Tight rigorous bounds to atomic information entropies

J. C. Angulo and J. S. Dehesa
Departamento de Fisica Moderna, Facultad de Ciencias, Universidad de Granada, 18071-Granada, Spain

(Received 2 April 1992; accepted 14 May 1992)

The position-space entropy S_ρ and the momentum-space entropy S_γ are two increasingly important quantities in the study of the structure and scattering phenomena of atomic and molecular systems. Here, an information-theoretic method which makes use of the Bialynicki–Birula and Mycielski's inequality is described to find rigorous upper and lower bounds to these two entropies in a compact, simple and transparent form. The upper bounds to S_ρ are given in terms of radial expectation values $\langle r^\alpha\rangle$ and/or the mean logarithmic radii $\langle \ln r\rangle$ and $\langle (\ln r)^2\rangle$, whereas the lower bounds depend on the momentum expectation values $\langle p^\alpha\rangle$ and/or the mean logarithmic momenta $\langle \ln p\rangle$ and $\langle (\ln p)^2\rangle$. Similar bounds to S_γ are also shown in a parallel way. A near Hartree–Fock numerical analysis for all atoms with $Z<54$ shows that some of these bounds are so tight that they may be used as computational values for the corresponding quantities. The role of the mean logarithmic radius $\langle \ln r\rangle$ and the mean logarithmic momentum $\langle \ln p\rangle$ in the improvement of accuracy of the aforementioned bounds is certainly striking.

I. INTRODUCTION

The position-space entropy S_ρ and the momentum-space entropy S_γ are two information-theoretic concepts which are increasingly important in the study of the structure[1–9] and collisional phenomena[10] of atomic and molecular systems. They have been shown to be related with some fundamental quantities such as, for example, the kinetic energy,[1,9] and to predict momentum-space properties[11–13] of those systems.

Let us consider a N-electron atomic system characterized by the one-electron charge density $\rho(\mathbf{r}_1)$ given by

$$\rho(\mathbf{r}_1) = \sum_{\sigma_i=-1/2}^{+1/2} \int |\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N;\sigma_1,\sigma_2,\ldots,\sigma_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \ldots d\mathbf{r}_N,$$

where $\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N;\sigma_1,\sigma_2,\ldots,\sigma_N)$ is the normalized wave function of the system which is antisymmetric in the pairs $(\mathbf{r}_i,\sigma_i)$ of position-spin electronic coordinates. The density function $\rho(\mathbf{r})$ is, then, normalized to unity. The information entropy S_ρ is defined as

$$S_\rho = -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r}. \quad (1)$$

The momentum-space information entropy S_γ of the one-electron momentum density $\gamma(\mathbf{p})$ is defined in a fully analogous way. Gadre *et al.* recently computed these two entropies in the Thomas–Fermi model for neutral atoms[7] as well as within a Hartree–Fock framework for some simple systems (harmonic oscillator and hydrogen atom) and for several atoms and ions.[8] In addition, they obtain[9] rigorous upper bounds to the information entropies S_ρ and S_γ in terms of the second moment of the respective single-particle densities (i.e., $\langle r^2\rangle$ and $\langle p^2\rangle$) by means of the maximum entropy method in its simplest way; that is, for example, in the position space, by maximizing S_ρ subject to two constraints: normalization of the density $\rho(\mathbf{r})$ to unity and the expectation value $\langle r^2\rangle$.

One would like to extend the work of Gadre *et al.* to find new and improved additional bounds to the aforementioned information entropies by including any moment-type constraint but this has not yet been done in spite of efforts of many authors.[14,15] The reason is that the solution of the integrals in the evaluation of the constant Lagrange multipliers of the probability density which maximizes the corresponding entropy cannot be expressed in terms of elementary functions, generally speaking. This maximum entropy problem can be analytically solved only in the case of one-moment constraint provided that moment is of positive order. Even more, the existence of a solution is already problematic in the general case. Recently, Mead and Papanicolau[15] have found necessary and sufficient conditions for the existence of a maximum entropy solution for one-dimensional densities with an arbitrary number of moment constraints on a finite interval. In cases where the interval is infinite or semiinfinite, the maximum entropy problem is much less known and with not so much mathematical rigor. For finite many-particle systems, the relevant interval is usually the semiinfinite one, $[0,\infty)$. In this case the only well-established analytical result possibly corresponds[15–19] to the mere existence of a solution to the problem having as constraints the two[16] or three[19] moments of lowest positive order in addition to the normalization to unity; partial generalization of this result was done by Einbu,[20] who also considered the question of uniqueness.

In the present work we use a method described in Sec. II to obtain several families of analytical upper and lower bounds to the atomic information entropies S_ρ and S_γ. Upper bounds to S_ρ are given by means of one and two radial expectation values of positive and negative order with and without the mean logarithmic radius $\langle \ln r\rangle$. Corresponding bounds to the momentum entropy S_γ are also given. The upper bounds to both atomic entropies are collected and proved in Sec. III and the lower bounds are contained in Sec. IV. Some numerical tests of the accuracy of these bounds are done in Sec. V for several neutral atoms within a Hartree–Fock framework. Briefly, they show that the inclusion of the mean logarithmic radius makes the new upper bounds to the entropy of information certainly tight in both position and momentum spaces. Finally, some concluding remarks are given.

II. THEORETICAL GROUND

The information entropy for an absolutely continuous distribution with probability density $p(\mathbf{r})$ is defined as[21]

$$S_p=-\int p(\mathbf{r})\ln p(\mathbf{r})d\mathbf{r}, \quad (2)$$

where $p(\mathbf{r})$ is assumed to be normalized to unity, i.e.,

$$\int p(\mathbf{r})d\mathbf{r}=1. \quad (3)$$

A generalization of this concept is the so-called relative entropy[22] $I(p,f)$ associated to two probability density functions $p(\mathbf{r})$ and $f(\mathbf{r})$ and normalized to unity:

$$I(p,f)=\int p(\mathbf{r})\ln\frac{p(\mathbf{r})}{f(\mathbf{r})}\,d\mathbf{r}. \quad (4)$$

The relative entropy is a measure of the deviation of $p(\mathbf{r})$ from $f(\mathbf{r})$, which is usually called reference density or prior density. It has been successfully applied to a remarkable variety of fields, going from statistics[22,23] to quantum physics,[1,24] because it has several useful properties.[22,23] In particular, it is non-negative, i.e., $I(p,f)\geqslant 0$, which allows us to write

$$S_p\leqslant-\int p(\mathbf{r})\ln f(\mathbf{r})d\mathbf{r}. \quad (5)$$

It is interesting to remark that

$$S_p\leqslant-\int p(\mathbf{r})\ln p(r)d\mathbf{r}, \quad (6)$$

where $p(r)$ is the spherically averaged density defined by

$$p(r)=\frac{1}{4\pi}\int p(\mathbf{r})d\mathbf{r}. \quad (7)$$

The inequality (6) easily follows from Eqs. (5) and (7) with the choice $f(\mathbf{r})=p(r)$ as prior density.

The method which will be used here to find lower and upper bounds to the atomic information entropies S_ρ and S_γ consists of two steps:

(1) We use in the inequality (5) as prior density, a n-parametric density function $f(\mathbf{r};\alpha_1,\alpha_2,...,\alpha_n)$ normalized to unity to obtain a family of upper bounds

$$S_0(\alpha_1,\alpha_2,...,\alpha_n)=-\int p(\mathbf{r})\ln f(\mathbf{r};\alpha_1,\alpha_2,...,\alpha_n)d\mathbf{r} \quad (8)$$

and then we optimize $S_0(\alpha_1,...,\alpha_n)$ to find the best upper bound. Specifically, we will take the following prior estimates:

$$f_1(\mathbf{r})=Ar^m\exp(-ar^\alpha) \quad \text{for} \quad a>0,\ (m+3)\alpha>0, \quad (9)$$

$$f_2(\mathbf{r})=Ar^m\exp\left(-\beta r^\alpha-\frac{\nu}{r^\alpha}\right) \quad \text{for} \quad \beta>0,\ \nu>0, \quad (10)$$

$$f_3(\mathbf{r})=Ar^m\exp(-\beta r^{2\alpha}-\nu r^\alpha) \quad \text{for} \quad \beta>0,\ (m+3)\alpha>0, \quad (11)$$

where A is a constant to be determined by means of the normalization condition and m, α, β, and ν are parameters to be calculated in the maximization process.

Taking the atomic charge density $\rho(\mathbf{r})$ as the function $p(\mathbf{r})$, one finds rigorous upper bounds to the position-space information entropy S_ρ in terms of one or two radial expectation values $\langle r^\alpha\rangle$ and the mean logarithmic radius $\langle\ln r\rangle$ defined as

$$\langle r^\alpha\rangle=\int r^\alpha p(\mathbf{r})d\mathbf{r}, \quad (12)$$

$$\langle\ln r\rangle=\int \ln r\,p(\mathbf{r})d\mathbf{r}, \quad (13)$$

respectively. In an analogous way, rigorous upper bounds to the atomic momentum information entropy may be obtained in terms of the corresponding momentum expectation values $\langle p^\alpha\rangle$ and the mean logarithmic momentum $\langle\ln p\rangle$.

