Information Entropies of Many-Electron Systems

R. J. YÁÑEZ, J. C. ANGULO, AND J. S. DEHESA
Departamento de Física Moderna and Instituto Carlos I de Física Teórica y Computacional, Universidad de Granada, 18071-Granada, Spain; E-mail: ryanez@ugr.es, dehesa@ugr.es, angulo@ugr.es

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ABSTRACT

The Boltzmann–Shannon (BS) information entropy $S_\rho = -\int \rho(r)\log \rho(r)\, dr$ measures the spread or extent of the one-electron density $\rho(r)$, which is the basic variable of the density function theory of the many electron systems. This quantity cannot be analytically computed, not even for simple quantum mechanical systems such as, e.g., the harmonic oscillator (HO) and the hydrogen atom (HA) in arbitrary excited states. Here, we first review (i) the present knowledge and open problems in the analytical determination of the BS entropies for the HO and HA systems in both position and momentum spaces and (ii) the known rigorous lower and upper bounds to the position and momentum BS entropies of many-electron systems in terms of the radial expectation values in the corresponding space. Then, we find general inequalities which relate the BS entropies and various density functionals. Particular cases of these results are rigorous relationships of the BS entropies and some relevant density functionals (e.g., the Thomas–Fermi kinetic energy, the Dirac–Slater exchange energy, the average electron density) for finite many-electron systems.

Introduction

The Boltzmann–Shannon (BS) information entropy of an N-electron system in position space is defined by [1, 2] by

$$S_\rho = -\int \rho(r)\log \rho(r)\, dr, \qquad (1)$$

where $\rho(r)$ denotes the one-electron density of the system, i.e.:

$$\rho(r) = N \sum_{\sigma_i = -1/2}^{+1/2} \int |\Psi(r_1, r_2, \ldots, r_N; \sigma_1, \ldots, \sigma_N)|^2 \times dr_2, \ldots, dr_N.$$

The symbols (r_i, σ_i) and Ψ denote the position–spin coordinates of the ith particle and the wave function of the physical state of the system under

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consideration, respectively. The wave function is assumed to be normalized and antisymmetrized in the pairs (r_i, σ_i). Then, the density $\rho(r)$ is normalized to N.

Contrary to most fundamental quantities (e.g., position, momentum, and angular momentum), the BS entropy is not an observable of the system, i.e., it does not correspond to the expectation value of an operator of the Hilbert space of the system. However, it has an exceptional role since (i) it is closely related to the concept of entropy and disorder in thermodynamics [3] and (ii) it measures the spread or extent of the one-electron density $\rho(r)$, which is the basic element of the modern density functional theory [3–5]. Moreover, the BS entropy S_ρ may be interpreted as a measure of the uncertainty in the localization of an electron in position space [6], which has been the center of significant contributions to the analysis of numerous macroscopic quantities of finite many-electron systems [7–11]. The interpretation together with the Bialynicki–Birula and Mycielski (BBM)'s inequality has allowed Gadre et al. [12] to derive a new, stronger version of the Heisenberg uncertainty relation, namely:

$$S_\rho + S_\gamma \geq 3N(1 + \log \pi) - 2N \log N, \quad (2)$$

where S_γ denotes the information entropy in momentum space; so, S_γ is given as in Eq. (1) for the one-electron momentum density $\gamma(p)$ and measures the uncertainty in predicting the momentum of the electron.

At this point, let us mention that many authors prefer to work with the normalized-to-1 density, in which information entropy $\bar{S}_\rho$ is related to S_ρ (corresponding to the normalized-to-N density) as

$$\bar{S}_\rho = \frac{S_\rho}{N} + \log N.$$

The exact determination of the BS entropies of the majority of the quantum mechanical systems is not possible, not even in simple quantum systems such as the isotropic harmonic oscillator and hydrogen atom [12–14] except for the ground state and the first few lowest-lying excited states [14]. For finite many-electron systems, the numerical values of both information entropies S_ρ and S_γ have been calculated in the ground-state neutral atoms within the Thomas–Fermi model [15] and in the ground state of several atoms and ions within a Hartree–Fock framework [12]. Also, the values of the entropies of the harmonic oscillator and hydrogen atom are now numerically known [12, 14] for a large class of excited states.

