Analysis of Compton profile through information theory in H-like atoms inside impenetrable sphere

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Abstract

Confinement of atoms inside various cavities has been studied for nearly eight decades. However, the Compton profile for such systems has not yet been investigated. Here we construct the Compton profile (CP) for a H atom radially confined inside a hard spherical enclosure, as well as in free condition. Some exact analytical relations for the CP’s of circular or nodeless states of free atom is presented. By means of a scaling idea, this has been further extended to the study of an H-like atom trapped inside an impenetrable cavity. The accuracy of these constructed CP has been confirmed by computing various momentum moments. Apart from that, several information theoretical measures, like Shannon entropy ($S$) and Onicescu energy ($E$) have been exploited to characterize these profiles. Exact closed form expressions are derived for $S$ and $E$ using the ground state CP in free H-like atoms. A detailed study reveals that, increase in confinement inhibits the rate of dissipation of kinetic energy. At a fixed $\ell$, this rate diminishes with rise in $n$. However, at a certain $n$, this rate accelerates with progress in $\ell$. A similar analysis on the respective free counterpart displays an exactly opposite trend as that in confined system. However, in both free and confined environments, CP generally gets broadened with rise in $Z$. Representative calculations are done numerically for low-lying states of the confined systems, taking two forms of position-space wave functions: (a) exact (b) highly accurate eigenfunctions through a generalized pseudospectral method. In essence, CPs are reported for confined H atom (and isoelectronic series) and investigated adopting an information-theoretic framework.

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I. INTRODUCTION

In quantum mechanics, electron density (ED) is the most important physical quantity and lies in the heart of chemistry. Because, it is inherently connected with the structure, bonding and reactions-the fundamental pillars. According to Hohenberg-Kohn theorem of density functional theory, when the exact density is known, any property of the system can be calculated exactly. It is larger near the nuclei and covalent chemical bonds. All kinds of chemical interactions affect ED. X-ray diffraction has provided the experimental information about ED. Similarly, electron momentum density (EMD) which is the momentum counterpart of ED, has also been used quite extensively to understand chemical systems. It can be extracted directly from \((e, 2e)\) spectroscopy, position annihilation spectroscopy or X-ray Compton scattering (CS) [1, 2].

Compton effect is an inelastic scattering process [1], with use as spectroscopic probe in both single-particle excitation as well as in collective mode [3]. Linear CS for weakly bound electrons is well explained by the so-called impulse approximation [4], where the electron is assumed to be quasi-free. It means that, the binding energy of the electron is insignificant compared to the energy acquainted to it by the photon, so that the ultimate state of an electron may be adequately represented by a plane wave [5]. Within such an approximation, one can write,

\[
\frac{d^2\sigma}{d\Omega d\epsilon_2} = C(\epsilon_1, \epsilon_2, \phi) J(q).
\]

This equation indicates that, double differential cross section \((\sigma)\) measures the quantity of photon scattered by matter having a solid angle \(\Omega\) with energy \(\epsilon_2\). Here, \(\epsilon_1\) signifies the energy of incident photon and \(\phi\) the scattering angle. \(C(\epsilon_1, \epsilon_2, \phi)\) depends on the experimental setup, while \(J(q)\) corresponds to the Compton profile (CP). It determines the projection of EMD along direction of scattering vector. Importantly it provides the intensity of Compton band. Finally, \(q\) is the projection of target electron momentum upon scattering vector. The concept of CS is well known; for its useful properties and features, one can consult some of the excellent elegant reviews [4, 6, 7].

CS provides information about EMD. They can then be employed to estimate various momentum moments, \(\langle p^n \rangle\). In atomic systems CP was utilized to compute momentum moments, which are directly connected to entropy optimization principle [8, 9]. It was also invoked to analyze isoelectronic atoms [8]. In last two decades, numerous attempts were made to adopt CPs in interpreting various physical and chemical properties in atoms, molecules and solids, both theoretically as well as experimentally [10]. The cutting-edge X-ray CS technique permits us to visualize the bonding in liquids [11] and imaging the hole states of dopants in complex materials [12]. Theoreti-
cal prediction of CP has also been a very fruitful and worthwhile research topic ever since the work of [13]. The agreement between theory and experiment was improved by incorporating electron correlation in the wave function progressively accurately. Substantial amount of work has been reported using wave-function based techniques as well as density functional theory (DFT). A large set of closed-shell molecules were studied at Hartree-Fock (HF), various post-HF and DFT levels [14]. Role of basis set in this context is very critical and has been examined [15]. Several such calculations adopting CI with singles excitation [16], singles-doubles excitations [17] and multiple excitations (up to six fold) [18] were reported. Further, CI calculation by perturbation with multi-configurational zeroth-order wave function via iterative processes has been presented [19]. In DFT, the accuracy of CPs strongly depends on quality of exchange-correlation functional [20].

Many important concepts in physics such as electron correlation [21, 22], EMD [23–25], Fermi surface determination [26–29], X-ray and γ-ray radiations [30–32], were probed through the help of CP. CP is successfully employed to understand the anisotropy in nature of hydrogen bond of crystalline ice [33]. Similarly, the hydrogen bond signature in NH$_4$F$_9$ has been studied [34]. Interestingly, it can explain the metal-insulator transition in La$_{(2-2x)}$Sr$_{(1+2x)}$Mn$_2$O$_7$ [35]. However, in spite of such wide range of applications, CP in confined quantum systems has been rarely investigated neither experimentally nor by theoretical methods (pertaining a few examples), which we attempt to explore in this work.

Ever since its inception, confinement of quantum system has emerged as a subject of topical interest in the field of physics, chemistry, biology, nano-science and nano-technology, attracting a large number of elegant books and review articles [36–43]. Atoms, molecules constricted under cavities of varying size and shape, exhibit distinct fascinating changes in their physical and chemical properties from their free counterpart. Very recently, a new virial-like theorem has been proposed for these systems [44]. Extreme high pressure (of the order of multi-megabar) always influences almost all properties of a chemical system, including (i) the fate of a chemical reaction, (ii) reduction in size of anion (iii) elongation of length in covalent bond (iv) increase in coordination number of an atom in a coordination complex, etc. At such high pressure range, new bond can be formed and existing ones gets deformed (usually shortened, but in certain cases, stretched too) [38]. Besides, the van der Waal’s space gets compressed [46]. Atom under high pressure was first studied as early as in 1937 [45]. Such a situation can be modeled by shifting the spatial boundary from infinity to a certain finite region. Depending upon the capacity of pressure one can simulate them by invoking two broad category of confining potentials, impenetrable (hard) and penetrable (soft). The effect of pressure on CP as well as on autocorrelation functions of MgO polymorphs
were studied in the framework of DFT employing periodic linear combination of atomic orbital method [47]. Interestingly, the experimental investigation of CS under high pressure was done before, for elemental silicon by utilizing synchrotron radiation and Mao-Bell version of the Merrill-Basset diamond anvil cell with a Be gasket up to a pressure of 20 GPa. Moreover, the use of Laue monochromator and a special assembly of compound refractive lenses made this novel experimental setup successful. The detailed description about such unique establishment is available in [48].

In the last twenty years, emergence of information theoretical concept has provided a major impetus in many diverse field of science and technology [49]. They characterize the single-particle density of a system (in conjugate \( r \) and \( p \) spaces) in different complementary ways. Arguably, these are the most eligible measures of uncertainty, as they do not make any reference to some given point of a corresponding Hilbert space [50]. Moreover, these are compactly connected to energetics and experimentally measurable quantities of a given system. Shannon entropy (\( S \)) is the arithmetic mean of uncertainty. Onicescu energy (\( E \)) is the expectation value of density and it is also termed as second-order moment of density [51]. \( E \) is also called \textit{dis-equilibrium}, as it measures the deviation of a distribution from \textit{equilibrium} [52]. Importantly, being reciprocally connected to \( S \), \( E \) usually upholds the inferences obtained from \( S \). Particularlly, in a given space, the increase of spreading in a density distribution is quantified by an increment in \( S \) and decay in \( E \). Both \( S, E \) are successfully employed to quantify various density-distributions produced from relevant theoretical or experimental processes. \( S \) has connection to Colin conjecture [53, 54], atomic avoided crossing [55], electron correlation effect [54], configuration interaction [56], quantum entanglement in artificial atom [57, 58], bond formation [59], elementary chemical reactions [60], orbital-free DFT [61], aromaticity [62] etc. Some of these like the avoided crossing occurs under confinement condition. Further, \( S \) has its distinct ability to characterize artificial quantum systems designed by placing an atom or molecule inside a foreign environment [40]. Likewise, \( E \) has been widely employed to investigate the correlation energy and first ionisation potential in atomic and molecular systems [63]. In stressed condition, the change in confinement strength leads to the variation in electron density distributions. This effect can be characterized by employing these information measures.

