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Some novel characteristics of atomic information entropies

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Near—Hartree-Fock information entropies $S_\rho = -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\mathbf{r}$ and $S_\gamma = -\int \gamma(\mathbf{p}) \ln \gamma(\mathbf{p}) d\mathbf{p}$, where $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$ are one-electron densities in coordinate and momentum space, respectively, have been computed for atoms in their ground and excited states. The information entropies for the harmonic oscillator and hydrogen atom as prototype systems are also discussed. The result of this exercise is a numerical discovery that for the ground state, $S_\rho + S_\gamma$ shows its minimum value. This study for atoms in their ground states, using wave functions of single-zeta, double-zeta, and near—Hartree-Fock quality, also unearths a startling feature that the entropy sum, $S_\rho + S_\gamma$, increases with an enhancement in the ground-state wave-function quality.

I. INTRODUCTION

Information-theoretical concepts have been used[1–6] in the recent years for synthesis and analysis of electron densities in momentum[1,2,4] and coordinate[3,5,6] spaces. Sears and Gadre[1,2] employed the technique of entropy extremization subject to the constraints of various $\langle p^n \rangle$ values for constructing Compton profiles of atoms and molecules. They found that the simultaneous knowledge of two moments (e.g., $\langle p \rangle$ and $\langle p^2 \rangle$) leads to Compton profiles fairly close to experimental or theoretical ones. Sears *et al.*[3,4] derived the information-theoretical justification for the kinetic energy functional, $T[\rho]$ in the density-functional formalism.[7] Maroulis *et al.*[5] suggested the use of information-theoretic concepts for evaluating basis-set quality in terms of various expectation values and proposed a new method for improving the quality of a wave function. This approach, however, demands the *exact* expectation values for analysis. Simas *et al.*[6] tested the quality of various orbital basis sets for a specific case, viz., helium atom, employing the above formalism.

An interesting uncertainty-type rigorous inequality has recently been derived by Białynicki-Birula and Mycielski.[8] For wave functions normalized to unity

$$-\langle \ln |\phi(\mathbf{r})|^2 \rangle - \langle \ln |\tilde{\phi}(\mathbf{p})^2| \rangle \geq n(1+\ln\pi) , \tag{1}$$

where $\phi(\mathbf{r})$ and $\tilde{\phi}(\mathbf{p})$ are wave functions in n dimensional coordinate and momentum space, respectively. On simplification[4] and substitution of $n = 3N$, N being the number of electrons, one obtains

$$S_\rho + S_\gamma \geq 3N(1+\ln\pi) - 2N\ln N . \tag{2}$$

Here, S_ρ and S_γ are the Shannon information entropies in the coordinate and momentum space, respectively,

$$S_\rho = -\int \rho(\mathbf{r}) \ln \rho(\mathbf{r}) d\bar{r} \tag{3}$$

and

$$S_\gamma = -\int \gamma(\mathbf{p}) \ln \gamma(\mathbf{p}) d\bar{p} . \tag{4}$$

The densities $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$ are normalized to N, the number of electrons in the system under consideration. The bound (2) stresses the reciprocity between the coordinate and momentum spaces: A highly localized $\rho(\mathbf{r})$ is associated with a diffuse $\gamma(\mathbf{p})$, leading to low S_ρ and high S_γ and *vice versa.* As pointed out by Białynicki-Birula and Mycielski,[8] the sum $S_\rho + S_\gamma$ cannot be decreased beyond a limit as expressed by the inequality (2) above. Recent years have witnessed a growing interest in the application of information entropies to fundamental problems of quantum mechanics.[9] A particularly interesting bound,[9] viz.,

$$S_\rho + S_\gamma \geq 1 - \ln 2 - \ln \left[\frac{\Delta x \, \Delta p_x}{h} \right]$$

has been derived by Białynicki-Birula.

