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Geometric Rényi divergence: A comparative measure with applications to atomic densities

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An alternative one-parameter measure of divergence is proposed, quantifying the discrepancy among general probability densities. Its main mathematical properties include (i) comparison among an arbitrary number of functions, (ii) the possibility of assigning different weights to each function according to its relevance on the comparative procedure, and (iii) ability to modify the relative contribution of different regions within the domain. Applications to the study of atomic density functions, in both conjugated spaces, show the versatility and universality of this divergence.

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I. INTRODUCTION

Many information-theoretic divergence measures between two probability distributions have been introduced and extensively studied from their mathematical properties [1–5]. The applications of these measures can be found in the analysis of contingency tables [6], the approximation of probability distributions [7], signal processing [8], inference problems [9], pattern recognition [10], biodiversity [11], classification [12], homology [13], neural networks [14], computational linguistics [15], study of electronic densities [16–20], molecular similarity [21,22], texture and image registration [23], sequence analysis [24], machine learning [25], artificial intelligence [26], fuzzy set theory [27], and quantum-information theory [28], in particular as a measure of entanglement [29].

Among the proposed measures, the best known is the Kullback-Leibler [30] divergence based on Shannon entropy [31]. Since then, many other measures of divergence have been proposed and studied, in particular by using both local (Fisher) [32,33] and global (Shannon) [31] theoretic-information magnitudes. Some generalized entropies such as the Rényi one [34] have also been used to formulate deeper or more precise measures of discrepancy or distinguishability [35]. Applications of similarity and divergence measures to the study of atomic systems have been carried out in recent years, including the use of the quantum similarity index (QSI) [18] and the Jensen-Shannon divergence (JSD) [36].

The recent development in knowledge-based chemical research has created a surge of interest in chemical similarity or dissimilarity. Molecular modeling, molecular similarity [37], and quantitative structure activity relationship (QSAR) are simple examples of such an interest [38]. More recently the molecular quantum similarity framework has been used to provide a new set of quantum quantitative structure-properties relationship procedures (QQSPR) [39].

The aim of this work is to propose, study, and apply a new one-parameter generalized divergence measure, the geometric Rényi divergence ($\text{GRD}^{(q)}$), which has important advantages over other studied divergences. Such improvement mainly

arises from the capability of $\text{GRD}^{(q)}$ to modify, by means of its characteristic parameter q , the relative contribution of relevant specific regions of the probability densities. The mathematical definition and properties of $\text{GRD}^{(q)}$ allow us to deal with arbitrary probability distributions, independently of their meaning or the specific fields of research, including all those previously mentioned.

We show the main properties of this divergence by comparing and studying a simple but highly hierarchical and organized set of quantum systems. We study the one-particle densities of atomic systems, in both conjugated spaces, which contain all the physical and chemical information through density-functional theory [40]. The obvious motivation is that the differences in the electronic charge densities of these species could be related to the differences in their respective physical and chemical properties, according to density-functional theory and the Hohenberg-Kohn theorem [41].

In this sense, especially remarkable are the applications carried out in this work by means of $\text{GRD}^{(q)}$, namely, (i) comparison among neutral atoms and interpretation in terms of shell-filling-patterns, (ii) study of ionization processes by analyzing the geometric divergence between the initial and final systems (neutral and cation) and its connection with the value of the ionization potential, (iii) study of divergence among densities, for a given system, computed with different models, and (iv) discrimination of whether an atom belongs to a set of systems with identical nuclear charges. The results here provided improve some of the aforementioned applications performed by using other measures, such as the quantum similarity index [18] or the Jensen-Shannon divergence [36]. Further applications to other systems and/or processes of physicochemical relevance (e.g., molecules and reactions) will be provided elsewhere.

The paper is organized as follows. In Sec. II we define the geometric Rényi divergence, showing its main mathematical properties. Section III is devoted to the application of $\text{GRD}^{(q)}$ to the study of one-particle densities of atomic systems, and in Sec. IV we summarize the main results of this work.

II. GEOMETRIC RÉNYI DIVERGENCE

The so-called Jensen-Rényi divergence ($\text{JRD}^{(q)}$) was first conceived [42] as a measure of dissimilarity or divergence

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95 between two distribution functions, say $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$, both
 96 of which are defined over the same d -dimensional domain
 97 $\Delta \in \mathbb{R}^d$. In doing so, the nonlinearity of the Rényi entropy [34]

$$R^{(q)}(\rho) \equiv \frac{1}{1-q} \ln \omega^{(q)}(\rho), \quad (1)$$

98 according to the properties of the q th-order frequency mo-
 99 ments

$$\omega^{(q)}(\rho) \equiv \int_{\Delta} \rho^q(\vec{r}) d\vec{r}, \quad (2)$$

100 was taken into account. In this way, the deviation from linearity
 101 allows us to define the Jensen-Rényi divergence between two
 102 distributions as [42]

$$\text{JRD}^{(q)}(\rho_1, \rho_2) = R^{(q)}\left(\frac{\rho_1 + \rho_2}{2}\right) - \frac{1}{2}[R^{(q)}(\rho_1) + R^{(q)}(\rho_2)], \quad (3)$$

103 which constitutes the difference between the Rényi entropy of
 104 the arithmetic mean and the arithmetic mean of the respective
 105 Rényi entropies of ρ_1 and ρ_2 . Generalizations of this diver-
 106 gence have been provided very recently [35] by considering
 107 mean values for an arbitrary number of distributions and their
 108 associated weights:

$$\text{JRD}^{(q)}(\rho_1, \dots, \rho_n) = R^{(q)}\left(\sum_{k=1}^n \alpha_k \rho_k\right) - \sum_{k=1}^n \alpha_k R^{(q)}(\rho_k), \quad (4)$$

109 with the weights verifying $\sum_{k=1}^n \alpha_k = 1$.

110 In what follows, the integration domain Δ will be omitted
 111 in the notation unless necessary, for the sake of simplicity. We
 112 will deal with normalized-to-unity distributions, a condition
 113 which can be expressed as $\omega^{(1)}(\rho) = 1$.

