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Shannon-information entropy sum as a correlation measure in atomic systems

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The interpretation of the entropy sum as a correlation measure is demonstrated for isoelectronic series via an analytical expression that models the asymptotic behavior of the electronic charge density in position space and the cusp behavior in momentum space. We also develop an expression for the entropy sum in neutral atoms with an explicit dependence on the ionization energy and the atomic number. The results obtained from these relations are in qualitative agreement with the behavior observed from *ab initio* calculations. A connection between the entropy sum and the correlation energy is obtained for the weakly inhomogeneous electron gas and demonstrated via calculations for the helium isoelectronic series.

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I. INTRODUCTION

One of the most well known problems in many-electron atomic physics is electron correlation. It was defined by Löwdin [1] in energetic terms as the difference between the exact nonrelativistic total energy and the Hartree-Fock approximation. However, there also exists other measures of electron correlation in the literature such as the statistical correlation coefficients introduced by Kutzelnigg *et al.* [2], and more recently, the concept of correlation entropy as introduced by Ziesche *et al.* [3] as a measure of the correlation strength. Liu *et al.* [4] have also used density-functional theory to relate the correlation energy with the moments $\langle r^n \rangle$ of the position space density distribution.

The Shannon entropy in position space is defined as

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

where $\rho(\mathbf{r})$ is the electronic charge density. The momentum space Shannon entropy, S_π, of the electronic momentum density, $\pi(\mathbf{p})$, is defined in a fully analogous way with both densities normalized to N, the number of electrons in the system. The Shannon entropy is a measure of the delocalization or the lack of *structure* in the underlying distribution.

Gadre *et al.* [5] have noted some interesting properties of the entropy sum, $S_t = S_\rho + S_\pi$, for atoms at the Hartree-Fock level: (i) S_t attains a minimum value for the ground state and (ii) S_t is invariant to scaling while the individual entropies are not. In a study of an isoelectronic series, the numerical value of S_t was noted to increase with the inclusion of electron correlation in the wave function [6]. S_t has also been studied as a measure of the basis set quality [5,7,8]. It has been shown [5] that in the case of neutral atoms there is no complementary behavior between the Shannon entropies of the position and momentum spaces, as has been noted for members of an isoelectronic series [6,9,10]. However, Gadre *et al.* [5] did note a periodic dependence of S_t in neutral atoms which was not studied in their paper but will be analyzed here.

The importance of the entropy sum is firmly established by noting that a stronger version of Heisenberg's uncertainty principle may be formulated in these terms for any quantum many-electron system [5,11],

$$\begin{aligned} S_t = S_\rho + S_\pi &\geqslant 3N(1+\ln \pi) - 2N \ln N \\ &= N(6.4342 - 2 \ln N). \end{aligned} \tag{2}$$

Upon analysis of this last equation, it was suggested [5] that one may use the entropy sum to provide a *balanced* measure by taking into account the Shannon entropies of both spaces.

The motivation for this paper is to illustrate and to provide evidence, via an analytical expression using cusp and asymptotic constrained densities, that the entropy sum may indeed be considered as a correlation measure. This expression is also used to explain the Z-dependent behavior of the entropy sum in an isoelectronic series. We also present an expression for the entropy sum in neutral atoms, dependent on the ionization energy and the atomic number, which is able to reproduce the periodic features. Our results for the model entropy sum are in good qualitative agreement with those obtained from CI (configuration interaction) and HF (Hartree-Fock) *ab initio* calculations. Also, a connection between the entropy sum and the correlation energy is obtained for the weakly inhomogeneous electron gas and demonstrated with calculations for the helium isoelectronic series.

II. RESULTS AND DISCUSSION

We begin the analysis of the entropy sum with the simplest noncorrelated systems, i.e., hydrogenlike atoms. We use the ground-state position space wave functions for the hydrogenlike atoms and obtain the corresponding momentum space wave functions by the Dirac-Fourier transformation. Atomic units are used in this paper. S_ρ and S_π for these systems as a function of the atomic number Z are

$$S_\rho = 3 - \ln\left(\frac{Z^3}{\pi}\right), \tag{3}$$

$$S_\pi = \ln(32 Z^3 \pi^2) - \frac{10}{3}. \tag{4}$$

Upon summing Eqs. (3) and (4), there is a cancellation of the Z dependence in S_t which yields a constant value of 6.5665.

