

Uncertainty inequalities among frequency moments and radial expectation values: Applications to atomic systems

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Rigorous and universal bounds on frequency moments of one-particle densities in terms of radial expectation values in the conjugate space are obtained. The results, valid for any d -dimensional quantum-mechanical system, are derived by using Rényi-like position-momentum inequalities in an information-theoretical framework. Especially interesting are the upper bounds on the Dirac exchange and Thomas-Fermi kinetic energies, as well as the disequilibrium or self-similarity of both position and momentum distributions. A variety of bounds for these functionals in a given space are known, but most usually in terms of quantities defined within the same space. Very few results including a density functional on one space, and expectation values on the conjugate one, are found in the literature. A pioneering bound on the disequilibrium in terms of the kinetic energy is improved in this work. A numerical study of the aforementioned relationships is carried out for atomic systems in their ground state. Some results are given in terms of relevant physical quantities, including the kinetic and electron-nucleus attraction energies, the diamagnetic susceptibility and the height of the peak of the Compton profile, among others. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4705275>]

I. INTRODUCTION

The one-particle density $\rho(\vec{r})$ of many-fermion systems is an essential quantity for the introspection on their main physico-chemical properties.¹ Consequently, the study of this density has called the attention of many researchers, especially after the formulation of the Hohenberg-Kohn theorem² concerning the existence of a universal density functional for the energy of these systems. The so-called “frequency moments” of the density (later defined, just as integrals of powers of the own density) play a relevant role within such a density functional theory framework.^{3,4}

Much effort has been made to obtain a similar formulation of this theory in the conjugate space, i.e., in terms of the momentum one-particle density $\gamma(\vec{p})$, with many successful results.⁵⁻⁸

Different studies based on the simultaneous use of quantities in the position and momentum spaces have been carried out. Most of them aim to provide uncertainty-like relationships. For instance, the well-known Heisenberg uncertainty principle⁹⁻¹¹ involves variances (defined by means of radial expectation values) in conjugate spaces. Since the formulation of the Heisenberg principle, many other uncertainty relations have been obtained, with a diversity of expectation values and/or density functionals. It is worth mentioning the lower bounds on products of radial expectation values $\langle r^\alpha \rangle$ and $\langle p^\beta \rangle$ ¹² emphasizing the particular case $\alpha = \beta = 2$. Bounds on the disequilibrium of the charge density,¹³ the product of logarithmic uncertainties¹² and the sum of Shannon¹⁴ or Rényi¹⁵ entropies

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are also known. Although these relationships are usually applied in three-dimensional systems (i.e., with vectors of three components \vec{r} and \vec{p}), all of them are valid for arbitrary dimensionality.^{16,17}

Such uncertainty relations are physically relevant, not only because of their importance in a theoretical quantum-mechanical framework,^{18–20} but also in the development of quantum information and computation.^{21,22} In this sense, the studies of entropic uncertainty relations²³ and their connection with entanglement²⁴ are also remarkable.

The aim of this study is to present uncertainty inequalities, in the form of bounds on a frequency moment (quantity defined in Sec. II) in a given space (position or momentum) in terms of two radial expectation values in the conjugate space. Such inequalities can handle radial expectation values of positive or negative orders. The bounds provided here are of universal validity (i.e., for any d -dimensional quantum mechanical system). By way of example, we carry out a numerical study for selected inequalities of physical interest in atomic systems, and the results are interpreted taking into account that some radial expectation values for atomic densities, in both position and momentum spaces, are physically relevant and/or experimentally accessible.

The paper is structured as follows: Section II is devoted to the definition of the one-particle densities from the wave function, as well as the main quantities we will deal with (radial expectation values, frequency moments, Rényi entropies). In Sec. III, the uncertainty relations associated to those quantities are provided, as universal bounds on frequency moments in terms of radial expectation values in the conjugate space. Particular cases of physical interest are detailed in Sec. IV, by providing rigorous inequalities whose accuracy is numerically analyzed in Sec. V for atomic one-particle densities. Some concluding remarks are finally given in Sec. VI.

II. FREQUENCY MOMENTS AND RÉNYI ENTROPIES OF QUANTUM SYSTEMS

Let us consider the one-particle density of a d -dimensional N -fermion system, defined by

$$\rho(\vec{r}) = \int |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_2 \dots d\vec{r}_N, \quad (1)$$

with Ψ its spinless wave function. The one-particle density in momentum space is defined similarly,

$$\gamma(\vec{p}) = \int |\tilde{\Psi}(\vec{p}, \vec{p}_2, \dots, \vec{p}_N)|^2 d\vec{p}_2 \dots d\vec{p}_N, \quad (2)$$

now in terms of the d -dimensional Fourier transform $\tilde{\Psi}$ of Ψ . In what follows, (i) normalization to unity will be considered, so that $\int \rho(\vec{r}) d\vec{r} = \int \gamma(\vec{p}) d\vec{p} = 1$, (ii) it is understood that all integrals are performed over the whole d -dimensional space \mathbb{R}^d , and (iii) atomic units (a.u.) will be used, so $\hbar = m = e = 1$.

These densities are interpreted, taking into account the aforementioned normalization, as probability distributions of finding a particle at a specific region within the respective domains of the densities (position or momentum).

Different expectation values and density functionals have been considered in order to characterize or to estimate the main physical properties of many-fermion systems. A relevant concept for the interpretation of different quantum-mechanical phenomena is that of “uncertainty,” in the Heisenberg sense, regarding the accuracy in the knowledge of the particle’s position and momentum at a given time.

The well-known Heisenberg relation, given by^{9–11}

$$\langle r^2 \rangle \langle p^2 \rangle \geq \frac{d^2}{4} \quad (3)$$

for arbitrary d -dimensional quantum systems, is expressed in terms of second order “radial expectation values” $\langle r^a \rangle$ of the one-particle densities, where

$$\langle r^a \rangle \equiv \int r^a \rho(\vec{r}) d\vec{r} \quad (4)$$

with $r \equiv |\vec{r}|$, and similarly for $\langle p^a \rangle$. The real exponent a will be referred to as the “order” of the radial expectation value, whose range of allowed values will be imposed by the conditions of convergence

of the involved integrals. For densities with finite value at the origin, the condition $a > -d$ has to be taken into account, according to the expression of the volume element $d\vec{r} = r^{d-1}dr d\Omega_d$, where $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the d -dimensional solid angle.

Notice that the quantity $\langle r^a \rangle$ does not depend on the angular variables of the distribution $\rho(\vec{r})$. This means that we can determine them from the spherically averaged density $\rho(r)$, whose moments over the interval $r \in [0, \infty)$

$$\mu_a \equiv \int_0^\infty r^a \rho(r) dr$$

are related to the aforementioned radial expectation values as $\langle r^a \rangle = \Omega_d \mu_{a+d-1}$. From a mathematical point of view, we can deal in similar ways with the quantities $\langle r^a \rangle$ or μ_a . In the present work, the radial expectation values $\langle r^a \rangle$ will be considered, because of their physical meaning.

