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Information measures of hydrogenic systems, Laguerre polynomials and spherical harmonics

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Abstract

Fisher's information and Shannon's entropy are two complementary information measures of a probability distribution. Here, the probability distributions which characterize the quantum-mechanical states of a hydrogenic system are analyzed by means of these two quantities. These distributions are described in terms of Laguerre polynomials and spherical harmonics, whose characteristics are controlled by the three integer quantum numbers of the corresponding states. We have found the explicit expression for the Fisher information, and a lower bound for the Shannon entropy with the help of an isoperimetric inequality.

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1. Introduction

The information theory of quantum-mechanical systems is a great scientific challenge of our present time because (i) it provides a deeper insight into the internal structure of the systems [10] and (ii) it is the strongest support of the modern quantum computation and information [12], which is basic for numerous technological developments [17]. Actually even for the one-dimensional single-particle systems

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with an analytically solvable Schrödinger equation, where the wavefunctions of their physical states are controlled by special functions of mathematical physics (classical orthogonal polynomials, spherical harmonics, Bessel functions, McDonald functions, ...) [11], the basic information-theoretic quantities remain to be computed. This is because of the lack of knowledge in the information-theoretic properties of special functions despite the so many results provided by the theory of orthogonal polynomials and potential theory [3].

A paradigmatic example among these systems is the hydrogenic system, which consists of a simple nucleus with a positive charge $+Ze$ and one electron of charge $-e$ bound by the electric force acting between them. The physical and chemical properties of this system in a given quantum-mechanical state described by three integer quantum numbers (n, l, m) , are controlled by the spread of the probability density $\rho(\vec{r})$ over the whole space. The latter can be quantitatively measured by two complementary measures of information: the Fisher information defined [6] by

$$I(\rho) := \int_{\mathbb{R}^3} \frac{[\bar{\nabla} \rho(\vec{r})]^2}{\rho(\vec{r})} d\vec{r} \quad (1)$$

and the Shannon entropy [15]

$$S(\rho) := - \int_{\mathbb{R}^3} \rho(\vec{r}) \ln \rho(\vec{r}) d\vec{r}, \quad (2)$$

which are local and global measures of (i) the extent and the concentration of the wavefunction of the system, respectively, as well as (ii) the uncertainty in the spatial localization of the electronic cloud. These two measures are intimately connected one to another [2,16,5,14].

Up until now most efforts have been focussed on the hydrogenic Shannon entropy from both analytical and numerical standpoints [18,4]; see also [1] for a brief review. Nevertheless its explicit expression is not yet known, mainly because it involves some entropic integrals of Laguerre and Gegenbauer polynomials whose analytical calculation is an open problem still nowadays, as it is explained later on in Section 5. On the other hand, the computation of hydrogenic Fisher information has never been attempted for arbitrary states, to the best of our knowledge. This is certainly striking because this measure (i) predates the concept of Shannon's entropy for more than 20 yr (1925 versus 1948), and (ii) may also be a more intuitive and powerful analytical tool in the approximation theory and quantum physics [7–9].

Here, the Fisher information and the Shannon entropy for arbitrary hydrogenic states are explicitly calculated and bounded, respectively, in terms of the three quantum numbers (n, l, m) which characterize them. To do that we only use known properties of Laguerre polynomials and spherical harmonics (which are the elements which basically conform the hydrogenic wavefunctions) and, for the Shannon case, an isoperimetric inequality [16,5,14].

The structure of the paper is as follows. First, the necessary physico-mathematical elements to find the probability distribution of arbitrary hydrogenic states, pertinent to our work, are summarized in Section 2. Then, in Section 3, the hydrogenic Fisher information is explicitly given in terms of the quantum numbers (n, l, m) of the state under consideration in a closed and simple form. Briefly, it is found out that this quantity does not depend on the orbital quantum number l . Later, in Section 4 the present knowledge on the hydrogenic Shannon entropy is described, the difficulties to obtain its explicit expression from an analytical point of view are discussed, and a lower bound in terms of the quantum numbers characterizing the state is found. Finally, some concluding remarks are pointed out.

