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Structure of LiPs ground and excited states

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The lithium atom in its ground state can bind positronium (Ps) forming LiPs, an electronically stable system. In this study we use the fixed node diffusion Monte Carlo method to perform a detailed investigation of the internal structure of LiPs, establishing to what extent it could be described by smaller interacting subsystems. To study the internal structure of positronic systems we propose a way to analyze the particle distribution functions: We first order the particle-nucleus distances, from the closest to the farthest. We then bin the ordered distances obtaining, for LiPs, five distribution functions that we call sorted distribution functions. We used them to show that Ps is a quite well-defined entity inside LiPs: The positron is forming positronium not only when it is far away from the nucleus, but also when it is in the same region of space occupied by the 2*s* electrons. Hence, it is not correct to describe LiPs as positronium "orbiting" around a lithium atom, as sometimes has been done, since the positron penetrates the electronic distribution and can be found close to the nucleus.

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I. INTRODUCTION

With the recent development of positron sources, there has been a renewed interest in the theoretical description of the interaction between positrons and atomic and molecular systems to form bound states, a field where theory is still ahead of the experiments [1–5].

The ability of positronium (Ps), a system composed of an electron and a positron, to attach to atoms has been known for a long time, starting with the pioneering calculation by Ore [6] which showed that Ps can attach to a hydrogen atom forming an electronically stable system: positronium hydride (PsH). Starting from the 1970s many researchers explored, with contrasting results, the possibility that a positron or positronium could attach to various atoms and molecules. Helium in its ground state is not able to bind either a positron or positronium. It took almost half a century after the theoretical prediction of the existence of PsH, to show that lithium can bind a positron, to form e^+Li [7], and even Ps to form LiPs, although neither of them has been so far experimentally detected.

Various theoretical calculations showed that at least 11 neutral atoms are capable of binding positronium in their ground state [2,8], although an experimental confirmation is still lacking for almost all of them. In contrast very little is known on the excited states of these complexes [8,9]. This is unfortunate since the existence of excited states of positronic compounds could provide a path to the experimental observation of these systems, similarly to what happened with the experimental observation of the dipositronium molecule [10] that exploited the existence of an excited state. Furthermore most theoretical investigations were aimed at computing energetic properties as accurately as possible, while the description of their internal structure, and in particular the detailed behavior of the positron in the electronic environment, has been only superficially explored, with the possible exception of PsH [11–13]. There is no consensus yet on the nomenclature of positronic compounds and this is a reflection of the fact that more studies are needed to better understand the internal structure of these systems. For example, positronic lithium, e^+Li, could well be named PsLi$^+$: The name should reflect, if possible, the real electronic and positronic distribution, which in this case seems to be better described as a Li$^+$ core interacting with a Ps system. Analogously the system formed by attaching Ps to lithium is generally described as LiPs, but *a priori* alternatives could be e^+Li$^-$ and even Ps$^-$Li$^+$. Although choosing an appropriate descriptive name, representing the real physical nature of the system, is to some extent only a matter of convention, we need to understand more deeply to what degree (and how) a positronic system can be considered "composed" by different interacting subsystems. This is of practical importance since in some cases it seems possible to describe Ps as an effective particle and develop effective potentials to model its interaction with the rest of the system [14–16]. This approach could then be used to model the interaction of Ps in cases where a full many-body calculation is not feasible.

In this work, we studied the interaction between Ps and the ground and a few excited states of lithium atom. We also performed a detailed investigation of the internal structure of these systems, establishing to what extent they could be described by smaller interacting subsystems.

The first dissociation channel for LiPs is the breakup into Li and Ps, with threshold energy of −7.728 04 hartrees. The dissociation into Li$^-$ and e^+ is higher in energy, with a threshold of −7.500 76 hartrees. The possibility that lithium could bind Ps was explored by Saito [17] using second-order variational perturbation theory but he was unable to see any binding. Subsequently two studies were published, both employing the fixed node diffusion Monte Carlo (FN-DMC) method, further investigating the possible binding. Harju and co-workers [18] predicted LiPs to be unbound. On the contrary, Yoshida and Miyako [19] reported a rather large binding energy of 0.028(5) hartree. These conflicting early results using the same computational method can probably be explained by a lack of convergence of those early Monte Carlo simulations, since both would be considered too short by today's standards.

The first to resolve the matter and rigorously prove that the lithium atom in its ground state can bind positronium were Ryzhikh and Mitroy in 1998 [20]. They performed the first large variational calculation of the LiPs system using explicitly correlated Gaussians (ECGs) within the stochastic variational method (SVM) as implemented by Varga and Suzuki [21,22]. They reported a total energy of −7.738 55 hartrees with a binding energy (B.E.) of 0.010 51 hartree. Of course, the LiPs system is stable only from the chemical point of view, since its total energy is below the sum of the fragments, but it is not stable against electron-positron annihilation. Later in the same year Bressanini and co-workers [23] published a statistically reliable FN-DMC simulation of that system, confirming the results of Ryzhikh and Mitroy, with a similar binding energy of 0.0096(8) hartree, showing that the FN-DMC method was indeed able to accurately describe the system, despite the early failures.