Rigorously, only some upper bounds to S_ρ and S_γ in terms of the second moment of the corresponding one-electron densities (i.e., $\langle r^2 \rangle$ and $\langle p^2 \rangle$, respectively) were known [16] until recently. Two of the authors [17, 18] extended this work by the determination of upper bounds to $S_\rho(S_\gamma)$ in terms of any radial expectation values $\langle r^\alpha \rangle(\langle p^\alpha \rangle)$, $\alpha > -3$, respectively, and/or the mean logarithmic radius $\langle \log r \rangle(\langle \log p \rangle)$. The combination of these results has led us to find new uncertainty-type relationships of radial and logarithmic character [18–20].

The structure of this article is the following: Briefly, in the second section, we summarize the known facts in the problem of the analytical determination of the information entropies in both position and momentum spaces of the harmonic oscillator and hydrogen atom for an arbitrary physical state and we point out the open problems to find the complete analytical solution. In the third section, we describe the known rigorous bounds to the position and momentum entropies of a many-electron system in terms of the radial and/or logarithmic expectation values of the two complementary spaces and we detail some related questions, not yet solved. Then, in the following section, we derive a general theorem which allows us to obtain rigorous inequalities which relate the position space entropy S_ρ to each of the following fundamental and/or experimentally accessible quantities: Thomas–Fermi kinetic energy T_0, exact kinetic energy T, Dirac exchange energy K_0, and the average electronic density $\langle \rho \rangle$. In the fifth section, we extend the previous theorem so that we are able to derive more complex rigorous relationships which involve the entropy $S_\rho(S_\gamma)$ and other various density functionals of the system in position (momentum) space. Finally, some concluding remarks are given.

Information Entropies of Simple Quantum Mechanical Systems: Analytical Calculation

Here, we consider the problem of calculating the information entropies in position and momentum spaces of the isotropic harmonic oscillator and the hydrogen atom in an arbitrary state. The numerical values of these quantities can be calculated in a large portion of the spectrum. However, this is no longer true for the high-lying Rydberg states. So, the exact calculation of the information entropies of these two physical systems is not only intrinsically relevant but also of a great practical interest, especially in the excited states with large quantum numbers. Recently [14], the analytical solution of this problem has been initiated for the D-dimensional harmonic oscillator and hydrogen atom. In this section, we briefly review the main findings in the three-dimensional case, pointing out the not-yet-solved question for a complete analytical solution of the problem. The situation is analogous in other dimensions.

HARMONIC OSCILLATOR, i.e., $V(r) = \frac{1}{2}\lambda^2 r^2$

The normalized-to-unity position and momentum densities for a state described by the quantum numbers (n, l, m) are

$$\rho(r) = \frac{2n!\,\lambda^{l+3/2}}{\Gamma(n+l+\frac{3}{2})} r^{2l} e^{-\lambda r^2} \times \left[L_n^{l+1/2}(\lambda r^2)\right]^2 |Y_{lm}(\Omega)|^2,$$

$$\gamma(p) = \lambda^{-3}\rho\left(\frac{p}{\lambda}\right),$$

respectively. The symbols $L_n^{\alpha}(x)$ and $Y_{lm}(\Omega)$ denote the well-known Laguerre polynomials and spherical harmonics, respectively. Then, the information entropies in position space S_ρ and in momentum space S_γ have the following expressions:

(i) Ground state:

$$S\rho = -\tfrac{3}{2}\log\left(\frac{\lambda}{\pi}\right) + \tfrac{3}{2},$$

$$S_\gamma = \tfrac{3}{2}\log(\lambda\pi) + \tfrac{3}{2}.$$

Note that the entropy sum saturates the uncertainty relation (2), with $N = 1$, i.e.,

$$S_\rho + S_\gamma \geq 3(1 + \log \pi).$$

(ii) Excited states: For arbitrary values of n, l, and m, one has that

$$S_\rho = -\log\left(\frac{2n!}{\Gamma(n+l+\frac{3}{2})}\right) + \tfrac{3}{2}(1 - \log\lambda) + 2n + l - \frac{n!}{\Gamma(n+l+\frac{3}{2})}(I_1 + I_2) - I_3,$$