114 Regarding the definition of $\text{JRD}^{(q)}$, any order $0 < q \neq 1$
 115 can be considered, as far as the involved frequency moments
 116 converge. The limiting case $q \rightarrow 1$ provides the so-called
 117 Jensen-Shannon divergence [43,44], $\text{JSD} = \text{JRD}^{(1)}$, defined
 118 as above but in terms of the Shannon entropy $S(\rho) \equiv$
 119 $-\int \rho(\vec{r}) \ln \rho(\vec{r}) d\vec{r}$ [31] instead of the Rényi one. This is due
 120 to the limiting equality $S = R^{(1)}$ among entropies.

121 However, an essential constraint in performing studies
 122 by means of $\text{JRD}^{(q)}$ has been the necessary condition of
 123 considering the order q not above unity. The reason is that
 124 the non-negativity of $\text{JRD}^{(q)}$ is guaranteed only for $q \leq 1$,
 125 while for $q > 1$ it does not have a definite sign. According
 126 to the interpretation of $\text{JRD}^{(q)}$ as a measure of distance or
 127 divergence among distributions, we must avoid values below
 128 zero, as usually done for arbitrary metrics in a given space.

129 Let us recall Eqs. (1) and (4). We can express $\text{JRD}^{(q)}$ in
 130 terms of frequency moments as

$$\text{JRD}^{(q)}(\rho_1, \dots, \rho_n) = \frac{1}{1-q} \ln \frac{\omega^{(q)}(\sum_{k=1}^n \alpha_k \rho_k)}{[\omega^{(q)}(\rho_1)]^{\alpha_1} \dots [\omega^{(q)}(\rho_n)]^{\alpha_n}}. \quad (5)$$

131 The non-negativity of $\text{JRD}^{(q)}$ for $q < 1$ arises from the value
 132 above unity of the fraction within the logarithm. The same
 133 property of $\text{JRD}^{(q)}$ for $q > 1$ would be verified in case of the
 134 fraction being below unity, what is not necessarily true.

To get a Rényi-like divergence measure, non-negative for
 arbitrary order, we apply a different procedure in the present
 work. The well-known generalized Hölder's inequality [45]
 establishes that

$$\left[\int (f_1 f_2)^m d\vec{r} \right]^{1/m} \leq \left[\int f_1^s d\vec{r} \right]^{1/s} \left[\int f_2^t d\vec{r} \right]^{1/t} \quad (6)$$

for any $m, s, t > 0$ verifying $\frac{1}{m} = \frac{1}{s} + \frac{1}{t}$. An iterative use of
 the above inequality allows us to assert that

$$\left[\int (f_1 \dots f_n)^m d\vec{r} \right]^{1/m} \leq \left[\int f_1^{p_1} d\vec{r} \right]^{1/p_1} \dots \left[\int f_n^{p_n} d\vec{r} \right]^{1/p_n}, \quad (7)$$

with $\sum_{i=1}^n \frac{1}{p_i} = \frac{1}{m}$. Through the identities $f_i = \rho_i^{q/p_i}$ for a
 given $q > 0$, we obtain

$$\int (g_1^{\lambda_1} \dots g_n^{\lambda_n})^q d\vec{r} \leq \left(\int g_1^q d\vec{r} \right)^{\lambda_1} \dots \left(\int g_n^q d\vec{r} \right)^{\lambda_n}, \quad (8)$$

where $\lambda_i \equiv m/p_i$ summing up to unity as $\sum_{i=1}^n \lambda_i = 1$. We
 can now provide, for arbitrary $q > 0$, a quotient above unity
 and consequently with its logarithm being above zero. The
 logarithm of the quotient is expressed in terms of frequency
 moments as

$$\lambda_1 \ln \omega^{(q)}(\rho_1) + \dots + \lambda_n \ln \omega^{(q)}(\rho_n) - \ln \omega^{(q)}(\rho_1^{\lambda_1} \dots \rho_n^{\lambda_n}) \geq 0, \quad (9)$$

or in terms of the Rényi entropies defined in Eq. (1) as

$$\text{GRD}^{(q)}(\rho_1, \dots, \rho_n) \equiv (q-1) \left[R^{(q)}(\rho_1^{\lambda_1} \dots \rho_n^{\lambda_n}) - \sum_{i=1}^n \lambda_i R^{(q)}(\rho_i) \right] \geq 0, \quad (10)$$

where the quantity $\text{GRD}^{(q)}$ will be referred to as the geometric
 Rényi divergence of order q for the set of distributions $\{\rho_i\}$
 with weights $\{\lambda_i\}$.

Some comments are in order:

(1) Let us notice the strong resemblance between the terms
 within brackets in Eq. (10) and those of the definition of
 the Jensen-Rényi divergence ($\text{JRD}^{(q)}$) in Eq. (4). In fact, all
 terms associated with individual distributions are identical, the
 difference between both expressions being determined by the
 multicomponent term. That term corresponds to the frequency
 moment of the arithmetic mean of the distributions in the
 $\text{JRD}^{(q)}$ case, while the geometric mean, instead, in $\text{GRD}^{(q)}$.

(2) The additional factor $(q-1)$ guarantees the non-
 negativity of $\text{GRD}^{(q)}$ for any $q > 0$, including the nonzero
 and finite-valued limiting case $q = 1$. Adding the same factor
 in the definition of $\text{JRD}^{(q)}$ would not solve the problem of the
 indefiniteness of sign for $q > 1$, as will be shown in Sec. III A.

(3) A particular case of physical relevance is obtained for
 $q = 2$:

$$\text{GRD}^{(2)}(\rho_1, \dots, \rho_n) = \ln \frac{[D(\rho_1)]^{\lambda_1} \dots [D(\rho_n)]^{\lambda_n}}{D(\rho_1^{\lambda_1} \dots \rho_n^{\lambda_n})}, \quad (11)$$

where the functional $D(\rho)$ is the so-called disequilibrium, a
 measure of departure of the distribution from uniformity [46].

170 So, $\text{GRD}^{(2)}$ for a set of distributions is expressed in terms of
 171 the quotient between the geometric mean of their respective
 172 disequilibria and the disequilibrium of the geometric mean
 173 of the distributions. Let us mention that the disequilibrium
 174 plays a relevant role also in what concerns the concept of
 175 shape complexity [47,48] and its physical interpretation for
 176 atomic [49] and molecular [50] systems.

