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Energetics and structure of $\mathrm{Ps}^-\mathrm{HPs}$ using a molecular approach

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Many atoms and negative ions are able to bind a positron. Their structure consists of an atomic core with an orbiting positron or positronium (Ps). A few systems can also bind two positrons, but much less is known about their internal structure. We examine the family $pe_n^-e_m^+$ with a proton p, $n \leqslant 4$ electrons, and $m \leqslant 2$ positrons. Using quantum Monte Carlo techniques, we study the energetics and structure of $pe_4^-e_2^+$. We compute its ground-state energy [$-1.05910(1)$ hartree] and its binding energy (0.0079 hartree). We show that to construct a bound variational wave function, despite having a single nucleus, we must adopt a molecular description of this system, using HPs, Ps^-, H^-, and Ps_2 as interacting fragments. The analysis of the electronic and positronic probability distributions reveals that at zero order, the internal structure of this system consists of a Ps^- interacting with the HPs core. Based on these results, we speculate about the existence of similar systems containing three positrons.

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The study of multipositronic systems is a new and largely unexplored field. Electrons and positrons, when no other particles are present, can form (disregarding annihilation) stable systems. Dipositronium (Ps_2) with two electrons and two positrons is a well-known example. It has been extensively studied theoretically [1–8] and it was detected experimentally [9]. Positrons can also bind to an atom or a molecule [10–12]. The positive nuclear charge repels the positrons, but they might attach to the whole system due to the attraction of the electrons.

Predicting the stability of Coulombic few-body systems containing positrons and electrons is a very difficult task requiring extremely accurate calculations, as particle correlation must be fully taken into account. Theoretical calculations have established the stability of a few multipositronic systems such as $\mathrm{Ps}_2\mathrm{O}$ [13], $e^+\mathrm{HPs}$ [14–16], $\mathrm{Li}^+\mathrm{Ps}_2$ and $\mathrm{Na}^+\mathrm{Ps}_2$ [17], $F^+\mathrm{Ps}_2$ and $\mathrm{Cl}^+\mathrm{Ps}_2$ [16], but so far they have not been detected experimentally.

In this paper, we study the stability diagram of the family $pe_n^-e_m^+$ composed of a proton p, $n \leqslant 4$ electrons, and $m \leqslant 2$ positrons. After a review of the known results, we study the energetics of $pe_4^-e_2^+$, establishing an accurate value of its binding energy (BE), and analyze its internal structure. We then discuss the stability of systems of the same family with three positrons and up to five electrons.

Figure 1 shows our current knowledge on the systems that can be built using one fixed proton and any number of electrons and positrons, with the caveat that in most cases only the $L = 0$ state has been investigated. Shaded boxes correspond to unstable combinations, while white boxes correspond to bound systems. For unstable systems, we used as a hypothetical name the combination of the two species corresponding to the lowest dissociation channel.

It is known that pe^-e^+, the hypothetical $e^+\mathrm{H}$ system, is unstable. The hydrogen atom is not able to bind a positron and this has been theoretically proved by Aronson and collaborators [18] and Armour [19]. Unsurprisingly, H^- is able to bind a positron to form HPs, which is also stable with respect to the dissociation into H + Ps. This system, theoretically predicted by Ore [20], was experimentally observed by Schrader and collaborators [21]. The next system $pe_3^-e^+$ is unstable with respect to the dissociation into e^- + HPs.

HPs can bind an additional positron to form $pe_2^-e_2^+$, a multipositronic system [14–16]. The analysis of its structure [15] revealed that this system is better described as $e^+\mathrm{HPs}$: a positron bound to positronium hydride.

$e^+\mathrm{HPs}$ has a positive charge, so one might try to add one electron to see if it remains stable. Varga [14] showed, however, that this system very likely is not bound since by increasing the basis size in stochastic variational method (SVM) calculations, the energy converges to the threshold HPs + Ps.