for the position-space entropy, and

$$S_\gamma = -\log\left(\frac{2n!}{\Gamma(n+l+\frac{3}{2})}\right) + \tfrac{3}{2}(1 + \log\lambda) + 2n + l - \frac{n!}{\Gamma(n+l+\frac{3}{2})}(I_1 + I_2) - I_3,$$

for the momentum-space entropy. The symbols I_1 and I_2 denote the integrals

$$I_1 = \int_0^\infty t^{l+1/2} e^{-t} \log t^l (L_n^{l+1/2}(t))^2\,dt,$$

$$I_2 = \int_0^\infty t^{l+1/2} e^{-t} (L_n^{l+1/2}(t))^2 \times \log(L_n^{l+1/2}(t))^2\,dt,$$

and the integral I_3 is given by

$$I_3 = \int |Y_{lm}(\Omega)|^2 \log |Y_{lm}(\Omega)|^2\,d\Omega = \log\left(\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right) + \left(\frac{(2l+1)(l-m)![(2m)!]^2}{2^{2m+1}(l+m)!(m!)^2}\right) \times (I_4 + I_5) + 2\log\left(\frac{(2m)!}{m!\,2^m}\right),$$

with

$$I_4 = \int_{-1}^{+1} \left[C_{l-m}^{m+1/2}(t)\right]^2 (1-t^2)^m \times \log(1-t^2)^m\,dt,$$

$$I_5 = \int_{-1}^{+1} \left[C_{l-m}^{m+1/2}(t)\right]^2 (1-t^2)^m \times \log\left[C_{l-m}^{m+1/2}(t)\right]^2\,dt,$$

where the symbol $C_k^{\alpha}(t)$ denotes the well-known Gegenbauer polynomial. Notice that the states (n, l, m) and $(n, l, -m)$ have the same entropies S_ρ and S_γ. Up to now, the analytical values of these entropies are not known for arbitrary (n, l, m) because it has not yet been possible to calculate neither the integrals I_1 and I_2 nor I_4 and I_5 in spite of the large body of knowledge on the classical orthogonal polynomials [21, 22]. Only in some very special cases, the situation is controlled such as in the first excited states $n = 0, l = 1$, where the entropies $S_\rho^{n,l,|m|}$ and $S_\gamma^{n,l,|m|}$ have the values

$$S_\rho^{0,1,0} = \log\left[2(\pi/\lambda)^{3/2}\right] + C + \tfrac{1}{2},$$
$$S_\gamma^{0,1,0} = \log[2(\pi\lambda)^{3/2}] + C + \tfrac{1}{2},$$

and

$$S_\rho^{0,1,1} = \tfrac{3}{2}\log[\pi/\lambda] + C + \tfrac{3}{2},$$
$$S_\gamma^{0,1,1} = \tfrac{3}{2}\log[\pi\lambda] + C + \tfrac{3}{2},$$

where $C = 0.5772156649\cdots$ is Euler's constant.

HYDROGEN ATOM, i.e., $V(r) = -(1/r)$

In this case, the normalized-to-unity position and momentum densities for a state described by the quantum numbers (n, l, m) are

$$\rho(r) = N_{n,l}^2 e^{-r/\lambda}\left(\frac{r}{\lambda}\right)^{2l}\left(L_{n-l-1}^{2l+1}\left(\frac{r}{\lambda}\right)\right)^2 |Y_{lm}(\Omega)|^2,$$

with

$$N_{n,l} = \lambda^{-3/2}\left(\frac{(n-l-1)!}{2n(n+l)!}\right)^{1/2}, \qquad \lambda = \frac{n}{2},$$

and

$$\gamma(p) = K_{n,l}^2 \frac{(np)^{2l}}{(1+n^2p^2)^{2l+4}} \times\left[C_{n-l-1}^{l+1}\left(\frac{1-n^2p^2}{1+n^2p^2}\right)\right]^2 |Y_{lm}(\Omega)|^2,$$

with

$$K_{n,l} = \left(\frac{(n-l-1)!}{2\pi(n+l)!}\right)^{1/2} 2^{2l+3}\Gamma(l+1)n^2,$$

respectively. Then, the information entropies S_ρ and S_γ have the following expressions:

