



## Research paper

## Fisher information in confined hydrogen-like ions

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## ABSTRACT

Fisher information ( $I$ ) is investigated for confined hydrogen atom (CHA)-like systems in conjugate  $r$  and  $p$  spaces. A comparative study between CHA and free H atom (with respect to  $I$ ) is pursued. A detailed systematic result of  $I$  with respect to variation of confinement radius  $r_c$  is presented, with particular emphasis on *non-zero*-( $l, m$ ) states. In certain respect, inferences in CHA are significantly different from free counterpart, such as (i) dependence on  $n, l$  quantum numbers (ii) appearance of maxima in  $I_p$  plots for  $|m| \neq 0$ . The role of atomic number and atomic radius is discussed.

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## 1. introduction

In the first half of the twentieth century, Michels et al. [1] designed and proposed a simple model in which a hydrogen atom was enclosed in an impenetrable spherical cavity keeping the nucleus at centre. For these confined quantum systems, the wave function vanishes at a particular boundary which lies at a finite distance but may be extended up to infinity. In such a situation, the particle shows interesting, distinctive changes in its observable properties [2,3]. Such a model of confinement can be exploited as a realistic approximation to various physical and chemical environments [4], with particular importance in the field of condensed matter, semiconductor physics, astrophysics, nano-science and technology, quantum dots, wires and wells [5,6,8]. In last few decades, confined quantum systems like atoms, molecules either in fullerene cage or inside the cavities of zeolite molecular sieves, and in solvent environments, have been explored extensively [6–8].

In recent years, information theory has emerged as a subject of topical interest. At a fundamental level, this explicitly deals with single-particle probability density  $\rho(\tau)$  of a system ( $\tau$  is a generalized variable). Hence, statistical quantities directly related to  $\rho(\tau)$  have their importance in predicting and explaining numerous interesting phenomena in both physics as well as in chemistry [9]. A few examples of them are information entropies like Rényi ( $R$ ) and Shannon ( $S$ ) entropy, Fisher information ( $I$ ), Onicescu energy ( $E$ ), etc. As a consequence of the fact that,  $I$  represents the gradient functional of density, it measures the local fluctuation of

space variable. An increase in  $I$  indicates localization of the particle. In other words with the rise in  $I$ , the density distribution gets concentrated as well as uncertainty reduces [9]. It is important to note that,  $I$  resembles the Weizsäcker kinetic energy functional ( $T_w[\rho]$ ) frequently used in density functional theory (DFT) [10]. Lately, a *Euler* equation in orbital-free DFT has been formulated with the help of  $I$  and  $S$  [11]. For spherically symmetric systems this equation can be formalized by using only a specific form of  $I$  [11]. Because of its ability to predict and explain versatile properties,  $I$  has been especially invoked to explore Pauli effects [12,13], ionization potential, polarizability [14], entanglement [15], avoided crossing [16], in atomic systems. In molecular systems,  $I$  has been exploited to investigate steric effect [17,18], bond formations [19], elementary chemical reactions [20].

About a decade ago, numerical investigation of  $I$  for ground-state of neutral atoms [21,22] was made. Some analysis from analytical standpoint was given in [23], where the authors formulated a pair of equations to compute  $I_r, I_p$  in *central potentials*. Accordingly, they are expressed in terms of four expectation values viz.,  $\langle p^2 \rangle, \langle r^{-2} \rangle$  and  $\langle r^2 \rangle, \langle p^{-2} \rangle$  respectively. In recent time,  $I$  in both  $r$  and  $p$  spaces have been reported for various model diatomic potentials, such as Pöschl-Teller [24], pseudo-harmonic [25], Tietz-Wei [26], Frost-Musulin [27], Generalized Morse [28], and exponential-cosine screened coulomb [29] potential.

