

# Positron and positronium chemistry by quantum Monte Carlo. IV. Can this method accurately compute observables beyond energy?

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Many different properties of the positron containing systems PsH, [Li,  $e^+$ ], LiPs, and [LiH,  $e^+$ ], were computed using both variational Monte Carlo and fixed node diffusion Monte Carlo methods, and explicitly correlated trial wave functions. Our results show that these techniques can accurately compute not only energy values, but also other observables. Our  $\langle \delta(r_{+-}) \rangle$  values for PsH, [Li,  $e^+$ ], and LiPs are in good agreement with the most recent *state of the art* correlated calculations, while for [LiH,  $e^+$ ] our calculations are the first to give reliable results. © 1999 American Institute of Physics. [S0021-9606(99)30725-X]

## I. INTRODUCTION

During the last few years, theoretical works on positron and positronium containing systems have paid particular attention to ground-state energies and properties.<sup>1</sup> So far, only two approaches have proved to be able to give results that are accurate enough to discuss relative stability, positron affinity, and positronium binding energy: the variational approach based on explicitly correlated Gaussians (ECG),<sup>2-4</sup> and quantum Monte Carlo (QMC) methods.<sup>5-14</sup> These two approaches explicitly introduce the instantaneous correlation among particles, but only QMC methods allow, in principle, to correctly describe the local behavior of the exact wave function of the system, i.e., the cusp due to the divergency of the potential energy when two particles collide. Unfortunately, both ECG and QMC methods have some drawbacks: By using ECG, one is limited when increasing the number of particles in the system, usually the number of electrons, by the exponential growth of the number of permutations that must be included to account for the antisymmetry. On the other hand, QMC, in the fixed node diffusion Monte Carlo (FN-DMC) approximation, suffers from the fact that it is not easy to reduce the nodal error.<sup>15</sup> For large electronic systems it is possible to use a trial wave function written as a product of a determinant of orbitals and a correlation factor, while for small and medium systems one can attempt to improve the nodal surfaces by adding a few more configurations.<sup>15</sup> For systems including positrons, the usual restricted open- and closed-shell determinants do not allow the electronic density to change in order to describe the actual distribution of the leptons after the positron has been added. Adding a positron to an atomic anion generates a spreading of the outer shell electronic density due to the probable formation of the Pos-

itronium Ps = ( $e^+$ ,  $e^-$ ), i.e., the system is more correctly described as a Ps polarized by the mean field of the neutral atom, rather than a positron bound to an anion by means of Coulomb interaction.<sup>11,13</sup>

In our previous work on atomic and molecular systems containing a positron,<sup>11-13</sup> we assumed a trial wave function of the form

$$\Psi_T = \text{Det}|\phi_\alpha| \text{Det}|\phi_\beta| e^{U(r_{\mu\nu})} \Omega(\mathbf{r}_p, r_{p\nu}), \quad (1)$$

$\phi_{\alpha,\beta}$  are orbitals and  $e^{U(r_{\mu\nu})}$  is the electronic correlation factor used by Schmidt and Moskowitz in their works on atoms and ions.<sup>16,17</sup> In Eq. (1) (see Refs. 18 and 19)

$$\Omega(\mathbf{r}_p, r_{p\nu}) = \sum_{i=1}^{N_{\text{terms}}} c_i \Phi_i(\mathbf{r}_p, r_{p\nu}), \quad (2)$$

where  $\mu, \nu$  are electrons,  $p$  is the positron and

$$\Phi_i(\mathbf{r}_p, r_{p\nu}) = f_i(\mathbf{r}_p) \exp \left[ k_{i,1} \sum_{\nu=1}^N r_{p\nu} - \sum_{n=1}^{N_{\text{nuc}}} k_{i,n+1} r_{pn} \right]. \quad (3)$$

The wave function was, therefore, the product of an electronic part, in a form that is almost standard in QMC calculations of electronic systems, and a function of the positron, written as a sum of exponentials of the positron–electron and positron–nucleus distances. The  $\phi_{\alpha,\beta}$  orbitals were obtained by means of a self-consistent field (SCF) calculation for the system without the inclusion of the positron, and they were not modified during the optimization procedure used to select the linear and nonlinear parameters of the  $\Omega(\mathbf{r}_p, r_{p\nu})$  function. As previously mentioned, this choice does not allow the electronic wave function to change and include the distortion introduced in the electronic density by the positron. Nevertheless, this approach was shown to be accurate enough to obtain reliable energetic quantities, especially positron affinity and positronium binding energy by means of diffusion Monte Carlo (DMC) simulations.<sup>5-14</sup>

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The constraints due to the “frozen” electronic part of the trial wave function and the use of only one parameter  $k_{i,1}$  to describe the positron–electron correlation in Eq. 3 have another important drawback: During the optimization of the parameters of the positronic part of the wave functions,  $k_{i,1}$  usually assumes quite small values, therefore, almost no correlation is introduced. This fact determines the small value of the electron–positron annihilation rate we found running variational Monte Carlo (VMC) simulations after the optimization of the trial wave function. Although DMC is able to correct the electron–positron distribution, it cannot accurately compute the annihilation rate due to the overall poor quality of the description given by the trial wave function. This fact can be easily understood if one considers that DMC samples the distribution  $f = \Psi_T \Psi_0$ , not the exact  $\Psi_0^2$  that is needed to compute average values of properties whose operators do not commute with the Hamiltonian.

