1} \quad (n \geqslant 1), \tag{17}$$

$$\Theta_n \geqslant n\Omega_D \mu_{Dn-1} \quad (0 < n \leqslant 1), \tag{18}$$

$$S_z \geqslant -1 - D\langle \ln r\rangle. \tag{19}$$

To see that, let us consider a density function $\rho(r)$ having local extrema at $r_1, r_2, \ldots, r_{2M-1}$, where the kth maximum and minimum are located at r_{2k-1} and r_{2k}, respectively (taking $r_1 \equiv 0$ if the first local extrema is a minimum), and define $r_0 \equiv 0$ and $r_{2M} \equiv +\infty$. Then, and following the same procedure as in Sec. II, let us define the functions $z_k(t)$ $(k=1,\ldots,2M)$, each one associated to the piece of $\rho(r)$ between consecutive extrema [what is allowed due to the monotonic character of $\rho(r)$ in such subintervals], with $z_k(t) \equiv 0$ out of its subinterval. Now, define $z(t):[0,\rho_{\max}^{1/3}] \to [0,\infty)$ as

$$z(t) \equiv \sum_{k=1}^{2M} (-1)^k z_k(t).$$

Taking into account that $z_k(t)$ is a monotonically increasing function for odd k and decreasing for even k, it is observed that $z(t)$ is monotonically decreasing, even for nonmonotonic $\rho(r)$.

For $z(t)$ defined in such a way, it is not difficult to show that Eqs. (11) and (13) also hold. Let us now prove the inequalities (17)–(19). In doing so, let us consider the nth frequency moment of $z(t)$,

$$\Theta_n \equiv \Omega_D \int_0^{\rho_{\max}^{1/D}} t^{D-1} \left[\sum_{k=1}^{2M} (-1)^k z_k(t) \right]^n dt \tag{20}$$

as well as the sum

$$S_n \equiv \sum_{k=1}^{M} [\Theta_n^{(2k)} - \Theta_n^{(2k-1)}] = n\Omega_D \int_0^\infty r^{Dn-1} \rho(r)\, dr = n\Omega_D \mu_{Dn-1}, \tag{21}$$

where

$$\Theta_n^{(k)} = (-1)^k \Omega_D \left[\frac{r_{k-1}^{Dn}\rho(r_{k-1}) - r_k^{Dn}\rho(r_k)}{D} + n\int_{r_{k-1}}^{r_k} r^{Dn-1}\rho(r)\, dr \right],$$

is the nth frequency moment of $z_k(t)$. Let us prove that $\Theta_n \leqslant S_n$ if $n \geqslant 1$, and $\Theta_n \geqslant S_n$ if $0 < n \leqslant 1$. To do that, consider the function

$$F_M(n) \equiv \left[\sum_{k=1}^{2M} (-1)^k z_k(t) \right]^n - \sum_{k=1}^{2M} (-1)^k [z_k(t)]^n. \tag{22}$$

Using induction on M, it can be proved that $F_M(n) \leqslant 0$ if $n \geqslant 1$ and $F_M(n) \geqslant 0$ if $0 < n \leqslant 1$. This result, together with Eqs. (20)–(22), gives rise to the desired inequalities (17) and (18) which, after taking into account Eq. (10), provide also the inequality (19).

In Secs. III and IV, different inequalities involving such kind of quantities are used to obtain a wide new set of relationships among them, and some particular cases corresponding to atomic systems will be explicitly given and analyzed.

III. APPLICATIONS: GENERAL INEQUALITIES

Let us consider any rigorous relationship involving moments and/or frequency moments of a monotonically decreasing function. This is, for instance, the case of ground-state neutral atomic systems, for which the electron density $\rho(r)$ is known to be monotonically decreasing. So, Eqs. (11)–(12) allow us to replace the involved moments by frequency moments, and conversely. Then, a new relationship among the same kind of quantites is obtained, being also valid for any decreasing density. Similarly, inequalities containing the information entropy and/or the mean logarithmic radius give rise to new relationships, by taking into account Eqs. (13)–(14). In some cases, the resulting inequalities will be also valid for nonmonotonic densities.

