Confined H$^-$ ion within a density functional framework

Sangita Majumdar$^1$, Neetik Mukherjee$^1$, and Amlan K. Roy$^{1,*}$

$^1$ Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur, Nadia, West Bengal 741246, India

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Abstract. Ground and excited states of a confined negative hydrogen ion have been pursued under Kohn–Sham density functional approach by invoking a physically motivated work-function-based exchange potential. The exchange-only results are of near Hartree–Fock quality. Local parameterized Wigner-type, and gradient- and Laplacian-dependent non-local Lee–Yang–Parr functionals are chosen to investigate the electron correlation effects. Eigenfunctions and eigenvalues are extracted by using a generalized pseudospectral method obeying Dirichlet boundary condition. Energy values are reported for $1s^2 \left(^1S\right)$, $1s2s \left(^3S\right)$ and $1s2p \left(^3P\right)$ states. The performance of the correlation functionals in the context of confinement is examined critically. The present results are in excellent agreement with the available literature. Additionally, Shannon entropy and Onicescu energy are offered for ground and low-lying singly excited $1s^2 \left(^1S\right)$ and $1s2p \left(^3P\right)$ states. The influence of electron correlation is more predominant in the weaker confinement limit, and it decays with an increase in confinement strength. In essence, energy and some information measures are estimated using a newly formulated density functional strategy.

1 Introduction

Atomic and molecular systems confined by different forms of external potentials show various novel and interesting properties which are significantly different from their free counterparts. Although the study of confined atoms started several decades earlier [1,2], spectroscopic analysis of energy levels and other structural properties of quantum systems under diverse external confinements have received attention in the recent years [3–14]. An atom under spatial constraints may be modeled for describing the effect of pressure on the system, which may impact the rearrangement of orbitals, energy spectrum, continuum lowering; also, bonding pattern and co-ordination number may undergo dramatic changes in a molecule. Interested reader can find some elegant reviews in the literature [4,9,15,16]. Such changes in structure play a crucial role for gaining insight into the unusual physicochemical properties in constrained systems. A systematic analysis of one- and two-electron atom/ion is, therefore, essential for a comprehensive understanding of quantum confinement.

A simple but interesting two-electron confined model is the hydrogen negative ion (H$^-$) restricted by a spherical barrier. Investigation on negative ions is an important research activity in atomic physics in their own right. Usually, they are fragile quantum systems possessing binding energies less than one order of magnitude than that in the atom. H$^-$ ion, in particular, plays a fundamental role in the understanding of effect of correlation in three-body quantum mechanical problems. As a result of this weaker binding, the correlation effects are rather sensitive and delicate, compared to an isoelectronic atom or positive ion. Several excellent reviews are available [17,18] on the subject. Almost eighty percent atoms are able to form stable negative ion. They play a dominant role in the context of electrical conductivity in weakly ionized gases and plasmas. The versatility of hydride ion has been well established. It acts as an efficient antioxidant in human body. In transition region of planetary nebula, it is present in high concentration. It also functions as the main source of opacity in sun atmosphere at red and infrared region. Unlike other negative ions, extensive theoretical study for H$^-$ ion has been done since 1962. However, similar works on its confined counterpart remain quite limited. It is to be pointed out here, as the confinement radius is reduced, the isotropic pressure on the negative hydrogen ion is higher than $\sim 1$ GPa. In this high-pressure regime, it behaves in a manner which is significantly different from the free counterpart.

Most of the studies in the literature have considered He atom as the prototypical two-electron confined system. Spatially confined H$^-$ works are not so prevalent in the literature, relatively speaking. Nevertheless, a decent number of methods exist. Some of these are Hartree–Fock (HF) calculation with B-spline method [19], a combination of quantum genetic algorithm and HF [6], Hylleraas-type wave function for variational cal-
calculation [20], quantum Monte Carlo [21], CI calculation using explicitly correlated Hylleraas basis [10], for ground and singly excited S states. Apart from that, there prevails a couple of Rayleigh–Ritz approaches: (a) with three-parameter correlated wave function for ground state [22] and (b) using explicitly correlated Hylleraas-type basis set for singly excited 1s2s and 1s3s \((^1S)\) [11], for 1s\(^2\) \((^1S)\), 2p\(^2\), 1snp \((^1P)\) with \((n = 2–5)\) \((^3P)\), in [14]. One also finds variational method based on (a) generalized Hylleraas basis (GHB) [8, 23] and (b) B-spline basis [24] as well. A detailed analysis of electron correlation has been published in [19]. A density functional theory (DFT) report is available in [25], within LDA and BLYP functional. Penetrable walls have also been undertaken as well. For example, energy spectrum for different confinement strengths is analyzed for H\(^-\) ion confined by an anisotropic harmonic oscillator potential, by (i) CI method within Gaussian basis [26] and (ii) adiabatic hyper-spherical approach [27].

Based on the known properties like static dipole polarizability [28, 29], second hyperpolarizability [29] for are also pursued. Energy levels and electric dipole polarizabilities of endohedrally confined H\(^-\) ion with CI method coupled with a B-spline approach are analyzed in [30]. Some works are also reported in the context of H\(^-\) ion embedded in plasma environment [31–44].

