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Internal structure of the positronium ion Ps^-

Dario Bressanini[*]
Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, via Valleggio 9, I-22100 Como Italy

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The positronium ion Ps^- is often qualitative described as a positronium Ps with a loosely bound second electron, since the value of the annihilation rate for Ps^- is nearly equal to that of the spin-averaged neutral positronium. This similarity however has never been fully explained. To study its internal structure, we decompose the electron-positron distribution function of Ps^- into the sum of two terms: one for the electron closest to the positron and the other for the farthest. We show that the inner electron behaves almost as if the outer electron were not present, forming a Ps substructure inside Ps^- and that the effect of electron correlation is such that the outer electron tries to stay as close as possible to the positron but without interfering too much with the distribution of the inner electron. We show that this phenomenon is closely related to the problem of the critical stability of the system $(Z^+,\ e^-,\ e^-)$ with varying Z charge.

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I. INTRODUCTION

In his seminal paper on "polyelectrons" in 1946, Wheeler [1] predicted the existence of a bound state of two electrons and a positron, followed shortly and independently by Hylleraas [2]. Wheeler called it trielectron, while Hylleraas called it positronium ion, following Ruark [3] who in 1945 coined the name positronium for the system composed by one electron and one positron.

The positronium negative ion is the simplest coulombic three-body system and as such is fundamental to the study of three-body quantum mechanics, to test fundamental physics, and in many other areas. We refer the reader to the article by Emami-Razavi and Darewych [4] for an up-to-date review of the field. The calculation of its binding energy (BE) and other properties, such as the annihilation rate and various geometrical expectation values, has a long history [1,2,5–29]. Table I shows a comprehensive chronological list of the ground state calculations.

In the three decades following Wheeler's paper, only a few studies investigated the energetics and structural properties of Ps^-. In 1960, in one of the first early calculations, Kolos *et al.* [5] computed the average electron-electron and electron-positron distances (respectively, 8.5476 and 5.506 bohr), commenting that "*the large size of this system is remarkable*", but without further analysis. In 1968 Ferrante [7] was the first to tackle the problem of computing the two-photon and the three-photon annihilation rate of Ps^-. He remarked that the value of the annihilation rate for the positronium ion is nearly equal to that of the spin-averaged neutral positronium ($\Gamma_{Ps} = 2.00 \times 10^9\ s^{-1}$). He also noted that the electron density at the positron in Ps^- is about the same as for the neutral positronium suggesting a qualitative picture of one electron more tightly bound to the positron, and a loosely bound second electron.

It was only in 1981 that this elusive system was finally produced and detected experimentally by Mills [30], guiding a beam of low-energy positrons against a thin carbon film. This landmark result was followed two years later by the measurement of its decay rate [31] ($\Gamma = 2.09(9)\ ns^{-1}$) that agreed with the theoretical prediction by Ho [9] and Bhatia and Drachman [10].

In their 1983 paper, Bhatia and Drachman [10] observed that the two nonlinear exponential parameters of the employed wave functions differed by about a factor of two. This was the basis for their intuition of "*the basic structure of the Ps^- ground state, which consists mainly of the Ps atom plus a loosely bound electron*". This picture was further substantiated by the observation that the annihilation rate of Ps^- was very close to that of Ps, as already noticed by Ferrante [7]. They, however, did not compute the interparticle distances or the electronic and positronic densities to clarify the similarity.

These papers [9,10,30,31] immediately sparked a renewed interest in the positronium ion, both experimentally and theoretically. Frolov [13] and Ho [19] did a highly accurate calculations of the bound-state properties for this system, and quickly many new theoretical studies followed exploring both the ground state and possible resonances.

On the experimental side progress has been slower [32] due to the low intensity of the Ps^- beam. In 2006 Fleischer *et al.* [33] measured the Ps^- annihilation rate to greater accuracy. In 2008 a more efficient process to generate Ps^- using Cs-coated tungsten surfaces was discovered [34] opening a new era of experimental observation on this peculiar ion, allowing for example, the observation of the photodetachment process [35,36]. The photodetachment of positronium ions can provide a source for energy tunable Ps beams [37,38]. In 2011 Ceeh *et al.* [39] using a high-intensity neutron induced positron source measured to high precision the Ps^- decay rate to be $2.0875(50)\ ns^{-1}$, in agreement with the most recent

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[*] dario.bressanini@uninsubria.it

theoretical value by Puchalski *et al.* [40]. In 2016, Michishio *et al.* [41] experimentally detected a shape resonance of the positronium negative ion. For a perspective on possible future experiments with positronium and its negative ion we refer the readers to the recent reviews of Cassidy [42], Mills [43], and Nagashima [32].