We will center our attention on the following known inequalities: (i) variational upper and lower bounds on ω_n in terms of two radial expectation values $\langle r^k\rangle$ and $\langle r^n\rangle$, and (ii) variational upper bounds on the information entropy S_ρ in terms of one radial expectation value and the mean logarithmic radius $\langle \ln r\rangle$. Carrying out the procedure described above, these inequalities transform, respectively, into (i) a relationship among one radial expectation value and two frequency moments, and (ii) a bound on S_ρ in terms of the mean logarithmic radius and one frequency moment. As particular applications, let us remark (i) an accurate inequality among the energies E_{eN}, K_0, and T_0, and (ii) a relationship involving S_ρ, $\langle \ln r\rangle$ and one of K_0 and T_0.

A. Inequalities involving $\{\langle r^k\rangle,\omega_a,\omega_b\}$

In Ref. 8, the following upper and lower bounds on frequency moments ω_n, valid for any D-dimensional density function $\rho(\mathbf{r})$, are variationally obtained in terms of two radial expectation values:

$$\omega_n \geqslant F_+(\alpha,\beta,n,D)\left[\frac{\langle r^\beta\rangle^{n(\alpha+D)-D}}{\langle r^\alpha\rangle^{n(\beta+D)-D}}\right]^{1/(\alpha-\beta)}, \quad \alpha>\beta>-D\,\frac{n-1}{n} \tag{23}$$

for any $n>1$, and

$$\omega_n \leqslant G(\alpha,\beta,n,D)[\langle r^\alpha\rangle^{-n(\beta+D)+D}\langle r^\beta\rangle^{n(\alpha+D)-D}]^{1/(\alpha-\beta)}, \quad \beta<D\,\frac{1-n}{n}<\alpha \tag{24}$$

for any $0<n<1$, and where

$$F_+(\alpha,\beta,n,D)=\frac{n^n(\alpha-\beta)^{2n-1}}{\left\{\Omega_D B\left[\frac{n(\beta+D)-D}{(\alpha-\beta)(n-1)},\frac{2n-1}{n-1}\right]\right\}^{n-1}}\left\{\frac{[n(\beta+D)-D]^{n(\beta+D)-D}}{[n(\alpha+D)-D]^{n(\alpha+D)-D}}\right\}^{1/(\alpha-\beta)} \tag{25}$$

and

$$G(\alpha,\beta,n,D)=n^n(\alpha-\beta)^{2n-1}\left\{\Omega_D B\left[\frac{n(\alpha+D)-D}{(\alpha-\beta)(1-n)},\frac{-n(\beta+D)+D}{(\alpha-\beta)(1-n)}\right]\right\}^{1-n}$$
$$\times\left\{\left[\frac{1}{-n(\beta+D)+D}\right]^{-n(\beta+D)+D}\left[\frac{1}{n(\alpha+D)-D}\right]^{n(\alpha+D)-D}\right\}^{1/(\alpha-\beta)}. \tag{26}$$

Consider Eqs. (23)–(26) applied to the function $z(t)$, i.e., after making the substitutions $\omega_n \to \Theta_n$ and $\{\langle r^\alpha\rangle,\langle r^\beta\rangle\}\to\{\langle t^\alpha\rangle,\langle t^\beta\rangle\}$, and replace the parameters $\{n,\alpha,\beta\}$ by $k\equiv D(n-1)$, $a\equiv 1+\alpha/D$ and $b\equiv 1+\beta/D$. Now, taking into account the identities (11)–(12) connecting moments and frequency moments of $\rho(r)$ and $z(t)$, upper and lower bounds on $\langle r^k\rangle$ in terms of two frequency moments of $\rho(r)$ are obtained; the lower ones for $k>0$,

$$\langle r^k\rangle \geqslant L_D(a,b,k)\left[\frac{\hat{\omega}_b^{a(D+k)-D}}{\hat{\omega}_a^{b(D+k)-D}}\right]^{1/[D(a-b)]}$$

for any $a>b>D/(D+k)$ and $k>0$, and the upper ones for $k<0$

$$\langle r^k\rangle \leqslant U_D(a,b,k)[\hat{\omega}_a^{D-b(D+k)}\hat{\omega}_b^{a(D+k)-D}]^{1/[D(a-b)]} \tag{27}$$

