Atomic quantum similarity indices in position and momentum spaces

J. C. Angulo
*Departamento de Física Atómica, Molecular y Nuclear, Universidad de Granada, 18071-Granada, Spain
and Instituto Carlos I de Física Teórica y Computacional, Universidad de Granada,
18071-Granada, Spain*

J. Antolín
*Departamento de Física Aplicada, EUITZ, Universidad de Zaragoza, 50009-Zaragoza, Spain
and Instituto Carlos I de Física Teórica y Computacional, Universidad de Granada, 18071-Granada, Spain*

Quantum similarity for atoms is investigated using electron densities in position and momentum spaces. Contrary to the results in position space, the analysis in the momentum space shows how the momentum density carries fundamental information about periodicity and structure of the system and reveals the pattern of Mendeleev's table. A global analysis in the joint *r-p* space keeps this result. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2429064]

I. INTRODUCTION

Quantum similarity theory[1,2] was originally developed in order to establish quantitative comparisons between molecular systems by means of their fundamental structure magnitudes: electron density functions. Applications of this important theory have been one of the cornerstones of recent chemical research in molecules.[3] Similarity of atoms in molecules has been extensively studied by the pioneering group of Carbó-Dorca and also by others researchers.[4] One of the most attractive applications of computer-aided techniques in molecular modeling stands on the possibility of assessing certain molecular properties before the molecule is synthesized. The field of quantitative structure activity/property relationships has demonstrated that the biological activity and the physical properties of a set of compounds can be mathematically related to some simple molecular structure parameters.[5]

The generality of the measure definitions makes possible to use them for comparing other quantum objects. In particular, a few quantum similarity measures (QSMs) between atoms and nuclei have already been defined and computed. Due to the simple structure of these quantum objects, atoms and nuclei are excellent benchmark systems for the general theory. Only a few papers deal with these fundamental quantum systems. In Ref. 6 simple and accurate relationships between atomic and nuclear quantum similarity measures and their constituent elements were found. In particular, for a wide range of atoms and nuclei, the QSM is described as a polynomial function of the number of electrons (degree 3) or nucleons (degree 1) of the system. Also exact quantum molecular overlaplike and Coulomb-type self-similarity measures have been studied in a selected series of mono- and polyatomic systems (atoms and molecules) with the same number of electrons.[7] The aim of the work was to study the concentration of electronic charge in molecules, and a good linear relationship between the overlap self-similarity measure and the volume was found. More recently, an information theory approach in a numerical Hartree-Fock framework

has been used to investigate quantum similarities of atoms (H–Xe).[8] The basic result is that a nearest neighbor similarity is retrieved, masking periodicity, and confirming the earlier work of Robert and Carbó-Dorca.[6] Nevertheless, the introduction of shape functions[9] and the information discrimination concept, with reference to the noble gas atom of the previous row, were found to reveal some periodicity.

Most of the work on quantum similarity has been done in the usual position representation *r*. Nevertheless, methods for assessing quantum molecular similarity have been also developed in the, less known, momentum space *p*.[10] Many of the problems associated with the conventional position-space procedures are avoided and particular emphasis is placed on the variation of the long-range position-space electron density. This approach is particularly suited to problems for which molecular activity depends more on features of this long-range slowly varying valence electron density and less on precise details of the bonding topology.

The principal aim of the present work is to investigate the unexplored, to the best of our knowledge, momentum-space similarity for atomic systems with nuclear charge $Z=1-103$ and to extract complementary information to that obtained in the position space ($Z=1-54$).[8]

Information entropy is a magnitude of paramount importance in the study of many-electron systems and has been extensively used as a measure of distance between two electron distributions or processes. Entropy of a system can be calculated in both position and momentum spaces. Moreover the sum of these two quantities provides uncertainty relations or principles similar to others derived in quantum theory. These principles are usually interpreted as statements about the precision of a quantum measurement. However, they may also be considered as due to intrinsic uncertainty in a phase-space description of quantum systems. Bialynicki-Birula and Mycielski have derived an important inequality in terms of the information entropies of position (S_ρ) and momentum (S_γ) one-particle densities [$\rho(\mathbf{r})$ and $\Pi(\mathbf{p})$, respectively][11]

$$S_\rho + S_\Pi \geqslant 3(1 + \ln \pi) \tag{1}$$

[normalization $\int \rho(\mathbf{r})d\mathbf{r} = \int \Pi(\mathbf{p})d\mathbf{p} = 1$ will be used throughout]. This means that when a system becomes more localized in position space, it becomes more delocalized in momentum space, and vice versa. Some other important results involving the entropy sum have also been obtained.[12,13]

The previous results on entropy suggest that new calculations in a joint phase-space r-p taking into account the properties of both spaces can give complementary information on the quantum similarity of atoms, nuclei, or molecules. We have employed, apart from the corresponding densities associated with both individual spaces, a joint r-p density which entropy is just the sum of the entropies in the separated spaces to calculate atomic quantum similarities in the joint space. This allows us to compare results on atomic similarity in position, momentum, and phase spaces.