Gadre[10] recently computed S_ρ and S_γ for neutral atoms within Thomas-Fermi (TF) theory. This result is particularly interesting since TF theory is exact in the high-Z limit. The sum of entropies for the TF theory turns out to be

$$S_\rho + S_\gamma \simeq N(6.65 - \ln N) . \tag{5}$$

Motivated by the studies in Refs. 1—10, it was felt worthwhile by the authors to embark upon a project to systematically compute and analyze S_ρ and S_γ for a wide variety of systems including atoms and molecules. In Sec. III, the ground and excited states of two exactly solvable systems, viz., the one-dimensional harmonic oscillator and the hydrogen atom will be examined for the sake of orientation.

II. INFORMATION ENTROPIES FOR MODEL SYSTEMS

A. Harmonic oscillator

Uniform scaling of the coordinates of a particle in a one-dimensional case gives rise to a scaled wave function

$$\phi_\lambda(x) = \lambda^{1/2}\phi(\lambda x) \ . \tag{6}$$

The entropies for the scaled wave function turn out to be

$$S_{\rho_\lambda} = S_\rho - \ln\lambda \tag{7}$$

and

$$S_{\gamma_\lambda} = S_\gamma + \ln\lambda \ . \tag{8}$$

Thus, it is sufficient to examine S_ρ and S_γ for only one value of ω, the frequency of the harmonic oscillator. The results of S_ρ and S_γ for the first six states for $\omega = 0.5$ are presented in Table I. It may be noticed that the entropies in both the spaces, and hence their sum, increase with n. It may also be readily verified that the inequality (1) becomes an equality for $n = 0$ as has earlier been pointed out by Białynick-Birula and Mycielski.[8] The entropies may be computed for any arbitrary value of ω by employing (7) and (8), and exhibit similar trends. The most interesting observation is that $S_\rho + S_\gamma$ increases with n. Also note that the uncertainty product $\Delta x \, \Delta p_x$ for a one-dimensional harmonic oscillator, being $(n+\frac{1}{2})$, increases with n.

B. Hydrogen atom

The coordinate and momentum space wave functions for the hydrogen atom are

$$\phi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_l^m(\theta,\varphi)$$

and

$$\tilde{\phi}_{nlm}(\mathbf{p}) = P_{nl}(p) Y_l^m(\theta_p,\varphi_p) \ .$$

The corresponding entropies are then given by

$$S_\rho = -\int |R_{nl}(r)|^2 \ln |R_{nl}(r)|^2 r^2 dr - \int |Y_{lm}|^2 \ln |Y_{lm}|^2 d\Omega \tag{9}$$

TABLE I. Information entropies S_ρ and S_γ of the one-dimensional harmonic oscillator for $\omega = 0.5$. All values are in atomic units. ($m = \hbar = 1$).

	S_ρ	S_γ	$S_\rho + S_\gamma$
$n=0$	1.418	0.726	2.145
$n=1$	1.689	0.996	2.686
$n=2$	1.845	1.152	2.997
$n=3$	1.956	1.263	3.220
$n=4$	2.043	1.350	3.393
$n=5$	2.115	1.422	3.537

TABLE II. Information entropies S_ρ and S_γ for hydrogenic orbitals. All values are in atomic units. ($m = \hbar = e = 1$).

Orbital	S_ρ	S_γ	$S_\rho + S_\gamma$
1*s*	4.1447	2.4218	6.5665
2*s*	8.1109	−0.7576	7.3533
3*s*	10.4265	−2.1883	8.2383
4*s*	12.0748	−3.1457	8.9291
2*p*[a]	7.6968	0.4744	8.1712
	(7.2649)	(0.042 41)	(7.3073)
3*p*	10.2378	−1.4570	8.7808
3*d*	9.8355	−0.7428	9.0927

[a] Parenthesized numbers are the information entropies for the p_z orbital employing the nonspherically averaged electron densities.

and

$$S_\gamma = -\int |P_{nl}(p)|^2 \ln |P_{nl}(p)|^2 p^2 dp - \int |Y_{lm}|^2 \ln |Y_{lm}|^2 d\Omega \ . \tag{10}$$