(2) The lower bounds to the atomic information entropies S_ρ and S_γ are obtained by combining the upper bounds encountered in the previous step with the Bialynicki–Birula and Mycielski (BBM) inequality given by[8,25]

$$S_\rho+S_\gamma\geqslant 3(1+\ln\pi), \quad (14)$$

where both electron and momentum densities are normalized to unity. This inequality and others involving information entropies have been already used in a variety of quantum-mechanical problems[25–31] and more specifically in the study of atomic systems.[7–9,11]

In this way one can rigorously find lower bounds to S_ρ in terms of one and two momentum expectation values $\langle p^\alpha\rangle$ and the mean logarithmic momentum $\langle\ln p\rangle$ as well as lower bounds to S_γ by means of one and two radial expectation values $\langle r^\alpha\rangle$ and the mean logarithmic radius $\langle\ln r\rangle$. Then, one has rigorous relationships between the information entropy in a space and fundamental and/or measurable quantities of the system *in the* complementary space, being given the latter ones by means of the aforementioned expectation values.

III. UPPER BOUNDS TO ATOMIC ENTROPIES

Here we will collect the main infinite sets of upper bounds that we have found for the atomic information entropies together with their corresponding proofs.

(i) If $\alpha > -3$ and $(m+3)\alpha > 0$, then

$$S_\rho \leqslant S_\rho(\alpha,m) \equiv \ln(A_{m,\alpha}\langle r^\alpha\rangle^{(m+3)/\alpha}) - m\langle \ln r\rangle \quad (15)$$

with the parameter

$$A_{m,\alpha} \equiv \frac{4\pi\Gamma[(m+3)/\alpha]}{|\alpha|[(m+3)/e\alpha]^{(m+3)/\alpha}}, \quad (16)$$

where e is the exponential number. For a fixed α, this inequality allows one to find an infinity of upper bounds $S_\rho(\alpha,m)$ for $(m+3)\alpha > 0$. For $m=0$ one has

$$S_\rho(\alpha,0) = \ln[A_\alpha\langle r^\alpha\rangle^{3/\alpha}] \quad \text{for} \quad 0<\alpha<\infty, \quad (17)$$

where $A_\alpha \equiv A_{0,\alpha}$. Some particular cases of this expression are

$$S_\rho(1,0) = \ln\left(\frac{8\pi}{27} e^3\langle r\rangle^3\right), \quad (18)$$

$$S_\rho(2,0) = \ln\left(\frac{2\pi e}{3}\langle r^2\rangle\right)^{3/2}. \quad (19)$$

Besides, Eq. (15) produces for $\alpha = -2$, -1, 1, and 2 the following families of bounds:

$$S_\rho(-2,m) = \ln\left(\frac{A_{m,-2}}{\langle r^{-2}\rangle^{(m+3)/2}}\right) - m\langle \ln r\rangle \quad \text{for} \quad m<-3, \quad (20)$$

$$S_\rho(-1,m) = \ln\left(\frac{A_{m,-1}}{\langle r^{-1}\rangle^{m+3}}\right) - m\langle \ln r\rangle \quad \text{for} \quad m<-3, \quad (21)$$

$$S_\rho(1,m) = \ln(A_{m,1}\langle r\rangle^{m+3}) - m\langle \ln r\rangle \quad \text{for} \quad m>-3, \quad (22)$$

$$S_\rho(2,m) = \ln(A_{m,2}\langle r^2\rangle^{(m+3)/2}) - m\langle \ln r\rangle \quad \text{for} \quad m>-3, \quad (23)$$

respectively. The optimization of Eqs. (20)–(23) allows one to find the m value which produces the best bounds to S_ρ although this is not analytically possible.

To prove the main inequality (15) it is enough to use the function $f_1(\mathbf{r})$ given by Eq. (9) as a prior estimate in Eq. (8) and to calculate the normalization constant A via the elementary integral[34]

$$\int_0^\infty x^{\nu-1}e^{-\mu x^p}dx = \frac{1}{|p|}\mu^{-\nu/p}\Gamma(\nu/p) \quad \text{for} \quad \mu,p\nu>0.$$

Then, the optimization with respect to the parameter a leads to Eq. (15) in a straightforward manner.

In a fully analogous way we can derive upper bounds to S_γ depending on the momentum expectation values $\langle p^\alpha\rangle$ and the mean logarithmic momentum $\langle \ln p\rangle$. Their corresponding expressions are similar to Eqs. (15)–(23) but keeping in mind that the only existing values $\langle p^\alpha\rangle$ are those with $-3<\alpha<5$ due to the p^{-8} asymptotic behavior of the atomic momentum density $\gamma(\mathbf{p})$ at large momenta.[32,33] In particular, one can write

$$S_\gamma \leqslant S_\gamma(\alpha,m) \equiv \ln(A_{m,\alpha}\langle p^\alpha\rangle^{(m+3)/\alpha}) - m\langle \ln p\rangle \quad (24)$$

for $-3<\alpha<5$ and $(m+3)\alpha>0$. Similarly, to Eqs. (20)–(23) one has

$$S_\gamma(-2,m) = \ln\left(\frac{A_{m,-2}}{\langle p^{-1}\rangle^{(m+3)/2}}\right) - m\langle \ln p\rangle \quad \text{for} \quad m<-3, \quad (25)$$

$$S_\gamma(-1,m) = \ln\left(\frac{A_{m,-1}}{\langle p^{-1}\rangle^{m+3}}\right) - m\langle \ln p\rangle \quad \text{for} \quad m<-3, \quad (26)$$

$$S_\gamma(1,m) = \ln(A_{m,1}\langle p\rangle^{m+3}) - m\langle \ln p\rangle \quad \text{for} \quad m>-3, \quad (27)$$

$$S_\gamma(2,m) = \ln(A_{m,2}\langle p^2\rangle^{(m+3)/2}) - m\langle \ln p\rangle \quad \text{for} \quad m>-3, \quad (28)$$

respectively. Since the kinetic energy is $T=N\langle p^2\rangle/2$ and taking into account Eq. (28), one can write

$$S_\gamma \leqslant \frac{3}{2}\left(1+\ln\frac{4\pi T}{3N}\right), \quad (29)$$

a relation recently obtained by Gadre and Bendale.[9] Expressions (24)–(28) considerably extend and improve this relationship.

(ii) If $\alpha > -3$, but $\alpha \neq 0$, then

$$S_\rho \leqslant S_\rho^*(\alpha) \equiv \ln\left[\left(\frac{32\pi^3 e}{\alpha^2}\right)^{1/2}(\langle r^{-\alpha}\rangle - \langle r^\alpha\rangle^{-1})^{1/2}\right] + \left(3+\frac{\alpha}{2}\right)\langle \ln r\rangle, \quad (30)$$

$$S_\rho \leqslant S_\rho^{**}(\alpha) \equiv \tfrac{1}{2}[4\langle r^{-\alpha}\rangle\langle r^\alpha\rangle - 3]^{1/2} + \frac{1}{2}\ln 8\pi^3\frac{(4\langle r^{-\alpha}\rangle\langle r^\alpha\rangle - 3)^{1/2}-1}{\alpha^2\langle r^{-\alpha}\rangle^3} + (3-\tfrac{3}{2}\alpha)\langle \ln r\rangle. \quad (31)$$

Some particular upper bounds from inequalities (30) and (31) are

$$S_\rho^*(1) = \ln(32\pi^3 e)^{1/2} + \ln[\langle r^{-1}\rangle - \langle r\rangle^{-1}]^{1/2} + \tfrac{7}{2}\langle \ln r\rangle, \quad (32)$$

$$S_\rho^*(2) = \ln(8\pi^3 e)^{1/2} + \ln[\langle r^{-2}\rangle - \langle r^2\rangle^{-1}]^{1/2} + 4\langle \ln r\rangle, \quad (33)$$

and

$$S_\rho^{**}(1) = \tfrac{1}{2}[4\langle r^{-1}\rangle\langle r\rangle - 3]^{1/2} + \frac{1}{2}\ln 8\pi^3\frac{[4\langle r^{-1}\rangle\langle r\rangle - 3]^{1/2}-1}{\langle r^{-1}\rangle^3} + \frac{3}{2}\langle \ln r\rangle, \quad (34)$$

$$S_\rho^{**}(2)=\tfrac{1}{2}(4\langle r^{-2}\rangle\langle r^2\rangle-3)^{1/2}+\frac{1}{2}\ln 2\pi^3\frac{[4\langle r^{-2}\rangle\langle r^2\rangle-3]^{1/2}-1}{\langle r^{-2}\rangle^3}. \quad (35)$$

The best upper bound of these two infinite families $S_\rho^*(\alpha)$ and $S_\rho^{**}(\alpha)$ is obtained by optimizing the corresponding expressions (30) and (31), respectively, but this may only be done numerically.