Over the years the various computational methods used to study Ps^- improved both accuracy and precision of the calculations and now we know, to many decimal places, the energy and many geometrical expectation values, such as angles and various powers of interparticle distances. The current best estimate of the ground state energy [29] is an impressive –0.262 005 070 232 980 107 770 400 51. In all these years, however, the similarity between Ps and Ps^- has never been fully clarified. Furthermore, even more surprisingly, to the best of our knowledge there are no published studies of the pair distribution functions, i.e., the probability that in Ps^- a pair of particles is at a given distance, and their graphs have never been compared to the Ps distribution to clarify the similarity between the Ps and Ps^- internal structure.

This paper is organized as follows: Sec. II presents the structure of the various wave function employed; Sec. III shows an attempt to include a three-body term into the wave function. Section IV presents various one and two-dimensional (2D) probability distribution functions to show that one electron in Ps^- behaves almost like in Ps, while the other is at larger distances. Finally, Sec. V shows that the presence of the Ps substructure inside Ps^- is closely related to the problem of the critical stability of the system $(Z^+,\ e^-,\ e^-)$ with varying Z charge.

TABLE I. Chronological list of calculations on the ground state energy and structure of Ps^-. The decimal digits in bold agree with the most accurate calculation to date, shown in the last row.

Year and Reference	Energy (Hartree)
Wheeler 1946 [1]	**–0.2**57036
Hylleraas 1947 [2]	**–0.2**5765
Kolos 1960 [5]	**–0.26**19956
Frost 1964 [6]	**–0.26200**11
Ferrante 1970 [7]	**–0.26**070122
Poshusta 1983 [8]	**–0.26**1787
Ho 1983 [9]	**–0.26200**4895
Bathia 1983 [10]	**–0.2620050**565
Frolov 1986 [11]	**–0.2620050**6975
Petelenz 1987 [12]	**–0.2620050**694
Frolov 1987 [13]	**–0.2620050702**0
Patil 1988 [14]	**–0.26**103
Ball 1988 [15]	**–0.26**19(2)
Haftel 1989 [16]	**–0.26200**486
Frolov 1989 [17]	**–0.262005070232**2
Ball 1990 [18]	**–0.26200**(6)
Ho 1990 [19]	**–0.2620050702**05
Frolov 1993 [20]	**–0.26200507023**19
Ho 1993 [21]	**–0.262005070232**855
Frolov 1994 [22]	**–0.262005070232**6
Cox 1996 [23]	**–0.26200507023**1742
Frolov 1999 [24]	**–0.2620050702329**757
Korobov 2000 [25]	**–0.262005070232980107**
Drake 2002 [26]	**–0.262005070232980107**627
Frolov 2005 [27]	**–0.2620050702329801077**6885
Frolov 2009 [28]	**–0.262005070232980107770**3745
Frolov 2015 [29]	–0.26200507023298010777040051

II. WAVE FUNCTION CONSTRUCTION

There is no shortage, as we have seen, of extremely accurate wave functions for Ps^- so our aim is not to compete with those expansions with thousands of terms. Instead, we try to build an accurate but extremely compact trial wave function with a clear physical meaning to get an insight on the internal structure of the positronium ion.

The ground state wave function has total angular momentum $L = 0$, so it can be described using the interparticle distances: $\Psi(r_{12},\ r_{13}, r_{23})$ where 1 and 2 are the electrons and 3 is the positron. In the ground state, the two electrons are in a $S = 0$ state and the wave function must be symmetric with respect to the exchange between them.

In the study of atomic and molecular systems the Hartree Fock (HF) approximation is of central importance, not only as a practical computational tool but also to establish well defined concepts – like the correlation energy or the orbital structure– that are very useful when one uses wave functions that go beyond the mean field approximation. Ps^- has three particles of identical mass and the HF approximation fails from the very beginning to give a realistic description of this system since the positive charge is not much heavier than the electrons like in atoms. The HF functional form corresponds to $\Psi = f(r_{13})f(r_{23})$ with the neglect of the electron-electron interaction and imposing the same electron-positron "orbital" for the two pairs. This structure can successfully describe the ground state of the helium atom but completely fails when applied to the hydrogen negative ion H^-, and it is not surprising that it also fails for Ps^-.