177 (4) For clarity, we give below the simplest case of two
 178 densities with uniform weights, namely,

$$\text{GRD}^{(q)}(\rho_1, \rho_2) = (q - 1) \left\{ R^{(q)}(\sqrt{\rho_1 \rho_2}) - \frac{1}{2} [R^{(q)}(\rho_1) + R^{(q)}(\rho_2)] \right\}, \quad (12)$$

179 to be compared with Eq. (3). The arithmetic mean is replaced
 180 by the geometric one, obtaining a non-negative divergence
 181 measure after including the factor $(q - 1)$.

182 (5) $\text{GRD}^{(q)}$ keeps other relevant properties of $\text{JRD}^{(q)}$,
 183 including (i) invariance under exchange of distributions,
 184 (ii) additivity, and (iii) reaching the minimal value zero if
 185 and only if all distributions are identical.

186 (6) Nevertheless, $\text{GRD}^{(q)}$ possesses an additional property
 187 not shared with $\text{JRD}^{(q)}$. The geometric divergence of a set
 188 of distributions is independent of the normalization of each
 189 one within the set. Such an invariance under changes of
 190 normalization also holds for $\text{JRD}^{(q)}$ as far as those changes
 191 are identical for all distributions. In this sense, the comparison
 192 among distributions established by means of $\text{GRD}^{(q)}$ is based
 193 on a dissimilarity according to the shapes of the distributions,
 194 rather than on sizes, masses, charges, or any other quantity for
 195 which normalization is relevant.

196 (7) The main usefulness of the geometric Rényi divergence
 197 arises from its ability to modify the relative contribution of
 198 specific regions within the domain of definition in obtaining
 199 the divergence value, by varying appropriately the order q . This
 200 is a fundamental feature in applications to atomic systems, as
 201 will be discussed in the numerical analysis performed in the
 202 next section.

203 An illustrative example will allow us to understand better
 204 the role played by the order q of GRD. Let us consider
 205 two one-dimensional Gaussians, one of them centered at the
 206 origin, $f(x) = e^{-x^2}$, and the other one centered at an arbitrary
 207 point, $g(x) = e^{-(x-a)^2}$. Both have identical long-range
 208 behaviors, but short-range dissimilarity will be determined
 209 by the amount of the shift a . We compute straightforwardly
 210 $\text{GRD}^{(q)}(f, g) = a^2 q / 4$. We notice that for fixed $a \neq 0$, the
 211 geometric divergence increases as q does, because of the
 212 emphasis in the comparison based on short-range values. For
 213 any fixed q , the saturation $\text{GRD}^{(q)}(f, g) = 0$ occurs for $a = 0$,
 214 that is, $f = g$.

215 III. NUMERICAL ANALYSIS WITH ATOMIC 216 ONE-PARTICLE DENSITIES

217 The geometric divergence introduced in this work possesses
 218 useful features, especially relevant when compared to previous
 219 measures of divergence. Let us remark that, on the one hand,
 220 the characteristic parameter q (order) enables us to modify the
 221 relative contribution of specific regions for the comparative
 222 process among densities. On the other hand, its non-negativity
 223 makes possible the interpretation as a “mean distance” (not in

a strict mathematical sense) among the distributions under
 224 comparison. The latter is true for any $q > 0$. Such is not
 225 the case for the pioneering measure of divergence built up
 226 by means of the Rényi entropy, namely, the Jensen-Rényi
 227 divergence. In Sec. II we mentioned that its non-negativity
 228 (necessary to be interpreted as a divergence) is guaranteed
 229 only for $q \leq 1$.
 230

For illustration, both the Jensen-Rényi and the geometric
 Rényi divergences between the one-particle densities of neutral
 atoms He and Fr are displayed in Fig. 1 for $0 < q \leq 6$, in both
 position and momentum spaces. The one-particle densities
 of N -electron systems are defined from the wave function
 $\Psi(\vec{r}_1, \dots, \vec{r}_N)$ and its Fourier transform $\tilde{\Psi}(\vec{p}_1, \dots, \vec{p}_N)$ as
 follows:
 237

$$\rho(\vec{r}) = \int |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_2 \cdots d\vec{r}_N \quad (13)$$

in position space, and
 238

$$\gamma(\vec{p}) = \int |\tilde{\Psi}(\vec{p}, \vec{p}_2, \dots, \vec{p}_N)|^2 d\vec{p}_2 \cdots d\vec{p}_N \quad (14)$$

in momentum space. Computations of $\rho(\vec{r})$ and $\gamma(\vec{p})$ for
 neutral and ionized atomic systems will be done, throughout
 this section, by means of accurate near-Hartree-Fock wave
 functions [51,52]. Atomic units (a.u.) will be used.
 242

It is observed in Fig. 1 that, as we should expect,
 $\text{GRD}^{(q)}(\text{He}, \text{Fr})$ remains positive (in both spaces) within the
 whole interval, in fact, for any $q > 0$. However, $\text{JRD}^{(q)}(\text{He}, \text{Fr})$
 reaches negative values for values of the order q above unity.
 In this example, negativity of the Jensen-Rényi divergence is
 observed for $q \geq 1.26$ in position space, and $1.08 \leq q \leq 3.00$
 in the momentum one. Let us notice the existence of values
 of q for which $\text{JRD}^{(q)}(\text{He}, \text{Fr}) = 0$, in spite of dealing with
 two different distributions. So, the requirement of having null
 divergence if and only if the distributions under comparisons
 are identical is also violated.
 253

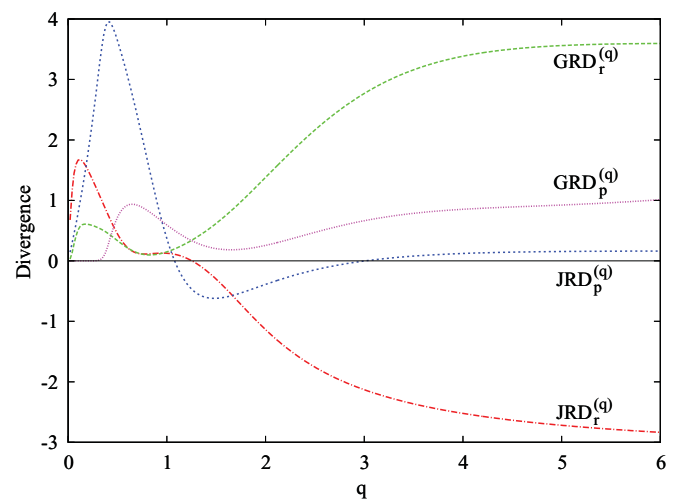


FIG. 1. Jensen-Rényi ($\text{JRD}^{(q)}$) and geometric Rényi ($\text{GRD}^{(q)}$)
 divergences between charge densities of He and Fr neutral atoms,
 for $q = 0.4$ and $q = 2$.