(i) Ground State:

$$S_\rho = 3 + \log\pi,$$
$$S_\gamma = -\tfrac{10}{3} + 5\log 2 + 2\log\pi.$$

It is interesting to remark that the sum of the entropies is

$$S_\rho + S_\gamma = 3(1 + \log\pi) - \tfrac{10}{3} + 5\log 2.$$

Notice that the sum is larger than $3(1 + \log\pi)$, in agreement with the uncertainty relation (2), with $N = 1$, i.e.:

$$S_\rho + S_\gamma \geq 3(1 + \log\pi).$$

(ii) Excited states: For arbitrary values of n, l, m, one has for the position-space entropy

$$S_\rho = -\log N_{n,l}^2 + \lambda^3 N_{n,l}^2 \times (J_1 - 2lJ_2 - J_3) - J_3,$$

where J_1 is

$$J_1 = \frac{(n+l+2)!}{(n-l-1)!} + 4\frac{(n+l+1)!}{(n-l-2)!} + \frac{(n+l)!}{(n-l-3)!},$$

and the integrals J_2 and J_3 are given by

$$J_2 = \int_0^\infty t^{\alpha+1}e^{-t}\log t[L_k^\alpha(t)]^2\,dt,$$
$$J_3 = \int_0^\infty t^{\alpha+1}e^{-t}[L_k^\alpha(t)]^2\log[L_k^\alpha(t)]^2\,dt,$$

with $k = n - l - 1$, and $\alpha = 2l + 1$. Also, for the momentum-space entropy, one has

$$S_\gamma = -\log K_{n,l}^2 + (2l+4)\log 2 - \frac{K_{n,l}^2}{n^3 2^{2l+4}}(lJ_4 + 4J_5 + J_6) - I_3,$$

where

$$J_4 = \int_{-1}^{+1}(1-t^2)^{\nu-1/2} \times \log(1-t^2)(C_k^\nu(t))^2\,dt,$$
$$J_5 = \int_{-1}^{+1}(1-t^2)^{\nu-1/2} \times (1+t)\log(1+t)(C_k^\nu(t))^2\,dt,$$
$$J_6 = \int_{-1}^{+1}(1-t^2)^{\nu-1/2} \times (C_k^\nu(t))^2\log(C_k^\nu(t))^2\,dt,$$

with $k = n - l - 1$ and $\nu = l + 1$.

A detailed analysis as well as an extensive numerical evaluation of the information entropies of these two systems has been carried out in [8] for arbitrary dimensions. Here, let us briefly state that the analytical determination of the two entropies essentially reduces to the calculation of the integrals

$$E_n := -\int p_n^2(x)\log p_n^2(x)\, d\mu(x),$$

where $p_n(x)$ are orthonormal polynomials with respect to a measure μ. Specifically, the polynomials which appear in two aforementioned physical problems are the classical orthogonal polynomials corresponding to the names of Gegenbauer and Laguerre. The integrals E_n are called "entropies of the orthonormal polynomials $p_n(x)$" for obvious reasons. Up to now, the values of E_n have been analytically determined for Chebyshev polynomials of the first type $T_n(x) = (n/2)\lim_{\alpha\to 0} C_n^{\alpha}(x)$ and of the second type $U_n(x) = C_n^1(x)$ in an exact form and for Gegenbauer polynomials $C_n^{\alpha}(x)$ in an approximate way [14]. Also, the asymptotical ($n \to \infty$) values of E_n were recently explored in both Gegenbauer [13] and Laguerre cases [23]. Further effort has to done so that this problem be fully solved.

Information Entropies of Many-Electron Systems and Radial Expectation Values

Here, we describe the only existing rigorous results on the BS information entropies in both position and momentum spaces of a finite many-electron system in a general state by means of an arbitrary charge or momentum radial expectation value, i.e., $\langle r^{\alpha}\rangle$ or $\langle p^{\alpha}\rangle$, respectively. These results are given as variational bounds:

- Upper bounds to $S_{\rho}(S_{\gamma})$ in terms of $\langle r^{\alpha}\rangle(\langle p^{\alpha}\rangle)$.
- Lower bounds to $S_{\rho}(S_{\gamma})$ in terms of $\langle p^{\alpha}\rangle(\langle r^{\alpha}\rangle)$.

