

Crámer-Rao complexity of the confined two-dimensional hydrogen

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Abstract

The internal disorder of the confined two-dimensional hydrogenic atom is numerically studied in terms of the confinement radius for the 1s, 2s, 2p, and 3d quantum states by means of the statistical Crámer-Rao complexity measure. First, the confinement dependence of the variance and the Fisher information of the position and momentum spreading of its electron distribution are computed and discussed. Then, the Crámer-Rao complexity measure (which quantifies the combined balance of the charge concentration around the mean value and the gradient content of the electron distribution) is investigated in position and momentum spaces. We found that confinement does distinguish complexity of the system for all quantum states by means of these two component measures.

KEYWORDS

confined two-dimensional hydrogen, Crámer-Rao complexity measure, Fisher information

1 | INTRODUCTION

The internal disorder of d -dimensional quantum mechanical nonrelativistic systems is conditioned by the spatial spreading/complexity of their Schrödinger single-particle probability density $\rho(\vec{r})$, $\vec{r} \in \mathbb{R}_d$.^[1,2] To best quantify it, three composite information-theoretic measures (the Fisher-Shannon, Lopezruiz-Mancini-Calvet [LMC], and Crámer-Rao complexities)^[3,4] and various generalizations (eg, the complexities of Fisher-Rényi and LMC-Rényi type) have been proposed beyond the single dispersion (the statistical variance) and information-theoretic measures (the Fisher information and the Shannon entropy) and their extensions (eg, the entropies of Rényi and Tsallis type).^[5] The latter measures are given as $V[\rho] = \langle r^2 \rangle - \langle r \rangle^2$, $r \equiv |\vec{r}|$, for the variance and

$$F[\rho] := \int_{\mathbb{R}_d} \frac{|\vec{\nabla}_d \rho(\vec{r})|^2}{\rho(\vec{r})} d\vec{r}, \quad S[\rho] := - \int_{\mathbb{R}_d} \rho(\vec{r}) \log \rho(\vec{r}) d\vec{r} \quad (1)$$

for the Fisher and Shannon information-theoretic entropies,^[6,7] respectively. The symbol $\vec{\nabla}_d$ denotes the d -dimensional gradient operator. These measures quantify a single facet of the density $\rho(\vec{r})$ of local (Fisher) or global (variance, Shannon) character, such as the concentration around the mean value (variance), the gradient content (Fisher information), and the total extent (Shannon entropy) of the density. They have been shown to be very useful in numerous scientific areas, particularly in identifying and characterizing many atomic, molecular, and chemical phenomena, such as correlation properties, level avoided crossings of atoms in external electromagnetic fields, and transition states and other stationary points in chemical reactions.^[8–12]

The composite information-theoretic measures have been recently shown to be the most appropriate to describe the intrinsic complexity of the quantum systems and to distinguish among their rich three-dimensional geometries, mainly because they jointly grasp different facets of their internal disorder. This is basically because (a) they are dimensionless; (b) they are invariant under replication (LMC), translation, and scaling transformations; and (c) they have, under certain mathematical conditions, minimal values for both extreme cases: the completely ordered systems (eg, a Dirac delta distribution and a perfect crystal in one and three dimensions) and the totally disordered systems (eg, an uniform or highly flat distribution and an ideal gas in one and three dimensions). The basic composite information-theoretic measures have the following two-ingredient expressions

$$C_{LMC}[\rho] = e^{S_V} \times \int_{R_0} [\rho(\vec{r})]^2 d\vec{r}, \quad C_{FS}[\rho] = F[\rho] \times \frac{1}{2\pi e} e^{3S_V} \quad (2)$$

for the Lopezruiz-Mancini-Calvet (LMC)^[13,14] and the Fisher-Shannon complexities $C_{FS}[\rho]$ ^[15,16] respectively, and

$$C_{CR}[\rho] = F[\rho] \times V[\rho] \quad (3)$$

for the Crámer-Rao complexity.^[17] Note that the LMC complexity measures the density nonuniformity through the combined effect of its total spreading and average height, while the Fisher-Shannon complexity grasps the oscillatory nature of the density together with its total extent in the configuration space, and the Crámer-Rao quantity takes into account the gradient content of the density along with its concentration around the centroid. The Crámer-Rao complexity measure occupies a special position among the intrinsic two-product complexity quantifiers of the internal disorder of the quantum systems. Indeed, it is the ONLY one that measures the localization of the probability density around its nodes (as given by the Fisher information) along with the concentration around the mean (as given by the variance). The variance measures an average of distances of outcomes of the probability distribution from the mean. Although the Shannon entropy, the disequilibrium, the Rényi entropies (which are components of the other two-product complexities), and the variance are measures of dispersion and uncertainty, the lack of a simple relationship between orderings of a distribution by these entropy-like and variance measures emanates from quite substantial and subtle differences. Both entropy-like and variance measures reflect concentration, but their respective metrics for concentration are different. Unlike variance, which measures concentration around the mean, entropy-like measures quantify diffuseness of the density irrespective of the location(s) of concentration.