To solve these difficulties, in this work we explore the possibility of extending the use of more flexible trial wave functions, similar to those used in our work on PsH ground and excited states,<sup>10</sup> to larger systems. These wave functions should allow us to compute more accurately energetic quantities and annihilation rates for systems containing positrons. Our goal is to show the ability of QMC to cope with this kind of systems. Moreover, we propose new areas of exploration to these problems that could allow the description of larger systems of experimental interest.

For all the systems we studied in this work except [LiH,  $e^+$ ], accurate results were published by Frolov and Smith,<sup>2</sup> and by Ryzhikh *et al.*<sup>3</sup> employing a linear expansion of ECG functions: We make direct reference to these papers to compare the quality of our mean values.

## II. TRIAL WAVE FUNCTION FORM AND MONTE CARLO SIMULATION

In the following the Latin  $n$  subscript denotes a nucleus, a Greek subscript denotes an electron, while the Latin  $p$  subscript denotes the positron.

In atomic units, the Hamiltonian operator (in the Born–Oppenheimer approximation) for any atomic and molecular system containing  $N$  electrons and a positron is

$$\mathcal{H} = -\frac{1}{2} \left( \sum_v^N \nabla_v^2 + \nabla_p^2 \right) + V(\mathbf{R}), \quad (4)$$

where  $V(\mathbf{R})$  is the Coulomb interaction potential

$$V(\mathbf{R}) = - \sum_{n=1}^{N_{\text{nuc}}} \sum_{v=1}^N \frac{Z_n}{r_{vn}} + \sum_{n=1}^{N_{\text{nuc}}} \frac{Z_n}{r_{pn}} + \sum_{v < \mu} \frac{1}{r_{v\mu}} - \sum_v \frac{1}{r_{pv}}, \quad (5)$$

between the particles (i.e., the  $N$  electrons, the positron and the  $N_{\text{nuc}}$  fixed nuclei of charge  $Z_n$ ), and  $\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{r}_p)$  is a point in configuration space.

We approximate the total trial wave function by the linear expansion<sup>18,19</sup>

$$\Psi_T = \sum_{i=1}^{N_{\text{terms}}} c_i \Phi_i(\mathbf{R}), \quad (6)$$

$$\Phi_i(\mathbf{R}) = \mathcal{A} \{ \mathcal{O}_{\text{symm}} [f_i(\mathbf{R}) \prod_{\mu=1}^{N_D} U(r_{\mu}, \mathbf{k}_{\mu})] \Theta_e \Theta_p \}, \quad (7)$$

where  $\mathcal{A}$  is the antisymmetrization operator,  $\mathcal{O}_{\text{symm}}$  is an operator used to fix the spatial symmetry of the state,  $\Theta_e$  and  $\Theta_p$  are the spin eigenfunctions for electrons and positron. In Eq. (7) the index  $\mu$  runs over the  $N_D$  interparticle distances  $r_{\mu}$ , and the term  $U(r_{\mu}, \mathbf{k}_{\mu})$  is a Pade’ factor whose analytical form is

$$U(r_{\mu}, \mathbf{k}_{\mu}) = \exp \left[ \frac{k_{\mu,1} r_{\mu} + k_{\mu,2} r_{\mu}^2}{1 + k_{\mu,3} r_{\mu}} \right], \quad (8)$$

$\mathbf{k}_{\mu}$  is a vector of three nonlinear parameters for the  $\mu$ th distance of the exponential term. In all cases we used a Pade’ factor with  $k_{\mu,2} = 0$  for electron–electron and electron–positron distances (Jastrow factor). The terms  $f_i(\mathbf{R})$  are monomials in the interparticle distances, and they are used to generalize the analytical form of the trial wave function to an Hylleraas-type *ansatz*: This means that only one exponential term is present in our wave function for all the systems we studied.

