Positron and positronium chemistry by quantum Monte Carlo. III. Ground state of [OH,Ps], [CH,Ps], and [NH_2,Ps] complexes

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The stability of the [OH,Ps], [CH,Ps] and [NH_2,Ps] complexes, where Ps = (e^+,e^-), have been studied using Monte Carlo techniques and explicitly correlated trial wave functions. For these systems we have computed the ground state energy values using both variational Monte Carlo and fixed node diffusion Monte Carlo methods. Diffusion Monte Carlo results allow us to predict [OH,Ps] and [CH,Ps] systems to be stable against positron and Positronium (Ps) loss. As far as [NH_2,Ps] is concerned, its small value of the Binding Energy (BE) does not allow us to conclude about its stability: this is discussed qualitatively including zero point motion of the atoms in the complex. © *1998 American Institute of Physics.* [S0021-9606(98)01838-8]

I. INTRODUCTION

While the increased possibility to obtain slow positrons opens up the possibility of a more careful study of the interaction between matter and antimatter,[1–3] the challenge represented by the calculation of accurate expectation values for positron and Positronium (Ps) containing systems is, up to now, far to be tackled successfully by means of standard *ab initio* techniques.[4] Only the use of explicitly correlated trial wave functions, e.g., in the form of a linear combination of correlated Gaussians,[5–10] and the Monte Carlo techniques[11–19] appear to be able to cope with the need to describe accurately the local behavior of the exact wave function when any two particles collide. While explicitly correlated Gaussians are in principle a very useful and flexible tool to get highly accurate results in Quantum Chemistry,[20] they have not been used so far to compute energy and other mean values for atomic and molecular systems containing more than five particles. Monte Carlo methods[21] are, instead, well suited to deal with explicitly correlated wave functions for larger systems, due to a more favorable scaling of the computational cost: on increasing the complexity of the system, i.e., the total number N_{tot} of particles, the computational cost to evaluate the trial wave function and its derivatives scales only as N_{tot}^3. These techniques allow one to avoid the problem of the calculation of the integrals needed to optimize the analytical form of the wave function chosen to describe the systems. This fact enlarges the possible choices of analytical forms that can be used, either increasing the chance to get a better description or decreasing the effort to get a given result.

This paper is the fourth of an ongoing project in our laboratory to investigate atomic and molecular complexes with positron and Positronium. In the previous papers we dealt with the leptonic structure and stability of ground and excited states of PsH,[17] with the ground state of the first-row atom Positronium complexes,[18] and with the stability of positron–polar molecule complexes.[19] In this paper we study the ground state of three Positronium complexes, [OH,Ps], [CH,Ps] and [NH_2,Ps] both with variational Monte Carlo (VMC) and fixed node diffusion Monte Carlo (FN-DMC).

The goal of this work is to obtain information about the relative stability of these systems and their fragments, in order to predict the energetic of various reactions that can take place in different environments. These complexes resemble the ''classic'' compounds H_2O, CH_2 and NH_3, and it is interesting to speculate on their stability, if one sees them as obtained by replacing a H with a Ps in the original species.[22] However, the really light mass of the positron prevents us from dealing with these complexes using the simple idea of potential energy surface and solving for the vibrational state of the ''isotopic'' substituted compound, so a complete simulation of the leptonic structure of the molecules has to be carried out to obtain meaningful information.

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 molecular system containing a positron has the form

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$$\mathcal{H}=-\frac{1}{2}\left(\sum_{\nu}^{N}\nabla_{\nu}^{2}+\nabla_{p}^{2}\right)+V(\mathbf{R}), \tag{1}$$

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

$$V(\mathbf{R})=-\sum_{n=1}^{N_{nuc}}\sum_{\nu=1}^{N}\frac{Z_n}{r_{\nu n}}+\sum_{n=1}^{N_{nuc}}\frac{Z_n}{r_{pn}}+\sum_{\nu<\mu}^{N}\frac{1}{r_{\nu\mu}}-\sum_{\nu}^{N}\frac{1}{r_{p\nu}}, \tag{2}$$

between the charged particles (i.e., the N electrons, the positron and the N_{nuc} fixed nuclei of charge Z_n), and $\mathbf{R}=(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{r}_p)$ is a point in configuration space. In this work we deal only with systems where $N=1+\Sigma_{n=1}^{N_{nuc}}Z_n$, i.e., with the complexes of a neutral molecule and a Positronium.