Thus, the entropies from the spherically nonaveraged densities are simply related to the entropies computed from the corresponding spherically averaged ones. The entropies for the hydrogen atom in the ground and a few excited states are displayed in Table II. Consider first the coordinate-space information entropy S_ρ. This entity is minimum for the most compact distribution, viz., the 1*s* orbital. The S_γ value is maximum for this orbital, as may be heuristically expected. However, as noted above, the information-entropy sum $S_\rho + S_\gamma$ is indeed minimum for the ground state. Consider now the orbitals 1*s*, 2*s*, 3*s*, and 4*s*. The S_ρ values enhance with the principal quantum number n. The respective S_γ values show a monotonic decrease with n. Similar trends are seen for the case of *p* orbitals. The nonspherically averaged S_ρ and S_γ values for the $2p_z$ orbital are shown in Table II for a comparison. These values are smaller by 0.4319 than their spherically averaged counterparts. It may thus be noted that the corrections to S_ρ and S_γ due to nonsphericity of ρ and γ would be rather small for the many-electron atoms. In Sec. III, we present and discuss our results on information entropies for atoms helium through xenon employing spherically averaged densities.

III. NEAR–HARTREE-FOCK ATOMIC INFORMATION ENTROPIES

The highly accurate analytic near–Hartree-Fock (NHF) wave functions reported by Clementi and Roetti[11] were employed for computing the entropies. It was verified that the corrections to S_ρ and S_γ values due to nonsphericity of densities are rather small. Let us consider, for example, the helium atom. The spherically averaged densities [computed from a configuration interaction (CI) wave function, due to Taylor and Parr from Ref. 12] yield 4.068 36, 6.455 13, and 10.523 49 a.u. for S_ρ, S_γ, and $S_\rho + S_\gamma$; the nonspherical counterparts being 4.068 35, 6.455 11, and 10.523 46 a.u. It may also be noted that the use of nonspherically averaged $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$ renders the entropy computations rather cumbersome. Thus the in-

TABLE III. Informational entropies S_ρ and S_γ for the ground and excited states of some randomly selected atoms evaluated from NHF wave functions of Ref. 14. All values are in atomic units ($m=\hbar=e=1$).

Atom	State	S_ρ	S_γ	$S_\rho+S_\gamma$	$-E$
Carbon	^3P	7.8357	20.1886	28.0743	37.69
	^1D	8.0846	20.0402	28.1248	37.63
	^1S	8.4166	19.8099	28.2265	37.55
Phosphorous	^4S	-5.2385	62.1095	56.8710	34.072
	^2D	-5.0156	61.9629	56.9473	34.065
	^2P	-4.8611	61.8645	57.0034	34.060
Titanium	^3F	-19.1919	95.3865	76.1946	848.41
	^1D	-19.1035	95.3414	76.2379	848.36
	^3P	-19.0892	95.3342	76.2450	848.35
	^1G	-19.0516	95.3159	76.2643	848.33
	^1S	-18.8070	95.2040	76.3970	848.23

formation entropies S_ρ and S_γ for all the atoms in their ground and excited states (reported in Ref. 11) were computed employing spherically averaged densities. These entropies and their sum, $S_\rho+S_\gamma$ are reported in Table III for a few randomly selected atoms.

Let us first investigate S_ρ and S_γ for atoms in their ground states shown pictorially in Fig. 1. The S_ρ values generally *decrease* with Z, though there are some notable exceptions around fully filled shells, such as Ne and Ar atoms. This physically means that $\rho(r)$ for these atoms is the most compact one when compared to the neighboring atoms. The S_γ values as well as the sum $S_\rho+S_\gamma$, however, show a strictly monotonic increase with Z. The least-squares fits of these ground-state NHF values to the form suggested in Ref. 10 along with the respective correlation coefficients X are given by

$$S_\rho = N(4.171-1.715\ln N),\quad X=-0.988 \tag{11a}$$

and

$$S_\gamma = N(2.086+0.784\ln N),\quad X=0.976\ , \tag{11b}$$

leading to

$$S_\rho+S_\gamma = N(6.257-0.933\ln N),\quad X=0.993\ . \tag{11c}$$

The fit (11c) is in reasonably good agreement with its TF counterpart (5), though the individual entropies, S_ρ and S_γ values do *not* match with the respective TF ones that well.