The chosen form for the trial wave function makes impossible to compute analytically the matrix elements of the Hamiltonian operator, and numerical methods must be used to obtain the energy and other mean values for a given trial wave function. The variational Monte Carlo method is well suited for this goal since it requires only the evaluation of the trial wave function, its gradient and Laplacian. Since this and other Monte Carlo methods are well described in the literature,<sup>15</sup> we refer the reader to it and to our previous work in this field for the details. However, it is relevant to point out that all the mean values were computed by means of the general integral

$$\langle \mathcal{O} \rangle = \frac{\int f(\mathbf{R}) \mathcal{O}_{\text{loc}}(\mathbf{R}) d\mathbf{R}}{\int f(\mathbf{R}) d\mathbf{R}}, \quad (9)$$

where

$$\mathcal{O}_{\text{loc}}(\mathbf{R}) = \frac{\mathcal{O} \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}, \quad (10)$$

and  $f(\mathbf{R}) = \Psi_T^2(\mathbf{R})$  for VMC, while  $f(\mathbf{R}) = \Psi_T(\mathbf{R}) \Psi_0(\mathbf{R})$  for DMC. In VMC calculations, Eq. (9) gives exactly the expectation values of the  $\mathcal{O}$  operator over the trial wave function  $\Psi_T$ , while in DMC simulations Eq. (9) gives only an improved estimate of the value, but not the exact one. This is true for all the  $\mathcal{O}$  operators that do not commute with the Hamiltonian. Jiang and Schrader<sup>14</sup> showed that one can give a second-order estimate (SOE) of  $\langle \mathcal{O} \rangle$  by means of the general equation

$$\langle \mathcal{O} \rangle_{\text{SOE}} = 2 \langle \mathcal{O} \rangle_{\text{DMC}} - \frac{\langle \mathcal{B} \rangle_{\text{DMC}}}{\langle \mathcal{B} \rangle_{\text{VMC}}} \langle \mathcal{O} \rangle_{\text{VMC}}, \quad (11)$$

where  $\mathcal{B}$  is a generic operator for the system. They proposed this equation as an improvement over the standard one, where  $\mathcal{B} = \mathcal{T}$ , we used in our previous work.<sup>10</sup> Unfortunately, it is difficult to assess the accuracy of the SOE results obtained by means of Eq. (11) if one starts from a trial wave function whose mean properties are quite different from the correct ones, both for the  $\mathcal{B} = \mathcal{T}$  and  $\mathcal{B} \neq \mathcal{T}$  cases. Since in

TABLE I. VMC, DMC, and ECG mean values for observables of the ground-state  $2^1S$  of the Positronium Hydride.

	VMC <sup>a</sup>	DMC <sup>a</sup>	VMC <sup>b</sup>	DMC <sup>b</sup>	ECG <sup>c</sup>
$\langle E \rangle$	-0.786 20(1)	-0.789 16(3)	-0.788 23(1)	-0.789 15(4)	-0.789 19
$\langle V \rangle$	-1.5704(2)	-1.5758(4)	-1.5756(3)	-1.5779(9)	
$\langle \delta_{+-} \rangle$	0.024(1)	0.0236(2)	0.024(1)	0.023(2)	0.02437
$\langle r_{+-} \rangle$	3.4807(4)	3.473(1)	3.4842(7)	3.468(1)	3.480
$\langle r_- \rangle$	2.3287(4)	2.3164(7)	2.3124(4)	2.310(1)	2.311
$\langle r_+ \rangle$	3.6225(6)	3.635(1)	3.6589(9)	3.648(2)	3.661
$\langle r_{--} \rangle$	3.6155(7)	3.590(1)	3.5755(8)	3.570(2)	3.574

<sup>a</sup>One term wave function.<sup>b</sup>28 term wave function.<sup>c</sup>References 2 and 3.

our opinion neither the possibility to overshoot the correct value when Eq. (11) is used, nor the chance to underestimate the correction can be ruled out, we decided not to compute SOE mean values and to test the quality of the trial wave function by directly comparing the VMC and DMC results. When these two mean values differ for a given operator  $\mathcal{O}$ , the wave function can be considered as accurate as the difference  $\langle \mathcal{O} \rangle_{\text{DMC}} - \langle \mathcal{O} \rangle_{\text{VMC}}$  for that particular property.

As to our general strategy to optimize the trial wave functions for the systems studied, we usually begin selecting the parameters of the exponential part in Eq. (8) by minimizing an estimate of the variance of the local energy over a fixed sample of configurations. Our experience, developed employing these flexible functional forms to describe small atomic and molecular systems containing only electrons, shows that the Pade' factor usually guarantees an accurate approximation.<sup>20</sup> Therefore, we expect it to give a good description also in the case of systems containing positrons. To test if this is the case, we always run both VMC and DMC simulations using this simple form and compute all the relevant expectation values. This strategy is driven by the hope to find an easily optimizable general function even for larger systems. Successively, the linear coefficients,  $c_i$  in Eq. (6) are obtained by solving the standard eigenvalue problem, whose matrix elements are computed by means of a VMC simulation using the previously optimized term of the expansion as guide function. Since this work focuses primarily on the study of the ability of QMC methods to compute accurate mean values for positron containing systems, we plan to give more details about this procedure somewhere else.<sup>20</sup>

Here, we want to stress that VMC calculations, employing this form for the trial wave function, satisfy the constraint posed by Schrader<sup>1</sup> for the methods that can be used to deal with the positron, i.e., that these methods should be able to compute the electron affinity for the systems studied with good accuracy.