The relation between information theoretic tool and quantum mechanical kinetic energy was established in [45]. Since then the importance of these measures in the context of DFT has been discussed in several papers [46–50]. In a recent work, the Euler equation in orbital-free DFT is formulated by invoking Shannon entropy \((S)\) and Fisher information [51] Over the years, these tools have emerged as versatile descriptors in analyzing atoms and molecules [25, 52–54]. They are functionals of density and can quantify it accurately in various complementary ways. In the present work, we are specifically interested in two such measures, namely Shannon entropy and Onicescu energy \((E)\). The former is the arithmetic mean of uncertainty and can characterize a given density distribution in global way. The latter refers to the expectation value of density and generally complements the behavior of \(S\). A decent amount of research work has been published to inspect these measures in free atom/ion. However, in confined situation, parallel reports are quite limited and scattered. One can mention the works on confined H atom (CHA), where \(S\) was studied with change in \(r, p\) in, in composite \(r, p\) spaces, in case of both \(l = 0\) and non-zero \(l\) states [13, 25, 55, 56]. It was found that effect of confinement is more pronounced on higher states. Study of \(S\) was also performed in [57] for the hydrogen atom submitted to four different potentials: (a) infinite potential; (b) Coulomb plus harmonic oscillator; (c) constant potential; and (d) dielectric continuum. In many electron atoms, \(S\) has been explored mostly using correlated Hylleraas-type wave function, in either attractive or repulsive conditions. Some DFT works are also reported. Thus, ground-state \(S\) was considered for two-electron iso-electronic series \((\text{H}^-, \text{He}, \text{Li}^+, \text{Be}^{2+})\) under hard (impenetrable rigid wall) confinement, by using the BLYP XC functional [25]; another DFT study for ground and excited states is recently published in [58] for He, Li\(^+\) and Be\(^{2+}\). Of late, there is a growing interest to treat the so-called finite (soft) confinement as well. Besides ground state, some limited works exist on low-lying excited states of \(S\)-mostly, for single [59] and double [60] excitations in He.

Thus, it appears that there is a need for DFT calculation for confined many electron systems, in particular the negative ions. The motivation of the present work lies in that. Here, we perform a detailed and systematic study of energy as well as \(S, E\), in composite \(r\) and \(p\) spaces, for ground and some low-lying singly excited states of H\(^-\) ion, trapped inside high-pressure environment. This is accomplished by invoking a simple work-function-based exchange potential, motivated from physical grounds. The correlation effect is incorporated by using (i) a local, parameterized Wigner-type functional and (ii) the popular Lee–Yang–Parr (LYP) functional. The relevant KS differential equation under Dirichlet boundary condition is solved by adopting an accurate and efficient generalized pseudospectral (GPS) scheme. This procedure has been effectively applied to ground and a large number of excited states in free atoms as well as in some confinement works, with considerable success. Electron density, \(S_r, E_p\) are estimated from self-consistent orbitals. The momentum-space orbitals are obtained by performing Fourier transformation to \(r\)-space orbitals in usual way. Electron momentum density is constructed from \(p\)-space orbitals, and subsequently, \(S_p, E_p\) are obtained therefrom. Our pilot calculation are done on ground and 1s2s, 1s2p excited states. Section 2 sums up the adopted methodology. Section 3 imprints the calculated results along with a comparison with available references. Finally, Sect. 4 concludes with the outlook and future prospects.

2 Methodology

Here, we briefly outline the proposed density functional method for a particular state of an arbitrary atom centered inside an impenetrable spherical cavity, followed by the GPS scheme for calculation of eigenvalues and energies of KS equation. This has been very successful for ground and various states (such as singly, doubly, triply excited states corresponding to low- and high-lying excitation, valence and core excitation, autoionizing, hollow, doubly hollow, Rydberg and satellite states) of free or unconfined neutral atoms as well as ions [61–67]. Very recently, this has been extended to confinement situations [58]. Our focus remains on essential portions, omitting the relevant details, which are available in the above references.

Our starting point is the non-relativistic single-particle time-independent KS equation with imposed confinement, which can be conveniently written as
(atomic unit employed unless otherwise mentioned):

\[
\left[ -\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \tag{1}
\]

where the “effective” potential is constituted of following terms:

\[
v_{\text{eff}}(\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + \frac{\delta E_{\text{xc}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} + v_{\text{conf}}(\mathbf{r}). \tag{2}
\]

In this equation, the first three terms in right-hand side correspond to usual electron–nuclear attraction, classical Hartree repulsion and XC potentials, respectively. The following perturbation accounts for the desired confinement (\(r_c\) refers to the radius of spherical cage):

\[
v_{\text{conf}}(\mathbf{r}) = \begin{cases} 0, & r \leq r_c \\ +\infty, & r > r_c. \end{cases} \tag{3}
\]

Despite the remarkable progress and success in ground-state electronic structure and properties of atoms/molecules, in past five decades, excited state-DFT has faced difficulties and challenges. This is mainly due to the lack of (i) an analogous Hohenberg–Kohn theorem and (ii) an accurate, proper XC functional for a general excited state. This work intends to extend the KS equation following the Dirichlet boundary condition. This is done here by adopting an accurate and efficient GPS prescription, providing a non-uniform, optimal spatial discretization. It is a simple but effective method giving excellent results on numerous physically and chemically relevant problems, such as singular and non-singular Coulomb, Hülthen, Yukawa, logarithmic, spiked oscillator, Hellmann potential, etc., along with its recent extension to quantum confinement. This will give the opportunity to examine and calibrate the performance of these functionals in the current situation.

By taking the \(v_x(\mathbf{r})\) and \(v_{\varepsilon}(\mathbf{r})\) as above, we proceed toward the solution of resulting KS equation following the Dirichlet boundary condition. The numerical \(p\)-space wave function is obtained by Fourier transforming of \(r\)-space counterpart, as follows:

\[
\xi(\mathbf{p}) = \int \phi(\mathbf{r}) e^{i\mathbf{p} \cdot \mathbf{r}} \, d\mathbf{r}. \tag{9}
\]

Here, \(\xi(\mathbf{p})\) needs to be normalized. The normalized \(r\)- and \(p\)-space densities are then expressed in the forms as \(\rho(\mathbf{r}) = \sum_{i=1}^{N} n_i |\phi_i(\mathbf{r})|^2\) and \(\Pi(\mathbf{p}) = \sum_{i=1}^{N} n_i |\xi_i(\mathbf{p})|^2\), respectively, where \(n_i\) indicates the occupation number of the \(i\)th orbital.