In 1944 Chandrasekhar [44] in his study on the negative hydrogen ion remarked that the relative success of the simple wave function $\psi = \exp(-a\ \mathrm{r}_1 - a\ \mathrm{r}_2)$ to qualitatively describe the He atom has a simple physical interpretation. Each electron moves in a suitable screened Coulomb field generated by the other and is described by a screened hydrogenlike orbital. This approach, however, fails to describe the hydrogen negative ion. Chandrasekhar argued that the case of H^-, with its barely bound second electron, is completely different, and suggested to assign a different screening constant to each electron and wrote $\psi = \exp(-a\ \mathrm{r}_1 - b\ \mathrm{r}_2) + \exp(-a\ \mathrm{r}_2 - b\ \mathrm{r}_1)$. The same can be said about the positronium ion. If the two electron-positron interactions are treated independently, we can write the functional form

$$\Psi = (1 + \hat{P}_{12})f_1(r_{13})f_2(r_{23}). \tag{1}$$

The functions f_i describe the attraction between the positron and the electrons and $\hat{P}_{12}$ is the permutation operator. We model each function with an exponential Padè functional form $f(r) = e^{\frac{-r/2+b\,r^2}{1+c\,r}}$ and different b and c parameters. The function f behaves as $e^{-\frac{r}{2}}$ near zero, satisfying the cups conditions, and as $e^{\frac{b}{c}r}$ asymptotically where c is always nonnegative. Previous studies [45–50] showed that by using this

TABLE II. Energy and binding energy (in Hartree) and percentage of the recovered binding energy with respect to the exact value for various wave functions.

Ψ	Energy	BE	% BE
$f(r_{13})f(r_{23})$	–0.2439(1)	unbound	
$(1+\hat{P}_{12})f_1(r_{13})f_2(r_{23})$	–0.25652(1)	0.0065	54.3
$(1+\hat{P}_{12})f_1(r_{13})\Psi(Ps_{23})$	–0.25642(1)	0.0064	53.5
$(1+\hat{P}_{12})J(r_{12})f_1(r_{13})\Psi(Ps_{23})$	–0.25894(1)	0.0089	74.6
$(1+\hat{P}_{12})g(r_{12})f_1(r_{13})\Psi(Ps_{23})$	–0.26133(1)	0.0113	94.4
$(1+\hat{P}_{12})g(r_{12})f_1(r_{13})f_2(\mathrm{r}_{23})$	–0.26135(1)	0.0114	94.6
$(1+\hat{P}_{12})g(r_{12})f_1(r_{13})f_2(\mathrm{r}_{23})g_3(r_{12}, r_{23})$	–0.26164(1)	0.0116	96.9
$(1+\hat{P}_{12})\sum_i^2 a_i g(r_{12})f_1(r_{13})f_2(\mathrm{r}_{23})g_3(r_{12}, r_{23})$	–0.26183(1)	0.0118	98.6
Exact[a]	–0.262005	0.0120	100

[a] Ref. [29]

kind of function it is possible to develop very compact but accurate wave functions for few particle systems.

We used variational Monte Carlo (VMC) to estimate the variational energy and the various distribution functions. We first roughly optimized the parameters minimizing the mean absolute deviation of the local energy [51], and then fine-tuned them using an energy optimization procedure.

Table II shows that the functional form in Eq. (1), with four variational parameters, can describe a bound Ps$^-$ ion and recovers 54% of the exact binding energy.

Inspecting the two optimized f functions reveals that one of them is almost superimposable to $e^{-r/2}$, the exact wave function for the ground state of Ps. The other function f has a slower exponential decay describing a more loosely bound electron. So, the intuitive and qualitative picture of Ps$^-$ being composed by a Ps with an additional electron at a larger distance comes out naturally by inspecting this compact wave function. We wish to point out that all the extremely accurate wave functions developed in the past (see Table I) are absolutely necessary to compare calculations with experimental data, but lack such a simple physical interpretation since their structure goes beyond the simple pairs approximation we have employed. As noted long time ago by Mulliken [52] just at the dawn of the massive use of computers for electronic structure calculations, "*the more accurate the calculations became, the more the concepts tended to vanish into thin air*".

We can directly write our compact wave function as $\Psi = (1+\hat{P}_{12})f_1(r_{13})\Psi(Ps_{23})$ where we have explicitly inserted the exact Ps wave function, at the expense of two variational parameters, with a negligible decrease in the binding energy. To improve the variational energy without changing the functional form, one strategy could be to use an exponential Padè of higher degree. The improvement, however, would be negligible. Instead the quality of the wave function can be greatly improved including a correlation factor $g(r_{12})$ to describe the instantaneous repulsion between electrons: $\Psi = (1+\hat{P}_{12})g(r_{12})f_1(r_{13})f_2(\mathrm{r}_{23})$. In fact, almost all published calculations on the Ps$^-$ ion expand the exact wave function in building blocks of this form.

