Stability and positron annihilation of positronium hydride $L=0,1,2$ states: A quantum Monte Carlo study

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States of positronium hydride having different angular momenta have been studied by means of quantum Monte Carlo techniques. Explicitly correlated wave functions for different states have been obtained using the variational Monte Carlo optimization method. These wave functions have been used in variational Monte Carlo and diffusion Monte Carlo (DMC) simulations to compute energies, annihilation rates, and other observables. Our DMC results compare well with the best published variational ground-state binding energy, and show that positronium hydride has metastable states with angular momentum $L=1$ and 2 above the ground-state dissociation threshold. The values of the other observables for the ground state are comparable with the best variational calculations. The results for the $L=1$ and 2 states are used to discuss a proposed model for the annihilation of positrons in alkali hydrides crystals. [S1050-2947(98)09502-X]

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I. INTRODUCTION

During the last few years, attention has been paid to the properties of systems containing one or more positrons with the aim to elucidate the problem of their stability and the annihilation behavior of positrons in ordinary matter. Among the systems studied, there are the positronium anion Ps^- [1,2], the dipositronium molecule Ps_2 [3–5], the positronium hydride PsH [6–18] and other small atomic and model systems [19]. These issues are still wide open, and there is a growing mass of experiments and experimental techniques that can accurately probe the interaction between matter and antimatter, and which need theoretical support to be interpreted. So far, few attempts have been devoted to solving the problems of stability and annihilation in a systematic way: Cade and Farazdel [20], Patrick and Cade [21], Kurtz and Jordan [22], and Gol'danskii, Ivanova, and Prokop'ev [8] proposed applying the Hartree-Fock method to compute the positron affinity and positronium (e^+,e^-) binding energy of atoms, ions, and molecules; the authors of Refs. [10,12], [14,15], and [13] used explicitly correlated trial wave functions to compute energies for small atomic systems containing positrons; attempts have been made to apply density-functional theory (DFT) to the calculation of average values for first-row atoms, ions, and solids [17,23–25]. Although the cited methods can help to rationalize the increasing amount of experimental data, each one has his own drawbacks: DFT theory lacks knowledge of the exact energy functional, and its results are dependent on the particular choice of the exchange and correlation potential used in the computation, while self-consistent-field (SCF) theory does not include electron-electron and electron-positron correlation. It relies on a ''mean-field'' description, missing the local behavior of the exact wave function near particle coalescence points; as a consequence it underestimates both positron affinity and positronium binding energy. To correct the SCF deficiencies, correlation has been introduced by means of standard molecular-orbital methods, like the Moller-Plesset perturbation theory [26] and the many-body-perturbation theory [16,27]. Recently, some attempts have been made to explore the possibility of using configuration-interaction techniques [28,29], but convergence of energy and other mean values has proved to be painfully slow. On the other hand, to correct for the lack of a description of the positron-electron cusp in DFT, a pair correlation correction has been developed [24]: by means of an enhancement factor one is able to estimate the annihilation properties simply using the positron and electron densities, but this is rather a heuristic approach to the problem since it has been developed starting from model systems and extrapolating their behavior to larger ones.

The best theoretical approach used so far to describe this class of systems exploits explicitly correlated trial wave functions to compute accurate values of the observables. Matrix elements between explicitly correlated wave functions are not easy to compute for systems containing more than two particles, unless one uses correlated Gaussians [30,4]. Since these functions do not reproduce the cusp conditions, i.e., the behavior of the exact wave function at small interparticle distances, very large basis sets must be employed, and also a careful and computationally expensive optimization of the nonlinear parameters of the trial wave function is required in order to obtain an accurate description.

Monte Carlo techniques are flexible and powerful methods to solve the Schrödinger equation for small atoms and molecules, even if they contain exotic particles like positrons or muons [31–38], or if one is interested in observables different from the energy [39]. In this work we present a nu-

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merical study of various states of PsH having different total angular momentum by means of variational and diffusion Monte Carlo (VMC and DMC) methods. The ground state of this system has been studied in the past using various standard methods, namely, SCF and Hartree-Fock methods [8,20,22,23], DFT [17], and DMC [33,36]. Also, explicitly correlated trial functions have been used [6,7,10–15], the most recent and accurate calculation being the one performed by Frolov and Smith [18] using a linear combination of explicitly correlated Gaussians. A compilation of the main results on the PsH ground state was published by Yoshida and Miyado [36] in their paper on the stability of PsH and $[\mathrm{Li},e^+]$. Although a lot of computational effort has been spent on the ground state of this system, and accurate information is now available, the results obtained so far need to be checked by independent calculations exploiting different methods, especially regarding the annihilation behavior of PsH. This position can be justified noticing that even the 396 term wave function by Ho [15], a reference calculation in this field, does not seem to be well converged to definitive results, if compared with the other values of the shorter linear combinations published in the same paper and with the results published in Ref. [18]. The ground state of PsH is a good candidate for the application of our methods since it contains all the relevant physics of this class of systems: without a complete description of the correlation between the particles, no meaningful information could be obtained, especially for properties like the annihilation rates that are strongly dependent on the quality of the description of the correlated motion. Our work is therefore motivated by the need to compute accurate values for these observables. In addition, we applied Monte Carlo methods to higher angular momentum states of this system, since these have been much less studied than the ground state and could be of relevant interest in scattering experiments with positron beams [40]. Furthermore these results will allow to test the model proposed in Ref. [8] to explain the annihilation behavior of slow positrons in alkali hydrides. It is also worth noting that during the last few years, experiments [40] with positron beams opened the possibility to detect positron systems in the gas phase, giving rise to a new amount of experimental information needing theoretical counterparts to be interpreted meaningfully.