2. Probability distribution of the hydrogenic system

In this section, we briefly summarize the analytical determination of the wavefunctions $\Psi(\vec{r}, t)$ of the quantum-mechanical states for a hydrogenic system, and consequently the associated probability distribution densities which are given by the square of the absolute value of the wavefunctions. They depend on three integer quantum numbers (n, l, m) , corresponding to the three degrees of freedom of the electron.

As usual, we will work in the reference system with polar coordinates (r, θ, φ) and the origin at the center of mass of the system, which practically coincides with the position of the nucleus because of its huge mass relative to that of the electron. Atomic units will be used throughout the paper. The potential energy of the electron has the Coulomb form $V(r) = -Z/r$. Then, the stationary states of the system are

$$\Psi_{nlm}(\vec{r}, t) = \Psi_{nlm}(\vec{r}) \exp(-iE_n t),$$

where (E_n, Ψ_{nlm}) are the eigensolutions of the Schrödinger equation of the system

$$\left(-\frac{1}{2\mu} \bar{\nabla}^2 - \frac{Z}{r} \right) \Psi_{nlm}(\vec{r}) = E_n \Psi_{nlm}(\vec{r}),$$

where μ is the reduced mass of the electron, and the gradient operator on \mathbb{R}^3 written in polar coordinates is $\bar{\nabla} = (\frac{\partial}{\partial r}, \frac{1}{r} \frac{\partial}{\partial \theta}, \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi})$. It is known that the energetic eigenvalues are $E_n = -\mu/(2n^2)$, and the associated eigenfunctions are

$$\Psi_{nlm}(\vec{r}) = R_{nl}(r) Y_{lm}(\Omega), \tag{3}$$

where the principal quantum number $n = 0, 1, \dots$, the orbital quantum number $l = 0, 1, \dots, n - 1$, and the magnetic or azimuthal quantum number $m = -l, -l + 1, \dots, +l - 1, +l$; and the solid angle Ω is defined by the angular coordinates (θ, φ) . Moreover, the radial eigenfunctions, duly normalized to unity, are given by

$$R_{nl}(r) = N_{nl} \left(\frac{2Z\mu}{n} r \right)^l e^{-\frac{Z\mu}{n} r} L_{n-l-1}^{(2l+1)} \left(\frac{2Z\mu}{n} r \right), \tag{4}$$

with the normalization factor

$$N_{nl} = \left[\left(\frac{2Z\mu}{n} \right)^3 \frac{(n-l-1)!}{2n(n+l)!} \right]^{1/2} \tag{5}$$

and the function $L_{n-l-1}^{(2l+1)}(x)$ is a particular case of the Laguerre polynomial

$$L_p^\alpha(x) = \sum_{s=0}^p (-1)^s \binom{p+\alpha}{p-s} \frac{x^s}{s!},$$

which is known to satisfy the orthogonality property

$$\int_0^\infty \omega_\alpha(x) L_p^\alpha(x) L_q^\alpha(x) dx = \frac{\Gamma(\alpha+p+1)}{p!} \delta_{pq}, \tag{6}$$

where $\omega_\alpha(x) := x^\alpha e^{-x}$ is the Laguerre weight function.