The previous Heisenberg relation was later generalized to arbitrary uncertainty products $\langle r^a \rangle^{1/a} \langle p^b \rangle^{1/b}$ with positive orders a and b , first for three-dimensional systems¹² and later extended to arbitrary dimensionality d .¹⁶ These relationships were obtained drawing upon the concept of ‘‘Shannon entropy,’’ a density functional defined by²⁵

$$S(\rho) \equiv - \int \rho(\vec{r}) \ln \rho(\vec{r}) d\vec{r}, \quad (5)$$

which is a measure of ‘‘spreading/delocalization’’ of the probability distribution. As suggested by the notion of uncertainty previously discussed, the Shannon entropies in position and momentum spaces, namely, $S(\rho)$ and $S(\gamma)$, fulfil the uncertainty relation given in Ref. 14:

$$S(\rho) + S(\gamma) \geq d(1 + \ln \pi), \quad (6)$$

what means that it is not possible to deal, simultaneously, with arbitrary low values of both entropies or, in other words, with extremely accurate values of the position and momentum variables. The above inequality, paying homage to its pioneering authors Bialynicki-Birula and Mycielski, will be referred as the BBM inequality. Other entropic inequalities are also known,^{23,26} with a variety of applications in a quantum-theoretical framework.²⁴

A very recent improvement of the above inequality on radial uncertainty products has been achieved²⁷ by considering a Rényi-like inequality instead of the Shannon-like BBM one, giving rise to a lower bound with a new parameter ‘‘ q ,’’ providing the original bound as $q = 1$. The optimization of this new bound with respect to the parameter q improves the well-known results with the particular value $q = 1$.

Rényi’s entropy²⁸ constitutes a generalization of Shannon’s one, and it is defined as follows:

$$R_q(\rho) \equiv \frac{1}{1-q} \ln \omega_q(\rho), \quad (7)$$

where the quantity

$$\omega_q(\rho) \equiv \int \rho^q(\vec{r}) d\vec{r} \quad (8)$$

is the ‘‘frequency (or entropic) moment of order q ,’’²⁹ of the distribution. Let us remark that, in spite of their names, the mathematical definition of the frequency moments (expectation values of powers of the density) strongly differs from that of the ‘‘usual’’ moments μ_a given after Eq. (4) (expectation values of powers of the independent radial variable).

The term ‘‘frequency moments’’ is usually employed in probability and statistics. Sichel^{30,31} employed them for the fitting of certain frequency curves. It happens that estimators based on frequency moments are, at times, much better than the ordinary moment estimates. Moreover, the frequency moments are fairly efficient in the range where the ordinary moments are very inefficient. This is so in some cases where the range is unlimited and the density is poorly known.²⁹

The quantities ω_q are also called ‘‘entropic moments’’ of the density function, because they are closely connected to the so-called Rényi and Tsallis entropies.^{28,32} The entropic adjective and the frequency term allow us to identify more appropriately the moments ω_q from the other type of

moments:²⁹ moments around the origin, central moments, factorial moments, absolute moments, etc. of a distribution.

The equality $R_1(\rho) = S(\rho)$ holds, taking into account that the normalization to unity of the distribution is expressed as $\omega_1(\rho) = 1$. The frequency moments play a central role in the description of many-fermion systems in terms of the one-particle density. In this sense, it is worth remarking the relevance of those with orders $q = 4/3$ and $5/3$, within a density functional theory (DFT) framework. They correspond, essentially, to the exchange and kinetic energy terms of the energy functional.¹ The frequency moment of order 2, namely, $\omega_2(\rho) = \int \rho^2(\vec{r})d\vec{r}$ is known as the “disequilibrium” of the probability distribution, which quantifies the departure from the equiprobability situation (equilibrium). The interpretation as a measure of departure from equiprobability arose in the framework of discrete and finite probability distributions.³³ Later on, this interpretation was generalized for the case of infinite and continuous probability distributions.³⁴ In spite of the nonexistence of uniform distributions in those cases, uniformity can be arbitrarily approached by means of sequences of distributions. In addition, the problem of fully characterizing the distribution by frequency moments was also addressed by considering the so-called Hausdorff entropic moment problem.³⁵

Similarly to the uncertainty inequality BBM for Shannon entropies, there exists a Rényi-like one given by¹⁵

$$R_q(\rho) + R_t(\gamma) \geq \ln \left[(2\pi)(2q)^{\frac{1}{2(q-1)}} (2t)^{\frac{1}{2(t-1)}} \right]^d \quad \text{as far as} \quad \frac{1}{q} + \frac{1}{t} = 2. \quad (9)$$

The BBM inequality is recovered for the particular case $q = t = 1$. Apart from the above mentioned case, it is clear that one of the orders must be above unity while the other is below unity. In what follows, let us choose the parameters in such a way that $q \geq 1 \geq t$. The opposite order will be considered by exchanging the distributions ρ and γ .

III. UPPER BOUNDS ON FREQUENCY MOMENTS IN TERMS OF RADIAL EXPECTATION VALUES

Let us notice that Eq. (9) can be expressed in terms of frequency moments as follows:

$$\omega_q(\rho) \leq \left[\frac{(q/\pi)^{q-1}}{(2q-1)^{\frac{2q-1}{2}}} \right]^d \omega_t^{\frac{1}{2t-1}}(\gamma), \quad \left(q \geq 1 \geq t \quad \text{with} \quad \frac{1}{q} + \frac{1}{t} = 2 \right), \quad (10)$$

and the opposite inequality holds for $q \leq 1 \leq t$.

Many expectation values are well-known relevant quantities which can be accessed or estimated from experiments (diamagnetic susceptibility, electron-nucleus attraction energy, height of the peak of the Compton profile, kinetic energy, and its relativistic correction due to mass variation, etc.).³⁶ That is not the case of frequency moments, in spite of their physical significance, especially in a density functional theory framework. Let us mention the relevant role played by the exchange and kinetic terms in the expansion of the functional for the total energy,¹ the Shannon entropy²⁵ (as a limiting case having its roots in information theory, statistical mechanics, and thermodynamics), or the disequilibrium³³ in the study of organization patterns in statistical mechanics, to mention a few of them. Additionally, let us remark that some of the previous functionals are essential ingredients in defining a variety of further information-theoretic concepts (e.g., complexity,³⁴ similarity,³⁷ and divergence^{38–40}).

The key point here, from a physical point of view, is that the radial expectation values of the one-particle densities (in position or momentum spaces) are physical observables, while the density functionals do not. It appears consequently of high interest to have at our disposal useful tools to get relevant information from density functionals by using the information we could get at the laboratory, or through alternative ways (theoretical, computational, etc.).

Due to the physical interest of the frequency moments, the variational procedure has been also employed in order to bound them in terms of physical observables. In Ref. 41, lower (upper) bounds on the d -dimensional frequency moments of order above (below) unity are given in terms of two radial expectation values, not necessarily of positive order. Regarding Eq. (10), let us take into

account the upper bound $\omega_t^*(\gamma)$ to the frequency moment $\omega_t(\gamma)$ with order below unity, as provided in Ref. 41 in terms of two radial expectation values:

$$\omega_t(\gamma) \leq \omega_t^*(\gamma) \equiv G(\alpha, \beta, t, d) \left[\langle p^\alpha \rangle^{-t(\beta+d)+d} \langle p^\beta \rangle^{t(\alpha+d)-d} \right]^{1/(\alpha-\beta)}, \quad \alpha > d \frac{1-t}{t} > \beta. \quad (11)$$

This bound is given in the aforementioned work, together with similar lower ones for order $t > 1$. Their analytical expressions, as well as that of the function $G(\alpha, \beta, t, d)$ can be found there.