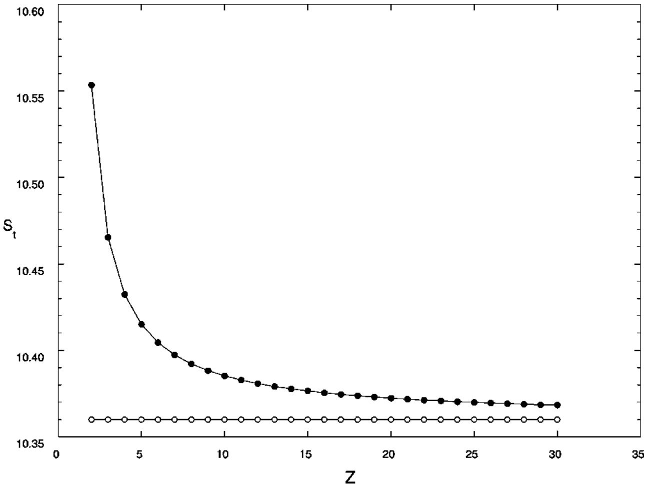

FIG. 1. The entropy sum, S_t, for the helium isoelectronic series with (solid circles) and without (open circles) electronic interaction using the two-parameter wave function.

Thus S_t is not a function of the atomic number in one-electron atomic systems. This behavior is also observed for excited states.

We now analyze the helium isoelectronic series to determine if the Z dependence of S_t is present with the inclusion of electronic interactions. For simplicity, we analyze wave functions corresponding to the singlet state. Considering the helium series without electronic interactions ($V_{ee}=0$), i.e., bare Coulomb field (BCF), we obtain that the electron density resembles that of the hydrogenlike atoms and thus the entropy sum is constant, as shown in Fig. 1. The same result is obtained if one uses screened hydrogenic functions. Next, we use simple ground-state wave functions, with different spatial orbitals for each electron but which allow a partial representation of the electron correlation [19],

$$\Psi(r_1,r_2)=C_N(e^{-Z_1r_1}e^{-Z_2r_2}+e^{-Z_2r_1}e^{-Z_1r_2}), \qquad (5)$$

where C_N is the normalization constant and Z_1 and Z_2 are variational parameters. We calculated the values of Z_1 and Z_2 by variationally optimizing the wave functions. Our ground-state energy for the helium atom is equal to that reported by Hylleraas [12] for the same type of function. In this model, the electron correlations are responsible for $Z_1\neq Z_2$. It is important to remark that when the interelectronic interaction is included and $Z\rightarrow\infty$, then $Z_1\rightarrow Z_2\rightarrow Z$ and the entropy sum tends to a constant value that is the same as that for the corresponding BCF atom.

In Fig. 1 we plot S_t against Z for the helium isoelectronic series with [Eq. (5)] and without (BCF atoms) interelectronic interaction. For the case of interelectronic interaction, S_t was obtained by summing the individual entropies which were calculated by numerically integrating the expressions for the spherically averaged densities in the respective spaces [see Eq. (1)]. Note that the plot corresponding to the inclusion of electronic interaction looks like a $(1/Z^n)$-type function and is distinct from the plot corresponding to no electronic interaction. If we fit our entropy sum to such a function, with n equal to 1.47, the correlation coefficient is 0.99. HF entropies, calculated from the Clementi-Roetti functions [13], and CI entropies, calculated from accurate Slater-basis CI wave functions for four isoelectronic series, are presented in Table I. The reported values of n were obtained by trial from fits of the data to $(1/Z^n)$ with the criteria that the correlation coefficient be greater than 0.99. Important to notice is that n is sensitive to the level of calculation and also increases when more electrons (more electron correlation) are included.