On the other hand, the angular part of the wavefunctions is given by the spherical harmonics

$$Y_{lm}(\Omega) = M_{lm} P_l^m(\cos \theta) e^{im\varphi}; \quad 0 \leq \theta \leq \pi, \quad 0 \leq \varphi \leq 2\pi, \quad (7)$$

where $P_l^m(x)$ is the associated Legendre function of the first kind and the constant M_{lm} is given by

$$M_{lm} = \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2}. \quad (8)$$

The spherical harmonics fulfill the orthogonality condition

$$\int Y_{lm}^*(\Omega) Y_{l'm'}(\Omega) d\Omega = \delta_{ll'} \delta_{mm'}, \quad (9)$$

where $d\Omega = \sin \theta d\theta d\varphi$, and the Legendre functions $P_l^m(x)$ satisfy the following orthogonality relationships

$$\int_{-1}^{+1} (1-x^2)^{-1} P_l^m(x) P_{l'}^{m'}(x) dx = \frac{(l+m)!}{m(l-m)!} \delta_{mm'}, \quad (10)$$

$$\int_{-1}^{+1} P_l^m(x) P_{l'}^m(x) dx = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!} \delta_{ll'} \quad (11)$$

and the recurrence relation

$$(2l+1)x P_{l-1}^m(x) = (l+m-1) P_{l-2}^m(x) + (l-m) P_l^m(x). \quad (12)$$

Then, the probability distribution density of the hydrogenic system in the state characterized by the quantum numbers (n, l, m) is given by

$$\rho(\bar{r}) \equiv \rho_{nlm}(\bar{r}) = |\Psi_{nlm}(\bar{r})|^2 = R_{nl}^2(r) |Y_{lm}(\Omega)|^2 = M_{lm}^2 R_{nl}^2(r) |P_l^m(\cos \theta)|^2,$$

which with the use of Eq. (4) can be written as

$$\rho(\bar{r}) = N_{nl}^2 \eta^{-1} \omega_{2l+1}(\eta) [L_{n-l-1}^{(2l+1)}(\eta)]^2 |Y_{lm}(\Omega)|^2. \quad (13)$$

This quantity gives the probability density for observing the electron as a function of r and the polar angle θ , since it does not depend on the azimuth.

3. The hydrogenic Fisher information

In this section we show the explicit expression of the Fisher information $I(\rho)$, given by Eq. (1), for the probability distribution $\rho(\bar{r})$ of an arbitrary quantum-mechanical state of the hydrogenic system, as given by Eq. (4) or (10), by use of general properties of the special functions involved in the state wavefunction; namely, Laguerre polynomials, spherical harmonics and associated Legendre functions of first kind. Our main result is

$$I(\rho) = \left(\frac{2Z\mu}{n} \right)^2 \frac{n - |m|}{n}, \quad (14)$$

where Z and μ are the nuclear charge and the reduced mass of the system, and the integer numbers (n, m) are the principal quantum number $n = 0, 1, \dots$, and the azimuthal quantum number $m = -l, -l + 1, \dots, +l$, which together with the orbital quantum number $l = 0, 1, \dots, n - 1$ characterize the state under consideration.

From a physical point of view let us first of all highlight that the Fisher information is independent of the orbital quantum number l . Moreover, for states s (which are characterized by the quantum numbers $(n, l=0, m=0)$) and for the circular states $(n, l=n-1, m=n-1)$ this quantity equals to $(2\mu Z)^2/n^2$ and $(2\mu Z)^2/n^3$, respectively. Finally, let us remark that for all cases the Fisher information rapidly decreases when the principal quantum number (and so the energy of the state) is increased, which is a clear prediction for the electronic cloud to be much less concentrated in excited states.

To prove Eq. (14), we use a method based on the properties of the involved special functions. We begin with Eq. (1) which gives the Fisher information I for a general density function $P(\vec{r})$ on \mathbb{R}^3 . Taking into account the gradient operator in polar coordinates $\vec{\nabla} = (\frac{\partial}{\partial r}, \frac{1}{r} \frac{\partial}{\partial \theta}, \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi})$ and the azimuthal independence of the probability density for an arbitrary hydrogenic state, as given by Eq. (13), one has the following expression for the hydrogenic Fisher information

$$I(\rho) = \int_{\mathbb{R}^3} \frac{1}{\rho(\vec{r})} \left[\frac{\partial \rho(\vec{r})}{\partial r} \right]^2 d\vec{r} + \int_{\mathbb{R}^3} \frac{1}{\rho(\vec{r})} \left[\frac{1}{r} \frac{\partial \rho(\vec{r})}{\partial \theta} \right]^2 d\vec{r} \equiv I_1 + I_2. \tag{15}$$