Study of  $I$  in a *confined* hydrogen atom (CHA) is quite scarce. We are aware of only the work of [30], where it was considered for CHA under soft and hard confinement for the ground state only. In this endeavor, our primary objective is to perform an explicit analysis of  $I$  in a CHA-like system, for any arbitrary state characterized by the principal, azimuthal and magnetic quantum numbers  $n, l, m$  in conjugate spaces with a special emphasis on  $l, m \neq 0$

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states. Elucidative calculations are performed with exact analytical wave functions in  $r$ -space; whereas the  $p$ -space, wave functions are obtained from numerical Fourier transform of the  $r$ -space counterpart. Representative results are given for  $1s, 2s, 2p, 3s, 3d, 4s, 4f$  as well as  $5s-5g$  and  $10s-10m$  states, to understand the various effects. Here, we have envisaged all the allowed  $m$ 's corresponding to a given  $n$  and  $l$ , which allows one to follow the detailed changes in the behavior of states with different  $m$  as the environment switches from free to confinement. Changes are also monitored with respect to  $Z$  in H-isoelectronic series under confinement. It may be relevant to mention a recent detailed study [31] of  $S$  in CHA along the same line. Section 2 gives a brief description of the theoretical method used; Section 3 offers a detailed discussion of results of  $I$ , while we conclude with a few comments in Section 4.

## 2. Methodology

The non-relativistic radial Schrödinger equation for a confined H-like ions, without any loss of generality, may be written as (atomic unit employed, unless otherwise mentioned),

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} + v(r) + v_c(r) \right] \psi_{n,\ell}(r) = \mathcal{E}_{n,\ell} \psi_{n,\ell}(r), \quad (1)$$

where  $v(r) = -Z/r$  ( $Z = 1$  for H atom). Our required confinement inside an impenetrable spherical cage is introduced by invoking the following form of potential:  $v_c(r) = +\infty$  for  $r > r_c$ , and  $0$  for  $r \leq r_c$ , where  $r_c$  implies radius of confinement.

Exact generalized radial wave function for a CHA is mathematically expressed as [32,33],

$$\psi_{n,l}(r) = N_{n,l} (2r\sqrt{-2\mathcal{E}_{n,l}})^l {}_1F_1 \left[ \left( l+1 - \frac{1}{\sqrt{-2\mathcal{E}_{n,l}}} \right), (2l+2), 2r\sqrt{-2\mathcal{E}_{n,l}} \right] e^{-r\sqrt{-2\mathcal{E}_{n,l}}}, \quad (2)$$

where  $N_{n,l}$  represents normalization constant and  $\mathcal{E}_{n,l}$  denotes energy eigenvalue of a given state distinguished by  $n, l$  quantum numbers, whereas  ${}_1F_1[a, b, r]$  is a confluent hypergeometric function. Allowed energies are enumerated by imposing Dirichlet boundary condition,  $\psi_{n,l}(0) = \psi_{n,l}(r_c) = 0$  in Eq. (2). In this work, generalized pseudospectral (GPS) method has been applied to compute  $\mathcal{E}_{n,l}$  of CHA. This method has produced very accurate results for the various model and real systems including atoms and molecules in the last decade; some of which could be found in Refs. [34–37].

The  $p$ -space wave functions are obtained numerically from Fourier transform of  $r$ -space counterpart, and as such given as,

$$\xi_{n,l}(\mathbf{p}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int_0^{r_c} \int_0^\pi \int_0^{2\pi} \psi_{n,l}(r) \Theta_{l,m}(\theta) \Phi_m(\phi) e^{ipr\cos\theta} r^2 \sin\theta dr d\theta d\phi. \quad (3)$$

Here  $\xi(\mathbf{p})$  needs to be normalized. The normalized  $r$ - and  $p$ -space densities are represented as,  $\rho(\mathbf{r}) = |\psi_{n,l,m}(\mathbf{r})|^2$  and  $\Pi(\mathbf{p}) = |\xi_{n,l,m}(\mathbf{p})|^2$  respectively. Let  $I_r, I_p$  denote net information measures in conjugate  $r$  and  $p$  space of CHA. It is well established that, for a single particle in a central potential, these quantities can be written in terms of radial expectation values  $\langle r^k \rangle$  and  $\langle p^k \rangle$ , ( $k = -2, 2$ ) [23], as below,

$$I_r = \int_{\mathcal{R}^3} \left[ \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \right] d\mathbf{r} = 4\langle p^2 \rangle - 2(2l+1)|m|\langle r^{-2} \rangle \quad (4)$$

$$I_p = \int_{\mathcal{R}^3} \left[ \frac{|\nabla \Pi(\mathbf{p})|^2}{\Pi(\mathbf{p})} \right] d\mathbf{p} = 4\langle r^2 \rangle - 2(2l+1)|m|\langle p^{-2} \rangle. \quad (5)$$