In this article, we intend to show the effect of high pressure on CP of a confined quantum system considering a H-like atom under a rigid impenetrable well (solid hydrogen), as test case. The \textit{first principles} study of an atom trapped inside a fullerene cavity can provide accurate results. But they may not direct us to a simple interpretation of the calculated properties [64]. The cavity model has been designed using experimental results [65]. In the present scenario, the motive is to extract
a qualitative idea about the impression of high pressure on CPs of CHA. To a certain extent, this can serve the purpose. The designed CPs are characterized by employing a few information-theoretic measures, which helps uncover the effect of confinement on CP. These measures will act as descriptor in interpreting the CPs. This investigation will act as a threshold to discern the influence of various confined environments (such as quantum dot, encapsulated atom in fullerene cavity [65] and so on) on CPs. It is worthwhile noting that, CP for a free H atom (FHA) was studied before by some researchers [5–7, 13], however, we are not aware of any similar work in a confined H atom (CHA). Besides, the information analysis of CP in either FHA or CHA is not reported as yet. Therefore, at first, we examine the CP in an FHA; it is found to be possible to obtain a generalized expression for circular \( (n - l = 1) \) states, while for other states it needs to be calculated numerically. In the next step, we analyze the Compton Shannon entropy \( (S^c) \), Compton Onicescu energy \( (E^c) \) and generalized entropic moment \( (\alpha \text{ order}) \) using the Compton density, in various states in FHA. As it turns out, these quantities can be derived in closed form only for the lowest state of FHA. Now to pursue the above relevant quantities in a CHA, we apply the following form of potential: \( v_c = \infty \) at \( r \geq r_c \), and zero elsewhere. Here, \( v_c \) represents the perturbing potential and \( r_c \) the confining radius. The calculated CPs were tested by evaluating several momentum moments. It is well established that one can calculate the expectation value of any of the desired momentum moments in a given state, starting from their respective CP [5]. Later, this entire idea has been envisaged to confined H-like atoms (with varying \( Z \), the nuclear charge) by introducing a novel scaling relation. For our calculations, we have chosen six states corresponding to \( n \leq 3 \), which suffices the current purpose. These are done by means of two wave functions, \( \text{viz, exact} \) wave function available in terms of Kummer hypergeometric function and the accurate wave function obtained through a generalized pseudospectral (GPS) method. It is verified that the results of these two methods are practically identical. The article is organized as follows. Section II presents a brief summary of various aspects of methodology used in this work. Section III provides an in-depth discussion of the results for both FHA and CHA. Finally we conclude with a few remarks and future prospects, in Sec. IV.

II. METHODOLOGY

A. Theoretical formalism
The radial Schrödinger equation for a spherically confined system is expressed as,

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

(2)

where \(v(r) = -Z/r\) (\(Z = 1\) for H atom). Our desired high pressure confinement is established by invoking the potential: \(v_c(r) = +\infty\) for \(r > r_c\), and 0 for \(r \leq r_c\), where \(r_c\) implies the radius of the box. This equation needs to be solved under Dirichlet boundary condition, \(\psi_{n,l}(0) = \psi_{n,l}(r_c) = 0\).

The exact wave function for CHA is obtained by solving Eq. (2), which is expressible in terms of Kummer’s M function (confluent hypergeometric) \[66\],

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

(3)

with \(N_{n,\ell}\) denoting normalization constant and \(\mathcal{E}_{n,\ell}\) corresponding to energy of a state represented by \(n, \ell\) quantum numbers. At \(r = r_c\), this equation becomes zero. It is a transcendental type equation and becomes useful when \(\mathcal{E}_{n,\ell}\) are known. At \(r = r_c\),

\[
\frac{1}{\Gamma\left(\ell + 1\right)} \frac{1}{\sqrt{-2\mathcal{E}_{n,\ell}}} \left(2\ell + 2\right) 2r_c \sqrt{-2\mathcal{E}_{n,\ell}} = 0.
\]

(4)

For a certain \(\ell\), first root confirms the energy of the lowest-\(n\) state (\(n_{\text{lowest}} = \ell + 1\)), with successive roots signifying excited states. It is instructive to mention that, to construct the exact wave function of CHA for a definite state, one needs to provide energy eigenvalue of that state.

In current purpose, \(\mathcal{E}_{n,\ell}\) are computed by means of the GPS method, which has produced highly accurate eigenvalues for a number of central potentials, in both free and confined condition \[67-69\].

In this present communication, our objective is to construct the spherically averaged EMD, which is the foundation to generate the CPs. In order to do that, at first, the \(p\)-space wave function can be obtained numerically by the following standard equation,

\[
\psi_{n,\ell}(p) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int_0^\infty \int_0^{\pi} \int_0^{2\pi} \psi_{n,\ell}(r) \Theta(\theta)\Phi(\phi) e^{ipr\cos\theta} r^2 \sin\theta \dr d\theta d\phi,
\]

(5)

\[
= \frac{1}{2\pi} \int_0^\infty \int_0^{\pi} \psi_{n,\ell}(r) P_\ell^0(\cos\theta) e^{ipr\cos\theta} r^2 \sin\theta \dr d\theta.
\]

Note that, \(\psi(p)\) needs to be normalized. Integrating over \(\theta\) and \(\phi\) variables, this equation can be further modified to,

\[
\psi_{n,\ell}(p) = (-i)^{\ell} \int_0^\infty \frac{\psi_{n,\ell}(r)}{p} f(r,p) \dr.
\]

(6)
Depending on $\ell$, this can be expressed in following simplified form ($m'$ starts with 0),

$$f(r, p) = \begin{cases} 
\sum_{k=2m'+1}^{m'=\frac{\ell}{2}} a_k \frac{\cos pr}{p^k r^{k-1}} + \sum_{j=2m'}^{m'} b_j \frac{\sin pr}{p^j r^{j-1}}, & \text{for even } \ell, \\
\sum_{k=2m'}^{m'=\frac{\ell-1}{2}} a_k \frac{\cos pr}{p^k r^{k-1}} + \sum_{j=2m'+1}^{m'} b_j \frac{\sin pr}{p^j r^{j-1}}, & \text{for odd } \ell.
\end{cases}$$

(7)

The coefficients $a_k, b_j$ of even-$\ell$ and odd-$\ell$ states are obtained analytically. In order to get further details, please see the Tables I and II in reference [43].

