Ps^- and H_2^+ Ions under Spatial Confinement

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Abstract. The ground state energy eigenvalues of the spatially confined symmetric three-body exotic ions Ps^- and H_2^+ have been determined under the framework of Rayleigh-Ritz variational method. The spatial confinement is simulated by considering an impenetrable spherical box of varying radius around the ion. The electron-electron correlation in Ps^- and the proton-proton correlation in H_2^+ are properly taken care of by expanding the trial wavefunction in explicitly correlated Hylleraas type basis set. The critical radius and the corresponding critical pressure, at which the respective ions destabilize are also reported.

Keywords. Spatial confinement; Exotic three-body ions; Hylleraas basis; Correlation; Variational method

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1. Introduction

Spatial confinement means a system (*i.e.*, an ion, atom, molecule) is enclosed inside a finite domain. Due to such spatial restriction, the system feels an external pressure, the magnitude of which depends on the radius of the cavity. This thermodynamic pressure pushes the energy levels of the ion towards continuum which itself is lowered due to effect of confinement. Such modifications in the structure of the system results in evolution of various novel properties of confined quantum mechanical systems. Though the study of confined atomic systems started

long ago [1, 2], in recent times it has received immense attention from researchers [3–8]. Such studies are necessary for estimating the modification of spectral properties of atomic systems in different environments from which indirect information about the environment may be obtained.

It is a challenging task, both from mathematical and computational aspects, to calculate the structure of three-body ions within a finite domain due to the truncation of wave function at the boundary. Several efforts have been made by researchers to incorporate the effect of correlation within a finite domain of arbitrary size. It is well known that explicitly correlated wave functions expanded in Hylleraas basis can produce highly precise non-relativistic energy values of three-body ions in Rayleigh-Ritz variational technique. However, the difficulty lies in using large dimensions of the wave functions in Hylleraas basis due to the loss of linear independence of the basis [3]. To use a fully flexible range of non-linear parameters, through which the entire space available to the system is spanned, also becomes difficult in this formalism. Recently, a general methodology to carry out finite domain two-particle correlated integrals in Hylleraas basis with flexible parameters has been developed by Bhattacharyya *et al.* [8, 23] where the problem of linear dependency in larger dimensions is avoided successfully.

Even after resolving the difficulty of theoretical calculations for three-body ions within a finite domain, there exists no such calculation for exotic systems. Such exotic ions may be formed in experiments via recapture or ionization processes. It is highly interesting to examine the behaviour of such three-body exotic ions placed inside a finite volume. In the present work we consider the positronium ion Ps^- ($e^+e^-e^-$) and also the molecular hydrogen ion H_2^+ ($p^+p^+e^-$) within a finite domain. The positronium negative ion is a purely leptonic system consisting of two electrons and one positron. It was first observed in the laboratory by Mills [9], and recently it has been gaining considerable experimental interest for measuring its annihilation rate [10]. For several years, it is an active area of research in various directions such as measuring the photo-ionization cross sections [11, 12], calculations of its ground state energy [13, 14] and doubly excited resonance states *etc*. The Ps^- ion has also found its application in monitoring work functions of surface plasma source [18], in astrophysical context [17]. On the other hand, the hydrogen molecular ion (H_2^+) has played a crucial role in the development of molecular quantum mechanics. This ion has an essential importance not only in atomic and molecular physics, but also in astrophysics and semiconductor physics, solid state and plasma physics [15]. The energy levels of confined H_2^+ ion has been studied by Molinar-Tabares and Campoy-Güereña [19] using numerical approach in prolate spheroidal coordinates. Very recently, Olivares-Pilón and Cruz [20] have also studed the energy levels of H_2^+ ion inside impenetrable spheroidal cavity in Lagrange-mesh approach. In this work, we have estimated the ground state energy values of the Ps^- ion and H_2^+ molecular ion within spherical confinement where the confinement is taken in a very wide range, from close to the '*free*' limit to the limit of destabilization of the system. The ground state energy levels of two body subsystems corresponding to both the systems, *i.e.* positron (e^+e^-) for Ps^- and hydrogen (p^+e^-) for H_2^+ ion, have also been studied within confined domain for a comprehensive analysis of the structure of three body ions.