Next, \(S_r\), \(S_p\) and Shannon entropy sum \(S_t\) are defined as given below:

\[
S_r = -\int_{\mathbb{R}^3} \rho(\mathbf{r}) \ln[\rho(\mathbf{r})] \, d\mathbf{r},
\]

\[
S_p = -\int_{\mathbb{R}^3} \Pi(\mathbf{p}) \ln[\Pi(\mathbf{p})] \, d\mathbf{p},
\]

\[
S_t = [S_r + S_p] \geq 3(1 + \ln \pi), \quad \text{in 3 dimension.} \tag{10}
\]

Similarly, \(E_r\), \(E_p\) and Onicescu energy product \(E_t\) are defined as given below:

\[
E_r = -\int_{\mathbb{R}^3} \rho^2(\mathbf{r}) \, d\mathbf{r}, \quad E_p = -\int_{\mathbb{R}^3} \Pi^2(\mathbf{p}) \, d\mathbf{p},
\]

\[
E_t = E_r E_p \tag{11}
\]
Here, both $\rho(\mathbf{r})$ and $\Pi(\mathbf{p})$ are normalized to unity.

All the computations are done numerically. The convergence is ensured by carrying out calculations with respect to variation in grid parameters, such as total number of radial points and maximum range of grid. It is observed that for entire regime of considered confinement strength, convergence is obtained with uniform accuracy and ease. A general convergence criteria in energy ($10^{-6}$) and potential ($10^{-5}$) during the iterative process were employed throughout the whole confinement region. All the quantities given in the following tables and plots have been checked for the above convergence.

3 Results and discussion

At the onset, it is convenient to mention a few general comments about the referred results for compressed H$^-$ ion. Non-relativistic energies will be reported for ground 1s$^2$ 1S and low-lying single excited 1s2s $^3$S, 1s2p $^3$P states. Results on $S$, $E$ in composite r- and p-spaces will be presented for 1s$^2$ 1S, 1s2s $^3$S and 1s2p $^3$P states. All results are in atomic units, unless stated otherwise. In order to organize the data in an appropriate manner, three sets of energies are attempted, viz. (i) exchange-only; (ii) involving Wigner correlation; (iii) considering LYP correlation. Throughout the discussion, these are termed as X-only, XC-Wigner and XC-LYP. Ground-state energies for confined H$^-$ ion are investigated with some interest. Consequently, a healthy amount of the literature is available, and they are compared with the present calculation whenever feasible. However, for excited state, such an attempt is very uncommon and only a handful of results are available to collate. Furthermore, investigation of $S$ and $E$ for confined H$^-$ ion is very scarce. Except [25] no such record is available for comparison.

3.1 Energy analysis

Let us begin the discussion with ground-state energies of confined H$^-$ ion given in Table 1 at certain representative $r_c$’s, starting from very strong confinement regime ($r_c = 0.05$) to free limit ($r_c \rightarrow \infty$). The present X-only results are reported in the second column. These outcomes are almost identical with HF results obtained by using B-spline approach employing the zeroth-order spherical Bessel function [19]. In this context, note that an analogous agreement with HF calculation [81] is also observed in the case of He-isoelectronic series and Li, Be atoms for which similar calculation has been done by the authors and it will be published soon [82]. Apart from that, the X-only values are also compared by invoking a combined quantum genetic algorithm (QGA) and RHF method [6]. A slightly compromised matching is observed at $r_c \leq 1$ region. However, similarity between these two results improves with a rise in $r_c$. At moderate to large $r_c$ ($\geq 3$), both the results become identical. All these literature values are available in the third column of Table 1.

The columns 4 and 5 of Table 1 now represent the Wigner and LYP energies, respectively, with corresponding references in column 6. At strong confinement zone ($\approx r_c \leq 3$), Wigner energies are lower compared to LYP. However, at moderate to large $r_c$ region, an opposite behavior is seen. The difference between these two energies remains in the range of $-0.0107$ to $1.5585$. Moving from free to confinement condition total energy increases. This happens mainly due to an abrupt rise in kinetic energy. In most cases (except $r_c = 0.05, 2.5, 2.8, 3$), either of the correlated present results (PR) shows appreciable agreement with explicitly correlated GHB [8,14,19,20,23] energies. In XC-Wigner and XC-LYP, the absolute deviations are 0.003–3.93 and 0.03–4.84%, respectively. At $r_c = 0.05$, Wigner energies show excellent agreement with reported results, but a slight deviation is seen relative to XC-LYP value. However, at $r_c = 2.5, 2.8, 3$, PR diverge from literature. It is important to mention that in almost all the cases, XC-LYP values are higher than the best possible results [8,14,20,23], but no such trend is seen in XC-Wigner. These references also suggest that at small $r_c$ region, Wigner performs better than LYP, but the scenario reverses with weakening of confinement strength. At strong confinement region ($r_c < 4$), PR are smaller than BLYP energies given in [25]. However, this pattern reverses at $r_c > 4$ range. Interestingly, at $r_c = 4$, Wigner and BLYP energies [25] become almost identical. A similar situation arises for LYP functional at $r_c = 5$. In essence, both Wigner and LYP produce reasonably good agreement with the BLYP results [25], recording absolute deviations of 0.13–13.65 and 0.08–3.54%, respectively. At certain $r_c$’s ($\geq 0.4$), these are also tallied with CI method coupled with a B-spline approach [30]. In this case, the absolute deviation involving Wigner and LYP is 0.14–4.91 and 0.64–10.02% successively. Besides these, PR produces good agreement with other correlated energies available in [22,79,80]. It is needless to mention that as usual, both X-only and correlated energies abate with a rise in $r_c$.