II. POSITION AND MOMENTUM-SPACE SIMILARITIES FOR ATOMS

The one electron densities of an N electron system in position and momentum spaces, $\rho(\mathbf{r})$ and $\Pi(\mathbf{p})$ respectively, are basic ingredients in the study of many physical properties from a density functional theory perspective. Much attention has been paid to the relevant role played by the position-space density $\rho(\mathbf{r})$ in the description of many-electron systems. However, a similar study in terms of the electron distribution in momentum space has still to be much more worked out.

The electron distribution of atomic systems in momentum space, described in terms of the monoparticular density $\Pi(\mathbf{p})$, allows to easily interpret numerous physical and chemical phenomena and plays a fundamental role in the description of important properties of these systems.[14,15] Also, $\Pi(\mathbf{p})$ is an experimentally accessible quantity by several techniques.[16,17]

The most straightforward means of obtaining momentum-space wave functions is to perform the Fourier transform of the familiar position-space wave function. The relationship in $\mathbf{p}$ space between the wave function $\Psi(\mathbf{p}_1, \ldots, \mathbf{p}_N)$ and the total electron momentum density $\Pi(\mathbf{p})$ is exactly the same as in r space. The contribution, for instance, to $\Pi(\mathbf{p})$ of an electron in molecular orbital $\Psi(\mathbf{p})$ is simply $|\Psi(\mathbf{p})|^2$. The momentum-space electron density falls very slowly with increasing $|\mathbf{p}|$, which corresponds in position space to the quickly varying outer valence electron density. The form of the electron density in r space $\rho(\mathbf{r})$ is determined largely by the core electron and consequently by the nuclear positions. $\Pi(\mathbf{p})$, in contrast, emphasizes the chemical interesting features of the valence electron distribution.

The QSM between isolated atoms is defined in a completely similar form as for molecules or other quantum systems,[7]

$$M_{AB} \equiv \int \rho_A(\mathbf{r}_1)\Omega(\mathbf{r}_1, \mathbf{r}_2)\rho_B(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2, \tag{2}$$

where $\rho_A(\mathbf{r}_1)$ and $\rho_B(\mathbf{r}_2)$ are the (spinless) electron density functions of both systems A and B, and $\Omega(\mathbf{r}_1, \mathbf{r}_2)$ is a separa-

ration operator. Most often, Ω is chosen as the Dirac delta function $\delta(\mathbf{r}_1 - \mathbf{r}_2)$ reducing Eq. (2) to an overlap-type integral, and the other most oftenly used operator being $\mathbf{r}_{12}^{-1}$, transforming Eq. (2) in a Coulomb-type integral. One can generalize these computations by using other positive powers $\mathbf{r}_{12}^n$ of the interdistance. Normalization is taken by defining a quantum similarity index (QSI),

$$\text{QSI} \equiv \frac{M_{AB}}{\sqrt{M_{AA}M_{BB}}}, \tag{3}$$

running between 0 and 1. Evaluation of a similarity index for atoms is straightforward using electron densities of sufficient quality for the isolated atoms. In a completely similar way one can compute similarity indices in momentum space by using the corresponding momentum densities $\Pi_A(\mathbf{p}_1)$ and $\Pi_B(\mathbf{p}_2)$.

M_{AA} (or M_{BB}) is called *quantum self-similarity* and is obtained, independently of the operator, when comparing a system with itself. It is related to the electronic charge density occupation in the space, that provides information on the charge concentration of the considered quantum object. When the selected operator is the overlap one, self-similarities can be considered as the square of the norm of the density function in the chosen metric. This is a very important measure of localization, also called as *linear entropy*,[18] in contrast with the (nonlinear) *Shannon entropy* [closely related to Renyi entropies $R_q(\rho)$ of orders 2 and 1, respectively, as $M_{AA} = e^{-R_2}$ and $S_\rho = R_1$], or in other contexts, informational energy and inverse participation number.[19]

Other related indices to the QSI one have been also defined and computed as the *dissimilarity* between two systems,[10]

$$D_{AB} \equiv M_{AA} + M_{BB} - 2M_{AB}, \tag{4}$$

which is the square of the L^2 norm.