II. TRIAL WAVE-FUNCTION FORM AND MONTE CARLO SIMULATION

In the following an alphabetic subscript denotes a positron, while a numerical subscript denotes an electron. In atomic units, the Hamiltonian operator for PsH system in the Born-Oppenheimer approximation has the form

$$\mathcal{H}=-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2+\nabla_a^2)+V(\mathbf{R}), \tag{1}$$

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

$$V(\mathbf{R})=-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{r_a}+\frac{1}{r_{12}}-\frac{1}{r_{1a}}-\frac{1}{r_{2a}}, \tag{2}$$

between the four-unit-charge particles (i.e., two electrons, the positron, and the nucleus), and $\mathbf{R}$ is a point in configuration space.

The breakup of this system in a three-particle cluster plus a free particle is not possible because the Coulomb attraction between the two fragments binds them together: so the lowest energy dissociation threshold for this system is given by [41]

$$E_{\mathrm{thr}}=E_{\mathrm{H_{gs}}}+E_{\mathrm{Ps_{gs}}}=-\tfrac{1}{2}-\tfrac{1}{4}=-\tfrac{3}{4}, \tag{3}$$

where PsH dissociates in two neutral fragments, both in their ground state. The stability of higher angular momentum states is relative to their own dissociation threshold, i.e., where the two fragments are resting at infinity and the positronium carries the total angular momentum L of the system:

$$E_{\mathrm{thr}}^{L}=E_{\mathrm{H_{gs}}}+E_{\mathrm{Ps}_{(L)}}=-\frac{1}{2}-\frac{1}{4(L+1)^2}. \tag{4}$$

The other possibilities, in which the hydrogen atom carries a nonzero angular momentum, or when for $L\geqslant 2$ the angular momentum is shared between the two fragments, always have a higher energy. To approximate the wave functions of states having different total angular momenta, we propose to use a linear combination of explicitly correlated functions [38,42,43]

$$\Psi_T=\sum_{i=1}^{N_{\mathrm{terms}}} c_i\Phi_i, \tag{5}$$

where

$$\begin{aligned}\Phi_i(\mathbf{R},\mathbf{k}_i)=\mathcal{A}\{&f_i(\mathbf{R})\\ &\times e^{-k_{i,1}r_1-k_{i,2}r_2-k_{i,3}r_a+k_{i,4}r_{12}+k_{i,5}r_{1a}+k_{i,6}r_{2a}}\\ &\times\Theta_{0,0}^{1,2}\Theta_{1/2,1/2}^{a}\}.\end{aligned} \tag{6}$$

In this equation $\mathcal{A}$ is the antisymmetrization operator; $f_i(\mathbf{R})$ is a function that explicitly contains the dependence on the spatial coordinates of the particles (we refer to this as the preexponential part of the trial wave function), but does not contain any variational parameter; $\Theta_{0,0}^{1,2}$ is the spin eigenfunction for the two electrons, while $\Theta_{1/2,1/2}^{a}$ is the spin function for the positron; and $\mathbf{k}_i$ is a vector of parameters for the ith term of the linear expansion. The first three components of this vector were forced to have only positive values for all the terms of the linear combination. As already stated in our previous work [43], it is possible to write this trial wave function in a spin-free formalism by means of a linear combination of spatial terms with exchanged particle indices, i.e.,

$$\begin{aligned}\Phi_i(\mathbf{R},\mathbf{k}_i)=\sum_{j=1}^{N_p}\mathcal{P}_j^{\mathrm{sym}}[&f_i(\mathbf{R})\\ &\times e^{-k_{i,1}r_1-k_{i,2}r_2-k_{i,3}r_a+k_{i,4}r_{1a}+k_{i,5}r_{2a}+k_{i,6}r_{12}}],\end{aligned} \tag{7}$$