The joint use of Eq. (10) and its ‘‘opposite version’’ for $q \leq 1$, together with the above mentioned variational upper and lower bounds on frequency moments,⁴¹ provides us with a variety of bounds (upper or lower) on $\omega_q(\rho)$ in terms of $\langle p^\alpha \rangle$ and $\langle p^\beta \rangle$. The symbol $B(x, y)$ stands for the beta function.

- (a) Upper bounds for $q > 1$ with $\alpha > d \frac{q-1}{q} > \beta$:

$$\begin{aligned} \omega_q(\rho) \leq & (\alpha - \beta) \left(\frac{\pi}{q} \right)^{d(1-q)} q^q (2q-1)^{d \frac{1-2q}{2}} \left[\Omega_d B \left(\frac{d+q(\alpha-d)}{(q-1)(\alpha-\beta)}, \frac{q(d-\beta)-d}{(q-1)(\alpha-\beta)} \right) \right]^{q-1} \\ & \times \left\{ \left[\frac{\langle p^\beta \rangle}{d+q(\alpha-d)} \right]^{d+q(\alpha-d)} \left[\frac{\langle p^\alpha \rangle}{q(d-\beta)-d} \right]^{q(d-\beta)-d} \right\}^{\frac{1}{\alpha-\beta}}. \end{aligned} \quad (12)$$

Let us notice the positivity of the order α , while β can be either positive or negative.

- (b) Lower bounds for $q < 1$ with $\alpha > \beta > -d \frac{1-q}{q}$:

$$\begin{aligned} \omega_q(\rho) \geq & (\alpha - \beta) \left(\frac{\pi}{q} \right)^{d(1-q)} q^q (2q-1)^{d \frac{1-2q}{2}} \left[\Omega_d B \left(\frac{q(\beta-d)+d}{(\alpha-\beta)(1-q)}, \frac{1}{1-q} \right) \right]^{q-1} \\ & \times \left\{ \left[\frac{\langle p^\beta \rangle}{d-q(d-\alpha)} \right]^{d-q(d-\alpha)} \left[\frac{q(\beta-d)+d}{\langle p^\alpha \rangle} \right]^{q(\beta-d)+d} \right\}^{\frac{1}{\alpha-\beta}}. \end{aligned} \quad (13)$$

In this case, each order α and β can be either positive or negative.

- (c) Lower bounds for $q < 1$ with $\beta < \alpha < -d \frac{1-q}{q}$:

$$\begin{aligned} \omega_q(\rho) \geq & (\alpha - \beta) \left(\frac{\pi}{q} \right)^{d(1-q)} q^q (2q-1)^{d \frac{1-2q}{2}} \left[\Omega_d B \left(\frac{q(d-\alpha)-d}{(\alpha-\beta)(1-q)}, \frac{1}{1-q} \right) \right]^{q-1} \\ & \times \left\{ \left[\frac{\langle p^\alpha \rangle}{q(d-\beta)-d} \right]^{q(d-\beta)-d} \left[\frac{q(d-\alpha)-d}{\langle p^\beta \rangle} \right]^{q(d-\alpha)-d} \right\}^{\frac{1}{\alpha-\beta}}. \end{aligned} \quad (14)$$

Now, both orders α and β of the radial expectation values are negative necessarily.

The same inequalities apply after exchanging the conjugated variables and densities, giving rise to bounds on frequency moments $\omega_q(\gamma)$ in momentum space in terms of radial expectation values in the position one.

IV. PARTICULAR CASES OF PHYSICAL INTEREST

For atomic systems, the expectation values $\langle r^n \rangle$ and $\langle p^n \rangle$ have been extensively used to bound and/or estimate other global quantities^{41,42} and the density itself.⁴³ Among those quantities, let us remark the frequency moments of both $\rho(\vec{r})$ and $\gamma(\vec{p})$. Additionally, different uncertainty-like inequalities have been derived by using information-theoretical tools.^{27,44}

It is worth mentioning that some of these expectation values are physically relevant and/or experimentally accessible in three-dimensional N-electron atoms. Some examples are³⁶ the following:

- (a) The kinetic energy T , given by $T = N \frac{\langle p^2 \rangle}{2}$, with its relativistic correction being proportional to $\langle p^4 \rangle$.

- (b) The height of the peak of the Compton profile $J(q)$, experimentally accessible from electron scattering experiments, is $J(0) = N \frac{\langle p^{-1} \rangle}{2}$.
- (c) The diamagnetic susceptibility χ , proportional to $\langle r^2 \rangle$.
- (d) The electron-nucleus attraction energy (absolute value) $E_{eN} = NZ \langle r^{-1} \rangle$, with Z being the nuclear charge.

Concerning the frequency moments and their corresponding Rényi entropies (see Sec. II), they have been considered as essential tools in a wide variety of fields, including the study of three-dimensional ($d = 3$) many-electron systems and physical processes. Many of those studies have emphasized the role played by the order “ q ” of the aforementioned density functionals, as also done in more recent applications based on the concepts of Jensen-Rényi,³⁹ Jensen-Tsallis,³⁸ and Kullback-Leibler⁴⁵ divergences, the quantum similarity index^{46,47} and its generalization⁴⁸ or the generalized shape complexity,⁴⁹ among others. In most of these applications, considering low enough values (usually below unity) of the order q appears very important in order to get non-trivial information, based on the features of the one-particle density in position space, regarding a variety of relevant properties of, e.g., atomic systems.

However, the main applications in the present work deal with frequency moments of order above unity. For N -fermion systems, it is well-known¹ that the frequency moments $\omega_{4/3}(\rho)$ and $\omega_{5/3}(\rho)$ are related to the local density approximations to the exchange and kinetic energies, K_0 and T_0 , respectively, as

$$K_0 = \frac{(3N)^{4/3}}{4\pi^{1/3}} \omega_{4/3}(\rho), \quad (15)$$

$$T_0 = \frac{(3N)^{5/3} \pi^{4/3}}{10} \omega_{5/3}(\rho), \quad (16)$$

and that

$$\omega_2(\rho) = \langle \rho \rangle \equiv D(\rho) \quad (17)$$

and

$$\omega_2(\gamma) = \langle \gamma \rangle \equiv D(\gamma) \quad (18)$$

are the average densities. It is worth mentioning the upper bound

$$\langle \rho \rangle \leq (8/3\pi^2)(2/3)^{1/2}(T/N)^{3/2} \approx 0.2206(T/N)^{3/2}, \quad (19)$$

due to Gadre and Chakravorty,¹³ and derived within a DFT framework by considering the relationship between the total kinetic energy functional T and its Weizsäcker term T_W . Let us remark that T is proportional to the radial expectation value $\langle p^2 \rangle$.

