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Shannon and Fisher entropies for a hydrogen atom under soft spherical confinement

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ABSTRACT

We calculate Shannon and Fisher entropies in the position and momentum space, and some complexity measures for a variationally described hydrogen atom confined in soft and hard spherical boxes of varying dimension r_c and selected values of strength U_0. We include calculations for a free particle trapped in impenetrable boxes. It is found that the Shannon entropy S_r becomes negative for small cavity radii and large values of U_0, due to the highly localized nature of the particle. For soft confinement and small cavity dimensions, the entropies change very rapidly over short radial intervals.

1. Introduction

In information theory, entropy is a measure of the uncertainty associated with a random variable. In this field, the term usually refers to the Shannon entropy, which measures the expected value of the information contained in a message, usually in units such as bits, i.e., it is a measure of the average information content that is missing when the value of the random variable is unknown. This concept was introduced by Claude E. Shannon in his 1948 paper "A Mathematical Theory of Communication" [1], in which, he sets out to find fundamental limits on signal processing operations such as compressing data and on reliably storing and communicating data. Since its proposal this theory has expanded into a number of applications in other areas, such as statistical inference, cryptography, thermal physics, quantum computing, atomic and molecular structure and chemical reactivity.

In quantum computation [2] Shannon's entropy represents an absolute limit on the best possible lossless compression of any communication, under some particular constraints. Shannon's entropy appears in the description of mean excitation energy [3] and it relates to certain features of the chemical bond [4]. Since the total entropy increases with the improvement of the basis, it has been used as a measure of basis quality in atomic and molecular calculations [5–7], and also to estimate the degree of correlation included in a wave function [8,9] as well as in several applications in physical chemistry [10]. In chemistry, such entropy is closely related to electron delocalization which plays a crucial role in aromatic compounds [11]. There is a connection between Shannon entropy and the lowest ionization potential in atoms, as obtained by means of Koopman's theorem [12]. It has been employed as a quantitative measure of spin polarization associated with the ground state of some atoms [13], and even to describe the spreading of wave packets in fractal models [14], and also to analyze eigenstates and coherent states supported by a Poschl–Teller [15] potential and bound states for various systems [16].

Shannon's entropy has recently received an increasing attention [17] in connection with studies of atoms confined in impenetrable boxes, where the latter represents a simplified model to analyze how the atomic structure is modified when subjected to high pressure [18]. Shannon's quantum entropy has been interpreted as the uncertainty associated with the particle position, which in turn relates to the corresponding degree of localization-delocalization [8]. Confined quantum systems such as atoms and molecules trapped in impenetrable boxes, quantum dots and quantum wells, are ideal systems to analyze the concept of localization-delocalization. The Shannon entropy behavior has recently been studied for the ground state of one-, two- and three-electron atoms and ions in hard spherical boxes [17]. For several of these systems, local maxima and minima have been found along the curve of Shannon's total entropy as a function of the confinement radius. It has also been found that Shannon's entropy in the position space becomes negative for a strong confinement regime (very small cavity dimensions) in impenetrable boxes. In this connection, introducing a cavity of padded walls (soft confinement) for

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an atomic or molecular system would represent a physically more realistic model. This is precisely the problem we undertake in the present report, where the behavior of several quantum mechanical properties of the hydrogen atom confined by soft spherical walls of varying strength is analyzed as a function of the box radius r_c.

The Shannon entropies in the position and momentum space are defined as

$$S_r = -\int_0^\infty \rho(r) \ln\left[\rho(r)\right] d^3r, \tag{1}$$

$$S_p = -\int_0^\infty \gamma(p) \ln\left[\gamma(p)\right] d^3p, \tag{2}$$

whereas the total Shannon entropy is given by

$$S_t = S_r + S_p. \tag{3}$$

A quantity that is closely related to the Shannon entropy which describes more adequately the degree of delocalization of the electronic cloud in a system corresponds to the Shannon entropy power[1,19]:

$$J_{r,p} = \frac{1}{2\pi e} e^{2S_{r,p}/3}. \tag{4}$$

The Fisher entropies [20] in the position and momentum space are given by

$$I_r = \int_0^\infty \frac{|\vec{\nabla}\rho(r)|^2}{\rho(r)} d^3r = \int_0^\infty 4\left[\frac{d\tilde{\psi}(r)}{dr}\right]^2 d^3r, \tag{5}$$

$$I_p = \int_0^\infty \frac{|\vec{\nabla}\gamma(p)|^2}{\gamma(p)} d^3p = \int_0^\infty 4\left[\frac{d\tilde{\phi}(p)}{dp}\right]^2 d^3p, \tag{6}$$

where ρ is the one-particle probability density of the system, measures the concentration (sharpness) of the electron density. Fisher's entropy and the Shannon entropy power fulfill a generalized uncertainty relation [19,21]:

$$\frac{1}{3} I_{r,p} J_{r,p} \geqslant 1. \tag{7}$$

By plotting $J_{r,p}$ vs $I_{r,p}$ one obtains the so-called *Fisher–Shannon information plane*, which provides us with a very useful tool to systematically analyze the electron correlation in atoms [22].