2. Method

Exploiting the translation symmetry of the Hamiltonian of any arbitrary quantum three-body system, it is possible to describe the motion of the system with respect to their center of mass in six co-ordinates. For a symmetric three-body system e.g. Ps^-, H_2^+,... etc., two particles are identical and the third one is different either with respect to charge or mass or both. We define the distances of the identical particles (of mass m) 1 and 2 with respect to the third particle (of mass M) as r_1 and r_2 and the distance between the particles 1 and 2 is r_{12}. For the spherically symmetric ground state ($^1S^e$) of a three-body system, the general variational equation [21] for arbitrary angular momentum reduces to,

$$\delta \int \left[\frac{1}{2}\left(\frac{1}{m}+\frac{1}{M}\right)\left\{\left(\frac{\partial\Psi}{\partial r_1}\right)^2 + \left(\frac{\partial\Psi}{\partial r_2}\right)^2\right\} + \frac{1}{m}\left(\frac{\partial\Psi}{\partial r_{12}}\right)^2 + \frac{1}{M}\cos(r_1,r_2)\frac{\partial\Psi}{\partial r_1}\cdot\frac{\partial\Psi}{\partial r_2} \right.$$
$$\left. + \frac{1}{m}\left\{\cos(r_2,r_{12})\frac{\partial\Psi}{\partial r_2}\cdot\frac{\partial\Psi}{\partial r_{12}} + \cos(r_1,r_{12})\frac{\partial\Psi}{\partial r_1}\cdot\frac{\partial\Psi}{\partial r_{12}}\right\} + (\mathcal{V}-E)\Psi^2 \right] d\tau = 0 \qquad (1)$$

where the volume element is $d\tau = r_1 r_2 r_{12} dr_1 dr_2 dr_{12}$ and we have defined,

$$\cos(r_i,r_j) = \frac{r_i^2 + r_j^2 - r_k^2}{2\,r_i\,r_j} \qquad (2)$$

where, the indices $i,j,k \equiv 1,2,12$ and the proton mass is taken as $m_p = 1836.1526675 * m_e$. It should be mentioned here that $m_e = 1$ is taken as we have considered atomic units throughout unless otherwise specified. Thus for Ps^-, $M = m = m_e$ and for H_2^+, $M = m_e$, $m = m_p$. The potential is given by

$$\mathcal{V} = -\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}} + \mathcal{V}_{ext}, \qquad (3)$$

where the external potential has the form of an impenetrable spherical box of radius R,

$$\mathcal{V}_{ext} = \begin{cases} 0 & \text{for } 0 \le r_1,\ r_2 \le R \\ \infty & \text{elsewhere.} \end{cases} \qquad (4)$$

Due to such spatial constraint, the trial radial wave function $\Psi(r_1,r_2,r_{12})$ can be written as,

$$\Psi(r_1,r_2,r_{12}) = (R-r_1)(R-r_2)f(r_1,r_2,r_{12}) \qquad (5)$$

where,

$$f(r_1,r_2,r_{12}) = \left[\sum_{i=1}^{3}\eta_i(1)\eta_i(2) + \sum_{i=1}^{3}\sum_{j=1}^{3}\eta_i(1)\eta_j(2)\right]g(1,2). \qquad (6)$$

In the second sum $i < j$ and $\eta_i(j) = e^{-\rho_i r_j}$, ρ being the non-linear parameter. The function $g(1,2)$ containing correlation terms, is expanded into Hylleraas type basis set as follows,

$$g(1,2) = \sum_{l \ge 0}\sum_{m \ge 0}\sum_{n \ge 0} C_{lmn} r_1^l r_2^m r_{12}^n \qquad (7)$$

subject to the box normalization condition

$$\int_0^R |\Psi(r_1,r_2,r_{12})|^2 d\tau = 1 \qquad (8)$$

The effect of the radial correlation is incorporated through different non-linear parameters ρ's in the wave function whereas, the angular correlation effect is taken care of through different

powers of r_{12}. The non-linear parameters ρ's are optimized using Nelder-Mead procedure [22]. After choosing the proper trial radial wave function, the energy eigenvalues are obtained by solving the generalized eigenvalue equation given by

$$\underline{\underline{H}}\,\underline{C} = E\underline{\underline{S}}\,\underline{C} \tag{9}$$

where $\underline{\underline{H}}$ and $\underline{\underline{S}}$ are Hamiltonian and overlap matrices, respectively. The necessary basis integrals of the form

$$A(R;m,n,l;a_1,a_2) = \int_{r_1=0}^{R}\int_{r_2=0}^{R}\int_{|r_1-r_2|}^{r_1+r_2} r_1^m r_2^n r_{12}^l e^{-a_1 r_1 - a_2 r_2}\,dr_1 dr_2 dr_{12} \tag{10}$$

with the condition, $m \geq 0$, $n \geq 0$, $l \geq 0$ and $a_1, a_2 > 0$ have been evaluated analytically, the details of which can be found in ref. [23]. All calculations are carried out in quadruple precision in order to achieve a better numerical accuracy.