Such a wave function has a clear physical meaning since each function describes the interaction between a different pair of particles. We know that the correlation factor must behave as $e^{\frac{r}{2}}$ close to the origin. In atomic and molecular calculations, it is common to assume that the correlation factor is an increasing function that reaches a constant value at infinity. However, a recent analysis by Lesiuk *et al.* [53] of the correlation factor for the helium atom showed that this is not necessarily the case: asymptotically the correlation factor can behave exponentially or even going to zero. Furthermore, Tew and Klopper [54] empirically found that the optimum correlation factor in their helium wave function is not monotonic and reaches a maximum before decreasing.

In order to accommodate for all possible behaviors at infinity, we described the functions g with the same functional form used before: $g(r) = e^{\frac{r/2+b\,r^2}{1+c\,r}}$. If $b = 0$ the function is commonly called the Jastrow factor and reaches an asymptotic value at infinity. For finite values of b, the correlation factor can either go to zero or to infinity depending on the sign of b. Using the exact Ps wave function for the function $f_2(r_{23})$ and a Jastrow correlation factor ($\Psi = (1+\hat{P}_{12})J(r_{12})f_1(r_{13})\Psi(Ps_{23})$), the recovered binding energy improves up to 75%. Releasing the b parameter in the correlation factor gives a much better wave function that recovers more than 94% of the binding energy (see Table II): an impressive result for such a compact wave function with only four variational parameters. On a side note, this is a strong indication that a Jastrow correlation factor is not a good description of the electron-electron interaction in the Ps$^-$ ion.

If we do not constrain the function f_2 to describe a pure Ps and release its parameters the total (and binding) energy improves very little: another sign that the Ps structure inside the total wave function comes out naturally.

Figure 1 shows the three optimized two-body functions. Note that the correlation factor increases up to about 7 bohr and then decreases to zero. At present, it is not clear why this form of correlation factor is superior to the commonly employed Jastrow factor and further studies are needed to investigate what is the best correlation factor in positronic systems.

III. THREE-BODY CORRECTIONS

The wave function $\Psi_{2B} = (1+\hat{P}_{12})g(r_{12})f_1(r_{13})f_2(\mathrm{r}_{23})$ is the most general wave function written as a symmetrized product of two-body functions. We call $E_{2\mathrm{B}}$ the lowest energy that can be obtained for infinitely flexible g and f two-body functions. The difference between the exact energy and the

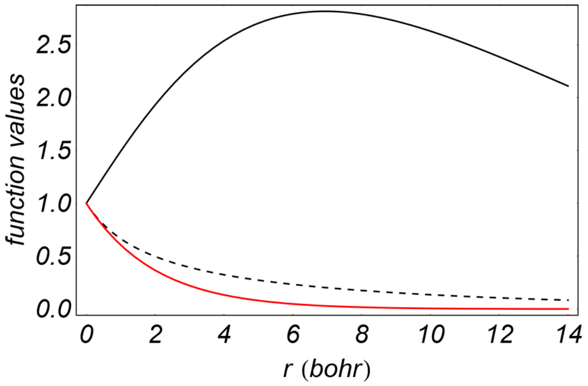

FIG. 1. Two-body functions for the optimized wave function of Ps⁻: g (black), f_1 (dashed black) and f_2 (thick red). Units are arbitrary.

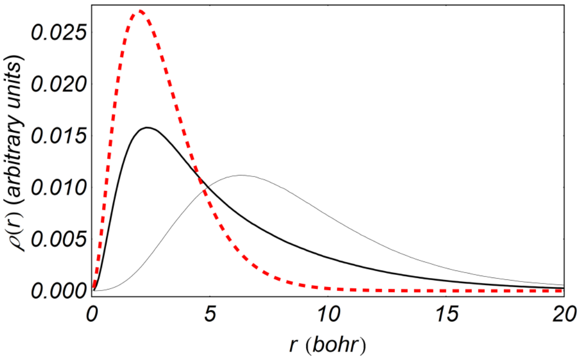

FIG. 2. Pair distributions functions: $\rho_{+-}(r)$ (thick black) and $\rho_{--}(r)$ (thin black) in Ps⁻. $\rho_{\mathrm{Ps}}(r)$ (dashed red) in positronium. All curves are normalized to 1.

limit two-body energy is a well-defined quantity and it is entirely due to three-body terms missing in the wave function. Using the functions g and f shown in the previous section, we recovered an energy of –0.26135(1) hartree, corresponding to 94.6% of the binding energy. In order to check how close we are to $E_{2\mathrm{B}}$ we employed a more sophisticated form for the two-body functions, adding a cubic term in the numerator of the exponent, and a quadratic term in the denominator of the exponent. After extensive optimizations the best energy we could get was –0.26143(1) hartree with a rather modest improvement. This means we are likely very close to the theoretical energy limit for that wave function functional form, and we estimate the three-body contribution to the exact energy $E_{3\mathrm{B}} \approx 0.0006$ hartree.