III. NUMERICAL ANALYSIS OF THE QSI FOR ATOMS IN CONJUGATE SPACES

In this section, a numerical analysis of the behavior of the QSI associated with the delta operator $\Omega(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2)$ for ground-state neutral atoms is carried out throughout the periodic table for systems with nuclear charge $Z = 1 - 103$. Such a study has been performed for both conjugate spaces (position $\mathbf{r}$ and momentum $\mathbf{p}$) as well as for the *phase space* corresponding to the pair $(\mathbf{r}, \mathbf{p})$. Phase-space density functions and entropies have been successfully used in other contexts, such as the study of dynamical properties and complexity of many-body quantum states.[20,21]

In order to obtain the one-particle densities $\rho(\mathbf{r})$ and $\Pi(\mathbf{p})$, and its product

$$f(\mathbf{r}, \mathbf{p}) \equiv \rho(\mathbf{r})\Pi(\mathbf{p}),$$

associated with the aforementioned spaces, it is necessary to compute the N-particle wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ and its Fourier transform $\Psi(\mathbf{p}_1, \ldots, \mathbf{p}_N)$. The position-space wave function is expressed as an N-dimensional determinant, which elements $\phi_i(\mathbf{r}_j)$ $(i, j = 1, \ldots, N)$ correspond to the one-electron orbitals, which radial part is expressed as a linear

combination of Slater-type functions $\xi(r) = r^n e^{-\alpha r}$, employing the accurate set of coefficients provided by Koga et al.,[22] from which consequently are also expanded functions $\Pi(\mathbf{p})$ (the radial part being a rational function on p^2) and $f(\mathbf{r},\mathbf{p})$. Concerning the systems considered in this work, i.e., isolated atoms, it is sufficient to deal with the spherical averages of the one-particle densities, namely, $\rho(r)$ and $\Pi(p)$, as well as the two-dimensional density $f(r,p)$ built up from the previous ones.

For the present case (i.e., delta operator), the calculation of the QSI involving the phase-space function $f(r,p)$ reduces to the product of the corresponding QSI in both separate spaces. However, its calculation is not a trivial task in other cases, such as those involving the variables $\mathbf{r}_{12}$ or $\mathbf{p}_{12}$. Nevertheless, as it will be shown below, even the choice of the simplest operator, i.e., the overlap one, reveals the relevant role played by the momentum variable in order to display structural and physical properties of the involved densities. Additional work employing more complex phase-space distributions $f(\mathbf{r},\mathbf{p})$ (e.g., Wigner[23] and Husimi[24] ones) will be also carried out.

Concerning the values of the QSI obtained for different pairs of atomic systems through the Periodic Table, the main results are given and discussed below, in order to study how the value of the QSI reflects the similarity in shell filling and structure.

In Fig. 1, the results concerning the QSI of each alkaline atom ($Z' = 3, 11, 19, 37, 55, 87$) with respect to the whole Periodic Table ($Z = 1 - 103$) are provided for position [Fig. 1(a)], momentum [Fig. 1(b)], and *phase* [Fig. 1(c)] spaces.

As pointed out by other authors,[4,8] the value of the QSI_$r(Z,Z')$ in position space [Fig. 1(a)] between atoms with nuclear charges Z and Z' mainly depends on $|Z - Z'|$, i.e., on how close they are located in the Periodic Table; in fact, for any fixed value Z' it is a unimodal function on Z, attaching its maximum value 1 (as should be expected) at $Z = Z'$, and no periodicity or shell structure is revealed by such a function.

However, such properties are clearly displayed in Figs. 1(b) (momentum space) and 1(c) (phase space), both involving the momentum variable p. Local extrema appearing in Fig. 1(b) are closely related to the process of shell filling. Maxima of QSI_p for all alkaline atoms are attached for atoms belonging to the same group and, additionally, for systems involved in the anomalous filling of subshells $5s$ and $6s$. However, QSI_p always displays a relative minimum when comparing a noble gas with an alkaline atom, as well as for anomalous filling of $4d$ and $5d$ as well as half filling of $4d$ subshell.

Similar comments can be done concerning Fig. 1(c) (phase space) which involves simultaneously both conjugate variables r and p. Location of extrema occurs at same position when only considering p [Fig. 1(b)], but the differences of the corresponding QSI_rp values are emphasized when adding the information provided by the position space.