The second-order frequency moment, also known as “disequilibrium” (D), “self-similarity” or “information energy,” plays a central role in the definition of the so-called “shape complexity,” a concept which has called the attention of many researchers in recent years for quantifying appropriately how far a composite system is from the extreme situations of perfect order and complete disorder.^{34,50,51} The aforementioned complexity, as well as the Fisher-Shannon one, includes in their definitions the Shannon entropy S , a measure of spreading of the distribution. The Shannon entropy is related to the frequency moments through the limiting expression

$$S(\rho) = - \int \rho(\vec{r}) \ln \rho(\vec{r}) d\vec{r} = - \left. \frac{d\omega_q(\rho)}{dq} \right|_{q=1}$$

and similarly for $S(\gamma)$.

V. NUMERICAL ANALYSIS WITH ATOMIC ONE-PARTICLE DENSITIES

The accuracy of the universal bounds on frequency moments and, in particular, to relevant physical quantities expressed in terms of them (see Sec. IV), will be analyzed in this section for

ground-state neutral atoms throughout the whole periodic table (nuclear charge $Z = 1-103$). In doing so, accurate near-Hartree-Fock wavefunctions^{52,53} will be employed, from which the one-particle densities in position and momentum space are built up.

Let us remind the normalization to unity of both densities, a condition expressed as $\omega_1(\rho) = \omega_1(\gamma) = 1$ or, equivalently, $\langle r^0 \rangle = \langle p^0 \rangle = 1$. The systems considered in these numerical applications are three-dimensional ones, so that $d = 3$ and $\Omega_3 = 4\pi$.

A. Disequilibrium or information energy

The disequilibrium D of a probability distribution³³ is defined as its mean value or, equivalently, the second-order frequency moment as given by Eqs. (8) and (17). In order to bound from above the disequilibrium in terms of radial expectation values in the conjugate space, we must choose $q = 2$ in Eq. (12). Due to the validity of these bounds in both conjugate spaces, we will deal with equations for the disequilibrium $D(\rho)$ of the position space density $\rho(\vec{r})$. Similar inequalities are obtained for $D(\gamma)$ after exchanging the conjugate variables and their corresponding distributions.

We consider first the general inequality

$$D(\rho) \leq \frac{128(\alpha - \beta)}{3^{9/2}\pi^2} \Gamma\left(\frac{2\alpha - 3}{\alpha - \beta}\right) \Gamma\left(\frac{3 - 2\beta}{\alpha - \beta}\right) \left\{ \left[\frac{\langle p^\alpha \rangle}{3 - 2\beta} \right]^{3-2\beta} \left[\frac{\langle p^\beta \rangle}{2\alpha - 3} \right]^{2\alpha-3} \right\}^{\frac{1}{\alpha-\beta}} \equiv D_\rho(\alpha, \beta), \quad (20)$$

providing an upper bound, denoted as $D_\rho(\alpha, \beta)$, in terms of any two moments $\langle p^\alpha \rangle$ and $\langle p^\beta \rangle$ with orders constrained as $\alpha > \frac{3}{2} > \beta$. We observe that the order α is positive necessarily, while β can be positive, negative, or zero. The notation of the bound as $D_\rho(\alpha) \equiv D_\rho(\alpha, 0)$ is employed for the particular choice $\beta = 0$, namely,

$$D(\rho) \leq \frac{128\alpha}{(2\alpha - 3)^{2-\frac{3}{\alpha}} 3^{\frac{9}{2}+\frac{3}{\alpha}} \pi^2} \Gamma\left(2 - \frac{3}{\alpha}\right) \Gamma\left(\frac{3}{\alpha}\right) \langle p^\alpha \rangle^{3/\alpha} \equiv D_\rho(\alpha). \quad (21)$$

Apart from normalization, the bound $D(\alpha)$ is defined in terms of a unique expectation value $\langle p^\alpha \rangle$ with $\alpha > 3/2$. Especially interesting are the cases $\alpha = 2$ and $\alpha = 4$, with the corresponding bounds determined, respectively, by the kinetic energy (proportional to $\langle p^2 \rangle$) and its relativistic correction (essentially $\langle p^4 \rangle$) due to mass variation.

In Figure 1(a), the disequilibrium $D(\rho)$ for the charge density of neutral atoms is displayed, together with the aforementioned two upper bounds, namely $D_\rho(2)$ and $D_\rho(4)$. These bounds are given by

$$D_\rho(2) = \frac{128}{729\pi} \langle p^2 \rangle^{3/2} \approx 0.05589 \langle p^2 \rangle^{3/2} \quad (22)$$

and

$$D_\rho(4) = \frac{2^{15/2}}{3^{21/4} 5^5 \pi} \langle p^4 \rangle^{3/4}. \quad (23)$$

It is worth remarking that our bound $D_\rho(2)$ improves Gadre's one¹¹ in Eq. (19), rewritten as

$$D(\rho) \leq \frac{4}{3^{3/2}\pi^2} \langle p^2 \rangle^{3/2} \approx 0.07800 \langle p^2 \rangle^{3/2}, \quad (24)$$

after taking into account that $\langle \rho \rangle = D(\rho)$ and $T = N\langle p^2 \rangle/2$. The improvement is quantified by a factor of 72% of the Gadre's one.

It should be noticed also the functional dependence on the nuclear charge Z of the disequilibrium and the above discussed upper bounds of the systems under study. Such a dependence is (roughly) a power-like one as Z^c , with c a constant. An approximate value $c = 1.3$ is induced for the disequilibrium $D(\rho)$, and $c = 2.1$ and $c = 2.4$ for the upper bounds $D_\rho(2)$ and $D_\rho(4)$, respectively. Those values of the power c imply a higher accuracy of the upper bounds for light atomic systems as compared to the heavier ones.