for any $a>D/(D+k)>b$ and $k<0$, and where

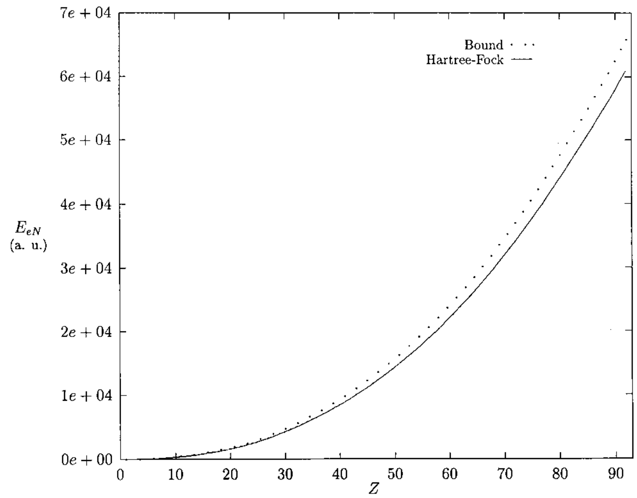

FIG. 1. Electron–nucleus attraction energy E_{eN} and upper bounds in terms of the exchange-correlation (K_0) and kinetic (T_0) energies and the nuclear charge Z, calculated in a Hartree–Fock framework (Refs. 14, 15). Atomic units (a.u.) are used.

$$L_D(a,b,k)=\frac{\left(1+\frac{k}{D}\right)^{k/D}[D(a-b)]^{1+(2k/D)}}{\left\{\Omega_D B\left[\frac{b(D+k)-D}{(a-b)k},2+\frac{D}{k}\right]\right\}^{k/D}}\left\{\frac{[ab(D+k)-aD]^{b(D+k)-D}}{[ab(D+k)-bD]^{a(D+k)-D}}\right\}^{1/[D(a-b)]},$$

and

$$U_D(a,b,k)=\frac{\left(1+\frac{k}{D}\right)^{k/D}[D(a-b)]^{1+(2k/D)}\left\{\Omega_D B\left[\frac{a(D+k)-D}{-k(a-b)},\frac{D-b(D+k)}{-k(a-b)}\right]\right\}^{-k/D}}{\{[ab(D+k)-bD]^{a(D+k)-D}[aD-ab(D+k)]^{D-b(D+k)}\}^{1/[D(a-b)]}}. \tag{28}$$

In some cases, and due to the relationship between ω_n and $\hat{\omega}_n$, the frequency moments $\hat{\omega}_a$ and $\hat{\omega}_b$ can be replaced by ω_a and ω_b, respectively. Such substitution is allowed (i.e., the involved inequalities are connected appropriately) when, additionally to the conditions on a and b given above, occurs that (i) $b\leqslant 1\leqslant a$ for the lower bounds, and (ii) $b\geqslant 1$ for the upper bounds.

For many-fermion systems in the three-dimensional case ($D=3$), especially interesting are the bounds corresponding to $k=-1$ (involving the electron–nucleus attraction energy) and $k=2$ (involving the diamagnetic susceptibility) in terms of the frequency moments of order 4/3, 5/3, and 2 (related to K_0, T_0, and $\langle\rho\rangle$, respectively). Among them, let us remark the inequality obtained by taking $k=-1$, $a=5/3$, and $b=4/3$ in Eqs. (27) and (28), valid for any atomic system with nuclear charge Z,

$$E_{eN}\leqslant(36K_0T_0)^{1/3}Z,$$

i.e., a relationship among three energies and the nuclear charge. For neutral atomic systems with $1\leqslant Z\leqslant 92$, the above inequality presents a high accuracy, which monotonically increases from 77% to 93%, (see Fig. 1), as observed in a Hartree–Fock framework by means of analytical wave functions.[14,15]

B. Inequalities involving $\{S_\rho, \omega_a, \langle \ln r \rangle\}$

Let us carry out the same procedure as before, starting from the known variational upper bounds on the information entropy S_ρ in terms of one radial expectation value $\langle r^k \rangle$ and the mean logarithmic radius $\langle \ln r \rangle$, namely[6,16]

$$S_\rho \leqslant A_D(k,m) + m \ln\langle r^k \rangle + (D-km)\langle \ln r \rangle$$

for all $m>0$, $k>-D$, where

$$A_D(k,m) \equiv m + \ln \frac{\Omega_D \Gamma(m)}{|k| m^m}.$$

This upper bound can be optimized in the parameter m for fixed values of $\langle r^k \rangle$ and $\langle \ln r \rangle$. However, such an optimization has to be numerically done.