All the VMC optimizations, and the VMC and DMC simulations were carried out using at least 5000 walkers; all the DMC simulations were run employing a time step of  $0.001 \text{ hartree}^{-1}$  and the accuracy of the results was checked running few more simulations with smaller time steps to ensure that the time step bias was negligible for all the expectation values.

Summarizing the steps of our computational strategy, we optimize a trial wave function for a system, and then com-

pute all the mean values using Eq. (9) by means of VMC and DMC simulations. All the wave functions are available from the authors upon request.

As a last issue related to the Monte Carlo simulations, we mention the problem of computing the mean value over the Dirac's delta function to obtain the annihilation rate in these compounds: As pointed out by Jiang and Schrader,<sup>14</sup> Eq. (14) of Ref. 10 is correct only if used in VMC simulations, while it gives only an approximate, even if quite accurate, value when used in conjunction with DMC simulations. In their work on the PsH system,<sup>14</sup> they preferred to employ a simple spherical well to approximate the Dirac's delta distribution during the DMC simulations.

Following their suggestion, to avoid possible pitfalls in our calculations, we chose to compute this quantity using a set of narrow Gaussians as a way to approximate a delta series, and extrapolating to zero width. As we show in the Appendix, this choice gives more accurate results than the use of a simple box to approximate the delta functions.

### III. VARIATIONAL AND DIFFUSION MONTE CARLO RESULTS

#### A. The $2^1S$ ground state of PsH

The  $2^1S$  ground state of PsH is usually selected as test problem to check if a method or a model wave function is able to accurately describe the physics related to positron containing systems.

As a starting point for the optimization of the wave function we chose the parameters of the one term wave function optimized in our previous work on PsH:<sup>10</sup> After few optimization steps the trial wave function converged to the final parameters. The results are shown in Table I. Our exponential part of the trial wave function is similar to the one proposed by Jiang and Schrader,<sup>14</sup> but we allowed complete flexibility to our parameters avoiding to exactly fix the cusp conditions by hand. Although we optimized the parameters minimizing the variance of the local energy instead of the energy itself as done by Jiang and Schrader, our energy is 9 mhartree lower. We do not know whether this difference is due to a better optimization procedure (in Ref. 14 this was carried out by hand) or to the improved flexibility due to the released constraints, or a combination of both effects.

When compared with our previous results,<sup>10</sup> it clearly appears that this analytical form for the trial wave function is

TABLE II. VMC, DMC, and ECG mean values for observables of the ground-state  $2^2S$  of the  $[\text{Li}, e^+]$  complex.

	VMC <sup>a</sup>	DMC <sup>a</sup>	VMC <sup>b</sup>	DMC <sup>b</sup>	ECG <sup>c</sup>
$\langle E \rangle$	-7.5251(1)	-7.531 65(8)	-7.530 18(9)	-7.532 29(2)	-7.532 323
$\langle V \rangle$	-15.049(6)	-15.054(4)	-15.047(5)	-15.057(2)	
$\langle \delta_{+-} \rangle$	0.0112(6)	0.0111(2)	0.0119(8)	0.0113(2)	0.01141
$\langle r_{+-} \rangle$	6.131(3)	6.462(5)	7.05(5)	7.63(1)	7.829
$\langle r_- \rangle$	2.660(1)	2.781(2)	3.06(3)	3.366(7)	3.443
$\langle r_+ \rangle$	7.490(4)	7.981(7)	8.85(9)	9.74(2)	10.030
$\langle r_{--} \rangle$	4.862(3)	5.105(5)	5.66(6)	6.27(1)	4.675

<sup>a</sup>One term wave function.<sup>b</sup>111 term wave function.<sup>c</sup>Reference 3.

much superior to the one we employed earlier: Our previous seven term function in Ref. 10 was only 0.5 mhartree lower in energy than the single term function optimized in this work.

We added to this optimized term a set of 27 functions having as pre-exponential part  $r_a$ ,  $r_a^2$ ,  $r_{ab}$ ,  $r_{ab}^2$ ,  $r_a r_b$ ,  $r_a r_{ab}$ ,  $r_{ab} r_{cd}$ , where the indices indicate both the positron and the electrons. We chose to restrict our calculation to these simple terms to reduce the computational effort to obtain the relevant integrals as well as to test if this simple form of three- and four-body correlation can be flexible enough to improve the description of these systems. We ran a VMC simulation to compute the matrix elements between these 28 basis functions, and optimized a new function of the form Eq. (6). The mean values obtained by means of this larger trial wave function are shown in Table I for VMC and DMC simulations.