Next, we move to employ this method in excited states. This provides an idea about its utility as well as performance in such states under hard confinement. Table 2 imprints energies of singly excited 1s2s $^3$S and $^1$S states of a trapped H$^-$ ion for a wide range of $r_c$. Reference theoretical results in this context are very rare. To the best of our knowledge, both X-only and correlated results are available only for $^3$S state and no such values are reported for $^1$S state. The second and sixth columns represent X-only results for triplet and singlet states. The X-only energies for $^3$S state can be compared with combined QGA-RHF method [6], and the results show good agreement. Similar to the ground state, here also the convergence between these two values increases with progress in $r_c$. The third and fourth columns of Table 2 offer the Wigner and LYP energies for $^3$S, whereas columns six and seven provide the same for $^1$S. Like the ground state, here also for both triplet
| $r_c$ | X-only | Literature | XC-Wigner | XC-LYP | Literature |
|------|--------|------------|-----------|--------|------------|
| 0.05 | 3885.9257 | 3885.925658$^a$ | 3885.7425 | 3887.3010 | 3885.922469$^e$, 3885.870899$^d$, |
| 0.1  | 955.9361  | 955.7694  | 956.7881 |        |            |
| 0.4  | 53.8264   | 53.7168   | 54.0735  |        | 54.1458, 54.3573$^k$ |
| 0.5  | 33.1632   | 33.18974$^b$ | 33.0645  | 33.3253 | 33.1120$^f$, 33.4358$^g$, 33.11307$^m$ |
| 0.7  | 15.5897   | 15.59244$^b$ | 15.5072  | 15.7069 | 15.5400$^h$, 15.7568$^i$, 15.5487$^m$ |
| 0.9  | 8.6106    | 8.61166$^b$ | 8.5305   | 8.6853  | 8.5621$^i$, 8.7073$^j$, 8.56299$^m$ |
| 1.0  | 6.6375    | 6.637526$^a$, 6.64209$^b$ | 6.5709   | 6.6969  | 6.633326$^c$, 6.589644$^d$, |
| 1.2  | 4.1341    | 4.13699$^b$ | 4.0749   | 4.1706  | 4.0875$^e$, 4.1826$^f$, 4.1492$^k$, |
| 1.4  | 2.6808    | 2.68124$^b$ | 2.6275   | 2.7011  | 2.6354$^g$, 2.7112$^h$, 2.63603$^m$ |
| 1.8  | 1.1764    | 1.17666$^b$ | 1.1315   | 1.1758  | 1.1330$^i$, 1.1834$^j$, 1.13357$^m$ |
| 2.0  | 0.7665    | 0.76664$^b$ | 0.7248   | 0.7591  | 0.7240$^i$, 0.7231$^j$, 0.7245$^l$, |
| 2.5  | 0.1799    |              | 0.1442   | 0.1616  | 0.1394$^i$, 0.1385$^i$, 0.167$^g$ |
| 2.8  | −0.0123   | −0.0145     | −0.0347  | −0.051936$^h$, −0.051936$^a$ |
| 3.0  | −0.1040   | −0.10408$^b$ | −0.1357  | −0.1284 | −0.1431$^e$, −0.1435$^f$, |
|      |           |            |          |        | −0.143084$^g$, −0.124$^h$, |
|      |           |            |          |        | −0.1427$^i$, −0.13915$^j$, |
|      |           |            |          |        | −0.14271$^k$, −0.143084$^l$, |
| 4.0  | −0.3420   | −0.34209$^b$ | −0.3685  | −0.3714 | −0.3790$^m$, −0.3794$^n$, |
|      |           |            |          |        | −0.379037$^o$, −0.369$^p$, |
|      |           |            |          |        | −0.3786$^q$, −0.3295$^r$, |
|      |           |            |          |        | −0.374641$^s$, −0.37875$^t$, |
| 5.0  | −0.4258   | −0.425815$^a$ | −0.4493  | −0.4564 | −0.438594$^u$, −0.461974$^v$, |
|      |           |            |          |        | −0.462093$^w$, −0.4620$^x$, |
|      |           |            |          |        | −0.4623$^y$, −0.4617$^z$, |
|      |           |            |          |        | −0.465$^a$, −0.462073$^b$, |
| 6.0  | −0.4595   | −0.45954$^b$ | −0.4813  | −0.4902 | −0.4958$^c$, −0.4958$^d$, |
|      |           |            |          |        | −0.495772$^e$, −0.492$^f$, |
|      |           |            |          |        | −0.4956$^g$, −0.440$^h$, |
|      |           |            |          |        | −0.49166$^i$, −0.49558$^j$, |
| 10.0 | −0.4861   | −0.486150$^a$, 0.48614$^b$ | −0.5056  | −0.5157 | −0.509209$^k$, −0.524688$^l$, |
|      |           |            |          |        | −0.524688$^m$, |
|      |           |            |          |        | −0.5247$^n$, −0.5230$^o$, |
|      |           |            |          |        | −0.5245$^p$, −0.5238$^q$, |
|      |           |            |          |        | −0.52455$^r$, −0.524688$^s$, |
|      |           |            |          |        | −0.528$^t$, −0.52775$^u$, |
|      |           |            |          |        | −0.52481$^v$, −0.52775$^w$, |

$^a$Ref. [19]
$^b$Ref. [6]
$^c$E$^{RL}$ result of Ref. [19]
$^d$E$^{2}$ result of Ref. [19]
$^e$Ref. [23]
$^f$Ref. [21]
$^g$Ref. [25]
$^h$Ref. [14]
$^i$Ref. [79]
$^j$Ref. [20]
$^k$Ref. [80]
$^l$Ref. [22]
$^m$Ref. [30]
$^n$Ref. [8]
and singlet states, LYP values are higher than Wigner data in $r_c \leq 5$ region. Further, in $^3$S, the matching between Wigner and LYP energies enhances with an advancement in $r_c$. Absolute difference between these two correlated values for both the states is almost identical, and it is in the range of 0.003–1.593. The present correlated energies for triplet state are in good agreement with the available GHB results [29]. In this case, absolute deviation for Wigner and LYP is 0.27–7.33 and 0.016–9.41% successively. It may also be noted that in both cases, deviation is higher in large $r_c$ regime.