TABLE I. Values of n obtained from fits of calculated values of the entropy sum to $(1/Z^n)$ for different isoelectronic sequences. Li series [9], Be series [6], Ne series [10].

Isoelectronic series	n (HF)	n (CI)
He	1.18	1.48
Li	1.50	1.68
Be	1.80	2.70
Ne	2.80	3.10

Asymptotic and cusp-constrained model densities have been used to obtain simple expressions for the Shannon entropy in position space (S_ρ^{asym},S_ρ^{cusp}) and in momentum space (S_π^{asym},S_π^{cusp}), respectively, as functions of the first ionization energy, I_1, and the atomic number, Z. The model position space entropy, which arises from constraining the asymptotic behavior in position space, S_ρ^{asym}, and the momentum space model entropy arising from constraining the cusp condition, S_π^{cusp}, were shown to be particularly effective in qualitatively explaining the behavior of the entropies as a function of Z [14]. Furthermore, it was shown that the inequality for the entropy sum in Eq. (2) is obeyed for (i) $S_\rho^{\text{cusp}}+S_\pi^{\text{cusp}}$, (ii) $S_\rho^{\text{asym}}+S_\pi^{\text{asym}}$, and (iii) $S_\rho^{\text{asym}}+S_\pi^{\text{cusp}}$, proving that these models do not violate this uncertainty principle. We would expect such a result for (i) and (ii) since the one-electron wave functions corresponding to the constrained densities in the respective spaces are related by a Dirac-Fourier transform, while the result for (iii) is less obvious since there is no such relationship between the wave functions. In (i) the Z dependence is canceled while in (ii) the ionization energy dependence is canceled, thus the entropy sum in both of these cases has a constant value and displays no Z dependence.

In order to obtain the Z dependence of the entropy sum, we consider (iii), i.e., we model the asymptotic behavior of the densities in the respective spaces. Now we test this model for the entropy sum. We obtain S_ρ^{asym}, S_π^{cusp}, and S_t as

$$S_\rho^{\text{asym}}=-\frac{3}{2}N\ln I_1-N\ln\left(\frac{2^{3/2}N}{\pi}\right)+3N, \qquad (6)$$

$$S_\pi^{\text{cusp}}=3N\ln Z+N\ln\left(\frac{32\pi^2}{N}\right)-\frac{10}{3}N, \qquad (7)$$

$$S_t=S_\rho^{\text{asym}}+S_\pi^{\text{cusp}}=-\frac{3}{2}N\ln I^{\text{rel}}+N\ln\left[\frac{32\pi^3}{N^2}\right]-\frac{N}{3}, \qquad (8)$$

where I^{rel} is the relative ionization energy defined as I_1/I^H, and $I^H(=Z^2/2)$ is the ionization energy of the corresponding

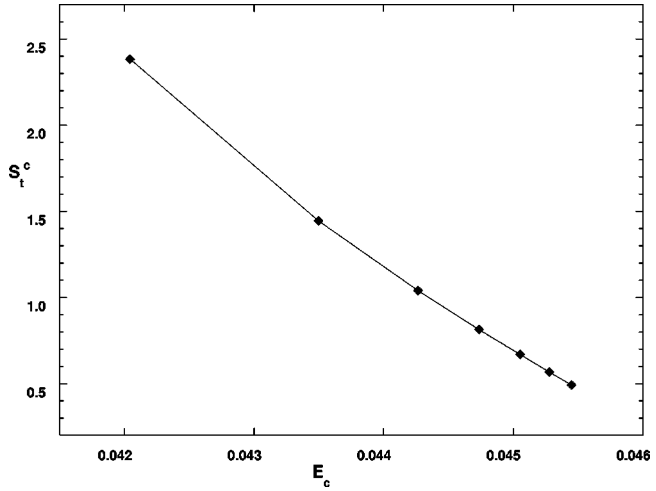

FIG. 2. The correlation measure, S_t^c, versus the absolute value of the exact correlation energy, E_c (a.u.), for the helium isoelectronic series.

hydrogenlike atom. This equation is interesting as it expresses the entropy sum as a function of the ionization energy, atomic number, and the number of electrons.