Let us first calculate the integral I_1 . From Eq. (13) one has

$$\frac{\partial \rho(\vec{r})}{\partial r} = N_{nl}^2 \frac{2Z\mu}{n} \eta^{2l} e^{-\eta} \left\{ \left(\frac{2l}{\eta} - 1 \right) [L_{n-l-1}^{(2l+1)}(\eta)]^2 - 2L_{n-l-1}^{(2l+1)}(\eta)L_{n-l-2}^{(2l+2)}(\eta) \right\} |Y_{lm}(\theta, \varphi)|^2,$$

where $\eta = \frac{2Z\mu}{n}r$. Then, the integral I_1 can be decomposed into a sum of five integrals denoted by I_{1i} , $i = 1 - 5$. Taking into account the volume element $d\vec{r} = r^2 dr d\Omega$ and the normalization to unity of the spherical harmonics, given by Eq. (9), one has the following values for the first four integrals of this sum

$$\begin{aligned} I_{11} &= 4l^2 \int_{\mathbb{R}^3} r^{-2} \rho(\vec{r}) d\vec{r} \equiv 4l^2 \langle r^{-2} \rangle \\ &= 4l^2 \left(\frac{2Z\mu}{n} \right) N_{nl}^2 \int_0^\infty \eta^{-1} \omega_{2l+1}(\eta) [L_{n-l-1}^{2l+1}(\eta)]^2 d\eta \\ &= \left(\frac{2Z\mu}{n} \right)^2 \frac{2l^2}{n(2l+1)}, \end{aligned} \tag{16}$$

$$\begin{aligned} I_{12} &= -\frac{8lZ\mu}{n} \int_{\mathbb{R}^3} r^{-1} \rho(\vec{r}) d\vec{r} = -\frac{4ln}{2Z\mu} N_{nl}^2 \int_0^\infty \omega_{2l+1}(\eta) [L_{n-l-1}^{2l+1}(\eta)]^2 d\eta \\ &= -\left(\frac{2Z\mu}{n} \right)^2 \frac{2l}{n}, \end{aligned} \tag{17}$$

$$\begin{aligned}
 I_{13} &= \left(\frac{2Z\mu}{n}\right)^2 \int_{\mathbb{R}^3} \rho(\vec{r}) \, d\vec{r} = \frac{n}{2Z\mu} N_{nl}^2 \int_0^\infty \eta \omega_{2l+1}(\eta) [L_{n-l-1}^{2l+1}(\eta)]^2 \, d\eta \\
 &= \left(\frac{2Z\mu}{n}\right)^2, \tag{18}
 \end{aligned}$$

$$I_{14} = 4 \frac{n}{2Z\mu} N_{nl}^2 \int_0^\infty \omega_{2l+2}(\eta) [L_{n-l-2}^{(2l+2)}(\eta)]^2 \, d\eta = \left(\frac{2Z\mu}{n}\right)^2 \frac{2(n-l-1)}{n}, \tag{19}$$

where integrals (16) and (18) can be calculated using (see, e.g. [13])

$$\begin{aligned}
 &\int_0^\infty dx \, x^s e^{-x} L_n^\alpha(x) L_m^\beta(x) \\
 &= \Gamma(s+1) \sum_{r=0}^{\min(n,m)} (-1)^{n+m} \binom{s-\alpha}{n-r} \binom{s-\beta}{m-r} \binom{s+r}{r} \tag{20}
 \end{aligned}$$

and the fifth integral I_{15} can be expressed as:

$$\begin{aligned}
 I_{15} &= -4 \frac{n N_{nl}^2}{2Z\mu} \left[2l \int_0^\infty \omega_{2l+1} L_{n-l-2}^{(2l+2)}(\eta) L_{n-l-1}^{(2l+1)}(\eta) \, d\eta \right. \\
 &\quad \left. - \int_0^\infty \eta \omega_{2l+1}(\eta) L_{n-l-2}^{(2l+2)}(\eta) L_{n-l-1}^{(2l+1)}(\eta) \, d\eta \right], \tag{21}
 \end{aligned}$$

where $\omega_\alpha(\eta) \equiv \eta^\alpha e^{-\eta}$ is the weight function with respect to which the Laguerre polynomials $L_p^\alpha(\eta)$ are orthogonal on the interval $[0, \infty]$. Then, keeping in mind the orthogonality property (6) of the Laguerre polynomials we have that (a) the first integral vanishes, and (b) the second integral equals

$$I_{15} = -\left(\frac{2Z\mu}{n}\right)^2 \frac{2(n-l-1)}{n},$$

where we have also used the ladder relationship of the Laguerre polynomials

$$x L_k^{\alpha+1}(x) = (k + \alpha + 1) L_k^\alpha(x) - (k + 1) L_{k+1}^\alpha(x),$$

for the product $\eta L_{n-l-2}^{(2l+2)}(\eta)$.

So, putting together the computed values for I_{1i} , $i = 1 - 5$, one has the following value for the integral I_1 :

$$I_1 \equiv \int_{\mathbb{R}^3} \frac{1}{\rho(\vec{r})} \left[\frac{\partial \rho(\vec{r})}{\partial r} \right]^2 \, d\vec{r} = \left(\frac{2Z\mu}{n}\right)^2 \frac{1}{n} \left[n + \frac{2l^2}{2l+1} - 2l \right]. \tag{22}$$

Let us now calculate the integral I_2 . From Eqs. (10) and (8) one has

$$\begin{aligned}
 \frac{\partial \rho(\vec{r})}{\partial \theta} &= N_{nl}^2 \omega_{2l}(\eta) L_{n-l-1}^{(2l+1)}(\eta) \frac{\partial |Y_{lm}(\theta, \varphi)|^2}{\partial \theta}, \\
 \frac{\partial |Y_{lm}(\theta, \varphi)|^2}{\partial \theta} &= 2M_{lm}^2 \left\{ \frac{l \cos \theta}{\sin \theta} [P_l^m(\cos \theta)]^2 - \frac{l+m}{\sin \theta} P_l^m(\cos \theta) P_{l-1}^m(\cos \theta) \right\},
 \end{aligned}$$

for $m \geq 0$, so that

$$\left[\frac{1}{r} \frac{\partial \rho(\bar{r})}{\partial \theta} \right]^2 = \frac{4\rho^2(\bar{r})}{r^2 \sin^2 \theta} \left[l \cos \theta - (l + m) \frac{P_{l-1}^m(\cos \theta)}{P_l^m(\cos \theta)} \right]^2.$$

Then, a straightforward manipulation shows that the integral I_2 can be decomposed into the sum of three integrals denoted by I_{2i} , $i = 1 - 3$. Taking into account the orthogonality relations of the Legendre functions, one has the following value for the first integral I_{21}

$$\begin{aligned} I_{21} &= l^2 \int_0^\infty \int_0^\pi \frac{\cos^2 \theta}{\sin \theta} \rho(\bar{r}) \, dr \, d\theta \\ &= M_{lm}^2 l^2 \langle r^{-2} \rangle \left\{ \int_{-1}^{+1} (1 - x^2)^{-1} [P_l^m(x)]^2 \, dx - \int_{-1}^{+1} [P_l^m(x)]^2 \, dx \right\} \\ &= \left(\frac{2Z\mu}{n} \right)^2 \frac{l^2}{8\pi n m} \left(1 - \frac{2m}{2l + 1} \right) \end{aligned}$$

and for the second integral

$$I_{22} = (l + m)^2 M_{lm}^2 \langle r^{-2} \rangle \int_{-1}^{+1} (1 - x^2)^{-1} [P_{l-1}^m(x)]^2 \, dx = \left(\frac{2Z\mu}{n} \right)^2 \frac{l^2 - m^2}{8\pi n m},$$

where the properties for the Legendre functions given by Eqs. (10) and (11) have been used.