After the successful attempt of the present method in $1s2s$ configuration, we now arrive at $1s2p$ case to investigate its $^1$P and $^3$P states under compression. Table 3 provides energies for these two states at the same range of $r_c$ given in the previous table. Similar to the earlier

### Table 2 Energies of $1s2s$ $^1S$ and $^3S$ states of radially confined $H^-$ for different $r_c$. See text for details.

| $r_c$ | $^3S$ X-only | $^3S$ XC-Wigner | $^3S$ XC-LYP | $^1S$ Literature |
|-------|--------------|----------------|--------------|-----------------|
| 0.1   | 2426.7390    | 2426.5730      | 2428.1661    | –               |
| 0.2   | 596.4463     | 596.3056       | 597.2946     | –               |
| 0.5   | 90.4448      | 90.3468        | 90.8032      | 91.20906        |
| 0.6   | 61.6373      | 61.5482        | 61.9275      | 62.15161        |
| 0.9   | 25.8082      | 25.7373        | 25.9755      | 25.97643        |
| 1     | 20.4697      | 20.4037        | 20.6111      | 20.52687        |
| 1.2   | 13.6038      | 13.5451        | 13.7057      | 13.64636    |
| 1.4   | 9.5381       | 9.4853         | 9.6118       | 9.56349    |
| 1.5   | 8.1075       | 8.0571         | 8.1699       | –               |
| 1.8   | 5.2083       | 5.1594         | 5.2406       | 5.22940    |
| 2     | 3.9798       | 3.9387         | 4.0043       | 3.99015    |
| 3     | 1.2171       | 1.1864         | 1.2093       | 1.22002    |
| 4     | 0.3435       | 0.3184         | 0.3245       | 0.34429    |
| 5     | 0.17539      | 0.16203        | 0.1754       | –               |

aRef. [6] (X-only energies)
bRef. [23] (Correlated energies)

### Table 3 Energies of $1s2p$ $^1P$ and $^3P$ states of radially confined $H^-$ for different $r_c$. See text for details.

| $r_c$ | $^3P$ X-only | $^3P$ XC-Wigner | $^3P$ XC-LYP | $^1P$ Literature |
|-------|--------------|----------------|--------------|-----------------|
| 0.1   | 1472.4664    | 1472.4815      | 1473.7385    | –               |
| 0.2   | 360.5257     | 360.3864       | 361.1685     | –               |
| 0.5   | 53.9750      | 53.8797        | 54.2403      | 54.02876        |
| 0.6   | 36.6134      | 36.5270        | 36.8264      | 36.64832        |
| 0.9   | 15.0984      | 15.0309        | 15.2173      | 15.10315        |
| 1     | 11.9084      | 11.8453        | 12.0075      | 11.92050        |
| 1.2   | 7.8186       | 7.7629         | 7.8875       | 7.82685        |
| 1.4   | 5.4079       | 5.3580         | 5.4551       | 5.41271        |
| 1.5   | 4.5627       | 4.5152         | 4.6013       | –               |
| 1.8   | 2.8547       | 2.8133         | 2.8737       | 2.85748        |
| 2     | 2.1393       | 2.10104        | 2.1488       | 2.14134        |
| 3     | 0.5434       | 0.5153         | 0.5281       | 0.54437        |
| 4     | 0.04955      | 0.02665        | 0.05905      | 0.04969        |
| 5     | 0.003639     | 0.003639       | 0.003639     | –               |
| 6     | 0.003639     | 0.003639       | 0.003639     | –               |
| 8     | 0.003639     | 0.003639       | 0.003639     | –               |
| 10    | 0.003639     | 0.003639       | 0.003639     | –               |
| 15    | 0.003639     | 0.003639       | 0.003639     | –               |

aRef. [6] (X-only energies)
bRef. [14] (Correlated energies)
Fig. 1 Energy changes in some low-lying states of confined H\textsuperscript{−} with \(r_c\) in (a). Panel b shows a magnification of a in \(\epsilon \leq 0.2\) region. See text for details

Table 4 Energy values of some singly excited singlet and triplet states in radially confined H\textsuperscript{−} at \(r_c = 0.1\). Energies are arranged in ascending order. See text for details

| Configuration | States | X-only | XC-Wigner | XC-LYP |
|---------------|--------|--------|-----------|--------|
| 1s2p          | \(^3\)P, \(^1\)P | 1472.6466, 1479.8278 | 1472.4815, 1479.6627 | 1473.7385, 1480.9194 |
| 1s3d          | \(^3\)D, \(^1\)D | 2127.2860, 2132.8279 | 2127.1219, 2129.8212 | 2128.6261, 2130.1984 |
| 1s2s          | \(^3\)S, \(^1\)S | 2426.7390, 2432.4082 | 2426.5730, 2432.2422 | 2427.8466, 2434.9986 |
| 1s4f          | \(^3\)F, \(^1\)F | 2909.1492, 2910.6018 | 2908.9858, 2910.4384 | 2910.7391, 2912.1918 |
| 1s3p          | \(^3\)P, \(^1\)P | 3445.2211, 3448.2732 | 3445.0558, 3448.1079 | 3446.9466, 3449.9986 |
| 1s5g          | \(^3\)G, \(^1\)G | 3815.8480, 3816.6892 | 3815.6851, 3816.5263 | 3817.6904, 3818.5316 |
| 1s4d          | \(^3\)D, \(^1\)D | 4600.3498, 4602.1893 | 4600.1849, 4602.0245 | 4602.3665, 4604.2060 |
| 1s6h          | \(^3\)H, \(^1\)H | 4844.9833, 4845.5142 | 4844.8208, 4845.3517 | 4847.0792, 4847.6102 |
| 1s3s          | \(^3\)S, \(^1\)S | 4891.8255, 4894.0532 | 4891.6597, 4893.7214 | 4893.9043, 4896.1319 |
| 1s5f          | \(^3\)F, \(^1\)F | 5891.7768, 5892.9728 | 5891.6124, 5892.6439 | 5894.0811, 5895.2772 |
| 1s4i          | \(^3\)I, \(^1\)I | 5994.5782, 5994.9344 | 5994.4160, 5994.7722 | 5996.9280, 5997.2843 |
| 1s4p          | \(^3\)P, \(^1\)P | 6403.9567, 6405.4891 | 6403.7913, 6405.3236 | 6406.3592, 6407.8914 |
| 1s8k          | \(^3\)K, \(^1\)K | 7263.0203, 7263.2706 | 7262.8583, 7263.1086 | 7265.6245, 7265.8746 |
| 1s6g          | \(^3\)G, \(^1\)G | 7317.1025, 7317.9240 | 7316.9384, 7317.7598 | 7319.6904, 7320.5136 |
| 1s5d          | \(^3\)D, \(^1\)D | 8055.1773, 8056.2696 | 8055.1022, 8056.1044 | 8057.8952, 8058.9874 |
| 1s4s          | \(^3\)S, \(^1\)S | 8343.8330, 8345.0383 | 8343.6671, 8344.8724 | 8346.6009, 8347.8063 |