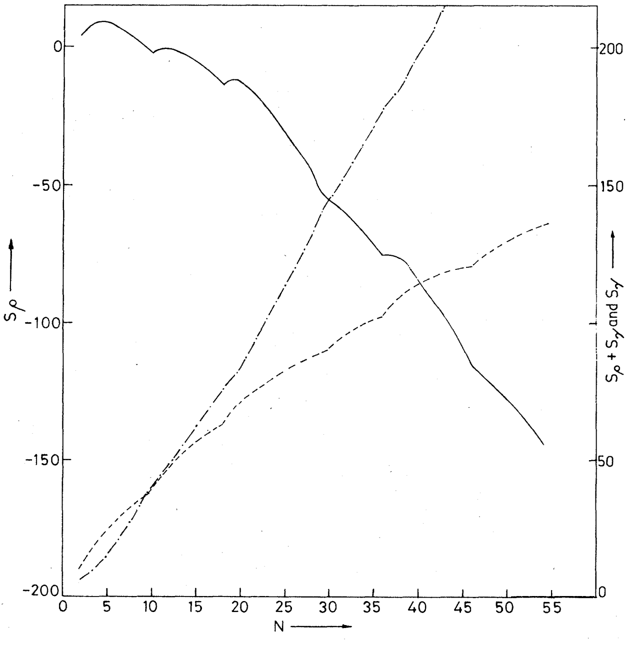

FIG. 1. Plot of near—Hartree-Fock information entropies for atoms with $2 \le N \le 54$. ——, S_ρ; — — —, $S_\rho+S_\gamma$; —·—·—·, S_γ.

TABLE IV. Informational entropies S_ρ and S_γ for atoms and ions in some isoelectronic series. All values are in atomic units ($m=\hbar=e=1$).

Isoelectronic series Atom/Ion	S_ρ	S_γ	$S_\rho+S_\gamma$
Be(^1S)			
Li^-	15.8266	4.6326	20.4592
Be	8.9511	11.2157	20.1668
B^+	5.0138	15.0808	20.0946
C^{2+}	2.1267	17.9329	20.0596
N^{3+}	-0.1757	20.2143	20.0386
O^{4+}	-2.0959	22.1207	20.0248
F^{5+}	-3.7460	23.7610	20.0150
Ne^{6+}	-5.1933	25.2010	20.0077
Br^{31+}	-21.2986	41.2683	19.9697
Kr^{32+}	-21.6470	41.6163	19.9693
Ne(^1S)			
F^-	3.9611	35.7618	39.7229
Ne	-2.4730	41.3447	38.8717
Na^+	-7.4893	45.9201	38.4303
Mg^{2+}	-11.6859	49.8319	38.1460
Al^{3+}	-15.3214	53.2619	37.9405
Br^{25+}	-52.3953	89.2960	36.9007
Kr^{26+}	-53.3410	90.2291	36.8881

Now consider the information entropies for atoms in their excited states. Three such cases are presented in Table III. It may be noted that S_ρ is *the lowest* for the ground state of an atom, in accordance with the intuitive notion that the ground state corresponds to the most compact electron density. The S_γ values are reciprocally expected to be the largest for the ground state. These trends are borne out fully by the present study. Thus, for all atoms reported in Ref. 11, the sum $S_\rho+S_\gamma$ is indeed a minimum for the ground state. Furthermore, the ordering of states is exactly identical with respect to entropy sum and electronic energy.

