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Excitons and the Positronium Negative Ion: Comparison of Spectroscopic Properties

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Abstract

In view of the analogy of an exciton, biexciton and trion to the positronium (Ps) atom, Ps molecule, and Ps negative ion, in this chapter, we review our recent works on the Ps atom, Ps negative ion (Ps^-), and Ps-Ps interaction with Coulomb and screened Coulomb interactions for better understanding of spectroscopic properties of excitons, and excitonic ions and molecules. For the Coulomb case, this chapter describes the recent theoretical developments on the ground state, resonance states, photodetachment cross sections, polarizability and the recent experimental advancement on the efficient formation, photodetachment, resonance state of Ps^- . The chapter also presents results for the lowest $^3\text{D}^e$ Feshbach and $^1\text{P}^o$ shape resonances for Ps^- using correlated exponential wavefunctions. The $^1\text{P}^o$ shape resonance parameter is in agreement with the recent experiment. For screened interactions, various properties of Ps and Ps^- along with the dispersion coefficients for Ps-Ps interaction have been reviewed briefly. This review describes the effect of screened interactions on various properties of Ps^- within the framework of both screened Coulomb potential (SCP) and exponential-cosine-screened Coulomb potential (ECSCP). The influence of ECSCP on the dipole and quadrupole polarizability of Ps^- as functions of screening parameter and photon frequency are presented for the first time.

Keywords: excitons, positronium atom, trions, positronium negative ion, bi-excitons, positronium molecule, correlated exponential wave functions, spectroscopic properties, variational methods

1. Introduction

An exciton is a bound state of an electron and a positive hole (an empty electron state in a valence band), which is free to move through a nonmetallic crystal as unit. The electron and the positive hole are attracted to each other by the electrostatic Coulomb force. Excitons are electrically neutral quasiparticles that exist in insulators, semiconductors, and in some liquids. Excitons are difficult to detect as an exciton as a whole has no net electric charge, but the

detection is possible by indirect means. Excitons can be described at various levels of sophistication; among them, the simplest and intuitive pictures can be understood using the effective mass approximation. Such approximation suggests that the Coulomb interaction between an electron and a positive hole leads to a hydrogen-like problem with a Coulomb potential term $-e^2/(4\pi\epsilon_0\epsilon|\mathbf{r}_e-\mathbf{r}_h|)$. Indeed, excitons in semiconductors form, to a good approximation, a hydrogen- or positronium-like series of states below the gap. The analogy of excitons to the hydrogen atom or even better the positronium atom can be pushed further. In analog to the formation hydrogen molecule or positronium molecule, two excitons can bind to form a new quasiparticle, the so-called bi-exciton or excitonic molecule. Similarly, in analog to the hydrogen molecular ion or the positronium negative ion, it is possible to form trions which are charged excitons or bi-excitons, i.e., quasiparticles of two electrons and one hole or vice versa. Like Ps molecule or Ps negative ion, bi-excitons or trions can also form bound states or quasi-bound states from the theoretical point of view. For detail discussions, classifications, and list of references on excitons, interested readers are referred to the review book authored by Klingshirn [1]. Keeping the above discussion in mind, it would be of great interest to review our works on the Ps atom, Ps negative ion, or Ps-Ps interaction for better understanding of spectroscopic properties of excitons, bi-excitons, or trions. The study of excitons under the influence of external environments is also of great interest both from theoretical and experimental sides. In this work, we have also discussed our recent study of the proposed systems under the influence screened Coulomb and cosine-screened Coulomb potentials.

The positronium negative ion (Ps^-) is the simplest bound three-lepton system (e^+ , e^- , e^-) for which the $^1\text{S}^e$ state is the only state stable against dissociation but unstable against annihilation into photons. The Ps^- has gained increasing interest from the theoretical studies and experimental investigations since its theoretical prediction [2] and discovery [3]. This ion is a unique model system for studying three-body quantum mechanics as the three constituents of the Ps negative ion are subject only to the electroweak and gravitational forces. This elusive ion is of interest in the various branches of physics including solid-state physics, astrophysics, and physics of high-temperature plasmas, etc. It is also important for workability of many technical devices, such as modern communication devices. The Ps^- has been observed first by Mills [4] almost 40 years ago, and he subsequently measured its positron annihilation rate [5]. Since then, several experiments have been performed on this ion. Review of the most recent experiments can be found in the article of Nagashima [6] which also contains a large number of useful references. This review [6] also includes discussion on efficient formation of ion, its photodetachment, and the production of an energy-tunable Ps beam based on the technique of the photodetachment. It is here noteworthy to mention the accurate measurement of the decay rate [7] and only measurement of the $^1\text{P}^o$ shape resonance of Ps^- [8]. Several theoretical studies have been calculated so far on various properties of this ion, such as bound state [9–17], annihilation rate [16–18], photodetachment cross sections [19, 20], resonance states [21–24], and polarizability [25–27], using the numerical approaches such as the variational principle of Rayleigh-Ritz [9, 15–17, 28, 29], the correlation function hyperspherical harmonics method

[30–32], the complex-coordinate rotation method [33–36], the stabilization method [36–40], and the pseudostate summation method [25–27, 41–43]. Full list of articles can be found in the next sections. Besides such properties in the Coulomb case, several properties of the Ps negative ion have been studied under the influence of screened Coulomb potential (SCP) and exponential cosine-screened Coulomb potential (ECSCP). It is important to mention here that the study of atomic processes under the influence of screened interactions is an interesting, relevant, and hot topic of current research [44–49]. The complete SCP in a general form can be written as [50, 51]

$$V(r) = \begin{cases} Ze^2 \left(\frac{1}{r} - \frac{1}{\lambda_D + \lambda_A} \right), & r \leq \lambda_A \\ \left(\frac{\lambda_D}{\lambda_D + \lambda_A} \right) \frac{Ze^2}{r} \exp \left(-\frac{r - \lambda_A}{\lambda_D} \right), & r \geq \lambda_A \end{cases}, \quad (1)$$

where Z , λ_D , and λ_A denote the nuclear charge, the screening length, and the mean radius of the ion sphere, respectively. In the limit when $\lambda_A \rightarrow 0$, Eq. (1) reduces to the Debye-Hückel potential [52]. The ECSCP in form can be written as [53]

$$V(r) = \left(\frac{Ze^2}{r} \right) \exp(-\mu r) \cos(\mu r), \quad (2)$$

where μ is the screening parameter. The SCP or ECSCP occurs in several areas of physics (solid-state physics, ionized plasma, statistical thermodynamics, and nuclear physics). The potentials are also used in describing the potential between an ionized impurity and an electron in a metal or a semiconductor and the electron-positron interaction in a positronium atom in a solid [44–55]. In the next sections, we will briefly describe the properties of Ps negative ion, such as bound state, positron annihilation, resonance states, photodetachment, and polarizability. Bound states of the Ps atom and the Ps₂ molecule and dispersion coefficients on Ps-Ps interaction have also been discussed in the next sections.