These results of Tables 1–3 encourage us to investigate the impact of confinement on excited states in a qualitative manner. Therefore, such energies are plotted in panels (a) and (b) of Fig. 1 for a few singlet and triplet singly excited states as a function of \(r_c\). In addition to the states investigated in the above three tables, in this occasion, we have considered some additional states, such as 1s3s and 1s4s \(^3\)S, 1s3p \(^3\)P and 1s3d \(^3\)D. In order to get a better insight about the crossing among various states, an amplified region (\(\epsilon \leq 0.2\)) of panel (a) is demonstrated in panel and (b) with improved resolution. X-only, XC-Wigner and XC-LYP energies generate qualitatively resembling plots. Hence, we take liberty to use X-only energies to point out some general features. In a free H\textsuperscript{−} ion, the possible ordering of states under consideration is: \(\epsilon_{1s4s} (\(^3\)S) > \epsilon_{1s4s} (\(^1\)S) > \epsilon_{1s4d} (\(^3\)D) > \epsilon_{1s4d} (\(^1\)D) > \epsilon_{1s3d} (\(^3\)D) > \epsilon_{1s3p} (\(^1\)P) > \epsilon_{1s3p} (\(^3\)P) > \epsilon_{1s3p} (\(^3\)S)\).
Correlation energies, with changes in $r_c$, for singly excited states of confined $\text{H}^-$, in a singlet b triplet states for Wigner correlation, while c, d give the same for LYP functional

$\epsilon_{1s2s}(1S) > \epsilon_{1s3d}(3S) > \epsilon_{1s2p}(1P) > \epsilon_{1s2p}(3P) > \epsilon_{1s2s}(1S) > \epsilon_{1s2d}(3S) > \epsilon_{1s2s}(1S)$. It has been found earlier that the influence of confinement seems to be more pronounced on valence orbitals leading to the rearrangement of atomic states at strong confinement regime [10,82]. Once we move from free to confinement limit, multiple crossovers between states occur, and the above order gets dissolved. This ordering is a function of $r_c$. From panel (a), it can be checked that at $r_c = 4, 5.6, 7.2$ and 8.1 crossovers between 1s2s 1S, 1s3d 1D; 1s2s 1S, 1s3d 3D; 1s2s 3S, 1s2p 3P; 1s2s 3S, 1s2p 1P occur, respectively. Moreover, the last three crossings are clearly visible from panel (b). It is to be noted that beyond the range of $r_c$ plotted here, several other crossings happen, which are not given this figure, to avoid clumsiness.

The outcomes of Fig. 1 motivate us to explore the ordering of various singly excited singlet and triplet states at strong confinement region. In this context, the energies for the first thirty-two singly excited triplet and singlet states arising from different singly excited configurations are provided in ascending order at $r_c = 0.1$ in Table 4. The third, fourth and fifth columns provide the X-only, XC-Wigner and XC-LYP results, respectively. It has been verified thoroughly that apart from the presented states, no intermediate singly excited state can be found to lie in between them. It is to be noted here that in this limit of confinement, for all the states under consideration, Hund’s rule is satisfied; singlet states possess higher energy than the triplets.

Till now we were involved in exploring the impact of confinement on total energy of $\text{H}^-$ ion. It has been found that both X-only and correlated energies diminish with an increase in $r_c$ and merge to respective free limits. At this point, it is sensible to investigate the variation in correlation with change in confinement strength. In this regard, Wigner and LYP correlation energies are plotted in panels (a)–(d) of Fig. 2, respectively. The left panels (a), (c) represent corresponding singlet states, and right panels (b), (d) indicate respective triplet states. From (a) and (b), it is evident that for both singlet and triplet states Wigner correlation energies accelerate with growth in $r_c$. This observation corroborates the pattern from a Hylleraas calculation [19]. Moreover, throughout the range in $r_c$, the Wigner correlation energies remain negative for all these states. It is noteworthy that correlation energy is the difference between exact energy and HF energy. Further, HF energy is always upper bound to the exact energy. Therefore, correlation energy should be negative. Here, Wigner correlation energies obey this criteria. Now we move to analyze the LYP correlation energy. On the
contrary, from panels (c) and (d) it can be seen that except for 1s4s $^3$1S states, LYP correlation energies for all other states decrease with progress in $r_c$. However, for 1s4s $^3$1S states, it initially decreases with $r_c$, attains a flat minimum and then increases again. However, in the entire range of $r_c$, such energies for all these given states attain both positive and negative values.

We have also examined the ratio of correlation energy and respective total energy in Fig. 3 for Wigner [(panels (a), (b)) and LYP (panels (c),(d)) functionals for the same set of excited states studied in Fig. 2. Here, also panels (a), (c) refer to singlet states and (b), (d) signify triplet states. For each of these states involving either of the functionals, a sudden jump occurs at a characteristic $r_c$. This jump is not due to the sign change in either of the energies. Because Wigner correlation energies are always negative, LYP can be both positive and negative. Thus, for all these states, these two energies connected to XC-Wigner change their domain from negative correlation energy and positive total energy in low $r_c$ to negative correlation energy and negative total energy in free limit. However, for XC-LYP case, same change occurs from positive correlation energy and positive total energy region to negative correlation energy and negative total energy.

**3.2 Shannon entropy and Onicescu energy**

Now we apply this method to compute $S_r, E$ in conjugate $r$ and $p$ spaces. This gives a scope to verify and assess the quality of density in such states under hard confinement. Because they act as descriptor in interpreting various chemical phenomena. Moreover, it will help us to understand the correlation contribution in the present endeavor.