The quantity $\ln[I^{\mathrm{rel}}]$ may be considered as a correlation measure since it is a logarithmic difference between the ionization energy of a hydrogenlike atom, which corresponds to noncorrelated electrons $(V_{ee}=0)$, and the experimental first ionization energy, which corresponds to correlated electrons. It is clear that when we treat a noncorrelated system $(\ln[I^{\mathrm{rel}}]\rightarrow 0)$, we obtain that the entropy sum is only a function of N. Thus, for the case of hydrogenlike atoms the entropy sum in Eq. (8) tends to the constant values shown above for these systems.

Now we apply the model given in Eq. (8) to the He series. Thus

$$S_t = -3\ln[I^{\mathrm{rel}}] + 10.360. \tag{9}$$

Physically, for an isoelectronic series the electron correlation tends to zero as $Z\rightarrow\infty$. Our entropy sum tends to a constant value as $Z\rightarrow\infty$. However, if we define a new correlation measure as $S_t^c = S_t - S_t^{Z\rightarrow\infty}$, where $S_t^{Z\rightarrow\infty}=10.360$, then it will have the same form as a relative correlation energy [3] (note that this measure is different from other commonly used ones which employ a difference from the HF level). Thus we have more evidence that the Z dependence of the entropy sum for the helium isoelectronic series can be related to the inclusion of electron correlation. As a test, we plot in Fig. 2 the new correlation measure, S_t^c (values of I_1 required to calculate S_t^c were taken from Ref. [15]), against the absolute value of the exact correlation energy, E_c [16], for the helium isoelectronic series. One notes that the behavior of the two quantities is similar, but not the same, as seen from the curvature in the plot. It is also important to note that the curve becomes more linear for larger values of E_c, which correspond to larger values of Z.

In our analysis, the ionization energy is an important factor in S_ρ^{asym} and hence in S_t. In order to obtain an analytical solution in terms of $1/Z$ for the entropy sum, such as that suggested by our numerical results, we will use the charge expansion of the nonrelativistic ground-state total energy [12,17],

$$E(Z,N) = Z^2\left[\varepsilon_0(N) + \left(\frac{1}{Z}\right)\varepsilon_1(N) + \cdots + \left(\frac{1}{Z^n}\right)\varepsilon_n(N) + \cdots\right]. \tag{10}$$

Its relationship with the original form of the density-functional theory [18] valid for large Z and N (Thomas-Fermi theory [19]) was studied by March and White [20], and the asymptotic form of the coefficients $\varepsilon_n(N)$ for sufficiently large N was given by $\varepsilon_n(N)\sim A_n N^{n+1/3}$. If we wish to obtain a similar expansion for the ionization energy, it is necessary to use the definition of ionization energy as $I_1 = E(N-1) - E(N)$, and using Eq. (10) we obtain

$$I_1(Z,N) = Z^2\sum_{n=0}^{\infty} \varepsilon_n'(N) Z^{-n}, \tag{11}$$

where the coefficients ε_n' are given by $\varepsilon_n(N-1) - \varepsilon_n(N)$.

Substituting Eq. (11) into Eq. (8) and considering the large-Z region using the MacLaurin expansion for $\ln(1-x)$, where x is the second most important contribution $(n=1)$ in Eq. (11), we may express the entropy sum for any isoelectronic series as

$$S_t \sim A + B\sum_{n=0}^{\infty} \frac{B'(n)}{(n+1)Z^{n+1}}, \tag{12}$$

where B is $(-3/2)N$ and A and $B'(n)$ are constants that depend analytically on the parameters of Eqs. (8) and (11). These terms may be obtained by fitting Eq. (12) to the known (calculated) entropy sum of any isoelectronic series. It is important to note that including more than two terms in Eq. (11) will yield the exact expression as in Eq. (12) but with different values for the constants. Though the present result is only valid in the limit of large Z, it is interesting to determine whether it may be generalized to a wider range of atomic number, since it is the first analytical expression of the entropy sum reported in the literature as a function of Z and N. Note that based on our numerical results, this equation verifies our conjecture that the entropy sum behaves as a $(1/Z^n)$-type function. Fitting by least squares the entropy sum of Eq. (12) to values obtained from CI calculations and considering two terms in the summation yields correlation coefficients greater than 0.99 for all the isoelectronic series studied. These fits are reported in Table II. With the inclusion of more terms in the expansion, we observed that the correlation coefficients moved closer to 1.