Ryzhikh *et al.* [24] made a first attempt to elucidate the structure of LiPs by plotting the probability of finding an electron or a positron as a function of the distance from the nucleus. They observed that the electronic and positronic probability densities have a similar decay, tending to merge at large distances from the nucleus. The authors suggested that it was a reflection of the fact that dissociation into Li+Ps (and not $\mathrm{Li}^- + e^+$) is the breakup process requiring the least energy. In other words, this was a strong suggestion, although not a rigorous proof, that in LiPs the positron could form a Ps system far from the nucleus. The preferred dissociation channel, however, does not necessarily dictate what happens to the positron when it is closer to the nucleus. As an example, consider the LiH molecule: It dissociates into Li+H but at the equilibrium distance the system is better described as H^- interacting with Li^+.

In 2001, using a larger basis, Mitroy and Ryzhikh [25] improved the energy (−7.740 208 hartrees) and the binding energy (0.012 148 hartree) but no further attempts to elucidate the structure were made. In the largest, to date, published calculation on LiPs [26], Mitroy using 2200 ECGs slightly improved the total energy (−7.740 431 6 hartrees) and the binding energy (0.012 371 hartree) but no new insight was gained on the structure of this system. In particular, the possible existence of a well-defined Ps subsystem, far from the dissociation region, has not been investigated.

Since LiPs can be formally built by adding a positron to Li^-, in this work we investigate the possibility of Li^- excited states to form LiPs in an excited state, analogously to what has been done for the lithium atom [9].

We also study the only LiPs excited state known: the ${}^{2,4}S^o$ state, found by Bromley and co-workers [27]. Bromley and co-workers, using the ECG-SVM method, obtained a total energy of −7.472 871 hartrees, proving that the system is bound with a binding energy of 0.000 215 hartree. They recognized, however, that the employed basis set was not large enough, and to give an estimate of the binding energy they resorted to the Configuration Interaction (CI) method with a frozen core approximation. The slow convergence of the CI method when applied to positronic systems is well known, and it was necessary to use a very large basis set to see the system bound, with a B.E. of 0.000 072 78 hartree. Extrapolating to a complete basis set they estimated the B.E. to be 0.000 441 hartree which, however, being the result of a frozen core approximation followed by an extrapolation, needs to be independently confirmed by a fully variational calculation. Furthermore a detailed analysis of the structure of this state has never been performed.

II. COMPUTATIONAL METHODS

The aim of this study was to elucidate the internal structure of these systems. We used the explicitly correlated functional form used by Bressanini and Morosi [13,28,29] for its compactness and flexibility to describe the wave function of Li, Li^-, and LiPs in their ground and various excited states. This type of wave function has been successfully employed in establishing that a positron can attach to an excited state of lithium [9].

The wave functions employed in this work include all particle-particle correlations:

$$\Psi = \hat{A}\left[\hat{O}\prod_{i=1}\varphi_i(\mathbf{R}_i)\prod_{i<j}g_{ij}(r_{ij})\right], \qquad (1)$$

where $\hat{A}$ is the antisymmetrizer operator and $\hat{O}$ is an operator used to fix the rotational symmetry, when needed. $\mathbf{R}_i$ are the space coordinates of particle i while r_{ij} is the distance between particles i and j. Each particle occupies its own orbital φ_i centered on the nucleus and the correlation between each pair of particles is described by a different function g_{ij}. This functional form has already been used with success in the past to describe PsH in a very compact form [13].

Since the purpose of this study was to perform an exploration of the possible Ps-lithium binding we described the $\varphi_i(\mathbf{R}_i)$ orbitals in a very compact way with no attempt to get the best possible form:

$$1s = e^{\frac{-Zr+br^2}{1+r}} \quad 2s = (r-c)e^{\frac{ar+br^2}{1+r}} \quad 2p_z = z\,e^{\frac{ar+br^2}{1+r}}. \qquad (2)$$

We employed a Jastrow factor to describe the correlation functions g_{ij}. Previous studies [28,29] showed that using this kind of functions it is possible to develop very compact, but nevertheless accurate wave functions for few-electron systems. The variational parameters are allowed to be different in the three orbitals.

We used the variational Monte Carlo (VMC) technique [30] to estimate the variational energy. The parameters were first roughly optimized by minimizing the mean absolute deviation of the local energy [31], a robust variant of the more common variance optimization, and then fine-tuned with an energy optimization procedure. The resulting wave functions have been employed in FN-DMC simulations to obtain an upper bound to the exact energy. The FN-DMC energies have been estimated using 5000 walkers. The time step bias has been eliminated by extrapolating to zero time step.

