Physica A 474 (2017) 370–379

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

On the correlation measure of two-electron systems

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HIGHLIGHTS

- Expressions for single-particle charge densities of correlated two-electron systems.
- Shannon information entropies in position(r) and momentum (p) spaces.
- Geometric realization for the change in sign of r-space entropy values.
- Role of correlation in modifying the uncorrelated entropies in r and p spaces.
- Response of entropies to inter-electronic repulsion and correlation measure.

ARTICLE INFO

Article history:
Received 3 May 2016
Received in revised form 13 November 2016
Available online 3 February 2017

Keywords:
Two-electron ions
Helium iso-electronic sequence
Correlated wave functions
Single-electron charge densities
Shannon's information entropies
Correlation measure

ABSTRACT

We make use of a Hylleraas-type wave function to derive an exact analytical model to quantify correlation in two-electron atomic/ionic systems and subsequently employ it to examine the role of inter-electronic repulsion in affecting (i) the bare (uncorrelated) single-particle position- and momentum-space charge distributions and (ii) corresponding Shannon's information entropies. The results presented for the first five members in the helium iso-electronic sequence, on the one hand, correctly demonstrate the effect of correlation on bare charge distributions and, on the other hand, lead us to some important results for the correlated and uncorrelated values of the entropies. These include the limiting behavior of the correlated entropy sum (sum of position- and momentum-space entropies) and geometrical realization for the variation of information entropies as a function of Z. We suggest that, rather than the entropy sum, individual entropies should be regarded as better candidates for the measure of correlation.

1. Introduction

Our understanding of atomic theory is largely based on the independent-electron model in which the effect of the inter-electronic repulsion, globally referred to as correlation, is disregarded. The correlation effects can, however, have major influence on measurable quantities of atomic systems. The correlation energy, defined by the difference between the exact total energy and Hartree–Fock energy, is traditionally used as a guide [1] for the amount of correlation in a given system. Relatively recently, it has been proposed that Shannon's information entropies [2] provide a useful basis for the measure of electron correlation in atomic systems [3].

For a many-electron atom, Shannon's position-space information entropy is defined by [2]

$$S_\rho = -\int \rho(\vec{r}) \ln \rho(\vec{r}) d\vec{r}, \tag{1}$$

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http://dx.doi.org/10.1016/j.physa.2017.02.003
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where

$$\rho(\overrightarrow{r}) = \int |\psi(\overrightarrow{r}, \overrightarrow{r}_2, \ldots, \overrightarrow{r}_N)|^2 d\overrightarrow{r}_2 \ldots, d\overrightarrow{r}_N \tag{2}$$

with $\psi(\overrightarrow{r}, \overrightarrow{r}_2, \ldots, \overrightarrow{r}_N)$, the normalized wave function of an N electron atom. The charge density $\rho(\overrightarrow{r})$ is also normalized to unity. Correspondingly, the momentum-space entropy is written as

$$S_\gamma = -\int \gamma(\overrightarrow{p}) \ln \gamma(\overrightarrow{p}) d\overrightarrow{p}. \tag{3}$$

The momentum-space single-particle density $\gamma(\overrightarrow{p})$ is similar to that given in (2) but characterized by the normalized momentum-space wave function $\phi(\overrightarrow{p}, \overrightarrow{p}_2, \ldots, \overrightarrow{p}_N)$ obtained by taking Fourier transform of the position-space wave function. The two entropies as introduced through (1) and (3) allowed Bialynicki-Birula and Myceilski [4] to introduce a stronger version of the Heisenberg uncertainty relation which for any 3-dimensional system reads

$$S_\rho + S_\gamma \geq 3(1 + \ln \pi). \tag{4}$$

Eq. (4), often referred to as BBM inequality, clearly indicates the reciprocity between the representation and momentum spaces such that high values of S_ρ are associated with low values of S_γ. For uncorrelated two-electron systems (separable wave functions) the entropy sum is independent of the atomic number Z and has a constant value 6.5665. But when the electron–electron interaction is switched on, the entropy sum appears to depend on Z [5]. Consequently, the correlated entropy sum $S_\rho + S_\gamma$ has also been used as measure of correlation in atomic systems.