3. Results and Discussion

The computed ground state energy eigenvalues of Ps^- and H_2^+ are presented in Table 1. The radius of the impentrable spherical cavity is varied for a wide range *i.e.* from a very large value corresponding to almost a free system to a small value which can lead the system towards destabilization. The size of the wavefunction is sufficient to explore the overall structural features of such confined exotic systems with resonable accuracy. To be precise, a 39 parameter triple-exponent correlated wavefunction is considered for Ps^- while a 66 parameter triple-exponent correlated wavefunction is taken for the H_2^+ ion. Thus, the maximum value of $\omega = l + m + n$ is 3 for Ps^- and 4 for H_2^+. For $R = 50$ a.u., the ground state energy of Ps^- is $-0.262\,004$ a.u. while that of free Ps^- is $-0.262\,005\,069\,97$ a.u. [24]. This comparison shows that the radius $R = 50$ a.u. can be considered as almost '*infinite*' radial distance for Ps^- and the system Ps^- can be considered almost free.

Table 1. Energy eigenvalues ($-E$ in a.u.) of the ground state of exotic Ps^- and H_2^+ ion within impenetrable cavity of radius R (in a.u.). The uncertainty of the calculated energy values is of the order of 10^{-5} a.u.

	$-E$ (in a.u.)			$-E$ (in a.u.)	
R	Ps^- ($e^+e^-e^-$)	Ps (e^+e^-)	R	H_2^+ ($p^+p^+e^-$)	H (p^+e^-)
50	0.262 004	0.249 999	60	0.588 398	0.499 727
30	0.261 907	0.249 999	30	0.588 248	0.499 727
20	0.260 635	0.249 999	10	0.588 020	0.499 727
15	0.256 139	0.249 970	5	0.577 427	0.496 131
10	0.229 743	0.248 208	3	0.414 485	0.423 547
9	0.214 167	0.246 103	2.8	0.362 789	0.396 207
8	0.189 169	0.241 633	2.6	0.290 580	0.358 569
7	0.147 631	0.232 178	2.4	0.197 246	0.305 826
6	0.074 947	0.211 984	2.3	0.138 387	0.271 883
5.5	0.018 137	0.194 182	2.2	0.069 136	0.231 377
5.38	0.001 521	0.188 734	2.12	0.004 757	0.193 243

We have also estimated the position of the respective thresholds *i.e.* the ground state energies of Ps and H for different values of R for a comprehensive understanding. The variational equation for $1s$ (^2S) states of one electron ion within a cavity of radius R can be written as

$$\delta \int_0^R \left[\frac{1}{2\mu} \left(\frac{\partial f}{\partial r} \right)^2 - \frac{1}{r} + \mathscr{V}_{ext} - E \right] r^2 dr = 0 \tag{11}$$

where $f(r)$ is the two-body radial function consistent with the boundary condition

$$f(r) = (R - r) \sum_{i=1}^{10} C_i r^{n_i} e^{-\alpha_i r} \tag{12}$$

which satisfies the box normalization condition

$$\int_0^R f^2 r^2 dr = 1. \tag{13}$$

It is evident from the table-1 that as R decreases, the energy values of both three-body and the corresponding two-body subsystem becomes more and more positive leading towards destabilization. The pattern of variation of ground state energy eigenvalues of both Ps^- and Ps vs. R is depicted in Figure 1 while that of H_2^+ and H vs. R is given in Figure 2. It seems that the general feature of both the patterns are quite identical *i.e.* down to a certain value of R, the energy value remains almost constant and further decrease in R leads the system towards rapid destabilization. Thus the pattern shows a '*knee*' like structure which is similar to that of the atomic systems [8, 25]. For Ps^- ion, the '*knee*' appears at around 10 a.u. whereas for H_2^+, it appears at around 4 a.u., as is seen from the figures.

Evolution of quasibound states [26, 27] is one of the interesting characteristics of such spatially confined atomic systems [25]. The ground state energy level of free Ps^- lies below that of free Ps. It is to be noted from Figure 1 that, as R decreases, the ground state of Ps^- approaches to that of Ps and thus the ionization potential decreases. But interestingly, at some value of R between 15 to 10 a.u., the energy level of Ps^- goes above the Ps level and hence Ps^- becomes quasibound. Similar feature is also evident for H_2^+ from Figure 2. H_2^+ becomes quasibound for a value of radius R ranging between 5 to 3 a.u.