It is interesting to remark that the limit case $\alpha\to 0$ of the two expressions (30) and (31) leads to a new upper bound for S_ρ by means of the mean logarithmic radius $\langle \ln r\rangle$ and the mean-square logarithmic radius $\langle(\ln r)^2\rangle$ as

$$S_\rho\leqslant S_\rho'\equiv\tfrac{1}{2}\ln\{32\pi^3 e[\langle(\ln r)^2\rangle-\langle\ln r\rangle^2]\}+3\langle\ln r\rangle. \quad (36)$$

To prove the two main inequalities (30) and (31), we have used in Eq. (8) the function $f_2(\mathbf{r})$ given by Eq. (10), properly normalized to unity, as a prior estimate. One obtains

$$S_\rho\leqslant -\ln A+\beta\langle r^\alpha\rangle+\nu\langle r^{-\alpha}\rangle-m\langle\ln r\rangle$$

with

$$A=\frac{|\alpha|(\beta/\nu)^{(m+3)/2\alpha}}{8\pi K_{(m+3)/\alpha}(2\sqrt{\beta\nu})},$$

where the K function is the modified Bessel function of the third kind or Basset function $K_\xi(x)$. Then the succesive choices of $(m+3)/\alpha=\pm\frac{1}{2}, \pm\frac{3}{2}$ followed by optimization with respect to β and ν produce the searched inequalities (30) and (31), respectively. Other choices for $(m+3)/\alpha$ would lead to new upper bounds. Here, once again the restriction $\alpha>-3$ comes from the nonexistence of moments of such orders of the atomic ρ density.

Working similarly in the momentum space, one obtains upper bounds to the momentum entropy S_γ fully analogous to those for S_ρ given in expressions (30)–(36), but in terms of $\langle p^\alpha\rangle$, $\langle p^{-\alpha}\rangle$, and $\langle\ln p\rangle$.

(iii) If z is a real number and $p=(m+3)/\alpha$ is positive, then

$$S_\rho\leqslant S_\rho(\alpha,p,z)\equiv\ln\left(\frac{4\pi\Gamma(p)}{|\alpha|}D_{-p}(z)\right)+\frac{z^2}{4}+p\ln x+(3-p\alpha)\langle\ln r\rangle+\frac{\langle r^{2\alpha}\rangle}{2x^2}+\frac{z\langle r^\alpha\rangle}{x} \quad (37)$$

with

$$x=\frac{1}{2p}[z\langle r^\alpha\rangle+(z^2\langle r^\alpha\rangle^2+4p\langle r^{2\alpha}\rangle)^{1/2}]$$

and where $D_{-p}(z)$ is the parabolic cylinder function[34] of order $-p$. A particular upper bound produced by this inequality is

$$S_\rho(\alpha,1,z)\equiv\frac{z^2}{2}+\frac{1}{2}\ln\frac{8\pi^3}{\alpha^2}[1-\phi(z/\sqrt{2})]^2x^2+(3-\alpha)\langle\ln r\rangle+\frac{\langle r^{2\alpha}\rangle}{2x^2}+\frac{z\langle r^\alpha\rangle}{x} \quad (38)$$

for any real z [where $\phi(x)$ is the so-called error function].

The best member of the family of upper bounds $\{S_\rho(\alpha,p,z)\}$ would be obtained via optimization with respect to the three parameters α, p, and z; however, we have not been able to do this analytically. To prove inequality (37) we have used in Eq. (8) the function $f_3(\mathbf{r})$ given by Eq. (11), properly normalized to unity, as prior estimate. One finds

$$S_\rho\leqslant -\ln A+\beta\langle r^{2\alpha}\rangle+\nu\langle r^\alpha\rangle-m\langle\ln r\rangle$$

with

$$A=\frac{|\alpha|(2\beta)^{(m+3)/2\alpha}e^{-\nu^2/8\beta}}{4\pi\Gamma[(m+3)/\alpha]D_{-(m+3)/\alpha}(\nu/\sqrt{2\beta})}.$$

Then, the notations $p\equiv(m+3)/\alpha$ and $z\equiv\nu/\sqrt{2\beta}$ together with the minimization with respect to β, lead to the searched inequality (37). One should also point out that to obtain the normalization constant A, the result[34]

$$\int_0^\infty x^{\mu-1}e^{-\beta x^2-\nu x}dx=(2\beta)^{-\mu/2}\Gamma(\mu)e^{\nu^2/8\beta}D_{-\mu}(\nu/\sqrt{2\beta}) \quad \text{for} \quad \beta,\mu>0$$

has been used.

In a fully analogous manner one would obtain in the momentum space a family of upper bounds $S_\gamma(\alpha,p,z)$ to the momentum entropy S_γ similar to expressions (37) and (38) but given in terms of $\langle p^\alpha\rangle$, $\langle p^{2\alpha}\rangle$, and $\langle\ln p\rangle$.

IV. LOWER BOUNDS TO ATOMIC ENTROPIES

The combination of the BBM's inequality (14) with each upper bound to the position (momentum) information entropy produces a lower bound to the momentum (position) information entropy. Thus, we may obtain lower bounds to the entropy in one space by means of the expectation values of the coordinate in the complementary space. Here, we will only quote some of them.

(i) If $-3<\alpha<5$ and $\alpha(m+3)>0$, then the expressions (14) and (24) give

$$S_\rho\geqslant 3(1+\ln\pi)-S_\gamma(\alpha,m)=3(1+\ln\pi)-\ln(A_{m,\alpha}\langle p^\alpha\rangle^{(m+3)/\alpha})+m\langle\ln p\rangle, \quad (39)$$

where the parameter $A_{m,\alpha}$ is given by Eq. (16). Some particular cases are the following.

For $m=0$,

$$S_\rho\geqslant 3(1+\ln\pi)-\ln(A_\alpha\langle p^\alpha\rangle^{3/\alpha}) \quad 0<\alpha<5. \quad (40)$$

For $\alpha=2$,

$$S_\rho\geqslant 3(1+\ln\pi)-\ln(A_{m,2}\langle p^2\rangle^{(m+3)/2})+m\langle\ln p\rangle, \quad m>-\tfrac{3}{4}. \quad (41)$$

TABLE I. Values, in atomic units, of the position entropy of information S_ρ, the radial expectation values $\langle r^\alpha\rangle$ with $\alpha=-2, -1, 1$, and 2, the mean logarithmic radius $\langle \ln r\rangle$ and the mean-square logarithmic radius $\langle(\ln r)^2\rangle$ for all the atoms with $Z<54$. The near Hartree–Fock atomic wave functions of Clementi and Roetti have been used.

Z	S_ρ	$\langle r^{-2}\rangle$	$\langle r^{-1}\rangle$	$\langle r\rangle$	$\langle r^2\rangle$	$\langle \ln r\rangle$	$\langle(\ln r)^2\rangle$
1	4.144 71	2.000 00	1.000 00	1.500 00	3.000 00	0.229 64	0.447 67
2	2.698 41	5.995 92	1.687 34	0.927 25	1.184 66	−0.270 82	0.510 37
3	3.701 38	10.072 30	1.905 18	1.673 27	6.210 46	−0.078 56	1.253 60
4	3.623 86	14.406 02	2.102 18	1.532 20	4.329 68	−0.100 50	1.279 75
5	3.405 40	18.732 65	2.275 89	1.362 10	3.169 94	−0.163 76	1.229 68
6	3.106 03	23.128 86	2.448 22	1.190 76	2.298 70	−0.250 07	1.172 20
7	2.801 61	27.602 83	2.619 43	1.049 98	1.725 81	−0.339 15	1.141 41
8	2.550 62	32.157 09	2.782 44	0.951 28	1.396 58	−0.415 87	1.143 80
9	2.298 86	36.785 78	2.946 51	0.864 20	1.137 49	−0.492 46	1.161 38
10	2.055 26	41.490 03	3.111 32	0.789 15	0.937 57	−0.566 61	1.193 52
11	2.330 05	46.316 85	3.220 94	0.985 74	2.468 19	−0.531 91	1.398 68
12	2.395 03	51.235 23	3.326 70	1.021 21	2.464 10	−0.527 17	1.486 31
13	2.445 55	56.180 56	3.423 06	1.055 02	2.572 99	−0.521 58	1.560 74
14	2.418 96	61.159 04	3.517 38	1.034 16	2.303 70	−0.531 07	1.590 12
15	2.358 81	66.170 64	3.609 85	0.998 09	2.017 48	−0.547 89	1.603 00
16	2.260 04	71.303 64	3.718 59	0.959 98	1.811 22	−0.576 16	1.626 54
17	2.221 89	76.279 08	3.786 61	0.930 76	1.625 64	−0.586 29	1.622 22
18	2.133 84	81.389 48	3.873 60	0.892 82	1.446 40	−0.609 94	1.626 81
19	2.301 66	86.536 96	3.941 76	1.023 75	2.694 44	−0.585 83	1.741 79
20	2.363 04	91.721 68	4.007 97	1.062 32	2.829 18	−0.575 95	1.797 80
21	2.298 11	96.873 05	4.081 38	1.022 68	2.531 17	−0.595 09	1.796 29
22	2.218 68	102.026 57	4.155 45	0.981 61	2.280 82	−0.617 87	1.793 70
23	2.135 14	107.195 02	4.229 26	0.942 63	2.065 98	−0.641 68	1.793 03
24	1.955 70	112.332 38	4.310 90	0.853 33	1.567 49	−0.686 66	1.758 63
25	1.962 58	117.563 03	4.376 38	0.871 50	1.723 14	−0.690 91	1.798 71
26	1.882 17	122.777 78	4.448 26	0.840 75	1.582 45	−0.714 13	1.805 39
27	1.800 09	127.999 61	4.520 27	0.811 49	1.459 57	−0.737 80	1.814 04
28	1.718 30	133.231 52	4.592 14	0.783 88	1.350 14	−0.761 44	1.824 62
29	1.563 29	138.426 79	4.671 66	0.726 35	1.113 23	−0.800 77	1.816 80
30	1.556 30	143.733 57	4.735 48	0.733 40	1.166 42	−0.808 34	1.851 34
31	1.574 27	149.032 29	4.795 17	0.754 66	1.319 66	−0.809 88	1.893 85
32	1.567 30	154.361 88	4.853 96	0.756 16	1.299 05	−0.815 20	1.921 22
33	1.549 75	159.709 70	4.911 87	0.750 91	1.243 96	−0.822 23	1.942 11
34	1.534 20	165.081 12	4.968 22	0.747 11	1.210 30	−0.828 67	1.962 48
35	1.510 58	170.461 61	5.023 96	0.739 12	1.157 12	−0.836 50	1.978 75
36	1.481 44	175.848 11	5.079 11	0.728 85	1.097 86	−0.845 28	1.992 51
37	1.576 17	181.235 23	5.126 32	0.805 38	1.842 85	−0.831 71	2.062 09
38	1.621 34	186.672 61	5.172 89	0.837 17	2.001 22	−0.824 35	2.104 31
39	1.614 03	192.094 24	5.221 12	0.829 48	1.877 40	−0.828 09	2.117 65
40	1.594 42	197.524 10	5.269 72	0.817 05	1.759 00	−0.834 50	2.126 55
41	1.523 34	202.942 17	5.321 12	0.773 04	1.426 58	−0.851 47	2.112 98
42	1.490 53	208.384 25	5.369 63	0.758 41	1.336 54	−0.860 46	2.119 11
43	1.461 66	213.825 44	5.417 37	0.747 32	1.278 76	−0.868 73	2.127 42
44	1.429 94	219.289 83	5.464 95	0.735 75	1.224 64	−0.877 63	2.135 26
45	1.395 41	224.751 59	5.512 31	0.723 48	1.170 43	−0.887 14	2.142 50
46	1.301 89	230.202 42	5.562 94	0.682 02	0.914 76	−0.906 67	2.129 75
47	1.323 23	235.698 01	5.606 32	0.699 48	1.073 11	−0.906 87	2.157 44
48	1.332 89	241.226 06	5.648 04	0.708 17	1.132 05	−0.907 74	2.178 11
49	1.351 83	246.735 53	5.689 70	0.724 70	1.253 68	−0.906 58	2.205 30
50	1.357 02	252.249 16	5.730 15	0.729 43	1.260 72	−0.907 30	2.223 14
51	1.354 93	257.773 28	5.770 04	0.729 37	1.236 54	−0.909 17	2.236 89
52	1.353 53	263.311 10	5.809 19	0.730 08	1.226 06	−0.910 83	2.250 45
53	1.346 66	268.858 67	5.848 03	0.727 68	1.197 24	−0.913 42	2.261 28
54	1.335 75	274.408 36	5.886 49	0.723 33	1.160 08	−0.916 69	2.270 22