Information entropies of two-electron systems can be expressed in closed analytic form for separable approximation of the wave function. This is, however, not possible for explicitly r_{12} - (inter-electronic separation) dependent wave functions which can account for correlation in the system. The object of the present work is to derive an exact analytic model to quantify correlation in two-electron systems described by wave functions depending explicitly on r_{12}. In particular, we shall use our model to study the effect of inter-electronic repulsion on Shannon's information entropies with a view to look for a new measure of correlation. The system of our interest consists of the first five members in the helium iso-electronic sequence.

There exist elaborate studies on the problem of determining accurate wave functions for the helium atom [6]. The constructed wave functions often involve very large number of variational parameters. Consequently, it is rather difficult to extend such approaches to deal with other ions in the helium iso-electronic sequence. Moreover, in applicative context, use of these wave functions leads to very large number of computations. In view of this, occasionally, there have been attempts to construct accurate correlated two-electron wave functions involving fewer numbers of parameters. One such attempt is due to Bhattacharyya et al. [7]. An important virtue of their work is that the proposed three-parameter correlated wave function could be used to construct exact analytic expression for the total energy of two-electron systems. But it was noted that the wave function of Ref. [7] satisfies cusp conditions [8] only approximately such that the total energy computed for the helium atom is higher than the experimental value. As a result there have been many attempts to improve on the quality of such few-parameter wave functions. A significant work along this line of investigation is due to Le Sech [9] who constructed a two-parameter wave function which not only satisfies the correlation cusp condition to a high degree of accuracy but also gives much improved values for the energies of two-electron atomic/ionic systems from H^- to B^{3+}. Recently, Chauhan and Harbola [10] reexamined the optimization procedure for the parameters in the wave function of Le Sech in order to make it more accurate than that used in Ref. [9] for the computation of ground-state energies of two-electron atoms and ions.

The wave function of our interest can be written in the form

$$\psi(\overrightarrow{r}_1, \overrightarrow{r}_2, r_{12}) = \frac{C_N}{2} e^{-Z(r_1+r_2)}(\cosh(ar_1) + \cosh(ar_2))(1 + \frac{\lambda}{2} r_{12} e^{-br_{12}}) \tag{5}$$

with Z, the atomic number of the system and C_N, the normalization constant of the wave function. Here a and b are variational parameters. For $\lambda = 1$ (5) gives the wave function of Le Sech [9] while for $\lambda = 0$ and $a = 0$ we get the well known separable two-electron wave function [11]. We shall construct closed form expressions for both single-particle coordinate- and momentum-space charge densities and then employ them to examine effect of correlation on individual entropies and entropy sum $S_\rho + S_\gamma$ by using the parameters of Chauhan and Harbola [10].

We begin Section 2 by noting that instead of using (2) and a similar result written in the momentum space, it is possible to obtain expressions for single-particle charge densities by following an alternative approach. The second viewpoint is particularly well suited to derive results for position- and momentum-space charge densities $\rho(\overrightarrow{r})$ and $\gamma(\overrightarrow{p})$ in the presence of correlation. We demonstrate that, due to the effect of inter-electronic repulsion, the bare or uncorrelated radial charge distribution is pushed apart. On the other hand, the bare momentum distribution is squeezed by the same effect. In Section 3 we present results for the position- and momentum-space information entropies computed on the basis of our expressions for $\rho(\overrightarrow{r})$ and $\gamma(\overrightarrow{p})$. We verify that the uncorrelated entropy sum is a constant which does not depend on the atomic number [5]. As opposed to this, in the presence of correlation the entropy sum becomes Z dependent. However, correlated entropy sum tends to the un-correlated Z-independent constant value as we go along the iso-electronic sequence. The position-space entropy S_ρ takes up negative values for high-Z atoms but values of momentum-space entropy S_γ are always positive. We provide a geometrical realization for this fact and thus try to visualize how the interplay between nuclear Coulomb interaction and inter-electronic repulsion determines the variation of S_ρ or S_γ as a function of Z. We observe that