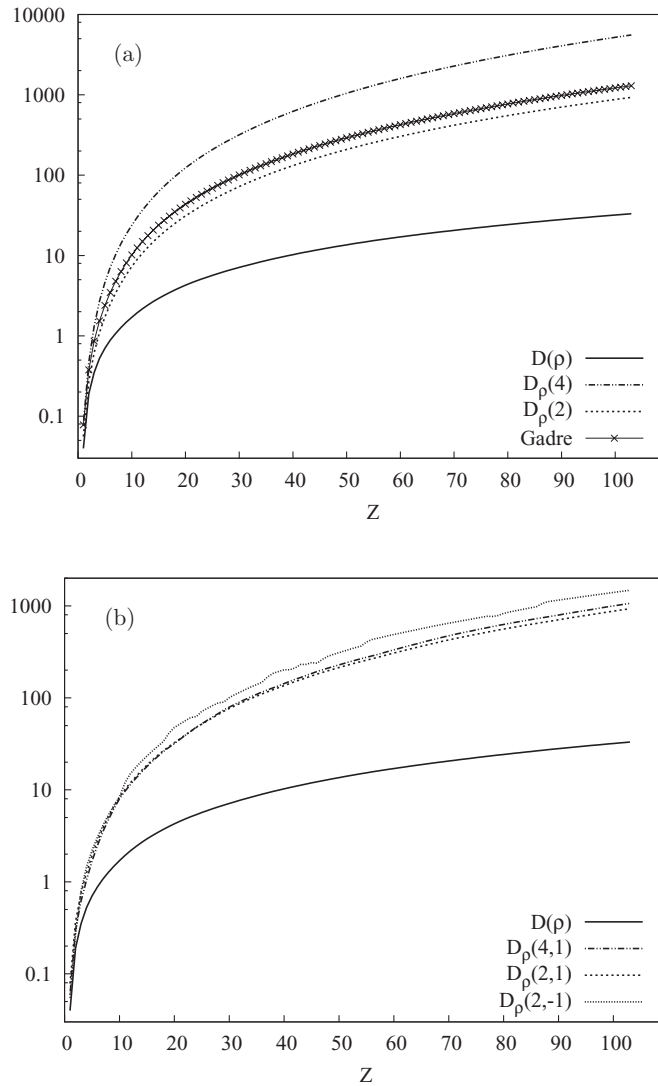


FIG. 1. Upper bounds on the disequilibrium $D(\rho)$ in position space (neutral atoms with nuclear charge $Z = 1-103$), in terms of (a) one, and (b) two radial expectation values in momentum space. Atomic units are used.

Considering non-zero orders α and β in Eq. (20) provides us with upper bounds on $D(\rho)$ in terms of two radial expectation values, constrained by the inequality $\alpha > 3/2 > \beta$. Consequently the order β can be either positive or negative. Some examples are displayed in Figure 1(b), corresponding to the analytical expressions given below:

$$D_\rho(2, 1) = \frac{128}{3^{9/2}\pi^2} \langle p \rangle \langle p^2 \rangle, \quad (25)$$

$$D_\rho(2, -1) = \frac{512}{3^5 5^{5/3} \pi} \langle p^{-1} \rangle^{1/3} \langle p^2 \rangle^{5/3}, \quad (26)$$

$$D_\rho(4, 1) = \frac{32\Gamma^2(1/4)}{3^{7/2} 5^{5/3} \pi^2} \langle p \rangle^{5/3} \langle p^4 \rangle^{1/3}. \quad (27)$$

It is observed in Figure 1(b) the similar behavior of the three bounds above mentioned, as also that of the own disequilibrium. To have an idea of the dependence on the nuclear charge Z of all bounds, the power-like dependence corresponds roughly to the constant $c = 2.1$. Attending to the value c

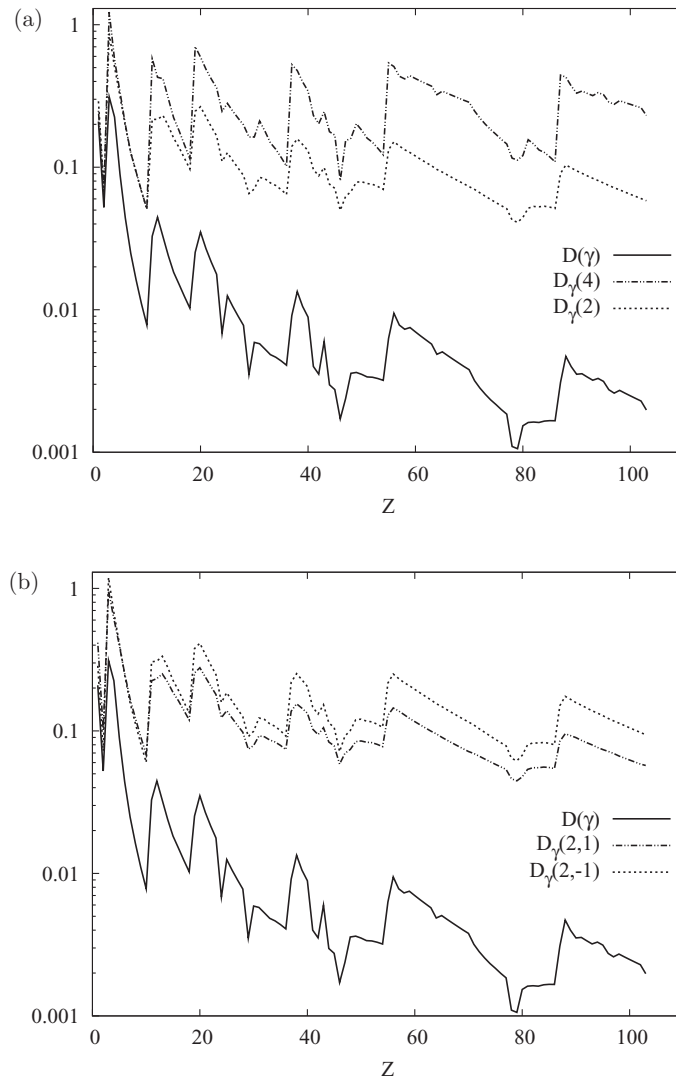


FIG. 2. Upper bounds on the disequilibrium $D(\gamma)$ in momentum space (neutral atoms with nuclear charge $Z = 1-103$), in terms of (a) one, and (b) two radial expectation values in position space. Atomic units are used.

$= 1.3$ for $D(\rho)$ as observed in Figure 1(a), similar comments apply in what concerns the accuracy of these bounds for light, medium, or heavy systems.

Let us now consider the study of the momentum-space disequilibrium $D(\gamma)$, with upper bounds expressed in terms of radial expectation values, now in position space. As done above regarding the numerical analysis of the bounds on $D(\rho)$, we study also the corresponding ones $D_\gamma(\alpha)$ and $D_\gamma(\alpha, \beta)$ to the momentum space one-particle distribution $\gamma(\vec{p})$.

The analytical expressions of these bounds, denoted as $D_\gamma(\alpha)$ and $D_\gamma(\alpha, \beta)$, are straightforwardly obtained from the previous ones, by only exchanging the conjugate variables r and p , as well as the one-particle densities $\rho(\vec{r})$ and $\gamma(\vec{p})$. One- and two-moment upper bounds are considered, with the orders of the involved moment(s) constrained as discussed previously.

The disequilibrium $D(\gamma)$ of the atomic momentum density, together with the one-moment bounds $D_\gamma(2)$ and $D_\gamma(4)$, is displayed in Figure 2(a), and two-moment bounds are shown in Figure 2(b). As compared to the position-space case (Figs. 1(a) and 1(b)), a very rich structure is observed for both the disequilibrium and its bounds, regarding their dependence on the atomic nuclear charge Z . The presence of local extrema (maxima or minima) is very apparent in the figures.

On a physical basis, the reason for finding a so rich structure is the enhancement, in the evaluation of the expectation values, of the contribution arising from the outermost (valence) region. The highest values of the momentum density occur (most usually) at the origin $p = 0$, or in its surrounding. The low-speed electrons (i.e., those with $p \approx 0$) correspond to the valence ones. Let us remark that the shell-filling pattern constitutes one of the main characteristics in atomic systems, determining most of their physical and chemical properties.

