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Rigorous relationships among quantum-mechanical kinetic energy and atomic information entropies: Upper and lower bounds

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An uncertainty-type lower bound [I. Bialynicki-Birula and J. Mycielski, Commun. Math. Phys. **44**, 129 (1975)] to the information-entropy sum in complementary spaces has recently been reformulated by Gadre *et al.* [Phys. Rev. A **32**, 2602 (1985)] in terms of the respective one-particle probability densities. This bound has been exploited to derive rigorous upper as well as lower bounds to the information entropies and their sum in terms of the corresponding second moments of their distributions. Thus the present work establishes a direct connection, as suggested by Sears, Parr, and Dinur [Israel J. Chem. **19**, 165 (1980)], between the quantum-mechanical kinetic energy and information entropy in position space. It has also been demonstrated that given at least one arbitrary moment-type constraint in each space, it is possible to derive an upper bound to the information entropy sum in complementary spaces.

I. INTRODUCTION

During the last decade there has been increasing interest[1–6] in the application of information theory to a variety of quantum-mechanical problems. An information-theoretical approach has been employed for the elucidation of fundamental concepts[1,3,6] as well as for a more practical purpose such as synthesis[4,5] of electron densities in position and momentum spaces. In the former category, the inequality due to Bialynicki-Birula and Mycielski[1] provides an interesting uncertainty-type relation in terms of the information entropies in complementary spaces,

$$-\langle \ln |\psi|^2\rangle - \langle \ln |\tilde{\psi}|^2\rangle > n(1+\ln\pi) , \tag{1}$$

where ψ and $\tilde{\psi}$ are the wave functions in n-dimensional coordinate and momentum spaces, respectively. As pointed out by Bialynicki-Birula and Mycielski[1] in their work, the inequality (1) is an expression of quantum-mechanical uncertainty, since a narrow distribution in a space must necessarily engender a diffuse one in the conjugate space. It has also been proved that the entropy sum in (1) is invariant to uniform scaling of coordinates.[2] The inequality (1) can readily be transcribed in terms of the corresponding one-particle probability densities, viz., $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$. Here,

$$\rho(\mathbf{r}) = N\int \psi^*(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)\psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)d\mathbf{r}_2\cdots d\mathbf{r}_N \tag{2}$$

and

$$\gamma(\mathbf{p}) = N\int \psi^*(\mathbf{p},\mathbf{p}_2,\ldots,\mathbf{p}_N)\times\psi(\mathbf{p},\mathbf{p}_2,\ldots,\mathbf{p}_N)d\mathbf{p}_2\cdots d\mathbf{p}_N . \tag{3}$$

The bound (1), after some simplification and use of the definitions in (2) and (3), assumes the form, shown in Ref. 2,

$$S_\rho + S_\gamma \geq 3N(1+\ln\pi) - 2N\ln N , \tag{4}$$

where the entropy $S_\rho = -\int \rho(\mathbf{r})\ln\rho(\mathbf{r})d\mathbf{r}$ is now defined with reference to three-dimensional electron density distribution. The Shannon entropy S_γ is defined analogously. In a recent work, several novel characteristics of atomic information entropies have been observed. The main observations reported in this work are that the information entropy sum $S_\rho + S_\gamma$ (1) enhances with excitation of a quantum-mechanical system and (2) seems to be an indicator of the wave function quality for fully optimized variational wave functions. Due to complete variation of all the parameters involved, these wave functions satisfy the quantum-mechanical Coulombic virial theorem, viz., $T=-E$. The studies carried out so far[2] investigating the atomic information entropies fully corroborate these findings. The wave functions employed in these studies include single-zeta, double-zeta, near Hartree-Fock, and some CI-type ones for atoms and ions.

A study portraying the quantum-mechanical kinetic energy as a measure of information in a probability distribution was earlier reported by Sears, Parr and Dinur.[3] In this interesting study they discussed the implications of information theory for density-functional theory of electronic structure. Several exact relationships were found,[3] the one of special interest being $T_\psi = T_w + (N/8)\langle I_f\rangle$, where the quantity on the left-hand side is the quantum-mechanical kinetic energy, T_w is the celebrated Weizsäcker term and the second term on the right-hand side denotes the average of the Fisher's information entropy associated with the N-

dimensional conditional density $|\psi(1,2,\ldots N)|^2/\rho(1)$, the averaging being done over the one-particle density $\rho(1)$. They thus noted that the Weizsäcker term is not so much of a "correction" term as thought of in the earlier literature, but provides a solid first approximation to the kinetic energy functional. The purpose of the present work is to establish a direct link between the quantum-mechanical kinetic energy and the Shannon entropy S_ρ associated with the position-space electron density, $\rho(\mathbf{r})$, via a rigorous inequality. Several bounds to S_ρ and S_γ as well as their sum and difference in terms of the second moments of the probability densities $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$, viz., the $\langle r^2\rangle$ and $\langle p^2\rangle$ values, will also be presented and discussed.