2. Bound states

It is well-described that variational methods are the most effective and powerful tool for studying the Coulomb three-body bound-state problem [8, 11, 12, 16, 17, 56]. From here, we will concentrate on the works based on the variational approach. As mentioned in the last section, the Ps⁻ has very simple bound-state spectra that contain only one bound (ground), singlet state with total angular momentum, $L = 0$, i.e., 1 ¹S state for short. To calculate ground state energy of such ion, one needs to obtain the solutions of the Schrödinger equation, $H\Psi = E\Psi$, where $E < 0$ following the Rayleigh-Ritz variational method. Here, we review our works using correlated exponential wave functions. The nonrelativistic screened Hamiltonian H (in atomic units) for a system having two electrons and a positron is given by

$$H = T + V, \quad (3)$$

with

$$T = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2}\nabla_3^2, \quad (4)$$

$$V = -V(\mu, \mathbf{r}_{13}) - V(\mu, \mathbf{r}_{23}) + V(\mu, \mathbf{r}_{12}), \quad (5)$$

$$V(\mu, r_{ij}) = \frac{\exp(-\mu|\mathbf{r}_i - \mathbf{r}_j|)}{|\mathbf{r}_i - \mathbf{r}_j|} \cos(-\xi\mu|\mathbf{r}_i - \mathbf{r}_j|), \quad (6)$$

where 1 and 2 denote the two electrons and 3 denotes the positively charged particle and $|\mathbf{r}_i - \mathbf{r}_j| = r_{ji} = r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$. In Eq. (6), $\xi = 0$ for SCP, $\xi = 1$ for ECSCP, and $\mu = 0$ for unscreened case (UC).

The variational wave functions for the 1S -state of positronium negative ion can be shown as

$$\Psi_0(\mu) = \left(1 + \widehat{P}_{12}\right) \sum_{i=1}^{N_{B0}} C_i^0(\mu) \exp(-\alpha_i^0 r_{13} - \beta_i^0 r_{23} - \gamma_i^0 r_{12}), \quad (7)$$

where the operator \widehat{P}_{12} is the permutation of the two identical particles 1 and 2. N_{B0} is the number of basis terms. The nonlinear variational parameters $\alpha_i^0, \beta_i^0, \gamma_i^0$ in the basis sets (7) are generated by the judicious implementation of a pseudorandom process of the following form

$$X_i^n = \left[\frac{1}{2}i(i+1)\sqrt{p_X} \right] (R_{2,X} - R_{1,X}) + R_{1,X}, \quad (8)$$

$[x]$ is the fractional part of x , $[R_{1,X}, R_{2,X}]$ ($X = \alpha, \beta, \gamma$) are real variational intervals which need to be optimized, and p_X assigns a separate prime number for each X . Quite a few theoretical studies have been performed to calculate binding energies of the proposed ion using variational wave functions (7) and the Hylleraas-type wave functions:

$$\Psi_{kmn} = \sum_{kmn} C_{kmn} (\exp[-\alpha(r_{13} + r_{23})] r_{12}^k r_{13}^m r_{23}^n + (1 \leftrightarrow 2)). \quad (9)$$

In Eq. (9), we also have $k + m + n \leq \Omega$, with Ω, l, m , and n being positive integers or zero. Detailed works in free atomic cases can be found from the earlier works [9–17, 57, 58]. In the screening environments, the ground state energy of Ps^- along with the electron affinity of Ps atom has been estimated variationally by Saha et al. [57] using multi-term correlated basis sets and SCP. The bound-state properties including ground state energies, radial and correlation cusp for this ion, and electron affinity of Ps have been investigated by us [58] using SCP and correlated wave functions (7). The bound states of Ps atom have also been described in our previous work under SCP ([59], references therein). To calculate the bound states of Ps atom, we have used standard Slater-type orbitals (see Eq. (40) in Section 7). Similar properties have been studied by Ghoshal and Ho [59] using ECSCP and wave function (9). The results show

interesting behavior in the screening environments. The binding energies of the Ps molecule have been reported in previous works [60, 61].

3. Positron annihilation

The (e^+, e^-) -pair annihilation (or positron annihilation, for short) can proceed with the emission of a number of photons, for illustration, $e^+ + e^- = \gamma_1 + \gamma_2 + \gamma_3 \dots + \gamma_K$, where γ_K is the emitted photons and K is the maximal number of such photons [16, 17]. Each of the annihilation processes has its unique annihilation width or annihilation rate $\Gamma_{k\gamma}$. For the proposed ion, the two-photon case would be the dominant annihilation process. However, the one-photon and three-photon, etc., annihilation are possible but in smaller rates. The annihilation rates $\Gamma_{2\gamma}$, $\Gamma_{3\gamma}$, $\Gamma_{4\gamma}$, $\Gamma_{5\gamma}$, and $\Gamma_{1\gamma}$ (arranged according to their numerical values) are important in applications. Here, we mention the formula for the one-, two-, three-, four-, and five-photon and total annihilation (Γ) rates, respectively [16, 17, 58]:

$$\Gamma_{1\gamma} = \frac{64\pi^2}{27} \alpha^8 c a_0^{-1} \langle \delta_{321} \rangle = 1065.7569198 \langle \delta_{321} \rangle s^{-1}, \quad (10)$$

$$\begin{aligned} \Gamma_{2\gamma} &= n\pi\alpha^4 c a_0^{-1} \left[1 - \frac{\alpha}{\pi} \left(5 - \frac{\pi^2}{4} \right) \right] \langle \delta(r_{31}) \rangle \\ &= 100.3456053781 \times 10^9 \langle \delta(r_{31}) \rangle s^{-1}, \end{aligned} \quad (11)$$

$$\begin{aligned} \Gamma_{3\gamma} &= n\alpha^5 c a_0^{-1} \frac{4(\pi^2 - 9)}{3} \langle \delta(r_{31}) \rangle \\ &= 271.8545954 \times 10^6 \langle \delta(r_{31}) \rangle s^{-1}, \end{aligned} \quad (12)$$

$$\Gamma_{4\gamma} \approx 0.274 \left(\frac{\alpha}{\pi} \right)^2 \Gamma_{2\gamma}, \quad (13)$$

$$\Gamma_{5\gamma} \approx 0.177 \left(\frac{\alpha}{\pi} \right)^2 \Gamma_{3\gamma}, \quad (14)$$

$$\begin{aligned} \Gamma \approx n(\Gamma_{2\gamma} + \Gamma_{3\gamma}) &= 2\pi\alpha^4 c a_0^{-1} \left[1 - \alpha \left(\frac{17}{\pi} - \frac{19\pi}{12} \right) \right] \langle \delta(r_{31}) \rangle \\ &= 100.61745997357 \times 10^9 \langle \delta(r_{31}) \rangle s^{-1}, \end{aligned} \quad (15)$$

