Positron Binding to Lithium Excited States

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In the last 15 years hundreds of papers have been devoted to the study of positron-atom or positron-molecule interaction. A large body of evidence has accumulated showing that many atoms in their ground state can bind a positron forming an electronically stable system. Studies on the possibility that a positron binds to an atomic excited state, however, are scarce. The first atom that was proved able to bind a positron in its ground state is lithium. Surprisingly, nothing is known on the possibility that a positron could bind to one of its excited states. In this Letter we study the positron attachment to the $1s^22p\ ^2P^o$, $1s2s2p\ ^2P^o$ and $2p^3\ ^4S^o$ excited states of the lithium atom. While the $^2P^o$ state cannot bind a positron, and the $^4S^o$ could at most form a metastable state, a positron can attach to the $^4P^o$ state of lithium forming a bound state with a binding energy of about 0.003 hartree. This state can alternatively be considered an excited state of the system e^+Li and it could be, in principle, exploited in an experiment to detect e^+Li, whose existence has been predicted theoretically but has not yet been observed experimentally.

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The ability of positronium (Ps), a system composed by an electron and a positron, to attach to atoms has been known for a long time, starting with the pioneering calculation by Ore [1] which showed that Ps can attach to an hydrogen atom and form an electronically stable system, positronium hydride (PsH). In contrast, the fact that a positron can attach to a neutral atom was established only in the last 15 years. Starting from the 1970s many researchers explored, with contrasting results, the possibility that a positron could attach to the lithium atom in its ground state forming positronic lithium (e^+Li), electronically stable against dissociation into both $\mathrm{Li}^+ + \mathrm{Ps}$ and $\mathrm{Li} + e^+$. In an early computational study of e^+Li Cavaliere and Ferrante found it to be bound [2]. Their calculations, however, used a model potential instead of the true one and the study could not be regarded as definitive. A few years later, Clary [3] studied a few positronic systems, including e^+Li, with the Hylleraas-CI method. While he was able to show that the system was stable against the dissociation into Li and e^+, the calculations failed to show stability with respect to the dissociation into Li^+ and Ps. The reasons why the Hylleraas-CI method failed to predict the existence of e^+Li have been recently clarified by Strasburger [4]. In 1996 Yoshida and Miyako [5] performed a diffusion Monte Carlo (DMC) calculation and found the system stable with respect to positron dissociation, but they concluded that probably it was unstable compared to the separated Ps and Li^+. The error bar of their calculated energy was quite large and probably their calculation was not converged. The definitive proof that a positron can attach to the ground state of the lithium atom and form an electronically stable system was due to Ryzhikh and Mitroy [6]. Ryzhikh and Mitroy performed a large variational calculation using the stochastic variational method (SVM) developed by Varga and Suzuki [7] and they were finally able to show that e^+Li is stable with respect to the dissociation into Ps and Li^+, with a binding energy of 0.002 17 hartree. Independently, and using a similar basis set of explicitly correlated Gaussians, Strasburger and Chojnacki [8] confirmed that the system is bound with a binding energy of 0.001 22 hartree. Their binding energy was smaller than the one by Ryzhikh and Mitroy due to the shorter expansion employed. Yuan *et al.* [9], using the adiabatic hyperspherical method and a model potential to describe Li^+, confirmed the existence of a bound state of e^+Li with a binding energy of 0.002 13 hartree. A diffusion Monte Carlo calculation by Mella *et al.* [10] finally showed that the DMC method was indeed able to accurately describe the system, despite the early failure [5], giving a binding energy of 0.002 38(2) hartree. Mitroy, in 2004 [11], estimated the exact ground state of the system at $-7.532\,895\,5$ hartree and a binding energy of 0.002 484 hartree using a large SVM calculation with 1200 explicitly correlated Gaussians. To our knowledge this is the current best estimate of the total and binding energy of this system.

Although an experimental observation is still lacking and all the evidence comes from extensive calculations, at least 11 neutral atoms are supposed to bind a positron in their ground state [12,13]. In contrast, very few computational studies have been performed on excited states, and this is unfortunate since the existence of excited states of positronic atoms could provide a path to the experimental observation of these systems, similarly to what happened with the recent experimental observation of the dipositronium molecule [14] exploiting the existence of an excited state.