Rather counterintuitively, even if $e^+\mathrm{HPs}$ is not able to bind a single electron, it can, however, capture two electrons, leading to the stable system $pe_4^-e_2^+$ [14]. The energies of the two lowest dissociation channels, computed using the known exact nonrelativistic energies [7], are HPs + Ps^- (-1.051201 hartree) and H^- + Ps_2 (-1.043754 hartree).

Using the SVM and a large correlated Gaussian basis, Varga [14] was able to conclude that $pe_4^-e_2^+$ is stable with respect to all dissociation channels. However, he commented that his estimate of the binding energy, 0.00423 hartree, was not converged and that additional calculations were needed to establish a more realistic value.

Varga speculated that this system could be considered as a three-body system with a proton p and two orbiting Ps^- ions, in analogy with H^- where the electrons have been replaced by the composite ion Ps^-. However, no further calculations have been published on this peculiar and intriguing system.

Method. We employed an explicitly correlated functional form,

$$\Psi = \hat{A}\prod_{i=1}^{6} f_i(r_i)\prod_{i<j} g_{ij}(r_{ij}), \qquad (1)$$

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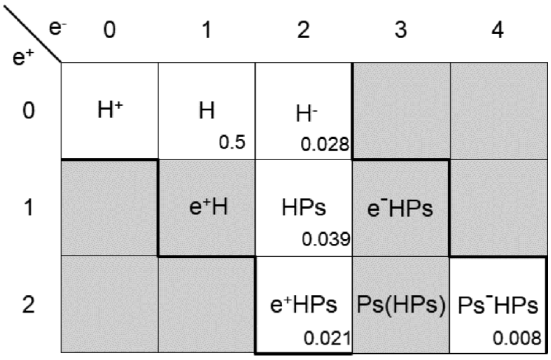

e^+ \ e^-	0	1	2	3	4
0	H^+	H 0.5	H^- 0.028	▨	▨
1	▨	▨ e^+H	HPs 0.039	▨ e^-HPs	▨
2	▨	▨	e^+HPs 0.021	▨ Ps(HPs)	Ps^-HPs 0.008

FIG. 1. Stability chart of the $pe_n^-e_m^+$ family. Systems in shaded boxes are unbound. The binding energy in hartree for a bound system is shown in white boxes.

to describe $pe_4^-e_2^+$. $\hat{A}$ is the antisymmetrizer operator, r_i is the distance between particle i and the proton, while r_{ij} is the distance between particles i and j. We assumed that both the positrons and the electrons are in a singlet state and the total angular momentum is 0. The functional form in Eq. (1) is the simplest, most general function where all two-body terms are taken into account. Since $pe_4^-e_2^+$ has a fixed proton with four electrons and two positrons, it is natural to view it as an atomic system with two positrons attached. In this picture, the electronic f functions describe the 1s and 2s orbitals, while the positronic f functions describe the two $1s_+$ orbitals.

Each particle occupies its own orbital centered on the nucleus. The f_i functions have the form

$$1s = 1s_+ = e^{\frac{ar+br^2}{1+cr}}, \quad 2s = (r-d)e^{\frac{ar+br^2}{1+cr}}, \tag{2}$$

where the parameters in each orbital are independent from each other and can assume different values. To reduce the number of variational parameters, we fixed the a parameter for the $1s_+$ and 1s orbitals, respectively, to their theoretical value of ±1.

The correlation function g_{ij} has the form $g(r) = \exp[(ar + br^2)/(1 + cr)]$. For electron-electron and positron-positron interactions, we set $b = 0$ and $a = 1/2$ or $a = 1/4$ for unlike and like spin, respectively. For electron-positron interactions, we fixed the cusps setting $a = -1/2$. We optimized all other parameters.

We used variational Monte Carlo (VMC) to estimate the variational energy. We first roughly optimized the parameters minimizing the mean absolute deviation of the local energy [22], and then finetuned them using an energy optimization procedure. We employed the resulting wave functions in fixed-node diffusion Monte Carlo (FN-DMC) simulations to obtain an upper bound to the exact energy. We estimated the FN-DMC energies using 10 000 walkers and eliminated the time-step bias by extrapolating to zero time step.