The integral I_{23} turns out to be

$$\begin{aligned} I_{23} &= -2l(l + m) M_{lm}^2 \langle r^{-2} \rangle \int_{-1}^{+1} \frac{x}{1 - x^2} P_l^m(x) P_{l-1}^m(x) \, dx \\ &= -2l(l + m) M_{lm}^2 \langle r^{-2} \rangle \frac{(l + m - 1)! (l - m)}{(l - m)! m} \\ &= - \left(\frac{2Z\mu}{n} \right)^2 \frac{2l(l - m)}{8\pi n m}, \end{aligned}$$

where the orthogonality and the recurrence relations given by Eqs. (10)–(12) have been used.

So, gathering the computed values of I_{2i} , $i = 1 - 3$, one has the following expression for the integral I_2 :

$$I_2 \equiv \int_{\mathbb{R}^3} \frac{1}{\rho(\bar{r})} \left[\frac{1}{r} \frac{\partial \rho(\bar{r})}{\partial \theta} \right]^2 \, d\bar{r} = \left(\frac{2Z\mu}{n} \right)^2 \frac{1}{n} \left[2l - m - \frac{2l^2}{2l + 1} \right] \tag{23}$$

for $m \geq 0$; and similarly, just with the opposite sign in front of m , for $m \leq 0$.

Taking the values of the integrals I_1 and I_2 , as given by Eqs. (22) and (23) respectively, into Eq. (15), one straightforwardly has the searched hydrogenic Fisher information $I(\rho)$ as given by Eq. (14).

4. The hydrogenic Shannon entropy

Recently, Dehesa et al. [18,4] have initiated the investigation of the Shannon information entropy of the D-dimensional single-particle systems in general central potentials. In doing so, these authors point out

the need for the previous knowledge of the so-called entropic integrals (or just, entropy) of the classical orthogonal polynomials and other special functions (e.g., spherical harmonics, Bessel functions, ...), depending on the specific analytical form of the potential. Their interest is focussed on the isotropic harmonic oscillator and the Coulomb potentials, as it is reviewed in Ref. [3]. Even for these simple systems, the explicit expression for their Shannon entropies is not known because the entropic integrals of the involved classical orthogonal polynomials (Hermite for the one-dimensional oscillator case, Laguerre for the Coulomb and D -dimensional ($D \geq 2$) oscillator cases and Gegenbauer in both cases) have not yet been successfully computed save for the ground- and very excited states. Indeed, in particular, the Shannon entropy of a hydrogenic system in an arbitrary state characterized by the quantum numbers (n, l, m) has been shown in [4,18], according to Eqs. (2) and (13), to have the expression

$$S(\rho) \equiv S_{nlm}(\rho) = S_{nl}(R) + S_{lm}(Y). \quad (24)$$

The radial part is

$$\begin{aligned} S_{nl}(R) &= - \int_0^\infty r^2 R_{nl}^2(r) \ln R_{nl}^2(r) dr \\ &= -3 \ln(Z\mu) - \ln \left[\frac{4(n-l-1)!}{n^4(n+l)!} \right] \\ &\quad + \frac{6(n-l-1)^2 + (2l+2)(6n-4l-3)}{2n} \\ &\quad - 2l \left[\frac{2n-2l-1}{2n} + \Psi(n+l+1) \right] + \frac{(n-l-1)!}{2n(n+l)!} E_1[L_{n-l-1}^{(2l+1)}(\eta)] \\ &= -3 \ln(Z\mu) - \ln \left(\frac{4}{n^4} \right) + \frac{6(n-l-1)^2 + (2l+2)(6n-4l-3)}{2n} \\ &\quad - 2l \left[\frac{2n-2l-1}{2n} + \Psi(n+l+1) \right] + \frac{1}{2n} E_1[\tilde{L}_{n-l-1}^{(2l+1)}]. \end{aligned} \quad (25)$$