## B. The $2^2S$ ground state of $[\text{Li}, e^+]$

The  $[\text{Li}, e^+]$  system owes its importance to the fact that it is the first neutral atom-positron complex that was proved to be bound by means of *ab initio* quantum-chemical methods using ECG.<sup>3</sup>

Previously, Yoshida and Miyako<sup>9</sup> had computed the value of  $-7.5203(48)$  hartree by means of a FN-DMC simulation. Unfortunately, the standard deviation of this result was too large to allow any definitive conclusion about the stability of  $[\text{Li}, e^+]$ , since the dissociation threshold is  $-7.529913$  hartree.

To optimize the one term trial wave function we started from a previously optimized function for the ground state of the Li atom and added the positron in the outer shell using a rough choice of parameters.

To carry out the optimization procedure, we employed DMC to select the new set of configurations instead of using distributions of walkers updated by means of VMC. This alternative way, although seldom used, has the advantage to push the distribution towards the correct one, biasing the selection of the parameters of the trial wave function toward better ones with respect to VMC. Our choice was dictated by the fact that we were not able to obtain any physically reasonable trial function using only VMC simulations. We do not know if this behavior is due to the lack of flexibility of the wave function, or to the optimization method, i.e., to the

minimization of the variance of the local energy instead of the energy itself. The VMC and DMC results for this wave function are shown in Table II. Comparing the VMC result with the threshold energy of  $-7.529913$  hartree for  $\text{Li}^+$  and Ps, it appears that our one term wave function is not able to correctly describe the binding of this system; however, the energy obtained by means of the DMC simulation with this function is  $0.00174(8)$  hartree below the threshold, that is, the binding energy is positive. This is another proof that our trial wave function can have good nodal surfaces.<sup>18</sup>

To correct for the deficiencies of this wave function, we added a set of 110 basis functions built using  $r_a$ ,  $r_a^2$ ,  $r_{ab}$ ,  $r_{ab}^2$ ,  $r_a r_b$ ,  $r_a r_{bc}$ ,  $r_{ab} r_{cd}$ ,  $(r_a r_b)^2$ ,  $(r_a r_{ab})^2$ , and  $(r_{ab} r_{cd})^2$  as pre-exponentials.

The solution of the standard secular equations, whose matrix elements were computed by a VMC simulation, gives a trial wave function whose mean values are shown in Table II together with the results obtained running a DMC simulation. The VMC energy predicts a binding energy for the system of  $0.00027(9)$  hartree, i.e., it is only slightly bound with respect to the dissociation in  $\text{Li}^+$  and Ps, while the DMC simulation predicts a binding energy of  $0.00238(2)$  hartree.

## C. The $2^1S$ ground state of LiPs

The ground state of the LiPs systems has been already investigated by means of DMC and VMC simulations, but no definitive results have been published so far for these methods. Specifically, the DMC calculation by Harju *et al.*<sup>6</sup> [ $-7.709(4)$  hartree] showed LiPs to be unstable with respect to the dissociation to Li and Ps, while it is predicted to be bound by both the Yoshida and Miyako result [ $-7.7562(5)$  hartree]<sup>9</sup> and our previous value [ $-7.7376(8)$  hartree].<sup>11</sup> However, the binding energies are quite different and, since this discrepancy could not be explained using simple arguments, we decided to resolve the issue running FN-DMC simulations employing a more accurate trial wave function. Using the same procedure followed for  $[\text{Li}, e^+]$ , we optimized a one term trial wave function. The results of the VMC and DMC calculations are shown in Table III, together with analytical ECG results.

Like in the  $[\text{Li}, e^+]$  case, we attempted to build a better wave function using a linear expansion of terms variously chosen, but all our efforts failed to obtain any significant

TABLE III. VMC, DMC, and ECG mean values for observables of the ground-state  $^2,1S$  of the LiPs complex.

	VMC	DMC	ECG <sup>a</sup>
$\langle E \rangle$	-7.726 16(8)	-7.739 59(6)	-7.739 682
$\langle V \rangle$	-15.434(5)	-15.458(9)	
$\langle \delta_{+-} \rangle$	0.0101(6)	0.0100(5)	0.0105
$\langle r_{+-} \rangle$	22.8(2)	10.38(5)	5.564
$\langle r_{-} \rangle$	8.55(5)	4.43(2)	2.824
$\langle r_{+} \rangle$	29.4(2)	12.73(7)	6.319
$\langle r_{--} \rangle$	16.1(1)	7.87(4)	4.675

<sup>a</sup>Reference 3.

improvement over the starting one term function. We believe this result is due to the joined effect of the higher dimensionality of the configuration space and of the diffuse nature of the electronic and positronic distributions in this system: These make the calculations of the matrix elements less accurate and computationally more expensive.