Given the importance of lithium in establishing a definitive theoretical proof that a neutral atom can bind a positron, it is surprising that there are no published studies on the possibility that it can bind a positron in some excited state. Such a state could be alternatively viewed as an excited state of the e^+Li system and would open the possibility of spectroscopic detection of this system.

Studies on positron binding to excited states of atoms are scarce and have been recently reviewed by Bromley and Mitroy [12]. It is known that the helium atom in its ground state cannot bind a positron [15]. Drachman *et al.* [16] and Clary [3] explored the possibility that the first triplet state $1s2s\ ^3S$ could bind a positron. Both attempts to establish binding were unsuccessful however. The first computational proof that the $1s2s\ ^3S$ state of helium can bind a positron, forming a very weakly bound state, came from Ryzhikh and Mitroy [17] whose SVM calculation gave a binding energy of only 0.000 591 6 hartree with respect to the $\mathrm{He}^+(1s) + \mathrm{Ps}(1s)$ dissociation channel. Unfortunately, helium in its ground state is incapable of binding a positron and so the binding of an excited state cannot be exploited to perform spectroscopic experiments.

The beryllium atom in its ^1S ground state is able to bind a positron [18]. A large scale CI calculation on the e^+Be ^3P excited state gave an energy above the dissociation threshold [19]. An analysis of the convergence patterns by successively increasing the maximum angular momentum of the basis functions suggested that this state might be bound, with a very small binding energy of 2.6 meV. A more robust confirmation, however, is needed. On more firm grounds is the establishment that the ^2P state of e^+Ca is bound [19]. However, even in this case the use of the fixed core approximation, and the same angular momentum extrapolation procedure, call for an independent confirmation with a variational method.

Apart from these cases, nothing else is known on positron binding to excited states, and, in particular, there are no fully variational calculations showing the existence of an excited positronic atom where the ground state is known to exist. In this Letter we explore the possibility that an excited state of Lithium binds a positron examining the following excited states of odd parity: $1s^2 2p\ ^2P^o$, $1s2s2p\ ^4P^o$ and $2p^3\ ^4S^o$.

Method.—The wave function of positronic compounds of the kind e^+A can be qualitatively understood considering the two limiting cases $\Psi(e^+A)$, where a positron can be considered attached to an unperturbed A atom, and $\Psi(\mathrm{Ps}A^+)$, where the positron detaches an electron, forming positronium, and the wave function describes Ps orbiting around the A^+ ion. The relative importance of the two structures depends on the ionization potential (IP) of the species A [20,21]. For this reason, it is extremely important that the employed functional form for the wave function has enough variational freedom to represent both limiting cases. We decided to use the explicitly correlated functional form used by Bressanini and Morosi [22–24] for both Li and e^+Li due to its compactness and flexibility.

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

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

where $\hat{A}$ is the antisymmetrizer operator, $\mathbf{R}_i$ 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 [22]: a single term with only seven variational parameters recovered roughly the same energy of 95.000 terms in a CI expansion.

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

$$1s = e^{ar+br^2/1+r}, \qquad 2s = (r-c)e^{ar+br^2/1+r}, \qquad 2p_z = ze^{ar+br^2/1+r}. \tag{2}$$

Previous studies [23,24] showed that using this kind of function it is possible to develop very compact but nevertheless accurate wave functions for few electron systems. In order to reduce the number of variational parameters, the a parameter for the $1s$ electronic orbital has been fixed to the theoretical hydrogenoid value —Z, to fix the cusp condition. The positronic orbital, denoted as $1s_+$ in the following, is similar in form to the $1s$ electronic orbital but with different parameters. In particular, the a parameter has been forced to be positive since the positron is pushed away from the positively charged nucleus.

As to the pair functions describing the electron-electron and electron-positron pairs, we employed a simple Jastrow factor $g_{ij}(r_{ij}) = e^{dr_{ij}/1+er_{ij}}$. To satisfy the cusp conditions, the d parameter has been fixed to $1/2$ or $1/4$ when considering the interaction between two unlike and like spins, respectively, and to $-1/2$ when considering a positron-electron interaction. The e parameters, different for each function g_{ij}, have been left free to be optimized. It is important to note that by choosing $e = 0$ and $d = -1/2$ the Ps system can be described exactly, a flexibility crucial to correctly describe positronic systems.