The TF expression for $S_\rho+S_\gamma$ suggests that the information entropy sum is a function of N and hence the dependence on the external potential may not be large. To test this conjecture, we have computed S_ρ and S_γ for some isoelectronic series. Some typical results are displayed in Table IV. It may be noted that S_ρ values diminish with increasing Z and the S_γ values are enhanced. Their sum, $S_\rho+S_\gamma$, is a rather slowly varying function of Z.

Having examined the ground and excited state information entropies, let us now study the effect of the ground-state wave function quality on the entropies.

IV. INFORMATION-ENTROPY SUM AS A MEASURE OF ATOMIC WAVE-FUNCTION QUALITY

In exploring the use of the sum $S_\rho+S_\gamma$ as a measure of wave-function quality, basis sets of single-zeta (SZ), double-zeta (DZ), and near—Hartree-Fock (NHF) types were employed. The entropies S_ρ and S_γ were computed numerically ensuring the normalizations in **r** and **p** spaces and $\langle p^2\rangle$ value correct to at least five significant places. The resulting values of the entropies and their sum, for some atoms selected at random, are shown in Table V. The trends exhibited by S_ρ, S_γ, and their sum are identical for all the basis sets employed: the S_ρ and $S_\rho+S_\gamma$ values enhance, and S_γ values decrease, with increasing Z. This is in qualitative agreement with the prototype Thomas-Fermi results.

Now consider the effect of enhancement of basis-set quality on information entropies. For any *atom*, the following three general trends may be noted. (i) The S_ρ values increase on passing from SZ to NHF wave functions. (ii) The corresponding S_γ values decrease. (iii) However, the sum $S_\rho+S_\gamma$ is a maximum for the NHF wave function and minimum for SZ ones. There is, indeed, not a single exception to the above observations.

The information-entropy sum has another attractive attribute, viz., invariance to scaling. Thus, generalizing the scaling arguments in Sec. II A, it can be readily proven that for an N-electron system

$$S_{\rho_\lambda}=S_\rho-3N\ln\lambda \tag{12}$$

and

$$S_{\gamma_\lambda}=S_\gamma+3N\ln\lambda\ , \tag{13}$$

leading to the result that the *entropy sum is invariant to scale transformations*. This result is indeed physically appealing, since the net information content $S_\rho+S_\gamma$ obtainable from a trial wave function is unaltered by uniform stretching or compression of the atom. In conclusion, the startling numerical discovery that the entropy sum strictly enhances with the atomic wave-function quality coupled with its invariance to scaling, justifies its use as a potential measure of wave-function quality.

V. CONCLUDING REMARKS

The first part of the present work (Secs. II and III) dealt with the variation of entropies for a given system with the state of excitation. These studies reveal that the entropy sum $S_\rho+S_\gamma$ is a minimum for the ground state of the system under consideration. We have, as yet, found not a single exception to this remarkable general observation. The rigorous proof of this result, however, does not seem to be straightforward and needs further attention. In the second part (Sec. IV), we advocated the use of the scale-invariant net information content $S_\rho+S_\gamma$ for assessing the quality of atomic wave functions. The trial wave functions analyzed here are of reasonably good quality. By this, it is meant that

(i) Their overlap with the *exact* ground-state wave function (or, the lower bound to it as determined by the Eckart criterion) is fairly large, say $S\simeq 0.95$.

(ii) The electron densities satisfy Kato's theorem, viz., $(d\rho/dr)_{r=0}=-2Z\rho(0)$, reasonably well.

(iii) The **r** space wave functions show a proper exponential "tail" and the **p** space wave functions die out asymptotically as $\sim p^{-8}$.