where $\mathcal{P}_j^{\mathrm{sym}}$ are the exchange operators generated by acting with $\mathcal{A}$ on Eq. (6) and collecting all the terms with the same spin product [e.g., $\alpha(1)\beta(2)\alpha(a)$]. This trial wave function, which has the correct spin and space symmetry, describes the correlation between the electrons and the positron by means of the exponential part depending on the explicit electron-

positron and electron-electron distances. This analytical form allows an accurate description of the correct behavior of the exact wave function at the coalescence point for equal and opposite sign charges. Satisfying the cusp condition usually accelerates the convergence [44] of the linear expansion and reduces its length for a chosen accuracy. This is useful to reduce the computational cost of the optimization of the parameters in the trial wave function, usually a quite heavy task. Moreover, for the specific system we are dealing with, the trial wave function must explicitly contain the positron-electron distance, otherwise the annihilation behavior and the ''pile-up'' effect of the electron density due to the positron are not correctly described.

The chosen form for the trial wave function makes it very difficult, if not impossible, to compute analytically the matrix elements of the Hamiltonian operator of the system. A numerical method must be used to obtain the energy mean value and other observables for a given trial wave function. The variational Monte Carlo method [45] is well suited for this goal since it requires only the evaluation of the wave function, its gradient, and its Laplacian. Since the VMC and other Monte Carlo methods are well described in the literature [45], we only summarize the main points relevant to this work.

The mean value of a local operator over a given trial wave function is computed using

$$\langle \mathcal{O} \rangle_{\mathrm{VMC}} = \frac{\int \Psi_T^2(\mathbf{R}) \mathcal{O}_{\mathrm{loc}}(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^2(\mathbf{R}) d\mathbf{R}}, \tag{8}$$

where

$$\mathcal{O}_{\mathrm{loc}}(\mathbf{R}) = \frac{\mathcal{O}\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}. \tag{9}$$

Here $\Psi_T^2(\mathbf{R})$ is interpreted as a probability distribution and it is sampled using Metropolis or Langevin algorithms [45]. As an explicit example, the expectation value of the Hamiltonian is written as

$$\langle \mathcal{H} \rangle_{\mathrm{VMC}} = \frac{\int \Psi_T^2(\mathbf{R}) \mathcal{H}_{\mathrm{loc}}(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^2(\mathbf{R}) d\mathbf{R}},$$

$$\mathcal{H}_{\mathrm{loc}}(\mathbf{R}) = \frac{\mathcal{H}\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}. \tag{10}$$

Other operators can be converted to form (9); for example, the mean value for the Dirac's delta operator $\delta(r_{ij})$ can be computed using the identity

$$\delta(r_{ij}) = -\frac{1}{4\pi} \nabla_{\mathbf{r}_i}^2 \frac{1}{r_{ij}}. \tag{11}$$

Introducing Eq. (11) into Eq. (8), and integrating by parts one obtains

$$\langle \delta(r_{ij}) \rangle = -\frac{1}{2\pi} \int \Psi_T^2(\mathbf{R}) \{ \nabla_{\mathbf{r}_i}^2 [\ln \Psi_T(\mathbf{R})] + 2[\nabla_{\mathbf{r}_i} \ln \Psi_T(\mathbf{R})]^2 \} \frac{1}{r_{ij}} d\mathbf{R}, \tag{12}$$

where Ψ_T is assumed to be normalized. Using the differential identity

$$\frac{\nabla_{\mathbf{r}_i}^2 f(\mathbf{R})}{f(\mathbf{R})} = \nabla_{\mathbf{r}_i}^2 \ln f(\mathbf{R}) + [\nabla_{\mathbf{r}_i} ln f(\mathbf{R})]^2, \tag{13}$$

Eq. (12) can be written as

$$\langle \delta(r_{ij}) \rangle = -\frac{1}{2\pi} \int \Psi_T^2(\mathbf{R}) \left\{ \frac{\nabla_{\mathbf{r}_i}^2 \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} + [\nabla_{\mathbf{r}_i} ln \Psi_T(\mathbf{R})]^2 \right\} \frac{1}{r_{ij}} d\mathbf{R}, \tag{14}$$

which is easy to implement in a VMC and DMC code, and has been used in this work to estimate the collision probability and the annihilation time of the PsH system.

To optimize the linear and nonlinear parameters in the trial wave function, we minimized the function

$$\mu^2(E_r) = \sum_{j=1}^{N_{\mathrm{conf}}} [E_{\mathrm{loc}}(\mathbf{R}_j) - E_r]^2, \tag{15}$$

where $\{\mathbf{R}_j, j = 1, N_{\mathrm{conf}}\}$ is a set of N_{conf} fixed configurations sampled from Ψ_T^2, and E_r is an approximation to the true value of the energy for the system. This method, proposed by Frost [46] and Conroy [47], has been described in detail by Umrigar, Wilson, and Wilkins [48] and by Mushinski and Nightingale [49] and has been proved to be much more stable than the optimization of the energy itself.