For $m=0$ and $\alpha=2$,

$$S_\rho \geq 3(1+\ln \pi) - \ln\left(\frac{2\pi e}{3}\langle p^2\rangle\right)^{3/2}. \tag{42}$$

The last inequality together with the definition $T=N\langle p^2\rangle/2$ allows to correlate the position entropy S_ρ and the quantum-mechanical kinetic energy T as

$$S_\rho \geq \frac{3N}{2}(1+\ln \pi) + \frac{1}{2} N \ln N - \frac{3}{2} N \ln \frac{4T}{3} \tag{43}$$

TABLE II. Values, in atomic units, of the momentum information entropy S_γ, the momentum expectation values $\langle p^\alpha \rangle$ with $\alpha=-2, -1, 1$, and 2, the mean logarithmic momentum $\langle \ln p \rangle$ and the mean-square logarithmic momentum $\langle (\ln p)^2 \rangle$ for all the atoms with $Z<54$. The near Hartree–Fock atomic wave functions of Clementi and Roetti have been used.

Z	S_γ	$\langle p^{-2} \rangle$	$\langle p^{-1} \rangle$	$\langle p \rangle$	$\langle p^2 \rangle$	$\langle \ln p \rangle$	$\langle (\ln p)^2 \rangle$
1	2.421 86	5.000 00	1.697 70	0.848 83	1.000 00	−0.333 33	0.467 38
2	3.913 52	1.022 35	0.535 15	0.699 75	1.430 85	0.145 41	0.415 89
3	3.996 88	2.950 67	0.576 20	0.545 07	1.651 67	0.033 87	1.099 56
4	4.190 12	1.580 70	0.394 90	0.464 63	1.821 62	0.089 85	1.169 93
5	4.705 90	0.650 48	0.239 18	0.425 96	1.962 32	0.275 15	1.057 36
6	5.156 52	0.326 62	0.159 85	0.401 72	2.093 83	0.440 34	1.056 75
7	5.549 33	0.185 76	0.114 23	0.384 96	2.220 43	0.584 90	1.121 92
8	5.867 34	0.117 21	0.086 76	0.370 64	2.337 75	0.701 43	1.219 32
9	6.163 32	0.078 35	0.067 94	0.360 08	2.454 56	0.809 08	1.339 51
10	6.437 02	0.054 80	0.054 56	0.351 97	2.570 90	0.908 06	1.474 75
11	6.483 07	0.267 25	0.071 99	0.336 63	2.675 27	0.861 33	1.766 08
12	6.515 25	0.256 65	0.071 49	0.323 13	2.772 33	0.849 12	1.919 84
13	6.619 18	0.164 78	0.060 93	0.311 98	2.862 38	0.877 97	1.969 98
14	6.733 72	0.114 03	0.052 12	0.302 45	2.947 43	0.916 02	2.013 16
15	6.848 63	0.083 23	0.045 04	0.294 15	3.028 60	0.957 03	2.059 03
16	7.002 42	0.064 89	0.039 90	0.286 33	3.104 94	1.014 09	2.146 77
17	7.052 09	0.050 57	0.035 14	0.279 75	3.179 71	1.031 90	2.162 26
18	7.155 27	0.040 45	0.031 26	0.273 77	3.251 83	1.070 88	2.217 46
19	7.172 56	0.139 56	0.038 14	0.266 54	3.319 37	1.042 70	2.388 40
20	7.180 00	0.152 05	0.039 37	0.259 83	3.383 75	1.030 57	2.492 86
21	7.303 20	0.122 14	0.034 75	0.255 62	3.445 57	1.077 04	2.537 12
22	7.426 70	0.103 30	0.031 07	0.252 02	3.505 77	1.123 55	2.594 01
23	7.547 04	0.087 95	0.027 93	0.248 81	3.564 83	1.168 91	2.656 54
24	7.751 33	0.048 10	0.021 27	0.247 41	3.622 75	1.262 37	2.679 40
25	7.776 80	0.065 91	0.022 95	0.243 31	3.679 52	1.255 55	2.795 46
26	7.882 52	0.057 15	0.020 92	0.240 77	3.734 92	1.295 21	2.865 44
27	7.985 97	0.033 90	0.016 45	0.239 74	3.789 63	1.333 97	2.939 03
28	8.086 37	0.044 39	0.017 62	0.236 39	3.844 29	1.371 58	3.014 49
29	8.250 39	0.028 37	0.014 14	0.235 65	3.897 59	1.447 97	3.071 81
30	8.278 50	0.035 08	0.015 03	0.232 67	3.950 67	1.443 59	3.169 69
31	8.323 80	0.028 27	0.014 42	0.229 85	4.002 58	1.451 52	3.231 02
32	8.371 38	0.023 24	0.013 67	0.227 15	4.053 44	1.462 98	3.283 00
33	8.418 10	0.019 75	0.012 95	0.224 54	4.103 33	1.475 80	3.331 38
34	8.458 27	0.017 38	0.012 36	0.221 96	4.152 06	1.487 04	3.378 01
35	8.499 34	0.015 24	0.011 75	0.219 49	4.199 71	1.499 81	3.422 19
36	8.540 76	0.013 49	0.011 17	0.217 14	4.246 94	1.513 36	3.465 05
37	8.544 18	0.043 36	0.013 38	0.214 47	4.292 43	1.495 23	3.567 87
38	8.542 20	0.050 23	0.014 19	0.211 89	4.337 37	1.484 71	3.639 14
39	8.590 46	0.041 88	0.013 18	0.209 76	4.380 77	1.501 60	3.668 12
40	8.640 51	0.036 78	0.012 35	0.207 80	4.423 50	1.519 67	3.702 27
41	8.732 60	0.020 10	0.010 10	0.206 31	4.465 85	1.564 31	3.703 08
42	8.782 24	0.018 04	0.009 53	0.204 56	4.507 14	1.583 08	3.743 58
43	8.828 75	0.016 89	0.009 07	0.202 84	4.547 91	1.600 26	3.785 67
44	8.875 45	0.015 81	0.008 65	0.201 22	4.588 18	1.617 60	3.828 66
45	8.922 05	0.014 79	0.008 24	0.199 67	4.628 00	1.635 15	3.871 98
46	8.988 63	0.004 50	0.006 65	0.198 53	4.666 96	1.678 06	3.885 62
47	9.013 78	0.013 03	0.007 52	0.196 75	4.705 74	1.669 86	3.960 71
48	9.024 81	0.017 09	0.008 00	0.194 94	4.743 13	1.663 96	4.019 83
49	9.048 75	0.014 51	0.007 84	0.193 34	4.781 43	1.666 71	4.059 90
50	9.072 79	0.012 75	0.007 63	0.191 71	4.818 40	1.671 28	4.093 86
51	9.096 56	0.011 30	0.007 39	0.190 13	4.854 71	1.677 05	4.124 79
52	9.116 93	0.010 29	0.007 20	0.188 57	4.890 19	1.682 01	4.155 76
53	9.138 06	0.009 38	0.006 99	0.187 05	4.925 66	1.687 94	4.185 05
54	9.159 75	0.008 57	0.006 77	0.185 57	4.960 19	1.694 64	4.212 88

which was first discovered by Gadre and Bendale[9] in 1987. This result is generalized by inequalities (39)–(41) via the inclusion of expectation values $\langle p^\alpha \rangle$ of index α other than 2 and/or the mean logarithmic momentum $\langle \ln p \rangle$. Moreover, the inequalities (14) and (15) lead to the following lower bound. If $\alpha > -3$ and $\alpha(m+3) > 0$, then

$$S_\gamma \geqslant 3(1+\ln \pi) - S_\rho(\alpha,m)$$

$$= 3(1+\ln \pi) - \ln(A_{m,\alpha} \langle r^\alpha \rangle^{(m+3)/\alpha}) + m\langle \ln r \rangle \qquad (44)$$