Table 5 tabulates the numerical values of $S_r$ and $S_p$ for H$^-$ ion in ground state at certain selected $r_c$ values. In all three occasions (X-only, XC-Wigner, XC-LYP), $S_r$ increases and $S_p$ decreases with growth in $r_c$. This amplifies the conclusion that electron density gets compressed with strengthening of confinement effect. At strong confinement zone, both X-only and correlated results in either space become identical. However, with the increase in $r_c$, this situation alters indicating the contribution of correlation effect in density. Similar observation was also reported in [58] for He-isoelectronic series involving He, Li$^+$ and Be$^+$. At $r_c \geq 1$ regime, X-only values of $S_r$ are higher compared to both Wigner and LYP results. However, in $p$-space, a reverse behavior is noticed. X-only values are smaller relative to correlated results. The BLYP [25] $S_r$ and $S_p$ are quoted in the last two columns of table. The
that (Wigner and LYP Shannon entropies are in complete
value of 3(1 + ln 3).

| $r_c$ | $S_r$ (X-only) | $S_p$ (X-only) | $S_r$ (XC-Wigner) | $S_p$ (XC-Wigner) | $S_r$ (XC-LYP) | $S_p$ (XC-LYP) | Literature |
|------|----------------|----------------|------------------|------------------|----------------|----------------|------------|
| 0.1  | -6.21007       | 14.1888        | -6.21007         | 14.1888          | -6.16007       | 13.0692        | -6.16007   |
| 0.2  | -4.13691       | 12.1115        | -4.13691         | 12.1115          | -4.88400       | 10.9927        | -4.88400   |
| 0.3  | -2.92960       | 10.9867        | -2.92960         | 10.9867          | -2.87704       | 9.7774         | -2.87704   |
| 0.5  | -1.40751       | 9.3668         | -1.40751         | 9.3668           | -1.35498       | 8.2477         | -1.35498   |
| 0.7  | -0.41162       | 8.3593         | -0.41177         | 8.3593           | -0.35658       | 7.2412         | -0.35658   |
| 1    | 0.63727        | 7.2955         | 0.63721          | 7.2956           | 0.69568        | 6.1776         | 0.69568    |
| 1.2  | 1.16957        | 6.7504         | 1.1699           | 6.7527           | 1.23929        | 5.6364         | 1.23929    |
| 1.5  | 1.81613        | 6.0918         | 1.81523          | 6.0923           | 1.87883        | 4.9779         | 1.87883    |
| 1.8  | 2.33015        | 5.5550         | 2.33780          | 5.5565           | 2.40340        | 4.4451         | 2.40340    |
| 2    | 2.63685        | 0.1578         | 2.63097          | 5.2493           | 2.70343        | 4.1406         | 2.70343    |
| 2.5  | 3.26494        | 4.6048         | 3.26811          | 4.6065           | 3.32850        | 3.5086         | 3.32850    |
| 3    | 3.76475        | 4.0003         | 3.76088          | 4.0029           | 3.82454        | 3.0127         | 3.82454    |
| 5    | 5.01519        | 2.7464         | 5.07112          | 2.7555           | 5.08496        | 1.8241         | 5.08496    |
| 6    | 5.50678        | 2.3211         | 5.492351         | 2.3341           | 5.46497        | 1.5157         | 5.46497    |
| 8    | 6.11312        | 1.7284         | 6.090080         | 1.7495           | 5.98988        | 1.1630         | 5.98988    |
| 10   | 6.52773        | 1.3347         | 6.4987           | 1.3619           | 6.36304        | 0.9543         | 6.36304    |
| 15   | 7.18923        | 0.7177         | 7.1486           | 0.7528           | 7.0703         | 0.5437         | 7.0703     |
| 25   | 7.9460         | -0.05127       | 7.8851           | 0.0932           | 7.8138         | -0.00327       | 7.8138     |

(a)Ref. [25]

| $r_c$ | $S_r$ (1s2s 3S) | $S_p$ (1s2s 3S) | $S_r$ (1s2p 3P) | $S_p$ (1s2p 3P) |
|------|----------------|----------------|----------------|----------------|
| 0.1  | -6.21007       | 14.1888        | -6.21007       | 14.1888        |
| 0.2  | -4.13691       | 12.1115        | -4.13691       | 12.1115        |
| 0.3  | -2.92960       | 10.9867        | -2.92960       | 10.9867        |
| 0.5  | -1.40751       | 9.3668         | -1.40751       | 9.3668         |
| 0.7  | -0.41162       | 8.3593         | -0.41177       | 8.3593         |
| 1    | 0.63727        | 7.2955         | 0.63721        | 7.2956         |
| 1.2  | 1.16957        | 6.7504         | 1.1699         | 6.7527         |
| 1.5  | 1.81613        | 6.0918         | 1.81523       | 6.0923         |
| 1.8  | 2.33015        | 5.5550         | 2.33780       | 5.5565         |
| 2    | 2.63685        | 0.1578         | 2.63097       | 5.2493         |
| 2.5  | 3.26494        | 4.6048         | 3.26811       | 4.6065         |
| 3    | 3.76475        | 4.0003         | 3.76088       | 4.0029         |
| 5    | 5.01519        | 2.7464         | 5.07112       | 2.7555         |
| 6    | 5.50678        | 2.3211         | 5.492351      | 2.3341         |
| 8    | 6.11312        | 1.7284         | 6.090080      | 1.7495         |
| 10   | 6.52773        | 1.3347         | 6.4987        | 1.3619         |
| 15   | 7.18923        | 0.7177         | 7.1486        | 0.7528         |
| 25   | 7.9460         | -0.05127       | 7.8851        | 0.0932         |

Wigner and LYP Shannon entropies are in complete correspondence with these cited values. It is evident that ($S_r + S_p$) always remains greater that its limiting value of 3(1 + ln r).

Next, $S_r$, $S_p$ values for 1s2s 3S and 1s2p 3P states are reported in Table 6. The second to seventh columns represent 3S, whereas the last six columns indicate 3P. No previous literature is available to match with our results. Analogous to the ground state, here also for either of the states, X-only and correlated entropies are uniform at strong confinement zone and the correlation contribution grows with a rise in $r_c$. Further, at $r_c \geq 1$ region, the X-only results are comparatively higher than those from Wigner and LYP. It has been found that at low to moderate $r_c$ region, energies of 1s2s 3S state are larger than 1s2p 3P, and crossing occurs when $r_c$ value lies in between 5 and 6. However, an exactly opposite trend is encountered here in the context of $S_r$. These
values for the former state are less than those of the latter, and a crossover happens at \( r_c \approx 6 \). However, \( S_p \) obeys the same pattern as observed in energy. As usual, the sum of \( r \)- and \( p \)-space \( S \) is higher than the bound value of 6.43418.