The estimation of the various average distances and probability distributions has been done using the second-order estimator (SOE) whose error is second order with respect to the error in the trial wave function. There are more advanced algorithms available in the literature to estimate the exact expectation values of a generic operator, but we found this simple estimate to be accurate enough for the purposes of investigating structural properties.

TABLE I. VMC, FN-DMC, and estimated NRL energies (in hartrees) of the various states of Li^- considered in this work.

Li^- states	VMC energy	FN-DMC	NRL
$1s^2\,2s^2\,{}^1S$	–7.49802(3)	–7.5006(1)	–7.500776[a]
$1s\,2s\,2p^2\,{}^5S^e$	–5.38221(3)	–5.3851(1)	–5.386603[b]
$1s\,2p^3\,{}^5S^o$	–5.25490(1)	–5.2559(1)	–5.256107[b]

[a] Reference [39].

[b] Reference [40].

The lithium atom can form only three stable anions: $1s^2\,2s^2\,{}^1S, 1s\,2s\,2p^2\,{}^5P^e$ and $1s\,2p^3\,{}^5S^o$. Since LiPs is formally composed by Li^- and e^+, and the $1s^2\,2s^2\,{}^1S$ state is known to form the ground state of LiPs, we investigated if the two stable excited states of Li^- could form an excited state of LiPs.

In the calculations discussed here, the spin of the positron and its coupling with the electrons is irrelevant.

III. RESULTS AND DISCUSSION

A. Energetics

Table I shows the VMC and FN-DMC energies obtained for the ground and excited states of the lithium negative ion, along with the best available estimate of the nonrelativistic limit (NRL) truncated to six decimal digits. The error bars of the VMC and FN-DMC energies are shown in parentheses.

The quality of the nodal structure of the wave function is crucial when computing the FN-DMC energy. Since the attached positron does not exchange with the electrons we expect the nodal structure of the positronic system to give roughly equally accurate results, which should guarantee an accurate estimation of the binding energy. Table II shows the FN-DMC results for a positron attached to the three stable lithium anions, together with the ${}^{2,4}S^o$ state of LiPs.

With our simple wave function the estimate of the LiPs binding energy is 0.011 87(6) hartree, that compares well with the almost exact 0.012 37 estimated by Mitroy [26].

To form the ${}^{2,4}S^o$ state of LiPs the positron can be considered in a $2p_+$ orbital and two electrons of like spin in two $2p$ orbitals. Taking into account only the electronic configuration, the system corresponds to Li^- $({}^3P^e)$ with an attached positron. However, the Li^- $({}^3P^e)$ state is unbound. For this reason Bromley and co-workers [27] described the ${}^{2,4}S^o$ state as *Borromean*, since considered as a four-body system $(\mathrm{Li}^+,e^-, e^-,e^+)$ it has no stable three-body state of the correct symmetry that can act as a parent. Considered as a many-body system, however, it is not truly Borromean since it can be formed by binding Li $(1s^2\,2p^2P^o)$ and Ps$(2p)$, with a dissociation threshold of $-7.472\,656$ hartree.

Our FN-DMC simulation succeeded in finding the system bound with a binding energy of 0.000 46(2) hartree. Since our calculation is variational, and the binding energy was computed against the exact threshold energy, this is a rigorous lower bound to the binding energy, within the level of statistical accuracy. The Configuration Interaction – Frozen Core (CI-FC) extrapolated estimate of Bromley and co-workers [27] agrees quite well with our result.

We extensively optimized the wave functions for the ${}^{4,6}S^o$ and ${}^{4,6}P^e$ states, but the variational energies were always above the dissociation threshold. When we used these wave functions in subsequent FN-DMC simulations, we observed a dissociation of the systems, with Ps going away, and the energy converging to the dissociation limit.

The energy computed with the FN-DMC method is an upper bound to the exact energy, and it depends on the quality of the node of the trial wave function that can be different from the exact nodes [29,32–37]. For this reason, we cannot completely rule out the possibility that a more sophisticated wave function, with different nodes, would give a bound state. However, we consider this possibility very unlikely since the employed wave function seems capable of describing the lithium atom, its anion, and two states of LiPs with high accuracy, and the presence of the positron should not significantly modify the nodal structure.

B. Structure

It is commonly believed that a positronic compound of the kind $[e^+,\mathrm{A}^-]$ can be qualitatively understood as lying somewhere between two limiting cases: e^+A^-, where a positron is attached to an unperturbed A negative ion, and *APs* (or *PsA*, there is no consensus yet on the nomenclature), where the wave function describes Ps orbiting around the A neutral atom. In order to give firm ground to this intuitive idea, and describe in a semiquantitative nonarbitrary way the relationship between the real system and the two limiting cases, we must resort to some sort of mathematical description of the different fragments.