The study of the internal disorder for the confined multidimensional quantum systems by means of entropy- and complexity-like measures is an area that has received increasing momentum per se (the confinement effects on the charge and momentum distributions of the quantum systems are not yet well established) because of the growing number of relevant applications in numerous fields of science and engineering, from surface chemistry to quantum technologies, where, for example, confined atoms have been recently suggested as building elements of qubits. This is illustrated by the various reviews/states-of-the-art that have appeared in the last few years.^[18–21]

Here, we are interested in the electronic complexity of the spherically confined two-dimensional hydrogen atom (in short, 2D-HA), both in position and momentum spaces. This atom is the prototype that has been used to interpret numerous phenomena and systems in surface chemistry,^[22–24] semiconductors (see, eg, Li et al.^[25]), quantum dots,^[26,27] atoms and molecules embedded in nanocavities (eg, fullerenes, helium droplets, ...),^[18,19,21,28–30] dilute bosonic and fermionic systems in magnetic traps of extremely low temperatures,^[31–33] and a variety of quantum-information elements.^[34,35] Up until now, contrary to the stationary states of the confined 3D-HA, where both the (energy-dependent) spectroscopic and the (eigenfunction-dependent) information-theoretic properties have received much attention,^[27,36–45] the knowledge of these properties for the confined 2D-HA is quite scarce.^[46–50] Just recently, the authors have determined^[51] the entropy-like (Shannon, Fisher) and complexity-like (Fisher-Shannon, LMC) measures for a few low-lying stationary states of the confined 2D-HA. The aim of this work is to extend this informational approach by means of the calculation of the confinement dependence of the variance and the Crámer-Rao complexity measure for the 1s, 2s, 2p, and 3d quantum states of the 2D-HA in the two conjugated spaces.

The structure of this work is as follows. In Section 2, we first analytically discuss the eigenvalue free (unconfined) d -dimensional hydrogen problem from an informational point of view, with application to the 1s, 2s, 2p, and 3d states of the free two-dimensional case. In Section 3, the computational method to solve the eigenvalue confined two-dimensional hydrogen problem is described, and the probability densities that characterize the stationary states of this system are given in both position and momentum spaces. In Section 4, we calculate and discuss the variance, the Fisher information, and the Crámer-Rao complexity of these densities in both conjugated spaces for various stationary states of the confined 2D-HA. Therein, it is explicitly shown how the values of these quantities progress toward the corresponding free constant values analytically found in Table 1 of Section 2, which is a further check of our results. Finally, some concluding remarks are made.

2 | THE EIGENVALUE D -DIMENSIONAL HYDROGEN PROBLEM: AN INFORMATIONAL APPROACH

In this section, we briefly describe the analytical solution of the nonrelativistic eigenvalue problem for the free (ie, unconfined) d -dimensional hydrogen atom in both position and momentum spaces. The main purpose of this section is to analytically obtain the expressions of the variance

TABLE 1 Variance, Fisher information, and Crámer-Rao complexity for various low-lying states of the free 2D-HA in position and momentum spaces

| State | $V[\rho]$ | $V[\gamma]$ | $F[\rho]$ | $F[\gamma]$ | $C_{Cr}[\rho]$ | $C_{Cr}[\gamma]$ |
|-------|-----------|-------------|-----------|-------------|----------------|------------------|
| 1s | 0.1250 | 1.5326 | 16.0000 | 1.5000 | 2.0000 | 2.2989 |
| s | 2.3750 | 0.2902 | 1.7777 | 58.2000 | 4.2220 | 16.8896 |
| p | 2.2500 | 0.0975 | 0.5925 | 18.0000 | 1.3331 | 1.7550 |
| d | 9.3750 | 0.0245 | 0.1280 | 62.5000 | 1.2000 | 1.5312 |

and the Fisher information of the free two-dimensional hydrogen atom and their corresponding products, which give the Crámer-Rao complexity measures in the two conjugated spaces as shown in Table 1 for various low-lying states. They will be used in Section 4 to check the validity of our confined complexity results when confinement becomes weaker and weaker. The resulting electron probability densities are used to determine the dispersion and Fisher information measures of the (ns) and circular states of this system in a rigorous way, with applications to the 1s, 2s, 2p, and 3d stationary states of the free 2D-HA. The Schrödinger equation of the free (ie, unconfined) d -dimensional hydrogenic system has the form

$$\left(-\frac{1}{2}\nabla_d^2 + \mathcal{V}(r)\right)\Psi(\vec{r}) = E\Psi(\vec{r}), \quad (4)$$

in atomic units, where $\vec{r} = (r, \theta_1, \theta_2, \dots, \theta_{D-1})$ in hyperspherical units and $r \in [0, +\infty)$. The symbols ∇_d and $\mathcal{V}(r)$ denote the d -dimensional gradient operator and the Coulomb potential $\mathcal{V}(r) = \frac{1}{r}$, respectively. It has been shown^[5,52] that the wavefunctions of this system are characterized by the energies

$$E = -\frac{1}{2\eta^2}, \quad \eta = n + \frac{d-3}{2}; \quad n = 1, 2, 3, \dots, \quad (5)$$

and the associated eigenfunctions

$$\Psi_{n,l,\{\mu\}}(\vec{r}) = R_{n,l}(\eta, r) \times Y_{l,\{\mu\}}(\Omega_{d-1}), \quad (6)$$