The aforementioned *structural* behavior of the QSI depending on the momentum-space variable (with or without taking into account position-space information) is also observed for all other groups of the Periodic Table. For in-
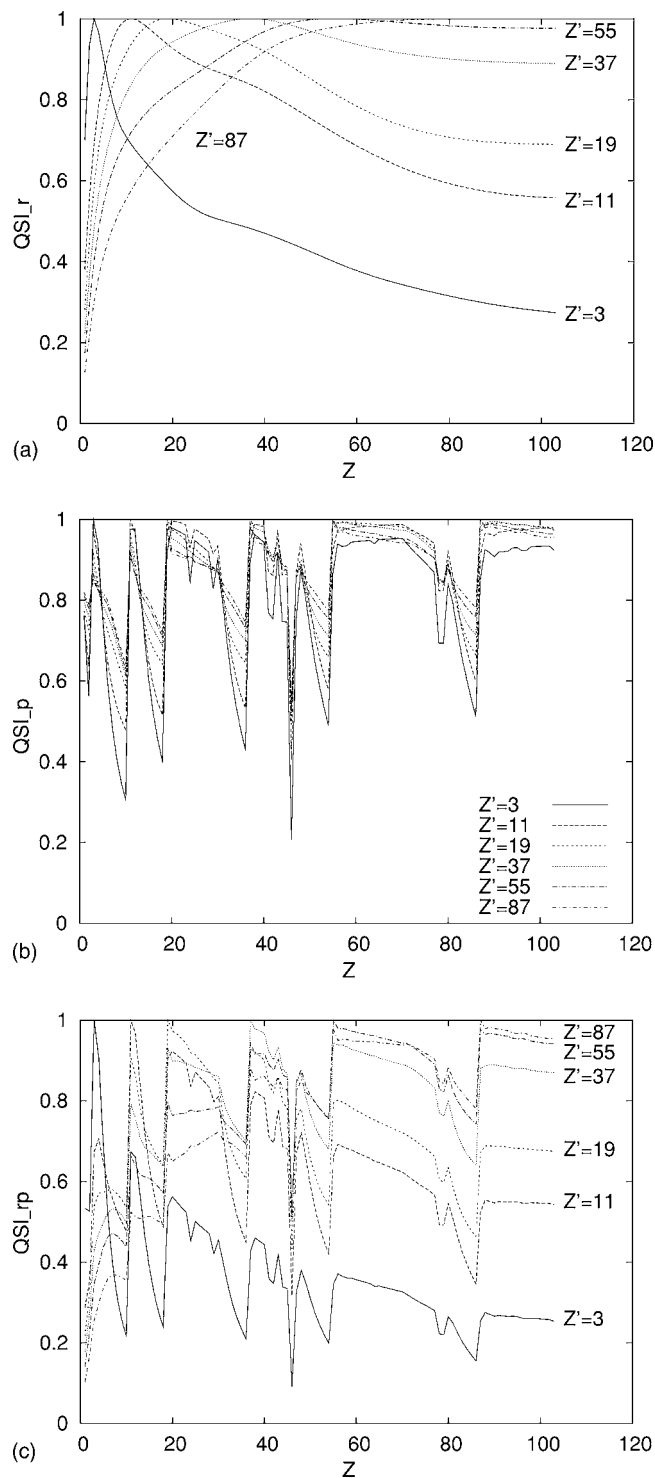

FIG. 1. Quantum similarity index (QSI) of alkaline atoms ($Z' = 3, 11, 19, 37, 55, 87$) in (a) position, (b) momentum, and (c) phase spaces.

stance, Fig. 2 provides the values obtained for the QSI_p associated with the momentum density of halogens ($Z' = 9$, 17, 35, 53, and 85) compared to the corresponding density of all atomic systems with $Z = 1 - 103$. Comments about the location of extrema in these curves are similar to those given previously for Fig. 1(b) corresponding to alkalines. As before, maxima appear when comparing two halogen atoms (i.e., systems belonging to the same group), and additional ones are displayed associated, in this case, with the anoma-
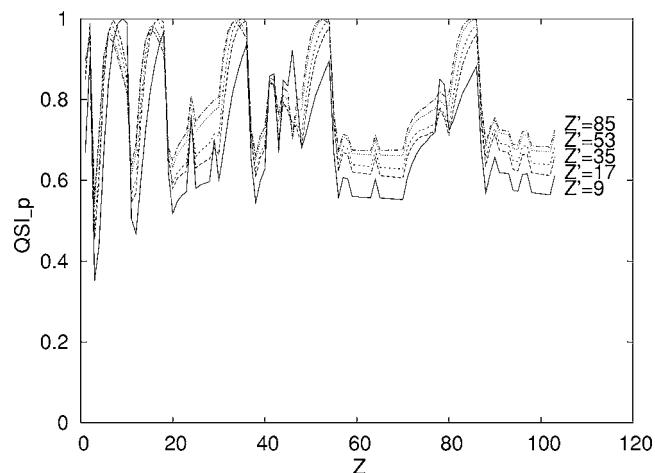
FIG. 2. Quantum similarity index (QSI) of halogen atoms (Z' = 9, 17, 35, 53, 85) in momentum space.