TABLE II. LiPs ground and excited states FN-DMC total energies and binding energies (B.E.). We report also the corresponding lowest dissociation channel, with its threshold energy. All energies are in hartrees.

LiPs state	Lowest dissociation channel	Threshold energy	FN-DMC energy	B.E.
$1s^2\,2s^2\,1s_+\,{}^2S$	Li $({}^2S)$ + Ps $(1s)$	–7.728060	–7.73994(6)	0.01187(6)
			–7.7404316[a]	0.01237[a]
			–7.73898[b]	0.011011[b]
$1s\,2p^3\,1s_+\,{}^{4,6}S^o$	Li $({}^4P^e)$ + Ps $(1s)$	–5.495409	Dissociate	
$1s\,2s\,2p^2\,1s_+\,{}^{4,6}P^e$	Li $({}^4P^o)$ + Ps $(1s)$	–5.618010	Dissociate	
$1s^2\,2p^2\,2\mathrm{p}_+\,{}^{2,4}S^o$	Li $({}^2P^o)$ + Ps $(2p)$	–7.472871	–7.47312(2)	0.00046(2)
				0.000441[c]

[a] Reference [26].

[b] Reference [14].

[c] Reference [27].

TABLE III. VMC energies of LiPs trial wave functions built using different fragments.

LiPs ground-state fragment	Energy (hartrees)
$\Psi(\mathrm{Li}^-)\Psi(e^+)f(\mathrm{Li}^-,e^+)$ VMC	−7.7226(1)
$\Psi(\mathrm{Li})\Psi(\mathrm{Ps})f(\mathrm{Li},\mathrm{Ps})$ VMC	−7.73429(3)
Threshold Li+Ps	−7.728060

There are at least two conceptually simple ways to compare the real physical system with the two limiting cases. The first is to analyze the wave function to see if it somehow "contains" the fragments, and to which extent they are perturbed. The second is to analyze the electronic and positronic densities. These two approaches are, obviously, intertwined in a nontrivial way, and give two different but complementary pictures of the system under study.

To give an illustrative example consider a generic $1s\,ns\,{}^1S$ state of the helium atom. When $n = 1$ we have the ground state, whose wave function cannot be accurately approximated by a simple product of two He^+ $1s$ wave functions, and the ground state of helium must be considered an entity of its own. However, as n is increased, the exact wave function can be well approximated by the symmetrized product $\hat{A}\Psi(\mathrm{He}^+(1s))\Psi(\mathrm{He}^+(ns))$ multiplied by a function f describing the interaction between the two electrons. The simple product must be properly symmetrized since the electrons are indistinguishable.

The second way to study the structure of the $1s\,ns\,{}^1S$ of the helium atom is to examine the electronic density which, again, can be related and compared to the electronic densities of the $1s$ and ns orbitals. Of course, with more particles involved it becomes more difficult, in practice, to analyze the wave functions and the densities.

Let us now analyze the structure of the ground state of LiPs. Following the above discussion, we constructed two different wave functions using, as building blocks, the wave functions of the possible fragments. We used the forms $\Psi(\mathrm{Li}^-)\Psi(e^+)f(\mathrm{Li}^-,e^+)$ and $\Psi(\mathrm{Li})\Psi(\mathrm{Ps})f(\mathrm{Li},\mathrm{Ps})$, properly antisymmetrized, to describe LiPs. The wave functions of the lithium atom, its anion, and Ps have been kept fixed, while the function $\Psi(e^+)$ and the two f functions describing the interaction between fragments have been optimized using VMC. These functions have been, again, constructed using products of the basis functions in Eq. (2). Table III shows the corresponding variational energies estimated using VMC. The first wave function, where we "forced" the structure of Li^- into the wave function, gives a quite poor description of the LiPs system. The energy is so poor, despite all the variational freedom given by the interaction function f, that it is even considerably higher than the dissociation threshold, suggesting that the contribution of this limit structure is negligible. On the other hand, the wave function of the form $\Psi(\mathrm{Li})\Psi(\mathrm{Ps})f(\mathrm{Li},\mathrm{Ps})$ is not only able to bind Ps to Li, but, remarkably, when we relaxed the variational parameters in the wave functions of the fragments, we could not improve the variational energy despite the additional variational freedom. This means that this wave function is the best functional form where all two-body correlations are taken into account, and this is a strong sign of the fact that describing LiPs as being composed of interacting Li and Ps is correct and not arbitrary. Since this was the best possible variational wave function we could construct, without including three- and higher-body effects, we used it in the FN-DMC simulations. We already saw that the FN-DMC energy of this wave function, shown in Table II, is very close to the estimated exact energy. In summary, the structure of the wave function strongly suggests that the LiPs picture is the correct one.