The optimized trial wave functions can be used to compute approximated mean values of the observables of the studied systems and to give upper and lower bounds to their energy. Unfortunately, the mean values strongly depend not only on the analytical form of the function employed, but also on the optimization method used [50] to define the trial wave function. In order to obtain the exact ground-state energy and improve the accuracy of the other mean values, the DMC method [51,45] is employed to simulate the time-dependent Schrödinger equation in imaginary time as a diffusion equation having source and sink terms. This method samples the distribution $f(\mathbf{R}) = \Psi_T(\mathbf{R}) \Psi_0(\mathbf{R})$, where $\Psi_0(\mathbf{R})$ is the ground-state wave function of the system with the same nodal surface of the trial wave function if we use the fixed node approximation to sample an antisymmetrized wave function. The value of the energy can be computed using the ''mixed estimator''

$$\langle \mathcal{H} \rangle_{\mathrm{DMC}} = \frac{\int \Psi_T(\mathbf{R}) \Psi_0(\mathbf{R}) \mathcal{H}_{\mathrm{loc}}(\mathbf{R}) d\mathbf{R}}{\int \Psi_T(\mathbf{R}) \Psi_0(\mathbf{R}) d\mathbf{R}}. \tag{16}$$

If the ground state has no nodes, or $\Psi_T(\mathbf{R})$ has the correct nodal structure, this equation gives the correct ground-state energy; otherwise one obtains an upper bound to it. To com-

TABLE I. Mean energy and various values and observables for the ground state $^{2,1}S$ of the positronium hydride.

N	$\langle E\rangle$	$\langle V\rangle$	$\langle r_{+-}\rangle$	$\langle r_{--}\rangle$	$\langle r_{-}\rangle$	$\langle r_{+}\rangle$	$\langle \delta_{+-}\rangle$	χ
3	−0.778 001(26)	−1.5332(2)	3.708 64(61)	4.3337(11)	2.7497(12)	4.3209(11)	0.022 00(10)	0.0115(3)
4	−0.782 189(24)	−1.5466(3)	3.789 33(57)	4.2071(10)	2.6647(11)	4.2071(10)	0.021 64(21)	0.0117(3)
5	−0.784 848(11)	−1.5587(2)	3.586 62(34)	3.972 88(55)	2.545 40(65)	3.972 88(55)	0.024 70(9)	0.0071(3)
6	−0.786 310(11)	−1.5562(2)	3.554 87(30)	3.757 13(47)	2.427 20(50)	3.862 14(49)	0.023 74(17)	0.0107(2)
7	−0.786 788(12)	−1.5514(3)	3.576 36(45)	3.739 90(59)	2.412 73(66)	3.834 84(66)	0.023 19(23)	0.0145(3)
DMC	−0.789 175(10)	−1.5652(3)	3.5236(8)	3.6550(9)	2.361(10)	3.743(1)	0.02438(20)	
SOE		−1.5895(3)	3.4708(8)	3.5701(9)	2.308(1)	3.651(1)	0.02556(30)	
Ho [a]	−0.778 45						0.0243	
Ho [b]	−0.788 945		3.849	3.556		3.644	0.0244	
FS [c]	−0.789 1794	−1.578 38	3.479	3.573	2.311	3.661	0.024 134	0.000 0131

[a]Ho's 126-term wave function [15].
[b]Ho's 396-term wave function [15].
[c]Frolov and Smith's wave function [18].

pute the mean values of dynamical observables whose operators do not commute with the Hamiltonian, i.e., the general case, one can still exploit the ''mixed estimator'' substituting the new operator to the Hamiltonian, but the value so computed is biased by the errors of the trial wave function. A simple strategy to partially correct for this bias is to use the quantity [45]

$$\langle \mathcal{O}\rangle_{\mathrm{SOE}} = 2\langle \mathcal{O}\rangle_{\mathrm{DMC}} - \langle \mathcal{O}\rangle_{\mathrm{VMC}}, \tag{17}$$

where

$$\langle \mathcal{O}\rangle_{\mathrm{DMC}} = \frac{\int \Psi_T(\mathbf{R})\Psi_0(\mathbf{R})\mathcal{O}_{\mathrm{loc}}(\mathbf{R})d\mathbf{R}}{\int \Psi_T(\mathbf{R})\Psi_0(\mathbf{R})d\mathbf{R}}. \tag{18}$$

Equation (17) gives an estimate of $\langle \mathcal{O}\rangle$ that is second order (SOE) on the error of the trial wave function.