Due to the truncation of wavefunction at a finite distance, a thermodynamic pressure is imposed on the exotic ions inside the sphere which increases with decrease of R. Under an adiabatic approximation, the critical pressure felt by the ions Ps^- and H_2^+ can be expressed as [1, 25]

$$P_c = -\frac{1}{4\pi R_c^2} \frac{dE_c}{dR_c} \simeq -\frac{1}{4\pi R_c^2} \frac{\Delta E_c}{\Delta R_c} \tag{14}$$

where E_c is the ground state energy of the ion inside the sphere of critical radius R_c at which the three-body system ceases to be in the bound state. In the present calculation, we have taken $\Delta R_c = 10^{-5}$ a.u. and calculated the corresponding expression $\Delta E_c = E(R_c) - E(R_c + \Delta R_c)$. It reveals that the critical pressure felt by the Ps^- ion is 8.09×10^{10} Pa corresponding to the critical radius of 5.38 a.u. while H_2^+ experiences critical pressure of 4.68×10^{11} Pa at the critical radius of 2.12 a.u. We have considered the conversion factor, 1 a.u. of pressure = 2.9421912 $\times 10^{13}$ Pa.
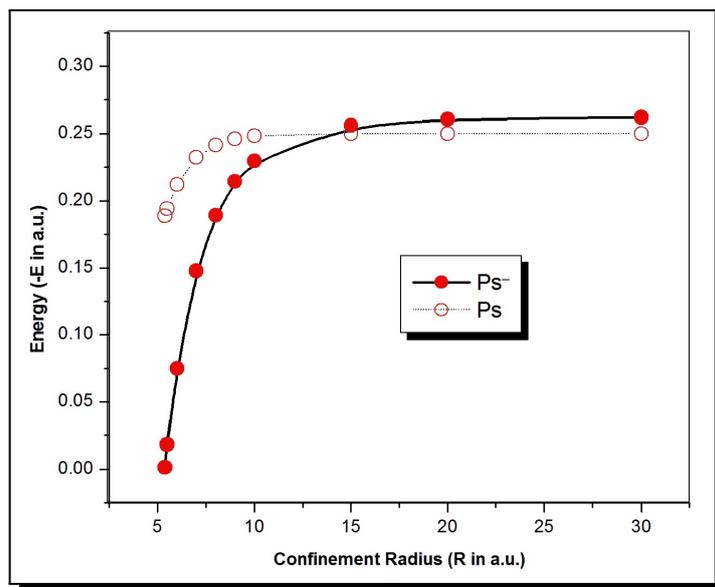
Figure 1. Variation of ground state energy eigenvalues ($-E$ in a.u.) of Ps^- and Ps with respect to the confinement radius (R in a.u.).
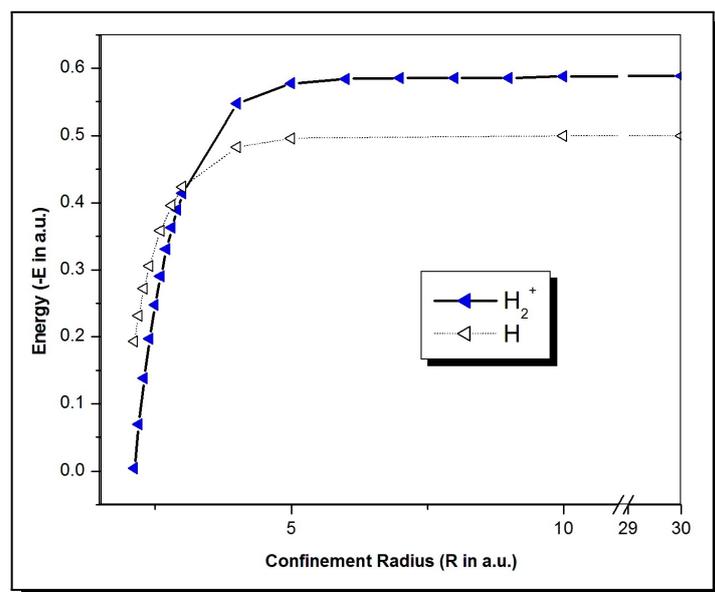
Figure 2. Variation of ground state energy eigenvalues ($-E$ in a.u.) of H_2^+ and H with respect to the confinement radius (R in a.u.).

4. Conclusion

The energy values of the ground state of the spatially confined exotic ions Ps^- and H_2^+ have been studied extensively. The effect of correlation that plays a crucial role in forming these ions has been considered explicitly through the wave function expanded in terms of triple-exponent Hylleraas type basis set. Evolution of the ground state of the three-body system as a quasi-bound states under spatial confinement is one of the interesting findings that comes

out of the present theoretical investigation. Calculation of singly and doubly excited states having nonzero angular momentum of such exotic atomic and molecular ions are in the pipeline. Moreover, muonic, pionic and kaonic molecular ions under spatial confinement can also be studied under the present theoretical framework.

Competing Interests

The author declares that he has no competing interests.

Authors' Contributions

The author wrote, read and approved the final manuscript.

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