To approximate the wave functions of the different states for the [M,Ps] systems, we use a trial wave function product of a function of the electronic coordinates times a function of the positron coordinates and of the positron–electron distances,[17–19]

$$\Psi_T=\mathrm{Det}|\phi_\alpha|\mathrm{Det}|\phi_\beta|e^{U(r_{\mu\nu})}\Omega(\mathbf{r}_p,r_{p\nu}); \tag{3}$$

$\phi_{\alpha,\beta}$ 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.[23,24] In Eq. (3),

$$\Omega(\mathbf{r}_p,r_{p\nu})=\sum_{i=1}^{N_{terms}}c_i\Phi_i(\mathbf{r}_p,r_{p\nu}), \tag{4}$$

where[30,16]

$$\Phi_i(\mathbf{r}_p,r_{p\nu})=f_i(\mathbf{r}_p)\exp\left[k_i\sum_{\nu=1}^{N}r_{p\nu}-\sum_{n=1}^{N_{nuc}}k_{i,n+1}r_{p,n}\right]. \tag{5}$$

In this equation $f_i(\mathbf{r}_a)$ is a function that contains explicitly the dependence on the spatial coordinates of the positron (we refer to this as the pre-exponential part of the trial wave function), $\mathbf{k}_i$ is a vector of parameters for the i–th term of the linear expansion. The last N_{nuc} components of this vector were forced to have only positive values for all the terms of the linear combination.

This trial wave function, which has the correct spin and space symmetry, describes the electron–electron and electron–positron correlation by means of the exponential parts depending on the explicit electron–electron and electron–positron 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 conditions usually accelerates the convergence of the wave function[25] to the exact one, and reduces its complexity 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 demanding task.

To compute the vertical Positron Affinity (PA),

$$PA_{[\mathrm{M}^-]}=E_{\mathrm{M}^-}-E_{[\mathrm{M,Ps}]}, \tag{6}$$

and the adiabatic Binding Energy (BE),

$$\mathrm{BE}_{[\mathrm{M,Ps}]}=E_{\mathrm{M}}-\tfrac{1}{4}-E_{[\mathrm{M,Ps}]}, \tag{7}$$

TABLE I. Variational and diffusion Monte Carlo energies and geometries for the neutral molecules and their anions.

	VMC (hartree)	DMC (hartree)	R (Bohr)	Angle (deg)
OH $^2\Pi$	−75.648(2)[a]	−75.7213(8)[a]		
OH^- $^1\Sigma^+$	−75.722(2)	−75.7874(4)	1.833[b]	
CH $^2\Pi$	−38.425(2)[a]	−38.4630(5)[a]		
CH^- $^3\Sigma^-$	−38.4673(8)	−38.4630(5)	2.1747[c]	
NH_2 $^2B_1$	−55.7428(9)[d]	−55.8640(7)[d]	1.9375[d]	96.7[d]
NH_2^- $^1A_1$	−55.7218(11)[d]	−55.8919(5)[d]	1.9521[d]	102.9[d]

[a]Reference 26.
[b]Experimental geometry. Reference 27.
[c]Experimental geometry. Reference 28.
[d]This work. Geometry optimized at the MP2/6-31G** level.

accurate energy values for the neutral molecules, the anions and the positron complexes are needed. In this work we computed both VMC and FN-DMC energies for Positronium complexes and anions using the same wave function for the electrons to exploit as much as possible the cancellation of the systematic error in FN-DMC simulations due to the non-exact nodal surface location. These methods were found quite effective by Lüchow and Anderson[26] in computing first-row hydride Binding Energies, and by ourselves in obtaining accurate values for Positronium Binding Energies of first-row atoms.[18] We refer to the results obtained by Lüchow and Anderson[26] for the total energy of the neutral molecules OH and CH, while the total energy for NH_2 was computed in our laboratory.