According to our model displayed in Eq. (8), we obtain for neutral atoms $(N=Z)$

$$S_t = -\frac{3}{2}Z\ln[I^{\mathrm{rel}}] - 2Z\ln[Z] + 6.5665Z. \tag{13}$$

TABLE II. Values of parameters and the correlation coefficient R resulting from fits $[a(1/Z)+b(1/Z)^2+c]$ of calculated values of the entropy sum in different isoelectronic series ($N=2,3,4,10$). Li series [9], Be series [6], Ne series [10].

Isoelectronic series	a	b	c	R
He	0.0856	0.2878	10.3644	0.9999
Li	0.3160	2.3846	16.1467	0.9996
Be	−1.1542	8.9122	20.1766	0.9984
Ne	−98.2344	837.9538	40.5624	0.9987

Note that for $Z=1$ in the above equation, we recover the exact value of 6.5665 for the hydrogen atom. In Fig. 3, we present plots of S_t versus Z for neutral atoms, from H through Kr, calculated from the model, along with corresponding values obtained from CISD (configuration interaction single and double excitations) calculations with a 6-311G Gaussian-type orbital basis set. One observes that our proposed model exhibits the same behavior as the *ab initio* values. Note also that our model with its explicit dependence on I_1 and Z is able to reproduce the periodic behavior present in S_t, especially the behavior around the noble gas atoms. We may also define a relative correlation measure, but now for neutral atoms, as $S_t^C=S_t-S_t^H$, where S_t^H is the total entropy corresponding to a hydrogenic density which is normalized to the number of electrons. Substitution in Eq. (13) yields $S_t^C=-\frac{3}{2}Z\ln[I^{\mathrm{rel}}]$. In Fig. 4, we plot S_t^C versus E_c for neutral atoms, from He through Ar. One observes that overall there is no obvious relationship between the two quantities, however one notes that the relationship is more intimate within a particular shell where a rough linearity is observed. Thus, on comparison to Fig. 2, it would seem that S_t^c is more suitable as a correlation measure for isoelectronic series than S_t^C is for neutral atoms when both are compared to the correlation energy.

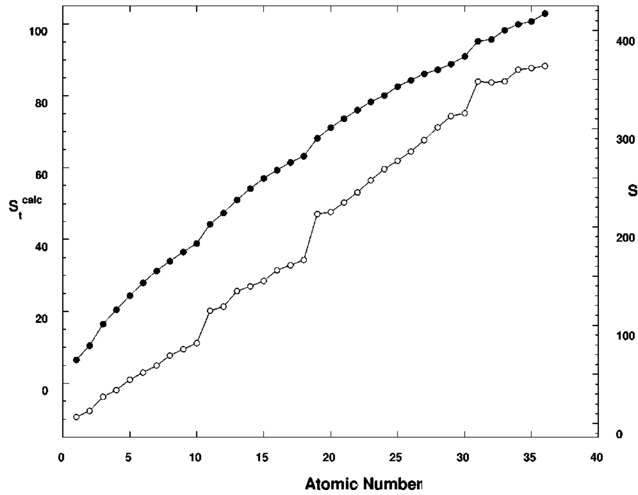

FIG. 3. The entropy sum, S_t, for neutral atoms, from H through Kr, obtained from *ab initio* calculations (S_t^{calc}, solid circles) and from the cusp-asymptotic constrained model (S_t^M, open circles).