The spherically averaged EMD or the mean radial distribution function for a definite $n, \ell$-state in $p$ space, $I_{n,\ell}(p)$, can be extracted as [5, 8],

$$I_{n,\ell}(p)dp = \int_{\omega} \left[ \psi_{n,\ell}(p)\psi_{n,\ell}^*(p)p^2 \right] dp = \psi_{n,\ell}(p)\psi_{n,\ell}^*(p)p^2dp,$$

(8)

where $\omega$ is an element of solid angle for $p$. In a given state, $I_{n,\ell}(p)dp$ signifies the probability that $p$ has a magnitude between $p$ and $p + dp$. Therefore, $\int_0^\infty I_{n,\ell}(p)dp = 1$. Now, assuming the impulse approximation, the desired spherically averaged CP of a CHA can be expressed as follows,

$$J_{n,\ell}(q) = \int_{|q|}^{\infty} \frac{I_{n,\ell}(p)}{p} dp.$$

(9)

$J_{n,\ell}(q)$ is a function merely of $q$, with its peak at $q = 0$, while $q$ is the projection of target-electron momentum upon the scattering vector. The momentum moments are then given by,

$$\left\langle \frac{1}{p} \right\rangle_{n,\ell} = 2J_{n,\ell}(q = 0), \quad \left\langle p^m \right\rangle_{n,\ell} = 2(m + 1) \int_0^\infty q^m J_{n,\ell}(q) dq.$$

(10)

Here, our interest is to estimate $S, E$ for CPs; these can be easily expressed in terms of $J(q)$ as,

$$S_{n,\ell}^c = -\int J_{n,\ell}(q) \ln J_{n,\ell}(q) dq, \quad E_{n,\ell}^c = \int J_{n,\ell}^2(q) dq.$$

(11)

A deeply bound electron has a very flat and broad momentum distribution [4]. As a consequence, its CP is also broad. This broadness of distribution can be quantified by $S_c, E_c$. Hence, these measures can act as descriptor about the bound effect on an electron within a quantum system. Our current study will convincingly establish this interpretation.

B. CHA isoelectronic series

In case of the isoelectronic series of CHA, it is interesting to investigate the influence of $Z$ on CPs. In this sub-section, analytical relations between CP and $Z$ have been established by
using some scaling properties. The required radial Schrödinger equation, in terms of a constrained Coulomb potential, can be written as,

\[-\frac{\hbar^2}{2m} \nabla^2 \psi_{n,\ell}(r) - \frac{Z}{r} \psi_{n,\ell}(r) + V_0 \theta(r - r_c) \psi_{n,\ell}(r) = \mathcal{E}_{n,\ell} \psi_{n,\ell}(r),\]

(12)

\[\theta(r - r_c) = 0 \quad \text{at} \quad r \leq r_c, \quad \theta(r - r_c) = 1 \quad \text{at} \quad r > r_c.\]

Here \(\theta(r - r_c)\) is the Heaviside theta function and \(V_0\) is taken to be an infinitely large positive number. After doing some straightforward mathematical manipulations, by transforming \(r = \lambda r_0\) and assuming \(\lambda = \frac{\hbar^2}{mZ}\) one leads to the following form of Hamiltonian,

\[-\frac{1}{2} \nabla_0^2 \psi_{n,\ell}(r_0) - \frac{1}{r_0} \psi_{n,\ell}(r_0) + V_0 \theta \left(r_0 - \frac{mZr_c}{\hbar^2}\right) \psi_{n,\ell}(r_0) = \frac{\hbar^2}{mZ} \mathcal{E}_{n,\ell} \psi_{n,\ell}(r_0).\]

(13)

where \(r_0\) is the new variable with dimension \(\text{M}^{-1}\text{L}^{-3}\text{T}^2\). We assume \(\frac{\hbar^2}{mZ} V_0 \approx V_0\) as \(V_0\) approaches to \(\infty\). Now, a comparison of Eqs. (12) and (13) yields,

\[\mathcal{E}_{n,\ell} \left(\frac{\hbar^2}{m}, Z, r_c\right) = \frac{mZ^2}{\hbar^2} \mathcal{E}_{n,\ell} \left(1, 1, \frac{mZr_c}{\hbar^2}\right),\]

\[\psi_{n,\ell} \left(\frac{\hbar^2}{m}, Z, r_c, r\right) = A \psi_{n,\ell} \left(1, 1, \frac{mZr_c}{\hbar^2}, r_0\right).\]

(14)

Applying the normalization condition, we obtain \(A = \lambda^{\frac{3}{2}}\). The \(p\)-space counterpart of \(\psi_{n,\ell}\) can be achieved by performing the Fourier transformation. It is important to mention that, \(p = \frac{\hbar^2}{\lambda}\).

\[\phi_{n,\ell} \left(\frac{\hbar^2}{m}, Z, r_c, p\right) = \lambda^{\frac{3}{2}} \phi_{n,\ell} \left(1, 1, \frac{mZr_c}{\hbar^2}, p_0\right).\]

(15)

Therefore, the spherically averaged momentum density \(I_{n,\ell}\) will take the form,

\[I_{n,\ell} \left(\frac{\hbar^2}{m}, Z, r_c, p\right) \frac{p^2}{m} dp = \phi_{n,\ell} \left(\frac{\hbar^2}{m}, Z, r_c, p\right) \phi^*_{n,\ell} \left(\frac{\hbar^2}{m}, Z, r_c, p\right) \frac{p^2}{m} dp = \lambda^3 \phi_{n,\ell} \left(1, 1, \frac{mZr_c}{\hbar^2}, p_0\right) \phi^*_{n,\ell} \left(1, 1, \frac{mZr_c}{\hbar^2}, p_0\right) \left(\frac{p_0}{\lambda}\right)^2 \frac{dp_0}{\lambda} \]

(16)

Some further manipulation leads to the expression,

\[\langle p^m \rangle_{n,\ell} = \int p^m I_{n,\ell} \left(\frac{\hbar^2}{m}, Z, r_c, p\right) \frac{p^2}{m} dp = \lambda^m \int \left(\frac{p_0}{\lambda}\right)^m I_{n,\ell} \left(1, 1, \frac{mZr_c}{\hbar^2}, p_0\right) \frac{p_0^2}{m} dp_0 \]

(17)

\[= \frac{1}{\lambda^m} \int p_0^m I_{n,\ell} \left(1, 1, \frac{mZr_c}{\hbar^2}, p_0\right) \frac{p_0^2}{m} dp_0 = \frac{\langle p^m \rangle_{n,\ell}}{\lambda^m}.\]

Our desired spherically averaged Compton density can be achieved adopting the following strategy,

\[J_{n,\ell} \left(\frac{\hbar^2}{m}, Z, r_c, q\right) = \int_{|q|}^\infty I_{n,\ell} \left(\frac{\hbar^2}{m}, Z, r_c, p\right) \frac{p^2}{|p|} dp.\]

(18)
Here, $p = \frac{m}{\lambda}$, then $|q| = \frac{|q_0|}{\lambda}$ and $dp = dp_0$. Hence, applying Eq. (16),

$$J_{n,\ell} \left( \frac{\hbar^2}{m}, Z, r_c, q \right) = \lambda \int_{|q_0|}^{\infty} I_{n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, p_0 \right) \frac{p_0^2 \ dp_0}{p_0}$$

$$= \lambda J_{n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, q_0 \right).$$

(19)

The above equation finally corresponds to the CP for CHA isoelectronic systems. Now, let us try to evaluate various momentum moments as below,

$$\langle p^m \rangle_{n,\ell} = 2(m+1) \int_0^\infty q^m J_{n,\ell} \left( \frac{\hbar^2}{m}, Z, r_c, q \right) dq$$

$$= 2(m+1) \int_0^\infty \left( \frac{q_0}{\lambda} \right)^m \lambda J_{n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, q_0 \right) \frac{dq_0}{\lambda}$$

$$= \frac{1}{\lambda^m} 2(m+1) \int_0^\infty q_0^m J_{n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, q_0 \right) dq_0 = \frac{\langle p^m \rangle_{n,\ell}}{\lambda^m}. $$

(20)

Thus Eqs. (17) and (20) have provided exactly identical expression, implying that our scaling formula in constructing CP for isoelectronic series is correct. Following a similar argument, one can easily write,

$$\langle \frac{1}{p} \rangle_{n,\ell} = \lambda \langle \frac{1}{p_0} \rangle_{n,\ell}. $$

Now, using Eq. (11) and Eq. (19) one can get,

$$S_{c,n,\ell} \left( \frac{\hbar^2}{m}, Z, r_c, q \right) = - \int J_{n,\ell} \left( \frac{\hbar^2}{m}, Z, r_c, q \right) \ln J_{n,\ell} \left( \frac{\hbar^2}{m}, Z, r_c, q \right) dq$$

$$= - \int \lambda J_{n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, q_0 \right) \left( \ln \lambda + \ln J_{n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, q_0 \right) \right) \frac{dq_0}{\lambda}. $$

(21)

Since $\int J_{n,\ell} \left( \frac{\hbar^2}{m}, Z, r_c, q \right) dq = \int J_{n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, q_0 \right) dq_0 = \frac{1}{2}$, we can write,

$$S_{c,n,\ell} \left( \frac{\hbar^2}{m}, Z, r_c, q \right) = - \frac{1}{2} \ln \lambda - \int J_{n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, q_0 \right) \ln J_{n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, q_0 \right) dq_0$$

$$= - \frac{1}{2} \ln \lambda + S_{c,n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, q_0 \right). $$

(22)

An analogous mathematical exercise will lead us to the following expression for Onicescu energy,

$$E_{c,n,\ell} \left( \frac{\hbar^2}{m}, Z, r_c, q \right) = \lambda E_{c,n,\ell} \left( 1, 1, \frac{mZr_c}{\hbar^2}, q_0 \right). $$

(23)

As mentioned earlier, the present calculations are done by engaging two different wave functions, namely, (i) exact wave function given in Eq. (3) and (ii) those obtained numerically through the GPS scheme. In either case, Compton profiles are established numerically in $p$ space. The two results are found to compliment each other in all occasions. Henceforth, we will report results produced from the exact wave function only. 