III. VARIATIONAL AND DIFFUSION MONTE CARLO RESULTS

A. $^{2,1}S$ ground state of PsH

The $^{2,1}S$ ground state of PsH was chosen as starting point of our investigation on systems containing positron. For this state the trial wave function must be written using only preexponential terms having spherical symmetry or containing explicitly the interparticle distances. Since the exponential part of the trial wave function already possesses an analytical form that should be able to describe the interparticle correlation correctly, the preexponential part of the analytical ansatz has been used only to modify the shape of the positronic density, expressing it as function of the positron-nucleus distance only. This choice makes it possible for the trial wave function to describe the positron-nucleus cusp condition correctly, reducing the probability to find the positron in the nuclear region.

To optimize the wave function, the simple one-term function given in Ref. [7] was used as starting point: its parameters were fully optimized minimizing the quantity $\mu^2(E_r)$ given by Eq. (15). Starting from this new wave function, more terms were added to reduce the variance of the local energy and to lower the mean energy. These steps were carried out using a stochastic selection procedure [42,43,52,53] for the nonlinear parameters of the new term, and choosing the linear coefficient c_{new} that minimizes the value of $\mu^2(E_r)$. Usually one or two thousand nonlinear parameter sets were randomly chosen, and the one that gave the lowest $\mu^2(E_r)$, once the linear parameter had been optimized, was kept as the new trial term. Usually, this procedure gives a small reduction of the variance of the local energy and a fairly good starting point for the following optimization. During all the optimization procedures, a set of 8000 configurations in the nine-dimensional configuration space was used. This set was chosen after sampling the best wave function previously optimized (e.g., the one-term function given by Ref. [7] for the first step of the optimization). After three or four optimization steps this ensemble was updated by means of a VMC run, usually 5×10^4 steps long, sampling the square of the new wave function. These VMC simulations are long enough to give reliable average values for all the observables. The variational results of the optimized trial wave functions for the $^{2,1}S$ ground state of PsH are reported in Table I for a number of terms $N=3-7$, together with the results obtained by Ho [15] using Hylleraas-type wave functions, and the results by Frolov and Smith [18]. In this table, $\langle V\rangle$ is the expectation value for the potential energy, while $\chi=|1+(\langle V\rangle/2\langle E\rangle-2\langle V\rangle)|$ is the so-called virial parameter. This parameter, since we did not optimize the expectation value of the energy, does not have to be equal to zero for a full optimized wave function written as a linear combination of a small number of terms. These results show that our expansion is quickly convergent toward an accurate value of the total energy, the three-term wave function already recovering more than 70%, and the seven-term one more than 93% of the binding energy computed by Frolov and Smith. Comparing the other mean values for our seven term, and Ho's 396-term trial wave function, it is worth noting that the mean distance between an electron and a positron is shorter for our trial wave functions than for that of Ho, while the mean distance between the two electrons is larger. These differences might be due to incomplete convergence of the two wave functions of different analytical forms, or to the optimization method used. Our mean distance between an elec-

TABLE II. Parameters of the optimized seven-term trial wave function.

N	c_i	$k_{i,1}$	$k_{i,2}$	$k_{i,3}$	$k_{i,4}$	$k_{i,5}$	$k_{i,6}$	f_i
1	1.00000	−0.36659	−1.00580	−0.34328	−0.37344	−0.04846	0.03263	r_a
2	0.35442	−0.12301	−0.75828	−0.14497	−0.30421	−0.81432	−0.05546	1
3	0.45760	−1.58378	−0.95978	−0.39332	−0.18145	0.11324	0.18718	1
4	−0.65857	−0.77919	−0.46739	−0.32126	−0.03521	−0.45572	−0.39182	r_a
5	0.72787	−0.46927	−1.26244	−0.28601	−0.89774	−0.10067	0.15699	1
6	0.23700	−0.86864	−0.22488	−0.38221	−0.11085	−0.79638	0.03429	r_a
7	−0.12385	−0.53677	−0.73638	−0.60591	−0.10452	0.00031	−0.03292	1

tron and the positron is in better agreement with the one computed by Frolov and Smith [18], being slightly larger like our mean electron-nucleus and positron-nucleus distances; that is, our VMC wave function describes a system less compact than Frolov and Smith [18] do. On the whole, our seven-term expansion, whose optimized parameters are shown in Table II, is a very compact and good quality wave function, well suited as guide function in a DMC calculation.

DMC simulations were performed to project out the remaining components of the excited states of the same symmetry of the ground state. Five simulations using different time steps spanning the range 0.001–0.012 hartree^{-1} have been carried out to obtain extrapolated zero time step values for the energy and other observables. These results (DMC) and their second-order estimates are shown in Table I. It is worth noting that our value for the ground-state energy of PsH, −0.78917(1) hartree, is 0.23(1) m hartree lower than the value computed by Ho: this is not a surprising result since the mean energy values published by Ho did not appear as conclusive, due to their slow convergence. Our energy is in good agreement with the two recently published DMC calculations of −0.7885(5) [33] and −0.789(1) hartree [36], but it is more accurate, due to the smaller standard deviation obtained in our simulation. Finally, we found complete agreement with the latest result −0.789179 hartree by Frolov and Smith [18].