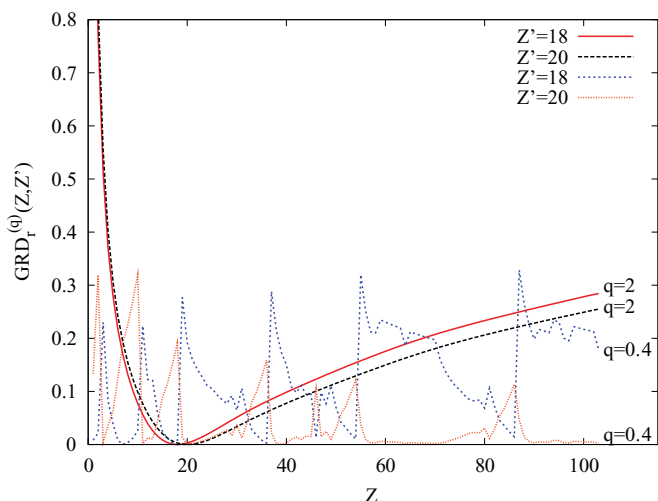


FIG. 2. $GRD_r^{(q)}(\text{Ar}, Z)$ and $GRD_r^{(q)}(\text{Ca}, Z)$ in position space, for $q = 0.4$ and $q = 2$ of both argon and calcium with respect to neutral atoms $1 \leq Z \leq 103$.

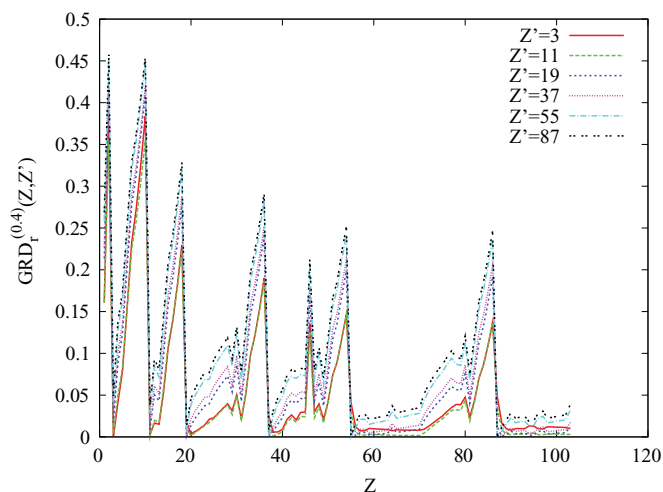


FIG. 3. $GRD_r^{(q)}(Z, Z')$ of order $q = 0.4$, in position space, of each alkali metal ($Z' = 3, 11, 19, 37, 55, 87$) and neutral atoms $1 \leq Z \leq 103$.

A. Neutral atoms

The purpose of a study based on the divergence among atomic one-particle densities is to give an answer to the following question: to what extent is the similarity or divergence of those densities related to how similar or different the physical and chemical properties of the corresponding atomic systems are? The same question is appropriate in the frameworks of a great variety of scientific and technological fields, such as molecular systems, reaction processes, image registration, and analysis of DNA sequences.

Let us consider, at a first stage, two significantly different atoms, such as argon (a noble gas, nuclear charge $Z = 18$) and calcium (an alkaline earth metal, $Z = 20$). We compare, in Fig. 2, each of their charge densities $\rho(\vec{r})$ with all those of neutral atoms throughout the whole Periodic Table ($Z = 1-103$). In doing so, the uniformly weighted geometric Rényi divergence ($GRD_r^{(q)}$) in Eq. (12) is employed for orders $q = 0.4$ and $q = 2$. Differences among the results obtained for each value of q are apparent: very “soft” and almost identical curves for both Ar and Ca are obtained with $q = 2$, while numerous local extrema appear for $q = 0.4$ with the structures of the curves being extremely different from one another.

To justify these results from a physical point of view, it is worth remarking that the main atomic physical and chemical properties are determined by the shell structure and, in particular, by the characteristics (quantum numbers, occupancy, etc.) of the outermost subshell (valence region). The computation of $GRD_r^{(q)}$ requires the computation of the q th-order frequency moments of each density and also of their geometric mean. Due to the exponential long-range behavior of the atomic charge densities, the relative contribution of the outermost region to the computation of the integrals involved is very small compared to that of the core. Such a contribution can be enhanced by raising the density to a relatively small power, as done when considering frequency moments of lower orders. Diminishing the value of $q = 2$ up to $q = 0.4$ allows us to gain enough information regarding valence features such that $GRD_r^{(q)}$ reveals in most cases whether the systems under

comparison share the above-mentioned features (e.g., if they belong to the same group of the Periodic Table). However, the closeness between both curves for $q = 2$ is due to the similar values of their nuclear charges (18 and 20), together with the enhancement, for the computation of integrals, of the surroundings of the nuclei, where the attractive potential governed by the nuclear charge Z determines (roughly) the shape and magnitude of the electronic cloud. A detailed discussion on the patterns for the appearance of extrema is carried out in the next figure.

Six curves are drawn in Fig. 3, corresponding to the position-space $GRD_r^{(q)}$ with $q = 0.4$ between each alkaline metal (group IA) and all neutral atoms with $1 \leq Z \leq 103$. The similar structure of all curves, appearing almost perfectly embedded, is clearly observed. A detailed analysis of the location of maxima and minima results in the following observations:

(1) An almost systematic appearance of local minima occurs when comparing any of the above-mentioned systems with another one belonging to its own group ($Z = 3, 11, 19, 37, 55, 87$). These minimum values should be interpreted as a low divergence among systems that share the fundamental features at the valence region and, consequently, have similar physicochemical properties. Those minima correspond to the main ones observed in Fig. 3.