9
III. RESULT AND DISCUSSION

The results will be discussed in three subsections. At first we present the CP and Compton information quantities on ground and some low-lying excited states of FHA. This offers an opportunity to derive the CPs in nodeless states in closed analytical form. This will help us to distinguish the manifestation of CP and all other measures from FHA to CHA, which is taken up in the second stage. Thus we will discuss and characterize the freshly built CPs of H-atom under high pressure environment, in detail. Finally, the above analysis will be extended to isoelectronic series of CHA.

A. Free H-like atom

In case of FHA like systems \((r_c \to \infty)\) the first-order hypergeometric function modifies to associated Laguerre polynomial with \(E_n = -\frac{Z^2}{2n^2}\). Therefore, Eq. (3) reduces to,

\[
\psi_{n,\ell}(r) = \frac{2}{n^2} \left[ \frac{(n-\ell-1)!}{\ell!} \right]^{\frac{1}{2}} \left[ \frac{2Z}{n} \right]^\ell e^{-\frac{Z}{n}r} L_{(n-\ell-1)}^{(2\ell+1)} \left( \frac{2Z}{n}r \right).
\]  

(24)

It is well-known that the Schrödinger equation of H-like atom in \(p\)-space can be solved exactly. The exact \(p\)-space wave function \([70]\), in this case, assumes the following form,

\[
\psi_{n,\ell}(p) = \frac{n^2}{Z^2} \frac{2}{\pi} \left[ \frac{(n-\ell-1)!}{\ell!} \right]^{\frac{1}{2}} 2^{(2\ell+2)\ell!} \frac{n^\ell}{\{|np|Z\}^{2\ell+2}} \frac{1}{\{(np)^2 + 1\}^{\ell+2}} \left( \frac{p}{Z} \right)^\ell C_{\ell+1}^{\ell+1} \left( \frac{|np|^2 - 1}{|np|^2 + 1} \right),
\]  

(25)

where \(C_{\ell}^{\eta}(t)\) signifies the Gegenbauer polynomial. In what follows, we attempt to provide an accurate analytical form of CP for nodeless states, by designing a generalized equation. From this, simplifying expressions are given for first five circular or nodeless states. For non-circular states, they become somehow involved and we have not pursued as it is aside the main objective of this work. On the other hand, the exact forms of \(S_{n,\ell}^c\) and \(E_{n,\ell}^c\) could be derived only for the ground state; for all excited states, recourse has been taken to numerical method.

We note that, in a circular state \((n-\ell) = 1\) and \(C_{n-\ell-1}^{\ell+1} \left( \frac{|np|^2 - 1}{|np|^2 + 1} \right)\) reduces to unity. Thus, the radial component in \(p\) space simplifies to,

\[
\psi_{n-\ell=1}(p) = \frac{n^2}{Z^2} \frac{2}{\pi} \left[ \frac{1}{(n+\ell)!} \right]^{\frac{1}{2}} 2^{(2\ell+2)\ell!} \frac{1}{\{|np|Z\}^{2\ell+2}} \left( \frac{p}{Z} \right)^\ell.
\]  

(26)

Therefore, the spherically averaged EMD or radial density in \(p\) space takes the form,

\[
I_{n-\ell=1}(p) = \frac{n^4}{Z^3} \frac{2}{\pi} \left[ \frac{1}{(n+\ell)!} \right]^{\frac{1}{2}} 2^{(4\ell+4)\ell!} \frac{1}{\{|np|Z\}^{2\ell+4}} \left( \frac{np}{Z} \right)^{2\ell}.
\]  

(27)

Now, using the definition in Eq. (9) and employing Eq. (27), the CP can be expressed as,

\[
J_{n-\ell=1}(q) = \frac{1}{2} \frac{n^4}{Z^3} \frac{2}{\pi} \left[ \frac{1}{(n+\ell)!} \right]^{\frac{1}{2}} 2^{(4\ell+4)\ell!} \frac{1}{\{|np|Z\}^{2\ell+4}} \left( \frac{np}{Z} \right)^{2\ell} \int_0^\infty \left( \frac{p}{Z} \right)^{2\ell} dp.
\]  

(28)
By setting $\left(\frac{mZ}{\pi}\right)^2 = y$, Eq. (28) can be rewritten as,

$$J_{n-\ell=1}(q) = \frac{n^2}{4Z} \left[ \frac{2}{\pi (n+\ell)!} \right] 2^{(4\ell+4)} (\ell)!^2 \int_0^\infty \frac{y^\ell}{(\frac{mZ}{\pi})^2 (y+1)^{2\ell+4}} \, dy.$$  \hspace{2cm} (29)

Now adopting the binomial expression and replacing $y^\ell = (y+1)^\ell - \sum_{k=1}^\ell \frac{\ell!}{k!(\ell-k)!} y^{(\ell-k)}$, in Eq. (29), one arrives at the following generalized form,

$$J_{n-\ell=1}(q) = \frac{n^2}{4Z} \left[ \frac{2}{\pi (n+\ell)!} \right] 2^{(4\ell+4)} (\ell)!^2 \int_0^\infty \frac{[(y+1)^\ell - \sum_{k=1}^\ell \frac{\ell!}{k!(\ell-k)!} y^{(\ell-k)}]}{(y+1)^{2\ell+4}} \, dy.$$  \hspace{2cm} (30)

This is our general expression for $J_{n-\ell}(q)$ in circular states of H-like atoms. Using appropriate values of $n, \ell$ in Eq. (30), following expressions can be written for five such lowest states:

\begin{align*}
J_{1s}(q) &= \frac{8}{3\pi Z} \left[ \frac{1}{(\frac{2q}{Z})^2 + 1} \right]^3, \quad (31) \\
J_{2p}(q) &= \frac{64}{15\pi Z} \left[ \frac{5}{(\frac{2q}{Z})^2 + 1} \right]^5, \quad (32) \\
J_{3d}(q) &= \frac{3072}{525\pi Z} \left[ \frac{21}{(\frac{3q}{Z})^4 + 7(\frac{3q}{Z})^2 + 1} \right], \quad (33) \\
J_{4f}(q) &= \frac{16384}{2205\pi Z} \left[ \frac{84}{(\frac{4q}{Z})^6} + 36(\frac{4q}{Z})^4 + 9(\frac{4q}{Z})^2 + 1 \right], \quad (34) \\
J_{5g}(q) &= \frac{131072}{14553\pi Z} \left[ \frac{330}{(\frac{5q}{Z})^8} + 165(\frac{5q}{Z})^6 + 55(\frac{5q}{Z})^4 + 11(\frac{5q}{Z})^2 + 1 \right]. \quad (35)
\end{align*}