In this sense, it is worth pointing out that the local minima of $D(\gamma)$ correspond to systems $Z = 2, 10, 18, 24, 29, 36, 42, 46, 54, 58, 64, 79, 86, 90, 93$, and 97 , which can be classified as follows: (i) noble gases ($Z = 2, 10, 18, 36, 54$, and 86), and (ii) systems suffering from the so-called ‘‘anomalous shell filling’’ ($Z = 24, 29, 42, 46, 58, 64, 79, 90, 93$, and 97). Similar sets of extrema and their classification are also found for the one- and two-moment upper bounds. As an example, let us mention the systematic presence of local maxima for most alkaline earths ($Z = 12, 20, 38, 56, 88$).

B. Thomas-Fermi kinetic energy

One of the earliest tractable schemes for solving the many-electron problem was proposed by Thomas⁵⁴ and Fermi.⁵⁵ In this model the electron density $\rho(\vec{r})$ is the central variable rather than the wavefunction, and the total energy of a system is written as a functional of the density. The Thomas-Fermi energy functional is composed of three terms, one of them the electronic kinetic energy T_0 associated with a system of non-interacting electrons in a homogeneous electron gas. This form, as provided in Eq. (16), is obtained by integrating the kinetic energy density of a homogeneous electron gas.

The expression of T_0 in terms of the frequency moment $\omega_{5/3}(\rho)$ allows to perform a bounding procedure as done in the previous subsection. In this way we obtain a variety of upper bounds in terms of radial expectation values in momentum space, as follows:

$$T_0 \leq N^{5/3} \frac{(\alpha-\beta)2^{5/3}3^{5/2}5^{8/3}}{7^{7/2}\pi^{1/3}} \left[\Gamma\left(\frac{5\alpha-6}{2(\alpha-\beta)}\right) \Gamma\left(\frac{6-5\beta}{2(\alpha-\beta)}\right) \right]^{2/3} \times \left\{ \left[\frac{\langle p^\alpha \rangle}{6-5\beta} \right]^{6-5\beta} \left[\frac{\langle p^\beta \rangle}{5\alpha-6} \right]^{5\alpha-6} \right\}^{\frac{1}{3(\alpha-\beta)}} \equiv T_0(\alpha, \beta), \quad (28)$$

for any $\alpha > \frac{6}{5} > \beta$.

Choosing $\beta = 0$ gives rise to one-moment bounds,

$$T_0 \leq N^{5/3} \frac{\alpha 2^{\frac{5}{3}-\frac{2}{\alpha}} 3^{\frac{5}{2}-\frac{2}{\alpha}} 5^{8/3}}{7^{7/2}(5\alpha-6)^{\frac{5}{3}-\frac{2}{\alpha}} \pi^{1/3}} \left[\Gamma\left(\frac{5}{2} - \frac{3}{\alpha}\right) \Gamma\left(\frac{3}{\alpha}\right) \right]^{2/3} \langle p^\alpha \rangle^{2/\alpha} \equiv T_0(\alpha), \quad (29)$$

for any $\alpha > \frac{6}{5}$. Figure 3(a) displays the value of the functional T_0 , together with the one-moment upper bounds $T_0(\alpha)$ for $\alpha = 2$ and $\alpha = 4$, namely, in terms of $\langle p^2 \rangle$ and $\langle p^4 \rangle$, respectively,

$$T_0(2) = N^{5/3} \frac{3^{3/2} 5^{8/3}}{2^{1/3} 7^{7/2}} \langle p^2 \rangle \approx 0.3322 N^{5/3} \langle p^2 \rangle \quad (30)$$

and

$$T_0(4) = N^{5/3} \frac{2^{2/3} 5^{8/3} \Gamma^{4/3}(3/4)}{3^{8/3} 7^{14/3} \pi^{1/3}} \langle p^4 \rangle^{1/2}. \quad (31)$$

As one should expect, the bound $T_0(2)$ is more accurate because of its dependence on $\langle p^2 \rangle$, a quantity proportional to the exact kinetic energy.

Similar comments to those provided in the discussion of results for disequilibrium in position space (Fig. 1(a)) apply for the results on T_0 , regarding the power-like functional dependence Z^c on the nuclear charge Z . While T_0 possesses a fit with $c = 4.1$, the corresponding values are $c = 4.7$

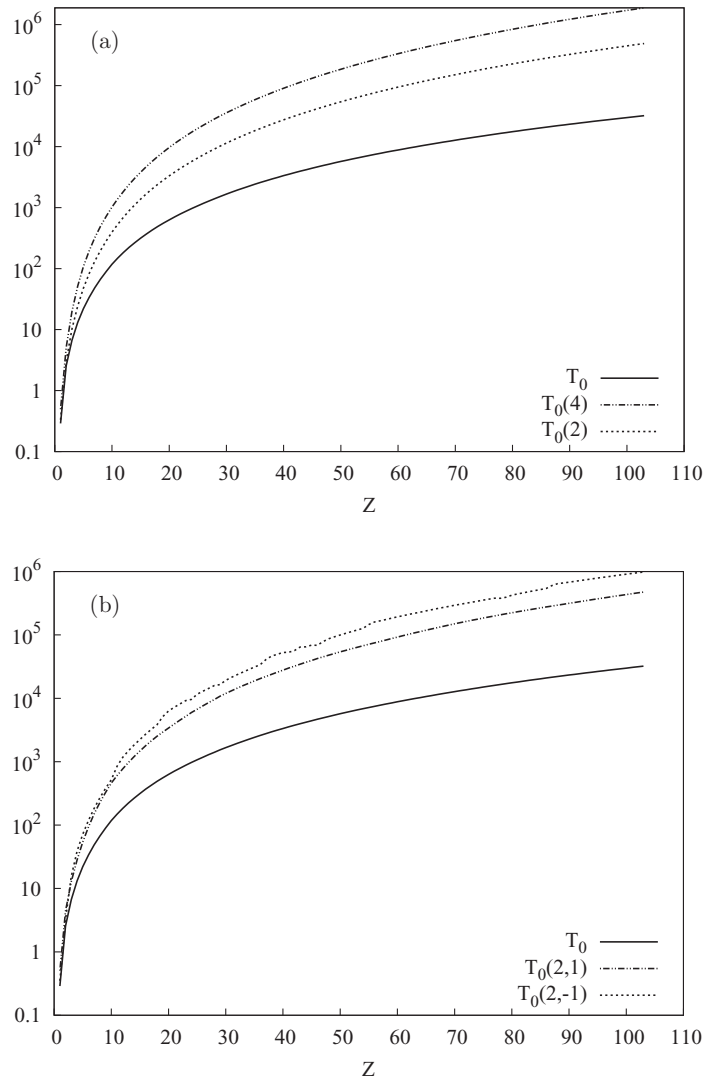


FIG. 3. Upper bounds on the Thomas-Fermi kinetic energy T_0 (neutral atoms with nuclear charge $Z = 1-103$), in terms of (a) one, and (b) two radial expectation values in momentum space. Atomic units are used.

for $T_0(2)$ and $c = 5.0$ for $T_0(4)$. This values justify (i) the higher accuracy of $T_0(2)$ as compared to $T_0(4)$, and (ii) the higher accuracy of both bounds for light systems as compared to heavy ones.