where $(l, \{\mu\}) \equiv (l \equiv \mu_1, \mu_2, \dots, \mu_{d-1})$ denotes the hyperquantum numbers associated with the angular variables $\Omega_{d-1} \equiv (\theta_1, \theta_2, \dots, \theta_{d-1})$, which may take all values consistent with the inequalities $l \equiv \mu_1 \geq \mu_2 \geq \dots \geq |\mu_{d-1}| \equiv |m| \geq 0$. The radial part of the eigenfunction is given by

$$R_{n,l}(\eta, r) = \left(\frac{\lambda^{-d}}{2\eta}\right)^{1/2} \left[\frac{\omega_{2l+1}(\vec{r})}{r^{d-2}}\right]^{1/2} L_{\eta-l-1}^{(2l+1)}(\vec{r}), \quad (7)$$

where $\lambda = \frac{\eta}{2}$, $\vec{r} = \frac{r}{\lambda}$, L is

$$L = l + \frac{d-3}{2}, \quad l = 0, 1, 2, \dots, \quad (8)$$

and the symbol $L_k^{(\alpha)}(x)$ denotes the orthonormal Laguerre polynomial of degree k with respect to the weight $\omega_\alpha(x) = x^\alpha e^{-x}$ on the interval $[0, \infty)$. The angular part of the eigenfunction is given by the known hyperspherical harmonics $Y_{l,\{\mu\}}(\Omega_{d-1})$.^[5,52]

Then, the position probability density for a generic $(n, l, \{\mu\}) \equiv (n, l \equiv \mu_1, \mu_2, \dots, \mu_{d-1})$ state of the free d -dimensional hydrogenic systems is

$$\rho(\vec{r}) = |\Psi_{n,l,\{\mu\}}(\vec{r})|^2 = R_{n,l}^2(\eta, r) \times |Y_{l,\{\mu\}}(\Omega_{d-1})|^2. \quad (9)$$

which is normalized so that $\int \rho(\vec{r}) d\vec{r} = 1$.

The probability density in momentum spaces $\gamma(\vec{p})$ is obtained by squaring the d -dimensional Fourier transform of the configuration eigenfunction, that is, the momentum eigenfunction,^[5]

$$\tilde{\Psi}_{n,l,\{\mu\}}(\vec{p}) = M_{n,l}(\eta, \vec{p}) \times Y_{l,\{\mu\}}(\Omega_{d-1}), \quad (10)$$

whose radial part is

$$M_{n,l}(p) = \left(\frac{\eta}{Z}\right)^{d/2} (1+\gamma)^{3/2} \left(\frac{1+\gamma}{1-\gamma}\right)^{\frac{d-2}{4}} \sqrt{\omega_{L+1}^{l+1}(\gamma) \tilde{C}_{\eta-L-1}^{l+1}(\gamma)}. \quad (11)$$

where $\gamma \equiv (1 - \eta^2 p^2)/(1 + \eta^2 p^2)$, and the symbol $\tilde{C}_m^a(x)$ denotes the orthonormal Gegenbauer polynomials with respect to the weight function $\omega_a^*(x) = (1-x^2)^{a-\frac{1}{2}}$ on the interval $[-1, +1]$. Then, the momentum probability density for a generic $(n, l, \{\mu\}) \equiv (n, l, \mu_1, \mu_2, \dots, \mu_{d-1})$ state of the free d -dimensional hydrogenic systems is

$$\gamma(\vec{p}) = |\tilde{\Psi}_{n,l,\{\mu\}}(\vec{p})|^2 = M_{n,l}^2(p) [Y_{l,\{\mu\}}(\Omega_{d-1})]^2, \quad (12)$$

which is normalized so that $\int \gamma(\vec{p}) d\vec{p} = 1$.

Let us highlight that all the dispersion, entropy-like, and complexity-like, which quantify the different facets of the electron delocalization and complexity of the free d -dimensional hydrogenic system in both position and momentum spaces, can be obtained by calculating the corresponding expressions given in the previous section for the position and momentum densities of the system that we have just found. In particular, as

$$\langle r^\alpha \rangle \equiv \int_{R_d} r^\alpha \rho(\vec{r}) d\vec{r} = \int_0^\infty r^{\alpha+d-1} R_n^2(r) dr = \frac{1}{2\pi} \left(\frac{\eta}{Z}\right)^\alpha \int_0^\infty \omega_{2l+1}(\tilde{r}) \left[\tilde{Z}_n^{(2l+1)}(\tilde{r})\right]^2 r^{\alpha+1} d\tilde{r}, \quad (13)$$

we have the values.^[5]

$$\langle r \rangle = \frac{1}{2} [3\eta^2 - L(L+1)]; \quad \langle r^2 \rangle = \frac{1}{2} \eta^2 [5\eta^2 - 3L(L+1) + 1], \quad (14)$$

so the variance $V[\rho] = \langle r^2 \rangle - \langle r \rangle^2$ has the value

$$V[\rho] = \frac{1}{4} [\eta^2 (\eta^2 + 2) - L^2 (L+1)^2]. \quad (15)$$

In addition, one can obtain the values^[53,54]

$$F[\rho] = 4\langle p^2 \rangle - 2|m|(2l+d-2)\langle r^{-2} \rangle \quad (16)$$