where α , c , and a_0 denote, respectively, the fine structure constant, the velocity of light, and the Bohr radius and $\langle \delta_{321} \rangle$ denotes the expectation value of three-particle delta function. It is obtained from the expectation value $\langle \Psi | \Psi \rangle$ evaluated for $r_{32} = r_{31} = r_{21} = 0$. Exploiting the results for $\langle \delta_{321} \rangle$ and $\langle \delta(r_{31}) \rangle$, one can easily calculate the values of $\Gamma_{1\gamma}$, $\Gamma_{2\gamma}$, $\Gamma_{3\gamma}$, $\Gamma_{4\gamma}$, $\Gamma_{5\gamma}$, and Γ using the explicit relation (10)–(15). The total annihilation rate along with the one-, two-, and three-photon annihilation rates, together with the values of $\langle \delta_{321} \rangle$ and $\langle \delta(r_{31}) \rangle$ for various Debye lengths, is reported in our earlier work. The annihilation rates obtained from our calculations [59] are in agreement with the reported results [16, 17]. Detailed calculations of

annihilation rate can be found from previous articles. As mentioned above, the positron annihilation process is of great interest in several areas of physics, such as astrophysics, solid-state physics, etc. It is also important for applicability of many technical devices, e.g., modern communication devices. In this review, we cited the recent references for free atomic case. For screened interaction, Kar and Ho [58] reported the annihilation rate under the influence of SCP, and Ghoshal and Ho [59] studied the similar features under ECSCP. The annihilation rates decrease with increasing screening strength.

4. Resonance states

A great number of theoretical studies on Ps^- have been performed in last few decades. Several studies have been performed on the resonances in e^- -Ps scattering using the theoretical methods such as the Kohn-variational method [20], adiabatic treatment in the hyperspherical coordinates [62, 63], adiabatic molecular approximation [64], the hyperspherical close coupling method [65], the complex-coordinate rotation method [23, 24, 66–71], and the stabilization method [67, 68, 72–74]. For the recent advances in the theoretical studies on the resonances in Ps^- , readers are referred to recent reviews [23, 24, 66, 67, 75–77]. Review on resonance states of the proposed ion can be found in the articles of Ho [21–24, 33, 67–71]. Here, we review the resonance calculations using correlated exponential wave functions within the framework of two simple and powerful variational methods: the stabilization method (SM) and the complex-coordinate rotation method (CRM). The variational correlated exponential wave functions for higher partial wave states can be written as

$$\Psi_n(\mu) = \left(1 + S_{pn}\hat{P}_{12}\right) \sum_{\substack{i=1 \\ l_1+l_2=L+\epsilon}}^{N_{Bn}} \sum_{l_1=\epsilon}^L C_i^n(\mu) (-1)^\kappa f(r_{13}, r_{23}, r_{21}) Y_{LM}^{l_1, l_2}(\mathbf{r}_{13}, \mathbf{r}_{12}), \quad (16)$$

with the radial function $f(r_{13}, r_{23}, r_{21})$ and the bipolar harmonics $Y_{LM}^{l_1, l_2}(\mathbf{r}_{13}, \mathbf{r}_{23})$,

$$f(r_{13}, r_{23}, r_{21}) = \exp[-\chi(\alpha_i^n r_{13} + \beta_i^n r_{23} + \gamma_i^n r_{21})], \quad (17)$$

$$Y_{LM}^{l_1, l_2}(\mathbf{r}_{13}, \mathbf{r}_{23}) = r_{13}^{l_1} r_{23}^{l_2} \sum_{m_1, m_2} \langle l_1 l_2 m_1 m_2 | LM \rangle Y_{l_1 m_1}(\hat{r}_{13}) Y_{l_2 m_2}(\hat{r}_{23}), \quad (18)$$

where $l_1 = i - (L + 1) \bmod \{i/(L + 1)\}$ for natural parity states, $l_1 = \bmod\{i/L\} + \kappa$ for unnatural parity states, $\bmod\{i/I\}$ denotes the remainder of the integer division i/I , N_{Bn} is the number of basis terms, $\kappa = 0$ for natural parity states, $\kappa = 1$ for unnatural parity states, and χ is a scaling factor. Now, we would like to point out briefly the computational aspects of SM and CRM.

4.1. Computational aspect of SM

In the first step of resonance calculations using the stabilization method [37–40, 55, 67, 68, 72–74], it is mandatory to obtain precise values of energy levels. Resonance position can be

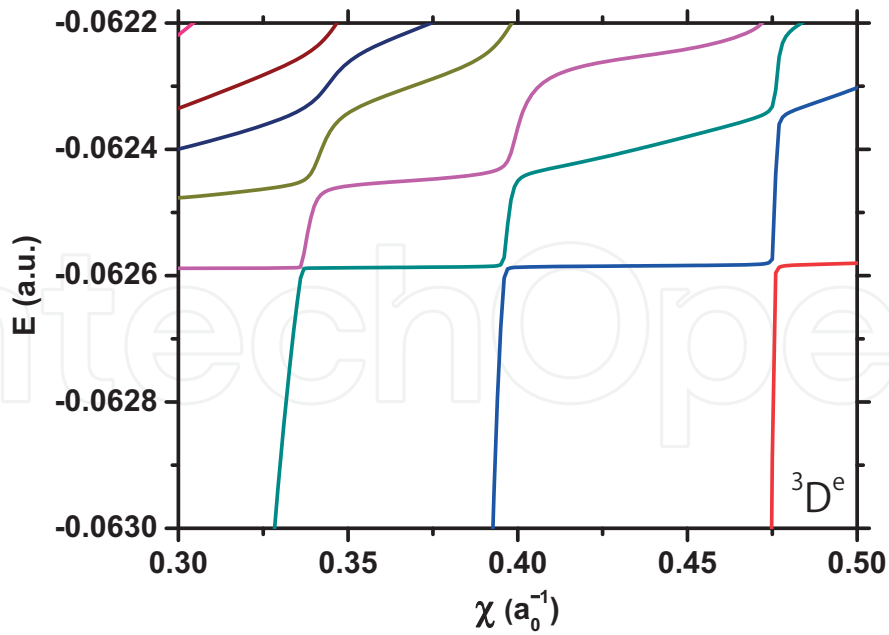


Figure 1. Stabilization diagram for the ${}^3D^e$ states of the Ps negative ion using 600 basis terms in Eq. (26).

identified after constructing stabilization diagram by plotting energy levels, E versus the scaling factor χ for certain μ . A stabilization diagram for the resonance states for the ${}^3D^e$ states of Ps^- for certain range of energy is depicted in **Figure 1**. The stabilized or slowly decreasing energy levels in the stabilization diagram indicate the position of the resonance at an energy E . Then to extract parameter (E_r, Γ) for a particular resonance state, one needs to calculate the density of the resonance states for each single energy level in the stabilization plateau using the formula

$$\rho_n(E) = \left| \frac{E_n(\alpha_{j+1}) - E_n(\alpha_{j-1})}{\alpha_{j+1} - \alpha_{j-1}} \right|_{E_n(\alpha_j)=E}^{-1} \quad (19)$$

where the index j is the j th value for α and the index n is for the n th resonance. After calculating the density of resonance states $\rho_n(E)$ using formula (18), we fit it to the following Lorentzian form that yields resonance energy E_r and a total width Γ , with

$$\rho_n(E) = y_0 + \frac{A}{\pi} \frac{\Gamma/2}{(E - E_r)^2 + (\Gamma/2)^2} \quad (20)$$

where y_0 is the baseline offset, A is the total area under the curve from the baseline, E_r is the center of the peak, and Γ denotes the full width of the peak of the curve at half height.