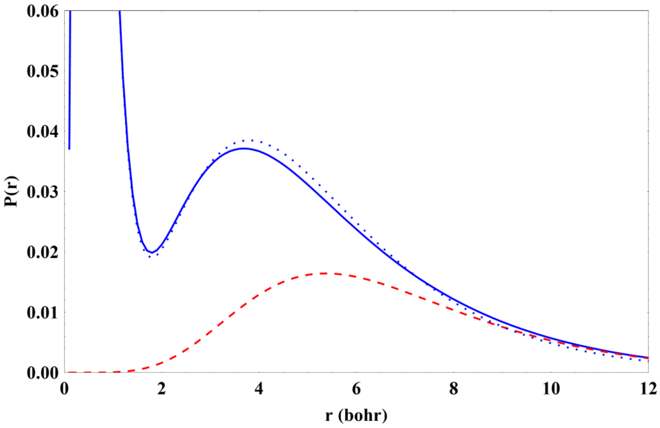

FIG. 1. Electron-nucleus (solid blue) and positron-nucleus (dashed red) distribution functions, in arbitrary units, for the ground state of LiPs. The dotted blue line is the electronic distribution of Li^-.

We now analyze the electronic and positronic density. The positron, on average, is at 6.5 bohrs from the nucleus while the average electron-nucleus distance is 2.9 bohrs and the average electron-positron distance is 5.7 bohrs. The average distances, however, are not very useful to get a clear insight of the structure since the particle-particle probability distribution functions are rather broad. For this reason we also computed the radial probability distribution functions of all the particles.

Figure 1 shows the electron-nucleus and positron-nucleus distribution functions for the ground state of LiPs, i.e., the probability to find the particle at a given distance from the nucleus. We also plot the electronic distribution of Li^-. The electronic and positronic curves are normalized, respectively, to 4 and 1. The size of the bins is 0.1 bohr. This plot agrees well with the one computed by Ryzhikh and co-workers [24].

The curve of the electrons, clipped close to the nucleus, shows the well-known shell structure, with the two $1s$ electrons tightly bound and the two more diffuse $2s$ electrons. The picture clearly shows that, passing from Li^- to LiPs, the electronic distribution of the first shell is unchanged. The second shell, however, is slightly different so the total electronic distribution of LiPs is not that of Li^-. This is consistent with the previously discussed finding that the wave function does not "contain" Li^-.

The positronic distribution is rather broad, confirming that geometrical properties cannot be discussed using the average distances only. In the distinguishable picture model the positron is moving in the same region of space around the nucleus where it is possible to find the two $2s$ electrons. Observing that at distances greater than about 8 bohrs the positronic curve superimposes to the electronic curve, Ryzhikh and co-workers [24] suggested the formation of Ps when the positron is far

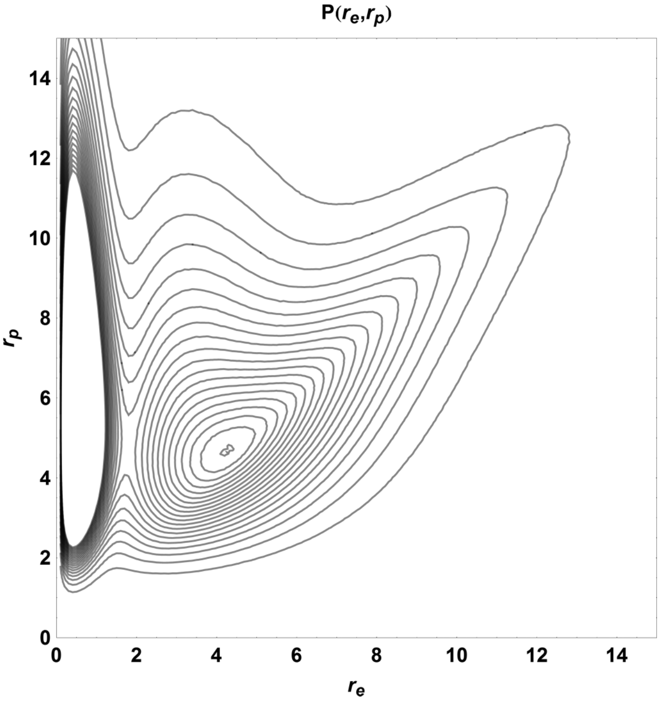

FIG. 2. Contour plot of $P(r_e,r_p)$: the probability of finding an electron at distance r_e from the nucleus and the positron at distance r_p from the nucleus. Distances are in bohrs.

away from the nucleus. Here we further analyze this observation to substantiate this intuition in a more rigorous way.

To get a better insight on the structure of the system we computed several two-dimensional probability distributions. Figure 2 shows the contour plot of $P(r_e,r_p)$: the probability of finding an electron at distance r_e from the nucleus and the positron at distance r_p from the nucleus.