A similar behavior is observed in Figure 3(b), where two-moment bounds are considered, in particular

$$T_0(2, 1) = N^{5/3} \frac{3^{5/2} 5^{8/3}}{2 \cdot 7^{7/2}} \langle p \rangle^{4/3} \langle p^2 \rangle^{1/3} \tag{32}$$

and

$$T_0(2, -1) = N^{5/3} \frac{2^{7/9} 3^{7/2} 5^{8/3}}{7^{7/2} 11^{11/9} \pi^{1/3}} [\Gamma(2/3)\Gamma(11/6)]^{2/3} \langle p^{-1} \rangle^{4/9} \langle p^2 \rangle^{11/9}, \tag{33}$$

both including the kinetic energy via $\langle p^2 \rangle$. The exponents of the nuclear charge have the values $c = 4.7$ and $c = 4.9$, respectively.

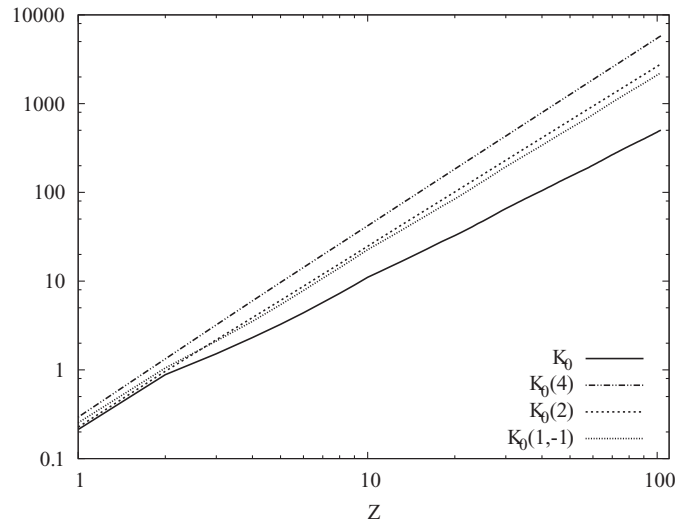


FIG. 4. Upper bounds on the Dirac exchange energy K_0 (neutral atoms with nuclear charge $Z = 1-103$), in terms of one and two radial expectation values in momentum space. Atomic units are used.

C. Dirac exchange energy

Shortly after the introduction of Thomas-Fermi theory, Dirac⁵⁶ developed an approximation for the exchange interaction based on the homogeneous electron gas. The resulting formula is simple, and is also a local functional of the density, as given by Eq. (15).

The bounds on the frequency moment $\omega_{4/3}(\rho)$ translate into upper bounds on K_0 :

$$K_0 \leq N^{4/3} \frac{8(\alpha-\beta)3^{5/2}}{5^{5/2}\pi} \left[\Gamma\left(\frac{4\alpha-3}{\alpha-\beta}\right) \Gamma\left(\frac{3-4\beta}{\alpha-\beta}\right) \right]^{1/3} \times \left\{ \left[\frac{\langle p^\alpha \rangle}{3-4\beta} \right]^{3-4\beta} \left[\frac{\langle p^\beta \rangle}{4\alpha-3} \right]^{4\alpha-3} \right\}^{\frac{1}{3(\alpha-\beta)}} \equiv K_0(\alpha, \beta), \quad (34)$$

for any $\alpha > \frac{3}{4} > \beta$. The one-moment bounds, obtained with the choice $\beta = 0$, are given by

$$K_0 \leq N^{4/3} \frac{8\alpha 3^{\frac{5}{2}-\frac{1}{\alpha}}}{5^{5/2}(4\alpha-3)^{\frac{4}{3}-\frac{1}{\alpha}}\pi} \left[\Gamma\left(4-\frac{3}{\alpha}\right) \Gamma\left(\frac{3}{\alpha}\right) \right]^{1/3} \langle p^\alpha \rangle^{1/\alpha} \equiv K_0(\alpha), \quad (35)$$

for any $\alpha > \frac{3}{4}$. Interesting particular cases are

$$K_0(2) = N^{4/3} \frac{8 \cdot 3^{7/3}}{5^{10/3}\pi^{2/3}} \langle p^2 \rangle^{1/2} \approx 0.2265 N^{5/3} \langle p^2 \rangle^{1/2} \quad (36)$$

and

$$K_0(4) = N^{4/3} \frac{32 \cdot 3^{9/4}}{5^{5/2}13^{13/12}\pi} [\Gamma(13/4)\Gamma(3/4)]^{1/3} \langle p^4 \rangle^{1/4}, \quad (37)$$

displayed in Figure 4, together with the bound

$$K_0(1, -1) = N^{4/3} \frac{8 \cdot 3^{17/6}}{5^{13/6}7^{7/6}\pi^{2/3}} \langle p^{-1} \rangle^{1/6} \langle p \rangle^{7/6} \quad (38)$$

as an illustrative example of the two-moment ones. In this figure, the power-like dependence on Z is emphasized by using a logarithmic scale in both axes. These bounds behave as Z^c with $c = 3.4, 3.5, 3.3$ for $K_0(2), K_0(4)$, and $K_0(1, -1)$, respectively, values to be compared with that for K_0 , namely, $c = 3.0$. Similar comments to those given in discussing results for T_0 apply now, also.

VI. CONCLUSIONS

The uncertainty inequality for Rényi entropies of conjugate distributions allowed us to perform a bounding procedure, whose main achievement is to provide upper and lower bounds on q th order frequency moments in terms of radial expectation values in the conjugate space. The procedure here employed provides results of universal validity, in the sense of being applicable to arbitrary one-particle densities arising from wavefunctions related by a Fourier transform.

We apply the above procedure to the study of physically relevant density functionals, defined in terms of the position and momentum one-particle densities of neutral atoms throughout the periodic table. Emphasis is laid on the one- and two-moment upper bounds on the position and momentum disequilibrium, the Thomas-Fermi kinetic energy, and the Dirac exchange energy. These bounds are expressed also in terms of physically meaningful and/or experimentally accessible expectation values. The power-like dependence of the position-space functionals and their upper bounds has been observed, and analyzed numerically in detail. On the other hand, the results for the momentum-space disequilibrium are interpreted according to shell-filling patterns, a feature shared by the corresponding upper bounds in terms of radial expectation values in position space.

Further applications are planned to be carried out in a near future. In this sense, we will take into account that the frequency moments and the Rényi and Tsallis entropies, including the Shannon one as a particular case, have been shown to play a fundamental role in the definition and applications of information-theoretical concepts such as complexity, similarity, and divergence. Additionally, other extensions of the present study will concern more sophisticated atomic models (e.g., configuration interaction), many-fermion systems (e.g., molecules), and physico-chemical processes (ionization, excitation, reaction).