Both DMC and SOE values show a decrease of their absolute values when compared with the VMC results: this effect can be attributed to a better description of the correlation between the various particles in the system. The SOE correction improves the agreement with the results of Ref. [18], but it appears that higher-order corrections are needed to obtain accurate predictions of these observables.

B. Lower $^{2,1}P$ and $^{2,1}D$ states of PsH

As to the $^{2,1}P$ state, we adopted the preexponential term

$$f_i(\mathbf{R}) = z_1 - z_a, \tag{19}$$

to describe both the relevant dissociative channel, i.e., the one that leads to the fragmentation of PsH in $H_{(L=0)}$ and $Ps_{(L=1)}$ both at rest, and the nodal surfaces due to a total angular momentum equal to 1. Using this analytical form for $\Phi_i(\mathbf{R},\mathbf{k}_i)$ in the linear expansion, a two-term wave function was optimized, as already explained for the ground-state calculations. As an initial guess for the one-term wave function, we wrote the total wave function as the product between the exact functions of the two fragments, modified introducing some correlation between the particles belonging to the two different fragments, in a way to produce a trial wave function that is square integrable: its parameters quickly rearranged into a pair of optimization steps to give a much better trial wave function, whose energy was below the dissociation threshold for this state. The second term was added using the previously described stochastic selection procedure, followed by full reoptimization of the wave function.

The VMC, DMC, and SOE results for the $^{2,1}P$ state, obtained using this function, are shown in Table III. DMC simulations were carried out using three different time steps, spanning the range 0.005–0.015 hartree^{-1}, to check for the time step bias: this appears smaller than the statistical error of the $\langle E \rangle$ values, as shown in Fig. 1.

For the $^{2,1}D$ state the preexponential part has the form

$$f_i(\mathbf{R}) = (x_1 - x_a)(y_1 - y_a), \tag{20}$$

and a one-term trial wave function has been optimized using the same procedure as for $^{2,1}P$ state. The VMC, DMC, and SOE results for this state are shown in Table IV.

IV. DISCUSSION

In this work we studied the PsH system, computing the energy and some mean values for the states carrying a total angular momentum $L=0$, 1, and 2. This has been done by optimizing explicitly correlated trial wave functions, written as linear combinations of different numbers of correlated terms, by means of the variational Monte Carlo technique, followed by diffusion Monte Carlo simulations.

Since a trial wave function always contains some errors

TABLE III. Mean energy and other observables for the $^{2,1}P$ state of positronium hydride: two-term trial wave function.

	$\langle E \rangle$	$\langle r_{+-} \rangle$	$\langle r_{--} \rangle$	$\langle r_{-} \rangle$	$\langle r_{+} \rangle$	$\langle \delta_{+-} \rangle$
VMC	−0.592 11(5)	9.472(4)	4.202(1)	2.574(1)	9.212(3)	0.001 25(5)
DMC	−0.615 28(5)	8.377(3)	3.953(2)	2.448(2)	8.172(5)	0.000 90(3)
SOE		7.822(4)	3.704(2)	2.332(2)	7.132(5)	0.000 55(5)

TABLE IV. Mean energy and other observables for the $^{2,1}D$ state of positronium hydride: one-term trial wave function.

	$\langle E \rangle$	$\langle r_{+-} \rangle$	$\langle r_{--} \rangle$	$\langle r_{-} \rangle$	$\langle r_{+} \rangle$	$\langle \delta_{+-} \rangle$
VMC	−0.543 40(2)	12.937(2)	4.5517(9)	2.788(1)	12.380(3)	0.000 066(13)
DMC	−0.566 72(3)	14.615(5)	4.147(1)	2.569(1)	14.345(5)	0.000 017(2)
SOE		16.293(5)	3.742(1)	2.350(1)	16.310(5)	

due to the incompleteness of the basis set used, the results will be incorrect by some amount. The DMC technique appears as a very useful tool to correct partially for this bias, since it is able to sample the correct wave function if the state has no nodal surfaces or if the trial function used to guide the simulation has the correct nodal structure. For the $^{2,1}S$ state of PsH, our optimized seven term trial wave function allows one to compute accurate values for both the energy and the other observables shown in Table I: for this state the relative error $(\langle \mathcal{O}_{\mathrm{DMC}} \rangle - \langle \mathcal{O}_{VMC} \rangle)/\langle \mathcal{O}_{\mathrm{DMC}} \rangle$ is always less than 0.04. Although it is not generally possible to estimate the quality of the DMC and SOE corrections to the VMC mean values, some relevant hints could be obtained using some model systems as a benchmark. In this regard, for the two systems Ps and X^Z Ps [19,33], i.e., the system composed by a fixed fractional charge $0 \leqslant Z \leqslant 1$ and a Ps atom, we found that for an order of magnitude of the relative error similar to the one we obtain for PsH, SOE values give an accurate approximation to the correct mean values, being in error by less than 1%. Therefore we estimate the values reported in Table I to have a similar accuracy.