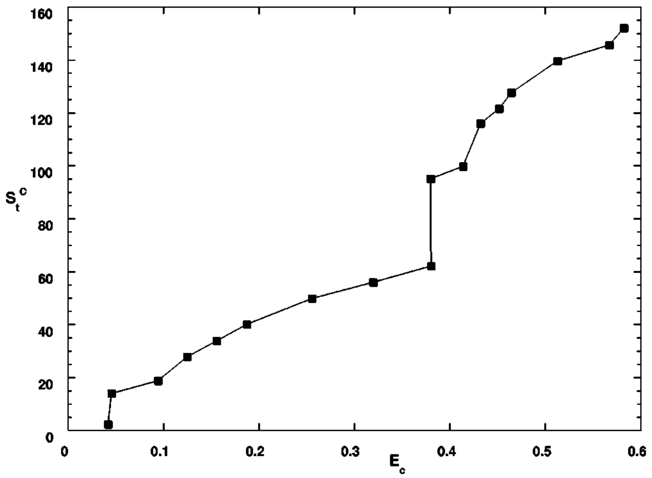

FIG. 4. The correlation measure, S_t^C, versus the absolute value of the exact correlation energy, E_c (a.u.), for neutral atoms, from He through Ar.

Gadre [21] has computed the information entropies for the Thomas-Fermi atoms as a prototype for atomic systems. He conjectured that the information entropies for atomic systems may be represented by the form $S=N(a+b\ln N)$, where a and b can be fitted using mathematical methods. We now propose another prototype for the information entropy of atomic systems using the expressions for S_π^{cusp}, S_ρ^{asym}, and S_t in Eqs. (6)–(8). In this case, our expression for S_π is of the same form as that used by Gadre, while our expressions for S_t and S_ρ are different and take the general form

$$S_{t,\rho}=N(a\ln I_1+b\ln N+c). \tag{14}$$

The difference between our atomic prototype and the one reported by Gadre, and hence its novelty, is the inclusion of the term with its dependence on the ionization energy, thus allowing the explanation of the observed periodic behavior. Fitting the values for the neutral atoms ($1\leqslant Z\leqslant 36$) obtained from the CISD calculations to Eq. (14), we obtain a correlation coefficient very close to 1, which indicates that our model is indeed a good representation of the actual behavior (see Table III).

It is also interesting to compare our prototype to the one in the Thomas-Fermi approximation as reported by Gadre [21]. In this way, we test our model in the asymptotic limit of a large number of electrons. For this approach, it is necessary to consider the asymptotic form of the coefficient $\varepsilon_n(N)$ in the expression for the ionization energy [Eq. (11)]. Thus, $\ln(I_1)\sim 2.333\ln(Z)+k$, where k is a constant that depends on the solution of the Thomas-Fermi problem. If we substitute

TABLE III. Values of parameters and the correlation coefficient R resulting from linear fits of S_ρ, S_π, and S_t to $S=N(a\ln I_1+b\ln N+c)$ for neutral atoms ($1\leqslant Z\leqslant 36$). Note that the missing value is not included since Eq. (7) has no $\ln I_1$ dependence.

	a	b	c	R
S_ρ	−0.4235	−1.7676	3.8526	0.9909
S_π		0.7380	2.2180	0.9680
S_t	−0.2158	−0.9966	6.2086	0.9953

this last expression into Eq. (13), we reproduce the general forms of the information entropies as reported by Gadre. This result corroborates that our new expressions are functionally equal to those of the Thomas-Fermi approximation in the limit of large *N*.

It would also be interesting to examine the relationship between the entropy sum and the correlation energy. Grassi *et al.* [22], for a weakly inhomogeneous electron gas, have connected S_ρ to the correlation energy using the work of Gell-Mann and Brueckner (GB) [23] and obtained the expression

$$E_c^{\mathrm{GB}}=AS_\rho+BN, \tag{15}$$

where A and B are constants, equal to 0.010 36 and $-0.062\,85$, respectively, and N is the number of electrons. Thus we see an interesting physical link between S_ρ and the correlation energy.