#### D. The $^2,1\Sigma$ ground state of $[\text{LiH}, e^+]$

As far as  $[\text{LiH}, e^+]$  is concerned, only few calculations<sup>12,21,22</sup> have been published on this interesting system that can be thought as a model for the annihilation in alkali hydride crystals. Only two papers<sup>12,22</sup> dealt with the problem of giving a correlated description of the molecule and no attempts were carried out to compute the annihilation rate.

In our previous work,<sup>12</sup> no change of the electronic distribution was allowed to take place, i.e., we kept frozen the electronic part of the wave function as obtained by an SCF calculation. The bond distance was taken to be the equilibrium distance of the LiH systems, 3.015 bohr.

As previously described for the LiPs and  $[\text{Li}, e^+]$  systems, we optimized a one term wave function starting from the parameters for the LiH system and adding an approximate description of the positron behavior. Since our previous experience on the LiH system<sup>20</sup> had shown that without the inclusion of the pre-exponential part of the expansion the description of the nodal surface was inaccurate, we did not perform a DMC simulation with this simple trial wave function. Instead we optimized a better wave function carrying out the standard VMC simulation to obtain the matrix elements needed to compute the coefficients of the linear combination. The basis set included 41 pre-exponential terms of the form  $r_{an}$ ,  $r_{an}^2$ ,  $r_{ab}$ ,  $r_{ab}^2$ , where the index  $n$  indicates a nucleus.

Due to the really fast increase of the number of term in the expansion, we were not able to include in the basis set the terms containing the product between particle distances. Moreover, the increased number of nuclei makes the simulations and optimization more time consuming.

The VMC and DMC energy, and some other expectation values for the 41 term wave function are shown in Table IV. Comparing the accurate energy of  $-8.0702(2)$  hartree for  $\text{LiH}^{20}$  at the same geometry with the VMC result in Table IV of  $-8.0913(2)$  hartree, it appears clearly that the 41 term function gives a correct qualitative description of the  $[\text{LiH}, e^+]$  system.

TABLE IV. VMC and DMC mean values for observables of the ground-state  $^2,1\Sigma$  of the  $[\text{LiH}, e^+]$  complex.

	VMC	DMC
$\langle E \rangle$	-8.0913(2)	-8.1023(1)
$\langle V \rangle$	-16.265(7)	-16.260(6)
$\langle \delta_{+-} \rangle$	0.0057(4)	0.0060(2)
$\langle r_{+-} \rangle$	6.055(6)	5.835(7)
$\langle r_{--} \rangle$	3.090(2)	3.081(2)

## IV. DISCUSSION

In this section we compare our VMC and DMC results, both energies and other expectation values, with the results published in other papers.

### A. Energies

As far as the PsH system is concerned, many calculations have been published so far having quite different accuracies both for the total energy and the mean values of other observables. As a general outcome, DMC<sup>6,9,10</sup> and ECG results<sup>2-4</sup> for the energy compare favorably: The most accurate DMC result published so far  $-0.789 18(1)$  hartree,<sup>10</sup> is in complete agreement with those obtained in this work for both the one term and 28 term wave functions, respectively,  $-0.789 16(3)$  and  $-0.789 15(4)$  hartree, and with the results by Jiang and Schrader<sup>14</sup> [ $-0.78918(5)$  hartree]. Moreover, these three values are statistically indistinguishable from the ECG results of  $-0.789 179 4$ ,  $-0.789 194 4$ , and  $-0.789 185$  hartree, obtained, respectively, by Frolov and Smith,<sup>2</sup> Ryzhikh *et al.*,<sup>3</sup> and Strasburger and Chojnacki.<sup>4</sup>

As to the  $[\text{Li}, e^+]$  system, less calculations have been published so far, the most accurate being the ones by Ryzhikh *et al.*,<sup>3</sup> and by Strasburger and Chojnacki.<sup>4</sup> They predicted for this system a total energy of  $-7.532 323$  and  $-7.531 137$  hartree, respectively, i.e., a positronium binding energy respect to  $\text{Li}^+$  of 0.002 410 and 0.001 224 hartree. Our energies of  $-7.531 65(8)$  and  $-7.532 29(2)$  hartree, respectively, from the one and 111 term wave functions, are in good agreement with those values, giving a binding energy of 0.001 74(8) and 0.002 38(2) hartree. Our results show that even the one term function, when used in DMC simulations, compares favorably for the energy with the 480 term ECG function of Strasburger and Chojnacki,<sup>4</sup> while our 111 term function generates a result statistically indistinguishable from that of the 860 term function of Ryzhikh *et al.*<sup>3</sup>