The variational upper bounds to the position entropy are [17]

$$S_{\rho} \le U(\alpha) = N\log\left[A_{\alpha}\langle r^{\alpha}\rangle^{3/\alpha}\right] - \frac{3+\alpha}{\alpha}N\log N, \qquad 0<\alpha<\infty, \quad (3)$$

with

$$A_{\alpha} = \frac{4\pi\Gamma(3/\alpha)}{\alpha(3/e\alpha)^{3/\alpha}}.$$

In particular, for $\alpha = 1, 2$, one finds that the centroide $\langle r\rangle$ of the one-electron density and the diamagnetic susceptibility $\langle r^2\rangle$ of the system bound from below the position entropy as

$$S_{\rho} \le N\log\left(\frac{8\pi}{27}e^3\langle r\rangle^3\right) - 4N\log N, \quad (3a)$$

and

$$S_{\rho} \le N\log\left(\frac{2\pi e}{3}\langle r^2\rangle\right)^{3/2} - \tfrac{5}{2}N\log N, \quad (3b)$$

respectively. There exist for the momentum entropies S_{γ} relations similar to (3), (3a), and (3b) in terms of the momentum expectation value $\langle p^{\alpha}\rangle$. At this point, it is convenient to highlight the case $\alpha = 2$, which gives the link between the momentum entropy and the exact kinetic energy of an N-electron system $T = N\langle p^2\rangle/2$, namely:

$$S_{\gamma} \le \frac{3N}{2}\left(1+\log\frac{4\pi T}{3}\right) - \tfrac{5}{2}N\log N. \quad (4)$$

The lower bounds to the position entropy are obtained by the combination of the upper bounds (3) and the inequality (2). They follow as [17, 18]

$$S_{\rho} \ge 3N(1+\log\pi) - N\log\left(A_{\alpha}\langle p^{\alpha}\rangle^{3/\alpha}\right) + \frac{3-\alpha}{\alpha}N\log N, \qquad 0<\alpha<5. \quad (5)$$

The particular case $\alpha = 2$ gives

$$S_{\rho} \ge \frac{N}{2}\left[3(1+\log\pi) + \log N - 3\log\frac{4T}{3}\right]. \quad (5a)$$

The corresponding inequality for the momentum entropy S_{γ} in terms of the diamagnetic susceptibility $\langle r^2\rangle$ is

$$S_{\gamma} \ge 3N(1+\log\pi) - N\log\left(\frac{2\pi e}{3}\langle r^2\rangle\right)^{3/2} + \tfrac{1}{2}N\log N. \quad (6)$$

The particular cases (4), (5a), and (6) were first observed by Gadre and Bendale [16] and later generalized and its accuracy numerically studied in all ground-state atoms [17, 18] within a Hartree–Fock framework. Let us only comment that the lower bounds are, of course, much less accurate than are the upper bounds.

The general upper and lower bounds given by Eqs. (3) and (5) have been extended [17, 18] by taking into account the logarithmic mean radius and momentum, $\langle \log r \rangle$ and $\langle \log p \rangle$, respectively. Moreover, it has been possible to find rigorous upper bounds only in terms of logarithmic mean radii, e.g., one has

$$S_\rho \leq \frac{N}{2} \log(32\pi^3 e) - 2N \log N + 3\langle \log r \rangle + \frac{N}{2} \log\left[N\langle (\log r)^2 \rangle - \langle \log r \rangle^2 \right],$$

and similarly for S_γ in terms of $\langle \log p \rangle$ and $\langle (\log p)^2 \rangle$.

Finally, we would like to point out an important problem still open: to find lower bounds to $S_\rho(S_\gamma)$ in terms of the expectation values $\langle r^\alpha \rangle (\langle p^\alpha \rangle)$ and, if necessary to improve accuracy, $\langle \log r \rangle (\langle \log p \rangle)$.

Position Entropy S_ρ of Many-Electron Systems and Physical Energies: Simple Bounds

Here, we derive a theorem which allows us to find rigorous bounds to the information entropies of many-electron systems by means of radial and/or logarithmic expectation values or some density functionals of the corresponding space. Then, as corollaries, we find inequalities which involve the position entropy S_ρ and one of the following physical quantities: Thomas–Fermi kinetic energy T_0, exact kinetic energy T, Dirac exchange energy K_0, and the average electronic energy $\langle \rho \rangle$.