Using Eq. (3) of Ref. [15] and our mean values for the δ_{+-} operator, we obtain 2.341(17), 2.461(20), and 2.580(30) ns^{-1}, respectively, for the VMC, DMC, and SOE two-photon annihilation rate $\Gamma_{2\gamma}$. These results are in good agreement with the value of 2.463 ns^{-1} published by Ho [15], and with the one of 2.4361 ns^{-1} computed by Frolov and Smith, but the SOE value seems to suggest a faster annihilation in PsH than the previously published results.

Due to the shorter length of the linear combinations used to approximate the states having higher angular momentum, the VMC results for these states are less accurate than the ones for the ground state. This fact is stressed by the differences between VMC and DMC values, usually of the order of 10% of the DMC values. This means that the observables computed for these states can be used only as indicators of the order of magnitude of the exact ones.

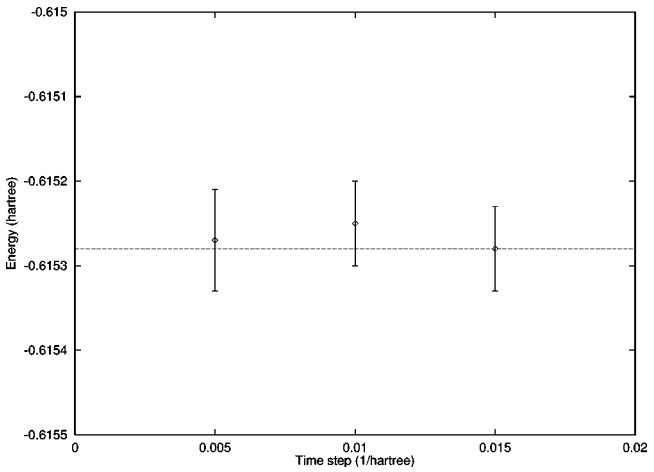

FIG. 1. DMC energy vs time step in the simulation of the $^{2,1}P$ state of PsH.

Although the mean values of the Dirac's delta operator δ_{+-} for the two excited states are not as accurate as for the ground state, they can be usefully employed to discuss annihilation of positrons in alkali hydrides [54]. To interpret the experimental results, Ref. [8] proposed a model where $^{2,1}S$ and $^{2,1}P$ states of PsH are assumed as responsible of the two different extrapolated annihilation rates $\Gamma_1 = 2.347(110)$ and $\Gamma_2 = 1.149(66)$ ns^{-1} that are seen experimentally. While their results based on Hartree-Fock calculations were not conclusive due to some computational error (see Ref. [10]), their model could not be definitely ruled out, and the problem is still waiting for a definitive answer. As already stated, accurate 2.463 and 2.4361-ns^{-1} values for the $\Gamma_{2\gamma}$ annihilation rate of the PsH ground state have been obtained respectively by Ho and Frolov and Smith, but for the $^{2,1}P$ state no explicitly correlated results are available to compare with. Our $\langle \delta_{+-} \rangle$ value for $^{2,1}P$ appears to be at least an order of magnitude less than the one for the ground state: assigning the Γ_1 annihilation rate to $^{2,1}S$, it appears obvious that the computed VMC $\Gamma_{2\gamma}$ rate for the $^{2,1}P$ state is too small by a factor of 10 at least. We strongly believe that this discrepancy cannot be resolved by means of a more accurate trial wave function: the DMC method is supposed to improve all the mean values computed, reducing the error in the sampled walker distribution, but it further decreases the $\langle \delta_{+-} \rangle$ value, indicating the need to further reduce the overlap between the positronic and electronic densities.

The VMC and DMC binding energies for the different L states,

$$\mathcal{E}^L_{\mathrm{VMC,DMC}} = E^L_{\mathrm{VMC,DMC}} - E^L_{\mathrm{thr}} \tag{21}$$

are shown in Table V. $^{2,1}P$ and $^{2,1}D$ states are bound if compared with the relevant threshold. The only previous result for $^{2,1}P$ excited state of PsH was published by Kurtz and Jordan [22]: their SCF total energy was −0.5873 hartree, giving a binding energy [Eq. (21)] of 0.0248 hartree, i.e.,

TABLE V. Binding energy (hartree) of PsH. VMC energies are computed using the best available wave function.