$$= \frac{4}{\eta^3} |\eta - |m||, \quad d \geq 2. \quad (17)$$

for the position Fisher information of an arbitrary state $(n, l \equiv \mu_1, \mu_2, \dots, \mu_{d-1})$ of the system. Similar expressions can be obtained for the variance and Fisher information of the d -dimensional hydrogen atom in momentum space.^[5] Indeed, one has

$$\langle p^2 \rangle = \frac{1}{\eta^2} \quad (18)$$

and

$$F[\gamma] = 4\langle r^2 \rangle - 2|m|(2l+d-2)\langle p^{-2} \rangle \quad (19)$$

$$= 2\eta^2 [5\eta^2 - 3L(L+1) - |m|(8\eta - 6L - 3) + 1]; \quad d \geq 2. \quad (20)$$

for the momentum expectation value $\langle p^2 \rangle$ and the momentum Fisher informations of an arbitrary state $(n, l, \{\mu\})$, respectively. Surprisingly, the mean momentum expectation value $\langle p \rangle$ is not yet explicitly known for any state but only for very-high lying (ie, Rydberg) states (where the value is $\frac{2}{\pi}$ ^[55]) and a few low-lying states of ns and circular types (see Appendix). Let us also mention that, with the previous considerations about the variance, and as the Fisher informations of the d -dimensional probability density $\rho(\vec{r})$ and the one-dimensional density $\rho(r)$ are equal for

unconfined spherically symmetrical systems, one finds that the Crámer-Rao products $\langle (r^2) - \langle r \rangle^2 \rangle \times F[\rho]$ and $\langle (p^2) - \langle p \rangle^2 \rangle \times F[\gamma]$ are upper bounded by unity. Moreover, the modified Crámer-Rao products $\langle r^2 \rangle \times F[\rho] \geq d^2$ and $\langle p^2 \rangle \times F[\gamma] \geq d^2$ are also fulfilled^[56-58]; in both cases, the minimal bound is reached by the ground state of the d -dimensional harmonic oscillator.

Finally, from the general position expressions (15) and (17) and the corresponding ones in momentum space, we can obtain the values gathered in Table 1 of the position and momentum variance and Fisher information for the 1s, 2s, 2p, and 3d quantum states of the free 2D-HA (where $d = 2$). Indeed, with $L = m + \frac{d-3}{2}$ and $d = 2$, one has, for example,

$$V[\rho] = \frac{1}{8}(2n^4 - 4n^3 + 7n^2 - 5n - 2m^4 + m^2 + 1), \quad F[\rho] = \frac{32(n-m-\frac{1}{2})}{(2n-1)^3} \quad (21)$$

for the variance and Fisher information of any quantum state (n, m) of the free 2D-HA in position space, respectively, and

$$V[\gamma] = \frac{4}{(2n-1)^2} \left(1 - \frac{\Gamma(n+\frac{1}{2})^4}{n^2 \Gamma(n)^4} \right), \quad F[\gamma] = \frac{1}{2}(2n-1)^2(n+2), \quad (22)$$

for the variance and Fisher information of any quantum state $(n, n-1)$ of the free 2D-HA in momentum space, respectively. See also the Appendix, where you also have $V[\gamma](2s) = \frac{4}{9} - \frac{\pi^2}{64} \simeq 0.2902$. Moreover, taking into account Equation (3), the last two columns of Table 1 collect the position and momentum Crámer-Rao complexity measures for the four states of the free 2D-HA under study.

3 | CONFINED 2D-HYDROGEN ATOM: COMPUTATIONAL METHODOLOGY

In this section, the computational methodology used to compute the electronic wavefunctions and the associated probability densities for the stationary states (n, m) of the confined two-dimensional hydrogen atom (ie, an electron moving around the nucleus in a circular region of radius r_0 with impenetrable walls and the nucleus clamped at the center) in both position and momentum spaces is described. This confined 2D-HA obeys the Schrödinger Equation (4) with $d = 2$ and $\vec{r} = (r, \theta)$, where $r \equiv |\vec{r}| \in [0, r_0]$ and $\theta \in [0, 2\pi]$; so, their stationary states are characterized by two quantum numbers (n, m) with $n = 1, 2, \dots$ and $m = 0, 1, \dots, n-1$. The states with $m = n-1$ are usually called circular states. This equation cannot be solved in an analytical way, except for the limiting case $r_0 \rightarrow \infty$, which corresponds to the free (ie, unconfined) system already considered in Section 2 for $d \geq 2$ dimensions.

To compute the eigensolutions $\Psi_{nm}^{(r_0)}(\vec{r}; \alpha)$ of the Schrödinger equation of the confined 2D-HA, we have used the variational methodology described by Aquino et al.^[48] in the two-dimensional case and by Rojas et al.,^[59] Marin and Cruz,^[60] Nascimento et al.,^[38] Rojas et al.,^[59] and Jiao et al.^[39] in the three-dimensional case. Then, we obtain

$$\Psi_{nm}^{(r_0)}(\vec{r}; \alpha) = R_{nm}^{(r_0)}(r; \alpha) \frac{e^{im\theta}}{\sqrt{2\pi}}, \quad (23)$$

where α is a variational parameter, and the approximate radial part $R_{nm}^{(r_0)}(r; \alpha)$ is given by

$$R_{nm}^{(r_0)}(r; \alpha) = N_{nm}'(\alpha) e^{-\alpha r} (ar)^{|m|} L_{n-|m|-1}^{2|m|}(\alpha r) \chi^{(r_0)}(r) \quad (24)$$

where the cut-off function $\chi^{(r_0)}(r) = \left(1 - \frac{r}{r_0}\right)$, $N_{nm}'(\alpha)$ denotes the normalization constant, and the optimized values of α are variationally derived. For further details about the role of the cut-off function, we refer to some careful and systematic studies recently published.^[38,59] The energies of the corresponding quantum states are numerically obtained as a function of the confinement radius r_0 by minimizing the functional $E(\alpha) = \langle \Psi | H | \Psi \rangle$ with respect to the variational parameter α . The confinement dependence of the first few low-lying states E_{10} , E_{20} , E_{21} , and E_{32} is shown in Figure 1.