TABLE V. Shannon entropies S_ρ, S_γ, and their sum $S_\rho+S_\gamma$ for neutral atoms in their ground state, computed from Hartree-Fock wave functions.[a]

		NHF[a]			DZ[a]			SZ[a]	
Atom	S_ρ	S_γ	$S_\rho+S_\gamma$	S_ρ	S_γ	$S_\rho+S_\gamma$	S_ρ	S_γ	$S_\rho+S_\gamma$
B	8.980	15.482	24.462	8.961	15.489	24.450	8.685	15.696	24.380
N	5.99	25.224	31.241	5.937	25.240	31.177	5.125	25.767	30.892
Ne	−2.473	41.345	38.872	−2.622	41.375	38.752	−4.669	42.426	37.758
K	−12.213	80.336	68.123	−12.239	80.348	68.109	−13.354	81.238	67.884
Cu	−52.316	141.613	89.297	−53.052	141.661	88.609	−58.261	143.614	85.352
Br	−71.567	173.045	101.479	−71.644	173.089	101.445	−75.110	175.264	100.154
Ru	−103.587	224.024	120.437	−103.814	224.046	120.232	−104.999	224.819	119.320
Xe	−143.274	279.233	135.959	−143.332	279.247	135.915	−146.360	281.536	135.166

[a] All values in a.u. Near—Hartree-Fock (NHF), double-zeta (DZ), and single-zeta (SZ) wave functions taken from Ref. 10.

For these "good" atomic wave functions, the entropy sum indeed is a good measure of the wave-function quality. We have, as yet found no rigorous proof of this fact.

The sum $S_\rho + S_\gamma$ is indeed an appealing measure of the net information content of a bound quantal system. It emphasizes the fundamental role played by the electron densities[7] in the density-functional formalism. It reflects a delicate balance between the coordinate and momentum spaces as may be seen from the bound by Białynicki-Birula and Mycielski.[8] The sum $S_\rho + S_\gamma$ is also invariant to scaling. Thus, the sum of the entropies in coordinate and momentum spaces (rather than the individual entropies S_ρ and S_γ) qualifies to be a measure of information content. This indeed has significant repercussions in the maximum entropy principle when employed for synthesizing atomic electron densities.[1–3]

The enhancement of $S_\rho + S_\gamma$ with wave-function quality for "reasonably good" wave functions deserves further studies. It would be worthwhile to study extremely good correlated wave functions in this light. The variation of the entropy sum during molecule formation is worth investigating. Thus, the information entropies seem to be a hidden treasure, which, as yet remains mostly unexplored.

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[1] S. R. Gadre and S. B. Sears, J. Chem. Phys. **71**, 432 (1979); S. B. Sears and S. R. Gadre, *ibid.* **75**, 4625 (1980).

[2] T. Koga, J. Chem. Phys. **79**, 1933 (1983).

[3] S. B. Sears, R. G. Parr, and U. Dinur, Isr. J. Chem. **19**, 165 (1980), and references therein.

[4] S. B. Sears, Ph.D. thesis, University of North Carolina at Chapel Hill, 1980.

[5] G. Maroulis, M. Sana, and G. Leroy, Int. J. Quantum Chem. **19**, 43 (1981).

[6] A. M. Simar, A. J. Thakkar, and V. H. Smith, Jr., Int. J. Quantum Chem. **24**, 527 (1983).

[7] See W. Kohn and P. Vashishta, in *Theory of the Inhomogeneous Electron Gas*, edited by N. H. March and S. Lundquist (Plenum, New York, 1983), p. 78; R. G. Parr, Annu. Rev. Chem. **34**, 631 (1983), for comprehensive reviews.

[8] I. Białynicki-Birula and J. Mycielski, Commun. Math. Phys. **44**, 129 (1975).

[9] See, for example, C. Deutsch, Phys. Rev. Lett. **50**, 631 (1983); M. H. Partovi, *ibid.* **50**, 1883 (1983); I. Białynicki-Birula, Phys. Lett. **103A**, 253 (1984).

[10] S. R. Gadre, Phys. Rev. A **30**, 620 (1984).

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

[12] L. C. Snyder, J. Chem. Phys. **33**, 1711 (1960); G. R. Taylor and R. G. Parr, Proc. Natl. Acad. Sci. U.S.A. **38**, 154 (1952).