The (clipped in the plot) structure on the left side of Fig. 2 represents the positron distribution corresponding to the region where two electrons, that we identify as the 1*s* electrons in the distinguishable picture model, stay close to the nucleus. The meaning of such a vertical elongated hill is that the electronic distribution in that region, from 0 to 2 bohrs, is practically not affected by the position of the positron. The maximum is located at approximately $r_e = 0.4$ bohr and $r_p = 5.6$ bohrs. In fact we already saw in Fig. 1 that the positron preferably stays outside the 1*s* shell.

More interesting, and revealing, is the heart-shaped structure for $r_e > 2$. The local maximum is at (4.3, 4.6), consistent with Fig. 1. The ridge along the direction where $r_e \approx r_p$ clearly shows that when the positron moves far from the nucleus it carries one electron with it. Figure 3 shows the radial probability distribution of the electrons when the positron is fixed at $r_p = 5$, 9, 13, and 17 bohrs (more precisely, in a bin of 0.1-bohr width). The distribution of the 1*s* electrons does not change while one electron moves following the positron, forming a local maximum.

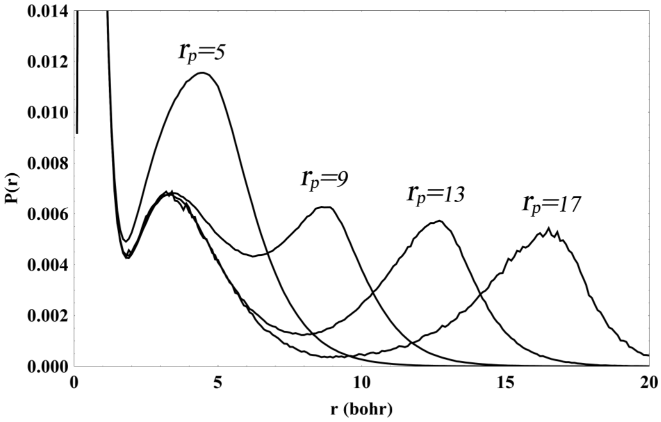

FIG. 3. Radial probability distribution, in arbitrary units, of the electrons when the positron is found at $r_p = 5$, 9, 13, and 17 bohrs from the nucleus.

As intuitively understood by different authors, the positron, far from the nucleus, forms a Ps system. However, it would not be correct to describe LiPs as positronium "orbiting" around a lithium atom, as sometimes has been done, since the positron penetrates the electronic distribution and can be found close to the nucleus, as shown in Fig. 1. What happens to the positron in the region between 2 and 8 bohrs from the nucleus? Does it stay, on average, close to only one electron or does it try to stay as close as possible to as many electrons as it can in order to maximize the interactions? In other words, does the Ps still exist even when the positron is between 2 and 8 bohrs?

To answer this question we propose an alternative way to analyze the distribution functions. We first order the particles-nucleus distances, from the smallest to the largest. In practice, we are temporarily labeling the particles from the closest to the nucleus to the farthest. We then bin the ordered distances obtaining, for LiPs, five distribution functions that we call sorted distribution functions because we sort the distance vector in ascending order. This does not violate the indistinguishability of the electrons since we are not assigning any permanent label to them. This kind of analysis is a generalization of the partitioning of the radial density function of two-electron systems into inner- and outer-electron radial density [38] where the distances from the two electrons to the nucleus are sorted before binning. Such an analysis is impossible to generalize to many-body systems when using an analytical integration method, but it is trivial using a Monte Carlo method.

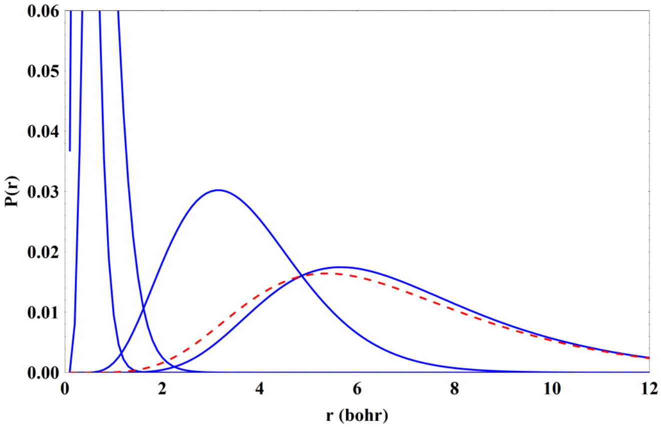

FIG. 4. Electronic distributions, in arbitrary units, of the sorted electrons (solid blue) and the positronic one (dashed red).