(2) The opposite occurs when comparing alkali metals with noble gases, with higher values (local maxima) of divergence. Let us recall the predisposition of alkali metals for reactivity, while noble gases ($Z = 2, 10, 18, 36, 54, 86$) are conformed so as to keep their closed-shell structure. According to the meaning of the divergence measure here considered, a high divergence should be expected, based on the one-particle densities, when comparing a pair of systems that are so different from a physical point of view. The appearance of local maxima when comparing alkali-metal–noble-gas atoms is absolutely systematic now.

(3) A number of additional extrema, not so relevant as for the above discussed, appear in each curve. The systems corresponding to minima can be classified, roughly, in two

331 different groups: (i) non-alkali-metal systems with a unique
 332 electron at the valence subshell ($Z = 13, 31, 49, 81$), and
 333 (ii) systems suffering from anomalous shell filling ($Z =$
 334 $29, 79, 93$). This similarly occurs for maxima, some of
 335 them corresponding to (i) closed-subshell systems ($Z =$
 336 $12, 30, 48, 80$) and (ii) anomalous shell filling again ($Z =$
 337 $42, 44, 46, 58, 64, 90, 97$).

338 In comparing a given system with all others throughout the
 339 Periodic Table, the structural features of the curves in position
 340 space, in what concerns the number and enhancement of
 341 extrema, are very apparent as far as q decreases. The opposite
 342 trend is observed in the momentum-space comparison, in the
 343 sense of having curves with a higher structure as far as q
 344 becomes higher. The reason for those trends in opposite spaces
 345 requires us again to consider the enhancement of the relative
 346 contributions of the valence and core regions.

347 **B. Ionization processes**

348 Our next purpose is to analyze the effects arising from
 349 the physical process of atomic ionization, attending to the
 350 changes experienced by the one-particle densities of the system
 351 considered. In doing so, we employ the geometric Rényi
 352 divergence in order to compare the respective densities of
 353 the initial and final products (that is, the neutral atom and
 354 the singly charged cation) involved in this physical process.
 355 Within this context, we employ the notation $GRD_r^{(q)}(NC)$ for
 356 the neutral-cation comparison in a given space.

357 For illustration, we consider the analysis in position
 358 space, i.e., for the quantity $GRD_r^{(q)}(NC)$, with NC pairs of
 359 nuclear charges $3 \leq Z \leq 55$, and consequently each system
 360 containing a number of electrons up to 54. This quantity is
 361 displayed in Fig. 4 for different values of q , together with an
 362 algebraic function of the atomic ionization potential (AIP).
 363 This function of AIP is considered, instead of the actual AIP,
 364 in order to make easier the interpretation of the correlation
 365 observed among the divergence and AIP values.

366 In what concerns $GRD_r^{(q)}(NC)$ for the considered q 's, some
 367 comments are in order:

- 368 (1) Systems displaying (in Fig. 4) higher values (local
 369 maxima) of divergence between the neutral and ionized species
 370 can be classified as follows:
 371 (a) $Z = 3, 11, 19, 37, 55$ (alkali metals) for which the ioniza-
 372 tion left empty the valence s subshell of the neutral atom,
 373 and the resulting cation possesses a closed-shell structure.
 374 These maxima occur in all curves with the exception of
 375 $q = 2$, a value too high to avoid the masking effect arising
 376 from the relatively sparse information on the valence
 377 features compared to the core ones.
 378 (b) Similarly for $Z = 5, 13, 31, 49$, but with the p subshell
 379 disappearing. The previous comment regarding the excep-
 380 tion $q = 2$ applies also to these systems. Additionally, a d
 381 subshell becomes empty for $Z = 39$, but a value as low as
 382 $q = 0.2$ is needed to detect it as a local maximum. Each
 383 of these systems provides (or not) a maximum according
 384 to the value of q .
 385 (c) $Z = 8, 16, 34, 52$ correspond to systems for which the
 386 outermost p subshell becomes half-filled. In this sense,
 387 we should emphasize the capability of $GRD_r^{(q)}(NC)$ to
 388 discriminate systems with half-filled valence subshells

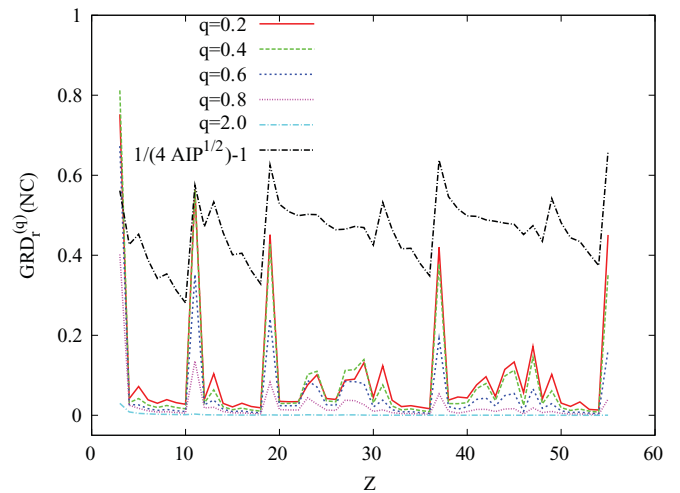


FIG. 4. $GRD_r^{(q)}(NC)$ between a neutral atom (N) and its singly-
 charged cation (C) with $3 \leq Z \leq 55$, and phenomenological corre-
 spondence with the atomic ionization potential (AIP) of the neutral
 system.

389 from others with a number of electrons (there) different 11
 390 from half the occupation number. These systems are
 391 displayed as maxima for all $q < 1$, while none for $q = 2$.
 392

393 (d) Additional maxima are found for $Z = (23 \text{ or } 24)$,
 394 (one of $27, 28, 29, 42, 45, 47$, depending on the curve. All
 395 these systems are characterized by an ionization process
 396 with the ejection of an electron from an inner s subshell,
 397 instead of the outermost one ($3d$ or $4d$). The only ones
 398 associated with maxima for $q = 2$ are $Z = 23, 27, 42$. The
 399 others require values of q below unity.