We computed various average distances and probability distributions using VMC and FN-DMC. If the employed wave function were exact, VMC and FN-DMC would give exactly the same values. We observed only small differences between the two, with no qualitative differences in the distributions; we combined these to further reduce the residual error using the second-order estimator (SOE).

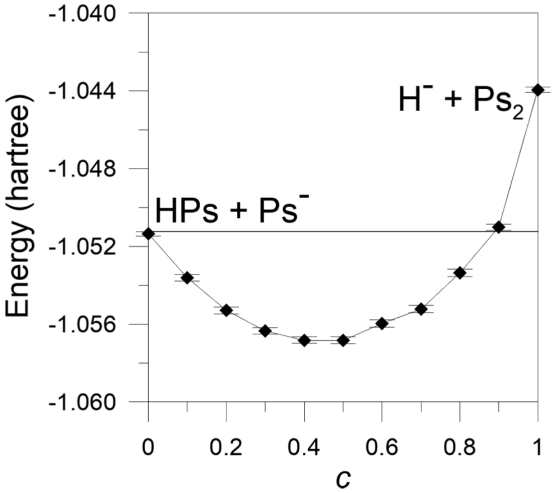

FIG. 2. DMC energies as a function of the mixing parameter c. The solid horizontal line is the lowest dissociation threshold.

Calculations. We extensively optimized all the orbitals and correlation factors in Eq. (1) but despite all efforts, we have been unable to obtain a bound system. Since in the past this functional form has been able to describe with great accuracy the essential physics of small electronic and positronic systems [23–26], its inability to do so in this case is a hint that some essential physics is missing. The implicit assumption of this picture is that the system has essentially an atomic character, and the trial wave function has been built accordingly.

The two lowest dissociation thresholds differ in energy by only 0.0074 hartree. The slow convergence of the SVM previously observed by Varga, and our inability to obtain a bound state using a single-term atomic wave function, despite the inclusion of all two-body correlations, led us to speculate that both limiting structures of the two dissociation channels could be important to describe the physics of the bound state. In other words, maybe we can view $pe_4^-e_2^+$ as a molecule that can dissociate into different fragments.

As a preliminary test of this hypothesis, we performed the following computational experiment. We first built the wave functions of the fragments using the same building blocks f and g already defined. The ground-state wave function of all fragments is positive everywhere and FN-DMC is able to recover, within the statistical uncertainty, their exact energy. We then built the total wave function mixing the two fixed structures, in a valence-bond-like framework (wave functions are not normalized),

$$\Psi = c\hat{A}\,\Psi(\mathrm{HPs})\Psi(\mathrm{Ps}^-) + (1-c)\hat{A}\Psi(\mathrm{H}^-)\Psi(\mathrm{Ps}_2). \tag{3}$$

When the mixing parameter c is either 0 or 1, one of the limiting structures is recovered with the corresponding energy dissociation threshold.

The Pauli principle dictates that the wave function of a four-electron system has a nontrivial nodal structure [27] and we expect its shape to vary as c changes, with a corresponding variation in the FN-DMC energy.

Figure 2 shows the result of several FN-DMC simulations with c varying from 0 to 1. The solid horizontal line is the

TABLE I. Total and binding energies of $p\,e_4^- e_2^+$.

$p\,e_4^- e_2^+$	Energy (hartree)	BE (hartree)
Threshold $H^- + Ps_2$	−1.043754	
Threshold HPs + Ps^-	−1.051201	
Varga[a]	−1.05542	0.00422
Eq. (3) with $c = 0.5$	−1.0574(1)	0.0062
VMC	−1.05424(1)	0.0030
FN-DMC	−1.05910(1)	0.0079

[a] Reference [14].

lowest dissociation threshold. Figure 2 also shows that by mixing into the lowest-energy structure even a small contribution from the second structure, the nodal structure changes and the system becomes bound. The lowest energy obtained with this crude experiment, reported in Table I is −1.0574(1) hartree. It is remarkable that such a simple nonoptimized wave function, with just a single tunable parameter, recovers a binding energy 50% larger than the one previously computed with the SVM with thousands of variational parameters.