We obtained the desired results for a particular resonance state by observing the best fit (with the least chi-square and with the best value of the square of the correlation coefficient) to the Lorentzian form. The best fitting (solid line, using formula (20)) of the calculated density of states (circles, using formula (18)) for the lowest ${}^3D^e$ state of the Ps negative ion is presented in

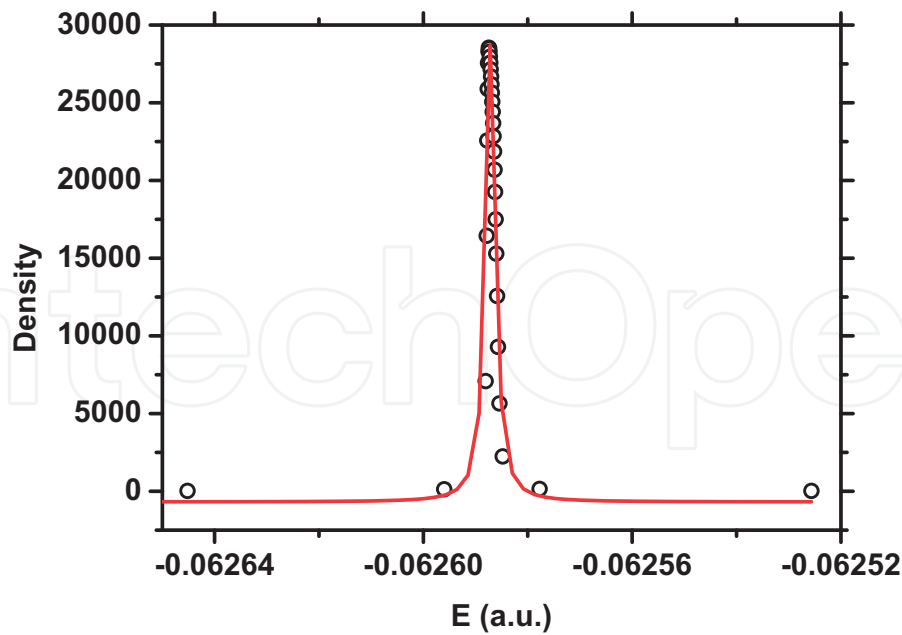


Figure 2. The best fitting (solid line) of the calculated density of states (circles) for the lowest $^3D^e$ state of the Ps negative ion.

Figure 2. The resonance position and width obtained from this work for the lowest $^3D^e$ state below the Ps ($N = 2$) threshold as $E_r = -0.06259(1)$ a.u. and $\Gamma = 2.2(8) \times 10^{-6}$ a.u. are comparable with the results $E_r = -0.0625878(10)$ a.u. and $\Gamma = 6.4(20) \times 10^{-6}$ a.u. reported by Bhatia and Ho (see Refs. [70, 71]). As the $^3D^e$ resonance states are too narrow, so it seems difficult to extract resonance parameters for the other states above the Ps ($N = 2$) threshold. However, a $^3D^e$ resonance parameter is obtained for the first time using the stabilization method, as well as using correlated exponential wave functions.

4.2. Computational aspect of CRM

In the complex-rotation method [23, 24, 33], the radial coordinates are transformed by

$$r \rightarrow re^{i\theta} \quad (21)$$

and the transformed Hamiltonian takes the form:

$$H \rightarrow T \exp(-2i\theta) + Ve^{-i\theta} \exp(-re^{i\theta}\mu) \quad (22)$$

where T and V are the kinetic and the Coulomb part of potential energies. The wave functions are those of Eqs. (7) and (9). In the case of non-orthogonal functions, there are overlapping matrix elements:

$$N_{ij} = \langle \psi_i | \psi_j \rangle \quad (23)$$

and

$$H_{ij} = \langle \psi_i | H(\theta) | \psi_j \rangle \quad (24)$$

The complex eigenvalues problem can be solved with

$$\sum_i \sum_j C_{ij} (H_{ij} - EN_{ij}) = 0 \quad (25)$$

Resonance poles can be identified by observing the complex energy levels, $E(\theta, \alpha)$. The complex resonance eigenvalue is given by

$$E_{res} = E_r - \frac{i\Gamma}{2}, \quad (26)$$

where E_r is the resonance energy and Γ is the width. The resonance parameters are determined by locating stabilized roots with respect to the variation of the nonlinear parameters in the wave functions and of the rotational angle θ .

Resonance states for P, D, and F states of the Ps^- were reported following the abovementioned wave functions (16) and CRM [23, 24]. We have also located an S-wave shape resonances of the Ps^- lying above the Ps ($N = 2$) threshold using wave functions (18) and (9) and CRM [78]. Later, S-wave resonance states associated with and lying above the Ps ($N = 2, 3, 4, 5$) thresholds are reported by Jiao and Ho [79] using the wave function (9) and CRM. We have mentioned that a $^1\text{P}^o$ shape resonance has been observed in the laboratory [8]. The observed $^1\text{P}^o$ shape resonance is in agreement with the available theoretical data [80–82] and the present work using correlated exponential wave functions and CRM. **Figure 3** shows the rotational path for the $^1\text{P}^o$ shape resonance of the Ps^- lying above the Ps ($N = 2$) threshold, in the complex plane for four different values of the scaling factor, χ using 500-term correlated exponential basis functions. From this work, we have obtained the lowest $^1\text{P}^o$ shape resonance parameters as $E_r = -0.06212$

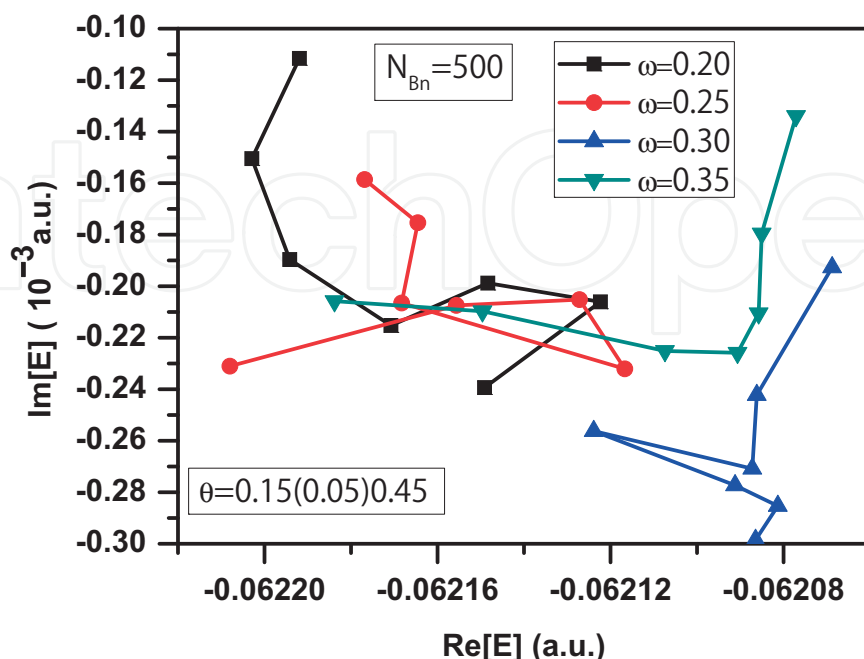


Figure 3. Rotational path of the $^1\text{P}^o$ shape resonance of the Ps^- lying above the $\text{Ps}(N = 2)$ threshold, in the complex plane for four different values of the scaling factor, χ using 500-term correlated exponential basis functions.