Keeping in mind the relationships (11), (13), and (14), the previous inequality applied to the function $z(t)$ gives rise to

$$[1-m(a-1)]\hat{S}_\rho \leqslant B_D(a,m) + m \ln \hat{\omega}_a + D\langle \ln r \rangle$$

for any $m, a>0$, where

$$B_D(a,m) \equiv ma + \ln \frac{\Omega_D \Gamma(m)}{D|a-1|(ma)^m},$$

and which is also valid for S_ρ instead of $\hat{S}_\rho$ if $m(a-1) \leqslant 1$. In such a case, the above inequality holds for ω_a instead of $\hat{\omega}_a$ if, additionally, $a \geqslant 1$. Then,

$$S_\rho \leqslant \frac{1}{1-m(a-1)}[B_D(a,m) + m \ln \omega_a + D\langle \ln r \rangle], \quad 1 \leqslant a \leqslant 1 + \frac{1}{m}. \tag{29}$$

Especially interesting are the particular cases $a=4/3$, $5/3$ in the three-dimensional case, which involve the quantities K_0 and T_0. It is numerically observed that, for most neutral atoms with $1 \leqslant N \leqslant 92$, the optimal value of the parameter m is around 1 for $a=4/3$ and around 2/3 for $a=5/3$. For those particular values, Eq. (29) reads as

$$S_\rho \leqslant C(N) + \tfrac{3}{2} \ln K_0 + \tfrac{9}{2}\langle \ln r \rangle \tag{30}$$

and

$$S_\rho \leqslant C'(N) + \tfrac{6}{5} \ln T_0 + \tfrac{27}{5}\langle \ln r \rangle, \tag{31}$$

where

$$C(N) = 2 + \ln \frac{8\pi^2}{\sqrt{3} N^2}$$

and

$$C'(N) = 2 + \ln \frac{\{9\pi[2\Gamma(2/3)]^9\}^{1/5}}{N^2}.$$

A numerical study of these inequalities within the aforementioned framework is carried out in Fig. 2 for all neutral atoms with $1 \leqslant N \leqslant 92$. Notice that both inequalities are quite accurate. Indeed, the accuracy of inequality (30) varies between 89% and 96%, while that of inequality (31) decreases

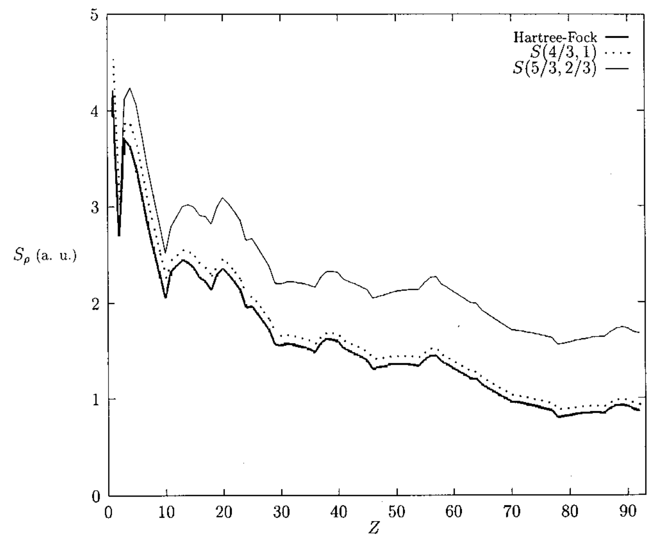

FIG. 2. Information entropy S_ρ and upper bounds in terms of the nuclear charge Z, the mean logarithmic radius $\langle \ln r \rangle$ and the exchange correlation (K_0) and kinetic (T_0) energies, respectively, calculated in a Hartree–Fock framework (Refs. 14, 15). Atomic units are used.

from 98% to 52% for increasing N. It is worthy to remark that this accuracy can be improved by choosing the exact optimal value of the free parameter m for each specific atom.

Let us also mention that other relationships involving moments and/or frequency moments can be obtained from known analytical inequalities. In this sense, expressions containing $\langle r^3 \rangle$ would provide equations on the average density $\langle \rho \rangle$, and the upper bounds[6] on S_ρ in terms of both $\langle r \rangle$ and $\langle r^2 \rangle$ give rise to inequalities involving $\langle \ln r \rangle$, K_0 and T_0, but much more cumbersome.