The results of this computational experiment show that the structures of both fragments are necessary to capture the physics of this system. Encouraged by this result, we then proceeded to optimize a wave function of the form

$$\Psi = \hat{A}\Psi(\mathrm{HPs})\Psi(\mathrm{Ps}^-)\varphi_1(\mathrm{HPs};\mathrm{Ps}^-) + c\hat{A}\Psi(\mathrm{H}^-)\Psi(\mathrm{Ps}_2)\varphi_2(\mathrm{H}^-;\mathrm{Ps}_2), \quad (4)$$

where the two functions φ describe the interaction between the fragments and are constructed using products of the functions f and g already described. We first optimized all the variational parameters of the φ functions and then relaxed the parameters of the fragments, both orbitals and correlation factors. Optimizing only the φ functions is not sufficient to obtain a bound wave function.

The optimized wave function has a variational energy of −1.05424(1) hartree, well below the dissociation threshold. We then performed a FN-DMC simulation. FN-DMC simulations can give an exact estimate of a fermionic ground state only if the wave function has the exact nodal surfaces [27]. In all other cases, such as this one, FN-DMC gives an upper bound to the exact energy. The estimate of the ground-state energy is −1.05910(1) hartree with a binding energy of 0.0079 hartree, almost double the previous estimate.

To investigate the internal structure, we computed the electronic and positronic distributions. Figure 3 shows the probability $p(r)$ to find an electron or a positron at a given distance from the nucleus. The distribution functions of the electrons and positrons are normalized, respectively, to 4 and 2. The electronic distribution shows two electrons close to the nucleus, with a maximum at 1.2 bohr, and the remaining two at a much larger distance, with a maximum at about 8.3 bohr. The positronic distribution is very broad and almost flat from 3 to 8 bohr with two slightly pronounced maxima.

As a comparison in e^+HPs the two positrons are closer to the nucleus [15] and the probability curve shows a single maximum. The two maxima of the positronic distribution immediately suggest to decompose it into the individual contributions of the inner and outer positrons [24,28] shown as dashed curves. The two interacting fragments emerge clearly: the inner positron is close to the two inner electrons, while the outer positron is closer to the two outer electrons. This is consistent with the molecular description we have adopted in the wave-function construction, and it is what we should expect from a Ps^- bound to a HPs.

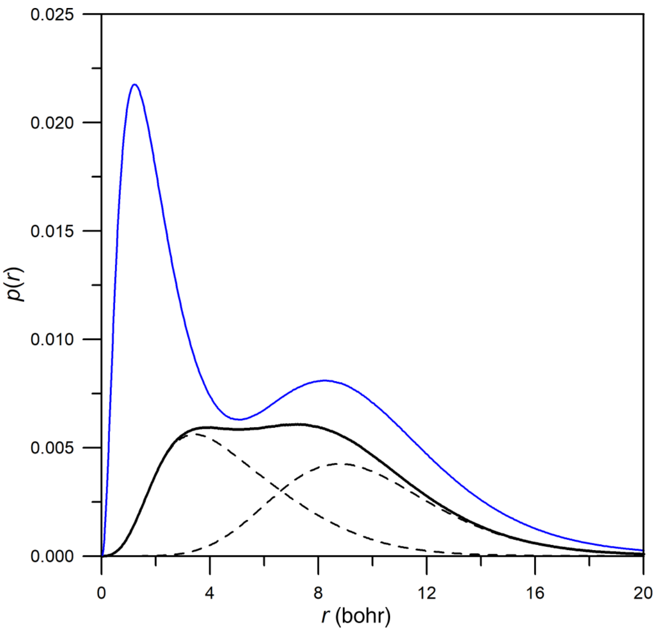

FIG. 3. Electronic (blue thin line) and positronic (black thick line) probability distributions, in arbitrary units, as a function of the distance from the nucleus. The curves are normalized to 4 and 2, respectively. The dashed lines are the probability distributions for the inner and outer positron.