lous filling of d subshells ($3d$, $4d$, $5d$, and $6d$); again, minima occur for the ns filling (n = 3, 4, 5, 6, 7) as well as to the previously mentioned maxima for the anomalous d filling, giving rise, in these cases, to a set of pairs maximum-minimum.

The aforementioned differences on the structure of the QSI involving or not the information coming from momentum space (dominated by the shell structure and the value of the nuclear charge, respectively) are also clearly observed in Fig. 3, in which QSI(Z, Z') are analyzed for two atoms with very close values of nuclear charge (namely, Z' = 18 and 20) throughout the whole Periodic Table. As should be expected, both curves appearing in Fig. 3(a), corresponding to QSI_r(Z, 18) and QSI_r(Z, 20) are very close everywhere due to the close values of the chosen nuclear charges, while the corresponding graph associated with the QSI_rp quantity presents a very strong difference between both curves, due to the fact that, as mentioned before, their structure is mainly the result of the shell-filling process. In fact, for the chosen atoms Z' = 18 and 20, with external orbitals $3p^6$ and $4s^2$, respectively, minima of one are located at maxima of the other, and vice versa. So, Fig. 3 again emphasizes the fundamental role played by the momentum-space properties in order to analyze and compare the shell structure of two many-electron systems.

IV. CONCLUSIONS

The comparison of two many-electron systems in what concerns the shell structure requires the consideration of the momentum-space variable **p** through the corresponding one-particle density. As previously known, the corresponding density in position space $\rho(\mathbf{r})$ only provides, by means of the quantum similarity index, information on how close the atoms are located at the periodic table. In order to get additional knowledge on the groups to which the systems belong, it is sufficient to deal with the momentum variable and, preferably, with both conjugate variables associated with the phase space in order to emphasize the aforementioned information.
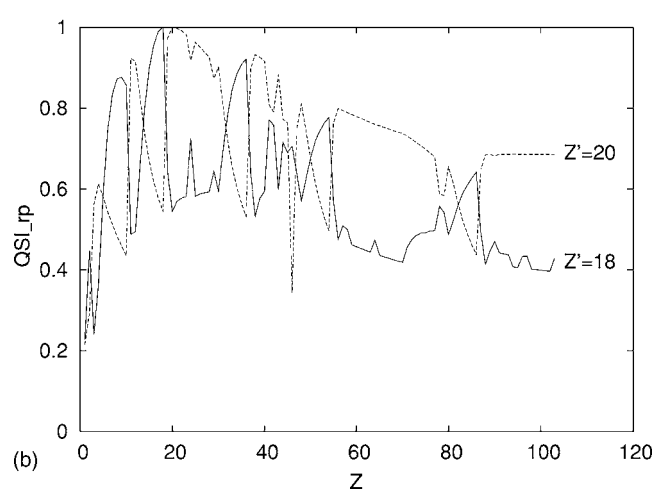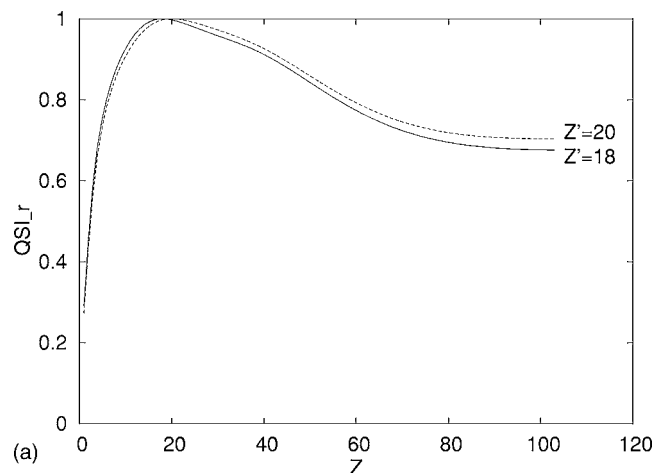

FIG. 3. Quantum similarity index (QSI) of Ar (Z' = 18) and Ca (Z' = 20) in (a) position and (b) phase spaces.

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