Theorem 1

The position-space information entropy S_ρ of an N-electron system in a physical state characterized by the (normalized to N) one-electron density $\rho(r)$ fulfills the inequality

$$S_\rho + \langle \log g(r) \rangle \leq \int g(r)\, dr - N, \qquad (7)$$

where $g(r)$ is an arbitrary positive function and the notation

$$\langle Q \rangle := \int Q(r) \rho(r)\, dr$$

is used.

Let us point out some consequences of this theorem, corresponding to various particular choices for $g(r)$.

1. If $g(r) = [\rho(r)]^{5/3}$, one has that

$$S_\rho \geq \frac{3}{2}\left[N - \int [\rho(r)]^{5/3}\, dr \right]. \qquad (8)$$

Since the Thomas–Fermi kinetic energy of the system is

$$T_0 = \tfrac{3}{10}(3\pi^2)^{2/3} \int [\rho(r)]^{5/3}\, dr, \qquad (9)$$

it is clear that

$$S_\rho \geq \frac{3}{2}\left[N - \frac{10}{3}\left(\frac{1}{3\pi^2} \right)^{2/3} T_0 \right].$$

Moreover, since the exact kinetic energy $T \geq T_0$ [24], one easily has the following lower bound:

$$T \geq \tfrac{3}{10}(3\pi^2)^{2/3}\left(N - \tfrac{2}{3} S_\rho \right),$$

which involves T and S_ρ differently from Eq. (5a).

2. If $g(r) = [\rho(r)]^{4/3}$, one has that

$$S_\rho \geq 3\left[N - \int [\rho(r)]^{4/3}\, dr \right]. \qquad (10)$$

Since the Dirac or semiclassical exchange energy of a many-electron system is [25]

$$K_0 = -\frac{3}{4}\left(\frac{3}{\pi} \right)^{1/3} \int [\rho(r)]^{4/3}\, dr, \qquad (11)$$

it is clear that

$$S_\rho \geq 3\left[N + \frac{4}{3}\left(\frac{\pi}{3} \right)^{1/3} K_0 \right].$$

3. If $g(r) = [\rho(r)]^2$, one has that

$$S_\rho \geq N - \langle \rho \rangle, \qquad (12)$$

which allows us to make firm statements about the disorder of the system from the data of the average electron energy, which may be obtained by measuring the intensity of X-rays elastically scattered by the system [26].

Proof. To prove this theorem, we use the nonnegativity of the function

$$\phi_n(x) = -\log x - \sum_{i=1}^{2n+1} \frac{(-1)^i}{i}(x-1)^i, \quad (13)$$

for all $n = 0, 1, 2, \cdots$. The case $n = 0$ leads to the inequality $\log x \leq x - 1$. Then, we consider an arbitrary nonnegative function f and an arbitrary positive function g on a space of measure $d\mu$. Taking $x = g/f$, one finds after integration that

$$\int f \log f d\mu - \int f \log g\, d\mu \geq \int f d\mu - \int g\, d\mu. \qquad (14)$$

The application of this inequality in the three-dimensional position space and with the choice $f = \rho(r)$ immediately produces the searched theorem, keeping in mind definition (1) of the information entropy S_ρ. It is worth saying that other choices of f as a density functional $F[\rho]$ gives rise to other interesting physical inequalities.

Theorem 2

The position-space entropy S_ρ of an N-electron system in a physical state characterized by the (normalized to N) one-electron density $\rho(r)$ fulfills the inequality

$$S_\rho + \langle \log g(r) \rangle \leq N \log\left[\frac{\int g(r)\, dr}{N}\right], \qquad (15)$$

where $g(r)$ is an arbitrary positive function.