We observe that, for large values of r_0 , these energies decrease monotonically toward their respective values for the free case. The free constancy is reached for a state-dependent critical value r_c of r_0 , having values of 2 a.u. (1s), 3 a.u. (2s, 2p), and 5 a.u. (3d). Moreover, for all quantum states, it was found that the greater the confinement (ie, the smaller r_0), the greater the energy. Note, nevertheless, that the confinement-dependent energetic lines E_{20} and E_{32} cross each other at $r_0 \simeq 1$ a.u., giving rise to the so-called (2s,3d) inversion. In fact, this is a common feature in systems confined by cavities with impenetrable walls.

The associated wavefunctions of the confined 2D-HA system in momentum space are determined by computing the Fourier transform of the position wavefunctions $\Psi_{nm}^{(r_0)}(\vec{r}; \alpha)$ given by Equation (23), obtaining

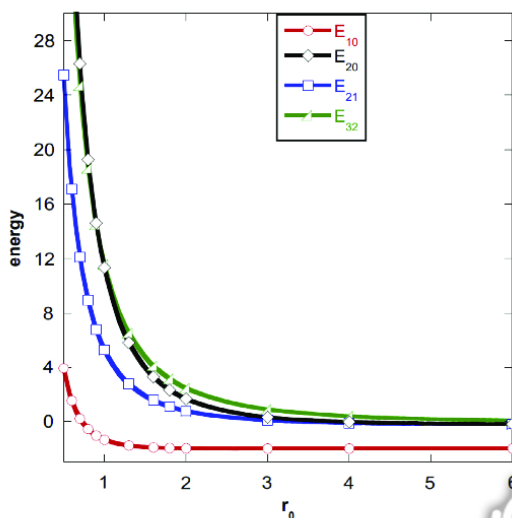


FIGURE 1 Confinement dependence of the energies E_{10} , E_{20} , E_{21} and E_{32} for the 1s, 2s, 2p, and 3d states of the 2D-HA, respectively. Atomic units have been used

$$\begin{aligned}\Phi_{n,m}^{(r_0)}(\vec{p}) &= \frac{1}{2\pi} \int_{R_2} \Psi_{n,m}^{(r_0)}(\vec{r}; \alpha) e^{-i\vec{p}\cdot\vec{r}} d\vec{r} \\ &= (2\pi)^{-\frac{3}{2}} \int_0^{r_0} R_{n,m}^{(r_0)}(r; \alpha) r \left[\int_0^{2\pi} e^{im\theta} e^{-i\vec{p}\cdot\vec{r}} d\theta \right] dr,\end{aligned}$$

which can be expressed as

$$\Phi_{n,m}^{(r_0)}(\vec{p}) = \frac{i^{3m} e^{im\theta_0}}{(2\pi)^{3/2}} \int_0^{r_0} R_{n,m}^{(r_0)}(r; \alpha) J_m(rp) r dr, \quad (25)$$

where we have taken into account the integral representation of the Bessel function, $J_n(z) = \frac{1}{2\pi i} \int_0^{2\pi} e^{inz} e^{iz \cos \theta} d\theta$, and its parity property, $J_n(-z) = (-1)^n J_n(z)$.

Finally, the position and momentum probability densities of the 2D-HA are given by

$$\rho_{n,m}(\vec{r}; r_0) = |\Psi_{n,m}^{(r_0)}(\vec{r}; \alpha)|^2; \quad \gamma_{n,m}(\vec{p}; r_0) = |\Phi_{n,m}^{(r_0)}(\vec{p}; \alpha)|^2, \quad (26)$$

respectively, which are the basic variables of the information theory of the confined two-dimensional hydrogenic system. They will be used to compute the dispersion- and complexity-like quantities of the system in the next sections.

4 | VARIANCE AND CRÁMER-RAO COMPLEXITY OF 2D-HYDROGENIC STATES

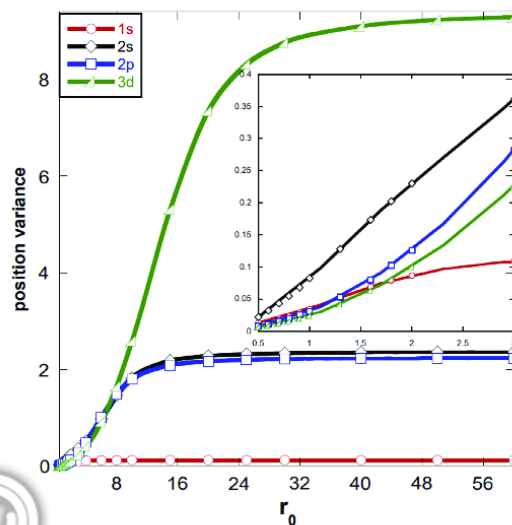
In this section, we study the confinement dependence of the variance, the Fisher information, and the Crámer-Rao complexity measure for the 1s, 2s, 2p, and 3d states of the confined two-dimensional hydrogenic atom in both position and momentum spaces. These measures quantify the confinement effects on the concentration around the mean value and the gradient content of the charge and momentum delocalization of the system in an individual and joint manner, respectively.