It is interesting to mention that the expressions for $1s, 2p$ states in Eq. (31) and (32) are the same as those given long times ago in [13]. However the generalized expression, Eq. (30) apparently has not been reported before. Similar exercise can also be undertaken for non-circular states as well. But these are cumbersome and outside the main focus of this work, as they have no bearing on the general conclusions made here. That is why they are not pursued here. Now following Eq. (10),
FIG. 1: CP for all six \( n \leq 3 \) states in CHA at \( r_c \) values 0.1, 10, 20 in panels (a)-(c). See text for details.

one can easily write,

\[
\langle \frac{1}{2p} \rangle_{1s} = \frac{8}{3\pi Z} = \frac{0.84882636}{Z},
\]

\[
\langle \frac{1}{2p} \rangle_{2p} = \frac{64}{15\pi Z} = \frac{1.35812218}{Z},
\]

\[
\langle \frac{1}{2p} \rangle_{3d} = \frac{3072}{525\pi Z} = \frac{1.86256756}{Z},
\]

\[
\langle \frac{1}{2p} \rangle_{4f} = \frac{16384}{2205\pi Z} = \frac{2.36516515}{Z},
\]

\[
\langle \frac{1}{2p} \rangle_{5g} = \frac{131072}{14553\pi Z} = \frac{2.86686859}{Z}.
\]

Now the focus is to investigate \( E^c_{n,\ell} \) and \( S^c_{n,\ell} \) of FHA. The ground-state \( E^c_{1,0} \) and \( S^c_{1,0} \) possess following closed forms (details are provided in Appendix I & II respectively).

\[
E^c_{1,0} = \omega^2 = \left( \frac{8}{3\pi} \right)^2 \frac{1}{Z} B\left( \frac{11}{2}, \frac{11}{2} \right) = \left( \frac{8}{3\pi} \right)^2 \frac{1}{Z} \frac{\Gamma(\frac{11}{2})\Gamma(\frac{11}{2})}{\Gamma(11)} = \left[ \frac{7}{8\pi Z} \right]
\]

(37)

\[
S^c_{1,0} = \frac{1}{2} \ln 24\pi + \frac{1}{2} \ln Z - \frac{7}{4}.
\]

(38)

Finally, when \( Z = 1 \), Eqs. (37), (38) produce \( E^c_{1s} = \frac{7}{8\pi} = 0.27852115 \) and \( S^c_{1s} = \frac{1}{2} \ln 24\pi - \frac{7}{4} = 0.411391858 \). Here, we have restricted ourselves to \( S^c_{n,\ell}, E^c_{n,\ell} \) in \( 1s \) state only. But for higher states, it is difficult to derive their closed forms. However, numerical values can be achieved. Results for some of these states are provided in Table II of Sec. III.B. These outcomes in \( 1s \) provide us an idea to predict the general trend in \( S^c_{n,\ell}, E^c_{n,\ell} \) with respect to \( Z \). Later, Sec. III.C establishes that \( S^c_{n,\ell} \) linearly increases with \( Z \), whereas, \( E^c_{n,\ell} \) is inversely proportional to \( Z \).
B. Confined H atom

Now we shift our focus to the central theme of this work, viz., CHA. The numerically calculated CPs, obtained from Eq. (9), are depicted in Fig. 1. The six lowest states (1s, 2s, 3s, 2p, 3p, 3d) having principal quantum number \( n \leq 3 \) at three \( r_c \) values 0.1, 10, 20, identifying strong, intermediate and weak confinement regions are offered in panels (a)-(c) respectively. Accuracy of these CPs have been thoroughly verified by independently computing selected expectation values, \( \langle \frac{1}{2p} \rangle, \langle p^2 \rangle \) and \( \langle p^4 \rangle \) in accordance with the right side of Eq. (10). The first one is directly connected to Compton profile, whereas \( \langle p^2 \rangle \) is proportional to kinetic energy. Similarly, \( \langle p^4 \rangle \) is related to relativistic kinetic energy. The results obtained using Eq. (10) are collected in Table I, for all six states at seven different box radii, namely, 0.1, 0.2, 0.5, 1, 5, 10, \( \infty \). It is a known fact that, these momentum moments can also be computed by either (a) using eigenfunction (Eq. (3)) in \( r \) space or (b) employing EMD in \( p \) space. The results obtained from Eq. (10) are in complete agreement with the reference values achieved for both free and confined H atom by adopting the above two methods. Due to the lack of space, only 1s state results of CHA are reported in the footnote. All the quantities in this table match up to all the decimal points reported. This convergence acts as a probe about the accuracy of the constructed CPs.

An in-depth analysis of panels (a)-(c) of Fig. 1 suggests that, there appears multiple humps in a given CP, which become prominent with rise in \( r_c \). Interestingly, in a particular state, the number of such humps corroborate the number of radial nodes in that state. Additionally, the sharpness of these CPs enhances with weakening of pressure effect. Similarly a careful examination of Table I reveals that, for a given state characterized by quantum numbers \( (n, \ell) \), the initial intensity \( \langle \frac{1}{2p} \rangle_{n,\ell}^{(q=0)} \) tends to grow with \( r_c \), while both \( \langle p^2 \rangle_{n,\ell} \) and \( \langle p^4 \rangle_{n,\ell} \) decay. The dependence of \( \langle p^2 \rangle_{n,\ell} \) and \( \langle p^4 \rangle_{n,\ell} \) on \( n, \ell \) quantum number at free and confined condition is very clear and supports our previous observation [42]. It may be recalled that, in FHA \( \langle p^2 \rangle \) is independent of \( \ell \) and decays with rise in \( n \). But in CHA it varies with both \( n, \ell \); at a fixed \( \ell \), it grows with \( n \), whereas at a given \( n \), decreases as \( \ell \) progresses. In contrast, \( \langle p^4 \rangle \), in both CHA and FHA, depends on \( n, \ell \), producing similar pattern as found here.

In order to get a further insight, dependency of \( \langle \frac{1}{2p} \rangle_{n,\ell} \) on \( n, \ell \) quantum numbers is addressed in Fig. 2. It may be noted that \( \langle \frac{1}{2p} \rangle \) and \( \langle p^m \rangle \) are inversely proportional to each other. Therefore, this particular study will automatically comment about the qualitative nature of \( \langle p^m \rangle \) with change in \( n, \ell \). From panel (a), it is seen that, at strong confinement region \( (r_c = 0.1) \), for all \( \ell \) initial intensity falls off at the end with rise in \( n \). However, at a fixed \( n \), it advances with rise in \( \ell \).
TABLE I: \(\langle \frac{1}{2p} \rangle, \langle p^2 \rangle, \langle p^4 \rangle\) for six low-lying states of CHA at seven \(r_c\). See text for detail.