Different choices of $g(r)$ yield the following relations:

1. If $g(r) = \rho(r)^{5/3}$, one has that

$$S_\rho \geq -\tfrac{3}{2} N \log\left[\frac{\int \rho(r)^{5/3}\, dr}{N}\right].$$

Taking into account definition (9), one obtains

$$S_\rho \geq -\tfrac{3}{2} N \log\left[\frac{10/3(3\pi^2)^{-2/3} T_0}{N}\right],$$

and from $T \geq T_0$, it follows that

$$T \geq \tfrac{3}{10}(3\pi^2)^{2/3} N \exp\left[-\frac{2S_\rho}{3N}\right].$$

2. If $g(r) = \rho(r)^{4/3}$, one has that

$$S_\rho \geq -3N \log\left[\frac{\int \rho(r)^{4/3}\, dr}{N}\right].$$

Using the definition of K_0, we have

$$S_\rho \geq -3N \log\left[-\frac{4}{3}\left(\frac{\pi}{3}\right)^{1/3} \frac{K_0}{N}\right].$$

3. If $g(r) = \rho(r)^2$, one has that

$$S_\rho \geq -N \log\left[\frac{\int \rho(r)^2\, dr}{N}\right].$$

Proof. To prove this theorem, we use Jensen's inequality [27], i.e.,

$$\varphi\left(\frac{\int f d\mu}{\int d\mu}\right) \leq \frac{\int \varphi(f)\, d\mu}{\int d\mu},$$

for all convex φ, $\int f d\mu < \infty$, and $d\mu$ as a nonnegative measure. Then, using the convexity of $\phi(x) = -\log x + x - 1$ with $f = g/\rho$ and $d\mu = \rho(r)\, dr$, we obtain the inequality (15).

Theorem 3

The power-type density functionals or frequency moments,

$$\omega_\alpha \equiv \omega_\alpha(\rho) := \int [\rho(r)]^\alpha\, dr,$$

of an arbitrary N-particle system in a physical state described by the (normalized to N) one-electron density $\rho(r)$ fulfills the inequalities

$$\omega'_\alpha \le \frac{\omega_\gamma - \omega_\beta}{\gamma - \beta} \quad \text{if} \quad \beta, \gamma \ge \alpha,$$

$$\omega'_\alpha \ge \frac{\omega_\gamma - \omega_\beta}{\gamma - \beta} \quad \text{if} \quad \beta, \gamma \le \alpha,$$

where

$$\omega'_\alpha \equiv \frac{d\omega_\alpha}{d\alpha} = \int [\rho(r)]^\alpha \log \rho(r)\, dr.$$

The following result follows from the previous theorem in the case $\alpha = 1$:

Corollary 3.1

The information entropy S_ρ of an N-particle system is bounded from below by two power-type density functionals ω_α as

$$S_\rho \ge \frac{\omega_\gamma - \omega_\beta}{(\beta - \gamma)} \quad \text{for} \quad \beta \ge 1 \quad \text{and} \quad \gamma \ge 1.$$

Moreover, this lower bound transforms into an upper bound in the cases that $0 < \beta \le 1$ and $0 < \gamma \le 1$.

Among all the lower bounds to S_ρ given in this corollary, let us point out those corresponding to the cases that β and γ take values of the set $\{\frac{4}{3}, \frac{5}{3}, 2\}$:

$$S_\rho \ge 3(\omega_{4/3} - \omega_{5/3}),$$

$$S_\rho \ge \tfrac{3}{2}(\omega_{4/3} - \omega_2),$$

$$S_\rho \ge 3(\omega_{5/3} - \omega_2),$$

which depend on two density functionals. Note that with the values $\gamma = 1$ and $\beta \in \{4/3, 5/3, 2\}$ one would find the lower bounds (8), (10), and (12), previously obtained by a fully different technique, which depend only on one density functional.

Proof. Theorem 3 is a direct consequence of the convexity of the functional $\omega_\alpha(\rho)$ [18].

Position Entropy S_ρ and Various Density Functionals

Here, we considerably extend the results of the previous section by means of the following result:

Theorem 4

An arbitrary density functional $F(\rho)$ of a many-electron system in a physical state described by the one-electron density $\rho(r)$ satisfies the inequality

$$\int \left\{ 3 \log F(\rho) + \left[\frac{g(r)}{F(\rho)}\right]^3 - \frac{9}{2}\left[\frac{g(r)}{F(\rho)}\right]^2 + 9\frac{g(r)}{F(\rho)} \right\} \rho(r)\, dr \ge 3 \int \rho(r) \log g(r)\, dr + \frac{11}{2} \int \rho(r)\, dr, \quad (16)$$

where $g(r)$ is an arbitrary positive function.