4.1 | The variance

As

$$\langle r^\alpha \rangle \equiv \int_{R_2} r^\alpha \rho_{n,m}(\vec{r}; r_0) d\vec{r} = \int_0^\infty r^{\alpha+d-1} |R_{n,m}^{(r_0)}(r; \alpha)|^2 dr,$$

FIGURE 2 Confinement dependence of the variance for the 1s, 2s, 2p, and 3d states of the confined 2D-HA in position space. Atomic units have been used



the variance of the probability density for a generic quantum state (n, m) of the confined 2D-HA is given by

$$V[\rho_{n,m}(\vec{r}; r_0)] = \int_0^{r_0} r^3 |R_{n,m}^{(r_0)}(r; \alpha)|^2 dr - \left(\int_0^{r_0} r^2 |R_{n,m}^{(r_0)}(r; \alpha)|^2 dr \right)^2 \quad (27)$$

in position space and by

$$V[\gamma_{nm}(\vec{p}; r_0)] = \int_0^{r_0} p^3 |\phi_{nm}^{(r_0)}(p)|^2 dp - \left(\int_0^{r_0} p^2 |\phi_{nm}^{(r_0)}(p)|^2 dp \right)^2 \quad (28)$$

in momentum space, where the symbol $\phi_{nm}^{(r_0)}(p)$ denotes the radial part of the momentum eigenfunction.

In Figures 2 and 3, we show the variance for the quantum states 1s, 2s, 2p, and 3d of the confined 2D-HA as a function of the confinement radius r_0 in both position and momentum spaces, respectively. First, we observe that both position and momentum values for the variance increase and decrease, respectively, to the rigorously calculated (as shown above in Table 1) free values when the confinement radius r_0 increases, reaching the free ones at a state-dependent critical value r_c around 8 a.u.(1s), 20 a.u.(2p), 30 a.u.(3d), and 60 a.u.(2s) in position space and around 2 a.u.(1s), 3 a.u.(2p), 5 a.u.(3d), and 7 a.u.(2s) in momentum space.

Note that, in the (strong) confinement region $(0, r_c)$, the position variance has an increasing first-convex-then-concave behavior, while the momentum variance decreases monotonically to their corresponding free constant values in a concave way. Moreover, from Figure 2, one also observes that, for the circular states (1s, 2p, 3d), the position variances of the electron distribution not only decrease when the confinement radius decreases from the critical values just mentioned, but they also cross each other; for example, the variance of the ground state has two crossings, one with the variance of the state 2p and another one with the variance of the state 3d. In addition, the variance of the state 3d has a crossing with the variance of each of the remaining states. From Figure 3, we realize that, for all quantum states, the greater the confinement (ie, the smaller r_0), the greater the momentum variance. This is a behavior similar to the confinement dependence of the energy shown in Figure 1. Note, however, that the confinement effect on the momentum variance provokes three crossings at around 1.2 a.u., 1.8 a.u., and 2.7 a.u. of (1s;2p), (1s;3d), and (1s;2s) character, respectively, while in Figure 1, we only had an energy (3d;2s) inversion at around 1 a.u.

4.2 | The Fisher information

The Fisher information for the stationary states of the confined two-dimensional hydrogenic atom, which are characterized by the position and momentum probability densities $\rho(\vec{r}; r_0)$ and $\gamma(\vec{p}; r_0)$, respectively, defined by Equation (26), is given^[6] (see also^[3]) by

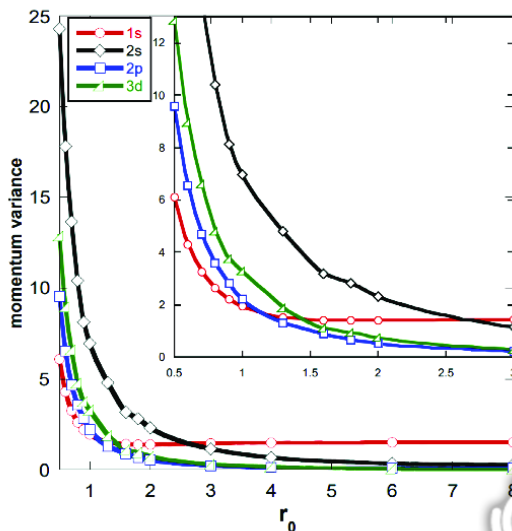


FIGURE 3 Confinement dependence of the variance for the 1s, 2s, 2p, and 3d states of the 2D-HA in momentum space. Atomic units have been used