(3) a.u. and $\Gamma = 0.00044(3)$ a.u. The numbers in the parentheses indicate the uncertainty in the last digits. The resonance states of Ps-Ps interaction were also studied by Ho [69].

In the screening environment, Kar and Ho [67, 68, 72–74] investigated the effects of SCP on the S-, P-, and D-wave resonance states of the Ps^- using correlated exponential wave functions, and Ghoshal and Ho [83] reported the effects of ECSCP on the lowest S-wave resonance state using the wave function (11) within the framework of SM. The resonance states have also successfully obtained using Hylleraas-type wave functions (9). Ho and Kar [76, 77] also investigated the S-wave resonance states of the proposed ion under the influence of SCP using CRM and wave function (9). In this work, wave functions (9) with up to $\Omega = 21$, $N_{B0} = 1078$, were used. The resonance parameters below the $N = 2, 3, 4, 5$, and 6 Ps thresholds, for various screening parameters, were reported. The lowest S-wave resonances of this ion interacting with ECSCP have also been studied by Ghoshal and Ho [83] using wave function (9) and ECSCP.

5. Photodetachment

The photoionization or photodetachment process is a subject of special interest in several areas of physics, such as astrophysics, plasma physics, and atomic physics due to its extreme importance in the atomic structures and correlation effects between atomic electrons [16, 17, 82, 84, 85]. The photoionization processes are also of great interest due to their applications in plasma diagnostics. Photodetachment of the Ps^- is also of particular interest as the experiments on Ps^- suggest that the Ps could be used to generate Ps beams of controlled energy, and this will involve acceleration of Ps^- and photodetachment of one electron. Photodetachment of the Ps^- is also of utmost importance due to its application in propagation of radiation in our galaxy. It is well known that the center of our galaxy, the Milky Way, contains a number of sources of the annihilation γ -quanta with $E_\gamma \approx 0.511$ MeV [86].

We reported the effect of screened Coulomb (Yukawa) potentials on the photodetachment cross sections of the positronium negative ion by using the asymptotic form of the bound-state wave function and a plane wave form for the final-state wave function. For detailed calculations and applications of the photodetachment of the positronium negative ion, interested readers are referred to the articles of Bhatia and Drachman [19], Frolov [17], Igarashi [82, 84, 85], Michishio et al. [8], Nagashima [6], and Ward et al. [20]. Here, we outlined the computational details in brief as mentioned in our earlier work [87] and in the works of Bhatia and Drachman [19].

In our previous work [87], we have considered the final-state wave function of the form $\Psi_f = \exp(i \vec{p} \cdot \vec{r})$ with $E = 3p^2/4$ and the initial bound-state wave function in the asymptotic region with the following form: $\Psi_i = C \exp(-\gamma r)/r$. The constant C for the Ps negative ion is obtained from the formula

$$C = G_{Ar} \exp(\gamma r) \Psi_i(r, 0, r), \quad (27)$$

where G_A is some normalization constant and $\gamma = \sqrt{4(E_{Ps} - E_{Ps^-})/3}$, with E_{Ps^-} and E_{Ps} , the ground state energies of the Ps^- ion and Ps atom, respectively. The ground state energy of the Ps atom has been calculated using basis functions (40) prescribed in Section 7.

The photodetachment cross sections (σ) having photon energy E_p can be expressed as

$$\sigma = \frac{2}{3} \alpha a_0^2 p g(E_p) \langle \Psi_f | \hat{\Lambda}(1, 2) | \Psi_i \rangle, \quad (28)$$

where α is the fine structure constant and $g(E) = E$ or E^{-1} for the dipole length and velocity approximations, respectively. The operator Λ represents the position and gradient operators for the length and velocity approximations, respectively, and can be written in explicit form as $\hat{\Lambda}(1, 2) = \Lambda(\vec{r}_{13}) + \Lambda(\vec{r}_{23})$.

The final form of σ in terms of wavelength takes the form

$$\sigma = 4.30255225 \times 10^{-17} \rho^5 \frac{C^2}{\gamma^3} \left[\frac{\lambda}{\lambda_0} \right]^{3/2} \left[1 - \frac{\lambda}{\lambda_0} \right]^{3/2} \text{ cm}^2, \text{ with } \lambda \leq \lambda_0, \quad (29)$$

and $\lambda_0 = 911.267057/\gamma^2$ (in Å), where ρ denotes the reduced electron mass. For the Ps^- ion, $\rho = (1 + M_c^{-1})^{-1}$ with $M_c = 2$. The required normalization constant has been determined in this from highly accurate, completely non-adiabatic wave functions in Eq. (7) for the three-particle systems. Similar type of work was reported by Ghoshal and Ho using ECSCP and wave function (9) [88].

6. Polarizability

The study of atomic and ionic polarizabilities (both static and dynamic) plays an important role in a number of applications in physical sciences ([25–27, 44, 45, 89–98], references therein). When an atom or ion or molecule is placed in an electric field, the spatial distribution of its electrons experiences a distortion, the extent of which can be described in terms of its polarizability. The dynamic (dc) polarizability describes the distortion of the electronic charge distribution of an atom, ion, or molecule in the presence of an oscillating electric field of certain angular frequency. In this review, we describe the polarizability calculations of the Ps negative ion reported by Bhatia and Drachman [25], Kar and Ho [99], and Kar et al. [26, 27]. We also describe the polarizability calculations with SCP and ECSCP. To obtain dipole and quadrupole polarizability for the Ps^- ion, it is an important task to determine precisely the energies and wave functions for the ground state and the final P and D states. The dynamic 2^l -pole polarizability of the Ps^- ion in the screening environment can be written as [27]

$$\alpha_l(\omega) = \alpha_l^+(\omega) + \alpha_l^+(-\omega) \quad (30)$$

with

$$\alpha_l^+(\omega) = \frac{8\pi}{2l+1} \left(\frac{M}{M+1} \right)^{2l+1} \sum_n \frac{f_{nl}}{E_n(\mu) - E_0(\mu) + \omega} \quad (\text{in units of } a_0^{2l+1}), \quad (31)$$

where

$$f_{nl} = \left| \left\langle \Psi_0(\mu) \left| \sum_{i=1}^2 r_i^l Y_{lm}(r_i) \right| \Psi_n(\mu) \right\rangle \right|^2 \quad (32)$$