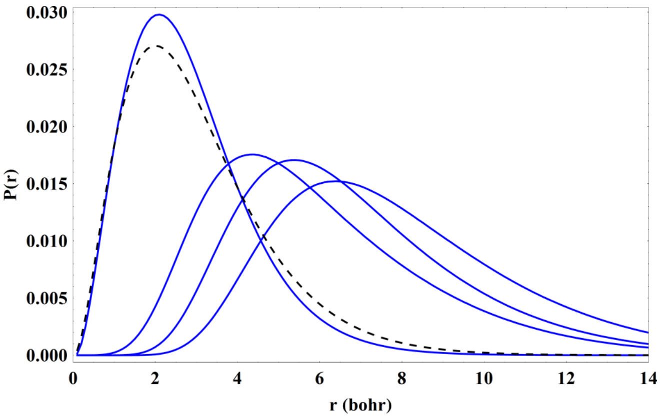

FIG. 5. Electron-positron sorted distances distributions (solid blue) and the exact electron-positron distribution of Ps (dashed black), in arbitrary units.

Figure 4 shows the sorted electronic distributions of the four electrons and the positronic one. The distribution of the last electron is amazingly similar to the positronic distribution, while the next to the last is quite different, and it peaks closer to the nucleus. This plot shows that for any given position of the positron, there is always, on average, an electron almost at the same distance from the nucleus. We now turn to the sorted electron-positron distributions.

Figure 5 shows the electron-positron sorted distances distributions with the exact distribution of Ps superimposed. The distribution of the closest electron, with respect to the positron, is very similar to the distribution of an isolated Ps, with the same maximum, while the other electrons are more distant on average. These graphs gives further support to the conclusion that positronium survives even when the positron is close to the nucleus. Of course we cannot say that the positron is always coupled to a specific electron, but only that the positron moves in the environment forming—with one electron at a time—a Ps system. It is like a dancer that, during the dance, exchanges partners, but is always dancing with only one partner at a time.

We performed a similar analysis on the structure of the $^{2,4}S^{o}$ state.

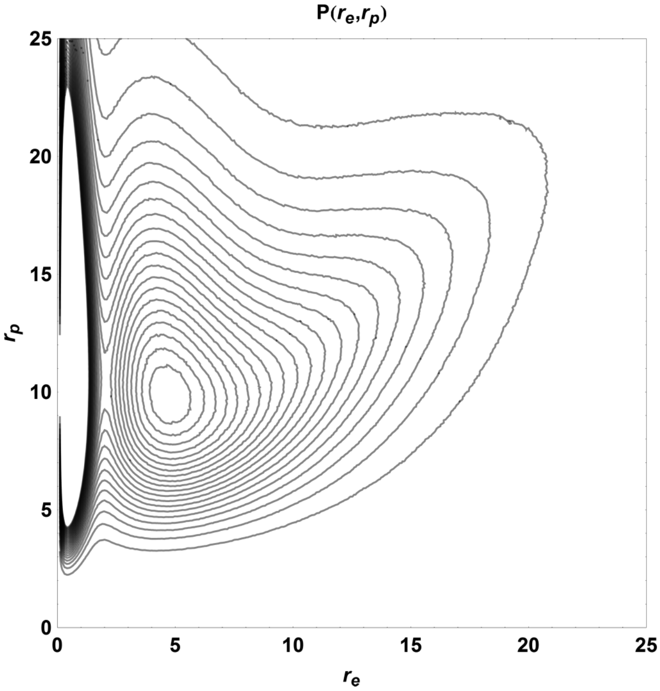

FIG. 7. Contour plot of $P(r_e,r_p)$ for the $^{2,4}S^{o}$ state of LiPs: the probability to find an electron at distance r_e from the nucleus and the positron at distance r_p from the nucleus. Distances are in bohrs.

Figure 6 shows the electronic and positronic distribution of this excited state. Compared with the LiPs ground state of Fig. 1, this state is much more diffuse. Both the positron and the $2p$ electrons are more distant from the nucleus, and again the two curves have the same decay. A contour plot of $P(r_e,r_p)$ distribution, analogous to Fig. 2, is shown in Fig. 7.

The heart-shaped structure, with maximum at (4.7,9.9), shows that the positron has the same behavior as in the LiPs ground state and again the Ps is a well-defined structure within the LiPs $^{2,4}S^{o}$ state. However, it is found at larger distances from the nucleus compared to the ground state.

The sorted distributions for this excited state are shown in Figs. 8 and 9.

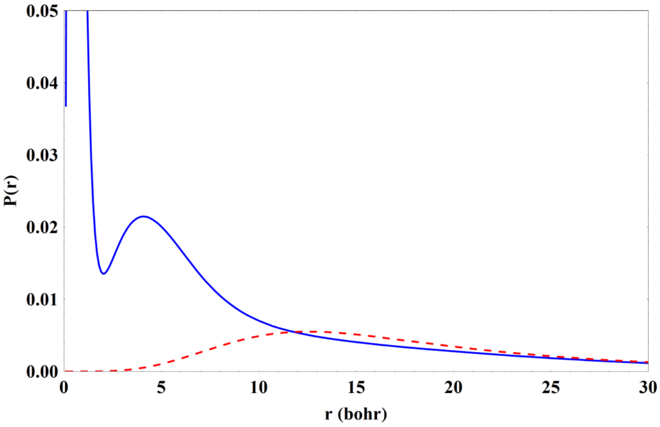

FIG. 6. Electron-nucleus (solid blue) and positron-nucleus (dashed red) distribution functions, in arbitrary units, of the $^{2,4}S^{o}$ state of LiPs.