Some particular cases are the following. For $m=0$,

$$S_\gamma \geqslant 3(1+\ln \pi) - \ln(A_\alpha \langle r^\alpha \rangle^{3/\alpha}), \quad 0<\alpha<\infty. \qquad (45)$$

For $m=0$ and $\alpha=2$,

$$S_\gamma \geqslant 3(1+\ln \pi) - \ln\left(\frac{2\pi e}{3}\langle r^2\rangle\right)^{3/2} \tag{46}$$

which is already known.[9]

For $\alpha=-1$,

$$S_\gamma \geqslant 3(1+\ln \pi) - \ln \frac{A_{m,-1}}{\langle r^{-1}\rangle^m + 3} + m\langle \ln r\rangle, \quad m<-3. \tag{47}$$

For $\alpha=1$,

$$S_\gamma \geqslant 3(1+\ln \pi) - \ln(A_{m,1}\langle r\rangle^m + 3) + m\langle \ln r\rangle, \quad m>-3 \tag{48}$$

For $\alpha=2$,

$$S_\gamma \geqslant 3(1+\ln \pi) - \ln(A_{m,2}\langle r^2\rangle^{(m+3)/2}) + m\langle \ln r\rangle, \quad m>-\tfrac{3}{4}. \tag{49}$$

Of course, for a fixed α the best lower bound is obtained in each case by optimizing with respect to m but this cannot be analytically done in general.

(ii) From inequalities (14) and (36), one has

$$S_\gamma \geqslant \tfrac{5}{2}(1-\ln 2) + \tfrac{3}{2}\ln \pi - \ln(\langle(\ln r)^2\rangle - \langle \ln r\rangle^2)^{1/2} - 3\langle \ln r\rangle. \tag{50}$$

A similar lower bound for the information entropy in position space, S_ρ, may be written by means of the expectation values $\langle \ln p\rangle$ and $\langle(\ln p)^2\rangle$.

V. NUMERICAL STUDY

Here we will study the quality of the bounds found in the two previous sections for all atoms with $Z \leqslant 54$ by means of the near Hartree–Fock atomic wave functions of Clementi and Roetti.[35] We will concentrate on the first set of upper bounds given in Sec. III; specifically, we will consider the quantities

$S_\rho(\alpha,m)$ with $\alpha=-2$, -1, 1, and 2 and $m=0,m_{\rm opt}$

given by Eqs. (18)–(23), and the corresponding ones $S_\gamma(\alpha,m)$ in the momentum space. The symbol $m_{\rm opt}$ denotes the value of m which gives the optimal (i.e., best) bound in the corresponding equation to the entropy. It is important to remark that $S_\rho(\alpha,m=0)\equiv S_\rho(\alpha)$ depends only on $\langle r^\alpha\rangle$, whereas $S_\rho(\alpha,m\neq 0)$ depends additionally on $\langle \ln r\rangle$, and similarly for $S_\gamma(\alpha,m)$ in momentum space. In addition, the accuracy of the upper bounds S'_ρ and its partner S'_γ in momentum space, will be analyzed. They are of enormous interest since they depend on the mean logarithmic radius and the mean-square logarithmic radius, only.

To carry out this numerical study, we evaluate firstly the Hartree–Fock values of the position space entropy S_ρ and the expectation values $\langle r^\alpha\rangle$, with $\alpha=-2$, -1, 1, and 2, $\langle \ln r\rangle$, and $\langle(\ln r)^2\rangle$. These are given in Table I. The values of the corresponding quantities in momentum space, that is S_γ, $\langle p^\alpha\rangle$, $\langle \ln p\rangle$, and $\langle(\ln p)^2\rangle$ are shown in Table II. Then, once we know these expectation values, any of the searched bounds may be easily calculated and compared with the Hartree–Fock (HF) value of the corresponding entropy. This is done in Tables III and IV and Figs. 1–6.

In Figs. 1 and 2 the bounds $S_\rho(\alpha)$ and $S_\gamma(\alpha)$ depending on a specific radial expectation value (only the cases $\alpha=1$, 2 are shown) are compared with the HF entropy, respectively. One notices that (i) the bounds with $\alpha=1$ are

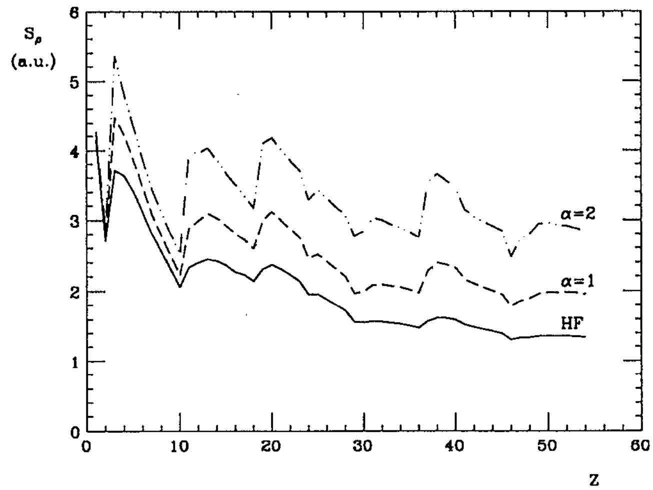

FIG. 1. Comparison between the Hartree–Fock value of the position entropy of information S_ρ for all the atoms with $1<Z<54$ and two upper bounds $S_\rho(\alpha)\equiv S_\rho(\alpha,m=0)$ which depend on a radial expectation value $\langle r^\alpha\rangle$. Atomic units are used throughout.

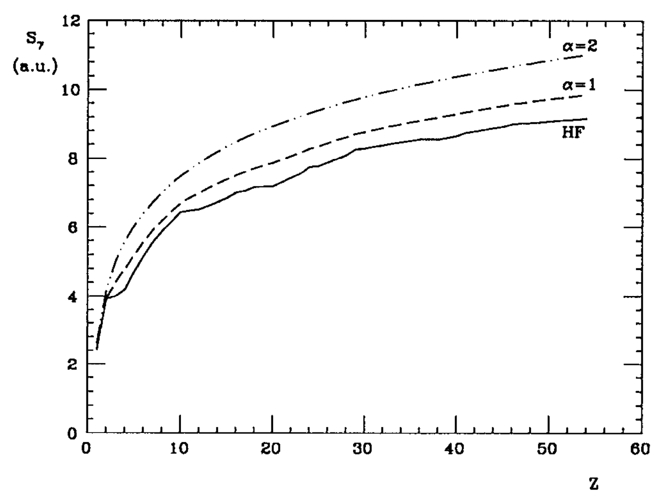

FIG. 2. Comparison between the Hartree–Fock value of the momentum entropy of information S_γ for all the atoms with $1<Z<54$ and two upper bounds $S_\gamma(\alpha)\equiv S_\gamma$ $(\alpha,m=0)$ which depend on a radial expectation value $\langle p^\alpha\rangle$. Atomic units are used throughout.

TABLE III. Values, in percent, of the upper bound $S_\rho(\alpha,m)$ to the position entropy S_ρ with $\alpha=-2$, -1, 1, and 2, and $m=m_{\rm opt}$ [i.e., the optimal value of m in the same sense that it produces, for a given α, the best upper bound as given by Eq. (15)] for all atoms with $Z<54$.