$$F_{\rho}(r_0) = \int_{R_2} \frac{|\nabla \rho(\vec{r}; r_0)|^2}{\rho(\vec{r}; r_0)} d\vec{r}; \quad F_{\gamma}(r_0) = \int_{R_2} \frac{|\nabla \gamma(\vec{p}; r_0)|^2}{\gamma(\vec{p}; r_0)} d\vec{p}, \quad (29)$$

which satisfy the uncertainty relation $F_{\rho} \times F_{\gamma} \geq 4 \times 2^2 = 16$ for the real wavefunctions of the system,^[61] which in our case occurs for the 1s and 2s states only. The Fisher information $F_{\rho}(r_0)$ for the state (n, m) of a 2D-HA is a local measure of spreading of the density $\rho_{nm}(\vec{r}; r_0)$ because it is a gradient functional of $\rho_{nm}(\vec{r}; r_0)$. The higher this quantity is, the more localized the density, the smaller the uncertainty, and the higher the accuracy in estimating the localization of the particle. Recently (see figure 3 of Estañón et al.^[51]), the Fisher information of the 2D-HA has been computed for the 1s, 2s, 2p, and 3d states. Therein, we found that the Fisher information decreases (position) and increases (momentum) when r_0 is increasing, so that they tend broadly and fast to the free values (analytically calculated in Section 2 and numerically given in Table 1) in such a way that the Fisher information-based uncertainty relation for the 1s and 2s states is always fulfilled because they are described by real wavefunctions.

4.3 | The Crámer-Rao complexity

The Crámer-Rao complexity measure for the stationary states of the 2D-HA, according to Equations (3) and (26), are given by

$$C_{CR}[\rho_{nm}(\vec{r}; r_0)] = F[\rho_{nm}(\vec{r}; r_0)] \times V[\rho_{nm}(\vec{r}; r_0)] \quad (30)$$

and

$$C_{CR}[\gamma_{nm}(\vec{p}; r_0)] = F[\gamma_{nm}(\vec{p}; r_0)] \times V[\gamma_{nm}(\vec{p}; r_0)] \quad (31)$$

in both position and momentum spaces, respectively. These measures quantify the combined balance of the gradient content of the density jointly with its concentration around the centroid in both conjugated spaces. So, they are statistical complexities of local-global character.

In Figures 4 and 5, we show the values of these Crámer-Rao measures for the quantum states 1s, 2s, 2p, and 3d of the confined 2D-HA as a function of the confinement radius r_0 in both position and momentum spaces, respectively. First, we observe that confinement does distinguish charge disorder and momentum complexity for the four quantum states under study. Moreover, these position and momentum measures appear

FIGURE 4 Confinement dependence of the Crámer-Rao complexity measure for the 1s, 2s, 2p, and 3d states of the confined 2D-HA in position space. Atomic units have been used

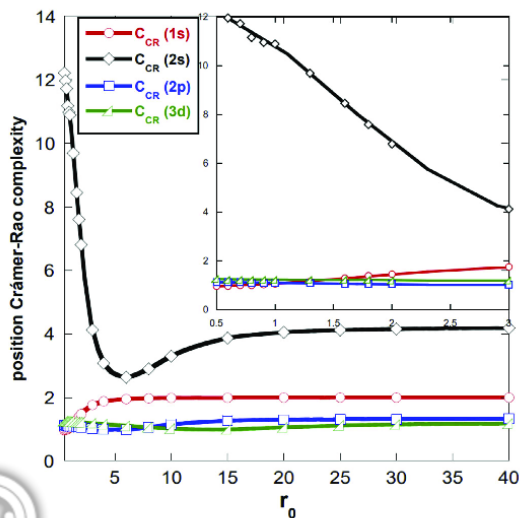
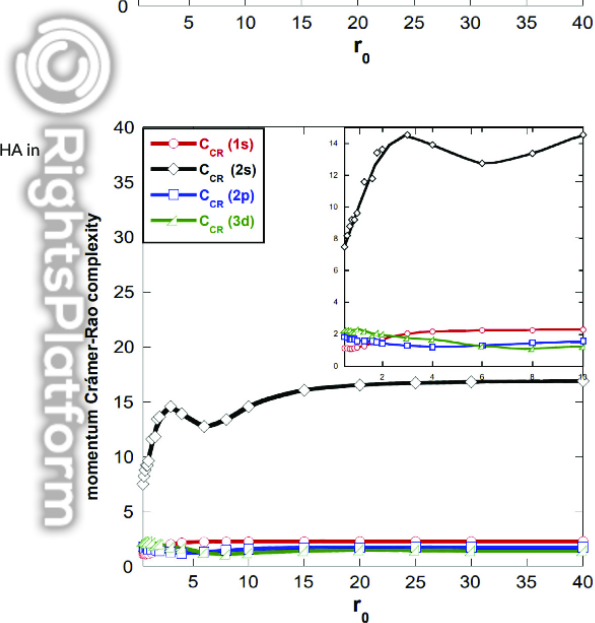


FIGURE 5 Confinement dependence of the Crámer-Rao complexity measure for the 1s, 2s, 2p, and 3d states of the 2D-CHA in momentum space. Atomic units have been used



to be lower-bounded by unity for all values of the confinement radius—that is, not only asymptotically where the system becomes unconfined—and then this property is rigorously fulfilled as already mentioned at the end of Section 2.