| State | Property   | \(r_c = 0.1\) | \(r_c = 0.2\) | \(r_c = 0.5\) | \(r_c = 1\) | \(r_c = 5\) | \(r_c = 10\) | \(r_c = \infty\) |
|-------|------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 1s    | \(\langle \frac{1}{2p} \rangle\)† | 0.0221757 | 0.044248 | 0.109759 | 0.215997 | 0.77876 | 0.84811 | 0.848826§ | 1.000000 |
|       | \(\langle p^2 \rangle\)† | 987.184273 | 246.969146 | 39.724028 | 10.146273 | 1.049068 | 1.000024 | 1.000000 |
|       | \(\langle p^4 \rangle\)† | 975768.196166 | 61315.262248 | 1630.135662 | 120.909615 | 5.170882 | 4.909913 | 4.999999 |
| 2s    | \(\langle \frac{1}{2p} \rangle\) | 0.010106 | 0.020928 | 0.051141 | 0.105489 | 0.76495 | 1.89844 | 2.716244 |
|       | \(\langle p^2 \rangle\) | 3947.9553 | 987.07315 | 158.02331 | 39.580724 | 1.536032 | 0.372064 | 0.249999 |
|       | \(\langle p^4 \rangle\) | 15590054.13617 | 975260.28106 | 25133.4985 | 1611.86976 | 5.682197 | 1.14715 | 0.812499 |
| 3s    | \(\langle \frac{1}{2p} \rangle\) | 0.00639 | 0.01278 | 0.03203 | 0.06439 | 0.35856 | 0.93869 | 4.87468 |
|       | \(\langle p^2 \rangle\) | 8882.714743 | 2220.730969 | 355.373136 | 88.888824 | 3.552168 | 0.829053 | 0.111111 |
|       | \(\langle p^4 \rangle\) | 78909217.8106 | 4933319.9437 | 126570.0272 | 7976.4667 | 17.372167 | 2.127063 | 0.259259 |
| 2p    | \(\langle \frac{1}{2p} \rangle\) | 0.011336 | 0.026655 | 0.066504 | 0.132535 | 0.639057 | 1.111514 | 1.358122§ | 0.249999 |
|       | \(\langle p^2 \rangle\) | 2019.114160 | 504.809879 | 80.805690 | 20.235456 | 0.873647 | 0.313022 | 0.249999 |
|       | \(\langle p^4 \rangle\) | 4077013.91352 | 254881.58402 | 6537.62441 | 411.62171 | 0.91591 | 0.185835 | 0.145833 |
| 3p    | \(\langle \frac{1}{2p} \rangle\) | 0.007478 | 0.014966 | 0.037522 | 0.075258 | 0.393877 | 0.866223 | 2.910261 |
|       | \(\langle p^2 \rangle\) | 5967.983470 | 1492.019831 | 238.750084 | 59.711670 | 2.417646 | 0.614379 | 0.111111 |
|       | \(\langle p^4 \rangle\) | 35617508.568154 | 2226295.030051 | 57029.814217 | 3572.84424 | 6.264438 | 0.535440 | 0.061728 |
| 3d    | \(\langle \frac{1}{2p} \rangle\) | 0.009830 | 0.019656 | 0.049111 | 0.098506 | 0.482851 | 0.935408 | 1.86256756 |
|       | \(\langle p^2 \rangle\) | 3321.761311 | 30.451738 | 132.885252 | 33.233236 | 1.348000 | 0.357810 | 0.111111 |
|       | \(\langle p^4 \rangle\) | 11034178.1130 | 689670.185288 | 17661.762592 | 1105.290838 | 1.860854 | 0.144078 | 0.022222 |

† Near-exact values of \(\langle p^2 \rangle\) for 1s state in CHA obtained by using Eq. (3) at \(r_c = 0.1, 0.2, 0.5, 1, 5, 10, \infty\) are: 987.18427303, 246.96914695, 39.724028075, 10.14627936, 1.049068068, 1.0000248591, 1 respectively.

‡ Near-exact values of \(\langle p^4 \rangle\) for 1s state in CHA obtained by using Eq. (3) at \(r_c = 0.1, 0.2, 0.5, 1, 5, 10, \infty\) are: 975768.19616638, 61315.26224861, 1636.15366289, 120.90961564, 5.17088297, 4.99991343, 5 respectively.

§ Exact values in FHA, from Eq. (30), for 1s, 2p, 3d states are: 0.84882636, 1.35812218, 1.86256756 respectively.

Consequently, with increase in radial nodes (so does kinetic energy), \(\langle \frac{1}{2p} \rangle\) decreases and vice-versa. On the contrary, as \(r_c \to \infty\) in panel (d), a completely opposite trend of \(\langle \frac{1}{2p} \rangle\) with respect to \(n, \ell\) emerges, where increase in radial nodes leads to the accumulation of \(\langle \frac{1}{2p} \rangle\). But as is known, in FHA, kinetic energy depends only on \(n\) \(\langle \frac{1}{2p} \rangle\). Moreover, panels (b) and (c) show the appearance of a maximum point, whose positions shift to right as \(r_c\) goes up. Actually, these two segments serve as a missing link in the evolution of H atom from CHA to FHA.

From the foregoing discussion of Figs. 1 and 2 as well as Table I, it is quite clear that the constructed CPs presented above are sufficiently accurate. Several interesting features may be emphasized, viz., (i) enhancement of sharpness of CP’s with relaxation of confinement (ii) alteration of behavioral pattern of momentum moments from CHA to FHA (iii) influence of radial nodes on CP. But the reasons behind these are not clear. Moreover, this analysis is inadequate to explain the significance of such broadening/sharpening of CP with pressure. In this context, information
based measures like $S, E$ may serve our purpose. Estimation of these two quantities may provide the required opportunity for CP in CHA, which we will be pursued now.

Both $S_{n,\ell}^c$ and $E_{n,\ell}^c$ values for six states (same as Table I) of CHA, at ten different $r_c$’s, $(0, 1, 2, 0.5, 1, 2.5, 5, 8, 10, 12, \infty)$ are given in Table II. In all cases, $S_{n,\ell}^c$ regresses and $E_{n,\ell}^c$ advances with progress in $r_c$. Since $S$ represents the measure of uncertainty in a given distribution, a sharp distribution has less uncertainty and hence low $S$ and a broad distribution corresponds to larger uncertainty and hence greater $S$. Therefore, for an arbitrary-(n, $\ell$) state, CP gets flattened with rise in pressure and conversely, with increase in cavity radius, CP becomes sharp. Thus, at strong confinement region, we get broader profile having higher uncertainty in kinetic energy as well as in momentum. Additionally at high pressure regime, boundedness of an electron enhances

FIG. 2: $\langle \frac{1}{2p} \rangle_{n,\ell}$ versus $n$ for s, p, d, f, g states of CHA, at four $r_c$’s in panels (a)-(d). See text for details.
TABLE II: $S_{n,\ell}^c, E_{n,\ell}^c$ for 1s, 2s, 3s, 2p, 3p, 3d states in CHA at ten $r_c$’s. See text for detail.

| $r_c$ | 1s  | 2s   | 3s   | 2p   | 3p   | 3d   |
|------|-----|------|------|------|------|------|
| 0.1  | 2.14595 | 2.48251 | 2.67471 | 2.32217 | 2.58115 | 2.44189 |
| 0.2  | 1.79988 | 2.13588 | 2.32852 | 1.97559 | 2.23462 | 2.09531 |
| 0.5  | 1.34408 | 1.67826 | 1.87058 | 1.51781 | 1.77381 | 1.63627 |
| 1    | 1.00466 | 1.33280 | 1.52472 | 1.17187 | 1.43015 | 1.29064 |
| 2.5  | 0.59679 | 0.87982 | 1.06517 | 0.71811 | 0.97342 | 0.83338 |
| 5    | 0.42686 | 0.51831 | 0.73501 | 0.38977 | 0.63244 | 0.48999 |
| 8    | 0.41196 | 0.22351 | 0.49872 | 0.20212 | 0.40834 | 0.26330 |
| 10   | 0.41188 | 0.09081 | 0.37264 | 0.13676 | 0.30206 | 0.16081 |
| 12   | 0.41174 | 0.00438 | 0.25721 | 0.10534 | 0.21138 | 0.08282 |
| ∞    | 0.411392 | -0.078101 | -0.297814 | 0.082991 | -0.195942 | -0.117328 |

| $r_c$ | 0.1  | 0.2  | 0.5  | 1    | 2.5  | 5    | 8    | 10   | ∞    |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1s   | 0.007964 | 0.003813 | 0.002537 | 0.005390 | 0.003092 | 0.004166 |
| 2s   | 0.015895 | 0.007625 | 0.005072 | 0.010774 | 0.006183 | 0.008331 |
| 3s   | 0.039441 | 0.019042 | 0.012669 | 0.026892 | 0.015469 | 0.020822 |
| 2p   | 0.077621 | 0.038045 | 0.025293 | 0.053608 | 0.030857 | 0.041580 |
| 3p   | 0.178217 | 0.096167 | 0.063166 | 0.132347 | 0.076835 | 0.103511 |
| 3d   | 0.265091 | 0.221328 | 0.127019 | 0.255510 | 0.152718 | 0.204978 |
|      | 0.278295 | 0.447362 | 0.217004 | 0.378673 | 0.249427 | 0.322178 |
|      | 0.278502 | 0.596075 | 0.291224 | 0.43985 | 0.311512 | 0.3961003 |
|      | 0.278514 | 0.713118 | 0.379233 | 0.474932 | 0.387316 | 0.465209 |
|      | 0.278521 | 0.860646 | 1.394031 | 0.505837 | 1.020566 | 0.732503 |

*Exact values of $S_{n,\ell}^c, E_{n,\ell}^c$ for 1s state in FHA, from Eqs. (51) and (46) are: 0.411391858 and 0.27852115 respectively.*

leading to increment in momentum uncertainty. Moreover, the rate of dissipation of Compton energy is slower in CHA compared to FHA. Note that CPs relate to kinetic energy dissipation curves; sharp CPs (less uncertainty in momentum) release kinetic energy faster compared to a broader CP (higher uncertainty momentum). Finally, one can conjecture that, a state having higher kinetic energy (implies larger $S^c$ and a resultant broad CP) releases Compton energy slowly.