400 (2) The display of low divergence (some local minima) of
 401 divergence in Fig. 4 corresponds to closed-shell and closed-
 402 subshell systems ($Z = 4, 10, 12, 18, 30, 36, 48, 54$), the range of
 403 q for which they appear as minima depends on the specific
 404 systems considered. The subshell from which the electron is
 405 ejected remains occupied in the cation, and, consequently,
 406 changes in one-particle densities arising from the ionization
 407 are not so strong because of the presence of exactly the same
 408 occupied orbitals in the neutral atoms and its cation.

409 (3) There exists a clear resemblance between the divergence
 410 of pairs NC and the value of the AIP of the neutral system.
 411 The complete list of the 15 local minima of AIP for the
 412 systems here considered (displayed in Fig. 5 as maxima in
 413 the corresponding curve, due to the functional fit employed) is
 414 $Z = 3, 5, 8, 13, 16, 19, 23, 28, 31, 34, 37, 47, 49, 55$. Let us notice
 415 that all these systems are included in the total list of high-
 416 divergence pairs.

417 To justify these results, let us notice that most systems with
 418 low AIP possess a valence subshell (independent of being
 419 the outermost one or not) containing a unique electron. Their
 420 ionization provokes the disappearance of that subshell, which
 421 translates in terms of changes experienced by the one-particle
 422 densities into a high value of the neutral-cation divergence. 12

423 Regarding the ionization analysis, we finally mention that
 424 similar conclusions to those here discussed, on the basis of the
 425 position-space densities, are obtained from the same analysis
 in momentum space.

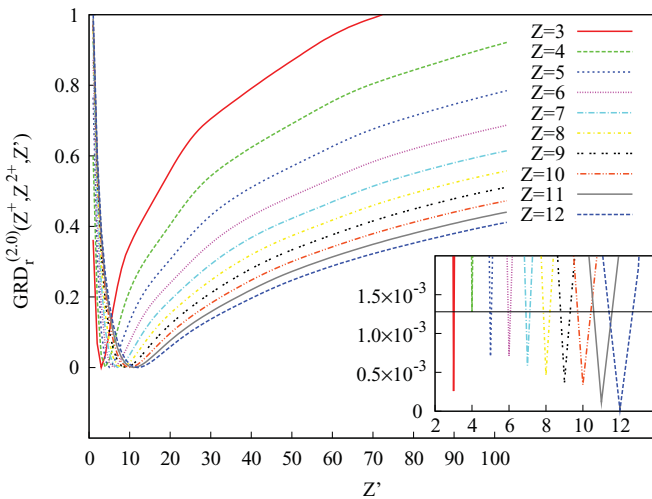


FIG. 5. $\text{GRD}_1^{(q)}(Z^+, Z^{2+}, Z')$ among singly and doubly charged cations with nuclear charge $3 \leq Z \leq 12$, together with a neutral system of nuclear charge $1 \leq Z' \leq 103$. A threshold of GRD values appears amplified in the inset.

C. Further applications

1. Computational models

We consider the extent to which the use of more simplified or sophisticated models for computing the wave function provokes more or less significant differences among the corresponding one-particle densities. To give a well-posed answer, it is first necessary to establish a quantitative measure of difference among densities. The $\text{GRD}^{(q)}$ divergence has been employed, both theoretically and numerically through this work, with the aim of quantifying how different two (or more) densities are.

In this sense, we could assert with a quantitative basis if, for instance, taking into account relativistic effects or correlations is worth doing in the study of multielectronic systems in terms of one-particle densities. Perhaps differences could be relevant when comparing wave functions, but not so important when dealing with densities. Similar analyses would be useful also for a comparative study of relevant distributions in physical systems (e.g., molecules and clusters), arising within different theoretical and/or numerical frameworks.

Let us analyze the effect of the interelectronic repulsion in the structural properties of the atomic charge and momentum densities. In doing so, we compute the densities using two different models: the accurate near-Hartree-Fock (HF) one employed for previous applications in this work, and the so-called bare Coulomb field (BCF) model [54], in which the interelectronic repulsive term of the Hamiltonian is neglected. This simplification provides a description of the multielectronic system as a superposition of hydrogenlike orbitals, in both spaces. The BCF system consists of a number of electrons within the attractive nuclear attraction, but noninteracting among themselves via repulsive forces.

Neglecting the interelectronic repulsion will provoke more or less significant changes in going from the HF situation to the BCF one. According to the previous description of these models, one should expect a more significant divergence among the HF and BCF densities as the number of electrons

N increases (with $N = Z$ for neutral atoms, that is, those here considered). This would result from the much higher neglect of interelectronic repulsive forces that occurs for high N .

Certainly an increasing trend is observed for the HF-BCF divergence curves. However, none is strictly increasing, but local extrema appear whose number and enhancement depend on the order q considered. Locations of maxima and minima are determined by the shell structure, as also observed in the two previous applications. These comments apply in both spaces.

The main conclusion regarding the present comparison among densities computed within the HF and BCF models is that the effects of the interelectronic repulsion on the atomic one-particle densities depend not only on the total number of electrons but also on the shell-filling features of the systems considered.

2. Discrimination of nuclear charges

It is worth remembering the capability of the geometric Rényi divergence to quantify the divergence of a number of functions higher than 2. The interpretation as a “mean distance” among two or more functions remains, independent of the number of densities considered. For simplicity, we restricted all previous applications in this work to one-to-one comparisons.

Nevertheless, there exist additional applications of $\text{GRD}^{(q)}$ among a set of distributions. We find it interesting to show one of them in the present work, but additional applications will be provided elsewhere.

Let us consider a number of atomic one-particle densities corresponding to systems sharing a specific property. Now we include in that set an additional distribution. A new question appears appropriate within this context: could we determine, in terms of the $\text{GRD}^{(q)}$ values, if the system added to the initial set shares the specific features which characterize the initial set? We provide here an example for which $\text{GRD}^{(q)}$ appears able to discriminate if the system added belongs or not to the initial set according to the features which characterize the set.