In order to get a better insight about the influence of confinement on entropies, \( S_r, S_p, S_t \) are plotted as a function of \( r_c \), in panels (a)–(c) of Fig. 4, for \( 1s^2 \, ^1S, 1s2s \, ^3S, 1s2p \, ^3P \) states. The correlation effect does not alter the qualitative nature of the graph. Hence, X-only results suffice. As seen, \( S_r \) progresses with a gain in \( r_c \), while \( S_p \) declines. In conformity with Table VI, panel (a) also indicates the crossover between \( 1s2s \, ^3S, 1s2p \, ^3P \) states at around \( r_c = 6 \). However, multiple crossovers between \( 1s^2 \, ^1S, 1s2s \, ^3S; 1s^2 \, ^1S, 1s2p \, ^3P \) are seen at \( r_c \approx 6,11 \), respectively, in panel (b). \( S_t \) in all these three cases initially declines, then attains a minimum and finally increases.

In one-electron system, \( S_t \) is independent of effective nuclear charge \( Z \) [52]. However, in a many-electron systems, this situation alters and it depends on \( Z \). Previously, \( S_t \) was employed in explaining the correlation effect in both free and confined conditions [52]. Now, \( S_t \) has been plotted as a function of correlation energy in Fig. 5. Panels (a) and (b) represent Wigner and LYP functionals. In the former case, for all these three states, it decays with a rise in \( \epsilon_{\text{corr}} \), then reaches a minimum and then sharply increases thereafter. On the contrary, for LYP functional involving \( 1s^2 \, ^1S, 1s2s \, ^3S \) states, it sharply decreases to a minimum and then gradually increases with a rise in \( \epsilon_{\text{corr}} \). Further, for \( 1s2p \, ^3P \) state, it always rises with \( \epsilon_{\text{corr}} \).

Now, we are interested to investigate \( E \) in the same three representative \( (1s^2 \, ^1S, 1s2s \, ^3S, 1s2p \, ^3P) \) states of confined \( H^- \) ion. It generally complements \( S \) by showing an opposite behavior. To the best of our knowledge, \( E \) for confined \( H^- \) ion has never been investigated before. Therefore, in future, the present work may offer important guideline in this context.

Next, Table 7 provides \( E_r \) and \( E_p \) for \( H^- \) ion in ground state at the same \( r_c \) values chosen in Table 5. X-only (columns 2, 3), Wigner (columns 4, 5) and LYP (columns 6, 7) results are given. \( E_r \) progresses and \( E_p \) abates with growth in \( r_c \). At \( r_c \rightarrow 0 \) region, X-only and correlated results in both spaces become very similar. Akin to \( S \), with an increase in \( r_c \), this situation alters implying the participation of correlation contribution in density. Then, \( E_r, E_p \) for \( 1s2s \, ^3S \) and \( 1s2p \, ^3P \) states are presented in Table 8. The arrangement is similar to Table 6. \( ^3S \) values are given in the second to sev-
enth columns, while \(^3P\) results are given in the last six columns. Similar to the ground state, here also for both states, the X-only and correlated results resemble each other at strong confinement limit. At low to moderate \(r_c\) region, \(E_r\) values of \(1s2s \, ^3S\) state lie higher than \(1s2p \, ^3P\) state and crossing occurs in between \(r_c = 5\) and \(6\). However, \(E_p\) follows a reverse pattern.

Finally, \(E_r\), \(E_p\), \(E_t\) for \(1s^2 \, ^1S\), \(1s2s \, ^3S\), \(1s2p \, ^3P\) states are plotted as functions of \(r_c\) in panels (a)-(c) of Fig. 6, respectively. As usual, here also consideration of X-only results is sufficient to illustrate the essential purpose. \(E_r\) declines with gain in \(r_c\), while \(E_p\) accelerates. As expected, multiple crossings between states take place, but they are not prominent from panel (a). However, panel (b) indicates the crossover between \(1s^2 \, ^1S\), \(1s2s \, ^3S\) and \(1s^2 \, ^1S\), \(1s2p \, ^3P\). \(E_t\) in all these three cases increases with \(r_c\).
4 Future and outlook

An appropriate and effective KS DFT method is presented for calculation of H⁻ ion trapped inside an impenetrable spherical cavity of varying radius. The proposed recipe is computationally achievable and can easily be applied to other atoms in both ground and excited states. Energies are reported for ground and selected singly excited (1s2s 3S, 1s2p 3P) states of H⁻ ion in wide range of rc covering strong, moderate and weak confinement regime. Accurate results for a given state can be achieved, provided the exchange contribution is properly taken into account, which, of course, is the key reason behind the general success of this approach. Wigner correlation energies show qualitative similar behavior with the high-quality result of Hylleraas method. The results are generally in good agreement with the available literature. X-only results are very close to HF. A detailed investigation involving the singly excited states has been done to understand the rearrangement of atomic orbitals in strong confinement region.

In order to test the quality of the constructed density, S, E in composite r and p-spaces have been studied for ground and 1s2s 3S, 1s2p 3P states. To the best of our knowledge, this is the first reporting of information entropy in both ground and excited states of confined atoms in very strong confinement (rc ≤ 0.1) region. This study reinforces the previous conclusion [58] that at strong confinement zone, contribution of correlation effect in density is small. In order to increase the correctness and accuracy of the method, better correlation energy functionals are required to be designed and incorporated. In future, the present method may be extended to other atoms as well. Further, it is encouraging to probe the current procedure for other important realistic confinement scenario (such as encapsulation of an atom in supramolecular cavity). Investigation of multipole polarizability, atomic avoided crossing, hyperpolarizability, influence of electric and magnetic field through dynamical study is highly desirable, some of which may be undertaken later.

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Author contributions

SM and AKR wrote the computer code for the problem. SM and NM generated the data, carried out the analysis of results, interpretation of the data and drafted the manuscript. AKR formulated the problem, drafted the manuscript, approved the version of the manuscript and procured the funding.

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