Formally we can decompose the exact wave function Ψ_0 into the product of two- and three-body contributions: $\Psi_0 = \Psi_{2B}\Psi_{3B}$. Unfortunately, almost nothing is known about Ψ_{3B}. It is likely that it must contains some logarithmic term in the triple collision region, i.e., where the three particles are very close [55–58] but at present its exact form is unknown. Three-body contributions to the exact wave function, however, are not limited to the triple collision region. To partially take into account three-body effects when one electron is at larger distance from the positron than the other, Patil [14] suggested the inclusion of the term $g_3(r_{12}, r_{23}) = \exp(p\,\boldsymbol{r}_{12} \cdot \boldsymbol{r}_{23}/\sqrt{r_{12}^2 + r_{23}^2})$ with an optimizable parameter p into the wave function. We multiplied our best two-body wave function with this term and obtained

$$(1 + \hat{P}_{12})g(r_{12})f_1(r_{13})f_2(\mathrm{r}_{23})g_3(r_{12}, r_{23}). \tag{2}$$

After optimizing all parameters, we observed a small improvement in the total energy, recovering 96.95% of the binding energy. Further research is needed to develop a better compact three-body correlation factor. Finally, we employed a linear combination of two such terms and after reoptimizing all linear and nonlinear parameters we obtained an energy of –0.26183(1) that recovers 98.6% of the binding energy.

IV. PAIR DISTRIBUTION FUNCTIONS

We have shown that, employing a symmetrized product of two-body functions, the presence of Ps inside the Ps⁻ wave function comes out naturally. Suggestive as it might be, however, we must remember that the two-body functions in the total wave function are not physical observables. To support our findings, we must look at the various geometrical observables. Of course, the average particle distances have been the focus of many calculations since the study by Kolos *et al.* [5]. The average electron-electron distance in Ps⁻ is 8.55 bohr while the average electron-positron distance is 5.49 bohr [29]. Since the average electron-positron distance in Ps is 3 bohr, it is clear that directly comparing average distances of the two systems is not very useful: the simple comparison of the average distances does not by itself reveal a picture of Ps⁻ as a positronium with a loosely bound second electron. It is likely that this apparent discrepancy is the reason why in all previous studies of Ps⁻ this intuitive picture has never been examined quantitatively going beyond the calculation of the average distances.

If our purpose is to get an insight into the geometrical structure and to understand to what degree there is a Ps "inside" Ps⁻, we must look at the pair distribution functions $\rho_{ij}(r)$, i.e., the probability that a pair of particles i and j is at a given distance r, defined as

$$\rho_{ij}(r) = \int \delta(r_{ij} - r)\Psi^2(R)dR, \tag{3}$$

where $\boldsymbol{R}$ indicates the coordinate vector of the three particles.

Using our best variational wave function, we have computed the probability distribution functions ρ_{--}(r) and ρ_{+-}(r), i.e., the probability to find a pair of particles at a specific distance.

Figure 2 shows the $\rho_{+-}(r)$ and the $\rho_{--}(r)$ pair distributions, along with the exact distribution of positronium $\rho_{\mathrm{Ps}}(r)$. All curves have been normalized to 1 for an easier comparison. The e^--e^- distribution has a maximum around 6.5 bohr but its tail extends to beyond 20 bohr. The e^+ e^- distribution has a maximum around 2.4 bohr whereas the maximum of the probability distribution in Ps is at exactly 2 bohr.

The curves in Fig. 2 support the intuitive picture of one electron close to the positron, while the second electron is at larger distances since $\rho_{--}(r)$ has a maximum at a larger distance and a more slowly decaying tail than $\rho_{+-}(r)$. The probability distribution $\rho_{+-}(r)$, however, is quite different from the distribution in Ps, and it is not directly comparable:

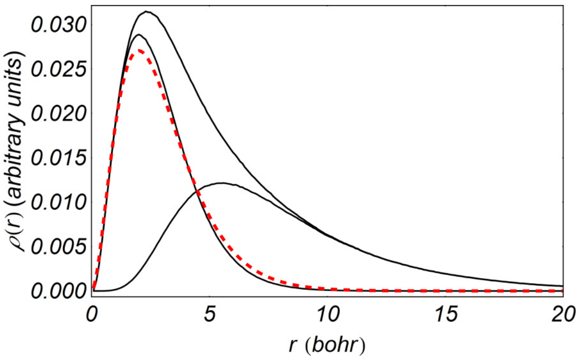

FIG. 3. Decomposition of $\rho_{+-}(r)$ (thick black, normalized to 2) into $\rho^{\rm in}_{+-}(r)$ and $\rho^{\rm out}_{+-}(r)$ (thin black, normalized to 1) along with the electron-positron distribution in Ps (dashed red).

since the two electrons are indistinguishable, the two electron-positron distances are averaged out.