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- ¹R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- ²P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1964).
- ³R. K. Pathak and L. J. Bartolotti, *Phys. Rev. A* **31**, 3557 (1985).
- ⁴R. K. Pathak and S. R. Gadre, *J. Chem. Phys.* **74**, 5925 (1981).
- ⁵M. Levy, *Proc. Natl. Acad. Sci. U.S.A.* **76**, 6062 (1979).
- ⁶G. A. Henderson, *Phys. Rev. A* **23**, 19 (1981).
- ⁷R. K. Pathak, P. V. Panat, and S. R. Gadre, *Phys. Rev. A* **26**, 3073 (1982).
- ⁸G. P. Das, S. K. Ghosh, and V. C. Sahni, *Solid State Commun.* **65**, 719 (1988).
- ⁹W. Heisenberg, *Z. Phys.* **43**, 172 (1927).
- ¹⁰W. Yue and L. J. Janmin, *Phys. Scr.* **30**, 414 (1984).
- ¹¹S. R. Gadre and S. J. Chakravorty, *J. Chem. Phys.* **84**, 7051 (1986).
- ¹²J. C. Angulo, *J. Phys. A* **26**, 6493 (1993).
- ¹³S. R. Gadre and S. J. Chakravorty, *Chem. Phys. Lett.* **132**, 535 (1986).
- ¹⁴I. Bialynicki-Birula and J. Mycielski, *Commun. Math. Phys.* **44**, 129 (1975).
- ¹⁵I. Bialynicki-Birula, *Phys. Rev. A* **74**, 052101 (2006).
- ¹⁶J. C. Angulo, *Phys. Rev. A* **50**, 311 (1994).
- ¹⁷S. Zozor and C. Vignat, *Physica A* **375**, 499 (2007).
- ¹⁸W. C. Price, in *The Uncertainty Principle and Foundations of Quantum Mechanics*, edited by W. C. Price and S. S. Chissick (Wiley, New York, 1977).
- ¹⁹G. B. Folland and A. Sitaram, *J. Fourier Anal. Appl.* **3**, 207 (1997).
- ²⁰P. Busch, T. Heinonen, and P. Lahti, *Phys. Rep.* **452**, 155 (2007).
- ²¹M. A. Nielsen and I. L. Chuang, *Quantum Computing and Quantum Information* (Cambridge University Press, Cambridge, 2000).
- ²²V. Vedral, *Introduction to Quantum Information Science* (Oxford University Press, Oxford, 2006).
- ²³J. I. de Vicente and J. Sánchez-Ruiz, *Phys. Rev. A* **77**, 042110 (2008).
- ²⁴O. Gühne and M. Lewenstein, *Phys. Rev. A* **70**, 022316 (2004).
- ²⁵C. E. Shannon and W. Weaver, *The Mathematical Theory of Communication* (University of Illinois Press, Urbana, 1949).
- ²⁶H. Maassen and J. B. M. Uffink, *Phys. Rev. Lett.* **60**, 1103 (1988).
- ²⁷S. Zozor, M. Portesi, P. Sánchez-Moreno, and J. S. Dehesa, *Phys. Rev. A* **83**, 052107 (2011).
- ²⁸A. Rényi, in *Proceedings 4th Berkeley Symposium on Mathematics, Statics and Probability*, (University of California Press, Berkeley, 1961), Vol. 1, p. 547.

- ²⁹M. G. Kendall and A. Stuart, *The Advanced Theory of Statistics* (Charles Griffin and Co. Ltd., London, 1969), Vol. 1.
- ³⁰H. S. Sichel, "Fitting growth and frequency curves by the method of frequency moments," *J. R. Stat. Soc., Ser. A* **110**, 337 (1947).
- ³¹H. S. Sichel, "The method of frequency moments and its applications to type VII populations," *Biometrika* **36**, 404 (1949).
- ³²C. Tsallis, *J. Stat. Phys.* **52**, 479 (1988).
- ³³O. Onicescu, "Energie informationelle," *Comptes Rendus de la Académie des Sciences Paris, Ser. A* **263**, 841 (1966).
- ³⁴R. López-Ruiz, H. L. Mancini, and X. Calbet, *Phys. Lett. A* **209**, 321 (1995).
- ³⁵E. Romera, J. C. Angulo, and J. S. Dehesa, *J. Math. Phys.* **42**, 2309 (2001).
- ³⁶I. R. Epstein, *Phys. Rev. A* **8**, 160 (1973).
- ³⁷R. Carbó-Dorca, J. Arnau, and L. Leyda, *Int. J. Quantum Chem.* **17**, 1185 (1980).
- ³⁸J. Antolín, S. López-Rosa, J. C. Angulo, and R. O. Esquivel, *J. Chem. Phys.* **132**, 044105 (2010).
- ³⁹J. C. Angulo, S. López-Rosa, J. Antolín, and R. O. Esquivel, *Int. J. Quantum Chem.* **111**, 297 (2011).
- ⁴⁰J. Antolín, P. A. Bouvrie, and J. C. Angulo, *Phys. Rev. A* **84**, 032504 (2011).
- ⁴¹J. S. Dehesa, F. J. Gálvez, and I. Porras, *Phys. Rev. A* **40**, 35 (1989).
- ⁴²J. C. Angulo and J. S. Dehesa, *J. Chem. Phys.* **97**, 6485 (1992).
- ⁴³J. Antolín, A. Zarzo, and J. C. Angulo, *Phys. Rev. A* **48**, 4149 (1993).
- ⁴⁴J. C. Angulo, *Phys. Rev. A* **83**, 062102 (2011).
- ⁴⁵S. Janssens, A. Borgoo, C. van Alsenoy, and P. Geerlings, *J. Phys. Chem. A* **112**, 10560 (2008).
- ⁴⁶*Fundamentals of Molecular Similarity*, edited by R. Carbó-Dorca, X. Gironés, and P. G. Mezey (Kluwer Academic/Plenum Press, New York, 2001).
- ⁴⁷A. Borgoo, M. Godefroid, P. Indelicato, F. de Proft, and P. Geerlings, *J. Chem. Phys.* **126**, 044102 (2007).
- ⁴⁸P. A. Bouvrie, J. Antolín, and J. C. Angulo, *Chem. Phys. Lett.* **506**, 326 (2011).
- ⁴⁹J. Antolín, S. López-Rosa, and J. C. Angulo, *Chem. Phys. Lett.* **474**, 233 (2009).
- ⁵⁰J. C. Angulo, J. Antolín, and K. D. Sen, *Phys. Lett. A* **372**, 670 (2008).
- ⁵¹R. O. Esquivel, J. C. Angulo, J. Antolín, J. S. Dehesa, S. López-Rosa, and N. Flores-Gallegos, *Phys. Chem. Chem. Phys.* **12**, 7108 (2010).
- ⁵²T. Koga, K. Kanayama, S. Watanabe, and A. J. Thakkar, *Int. J. Quantum Chem.* **71**, 491 (1999).
- ⁵³T. Koga, K. Kanayama, S. Watanabe, T. Imai, and A. J. Thakkar, *Theor. Chem. Acc.* **104**, 411 (2000).
- ⁵⁴L. H. Thomas, *Proc. Cambridge Philos. Soc.* **23**, 542 (1927).
- ⁵⁵E. Fermi, *Z. Phys.* **48**, 73 (1928).
- ⁵⁶P. A. M. Dirac, *Proc. Cambridge Philos. Soc.* **26**, 376 (1930).