Note in Figure 4 that the position Crámer-Rao measures behave differently for the four states when r_0 increases, although all of them tend toward constancy when r_0 is sufficiently large, that is, when confinement is sufficiently weak, and then, the 2D-HA system becomes practically free. Such a constancy is reached at 15 a.u. (or even earlier) for the circular states and at 25 a.u. for the state 2s. Above this critical confinement radius, the Crámer-Rao measure satisfies the inequality chain

$$C_{CR}[3d] < C_{CR}[2p] < C_{CR}[1s] < C_{CR}[2s].$$

Note that these constant free values for the position Crámer-Rao measure are 1.2000 (3d), 1.3331 (2p), 2.0000 (1s), and 4.2220 (2s), which coincide with the values collected in the last two columns of Table 1, which were obtained in a rigorous analytical way; this is a further check of our numerical results.

For stronger confinements, the situation becomes much more involved. Note that the Crámer-Rao ordering for the circular states is altered for values of r_0 less than 10 a.u., and the Crámer-Rao measure $C_{CR}[2s]$ shows a minimum at around 6 a.u. because of the delicate balance of the charge concentration around the centroid and the oscillatory character of the electron density at such a value of the confinement radius.

Similar considerations can be made from Figure 5 for the momentum Crámer-Rao complexity measures of the states 1s, 2s, 2p, and 3d. Here, again, we observe that, for all ground and excited states, this quantity tends toward the corresponding constant known free values when r_0 increases (ie, when the confinement is weaker and weaker) so that it fulfils the same complexity ordering pointed out previously in position space. This constancy is reached at 15 a. u. (or even earlier) for circular states and at 25 a.u. for the state 2s, as in position space. This behavior toward free constancy is, of course, different for each quantum state. In the ground state, the measure smoothly increases when r_0 increases up until the free constant value, which is reached at 4 a. u.. In the first excited state (2s), the momentum Crámer-Rao complexity has a completely different behavior with respect to the position when r_0 increases: the former measure has a pronounced maximum at about $r_0 = 5$ a. u., from which it oscillates to the free constancy. For the circular states 2p and 3d, the values of this momentum measure smoothly vary toward the corresponding free constant values rigorously calculated in Section 2 and collected in Table 1; note that they cross each other at $r_0 = 6$ a. u. All this suggests a strong dependence of the Crámer-Rao complexity measure on the quantum number difference $n - |m|$.

For stronger confinements (eg, when $r_0 < 10$ a. u.), the previous complexity ordering changes, mainly among the momentum complexities of the ground state and the other two circular states; this is basically because of the delicate interplay of the momentum concentration around the centroid and the gradient content of the electron density.

5 | CONCLUSIONS

In this work, the internal disorder of the confined two-dimensional hydrogen atom is studied in a few low-lying quantum states (1s, 2s, 2p, 3d) by means of the variance and the Crámer-Rao complexity measure in both position and momentum spaces as a function of the confinement radius r_0 . These measures, which do not depend on the energy but on the eigenfunction of the state, quantify the pointwise concentration of the electronic charge around the centroid and the combined balance of this concentration and the gradient content of the electron density all over the confinement region, respectively.

We have found that the position and momentum variances increase and decrease, respectively, when the confinement becomes weaker and weaker (ie, when r_0 is increasing) so that, for a critical confinement radius onward, the variances have the values of the free (unconfined) 2D-HA, which are rigorous and analytically determined. This critical radius is bigger in position space than in momentum space for each state. Moreover, the variances move monotonically up (in position space) and down (momentum space) without crossing, except for the ground state, to the corresponding free values. Then, the greater the confinement (ie, the smaller r_0), the smaller the position variance and the greater the momentum variance.

We have also shown here that confinement does distinguish complexity of the 2D-CHA for all stationary states by means of the Crámer-Rao measure in the two conjugated spaces. These quantities tend in various ways toward the corresponding constant free values for both ground and excited states when the confinement radius r_0 increases. This constancy, which is also analytically calculated, is reached at a critical confinement radius, which is much lower for circular states than for the state 2s basically because of the bigger relative gradient content. So, this complexity measure best detects the confinement effects when the impenetrable wall of the system is located at a gradually smaller critical radius.

The present results, together with some recent efforts on information entropies of global (Shannon, Rényi, Tsallis)^[37,40,41] and local (Fisher, relative Fisher)^[37,42,44,62,63] character for numerous excited states of three-dimensional free and confined hydrogen-like systems, illustrate how and how much confinement is crucial not only for the energy spectrum of multidimensional hydrogen^[20,64] but also for its eigenfunction-dependent information-theoretical properties that control all the chemical and physical properties.

AUTHOR CONTRIBUTIONS

Carlos Estañón: Data curation; formal analysis; investigation; methodology. **Norberto Aquino:** Conceptualization; investigation; methodology; validation. **David Puertas-Centeno:** Data curation; investigation; methodology; validation. **Jesus Sanchez-Dehesa:** Conceptualization; funding acquisition; investigation; methodology; supervision; writing-original draft; writing-review and editing.

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REFERENCES

- [1] K. D. Sen Ed., *Statistical Complexities: Application to Electronic Structure*, Springer, Berlin 2011.
- [2] D. R. Herschbach, J. Avery, O. Goscinski Eds., *Dimensional Scaling in Chemical Physics*, Kluwer, Dordrecht, The Netherlands 1993.