The summation in the above expression includes all the discrete and continuum eigenstates. Ψ_0 and Ψ_n describe the ground state eigenfunction with the corresponding energy eigenvalue E_0 and the n^{th} intermediate eigenfunction for the final states with the corresponding eigenvalue, E_n , respectively. In the limit when $\omega \rightarrow 0$, $\alpha_l(\omega)$ is the static polarizability. For precise determination of eigenvalues and eigenfunction for each frequency and for each screening parameter for a particular system, one needs to solve the Schrödinger equation, $H\Psi = E\Psi$, by diagonalization of the Hamiltonian with the properly chosen wave functions in Eqs. (7) and (10). We rewrite the explicit form of wave function in Eq. (10) for polarizability calculations of this ion as

$$\Psi_n(\mu) = \left(1 + \hat{P}_{12}\right) \sum_{\substack{i=1 \\ l_1+l_2=L}}^{N_{Bn}} C_i^n(\mu) \exp(-\alpha_i^n r_{13} - \beta_i^n r_{23} - \gamma_i^n r_{21}) Y_{LM}^{l_1, l_2}(\mathbf{r}_{13}, \mathbf{r}_{12}) \quad (33)$$

where $l_1 = i - (L+1) \bmod \{i/(L+1)\}$, $\bmod\{i/(L+1)\}$ denotes the remainder of the integer division $i/(L+1)$, and N_{Bn} is the number of basis term.

The static dipole and quadrupole polarizability for Ps^- has been reported by Bhatia and Drachman [25]. Kar and Ho also reported the static dipole polarizability of this ion in the screening environments as well in free atomic system [99]. Kar et al. also reported the dipole and quadrupole polarizabilities (static and dynamic) of this ion using SCP and exponential wave functions (33) [26, 27]. The dynamic dipole polarizability of the Ps^- was also studied by Kar et al. [27] in the screening environments. In this present work, we calculate the dipole and quadrupole polarizabilities (static and dynamic) under the influence of ECSCP and wave functions (33). The polarizabilities as functions of screening parameter and photon frequency are reported in **Figures 4** and **5** and **Tables 1** and **2**.

7. Dispersion coefficients for Ps-Ps interaction

Knowledge of the Van der Waals two-body dispersion coefficients in the multipole expansion of the second-order long-range interaction between a pair of atoms is of utmost importance for the quantitative interpretation of the equilibrium properties of gases and crystals, of transport phenomena in gases, and of phenomena occurring in slow atomic beams ([93, 100–102], references therein). The long-range part of the interaction potential between two spherically

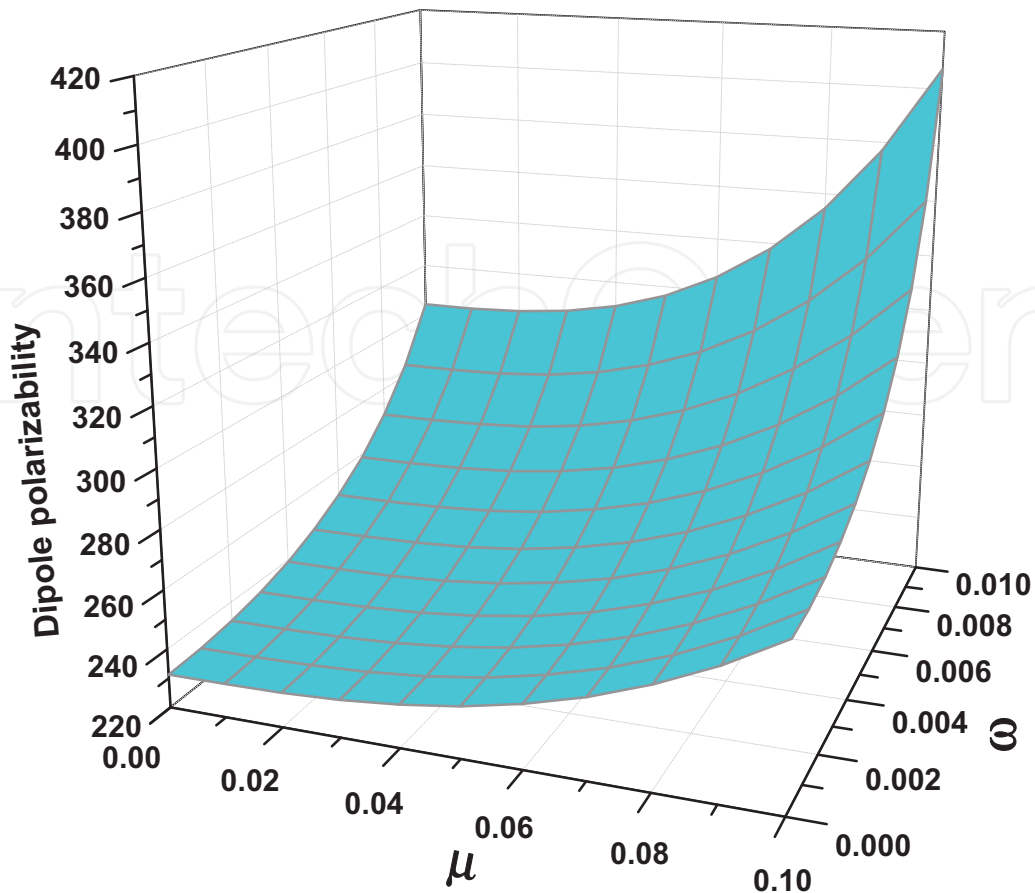


Figure 4. The dipole polarizability of the positronium negative ion as a function of screening parameter and photon frequency.

symmetric atoms a and b separated by a distance R can be written as a series with coefficients C_n denoted as dispersion coefficients [93, 100–102]:

$$V_{ab} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots, \quad (34)$$

with

$$C_6 = \frac{3}{\pi} G_{ab}(1, 1), \quad (35)$$

$$C_8 = \frac{15}{2\pi} [G_{ab}(1, 2) + G_{ab}(2, 1)], \quad (36)$$

$$C_{10} = \frac{14}{\pi} [G_{ab}(1, 3) + G_{ab}(3, 1)] + \frac{35}{\pi} G_{ab}(2, 2), \quad (37)$$

where

$$G_{ab}(l_a, l_b) = \frac{\pi}{2} \sum_{nm} \frac{f_{n0}^{(l_a)} f_{m0}^{(l_b)}}{E_{n0}^a E_{m0}^b (E_{n0}^a + E_{m0}^b)}, \quad (38)$$