We may refine Eq. (15) by noting that this expression or any of the local-spin-density (LSD) type in the correlation functional overestimates the correlation energy by a factor of 2. The most important physical effect that causes this problem in the LSD approximation is the self-interaction that can be avoided using the procedures of Perdew *et al.* [24] or Stoll *et al.* [25]. Perdew *et al.* [24] removed the spurious orbital self-correlation using a simple scheme of self-interaction correction (SIC),

$$E_c^{\mathrm{SIC}}=E_c^{\mathrm{LSD}}[\rho_\uparrow,\rho_\downarrow]-\sum_{\alpha\sigma}E_c^{\mathrm{LSD}}[\rho_{\alpha\sigma},0], \tag{16}$$

where $\rho_{\alpha\sigma}$ is the density of the occupied orbital $\alpha\sigma$. Stoll *et al.* [25] proposed the correction only for antiparallel-spin correlation as

$$E_c^{\mathrm{Stoll}}=E_c^{\mathrm{LSD}}[\rho_\uparrow,\rho_\downarrow]-E_c^{\mathrm{LSD}}[\rho_\uparrow,0]-E_c^{\mathrm{LSD}}[\rho_\downarrow,0]. \tag{17}$$

Perdew *et al.* [27] fitted the Ceperley-Alder correlation energies per electron, ε [26], to the simple expressions

$$\varepsilon(\rho/2,\rho/2)=0.0311\ln r_s-0.048+0.0034r_s\ln r_s-0.0116r_s, \tag{18}$$

$$\varepsilon(\rho,0)=0.015\,55\ln r_s-0.0269+0.0013r_s\ln r_s-0.0048r_s, \tag{19}$$

with an error of 1%. r_s is defined in terms of the density as $\rho=(4\pi r_s^3/3)^{-1}$. These expressions are valid for high densities $(0<r_s<5)$, i.e., those of the greatest importance in atoms.

Using both of the above procedures, and considering that in typical atomic densities the first two terms in each of Eqs. (18) and (19) are dominant [27], we may substitute these expressions into Eqs. (16) and (17), respectively, and using Eq. (1), we rewrite the correlation energy in terms of the Shannon entropy as

$$E_c^{(\mathrm{SIC})}=A'S_\rho+B'N, \tag{20}$$

$$E_c^{(\mathrm{Stoll})}=A'S_\rho+B''N, \tag{21}$$

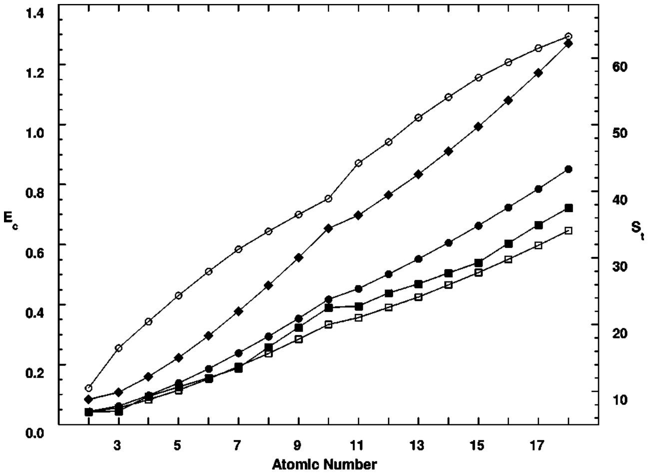

FIG. 5. The absolute value of the exact correlation energy, E_c (solid squares), $E_c^{(\mathrm{SIC})}$ (solid circles), $E_c^{(\mathrm{Stoll})}$ (open squares), E_c^{GB} (solid diamonds), and S_t (open circles), for neutral atoms. Values for the correlation energies are in atomic units.

where $A'=0.005\,18$, $B'=-(0.028\,52+0.005\,18\ln N)$, and $B''=-0.032\,12$. In Fig. 5, we present the exact correlation energy [16] and E_c calculated from Eqs. (15), (20), and (21) for neutral atoms where S_ρ was obtained from the CISD calculations. One observes a similarity among these quantities, however one notes that the behavior of $E_c^{(\mathrm{SIC})}$ and $E_c^{(\mathrm{Stoll})}$ is closer to the exact correlation energy than that of E_c^{GB}. We shall use the expression in Eq. (21) because of its simplicity and the fact that it reproduces well the values of atomic correlation energies. A reasonable question would be the use of the asymptotic model for S_ρ in Eqs. (15), (20), and (21). This form, with its I_1 dependence, would provoke a highly periodic behavior which is not present in the actual correlation energy, as can be seen in Fig. 5.