For LiPs, our DMC result of  $-7.739 59(6)$  hartree, together with the result of  $-7.739 682$  hartree by Ryzhikh *et al.*,<sup>3</sup> settles the questions on the total energy and positronium binding energy we raised in our previous work. The good agreement between our energy and the one computed analytically rules out the possibility of an error in our code and definitely marks the value of  $-7.7562(50)$  hartree by Yoshida and Miyako<sup>9</sup> to be too low, and the value of  $-7.709(4)$  hartree of Harju *et al.*<sup>6</sup> to be too high. Although we are not able to say what went wrong in the DMC simulations of Yoshida and Miyako<sup>9</sup> and Harju *et al.*,<sup>6</sup> we wish to remind the Monte Carlo practitioner that the most common error in Monte Carlo simulations is to stop them too early,

being fooled by a false convergence. Moreover, these accurate results seem to show that the hypothesis we proposed about the accuracy of our previous calculations on positronium–atom complexes, i.e., that positron affinity and positronium binding energy had the same accuracy of the electron affinity, was correct.

As to  $[\text{LiH}, e^+]$ , we were not able to find in the literature any accurate calculation for the properties of this systems. In our previous work<sup>12</sup> we focused only on the energy as a test for the ability of DMC to compute an accurate positron affinity, and to understand how much of the energy is due to correlation between positron and electrons. The new result obtained in this work appears to be in fair agreement with the previous one  $-8.1037(4)$  hartree, the difference being due primarily to the different nodal location in the two trial functions. Since FN-DMC results are variational with respect to the nodal placement, we can conclude that, at least for  $[\text{LiH}, e^+]$ , the determinant for the electronic part gives better nodal surfaces than our 41 term correlated function. This result was already found for  $\text{LiH}^{20}$  and corrected using a larger expansion than the one employed in this work.

## B. Properties

As far as PsH is concerned, the mean values in Table I show that both the one term and the 28 term wave functions give values that are in good agreement with the ECG calculations. Moreover, the small differences between the VMC and DMC results indicates the overall good performance of these model functions for this small system. While the one term function values differs at most a few part over a thousand from the accurate results of Frolov and Smith<sup>2</sup> and those of Ryzhikh *et al.*,<sup>3</sup> the 28 term function VMC expectation values are in optimal agreement with those results, and the DMC calculation corrects them by really small amounts. It is interesting to note that for the 28 term function, these corrections reduce  $\langle r_{+-} \rangle$  and  $\langle r_+ \rangle$  respect to the ECG results: We are unable to explain the reason for this behavior, since we can not check the convergency of the mean values computed by means of the ECG method. Nevertheless, we believe these small corrections to be the most stringent test for the accuracy of a model wave function, to be sure that the expectation values computed by means of the simulations are, indeed, representative of the relevant physics beneath this system.

Moreover, our VMC and DMC results for the Dirac's delta operator are now in agreement with those published so far and obtained by means of ECG and DMC calculations.<sup>14</sup> Nevertheless, we want to clarify an issue raised by Jiang and Schrader<sup>14</sup> about the second-order estimate published in our previous work:<sup>10</sup> Those results were obtained using  $\mathcal{B}=\mathcal{I}$  in Eq. (11). We recomputed this value for our previous seven term function using  $\mathcal{B}=\mathcal{H}$  as they suggest, obtaining a value that is statistically equal to our previous result, since the ratio  $\langle \mathcal{B} \rangle_{\text{DMC}} / \langle \mathcal{B} \rangle_{\text{VMC}}$  for the seven term function is 1.0038. We believe that the discrepancy between our previous value and the most accurate ones published so far is due only to some inaccuracy in the positron–electron distribution description as given by our trial function. What seems surprising to us is the good agreement between the Jiang and

Schrader result and the ECG one: Their trial wave function appears to be less accurate than our previous seven term function when the VMC results are compared. Since the correction due to the general Eq. (11) does not explain this outcome, there is the possibility that this is simply due to a fortuitous cancellation of error.

As to  $[\text{Li}, e^+]$ , comparing both VMC and DMC results in Table II for the one and 111 term functions, one is led to conclude that convergence has not been achieved for the different properties. The only exception appears to be the value of  $\langle \delta_{+-} \rangle$  that is statistically equal in all the four calculations we carried out. Our results are in optimal agreement with the value 0.001 141 computed by Ryzhikh *et al.*<sup>3</sup> using a 860 term function. This is an important point to keep in mind when one is facing the problem of computing the annihilation rate. It suggests that our trial function, although not accurate enough to describe all the particular features of these systems, can easily give good results for the  $\langle \delta_{+-} \rangle$ , especially when used in conjunction with DMC simulations.

Similarly to the  $[\text{Li}, e^+]$  case, the one term wave function for LiPs gives VMC expectation values different from the results of the DMC simulation, showing that this model function must be improved before being able to predict accurate geometric quantities. Nevertheless, the mean Dirac's delta function values for the VMC, DMC, and ECG calculations are in good agreement, showing again the ability to correctly describe the local relative distribution between the positron and the electrons, and the pile-up effect generated in the electronic density by the positron itself.