IV. CONVEXITY OF INVERSE ATOMIC DENSITIES

In addition to the monotonically decreasing character of the charge density $\rho(r)$ for all neutral atoms with $1 \leqslant Z \leqslant 92$, higher monotonicity properties have been numerically[17–19] studied by means of analytical Hartree–Fock wave functions.[14,15] Among those properties, it is worthy to mention the charge convexity, i.e., the non-negativity of the second derivative $\rho''(r)$ of the charge density. It is known[17,19] that such a property is valid for a great group of atoms ($Z=1-2,7-15,33-44$) of the Periodic Table, while for the rest ($Z=3-6,16-32,45-92$) convexity is very weakly violated [i.e., the function $\rho''(r)$ shows up a very small region of negativity]. In Ref. 17, it is shown that the convexity of $\rho(r)$ allows one to improve many different relationships among radial expectation values and/or other relevant quantities.

As described in Sec. II, the inverse function $z(t)$ associated with $\rho(r)$ is a monotonically decreasing function. The next step is to study the convexity of $z(t)$, i.e., the condition $z''(t) \geqslant 0$. If convexity would be valid for a given system, one should wonder on the improvement on the relationships described in the previous sections when taking into account such a property. Notice that the convexity of the function $z(t)$ for the three-dimensional case is equivalent to the convexity of its inverse, i.e., of the function $f(r)=[\rho(r^{1/3})]^{1/3}$. Then, it is not difficult to observe that the condition $f''(r) \geqslant 0$ transforms into

$$3r\rho(r)\rho''(r) - 6\rho(r)\rho'(r) - 2r[\rho'(r)]^2 \geqslant 0.$$

There is not an *a priori* relation between the convex character of $\rho(r)$ and $z(t)$ [i.e., neither the convexity of $\rho(r)$ implies the convexity of $z(t)$ nor conversely].

We have numerically studied the second derivative $z''(t)$ for the charge density $\rho(r)$ of all neutral atomic systems with nuclear charge $1 \leqslant Z \leqslant 92$, by means of the analytical Hartree–Fock wave functions of Refs. 14 and 15. It is observed that all the atoms with a nonconvex $z(t)$, i.e., $Z=16, 20, 49-92$ (46 atoms), also have a nonconvex $\rho(r)$ (69 atoms). Moreover, the nonconvexity region (when exists) of $z(t)$ is very small; its width is typically only 10^{-6}–10^{-5} times the length of the total support interval $[0,\rho^{1/3}(0)]$.

For a convex function $z(t)$, let us consider the density function given by its second derivative, i.e., $z''(t)$. Its moments $\nu_n^{(2)}$ are related to those of $z(t)$ by

$$\nu_n^{(2)}=n(n-1)\nu_{n-2} \quad (n>1)$$

and they are proportional to the frequency moments of $\rho(r)$ as

$$\nu_n^{(2)}=\frac{nD}{\Omega_D}\hat{\omega}_{\frac{n-1}{D}} \quad (n>1).$$

Then, for convex $z(t)$, inequalities involving its moments are improved by considering the quantities $\nu_n^{(2)}$ instead of ν_n. For illustration, the expression $\nu_2\nu_4\geqslant\nu_3^2$ (obtained from Hölder's inequality[20]) which leads to

$$\hat{\omega}_{5/3}\geqslant \tfrac{15}{16}\hat{\omega}_{4/3}^2$$

for the three-dimensional case, is improved by the inequality $\nu_4^{(2)}\nu_6^{(2)}\geqslant\nu_5^{(2)}$, since this gives

$$\hat{\omega}_{5/3}\geqslant \tfrac{25}{24}\hat{\omega}_{4/3}^2.$$

A similar comment can be done for other inequalities involving expectation values of the density.

V. UNCERTAINTY-LIKE RELATIONSHIPS

As mentioned in Sec. I, the information entropy of a density is a measure of its degree of delocalization. It means that many-electron systems having a very peaked density ρ (i.e., with the complete electron cloud almost located around some position) have a very low information entropy S_ρ. And, conversely, systems with a very flat or uniform density (corresponding to a very delocated electronic cloud) present a high value of their information entropy.