While the electrons are indistinguishable, and the spatial wave function is symmetric with respect to the exchange of the two, at any given instant we can pick the electron closer to the positron and compute the probability distribution of its distance from the positron, and we can do the same with the more distant electron. We are effectively partitioning the $\rho_{+-}(r)$ distribution, without violating the indistinguishability principle, into two distributions with an immediate physical and geometrical meaning, one for the inner electron and the other for the outer electrons, with respect to the positron: $\rho_{+-}(r) = \rho^{\rm in}_{+-}(r) + \rho^{\rm out}_{+-}(r)$. Formally

$$\rho^{\rm in}_{+-}(r) = \int \delta(\min(r_{13}, {\rm r}_{23}) - r)\Psi^2(R)dR \tag{4}$$

and

$$\rho^{\rm out}_{+-}(r) = \int \delta(\max(r_{13}, {\rm r}_{23}) - r)\Psi^2(R)dR. \tag{5}$$

We wish to point out that usually the analytical calculations to obtain such distributions can be quite difficult and sometimes even impossible for some basis set expansions. They have been recently obtained for the two-electron atoms [59] with a basis of Laguerre functions in scaled perimetric coordinates, and to our knowledge they have never been computed for the positronium ion. These distributions instead are completely trivial to compute within a Monte Carlo simulation, since it only amounts to sorting the two electron-positron distances and binning them separately in two vectors.

Figure 3 shows the partitioning of $\rho_{+-}(r)$ into $\rho^{\rm in}_{+-}(r)$ and $\rho^{\rm out}_{+-}(r)$ along with the electron-positron distribution in Ps.

Now the strong similarity between the Ps probability distribution and $\rho^{\rm in}_{+-}(r)$ is clear and indeed we can say that there is (almost) a positronium inside Ps$^-$, with one electron that behaves almost as if it were in a Ps, and a second electron more loosely bound, since the maximum of $\rho^{\rm out}_{+-}(r)$ is at about 5.5 bohr. It is remarkable that the inner electron behaves almost as if the outer electron were not present, and that the effect of electronic correlation is such that the outer electron tries to stay as close as possible to the positron but without interfering too much with the distribution of the inner electron.

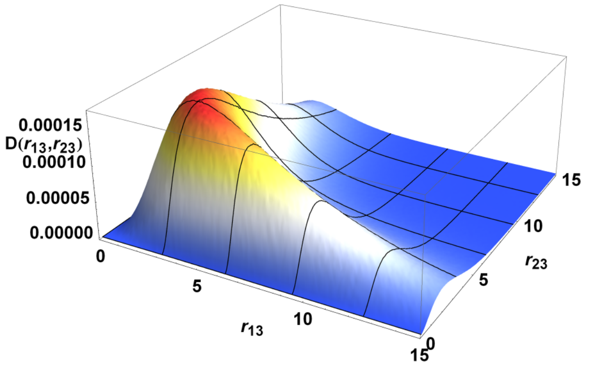

FIG. 4. (r_{13}, r_{23}) probability distribution, in arbitrary units, as a function of the two electron-positron distances in Ps$^-$. Distances are in bohr.

Figure 4 and 5 show, respectively, the 2D distribution for the two electron-positron distances $D(r_{13}, r_{23})$ and its contour plot.

Since the wave function is symmetric with respect to the exchange of the two electrons, the 2D distribution is symmetric along the line $r_{13} = r_{23}$. The maximum of the $D(r_{13}, r_{23})$ probability distribution is at (3.2,3.2), but the tendency of one electron to stay at larger distances from the positron is apparent from the peculiar shape of the distribution, with the two ridges where one electron forms a Ps substructure, as we have seen, and the other is more distant.

To elucidate how the second electron distributes itself around the Ps substructure, we computed a second 2D probability distribution. Figure 6 shows the probability distribution of the more distant electron on the *xy* plane defined by the three particles. The x axes is along the Ps with the origin of the coordinate at the center of the two particles.