The above equations can be further recast in the following forms,

$$I_r = 8\mathcal{E}_{n,l} - 8\langle v(r) \rangle - 2(2l+1)|m|\langle r^{-2} \rangle \quad (6)$$

$$I_p = 8\mathcal{E}_{n,l} - 8\langle v(p) \rangle - 2(2l+1)|m|\langle p^{-2} \rangle. \quad (7)$$

where  $v(p)$  is the  $p$ -space counterpart of  $v(r)$ .

In case of H-isoelectronic series,  $I$ 's in  $r$  and  $p$  space are expressed as;

$$I_r(Z) = Z^2 I_r(Z=1), \quad I_p(Z) = \frac{1}{Z^2} I_p(Z=1). \quad (8)$$

Hence, an increase in  $Z$  leads to rise in  $I_r(Z)$  and fall in  $I_p(Z)$ . However, it is obvious that  $I_t (= I_r I_p)$  remains invariant with  $Z$ . Throughout this work,  $I_r(Z=1)$  and  $I_p(Z=1)$  will be denoted as  $I_r, I_p$  respectively.

When  $m = 0$ ,  $I_r$  and  $I_p$  in Eqs. (4) and (5) reduce to simplified forms as below,

$$I_r = 4\langle p^2 \rangle, \quad I_p = 4\langle r^2 \rangle. \quad (9)$$

It is seen that, at a fixed  $n, l$ , both  $I_r$  and  $I_p$  are maximum when  $m = 0$ , decreasing with rise in  $m$ . Hence one obtains the following upper bound for  $I_t$ ,

$$I_r I_p (= I_t) \leq 16\langle r^2 \rangle \langle p^2 \rangle \quad (10)$$

Further manipulation using Eqs. (4) and (5) leads to following uncertainty relations [23],

$$\frac{81}{\langle r^2 \rangle \langle p^2 \rangle} \leq I_r I_p \leq 16\langle r^2 \rangle \langle p^2 \rangle. \quad (11)$$

Therefore, in a central potential,  $I$ -based uncertainty product is bounded by both upper and lower limits. They are state dependent, varying with alterations in  $n, l, m$ .

## 3. Result and discussion

Before we begin, let us examine the nature of the radial probability density for some arbitrary states in CHA. For this purpose we offer Fig. S1 in supplementary material (SM), where these distributions have been plotted for  $5s-5g$  states at four different  $r_c$  values namely 1, 5, 10, 20 (panels (a)–(d)). As expected, in all these states delocalization predominates with an increase in  $r_c$ . Also one gets the desired number of nodes in the plots.

Now, it is appropriate to mention a few points for ease of discussion. To ensure a good accuracy of calculated quantities in  $r$  space, two sets of  $I_r$  were calculated: the first route involves the use of Eq. (4) requiring  $\nabla \rho(\mathbf{r})$ , and the second route employs a simplified expression for central potentials through the expectation values, given in Eq. (6). However, the  $p$ -space calculations are done completely numerically via Eq. (5) and convergence is checked with respect to variation in grid parameter ( $n_r$ , the number of radial points in  $p$  space). Table S1 of SM offers our computed  $I_r, I_p$  values, side by side, to illustrate their convergence. For all states under consideration, convergence is ensured in this manner; so all the results reported in future tables show only those decimal places up to which convergence was attained. The net  $I$  in both space can be separated into radial and angular parts. But in both  $I_r$  and  $I_p$  expressions, angular part is normalized to unity. Hence, evaluation of all these desired quantities using only radial part will serve the purpose. The radial parts of the wave function in  $r, p$  spaces depend on  $n, l$  quantum numbers. Hence,  $p$ -space radial wave function can be generated by putting  $m = 0$  in Eq. (3). Further, a change in  $m$  from zero to non-zero value will not affect the form of the radial wave function in  $p$  space. Confinement in the hydrogen atom is accomplished by pressing the radial boundary from infinity to a finite region. To achieve this effect, pilot

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