Z	m	S_ρ (−2,m)	m	S_ρ (−1,m)	m	S_ρ (1,m)	m	S_ρ (2,m)
1	−4.09	91.7	−5.33	96.7	0.00	100.0	−1.17	99.6
2	−4.01	87.9	−5.13	95.2	−0.28	100.0	−1.34	99.0
3	−3.63	92.4	−4.02	95.9	−2.02	95.2	−2.32	93.8
4	−3.56	89.9	−3.91	93.7	−1.92	96.5	−2.21	96.2
5	−3.54	87.8	−3.89	92.2	−1.80	97.2	−2.12	97.3
6	−3.53	85.5	−3.91	90.7	−1.68	97.6	−2.04	97.9
7	−3.53	83.3	−3.93	89.3	−1.57	97.8	−1.97	98.3
8	−3.53	81.4	−3.96	88.3	−1.49	98.0	−1.92	98.5
9	−3.54	79.3	−3.98	87.0	−1.41	98.1	−1.88	98.6
10	−3.54	77.0	−4.01	85.7	−1.34	98.2	−1.84	98.6
11	−3.51	82.6	−3.91	90.6	−1.90	95.1	−2.31	90.2
12	−3.49	83.7	−3.87	91.5	−1.95	95.9	−2.31	92.4
13	−3.48	84.2	−3.83	91.8	−2.00	96.2	−2.32	93.3
14	−3.47	83.7	−3.81	91.3	−1.98	96.7	−2.29	94.5
15	−3.46	82.7	−3.81	90.5	−1.95	97.0	−2.26	95.3
16	−3.46	81.6	−3.80	89.6	−1.93	96.7	−2.24	95.4
17	−3.46	80.8	−3.80	88.9	−1.89	97.3	−2.21	96.4
18	−3.45	79.5	−3.80	87.9	−1.86	97.3	−2.18	96.7
19	−3.44	82.8	−3.76	90.9	−2.05	96.6	−2.37	92.6
20	−3.43	83.6	−3.74	91.5	−2.08	97.0	−2.37	93.6
21	−3.43	82.9	−3.74	91.1	−2.06	97.3	−2.36	94.1
22	−3.43	82.0	−3.74	90.5	−2.03	97.5	−2.34	94.2
23	−3.43	81.0	−3.75	89.9	−2.01	97.6	−2.33	94.2
24	−3.43	78.5	−3.77	88.1	−1.92	97.9	−2.27	94.6
25	−3.43	78.9	−3.76	88.6	−1.96	97.6	−2.30	93.8
26	−3.43	77.9	−3.77	87.9	−1.94	97.6	−2.29	93.7
27	−3.43	76.8	−3.77	87.2	−1.92	97.6	−2.28	93.5
28	−3.43	75.7	−3.78	86.5	−1.90	97.5	−2.27	93.2
29	−3.44	72.9	−3.80	84.4	−1.82	97.6	−2.23	92.9
30	−3.43	73.2	−3.80	84.9	−1.86	97.3	−2.25	92.5
31	−3.43	73.9	−3.79	85.6	−1.92	96.7	−2.29	91.3
32	−3.43	74.0	−3.78	85.8	−1.93	96.8	−2.29	91.8
33	−3.43	73.7	−3.77	85.6	−1.93	96.9	−2.28	92.5
34	−3.42	73.5	−3.77	85.5	−1.93	97.0	−2.28	93.0
35	−3.42	73.1	−3.77	85.2	−1.93	97.2	−2.27	93.5
36	−3.42	72.5	−3.77	84.7	−1.92	97.3	−2.25	93.9
37	−3.41	75.2	−3.75	87.2	−2.06	95.5	−2.39	88.4
38	−3.41	76.2	−3.73	88.1	−2.10	95.3	−2.41	88.9
39	−3.41	76.1	−3.73	88.0	−2.09	95.8	−2.40	89.8
40	−3.41	75.8	−3.73	87.8	−2.08	96.2	−2.39	90.5
41	−3.41	74.3	−3.73	86.5	−2.03	97.0	−2.34	92.1
42	−3.41	73.6	−3.73	86.0	−2.01	97.2	−2.33	92.5
43	−3.40	73.0	−3.73	85.5	−2.00	97.3	−2.32	92.7
44	−3.40	72.3	−3.73	85.0	−1.99	97.4	−2.31	92.7
45	−3.40	71.5	−3.73	84.4	−1.98	97.4	−2.30	92.7
46	−3.41	68.9	−3.74	82.0	−1.91	97.7	−2.23	95.0
47	−3.40	69.9	−3.73	83.1	−1.95	97.4	−2.29	92.6
48	−3.40	70.4	−3.73	83.6	−1.98	97.3	−2.31	92.2
49	−3.40	71.0	−3.72	84.3	−2.01	96.8	−2.33	91.2
50	−3.40	71.2	−3.72	84.5	−2.02	96.9	−2.34	91.5
51	−3.39	71.2	−3.71	84.5	−2.02	97.0	−2.33	92.0
52	−3.39	71.2	−3.71	84.4	−2.03	97.1	−2.33	92.4
53	−3.39	71.0	−3.71	84.3	−2.03	97.2	−2.33	92.8
54	−3.39	70.7	−3.71	84.0	−2.02	97.2	−2.32	93.2

TABLE IV. Values, in percent, of the upper bound $S_\gamma(\alpha,m)$ to the momentum entropy S_γ with $\alpha=-2$, -1, 1, and 2, and $m=m_{\rm opt}$ (i.e., the optimal value of m in the same sense that it leads, for a given α, the best upper bound) for all atoms with $Z<54$.

Z	m	S_γ (−2,m)	m	S_γ (−1,m)	m	S_γ (1,m)	m	S_γ (2,m)
1	−4.30	89.5	−5.71	96.4	0.11	99.4	−1.24	96.9
2	−4.22	93.6	−5.50	98.0	−0.22	99.5	−1.43	97.5
3	−3.61	91.4	−3.99	94.9	−1.77	98.0	−2.15	97.1
4	−3.67	93.8	−4.05	96.4	−1.92	96.8	−2.26	95.4
5	−3.77	95.7	−4.24	98.1	−1.82	97.4	−2.24	95.7
6	−3.84	96.5	−4.40	98.8	−1.72	97.8	−2.20	95.8
7	−3.90	97.0	−4.53	99.1	−1.63	98.0	−2.17	95.9
8	−3.96	97.3	−4.63	99.3	−1.56	98.0	−2.15	96.0
9	−4.00	97.5	−4.72	99.4	−1.49	98.2	−2.12	96.1
10	−4.04	97.7	−4.80	99.5	−1.43	98.3	−2.10	96.2
11	−3.51	92.5	−3.93	96.2	−1.74	99.0	−2.21	97.5
12	−3.50	93.4	−3.85	96.3	−1.87	99.0	−2.26	97.7
13	−3.55	94.8	−3.91	97.2	−1.91	99.0	−2.28	97.7
14	−3.60	95.7	−3.96	97.9	−1.92	99.0	−2.29	97.6
15	−3.64	96.4	−4.02	98.3	−1.92	98.9	−2.29	97.5
16	−3.66	96.5	−4.02	98.1	−1.88	98.9	−2.29	97.4
17	−3.70	97.2	−4.10	98.8	−1.92	98.6	−2.30	97.1
18	−3.73	97.5	−4.15	98.9	−1.91	98.5	−2.30	97.0
19	−3.47	94.2	−3.82	97.4	−2.00	99.1	−2.34	97.8
20	−3.45	94.4	−3.76	97.2	−2.06	99.2	−2.37	97.9
21	−3.46	94.5	−3.78	97.3	−2.04	99.2	−2.36	97.9
22	−3.47	94.5	−3.80	97.4	−2.02	99.1	−2.35	97.8
23	−3.47	94.5	−3.82	97.4	−2.00	99.1	−2.34	97.8
24	−3.53	94.8	−3.98	98.0	−1.90	98.9	−2.31	97.4
25	−3.48	94.4	−3.84	97.4	−1.96	99.1	−2.33	97.7
26	−3.48	94.4	−3.86	97.4	−1.94	99.1	−2.32	97.7
27	−3.54	95.5	−4.09	99.2	−1.93	99.0	−2.31	97.7
28	−3.48	94.3	−3.88	97.4	−1.90	99.1	−2.30	97.6
29	−3.52	94.4	−4.03	97.9	−1.81	98.9	−2.27	97.4
30	−3.49	94.2	−3.90	97.3	−1.86	99.1	−2.29	97.6
31	−3.51	94.9	−3.90	97.6	−1.89	99.2	−2.30	97.7
32	−3.53	95.5	−3.92	97.9	−1.90	99.2	−2.31	97.8
33	−3.55	95.9	−3.93	98.1	−1.92	99.2	−2.31	97.9
34	−3.57	96.2	−3.94	98.2	−1.93	99.2	−2.32	97.9
35	−3.58	96.5	−3.95	98.4	−1.94	99.2	−2.32	97.9
36	−3.60	96.8	−3.96	98.5	−1.94	99.2	−2.32	97.8
37	−3.42	94.3	−3.75	97.3	−2.00	99.4	−2.35	98.2
38	−3.41	94.3	−3.70	97.0	−2.04	99.5	−2.36	98.3
39	−3.42	94.5	−3.72	97.3	−2.03	99.5	−2.36	98.3
40	−3.43	94.7	−3.74	97.4	−2.03	99.5	−2.36	98.3
41	−3.49	95.4	−3.86	98.1	−1.99	99.3	−2.35	98.0
42	−3.49	95.5	−3.88	98.2	−1.99	99.3	−2.35	98.0
43	−3.49	95.5	−3.89	98.2	−1.98	99.2	−2.34	97.9
44	−3.50	95.5	−3.90	98.3	−1.98	99.2	−2.34	97.9
45	−3.50	95.5	−3.91	98.3	−1.97	99.2	−2.34	97.9
46	−3.75	98.3	−4.15	99.3	−1.93	98.8	−2.33	97.4
47	−3.50	95.4	−3.93	98.3	−1.96	99.1	−2.34	97.8
48	−3.46	95.1	−3.83	97.9	−1.99	99.2	−2.35	97.9
49	−3.48	95.6	−3.83	98.0	−2.01	99.3	−2.36	98.0
50	−3.49	95.9	−3.83	98.2	−2.02	99.3	−2.36	98.1
51	−3.51	96.2	−3.84	98.3	−2.03	99.3	−2.37	98.1
52	−3.52	96.4	−3.84	98.4	−2.04	99.3	−2.37	98.1
53	−3.53	96.7	−3.85	98.5	−2.04	99.3	−2.37	98.1
54	−3.54	96.8	−3.85	98.5	−2.05	99.3	−2.38	98.1

considerably better than those with $\alpha=2$ in both position and momentum spaces, and (ii) the bounds $S_\rho(\alpha)$, which depend on $\langle r^\alpha\rangle$, show up the same structure as the position entropy S_ρ; this is not true in the momentum case, although the general shape is very similar.