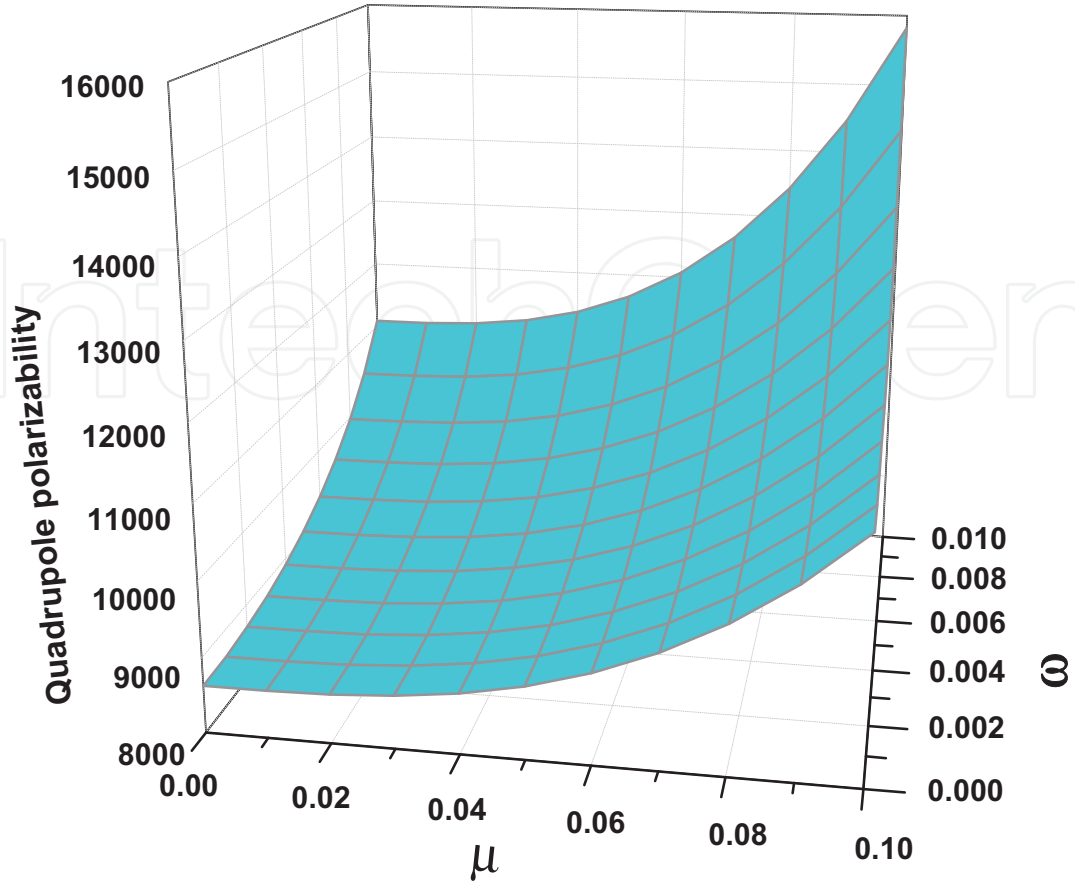


Figure 5. The quadrupole polarizability of the positronium negative ion as a function of screening parameter and photon frequency.

$E_{n0}^i = E_n^i - E_0^i$ is the excitation energy for atom i and is positive for the atoms in the ground state, and $f_{n0}^{(l)}$ denotes the 2^l -pole oscillator strengths and defined by

$$f_{n0}^{(l)} = \frac{8\pi}{2l+1} (E_n - E_0) \left| \left\langle \Psi_0 \left| \sum_i r_i^l P_l(\cos \vartheta_i) \right| \Psi_n \right\rangle \right|^2, \quad (39)$$

with $i = 1$ for Ps and H atom. We also review here the dispersion coefficients for H-H interactions to establish a relation of dispersion coefficients with Ps-Ps and H-H interaction.

For positronium and hydrogen atoms, we have employed the Slater-type basis set:

$$\Psi = \frac{\sqrt{2l+1}}{4\pi} \sum_{i=1}^N D_i r^{i+l} e^{-\lambda r} P_l(\cos \theta_1), \quad (40)$$

where λ is the nonlinear variation parameters; $l = 0, 1$ for S and P states, respectively, and $D_i (i=1, \dots, N)$ are the linear expansion coefficients.

ω	$\mu = 0.01$	$\mu = 0.02$	$\mu = 0.04$	$\mu = 0.05$	$\mu = 0.06$	$\mu = 0.08$	$\mu = 0.09$	$\mu = 0.10$
0.000	231.3779	231.7355	234.4589	237.308	241.438	254.3094	263.4554	274.709
0.001	231.8534	232.2127	234.9495	237.813	241.964	254.9026	264.0985	275.416
0.002	233.2980	233.6626	236.4406	239.348	243.563	256.7081	266.0575	277.572
0.003	235.7687	236.1426	238.9923	241.976	246.302	259.8077	269.4255	281.285
0.004	239.3685	239.7562	242.7131	245.810	250.304	264.3508	274.3733	286.755
0.005	244.2600	244.6673	247.7751	251.033	255.763	270.5782	281.1787	294.311
0.006	250.6914	251.1256	254.4422	257.922	262.979	278.8678	290.2821	304.479
0.007	259.0429	259.5144	263.1203	266.908	272.423	289.8223	302.397	318.132
0.008	269.917	270.441	274.458	278.687	284.857	304.455	318.753	336.819
0.009	284.332	284.935	289.567	294.457	301.624	324.642	341.717	363.680
0.010	304.207	304.939	310.583	316.576	325.43	354.54	376.95	407.13
0.011	334.00	334.98	342.67	350.97	363.53	408.6	4.53[2]	
0.012	392.9	395.2	4.17[2]					

The numbers in square brackets indicate the power of 10.

Table 1. The dipole polarizability of the Ps negative ion for different screening parameters and photon frequencies.

ω	$\mu = 0.01$	$\mu = 0.02$	$\mu = 0.03$	$\mu = 0.05$	$\mu = 0.06$	$\mu = 0.07$	$\mu = 0.09$	$\mu = 0.10$
0.000	8630.1	8649.4	8701.3	8962.1	9198.5	9522.9	10496.4	11182.1
0.001	8647.3	8666.7	8718.8	8980.7	9218.0	9543.7	10521.4	11210.1
0.002	8699.5	8719.2	8771.9	9036.9	9277.2	9607.0	10597.3	11295.5
0.003	8788.6	8808.6	8862.4	9132.9	9378.2	9715.0	10727.4	11442.0
0.004	8917.6	8938.2	8993.7	9272.3	9525.0	9872.2	10917.3	1.1656[4]
0.005	9091.6	9113.1	9170.8	9460.7	9723.7	10085.4	1.1176[4]	1.1950[4]
0.006	9318.1	9340.7	9401.4	9706.6	9983.6	10364.9	1.1518[4]	1.2339[4]
0.007	9608.2	9632.3	9697.0	10022.7	1.0319[4]	1.0726[4]	1.1965[4]	1.2852[4]
0.008	0.9978[4]	1.0005[4]	1.0075[4]	1.0428[4]	1.0750[4]	1.1195[4]	1.2554[4]	1.3534[4]
0.009	1.0456[4]	1.0485[4]	1.0563[4]	1.0956[4]	1.1314[4]	1.1811[4]	1.3343[4]	1.4465[4]
0.010	1.1086[4]	1.1119[4]	1.1209[4]	1.1660[4]	1.2074[4]	1.2650[4]	1.446[4]	1.582[4]
0.011	1.196[4]	1.200[4]	1.211[4]	1.266[4]	1.317[4]	1.388[4]	1.62[4]	1.81[4]
0.012	1.330[4]	1.336[4]	1.350[4]	1.43[4]	1.50[4]	1.60[4]		

The numbers in square brackets indicate the power of 10.