Next the focus is to understand the effect of state indices $n, \ell$ on $S^c$, which can help to interpret the influence of radial nodes on CPs. This can be discerned from Fig. (3), where $S^c$ plots are displayed for $\ell = 0 - 5$ states of CHA at $r_c$ values 0.1 (a), 10 (b), 20 (c), and $\infty$ (d), with $n$ up to 9. This first panel imprints that, at strong confinement regime ($r_c = 0.1$) $S^c_{n,\ell}$ grows with $n$, for a given $\ell$; however at a fixed $n$, it diminishes as $\ell$ goes up. That effectively implies, an increase in node in a system leads to growth of $S^c$ and consequently the broadening in CP. Moreover, at fixed radial node condition, states with higher $n$ possesses higher uncertainty in momentum. For
example, a 2p state imprints broader CP compared to a 1s state. This leads to an important conclusion that the effect of confinement on a given state is completely governed by its principal quantum number and number of nodes. In CHA, both $S_c$ as well as kinetic energy increase with $n$, leading to flattening of CP. Finally, the rate of release of Compton energy falls off as $n$ and nodes increase. In contrast, in panel (d), an exactly opposite trend of $S^c$ is witnessed, for the limiting case of FHA, where it reduces with increase in number of nodes. In FHA due to the presence of accidental degeneracy (fixed $n$) the kinetic energy is independent of $\ell$. But its uncertainty decreases with rise in $\ell$. However, at a fixed $n$, $S^c$ increases with $\ell$. It is a contradictory fact relative to CHA, where an enhancement in $S^c$ always stipulates the rise in uncertainty in both kinetic energy and momentum. Therefore, in FHA CP gets flattened with decrease in number of nodes. Similarly, at fixed $\ell$, $S^c$ abates with progress in $n$, explaining the increase in sharpness in CPs with rise in

FIG. 3: $S_{n,\ell}^c$ versus $n$ for s, p, d, f, g states of CHA, at four $r_c$'s in panels (a)-(d). See text for details.
FIG. 4: $E_{n,\ell}^c$ versus $n$ for $s, p, d, f, g$ states of CHA, at four $r_c$’s in panels (a)-(d). See text for details.

nodal structure. This investigation clearly suggests that, in both FHA and CHA, CP can only be characterized and interpreted by invoking $S^c$. Therefore, this exploration establishes the role of $S^c$ as a descriptor in both CHA and FHA. It is a known fact that, while moving from cha to FHA, behavioral pattern gets reversed. It can be explained by pointing out that, in FHA an increase in number of nodes shifts an orbital more away from the nucleus. However, in CHA rise in nodal structure squeezes the orbital more towards the centre. The remaining two intermediate panels (b), (c) suggest the appearance of minima points in these plots, which, for a given state, moves towards right as $r_c$ enhances. Note that, in this figure, the minima are observable only for 1s and 2p; for other states they become visible only at some sufficiently large $r_c$, which is not approached. This again concludes that, they act as bridge between CHA and FHA.

In order to revalidate the inferences drawn in Fig. 3, we have plotted $E_{n,\ell}^c$ of $s, p, d, f, g$ states
FIG. 5: Shannon entropy density, \((-J_{n,\ell}(q)\ln J_{n,\ell}(q))\), for all \(n \leq 3\) states in CHA at three \(r_c = 0.1, 10, 20\), in panels (a)-(c) respectively. See text for details.

(for \(n\) up to 9) at four representative \(r_c\)’s namely 0.1, 10, 20, \(\infty\). Four panels (a)-(d) in Fig. 4 exhibit the same. As usual in all these four \(r_c\), \(E_{n,\ell}^c\) displays exact opposite behavior of \(S_{n,\ell}^c\) of previous figure. As presumed, at \(r_c = 0.1\) in panel (a), \(E_{n,\ell}^c\) decreases with rise in both \(n\) and radial nodes respectively. On the contrary, panel (d) shows that, in case of FHA it increases for the same. This again reinforce the concept that (i) in CHA, pressure effect magnifies with growth in \(n\) and nodes (ii) rate of release in Compton energy reduces with \(r_c\). In two middle panels (b) and (c), a maximum point is seen. Like \(S_{n,\ell}^c\), this maximum point moves to right for greater \(r_c\). It is also evident that, the qualitative behavior of \(E_{n,\ell}^c\) and \(\langle \frac{1}{2p}\rangle_{n,\ell}\) resemble each other.

Finally, in panels (a)-(c) of Fig. 5, Shannon entropy density, \((-J(q)_{n,\ell}\ln J(q)_{n,\ell})\), has been plotted at three representative \(r_c\) (0.1, 10, 20) respectively. Moving from left to right panels, the intensity of a given curve (for a fixed \(n,\ell\) state) amplifies. Therefore, an increase in \(r_c\) reduces the area under a given density curve. This was clearly manifested in first section of Table II, where \(S_{n,\ell}^c\) for a given state decayed with growth in \(r_c\). At small \(r_c\) region in panel (a), like CP, there appears several numbers of plateau in these curves. As usual, in a given state, number of such humps corresponds to the number of nodes. In moderate to large \(r_c\) regions (b,c) the pattern of density curves changes. In left panel, for all six states, global maximum was located at \(q = 0\). But positions of such minima moves towards right direction in other two panels. Moreover, the number of humps in a given curve does not tally with number of nodes in that state.
TABLE III: $S^c$ and $E^c$ in the ground state of He$^+$, Li$_2^{2+}$, Be$_2^{3+}$, B$_3^{4+}$ ions at six $r_c$. See text for details.

| $r_c$ | $r_c$ | $S^c$ | $E^c$ |
|------|------|------|------|
|      | 2    | 3    | 4    | 5    | 2    | 3    | 4    | 5    |
| 0.1  | 1.69065 | 1.89338 | 2.03723 | 2.14880 | 0.007945 | 0.00793 | 0.00791 | 0.00789 |
| 0.5  | 0.94337 | 1.14610 | 1.28994 | 1.40151 | 0.03881 | 0.03799 | 0.03694 | 0.03564 |
| 1    | 0.77344 | 0.97617 | 1.12001 | 1.23158 | 0.073875 | 0.06822 | 0.06093 | 0.05302 |
| 2    | 0.75799 | 0.96082 | 1.10499 | 1.21666 | 0.12186 | 0.09142 | 0.06957 | 0.05572 |
| 10   | 0.75796 | 0.96070 | 1.10458 | 1.21641 | 0.139345 | 0.09290 | 0.06967 | 0.05574 |
| ∞    | 0.757965 | 0.960698 | 1.104539 | 1.2161108 | 0.13926057 | 0.092840 | 0.069630287 | 0.05570423 |

C. Confined Hydrogen isoelectronic series

The effect of $Z$ on confinement can easily be understood by analyzing Eqs. (20), (22) and (23). Let us assume that, both $\hbar = 1$ and $m = 1$. Therefore, the moments becomes lead to,

$$\langle \frac{1}{p} \rangle_{n,\ell} = \frac{1}{Z} \langle \frac{1}{p_0} \rangle_{n,\ell}, \quad \langle p^m \rangle_{n,\ell} = Z^m \langle p_0^m \rangle_{n,\ell},$$

whereas the information entropies, in this case, turn out to be,

$$S^c_{n,\ell}(1, Z, r_c, q) = \frac{1}{2} \ln Z + S^c_{n,\ell}(1, 1, Z r_c, q_0), \quad E^c_{n,\ell}(1, Z, r_c, q) = \frac{1}{Z} E^c_{n,\ell}(1, 1, Z r_c, q_0).$$