II. ATOMIC INFORMATION ENTROPIES AND KINETIC ENERGY

Consider all spherically symmetric distributions $\gamma(\mathbf{p})$, leading to a given value of the kinetic energy $T=\int\gamma(\mathbf{p})p^2dp/2$. Out of all these distributions, the one of the form $\gamma_{\max}(\mathbf{p})=A\exp(-\alpha p^2)$ has the maximum value of the information entropy S_γ. Here A is the normalization constant and α is an appropriate Lagrange multiplier. It turns out that $A=\alpha^{3/2}N/\pi^{3/2}$ and $\alpha=3N/4T$ where N is the number of electrons and T is the kinetic energy. Thus the maximum value of the momentum space entropy (for all distributions having a prescribed kinetic energy T) is given by $-\int\gamma_{\max}(\mathbf{p})\ln\gamma_{\max}(\mathbf{p})d\mathbf{p}$, leading to

$$S_\gamma\le-\int\gamma_{\max}(\mathbf{p})\ln\gamma_{\max}(\mathbf{p})d\mathbf{p}\ , \tag{5}$$

which on simplification yields

$$S_\gamma\le 3N(1+\ln\pi)/2-N\ln N-3N\ln(3N/4T)/2\ , \tag{6}$$

wherein the equality is attained by a Gaussian momentum density. From relations (4) and (6) one obtains a lower bound to S_ρ,

$$S_\rho\ge 3N(1+\ln\pi)/2+(N\ln N)/2-3N\ln(4T/3)/2\ , \tag{7}$$

which is a rigorous relationship between the exact quantum-mechanical kinetic energy and the information entropy in position space S_ρ. Addition of (6) and (7) leads to a lower bound to the excess information entropy in the position space over that in the momentum space,

$$S_\rho-S_\gamma\ge 3N\ln N-3N\ln(4T/3)\ . \tag{8}$$

The physical meaning of bound (8) is quite transparent: a large value of the kinetic energy is reflected in a lower bound to the excess information entropy in position space over that in the conjugate one. Similar upper as well as lower bounds can be worked out in terms of $\langle r^2\rangle$, the second moment of the position-space electron density, $\rho(\mathbf{r})$. These bounds are given by

$$S_\rho\le 3N(1+\ln\pi)/2+3N\ln(2\langle r^2\rangle/3)/2-5(N\ln N)/2 \tag{9}$$

$$S_\gamma\ge 3N(1+\ln\pi)/2+(N\ln N)/2-3N\ln(2\langle r^2\rangle/3)/2 \tag{10}$$

leading to

$$S_\gamma-S_\rho\ge 3N\ln[3N/(2\langle r^2\rangle)]\ . \tag{11}$$

Addition of (8) and (10) leads to

$$0\le 2N\ln(3N)-\ln(4\langle r^2\rangle\langle p^2\rangle)\ ,$$

or, equivalently,

$$\langle r^2\rangle\langle p^2\rangle\ge 9N^2/4\ . \tag{12}$$

Note that this is a bound[7] obtained by Gadre and Chakravorty employing an inequality due to Redheffer. This bound was also derived earlier by Yue and Janmin[7] via the use of commutator relations. It is indeed gratifying to note that the *same result* could also be obtained by the addition of inequalities (6) and (9) and may be represented by

$$S_\rho+S_\gamma\le 3N(1+\ln\pi)+3N\ln(4\langle r^2\rangle\langle p^2\rangle/9)/2 \\ -5N\ln N\ . \tag{13}$$

This means that an upper bound to the information-entropy sum can be prescribed in terms of the second moments in position and momentum space. It may be noted here that for an atomic or molecular system, the $\langle p^2\rangle$ expectation value, which is numerically twice the electronic energy via the virial theorem for Coulombic interactions, is measurable from thermochemical as well as spectroscopic experiments. It can also be obtained by integrating out suitably weighted Compton profiles measured from x-ray or γ-ray scattering as well as $(e,2e)$ experiments. The second moment of the coordinate space-charge density, viz., the $\langle r^2\rangle$ expectation value, can, however, be extracted from the experimental diamagnetic susceptibility data. However, it can be directly seen that the use of any moment-type constraint in either position or momentum space leads to an upper bound to the information entropy therein. Thus, the present results can be generalized to the case of an arbitrary number of known moment constraints; at least one in each space must be prescribed in order to obtain an upper bound to the information-entropy sum as expressed by inequality (12).