We used the variational Monte Carlo (VMC) technique [25] to estimate the value of the variational energy. The parameters were first roughly optimized by minimizing the mean absolute deviation of the local energy [26], 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 fixed node diffusion Monte Carlo simulations (FN-DMC) to obtain an upper bound to the exact energy. The more the nodes of these wave functions are close to the nodes of the exact

TABLE I. VMC, FN-DMC, and estimated NRL energies in hartree of the various states considered in this work.

Li excited state	VMC	FN-DMC	NRL
$1s^2\ 2p\ {}^2P^o$	$-7.408\,49(4)$	$-7.410\,14(1)$	$-7.410\,156$[a]
$1s\ 2s\ 2p\ {}^4P^o$	$-5.365\,52(2)$	$-5.367\,33(3)$	$-5.368\,010$[b]
$2p^3\ {}^4S^o$	$-2.103\,20(1)$	$-2.103\,65(4)$	$-2.103\,588$[c]

[a] Ref. [27].
[b] Ref. [28].
[c] Ref. [29].

wave functions of the various excited states considered, the more the FN-DMC energy is closer to the exact nonrelativistic energy. The FN-DMC energies have been obtained with 5000 walkers and eliminating the time step bias by extrapolating to zero time step.

Results.—Table I shows the VMC and FN-DMC energies obtained for the excited states of Li considered in this work, along with the best available estimate of the nonrelativistic limit (NRL) truncated to six decimal places. The error bars of the VMC and FN-DMC energies are shown in parenthesis. Comparing the FN-DMC results with the NRL energies shows that the nodal structure of the employed wave functions is extremely accurate, giving an error always less than 0.001 hartree and in all cases except the ${}^4P^o$ state close to 0.0001 hartree.

Since the attached positron does not exchange with the electrons we expect the nodal structure of the positronic moieties to give roughly equally accurate results.

Table II shows the FN-DMC results for a positron attached to the Li excited states considered in this work. The important role of the ionization potential of an atom in the possible binding of a positron has been already pointed out in the past [20,21]. The IP shown in Table II has been computed using the energy of the appropriate states of Li^+ reported in Refs. [30,31] truncated to three decimal digits.

Previous VMC calculations on the ground state of e^+Li [10] showed that using the single term in Eq. (1) VMC calculations were not able to show the binding of the positron. The subsequent FN-DMC calculation, however, gave a total energy very close to the exact value and a binding energy in agreement with other published calculations, as discussed in a previous section, showing the very good quality of the nodal structure of the employed wave function. A similar behavior was observed here in the simulations of e^+Li excited states: the VMC energies were statistically indistinguishable from the relevant dissociation threshold energies. For this reason Table II shows only the FN-DMC energies.

TABLE II. FN-DMC energies of the e^+Li excited states and the corresponding IP of the parent Li state. Energies are in hartree.

e^+Li state	Threshold	Lithium IP	FN-DMC
$1s_+\ 1s^2\ 2p\ {}^2P^o$	$\mathrm{Li}^+({}^2S) + \mathrm{Ps}(1s)$	0.130	dissociate
$1s_+\ 1s\ 2s\ 2p\ {}^4P^o$	$\mathrm{Li}({}^4P^o) + e^+(1s)$	0.257	$-5.3710(2)$
$1s_+\ 2p^3\ {}^4S^o$	$\mathrm{Li}({}^4S^o) + e^+(1s)$	0.306	$-2.1118(2)$

In the calculations discussed here the spin of the positron and its coupling with the electrons is irrelevant, so we drop it from the state symbol, showing only the spin multiplicity of the electrons. It is however of great importance when computing the annihilation rate of these systems, something that we plan to do in the future.

Discussion.—The $1s^2 2p\ {}^2P^o$ state of lithium, the first excited state, using the employed wave function is not able to bind a positron and the system dissociates into $\mathrm{Li}^+({}^2S) + \mathrm{Ps}(1s)$. 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. For this reason it cannot be completely ruled out the possibility that using a more flexible functional form the system is bound. We believe, however, that this is unlikely since our wave function seems capable of describing the lithium atom and ion with high accuracy, and the presence of the positron should not modify the nodal structure significantly. Furthermore, the IP of the ${}^2P^o$ state is 0.13 hartree, a value that seems too low [32] to support the formation of a positronic compound.