Equation (39) suggests that, as one passes from $Z = 2$ to 4, $\langle \frac{1}{p} \rangle_{n,\ell}$ lessens while $\langle p^m \rangle_{n,\ell}$ goes up. It is a known fact that, a rise in $\langle p^m \rangle_{n,\ell}$ is always accompanied by a drop in $\langle \frac{1}{p} \rangle_{n,\ell}$ and vice-versa. Like other instances, here also $J_{n,\ell}(q = 0)$ will provide a smooth monotonic decreasing curve, if plotted against $|E|$. Moreover, it is seen from Eq. (40) that, $S^c_{n,\ell}$ progresses and $E^c_{n,\ell}$ regresses with growth in $Z$. That means, the intensity of CP abates with rise in $Z$, which enhances the boundedness of electron. The ground-state $S^c, E^c$ of He$^+$, Li$_2^{2+}$, Be$_2^{3+}$, B$_3^{4+}$ are reported in Table III at six distinct $r_c$ values, i.e., 0.1, 0.5, 1, 2, 10 and $\infty$. These results demonstrate the validity of expressions given in Eqs. (40); in all four occasions, $S^c$ advances and $E^c$ declines with lengthening of box radius. Therefore, with relaxation in confinement, the rate of dissipation in kinetic energy magnifies. However, an enhancement in $Z$ value, inhibits the process.

IV. FUTURE AND OUTLOOK

Within the impulse approximation, CPs for confined H-like atoms, has been presented, for the first time. The accuracy and reliability has been verified by calculating several momentum moments. Besides, $S^c$ and $E^c$ were also invoked in a novel way to analyze the CPs–their correctness
suggests the impulse approximation to hold good in confined conditions. Such calculations are also performed in the respective unconfined systems. To the best of our knowledge, this is the first undertaking of such calculations. Moreover, they are found to play the role of good descriptors, as they offer a proper interpretation about the boundedness of electron, and influence of radial node on a given state. As an offshoot, several interesting analytical relations involving $S_c, E_c, \langle \frac{1}{r} \rangle, \langle p^m \rangle$, with $Z$, have been derived. It is observed that, the effect of $Z$ on CP’s remains similar in both confined and free conditions.

Experimental verification of these results is highly desirable. This will open up a new dimension in the high-pressure physics and chemistry. It is well known that, confined systems are generally, not exactly solvable; and moreover, accurate calculation of energy and density may be quite demanding and challenging for conventional theoretical approximations. However, once CP is available experimentally, one can follow the usual route used in free condition to construct EMD, and subsequently wave function and energy. This may be an interesting recipe to explain the bonding pattern, coordination number and reactivity in such stressed systems. Also, a theoretical exploration in many-electron systems would be quite helpful. Similar study for confined molecular systems may provide vital insight about the effect of confinement in chemical bonding.

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VI. APPENDIX I: ONICESCU ENERGY CALCULATION

At first let us work out the $\alpha$-order entropic moment, $\omega^\alpha$. It will provide an opportunity to calculate an arbitrary-order entropic moments. It can be derived as follows,

$$\omega^\alpha = \int_0^\infty \left( \frac{8}{3\pi Z} \right)^\alpha \frac{1}{\left( \frac{2}{Z} \right)^2 + 1}^{3\alpha} dq. \quad (41)$$

Assuming $\frac{q}{Z} = u$, this equation can be transformed in to,

$$\omega^\alpha = \int_0^\infty \left( \frac{8}{3\pi} \right)^\alpha Z^{1-\alpha} \frac{1}{\left[ u^2 + 1 \right]^{3\alpha}} du. \quad (42)$$
Further substitution of \( u = \tan \theta \) in Eq. (42) produces,

\[
\omega^\alpha = \int_0^{\frac{\pi}{2}} Z^{1-\alpha} \frac{\sec^2 \theta}{[\tan^2 \theta + 1]^{3\alpha}} d\theta
\]

\[
= \left( \frac{8}{3\pi} \right)^\alpha Z^{1-\alpha} \int_0^{\frac{\pi}{2}} \cos^{6\alpha-2} \theta d\theta.
\] (43)

Now, making use of the standard integral, \( \int_0^{\frac{\pi}{2}} \cos^{(\mu-1)} \theta d\theta = 2^{(\mu-2)} B \left( \frac{\mu}{2}, \frac{\mu}{2} \right) (\mu = 6\alpha - 1) \), in Eq. (42), gives us the final result as,

\[
\omega^\alpha = \left( \frac{8}{3\pi} \right)^\alpha Z^{1-\alpha} 2^{(6\alpha-3)} B \left( \frac{6\alpha-1}{2}, \frac{6\alpha-1}{2} \right).
\] (44)

It is needless to mention that, at \( \alpha = 2 \), this entropic moment in Eq. (45) reduces to \( E_{c,n,l} \). Therefore,

\[
E_{c,1,0}^2 = \omega^2 = \left( \frac{8}{3\pi} \right)^2 Z \left( \frac{11}{2}, \frac{11}{2} \right) = \left( \frac{8}{3\pi} \right)^2 Z \frac{1}{11} \frac{\Gamma(\frac{11}{2})\Gamma(\frac{11}{2})}{\Gamma(11)} = \frac{7}{8\pi Z}
\] (45)

VII. APPENDIX II: SHANNON ENTROPY CALCULATION

In a similar fashion, \( S_{c,n,l}^2 \) for 1s state will take the form,

\[
S_{1,0}^c = -\int_0^{\infty} \left( \frac{8}{3\pi Z} \right) \frac{1}{\left( \left( \frac{Z}{2} \right)^2 + 1 \right)^3} \ln \left( \frac{8}{3\pi Z} \right) \frac{1}{\left( \left( \frac{Z}{2} \right)^2 + 1 \right)^3} dq.
\] (47)

Once again putting \( q = u \) and \( u = \tan \theta \), Eq. (47) can be recast in to,

\[
S_{1,0}^c = \left[ \ln \left( \frac{3\pi}{8} \right) + \ln Z \right] \left( \frac{8}{3\pi} \right) \int_0^{\frac{\pi}{2}} \cos^4 \theta d\theta - \frac{16}{\pi} \int_0^{\frac{\pi}{2}} \cos^4 \theta \ln \cos \theta d\theta,
\]

\[
S_{1,0}^c = \left[ \ln \left( \frac{3\pi}{8} \right) + \ln Z \right] \left( \frac{8}{3\pi} \right) A_1 - \frac{16}{\pi} A_2.
\] (48)

Now invoking the following standard integrals [71],

\[
\int_0^{\frac{\pi}{2}} \cos^{2m} \theta d\theta = \frac{(2m-1)!! \pi}{(2m)!! 2},
\]

\[
\int_0^{\frac{\pi}{2}} \cos^{2k} \theta \ln \cos \theta d\theta = -\frac{(2k-1)!! \pi}{2^{2k} k!} \left[ \ln 2 + \sum_{m_1=1}^{k} \frac{(-1)^{m_1}}{m_1} \right],
\] (49)

we obtain \( A_1, A_2 \) as,

\[
A_1 = \int_0^{\frac{\pi}{2}} \cos^4 \theta d\theta = \frac{3\pi}{16},
\]

\[
A_2 = \int_0^{\frac{\pi}{2}} \cos^4 \theta \ln \cos \theta d\theta = -\frac{3\pi}{16} \left[ \ln 2 - \frac{7}{12} \right].
\] (50)
Finally inserting the values of $A_1$ and $A_2$ in Eq. 48 one gets,

$$S_{1,0}^c = \frac{1}{2} \ln 24\pi + \frac{1}{2} \ln Z - \frac{7}{4}. \tag{51}$$
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The diagram shows plots of various electron orbitals as a function of nuclear charge ($r_c$), with labels for 1s, 2s, 3s, 2p, 3p, and 3d orbitals.