Table 2. The quadrupole polarizability of the Ps⁻ in terms of screening parameter and photon frequency.

To investigate the effect on the dispersion coefficients C_6 in the screening environments, one can assume that the leading term in the Van der Waals interaction between two atoms a and b in their ground states still has a form of R^{-6} , as [101, 102]

$$V_{ab} = -\frac{C_6(\mu)}{R^6} + O(1/R^8) + \dots \quad (41)$$

Here, the plasma effect on V_{ab} is reflected on the value of C_6 , which now depends on the screening parameter μ , and is denoted by $C_6(\mu)$. Similarly, to consider the plasma effect on the dispersion coefficients C_8 and C_{10} , we assume the coefficients depend on the screening parameter μ and are denoted, respectively, by $C_8(\mu)$ and $C_{10}(\mu)$. To calculate the dispersion coefficients for the interactions for Ps-Ps or H-H interactions, one needs to obtain the energy levels for the positronium atom or the hydrogen atom in the different partial wave states with the optimum choices of nonlinear parameters. To obtain the energy levels for hydrogen and positronium atoms with different Debye lengths, we diagonalize the Hamiltonian

$$H = -\frac{\eta}{2}\nabla^2 - \frac{\exp(-r/\lambda_D)}{r} \quad (42)$$

with the wave functions (40). Here, $\eta = 1$ is for the hydrogen atom and $\eta = 2$ for the positronium atom. In our previous work, we have reported the C_6 , C_8 , and C_{10} coefficients for Ps-Ps interactions under the influence of SCP. We have found from our calculations that the C_6 , C_8 , and C_{10} coefficients are, respectively, 2^5 , 2^7 , and 2^8 times larger than the corresponding coefficients of hydrogen-hydrogen interactions [103].

8. Comparison of spectroscopic properties and concluding remarks

To describe a semiconductor, one needs in principle to solve the Schrödinger equation for the problem. Depending on the coordinates of the ion cores having the nucleus and the tightly bound electrons in the inner shells and the outer or valence electrons with coordinates R_j and r_i and masses M_j and m_0 , respectively, the Hamiltonian looks as ([1], Chapter 7)

$$H = -\frac{\hbar^2}{2} \sum_{j=1}^M \frac{1}{M_j} \nabla_{R_j}^2 - \frac{\hbar^2}{2m_0} \sum_{j=1}^M \nabla_{r_i}^2 + \frac{1}{4\pi\epsilon_0} \left(\sum_{j>j'} \frac{e^2 Z_j Z_{j'}}{|R_j - R_{j'}|} + \sum_{i>i'} \frac{e^2}{|r_i - r_{i'}|} + \sum_{i,j} \frac{e^2 Z_j}{|R_j - r_i|} \right), \quad (43)$$

where Z_j is the effective charge of the ion core j and the indices j and i run over all M ion cores and N electrons, respectively. The wave function solving (43) can be constructed using all coordinates R_j and r_i including spins. The optical properties of the electronic system of a semiconductor or an insulator or even a metal can be understood as a description of the excited states of the N particle problem. The quanta of these excitations are known as “excitons” in semiconductors and insulators. The ground state of the electronic system for a perfect semiconductor can be described from various points of view as a completely filled valence band

and a completely empty conduction band [1]. However, from the theoretical side, the wave function of the bound state for excitons is said to be *hydrogenic*, an exotic atom (such as positronium atom) state akin to that of a hydrogen atom or even much better positronium atom. However, the binding energy is much smaller and the particle's size much larger than a hydrogen atom or larger than a positronium atom. This is due to the screening of the Coulomb force by other electrons in the semiconductor and due to the small effective masses of the excited electron and positive hole. However, it can be understood that the Hamiltonian for an exciton can be similar to a positronium atom if one can consider units using the Bohr radius for the respective system. The exciton Bohr radius is $a_B^{ex} = a_B^H \varepsilon \frac{m_0}{\tau}$ where the reduce exciton mass $\tau = \frac{m_e m_h}{m_e + m_h}$; m_e and m_h indicate the effective mass of electron and hole, respectively, and m_0 is the free electron mass. Exciton Rydberg energy is $Ry^* = 13.6\text{eV} \frac{\tau}{m_0} \frac{1}{\varepsilon^2}$ [1]. In similar way, the Hamiltonian for a trion and a bi-exciton can be related, respectively, with the Hamiltonian Ps negative ion and the Ps molecule. Wave functions for a trion or a bi-exciton could be similar with the Ps atoms or the Ps molecule. So, it is expected that the spectroscopic properties of the Ps atom, Ps negative ion, or Ps molecule might be useful to understand the spectroscopic properties of an exciton, trion, or bi-exciton.

Let us describe other types of comparison with bound excitons which are well studied in semiconductor, especially in gallium phosphide doped by nitrogen (GaP:N). The role and application of bound excitons in nanoscience and technology have been discussed in the article of Pyshkin and Ballato [104]. This investigation [104] observes something like neutral short-lived atom analog—a particle consisting of heavy negatively charged nucleus (N atom with captured electron) and a hole. Using bound excitons as short-lived analogs of atoms and sticking to some specific rules, Pyshkin and Ballato have been able to create a new solid-state media—consisting of short-lived nanoparticles excitonic crystal, obviously, with very useful and interesting properties for application in optoelectronics, nanoscience, and technology. Note that such specific rules include the necessity to build the excitonic superlattice with the identity period equal to the bound exciton Bohr dimension in the GaP:N single crystal. This study [104] also reports that the excitonic crystals yield novel and useful properties. These properties include enhanced stimulated emission and very bright and broadband luminescence at room temperature. With such development of bound excitons as short-lived analogs of atoms under some specific rules, it is also important to mention here that the emission spectra of representatives of exciton and positronium negative ion families can be realized from the earlier articles [104–108]. These articles support the usefulness of such comparisons of spectroscopic properties of excitons and the positronium negative ion. We hope that this chapter will provide a new direction and would be a remarkable reference for the future studies on excitons, bi-excitons, or trions as well as positronium, positronium molecule, and positronium negative ion.

Finally, we should also mention recent investigations on quantum information and quantum entanglement in few-body atomic systems, including the positronium negative ion. Quantification of Shannon information entropy, von Neumann entropy and its simpler form, linear entropy, for the two entangled (correlated) electrons in Ps^- , has been reported in the literature [109–111].

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