In Tables III and IV the bounds $S_\rho(\alpha,m_{\rm opt})$ and $S_\gamma(\alpha,m_{\rm opt})$ are compared with the position and momentum entropies S_ρ and S_γ, respectively. This is done by giving the values of the bounds in percent. A few observations are in order. First of all, the bounds are very accurate in

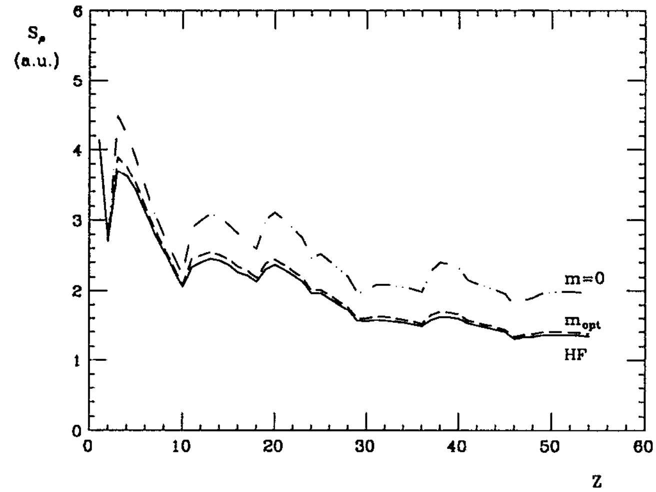

FIG. 3. Quality of the upper bounds $S_\rho(1,m)$ with $m=0$ and $m_{\rm opt}$ (the value of m which leads to the best upper bound to the position entropy S_ρ as given by Eq. (15); its value is shown in the sixth column of Table III) for all atoms, from hydrogen through xenon. Comparison between these bounds and the Hartree–Fock value is done. Notice that $S_\rho(1,0)$ only depends on $\langle r\rangle$ but $S_\rho(1,m_{\rm opt})$ depends additionally on $\langle \ln r\rangle$. Atomic units are used throughout.

the whole region of the periodic table. Generally speaking, the bounds with $\alpha=1$ [i.e., $S_\rho(1,m_{\rm opt})$ and $S_\gamma(1,m_{\rm opt})$] are again the tightest ones. The worst case occurs for $Z=11$ in position space where the bound lies within 4.8% of the HF value, and for $Z=4$ in momentum space where the bound lies within 3.2% of the corresponding HF value.

To gain insight into the bounds $S_\rho(\alpha,m)$, we compare in Fig. 3 the HF position entropy and the bounds $S_\rho(\alpha,0)\equiv S_\rho(\alpha)$ and $S_\rho(1,m_{\rm opt})$. Now we observe more transparently the considerable improvement brought by both the inclusion of the mean logarithmic radius and the

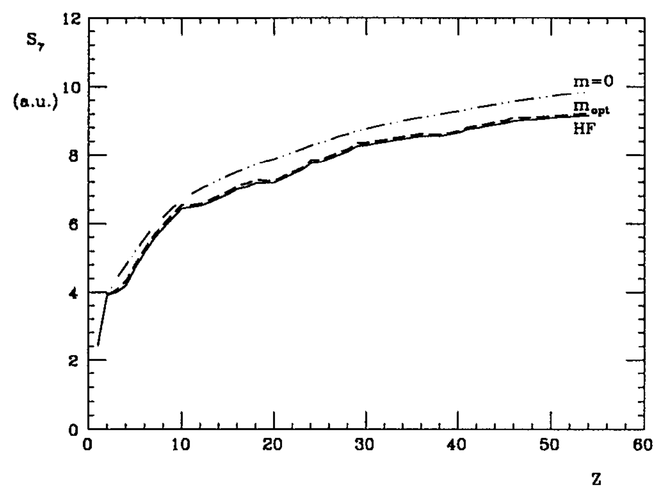

FIG. 4. Quality of the upper bounds $S_\gamma(1,m)$ with $m=0$ and $m_{\rm opt}$ (i.e., the value of m which leads to the best upper bound to the momentum entropy S_γ; its value is given in the sixth column of Table IV) for all atoms, from hydrogen through xenon. Comparison between these bounds and the Hartree–Fock value is done. Notice that $S_\gamma(1,m_{\rm opt})$ depends on $\langle r\rangle$, as $S_\gamma(1,0)$ does, but also on $\langle \ln p\rangle$. Atomic units are used throughout.

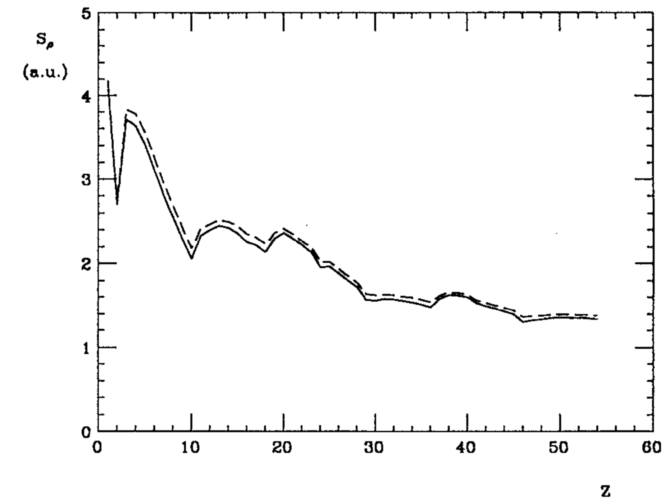

FIG. 5. Comparison between the Hartree–Fock value of the position entropy of information S_ρ and the upper bound S'_ρ, as given in Eq. (36) in text, for all atoms from hydrogen through xenon. The bound S'_ρ depends on both the mean logarithmic radius, $\langle \ln r\rangle$, and the mean-square logarithmic radius, $\langle (\ln r)^2\rangle$. Atomic units are used throughout.

m optimization. A similar comparison and observation may be done from Fig. 4 in momentum space for the bounds $S_\gamma(1,m)$. In this case, an additional remark should be mentioned: the bound $S_\gamma(1,m_{\rm opt})$ shows up, contrary to $S_\gamma(1,0)$, the same structure as the HF value S_γ.

In Figs. 5 and 6 we analyze the quality of the bounds S'_ρ and S'_γ, respectively, in the same Hartree–Fock framework. These new bounds depend only on the mean logarithmic radius and the mean-square logarithmic radius of the charge and momentum densities, respectively. Indeed, in Fig. 5 the comparison between the bound S'_ρ and the HF value S_ρ is shown. The analogous comparison in momentum space is done in Fig. 6. One notices that both bounds

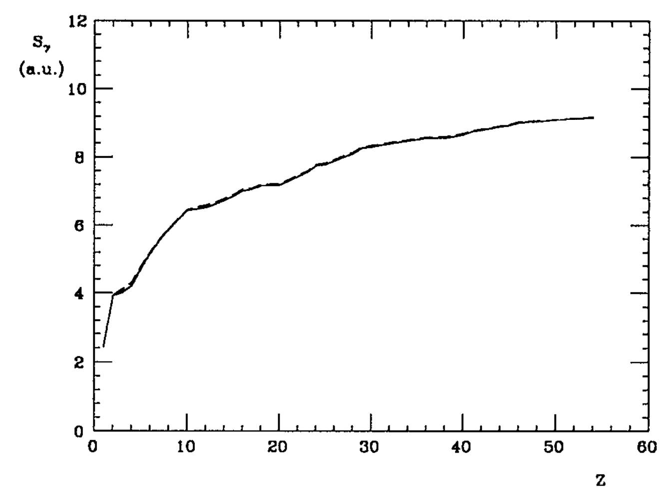

FIG. 6. Comparison between the Hartree–Fock value of the momentum entropy of information S_γ and the upper bound S'_γ for all atoms from hydrogen through xenon. The bound S'_γ depends on both the mean logarithmic momentum, $\langle \ln p\rangle$, and the mean-square logarithmic momentum, $\langle (\ln p)^2\rangle$. Atomic units are used throughout.