The $2p^3\ {}^4S^o$ state of lithium is a triply excited bound state embedded in the continuum of Li^+ but uncoupled from it due to its spin state and unnatural parity. Since the IP of this state is greater than 0.25 hartree the dissociation channel for the hypothetical e^+Li system is Li $({}^4S^o) + e^+$, the other $\mathrm{Li}^+\ ({}^3P^e) + \mathrm{Ps}(1s)$ being higher in energy. The FN-DMC calculation gave a binding energy of 0.0085 hartree, supporting the existence of a bound state. The angular momenta of the electrons and the positron however are not individually conserved, and a state of total S^o symmetry can be constructed also by coupling the $1s2p^2$ ${}^4P^e$ state of lithium with a positron in a $2p$ orbital. Since the ${}^4P^e$ state of lithium plus $e^+(2p)$ at infinity has an energy below our FN-DMC estimate, the e^+Li $({}^4S^o)$ cannot be considered a true bound state. Although this could be an indication of a resonance, further work and different computational techniques will be needed to investigate this matter.

The $1s2s2p\ {}^4P^o$ state of Lithium has an ionization potential of 0.257 hartree. It has been convincingly argued in the past [21,32] that an ionization potential close to 0.25 hartree, the binding energy of positronium, can be an indication of a possible positron binding to the neutral species. The first dissociation channel is $\mathrm{Li}({}^4P^o) + e^+$ with an energy of $-5.368\,010$ hartree. The FN-DMC simulation of e^+Li in a ${}^4P^o$ state gives an energy lower than this threshold, proving that the system is bound. Since the FN-DMC energy is an upper bound to the exact energy, using the estimated NRL of Li $({}^4P^o)$ in Table I gives a lower bound on the binding energy of about 0.003 hartree. Since the wave functions for both Li $({}^4P^o)$ and e^+Li $({}^4P^o)$

have a residual nodal error, due to nonexact nodal structure; assuming this is roughly the same gives an estimate of the binding energy, subtracting the respective energies, of 0.0037(2) hartree. This value, however, must be considered only as an indication and wave functions of better quality should be employed to give a more accurate estimation of the binding energy. There are no doubts however that the system is a true bound state since, unlike the e^+Li ($^4S^o$) case, its energy is below all relevant thresholds.

Conclusions.—In this work we investigated the binding of a positron to different excited states of odd parity of lithium using fixed node diffusion Monte Carlo calculations. A positron does not bind to the $1s^22p\ ^2P^o$ state; however, it can form a bound state attaching to the $1s2s2p\ ^4P^o$ state. The resulting system can alternatively be considered as an excited state of the e^+Li ground state whose existence has been predicted in the past but not yet observed experimentally. A positron can also attach to the $2p^3\ ^4S^o$ state of lithium but this state is unstable with respect to the dissociation into lithium ($^4P^e$) and $e^+(2p)$. This is the first time that a variational technique shows that a positron can bind to an excited state of the lithium atom. A similar investigation on excited states of even parity is under way. The existence of such excited states could in principle be exploited experimentally to detect the elusive e^+Li system. The theoretical prediction that the positronium molecule possesses an excited state has been recently exploited [14] in an experiment: Ps$_2$ molecules were formed in porous silica, resonantly excited, and then photoionized using a pulsed laser, providing a definitive evidence of its existence. It is possible that the discovery of the existence of an excited state of e^+Li could similarly help to devise an experiment to finally detect this system. The autoionizing $1s2s2p\ ^4P^o$ state of lithium might be produced by electron impact excitation of ground state atoms [33]. It has a rather long lifetime, of about 5.8 μs, compared to the lifetime of ortho-Ps of 142 ns, while the doublet states in lithium have lifetimes of the order of 10^{-14} s. As shown in this work, this state could pick up a positron and form a stable system, before annihilation occurs when the different products could be analyzed and measured. An alternative experimental route could be to attach the positron to the lithium ground state and then excite the system to the desired state and measuring the energy difference, although the different spin multiplicity between states renders this route a more difficult one.

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