As far as  $[\text{LiH}, e^+]$  is concerned, the Dirac's delta mean value is similar for both the VMC and DMC calculations showing good accuracy for this expectation value. When compared with the results for the other systems studied in this work,  $\langle \delta_{+-} \rangle$  for  $[\text{LiH}, e^+]$  appears smaller than the other values, in particular smaller than the one for PsH to which it resembles most. This large difference can be understood by noticing that, differently to what happens in the other systems, the positron distribution is no longer isotropic around the H nucleus, but strongly polarized outward the bond region due to the repulsive interaction with the Li nucleus. This repulsion decreases the overlap between the electronic and positronic distributions, reducing in this way the probability of an annihilative collision between the two different leptons. Moreover, the two mean values for the  $r_{--}$  operator are in fair agreement, showing that our trial wave function correctly describes the interelectronic distribution for this system.

## V. CONCLUSION

In this paper we tried to answer the question: “Can quantum Monte Carlo accurately compute observables beyond energy?” exploiting the flexibility of QMC to obtain useful information for systems containing positron. On the basis of the present results and the strategy we applied in this work, we feel the answer should be positive, at least for the average  $\langle \delta_{+-} \rangle$  values of the systems we studied. Unfortunately, our model wave function seems to have problems to describe atomic and molecular systems containing five particles: One of the causes seems to be the lack of description

of the three body ( $e^+, e^-, e^-$ ) correlation in the exponential part. Neutral systems like LiPs appear to be bound by means of the polarization of Ps in the field of the Li atom: This polarization should be accurately described to obtain positive binding energy between Li and Ps fragments. Moreover, the complete freedom we give to the parameters makes their number increasing quadratically with the number of particles, therefore, rapidly increasing the computational cost. This problem might be avoided using less flexible functions, or reducing the number of permutation in Eq. (8). This can be done correctly, forcing the analytical form of the model wave function to be symmetric under some particle exchange, e.g., the exchange of core electrons, without including explicitly the exchange operator. Nevertheless, if one accepts to work with frozen core potentials for larger systems, these trial wave functions can be used to describe the valence region and to obtain accurate results up to four valence electron. At present, we are pursuing this approach for atoms and molecules larger than those we considered in this work.

Another possible avenue of exploration could be the possibility of computing directly the mean values during a DMC simulation by means of the descendant weighting procedure<sup>15</sup> or by means of the perturbation theory approach developed by Sandler *et al.*:<sup>23</sup> Even in the presence of nodal surfaces partitioning the configuration space, these methods allow to get “exact” result for the nodal region where the simulation is carried out. This might not be as efficient as the standard FN-DMC for the energy, but nevertheless could give interesting results for systems as large as PsF.

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## APPENDIX: GAUSSIANS VERSUS SPHERICAL WELL TO COMPUTE DIRAC'S DELTA MEAN VALUES

In this Appendix we discuss the difference between computing delta mean values using Gaussians and spherical wells. Let us start defining the two normalized delta sequences

$$\delta_{\alpha}^g(r_{+-}) = \left[ \frac{1}{\pi\alpha} \right]^{3/2} e^{-(r_{+-}^2/\alpha)} \quad (\text{A1})$$

and

$$\delta_{\alpha}^w(r_{+-}) = \frac{3}{4\pi\alpha^3} \quad \text{for } r_{+-} \leq \alpha, \quad (\text{A2})$$

$$\delta_{\alpha}^w(r_{+-}) = 0 \quad \text{otherways.}$$

Using different  $f(r_{+-})$  to compute the integral

$$f(0)_{\alpha} = \int f(r_{+-}) \delta_{\alpha}(r_{+-}) r_{+-}^2 dr_{+-}, \quad (\text{A3})$$

one can show that both the delta series converge to the correct result in the limit  $\alpha \rightarrow 0$ . For  $f(r_{+-})$  having cusplike behavior near  $r_{+-} = 0$ , it is possible to show that  $f(0)_{\alpha}$  converges linearly with  $\alpha$  for  $\delta^w$ , while it follows the asymptotic behavior  $\alpha^{(1/2)}$  for  $\delta^g$ . This result could lead to the erroneous conclusion that the well should be preferred to the Gaussian due to the more favorable law of convergency. However, in the Monte Carlo methods it is important to be able to estimate a mean value with the smallest possible standard deviation. If one computes the mean-square value of the  $\delta_{\alpha}$  over the distribution  $f(r_{+-})$ , it is not surprising that this value diverges for both series when the width parameter shrinks the two distributions (to our knowledge, this is an expected result), but surely it is not expected that the divergency goes like  $1/\alpha^3$  for the well, while it follows  $[1/\alpha]^{(3/2)}$  for the Gaussian. For this reason we prefer to use a Gaussian series like Eq. (A1) even if we are forced to extrapolate against  $1/\alpha^{(1/2)}$ .

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