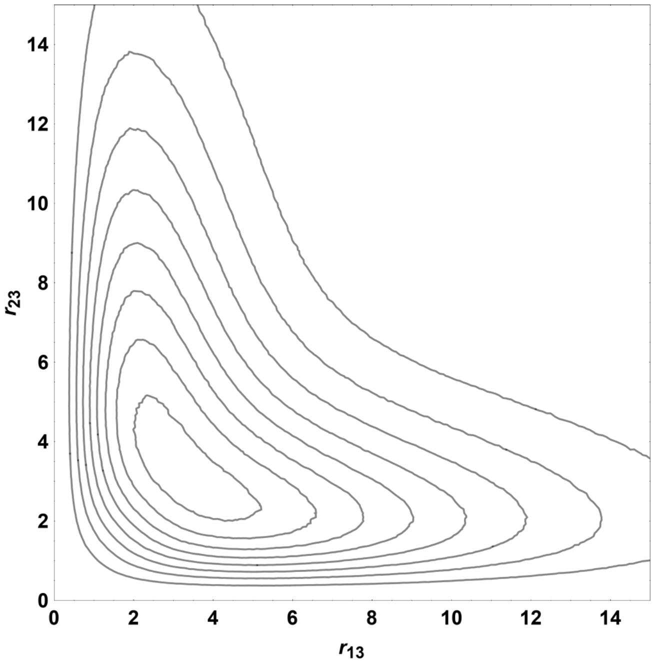

FIG. 5. Contour plot of $D(r_{13}, r_{23})$ in Fig. 4. Distances are in bohr.

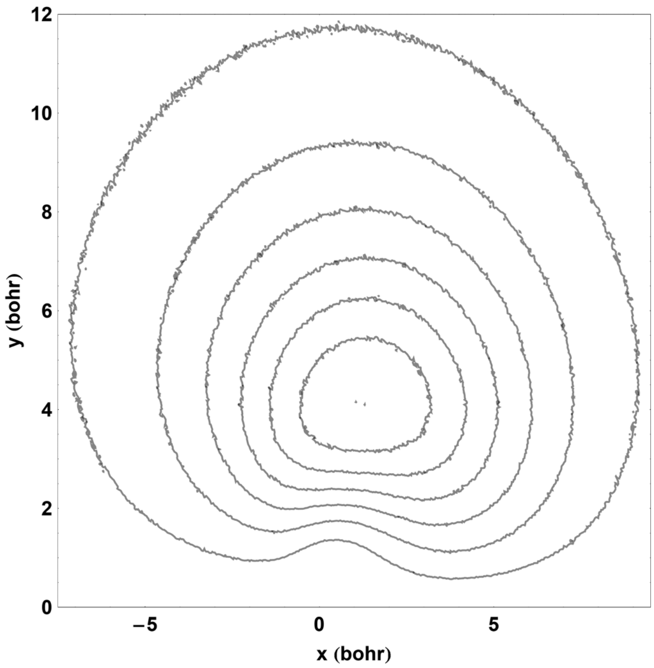

FIG. 6. Contour plot of the distribution of the second electron around Ps. The x axes is defined by the direction from e^- to e^+ in Ps, the origin is in the middle. The xy plane is defined by the three particles.

In the plane defined by the three particles, the distribution of the loosely bound electron has a maximum for $(x, y) = (1.3,\ 4.1)$ (distances are in bohr), closer to the positron, on the positive side of the x axes.

V. CRITICAL POSITIVE CHARGE TO BIND TWO ELECTRONS

To better understand why in Ps^- the outer electron is so loosely bound that the system resembles Ps in some properties, let us consider the system of three charges with unit masses $(Z^+,\ e^-,\ e^-)$. For $Z = 1$ we just have the positronium ion. For $Z \to 0$ this system dissociate into $(Z^+,\ e^-) + e^-$. Evidently there must exist a critical charge Z_c such that the three-particle system has exactly the same ground state energy than the threshold energy $-Z_c^2/4$. There is an extensive literature on the critical stability of three and four particle systems with varying charges and masses. We refer the reader to the article by Armour *et al.* [60] for a comprehensive review of the field. The first to study this particular system was Rebane [61] who, from purely theoretical arguments, established that $0.9070 < Z_c < 0.9276$. More recently Li and Shakeshaft [62] using a Pekeris-type wave function gave the accurate estimate $Z_c = 0.921802$. We performed several VMC simulations varying Z_c, using the best functional form developed in the previous section reoptimizing all variational parameters. Subsequently, we performed diffusion Monte Carlo (DMC) simulations to estimate the exact ground state energy obtaining the bound $0.9218 < Z_c < 0.9219$, in optimal agreement with Li and Shakeshaft. We could not go beyond four decimal digits in the determination of Z_c due to the statistical noise inherent in Monte Carlo simulations.