Numerous inequalities which involve various density functionals of the system follow from this theorem in a straightforward manner. Let us just write down the two following corollaries which involve the information entropy S_ρ together with three power-type density functionals of special interest. They are found by taking $F(\rho)$ equals to $[\rho(r)]^{-\alpha}$ and $[\rho(r)]^{+\alpha}$, $\alpha \ge 0$, respectively.

Corollary 4.1

The information entropy S_ρ of an N-electron system fulfills that

$$S_\rho + \frac{1}{3\alpha} \int g^3(r) [\rho(r)]^{1+3\alpha}\, dr - \frac{3}{2\alpha} \int g^2(r) [\rho(r)]^{1+2\alpha}\, dr + \frac{3}{\alpha} \int g(r) [\rho(r)]^{1+\alpha}\, dr \ge \frac{1}{\alpha} \langle \log g(r) \rangle + \frac{11}{6\alpha} N, \quad (17)$$

for any $\alpha \ge 0$.

Corollary 4.2

The information entropy S_ρ of an N-electron system fulfills that

$$S_\rho - \frac{1}{3\alpha}\int g^3(r)[\rho(r)]^{1-3\alpha}\,dr + \frac{3}{2\alpha}\int g^2(r)[\rho(r)]^{1-2\alpha}\,dr - \frac{3}{\alpha}\int g(r)[\rho(r)]^{1-\alpha}\,dr \le -\frac{1}{\alpha}\langle \log g(r)\rangle - \frac{11}{6\alpha}N, \qquad (18)$$

for all $\alpha \ge 0$.

Particular choices of $g(r)$ together with specific values of α give rise to different inequalities which allow us to correlate the information entropy with various power-type density functionals. Let us just mention the case in which $g(r) = 1$ and $\alpha = \frac{1}{3}$; then, Corollary 4.1 leads to

$$S_\rho - \frac{9}{2}\int [\rho(r)]^{5/3}\,dr + 9\int [\rho(r)]^{4/3}\,dr + \langle \rho\rangle \ge \tfrac{11}{2}N. \qquad (19)$$

Definitions (9) and (11) allows us to rewrite this inequality as

$$S_\rho - \frac{15}{(3\pi^2)^{2/3}}T_0 - 12\left(\frac{\pi}{3}\right)^{1/3}K_0 + \langle \rho\rangle \ge \tfrac{11}{2}N, \qquad (20)$$

which bounds from below this specific combination of the position entropy S_ρ, the Thomas–Fermi kinetic energy T_0, the Dirac exchange energy K_0, and the average electronic energy $\langle \rho\rangle$ by means of the normalization of the one-electron density of the system under consideration. One should recall at this point that combinations of this type have been encountered in the description of some physical quantities within the framework of the density functional theory, e.g., the total ground-state energy of a homogeneous electron gas [28].

Proof. To prove Theorem 4, we use again the nonnegativity of the function $\phi_n(x)$ given by Eq. (13). In the case $n = 1$, this property leads to the inequality

$$\log x \le \tfrac{1}{3}x^3 - \tfrac{3}{2}x^2 + 3x - \tfrac{11}{6}. \qquad (21)$$

Taking $x = g(r)/F(\rho)$ and integrating over $\rho(r)\,dr$, we obtain the desired inequality.

Summary and Conclusions

Some of the many facets of the Bolzmann–Shannon (BS) information entropies of the simple quantum mechanical systems like the harmonic oscillator (HO) and the hydrogen atom (HA) as well as the finite many-electron systems are briefly and critically discussed in both position and momentum spaces. Various opened questions are pointed out, such as, e.g., (i) the exact determination of the BS entropies of the HO and HA systems at any excited state, and (ii) the bounding of the position (momentum) space entropy in terms of the charge (momentum) radial expectation values.

Then, we found a number of universal relationships of inequality-character which have the virtue of yielding rigorous bounds to the BS entropy of an N-electron system in terms of one or more power-type density functionals (also called frequency moments of the electron density of the system). As particular cases, we obtained inequalities which link the information entropies with other theoretical and experimental quantities of the system under consideration.

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