Much effort has been devoted to Fisher's information measure, giving rise to a wide spectrum of physical applications [23]. For example, minimizing of Fisher's measure leads to a Schrödinger-like equation for the probability amplitude, where the ground state describes equilibrium physics and the excited states account for non-equilibrium situations [24]. In analogy to Shannon entropy's classical meaning, known to be connected with disorder, Frieden et al. [25] extensively studied the concept of order or complexity and showed that it is associated with the Fisher entropy. Another measure of complexity is due to López-Ruiz, Mancini and Calbet (LMC) [26], which was used in the context of electronic structure of atoms and molecules [27]. The Fisher–Shannon entropy power is a good descriptor of the complexity and it is related to the LMC complexity [28–32].

Shannon [1] and Fisher [20] entropies can thus be utilized to estimate the degree of localization for a quantum mechanical system both in position and momentum space when analyzing statistical complexity measures.

Calculations of Shannon entropies have been reported for one-electron atoms by Sen [17] and of Fisher–Shannon plus statistical complexity measures for two-electron atoms by Howard et al. [33], and also for the molecular ion H_2^+ by Montgomery and Sen [34]. Very recently, similar calculations for confined one-electron systems have been addressed in a review article by Sen et al. [35].

In this report, Shannon and Fisher entropies are calculated in the position (S_r, I_r) and momentum space (S_p, I_p) plus the complexity measures given by the so-called Fisher–Shannon products $(J_{r,p}I_{r,p})$, also expressed in both spaces, for the hydrogen atom spherically confined in soft and impenetrable (as a limiting case) boxes. For the latter, calculations for a free particle in a box are also included. For the atomic system and the free particle the evolution of these quantities is analyzed in terms of the cavity dimension r_c and strength U_0.

The densities

$$\rho(r) = \left|\tilde{\psi}(r)\right|^2; \tag{8}$$

$$\gamma(p) = \left|\tilde{\phi}(p)\right|^2, \tag{9}$$

are defined in terms of the one-particle system wave functions $\tilde{\psi}(r), \tilde{\phi}(p)$ in position and momentum coordinates, respectively.

The Fisher–Shannon products, expressed in both spaces, are $P_r = J_r I_r$ and $P_p = J_p I_p$, respectively, where J_r and J_p are the aforementioned quantities, Shannon entropy powers,

$$J_r = \frac{1}{2\pi e} e^{2S_r/3}; \tag{10}$$

$$J_p = \frac{1}{2\pi e} e^{2S_p/3}. \tag{11}$$

In Section 2 we discuss the free-particle-in-a-box case and briefly review the variational method based on atomic wave functions expanded in Slater-type basis sets where, for soft confinement (finite U_0), the radial coordinate extends over the whole space (r goes from 0 to ∞). When $U_0 \longrightarrow \infty$ (hard spherical confinement) the atomic wave function includes a cut-off factor to ensure correct fulfillment of Dirichlet boundary condition (vanishing wave function at the box edge, where the integral is performed from 0 to r_c). Section 3 is devoted to the presentation and discussion of results obtained by this method, whereas some concluding remarks are left for Section 4.

2. Method of calculation

The eigenfunctions for a free particle in a spherical box of radius r_c are given by

$$\psi_{nlm}(r,\theta,\phi) = A_{nl} j_l(x_{nl} r/r_c) Y_{lm}(\theta,\phi), \tag{12}$$

with energies

$$E_{nl} = \frac{x_{nl}^2}{2r_c^2}, \tag{13}$$

where A_{nl} is a normalization constant, x_{nl} is the nth-root of the spherical Bessel function j_l and the Y_{lm}'s are the spherical harmonics.

Since we consider in particular the ground state, the corresponding wave function is

$$\begin{aligned}\psi_{100}(r,\theta,\phi) &= A_{10} j_0(x_{10} r/r_c) Y_{00}(\theta,\phi) \\ &= \frac{A_{10}}{\sqrt{4\pi}} j_0(x_{10} r/r_c), \quad j_0(\tau) = \mathrm{Sin}(\tau)/\tau.\end{aligned} \tag{14}$$

The normalized ground state wave function for a spherically confined free particle in an impenetrable box is thus given by