This property provides a different formulation[21] of the Heisenberg uncertainty principle in terms of the information entropies of the one-particle densities in position (ρ) and momentum (γ) spaces. This principle states the impossibility of having a quantum system highly localized in both complementary spaces simultaneously, and its reformulation in terms of information entropies is given by[21]

$$S_\rho+S_\gamma\geqslant 3(1+\ln\pi). \tag{32}$$

A similar statement can be done concerning the entropies of the two complementary (in some sense) densities $\rho(r)$ and $z(t)$. Attending to the definition of $z(t)$, it should be also expected some kind of connection between the entropies S_ρ and S_z [a peaked $\rho(r)$ provide a flat $z(t)$, and conversely].

In this section we numerically study the sum $S_\rho+S_z$ for all neutral atoms with nuclear charge $1\leqslant Z\leqslant 92$ in a Hartree–Fock framework,[14,15] and we compare them to the corresponding quantity for hydrogen-like systems with the same nuclear charge. From the well-known expressions of the electron density for hydrogenic atoms with nuclear charge Z (see Sec. II), one easily obtains that

$$S_\rho=3+\ln\pi-3\ln Z \tag{33}$$

and

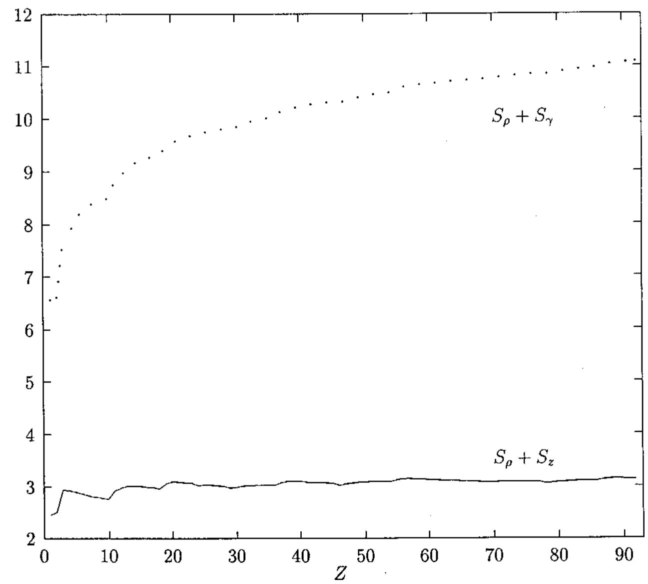

FIG. 3. Sums of information entropies $S_\rho + S_\gamma$ and $S_\rho + S_z$, calculated in a Hartree–Fock framework (Refs. 14, 15). Atomic units are used.

$$S_z = 3C + \ln 8 - \frac{11}{2} + 3\ln Z, \tag{34}$$

where $C = 0.5772\ldots$ is Euler's constant. Then, remark that hydrogenic atoms for the sum of entropies is constant (i.e., does not depend on the nuclear charge Z),

$$S_\rho + S_z = 3C + \ln 8\pi - \tfrac{5}{2} = 2.455\,818\ldots. \tag{35}$$

In Fig. 3, the entropy sums $S_\rho + S_z$ and $S_\rho + S_\gamma$ are plotted for the aforementioned neutral atoms. First, we observe that the sum $S_\rho + S_z$ is always greater for a neutral atom than for the hydrogenic one with the same nuclear charge Z, i.e., $S_\rho + S_z \geqslant 3C + \ln 8\pi - 5/2$. This may indicate that this entropy sum is a good atomic correlation measure. Moreover, we notice that the values of this sum through the Periodic Table lie in the interval $2.45 \leqslant S_\rho + S_z \leqslant 3.15$, which is much narrower than the interval of the corresponding values of the sum $S_\rho + S_\gamma$. Then, the entropy S_z [and, consequently with Eq. (14), the mean logarithmic radius $\langle \ln r \rangle$] can also be considered as a measure of the delocalization of the density. We are presently studying the implications of these two observations in the physics of many-fermion systems.

VI. SUMMARY

Different density functionals (e.g., frequency moments, information entropy) of D-dimensional many-particle systems have been expressed in terms of expectation values (radial and logarithmic) of a density function with finite support. This connection allows one to obtain many rigorous relationships among those quantities (some of them physically relevant and/or experimentally accessible) by means of known inequalities of variational type or based on classical integral inequalities. In some cases, the resulting new inequalities are of great accuracy, and have been even improved by taking into account additional analytic properties (e.g., convexity) of the densities involved.

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