On the other hand, the angular part is

$$S_{lm}(Y) = \ln(2\pi) - 2m \left[\Psi(l+m+1) - \Psi \left(l + \frac{1}{2} \right) - \ln 2 - \frac{1}{2l+1} \right] + E_0[\tilde{C}_{l-m}^{m+\frac{1}{2}}]. \quad (26)$$

In Eqs. (25) and (26) we have used the digamma function $\Psi(x) = \Gamma'(x)/\Gamma(x)$, and the entropy-like integrals $E_i(p)$ defined by

$$E_i(p_k) = - \int_a^b x^i p_k^2(x) \ln p_k^2(x) \omega(x) dx,$$

for $i = 1$ and 0 , respectively, and where p_k (\tilde{p}_k) denote the orthogonal (respectively, orthonormal) polynomials with respect to the weight function $\omega(x)$ on the interval (a, b) .

Since the calculation of the entropy-like integrals of the Laguerre and Gegenbauer polynomials (which are involved in the evaluation of the hydrogenic Shannon entropy S according to Eqs. (24)–(26)) is a difficult, not-yet-accomplished task, it is very helpful and natural to ask for rigorous and accurate bounds for S . This is the main purpose of this section: to derive a lower bound for the Shannon entropy

of a hydrogenic system in an arbitrary quantum-mechanical state described by the quantum numbers (n, l, m) . To this end we will use the isoperimetric inequality [2,5,14]

$$J(\rho)I(\rho) \geq 3,$$

where $J(\rho) = (2\pi e)^{-1} \exp[\frac{2}{3}S(\rho)]$ defines the Shannon entropy power of the probability density $\rho(\vec{r})$. Then, one has that the Shannon entropy $S(\rho)$ is bounded from below by the Fisher information $I(\rho)$ as

$$S(\rho) \geq \frac{3}{2}[1 + \ln(6\pi) - \ln I(\rho)]. \quad (27)$$

For hydrogenic systems the Fisher information is given by Eq. (14) so that

$$\ln I(\rho) \leq 2 \ln(Z\mu) - \ln n - \ln |m|,$$

which saturates for $|m| = \frac{n}{2}$. Here we have taken into account that $|m|(n - |m|) \leq \frac{n^2}{4}$, where the equality is reached for $|m| = \frac{n}{2}$.

The last two equations yield the following inequality:

$$S(\rho) \geq \frac{3}{2} \ln \left[\frac{6\pi en|m|}{(Z\mu)^2} \right]$$

which gives a lower bound for the Shannon entropy of any hydrogenic state characterized by the quantum numbers (n, l, m) . Since $n = 1, 2, \dots; l = 0, 1, \dots, n - 1$, and $|m| \geq l$, it follows that this bound is always non-negative.

5. Concluding remarks

The analytical determination of two information measures (Fisher, Shannon), which quantitatively and complementarily describe the spreading and concentration of the electronic cloud of a hydrogenic system in a general quantum-mechanical state, is considered in terms of the nuclear charge Z , the reduced mass μ and the quantum numbers (n, l, m) which characterize the system.

We have found an explicit expression for the Fisher information by means of an extensive use of the algebraic properties of Laguerre polynomials, the associated Legendre functions of first kind and spherical harmonics. Finally, for the Shannon entropy, let us comment that we have not been able to do the same task up to now, essentially because the involved entropy-like integrals of Laguerre and Gegenbauer polynomials are very difficult to compute, save for some exceptional cases (i.e. for the lowest and the highest values of their degrees). Here, we have derived a lower bound for the hydrogenic Shannon entropy, valid for all states of the system, with the help of a well-known isoperimetric inequality.

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