We substitute $S_\rho=S_t-S_\pi$ in the previous expression and use for the momentum space entropy the cusp model presented in Eq. (7). We now focus on the helium isoelectronic series. For simplicity, instead of Eq. (7), we use its fit to CI calculations $(S_\pi=6.6246\ln Z+1.9617)$, [28] which yields

$$E_c^{(\mathrm{Stoll})}=A'S_t-0.0343\ln Z-0.0743. \tag{22}$$

This equation gives the correlation energy in terms of the entropy sum. There is one aspect of Eq. (22) that deserves attention. In light of the connection between the entropy sum and the correlation energy in Eq. (22), it is not surprising that we obtained the relationship in Eq. (12) (substantiated by calculations presented in Table II) that is similar to the $1/Z$ expansion for the correlation energy. Hence we note that the entropy sum in an isoelectronic series would tend to a constant value as Z is increased (for non-near-degenerate systems) in a similar fashion to that observed for the correlation energy [16].

We may use the last expression as a guide to examine the connection between the correlation energy and entropy sum. In Fig. 6, we present values of the exact correlation energies of the helium isoelectronic series [16] against the entropy sum obtained from CI calculations. One notes the linear be-

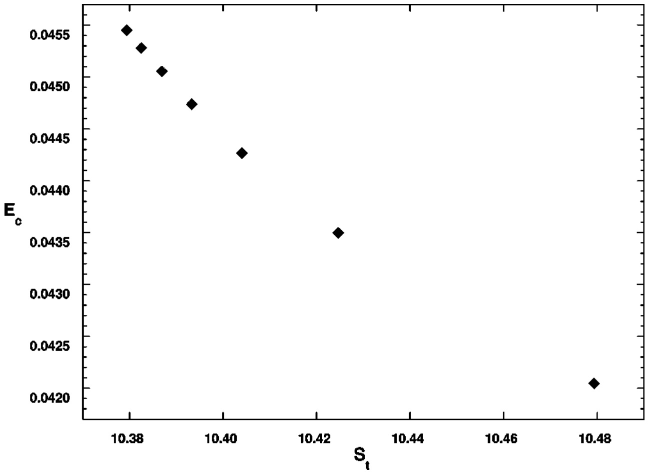

FIG. 6. The absolute value of the exact correlation energy, E_c (a.u.), versus S_t, the entropy sum obtained from CI wave functions, for the helium isoelectronic series.

havior, with small deviations occurring for the points at the extreme right-hand side of the plot. These points correspond to small Z, precisely where the large Z criteria used to construct the $1/Z$ expansion of the entropy sum in Eq. (12), and hence the connection to the correlation energy, would be less valid. In Fig. 5, for neutral atoms, we also compare the behavior of the entropy sum with the exact correlation energy, where one can note a similarity in their behavior with the largest differences in behavior occurring at the noble gas atoms.

III. CONCLUSIONS

In conclusion, the Z dependence of the entropy sum appears when the electron-electron interaction is switched on or correlation is taken into account. We obtain a relationship for the entropy sum in terms of the logarithmic difference between the experimental first ionization energy and the ionization energy of the corresponding hydrogenlike atom. This expression illustrates and provides evidence that the entropy sum may be used as a correlation measure. An analytical expression in terms of a $1/Z$ expansion for large Z may be obtained for the entropy sum in isoelectronic series using the charge expression for the nonrelativistic ground-state total energy. In the limit of large N, our new atomic prototype for S_t is similar to that of the Thomas-Fermi model reported by Gadre. We also obtain a connection between the entropy sum and the correlation energy in a weakly inhomogenous electron gas which is demonstrated with calculations for the helium isoelectronic series. Also, for neutral atoms, we have shown a similar tendency between the exact correlation energy and the entropy sum.

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