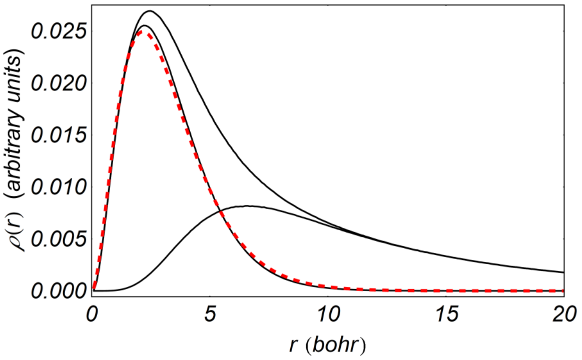

FIG. 7. Decomposition of $\rho_{+-}(r)$ (thick black, normalized to 2) into $\rho_{+-}^{\mathrm{in}}(r)$ and $\rho_{+-}^{\mathrm{out}}(r)$ (thin black, normalized to 1) along with the electron-positron distribution in the $(Z^+,\ e^-)$ system (dashed red) for $Z = 0.921802$.

Since for $Z < Z_c$ the system dissociates, it is a natural question to ask what happens to the wave function exactly at $Z = Z_c$ where the ground state energy is equal to the threshold energy $-Z_c^2/4$. This problem has never been studied before, but there is an extensive literature on the closely related system consisting of two electrons and a fixed nucleus of charge Z. The critical charge Z_c for the two-electron atomic systems, after many years of controversies, has finally been established by Estienne *et al.* [63] to be $Z_c = 0.911\,028\,224\,077\,255\,73$ and independently confirmed by Pilón and Turbiner [64]. Estienne *et al.* [63] found that not only the wave function at the critical charge is square integrable, as theoretically predicted, but it also remains localized at a finite distance from the nucleus.

King *et al.* [59] studied the electronic distributions of the inner and outer electrons for the two-electron atoms at various Z and at Z_c. They found that as the nuclear charge decreases, the inner electron distribution becomes more hydrogeniclike, to the extent that there is very little discernible difference between the distribution for the hydrogenic system and that calculated as the inner electron distribution for $Z = Z_c$. It is still an open question whether the inner electron distribution at the critical charge is exactly that of the hydrogenlike system, or it is slightly different. The numerical study of this problem using the variational principle requires extremely accurate trial wave functions: if the deviation of the approximated wave function from the exact one is of order ε, the variational energy has a quadratic error ε^2, much smaller, and so the variational principle is not very sensitive to slight variations in the wave functions.

We have reoptimized the parameters of our best wave functions to simulate our three-particle system for $Z = 0.921802$, the value of the critical charge estimated by Li and Shakeshaft [62]. To reduce the error still present in the optimized wave function we performed a DMC simulation, to obtain a better approximation to the exact distributions, and finally used the second order estimator to obtain the desired distributions. Figure 7 shows the partitioning of $\rho_{+-}(r)$ into $\rho_{+-}^{\mathrm{in}}(r)$ and $\rho_{+-}^{\mathrm{out}}(r)$ along with the electron-positron distribution of Ps for the system at the critical charge.

We observe the same phenomenon described by King *et al.* [59]: the closer Z is to the critical charge, the closer the inner electron distribution to that of the $(Z^+,\ e^-)$ system. Our wave function is not accurate enough to establish if, at the critical charge, the inner electron distribution is exactly equal to the $(Z^+,\ e^-)$ system or it is slightly different. Nevertheless, it is now clear why the inner electron in Ps⁻ behaves almost like in Ps: the critical charge $Z_c = 0.921802$ is very close to the $Z = 1$ charge in the physical system. If the critical charge had been much smaller, Ps⁻ could not be described as a Ps with a loosely bound electron.

VI. SUMMARY AND CONCLUSIONS

We clarified the empirical observation that some properties of Ps⁻ are nearly equal to that of the spin-averaged neutral Ps. We showed that writing the Ps⁻ wave function as a product of pair functions, the description of this ion as a Ps with a loose electron orbiting around comes out naturally. We then partitioned the electron-positron distribution $\rho_{+-}(r)$ into the sum of two terms: $\rho^{\text{in}}_{+-}(r) + \rho^{\text{out}}_{+-}(r)$. We showed that the distribution of the electron closest to the positron, $\rho^{\text{in}}_{+-}(r)$, is almost superimposable to the electron-positron distribution in Ps, and this is the reason why we could say that there is "almost" a Ps inside Ps⁻.

We finally related this phenomenon to the determination of the critical constant Z_c of the system of three moving charges with unit masses $(Z^+,\ e^-,\ e^-)$: $\text{Ps}^-(e^+,\ e^-,\ e^-)$ is very close to the critical system $(Z_c^+,\ e^-,\ e^-)$ where one electron is detaching from $(Z_c^+,\ e^-)$.

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