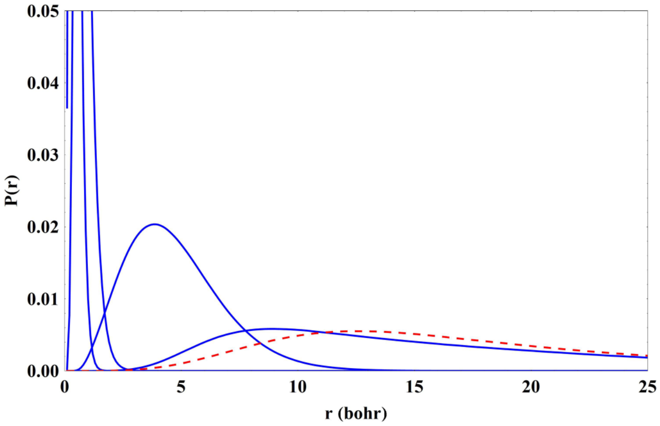

FIG. 8. Electronic distributions, in arbitrary units, of the sorted electrons (solid blue) and the positronic one (dashed red) for the $^{2,4}S^{o}$ state of LiPs.

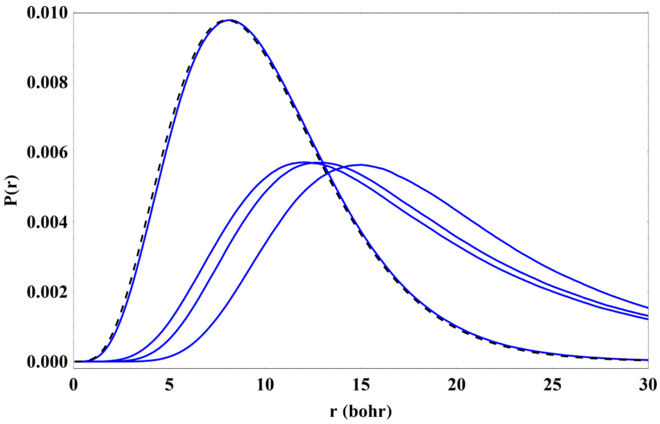

FIG. 9. Electron-positron sorted distances distributions (solid blue) for the $^{2,4}S^{\mathrm{o}}$ state of LiPs and the exact electron-positron distribution of Ps in a P state (dashed black), in arbitrary units.

As already found for the ground state, in the $^{2,4}S^{\mathrm{o}}$ state the positronic distribution follows the distribution of the outer electron. Consistently with Figs. 6 and 7, the positron is found at much larger distances from the nucleus than in the ground state. Also, it overlaps less with the electronic distributions of the other three electrons, and in particular with the inner $2p$ electron, while in the ground state the positron occupies a region of space where the inner $2s$ electron can be found more frequently. In other words, the positron in the $^{2,4}S^{\mathrm{o}}$ state interacts mainly with the outer electron. This can be seen more clearly looking at the electron-positron sorted distances distribution of Fig. 9. The dashed curve is the theoretical distribution of the P state of positronium, since both the electron and the positron occupy a $2p$ orbital. The overlap is almost perfect, as a result of the reduced perturbation from the more distant electrons.

IV. CONCLUSIONS

In this work we investigated the binding of a positron to all the known excited states of the lithium anion using the fixed node Diffusion Monte Carlo method. The positron does not form a bound state with the $^5S^{\mathrm{o}}$ or $^5P^{\mathrm{e}}$ state of Li^-. We have confirmed that the $^{2,4}S^{\mathrm{o}}$ excited state is bound, and give the best, to date, variational estimation of the total energy and a rigorous lower bound of the binding energy.

We examined in detail the structure of the ground state of LiPs. The inspection of various one- and two-dimensional distribution functions led to the conclusion that Ps is a reasonably well-defined entity within LiPs, not only when the positron is far away as has been already suggested in the past, but also closer to the nucleus. A similar analysis of the $^{2,4}S^{\mathrm{o}}$ state suggests a similar structure, with a Ps subsystem found at larger distances from the nucleus with respect to the ground state.

We introduced the sorted radial distribution functions and the two-dimensional distribution functions as a useful tool to get a better insight on the internal structure of many-body systems, and in particular of positronic systems. These distributions are extremely easy to compute in a Monte Carlo simulation of a many-body system, while they are impossible to estimate using a standard computational technique based on analytic integration. This is probably the main reason why such an analysis has never been performed before on LiPs.

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