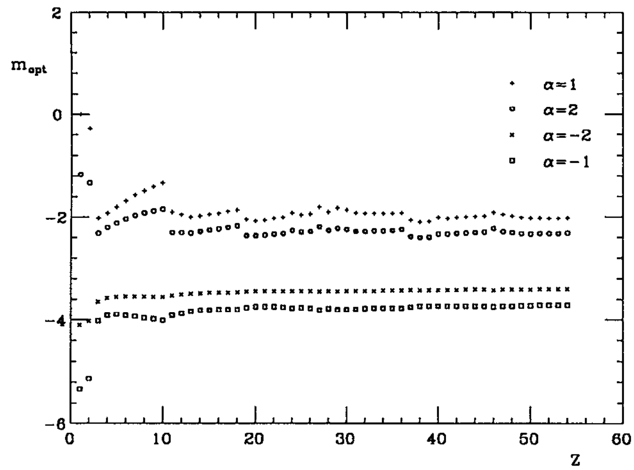

FIG. 7. Dependence of the optimal parameter m_{opt} of the upper bound to the position entropy for $\alpha=-2$, -1, 1, and 2 [see Sec. V and Eqs. (20)–(23) of Sec. III] with the atomic number Z in the whole periodic table up to Xe.

S'_ρ and S'_γ are strikingly accurate. Certainly, the quantities $S_\rho(1,m_{opt})$, S'_ρ, $S_\gamma(1,m_{opt})$, and S'_γ are tight upper bounds to the atomic information entropies.

A similar numerical study of the quality of the lower bounds discussed in Sec. IV may be performed in a parallel way. In that case the novelty lies in that the lower bound in a space depend on expectation values of quantities in the complementary or dual space.

Finally, it is worth emphasizing the general behavior of the optimal value m_{opt} of the m parameter with respect to Z. In both position and momentum spaces, one realizes that m_{opt} is practically constant for all atoms with $Z<54$ except for H and He cases, as it is shown in Tables III and IV. This dependence with Z is plotted in Figs. 7 and 8 for the sake of transparency. Therein, one realizes that a closer examination of this behavior indicates that deviations from the general constancy arises for those cases where the outer shell gets completed. This constant tendency is more apparent for negative values of α in position space. Moreover, the values of m_{opt} are higher for the positive values of α than for the negative ones in both spaces. Further research to know the physical meaning of this phenomenon needs to be done.

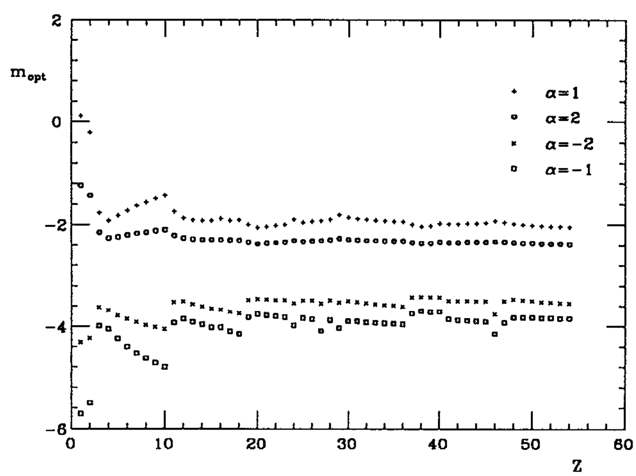

FIG. 8. Dependence of the optimal parameter m_{opt} of the upper bound to the momentum entropy for $\alpha=-2$, -1, 1, and 2 [see Sec. V and Eqs. (25)–(28) of Sec. III] with the atomic number Z in the whole periodic table up to Xe.

VI. CONCLUDING REMARKS

An information-theoretic method to find infinite sets of rigorous upper and lower bounds to the atomic information entropies, S_ρ and S_γ, in an analytical way, is described. The upper bounds to the entropy in a space (position or momentum) are given in terms of the moments (expectation values) of the associated single-particle density and/or a mean logarithmic radius. Contrary to this, the lower bounds to the entropy in a space depend on the moments of the single-particle density in the dual or complementary space and/or an associated mean logarithmic radius.

In particular, upper bounds to the position entropy S_ρ are given in terms of one or two radial expectation values $\langle r^\alpha \rangle$ and/or the mean logarithmic radius $\langle \ln r \rangle$. Additionally, a new bound S'_ρ depending only on $\langle \ln r \rangle$ and $\langle (\ln r)^2 \rangle$ is also found. The corresponding lower bounds to S_ρ are given by means of the expectation values $\langle p^\alpha \rangle$, $\langle \ln p \rangle$ and $\langle (\ln p)^2 \rangle$. Similar bounds are given for the momentum information entropy.

Finally, a numerical analysis of the accuracy of several upper bounds in both position and momentum spaces has been performed in a Hartree–Fock framework for all atoms with $Z \leqslant 54$. It shows that some of these bounds are so tight that they may be used as computational values of the corresponding quantities. Moreover, one realizes the important role of the mean logarithmic radii, $\langle \ln r \rangle$ and $\langle \ln p \rangle$, in the improvement of accuracy of the corresponding atomic entropies.

[1] S. B. Sears, R. G. Parr, and U. Dinur, Israel J. Chem. **19**, 165 (1980).
[2] C. Aslangul, R. Constanciel, R. Daudel, and P. Kottis, Adv. Quantum Chem. **6**, 94 (1972).
[3] S. R. Gadre and S. B. Sears, J. Chem. Phys. **71**, 4321 (1979).
[4] T. Koga, Theor. Chim. Acta. **58**, 173 (1981).
[5] S. B. Sears and S. R. Gadre, J. Chem. Phys. **75**, 4626 (1981).
[6] T. Koga and M. Morita, J. Chem. Phys. **79**, 1933 (1983).
[7] S. R. Gadre, Phys. Rev. A **30**, 620 (1984).
[8] S. R. Gadre, S. B. Sears, S. J. Chakravorty, and R. D. Bendale, Phys. Rev. A **32**, 2602 (1985).
[9] S. R. Gadre and R. D. Bendale, Phys. Rev. A **36**, 1932 (1987).
[10] Y. Alhassid and R. D. Levine, J. Chem. Phys. **67**, 432 (1977); Z. Gburski, C. G. Gray, and D. E. Sullivan, Chem. Phys. Lett. **106**, 55 (1984); C. G. Joslin, S. Singh, and C. G. Gray, Chem. Phys. Lett. **121**, 134 (1985).
[11] S. R. Gadre and R. D. Bendale, Current Sci. **5**, 970 (1985); Intern. J. Quantum Chem. **28**, 311 (1985).
[12] S. K. Ghosh, M. Berkowitz, and R. G. Parr, Proc. Natl. Acad. Sci. USA **81**, 8028 (1984).
[13] R. G. Parr, K. Rupnik, and S. K. Ghosh, Phys. Rev. Lett. **56**, 1555 (1986).
[14] *The Maximum Entropy Formalism*, edited by R. D. Levine and M. Tribus (M.I.T. Press, Cambridge, 1979).
[15] L. R. Mead and N. Papanicolau, J. Math. Phys. **25**, 2404 (1984).
[16] A. Wragg and D. C. Dowson, IEEE Trans. Inform. Theory **IT-16**, 226

(1970); D. C. Dowson and A. Wragg, IEEE Trans. Inform. Theory IT-19, 689 (1973).

[17] G. A. Wilson and A. Wragg, J. Int. Math. Appl. **12**, 165 (1973).

[18] R. Collins and A. Wragg, J. Phys. A **10**, 1441 (1977).

[19] A. Kociszewski, J. Phys. A **19**, L823 (1986).

[20] J. M. Einbu, IEEE Trans. Inform. Theory **IT-23**, 772 (1977).

[21] C. E. Shannon, Bell Syst. Tech. J. **27**, 379 (1948); **27**, 623 (1948).

[22] S. Kullback and R. A. Leibler, Ann. Math. Stat. **22**, 79 (1951); S. Kullback, *Statistics and Information Theory* (Wiley, New York, 1959).

[23] J. E. Shore and R. W. Johnson, IEEE Trans. Inform. Theory **IT-26**, 26 (1980); **IT-27**, 472 (1981).

[24] A. Wehrl, Rev. Mod. Phys. **50**, 221 (1981).

[25] I. Bialynicky-Birula and J. Mycielski, Comm. Math. Phys. **44**, 129 (1975).

[26] H. Maassen and J. B. M. Uffink, Phys. Rev. Lett. **60**, 1103 (1988).

[27] W. Beckner, Ann. Math. **102**, 159 (1975).

[28] W. G. Faris, J. Math. Phys. **19**, 461 (1978).

[29] I. I. Hirschman, Am. J. Math. **79**, 152 (1957); R. Leipnik, Inform. Control **2**, 64 (1959); **3**, 18 (1960).

[30] C. Deutsch, Phys. Rev. Lett. **50**, 631 (1983); M. H. Partovi, *ibid.* **50**, 1883 (1983).

[31] I. Bialynicki-Birula, Phys. Lett. **103A**, 253 (1984).

[32] R. Benesch and V. H. Smith Jr., in *Wave Mechanics: The First Fifty Years*, edited by W. C. Price, S. S. Chissick, and T. Ravensdale (Butterworths, London, 1973), pp. 357–377.

[33] A. J. Thakkar, J. Chem. Phys. **86**, 5060 (1987).

[34] I. S. Gradshteyn and I. M. Rizhik, *Table of Integrals, Series and Products* (Academic, New York, 1980).

[35] E. Clementi and C. Roetti, At. Data. Nucl. Data Tables **14**, 177 (1974).