	$^{2,1}S$	$^{2,1}P$	$^{2,1}D$
$\mathcal{E}_{\mathrm{VMC}}$	0.036 79(1)	0.029 61(5)	0.015 62(2)
$\mathcal{E}_{\mathrm{DMC}}$	0.039 17(1)	0.052 78(5)	0.039 97(3)
$\mathcal{E}_{\mathrm{analytic}}$	0.039 179 4 [a]	0.0248 [b]	

[a]Frolov and Smith's result [18].
[b]Kurtz and Jordan's result [22].

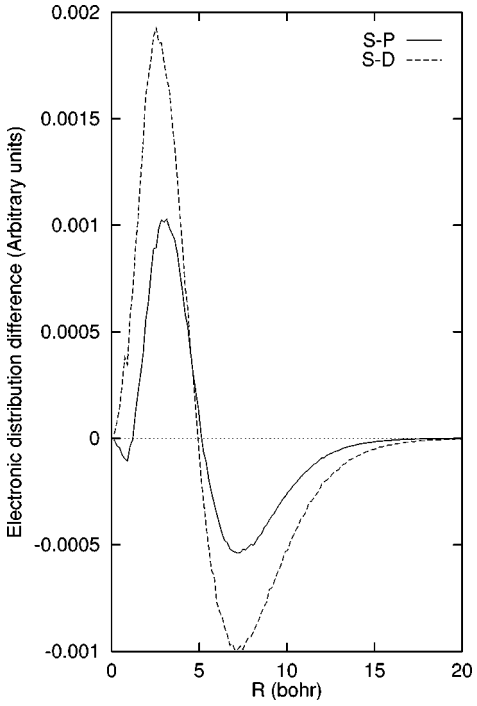

FIG. 2. Difference of the electronic distribution of the $^{2,1}P$ and $^{2,1}D$ states with the electronic distribution of the $^{2,1}S$ ground state.

47% of our DMC result. Our two-term trial wave function is already better than the SCF description, recovering 56% of the DMC binding energy.

As far as it is concerned with the experiment carried out in Ref. [40] by means of the reaction

$$e^+ + \mathrm{CH_4} = \mathrm{CH_3} + \mathrm{PsH}_{(L)} \tag{22}$$

whose energetic balance is given by

$$14.35\ \ \mathrm{eV} - \frac{6.8025}{(L+1)^2} - \mathcal{E}^{(L)}_{\mathrm{PsH}} \tag{23}$$

our energy values do not change the interpretation of these results, but suggest the onset of the production of PsH in higher angular momentum states at the threshold energy of 11.22 eV for the P state, and of 12.51 eV for the D state. Unfortunately these regions of kinetic energy of the positron beam were not explored in the experiment [40].

While the electronic distribution changes only slightly, increasing the angular momentum, as is shown in Fig. 2,

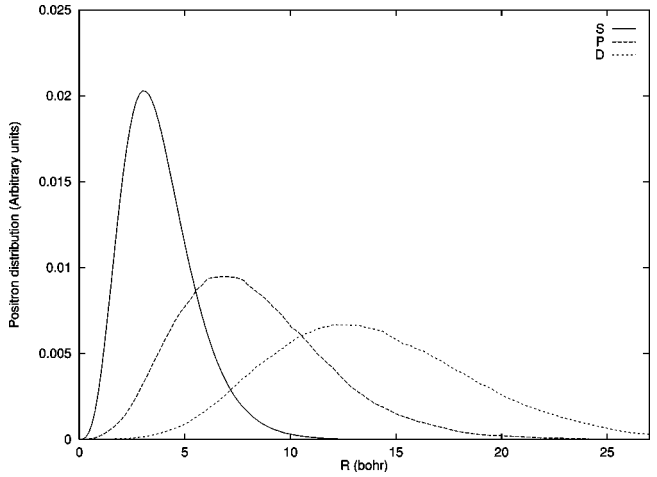

FIG. 3. Positronic distribution for the $^{2,1}S$, $^{2,1}P$, and $^{2,1}D$ states.

being polarized outward by the positron-electron interaction, both the SOE value of $\langle r_+ \rangle$ and the SOE positron distributions shown in Fig. 3 for different L values show that positron carries almost all the total angular momentum of the system. This physical picture was already pointed out by Kurtz and Jordan [22] using SCF calculations, even for the highly polarizable hydride anion.

Using the SOE positron-electron distribution $d(r_{+-})$, one could obtain useful information about the analytical form that should be used to describe the correlation between these two particles: for all three states these distributions can be accurately fitted by means of the function

$$d(r_{+-}) = r_{+-}^2 \sum_{i=1}^{N_d} c_i e^{-\alpha_i r_{+-}}, \tag{24}$$

using $N_d = 2$, showing that a good way to describe the correlation between light particles having opposite charges is given by an exponential form, such as the one used in this work.

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