Consider a pair of cations with identical nuclear charge Z , one of them singly charged and the other doubly charged. We denote them as Z^{+1} and Z^{+2} , where the superscripts correspond to the respective global charges. Let us notice that a pair of systems as chosen above share the property of having the same nuclear charge Z . Now we add to this two-element set a third system: a neutral atom (global charge zero) with nuclear charge Z' . To perform the study of the uniformly weighted three-density divergence $\text{GRD}_1^{(q)}(Z^{+1}, Z^{+2}, Z')$, we choose $q = 2$ for illustration. For the doubly charged ion, we use the near-Hartree-Fock wave functions of Ref. [53] for isoelectronic series with a number of electrons $N = 2-10$. They allow us to consider, for the present comparative purpose, values of the nuclear charges in the range $Z = 3-12$ for the systems comprising the initial set.

In Fig. 5, each curve corresponds to the election of Z for the initial two cations. Consequently, ten curves are displayed ($Z = 3-12$), each one as a function of $1 \leq Z' \leq 103$, the nuclear charge of the neutral atom added to the previous set. The first observation from Fig. 5 is the unimodal shape of all curves, decreasing quickly as Z' increases, until reaching

521 a minimum value (which is shown amplified in the inset)
 522 and increasing hereinafter. It is observed that the absolute
 523 minima occur when $Z' = Z$ in each curve. The horizontal
 524 line establishes a threshold in the following sense: values
 525 of $\text{GRD}_r^{(2)}(Z^{+1}, Z^{+2}, Z')$ above the aforementioned threshold
 526 allow us to assert that the neutral system added does not share
 527 the nuclear charge of the first two cations, that is, $Z' \neq Z$.
 528 However, any value below the line corresponds, necessarily,
 529 to the comparison of three systems with the same nuclear
 530 charge, which means that $Z' = Z$.

531 Summarizing this application, $\text{GRD}^{(q)}$ has been shown to
 532 be a useful tool for discriminating atomic systems, in the sense
 533 of the ability to determine if a system added to a set of atoms
 534 characterized by some physical properties should belong to
 535 that set, or, in other words, if the new atom included in the set
 536 shares the properties common to all the others.

537 Further applications will be provided elsewhere. They
 538 should include (i) the use of different values of q ,
 539 (ii) employment of weights other than the uniform ones, and
 540 (iii) a study based on properties (e.g., long-range behaviors)
 541 associated with the outermost regions, instead of the inner ones
 542 as done here.

543 IV. CONCLUSIONS AND OPEN PROBLEMS

544 An alternative measure of dissimilarity among probability
 545 distributions, the geometric Rényi divergence has been intro-
 546 duced in the present work. It is expressed in terms of the Rényi
 547 entropy, as also happens with the well-known Jensen-Rényi
 548 divergence. Both measures include a positive characteristic
 549 parameter in their definitions. The interpretation of JRD as a
 550 divergence measure constrains the parameter to values below
 551 unity, while no constraints at all are imposed on the GRD
 552 divergence.

553 The GRD statistical measure of divergence is used to
 554 compare atomic one-particle densities. The capability of GRD
 555 to gain physical insight into the structural properties of
 556 many-electron systems has been shown. In doing so, we have
 557 taken advantage of its characteristic parameter in order to
 558 enhance or diminish the short- and long-range contributions in
 559 a divergence-based analysis. The geometric Rényi divergence
 560 allows us to deal with a set of an arbitrary number of

density functions, assigning different weights to each one in
 accordance with their roles within the comparative purpose
 considered. For atomic systems, a study based on one-particle
 densities in both position and momentum spaces provides
 clearly an interpretation by means of shell structure.

A detailed numerical analysis clearly established the rela-
 tionship between valence subshell properties of the systems
 under comparison and the GRD values, as well as the detection
 of the presence of systems suffering from anomalous shell
 filling. The usefulness of the tool here defined has been shown
 in the study of ionized systems, by considering the analysis
 of atomic neutral-cation pairs. A strong resemblance appears
 among the extrema of divergence and those of the atomic
 ionization potential, mostly determined by occupancy numbers
 of the outermost subshell in neutral and cationic systems.
 Further applications of the generalized index, arising from its
 rigorous mathematical properties here described, have been
 carried out in this work, including studies (i) on the ability
 in comparing different quantum models, and (ii) detection of
 systems which do or do not share specific physical properties
 with their partners within an atomic set.

Additional studies are planned to be performed in a near
 future: (i) use of more sophisticated atomic models including
 relativistic effects and/or correlations, (ii) comparing more
 than two functions, e.g., sequence anion-neutral-cation, groups
 or periods of the Periodic Table, isoelectronic series, and
 subsystems of a given composite system, (iii) assigning
 appropriate weights to each system according to relevant
 physical and/or chemical properties, such as mass, number of
 electrons, and volume, and (iv) other quantum systems (e.g.,
 molecules) and processes (reaction or excitation). It is worth
 remarking that the universality of GRD, in what concerns its
 definition and mathematical properties, allows its use in a wide
 variety of fields. systems, and processes, far beyond atoms,
 molecules, or reactions.

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- [1] J. Aczel and Z. Daroczy, *On Measures of Information and Their Characterizations* (Academic, New York, 1975).
 [2] T. M. Cover and J. A. Thomas, *Elements of Information Theory* (Wiley Interscience, New York, 1991).
 [3] J. Lin, *IEEE Trans. Inf. Theory* **37**, 145 (1991).
 [4] I. J. Taneja and P. Kumar, *Inf. Sci.* **166**, 105 (2004).
 [5] J. Briët and P. Harremoës, *Phys. Rev. A* **79**, 052311 (2009).
 [6] D. V. Gokhale and S. Kullback, *Information in Contingency Tables* (Marcel Dekker, New York, 1978).
 [7] C. K. Chow and C. N. Liu, *IEEE Trans. Inform. Theory* **14**, 462 (1968).
 [8] Y. He, A. Ben Hamza and H. Krim, *IEEE Trans. Signal Process.* **51**, 1211 (2003).
 [9] L. Pardo, *Statistical Inference Based on Divergence Measures* (Taylor and Francis, New York, 2005).
 [10] X. Huang, S. Z. Li, and Y. Wang, *Proceedings of the IEEE Computer Society Conference on Computer Vision and Pattern Recognition (CVPR-2005)* **2**, 144 (2005).
 [11] S. Pavoine, S. Ollier, and D. Pontier, *Theor. Popul. Biol.* **67**, 231 (2005).
 [12] R. O. Duda, P. E. Hart, and D. G. Stork, *Pattern Classification* (Wiley, New York, 2001).
 [13] S. Y. Chung and S. Subbiah, *Structure* (London) **4**, 1123 (1996).
 [14] K. Suzuki, H. Yamada, and S. Hasimoto, *Pattern Recogn. Lett.* **28**, 1104 (2007).