However, as discussed previously, this limiting structure alone is unable to correctly describe this system since we must include into the wave function the two other possible fragments: $H^- + Ps_2$. This implies that the two positrons are not independently distributed around the nucleus, but they rather try to stay closer, to partially form dipositronium. From now on, we name this system Ps⁻HPs, after the lowest dissociation channel. A detailed study of the internal structure of Ps⁻HPs will be published elsewhere.

This structure can now explain why e^+HPs can bind two electrons, but not just one. In a molecular description, two electrons are needed to form the stable Ps^- that interacts with HPs, and at the same time the $H^- + Ps_2$ resonant structure. A single electron added to e^+HPs would form the hypothetical Ps-HPs that cannot be stabilized by resonance since the H + Ps_2 channel is much higher in energy.

Discussion. We now discuss the stability diagram of the entire family $p\,e_n^- e_m^+$. It is tempting to speculate on the possible existence of systems containing more than two positrons. We restrict our discussion to hypothetical systems with three positrons. In all systems considered so far, the two positrons have been assumed to have opposite spin. By adding an additional positron, the Pauli principle comes into play, introducing an additional nodal surface into the wave function since the electrons and positrons are antisymmetrized separately. Two like-spin positrons must avoid each other, raising the total energy and destabilizing the system. When we try to add a third electron to helium, for example, the system becomes unstable due to the newly formed nodal surface produced by the two electrons with the same spin. A way to overcome the effective repulsion and the destabilization is to increase the attraction due to the nuclear charge. This explains why the $1s^2\,2s\,^2S$ Li exists, while the $1s^2\,2s\,^2S$ He$^-$ does not. There is another way to accommodate the effective repulsion between like-spin identical fermions: the four electrons in the bound system Ps$^-$HPs do just that by distributing themselves in a sort of molecule where the electrons with the same spin belong to different fragments.

There are three possible tripositronic systems, with three to five electrons and at present it is unknown if they are stable species. Based on the discussion above, if they exist at all, they should be molecular systems with two interacting fragments. We assume that their structure mimics the two fragments of the lowest dissociation channel, with a possible stabilization due to the interaction of higher channels. In our discussion, we make the further assumption that Ps$_3$ and Ps$_3{}^-$ do not exist as stable isolated species [29].

If $pe_3^-e_3^+$ exists, it would probably be described as e^+HPs + Ps ($E_{th} = -1.0603$ hartree) rather than HPs + Ps$^+$ ($E_{th} = -1.0512$ hartree). Ps does not seem able to bind to charged species, but since the energy difference between the two channels is 9 mhartree, slightly bigger than for Ps$^-$HPs, this system might exist due to resonance stabilization.

Consider now $pe_4^-e_3^+$. The lowest dissociation channel is HPs + Ps$_2$ ($E_{th} = -1.3052$ hartree). Both Ps$_2$ and HPs need a charged system to bind, but the next dissociation channel, e^+HPs + Ps$^-$ ($E_{th} = -1.0723$ hartree), is much higher in energy and a resonance stabilization is unlikely. So this system is probably unstable.

Finally, consider $pe_5^-e_3^+$. Since Ps$_3$ and Ps$_3{}^-$ are probably unbound and $pe_3^-e_2^+$ and $pe_3^-e^+$ do not exist, the only possible way to build this system is Ps + Ps$^-$HPs ($E_{th} = -1.3091$ hartree) with no possible resonance stabilization: in conclusion, $pe_5^-e_3^+$ should be unstable.

In conclusion, using quantum Monte Carlo techniques, we studied the system composed of one proton, two positrons, and four electrons. We showed that this system has a molecular character, with a Ps$^-$ bound to a HPs, but with a contribution from the higher dissociation channel, H$^-$ + Ps$_2$, that leads to an energetic stabilization. We have computed its ground-state energy, estimating its binding energy at 0.0079 hartree. The analysis of various probability distributions showed that the inner positron stays closer to the two inner electrons, while the outer positron is closer to the two outer electrons. We also speculated about the possible existence of three-positron systems.

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