III. NUMERICAL TESTS AND CONCLUDING REMARKS

Let us begin by testing out the inequality (7), viz., $S_\rho\ge 3(1+\ln\pi)/2-3\ln(4T/3)/2$ which supplies a lower bound to T, the kinetic energy in terms of S_ρ for the case of hydrogen atom ($N=1$). Use of the value $S_\rho=4.14$ leads to a lower bound of approximately 0.41 a.u. (the exact value being 0.5) to the kinetic energy of the hydrogen atom. Note that (7) furnishes a lower bound to the kinetic energy, similar to the one used by Lieb[8] in his discussion of the stability of matter. However, Lieb's bound is given in terms of the integral of the cube of the electron density, viz., $T>K_s(\int\rho^3dr)^{1/3}$ where the best possible constant K_s is determined to be $3\delta(\pi/2)^{4/3}/2$. Lieb's inequality leads to a value of 0.43 a.u. for the lower bound to the kinetic energy. This is only about 5% higher than that offered by our bound (7). An additional attractive feature of our bound (7) is that it provides a connection between an interesting information-theoretical entity defined in terms of the experimentally measurable position-space probability density and the quantum-mechanical kinetic energy. The application of inequalities (4) and (13) leads to a lower and upper bound, respectively, viz., $S_\rho+S_\gamma \geq 3(1+\ln\pi)$ and $S_\rho+S_\gamma \leq 3(1+\ln\pi)\ +3\ln(4\langle r^2\rangle\langle p^2\rangle/9)/2$ to the information-entropy sum $S_\rho+S_\gamma$ for the case $N=1$. Thus, for the hydrogen atom, assuming $\langle p^2\rangle=1$ and $\langle r^2\rangle=3$ (all values in a.u.) leads to $6.43 \leq S_\rho+S_\gamma \leq 6.87$. Note that the true value of the information-entropy sum $S_\rho+S_\gamma$ is approximately 6.56 (correct to three significant digits) which is bracketed to within 5% on either side by the bounds (4) and (13). The bounds to information entropy in individual spaces turn out to be $3.83 \leq S_\rho \leq 4.26$ (actual values being 4.14 bracketed to within 8%) and $2.18 \leq S_\gamma \leq 2.61$ (true value being 2.42 which lies within 10% of the bounded values).

Some more tests of the upper and lower bounds to S_ρ, S_γ, and $S_\rho+S_\gamma$ are presented below in terms of the near Hartree-Fock expectation values $\langle r^2\rangle$ and $\langle p^2\rangle$ computed from the Clementi-Roetti wave functions.[9] For the helium atom, the bounds to S_ρ and S_γ predicted using the values of $\langle r^2\rangle=2.3697$ and $\langle p^2\rangle=5.7234$ (all values in a.u.) turn out to be $3.110 \leq S_\rho \leq 4.340$ and $5.756 \leq S_\gamma \leq 6.986$. The lower bounds to the entropy sum are given by $10.096 \leq S_\rho+S_\gamma \leq 11.326$. These may be compared to the near Hartree-Fock values[2] $S_\rho=4.011$, $S_\gamma=6.440$ and $S_\rho+S_\gamma=10.451$ a.u., respectively.

A similar test for the neon atom yields $-23.476 \leq S_\rho \leq 2.0963$, $16.194 \leq S_\gamma \leq 51.766$, and $18.290 \leq S_\rho+S_\gamma \leq 53.862$ (a.u.), the respective near Hartree-Fock counterparts being -2.473, 41.345, and 38.872 a.u. From these tests it may be seen that knowledge of $\langle r^2\rangle$ and $\langle p^2\rangle$, which is experimentally determinable, leads to rigorous upper and lower bounds to information entropies. These bounds are rather loose but could be made tighter by utilizing additional experimental-moments data.

To summarize, in the present work a variety of upper as well as lower bounds to information entropies in conjugate spaces have been derived exclusively in terms of the second moments of the respective one-particle densities. These inequalities employ the quantum-mechanical entropic uncertainty relation derived by Bialynicki-Birula and Mycielski.[1] It is noteworthy that our bounds are expressed in terms of electron densities. In fact, the inequalities derived in the present study furnish yet another crucial link between the electron densities in position and momentum spaces. Many other connections between these spaces have earlier been established in this laboratory. Some of these connections are based on the semiclassical phase-space treatment whereas some incorporate more rigorous conditions on the exchange hole.[10] The link between the conjugate-space densities is provided by the autocorrelation function in the latter approach. Some other connecting relationships are furnished by rigorous bounds among the moments of the probability densities in complementary spaces.[7] The highlight of the present work is the demonstration of upper as well as lower bounds to the information entropies in coordinate as well as momentum spaces furnished in terms of the second moment of the respective probability densities. It may be reemphasized here that a variety of bounds to the information entropies can be obtained in terms of other moments as well. It is also possible to obtain inequality-type relations among the position and momentum-space moments [as exemplified by the bound (12) in the present work] by invoking information-theoretical considerations.

The use of the information-entropy sum in conjugate spaces as a joint measure of the "uncertainty" of a quantum-mechanical distribution appears very rewarding. The existence of an upper bound to $S_\rho+S_\gamma$ proven in the present work indeed fortifies the recently enunciated maximum-entropy principle[11] for quantum-mechanical systems. Thus the present work points towards the possibility of a maximum entropy construction of electron densities in position and momentum spaces. Here, one can model the wave function in terms of an orbital basis, compute $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$, and maximize subject to certain prescribed moment-type constraints. This represents a new approach to electron-density synthesis which is similar in spirit to recent work of Massa *et al.*[12] in which an attempt to obtain a "Slater determinant" from the experimentally measured x-ray scattering factors is reported. That such an attempt is a valid one is vindicated by the upper bound to the information-entropy sum derived in the present study.

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