- [15] P. Resnik, *J. Artif. Intell. Res.* **11**, 95 (1999).
- [16] M. Ho, V. H. Smith Jr., D. F. Weaver, C. Gatti, R. P. Sagar, and R. O. Esquivel, *J. Chem. Phys.* **108**, 5469 (1998).
- [17] S. Janssens, A. Borgoo, C. van Alsenoy, and P. Geerlings, *J. Phys. Chem. A* **112**, 10560 (2008).
- [18] J. C. Angulo and J. Antolín, *J. Chem. Phys.* **126**, 044106 (2007).
- [19] S. López-Rosa, J. Antolín, J. C. Angulo and R. O. Esquivel, *Phys. Rev. A* **80**, 012505 (2009).
- [20] R. P. Sagar and N. L. Guevara, *J. Mol. Struct.* **857**, 72 (2008).
- [21] J. Cioslowski and A. Nanayakkara, *J. Am. Chem. Soc.* **115**, 11213 (1993).
- [22] *Fundamentals of Molecular Similarity*, edited by R. Carbó-Dorca, X. Gironés, and P. G. Mezey (Kluwer Academic/Plenum, New York, 2001).
- [23] B. Balas, *Pattern Recogn.* **41**, 972 (2008).
- [24] P. Bernaola Galván, I. Grosse, P. Carpena, J. L. Oliver, R. Román-Roldán, and H. E. Stanley, *Phys. Rev. Lett.* **85**, 1342 (2000).
- [25] G. Chechik, V. Sharma, U. Shalit, and S. Bengio, *J. Mach. Learn. Res.* **11**, 1109 (2010).
- [26] P. Faratin, C. Sierra, and N. R. Jennings, *Artif. Intell.* **142**, 205 (2002).
- [27] C. Zhang and H. Fu, *Pattern Recogn. Lett.* **27**, 1307 (2006).
- [28] P. W. Lamberti, A. P. Majtey, A. Borrás, M. Casas, and A. Plastino, *Phys. Rev. A* **77**, 052311 (2008).
- [29] A. P. Majtey, A. Borrás, M. Casas, P. W. Lamberti, and A. Plastino, *Int. J. Quantum Inform.* **6**, 715 (2008).
- [30] S. Kullback and R. Leibler, *Ann. Math. Stat.* **22**, 79 (1951).
- [31] C. E. Shannon and W. Weaver, *The Mathematical Theory of Communication* (University of Illinois, Urbana, IL, 1949).
- [32] R. A. Fisher, *Proc. Cambridge Philos. Soc.* **22**, 700 (1925).
- [33] B. R. Frieden, *Science from Fisher Information* (Cambridge University, Cambridge, England, 2004).
- [34] A. Rényi, in *Proceedings 4th Berkeley Symposium on Mathematics, Statistics and Probability* (University of California, Berkeley, CA, 1961), Vol. 1, pg. 547.
- [35] J. C. Angulo, S. López-Rosa, J. Antolín and R. O. Esquivel, *Int. J. Quantum Chem.* **111**, 297 (2011).
- [36] J. Antolín, J. C. Angulo, and S. López-Rosa, *J. Chem. Phys.* **130**, 074110 (2009).
- [37] R. Carbó-Dorca, J. Arnau, and L. Leyda, *Int. J. Quantum Chem.* **17**, 1185 (1980).
- [38] R. Carbó-Dorca, L. Amat, E. Besalú, X. Gironés and D. Robert, *J. Mol. Struct.* **504**, 181 (2000).
- [39] R. Carbó-Dorca and S. van Damme, *Theor. Chem. Acc.* **118**, 673 (2007).
- [40] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- [41] P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1964).
- [42] J. Burbea and C. R. Rao, *IEEE Trans. Inf. Theory* **28**, 489 (1982).
- [43] A. K. C. Wong and M. You, *IEEE Trans. Pattern Anal. Machine Intell.* **7**, 599 (1985).
- [44] C. R. Rao and T. Nayak, *IEEE Trans. Inf. Theory* **31**, 589 (1985).
- [45] A. W. Marshall and I. Olkin, *Theory of Majorization and Its Applications* (Academic, New York, 1979), p. 460.
- [46] R. López-Ruiz, H. L. Mancini, and X. Calbet, *Phys. Lett. A* **209**, 321 (1995).
- [47] R. G. Catalán, J. Garay, and R. López-Ruiz, *Phys. Rev. E* **66**, 011102 (2002).
- [48] R. López-Ruiz, *Biophys. Chem.* **115**, 215 (2005).
- [49] J. C. Angulo and J. Antolín, *J. Chem. Phys.* **128**, 164109 (2008).
- [50] R. O. Esquivel, J. C. Angulo, J. Antolín, J. S. Dehesa, S. López-Rosa, and N. Flores-Gallegos, *Phys. Chem. Chem. Phys.* **12**, 7108 (2010).
- [51] T. Koga, K. Kanayama, S. Watanabe, and A. J. Thakkar, *Int. J. Quantum Chem.* **71**, 491 (1999).
- [52] T. Koga, K. Kanayama, S. Watanabe, T. Imai, and A. J. Thakkar, *Theor. Chem. Acc.* **104**, 411 (2000).
- [53] T. Koga, M. Omura, H. Teruya, and A. J. Thakkar, *J. Phys. B* **28**, 3113 (1995).
- [54] N. H. March, *Phys. Rev. A* **33**, 88 (1986).