The chosen form for the trial wave function Ψ_T [see Eq. (3)] 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[21] is well suited for this goal since it requires only the evaluation of the wave function, its gradient and its Laplacian. Since VMC, FN-DMC and other Monte Carlo methods are described in the literature;[21] for the sake of brevity we avoid describing them in this paper.

III. MONTE CARLO RESULTS

In this work the ground state energies of M^- and [M,Ps] systems, where $M=$OH, CH, NH_2, were computed by means of VMC and FN-DMC simulations. The VMC and DMC energies of the neutral molecular systems M and of the anionic species M^- are reported in Table I together with the geometry used in the calculations. The trial wave functions used to describe these molecules have the usual determinantal form times a correlation factor $U(r_{\mu\nu})$, similar to the one described above for the positron–molecule systems. The length, and hence the quality, of the correlation factor $U(r_{\mu\nu})$ used in this work was kept equal to the one used by Lüchow and Anderson[26] (i.e., nine terms for each atom present) for all the molecules, in order to be consistent with their VMC results. The task to optimize this correlation factor was accomplished minimizing the variance of the local energy $\mathcal{H}\Psi_T/\Psi_T$ over a fixed set of configurations, as well described in the literature.[21] All our DMC results for the M

TABLE II. Variational and diffusion Monte Carlo energies and geometries for the Positronium complexes.

	VMC (hartree)	DMC (hartree)	R (bohr)	Angle (deg)
$[OH,Ps]\ ^{2,1}\Sigma^+$	−75.726(3)	−75.9815(9)	1.833[a]	
$[CH,Ps]\ ^{2,3}\Sigma^-$	−38.6203(5)	−38.7291(3)	2.1747[b]	
$[NH_2,Ps]\ ^{2,1}A_1$	−55.9282(33)[c]	−56.1196(5)[c]	1.9521[c]	102.9[c]

[a]Experimental geometry. Reference 27.
[b]Experimental geometry. Reference 28.
[c]This work. Geometry optimized at the MP2/6-31G** level.

and M^- systems were computed using a time step of 0.001 hartree^{-1}, and their accuracy was checked employing smaller time steps and comparing the results, which were found to be in statistical agreement.

The calculation on the [M,Ps] complexes were performed at the same geometry as the anionic species, and the same set of parameters obtained by optimization of the correlation factor for the anions was used to carry out the calculations on the complexes. The parameters of the positronic part of the trial wave function were optimized, again, minimizing the variance of the local energy, the Ω function including $N_{terms}=1$ [see Eq. (4)]. During all the optimization processes a set of 5000 configurations in the $3(N+1)$ dimensional configuration space was used; every three or four optimization steps this ensemble was updated by means of a VMC run. The variational results of the optimized trial wave functions for the [M,Ps] systems are reported in Table II together with the results of the DMC simulations. These were carried out using the same procedures and checks employed for DMC simulations of the anionic systems.

Using the above mentioned results for the complexes and their fragments, PA and BE values were calculated using Eqs. (6) and (7), and are shown in Table III, together with the computed FN-DMC electron affinities (EA) of the neutral molecules.

IV. DISCUSSION

As discussed in our previous papers on these topics,[18,19] the different approaches and approximations used in the literature rule out the possibility of comparing absolute energy values: our discussion will be limited to PA's and BE's.

As a former test of the ability of FN-DMC to correctly describe the correlation between particles in these systems, we computed the EA of OH, CH and NH_2 as proposed by Schrader.[4] Comparing our results shown in Table III with the experimental data, it is clear that for all the three systems they are in really good agreement, showing an almost completely cancellation of the fixed node error. This behavior was already exploited by Lüchow and Anderson[26] to compute accurate binding energy for first-row hydrides, and by us to obtain EA, PA and Positronium BE for first-row atoms.[18]

Both the [OH,Ps] and [NH_2,Ps] systems were described by Tao and Green[30] in their work on the reactivity of Ps atoms in aqueous solutions containing H_2O_2 and NH_3. These two complexes could play some role in explaining the behavior of the quenching effect in their aqueous solutions. For [OH,Ps] Tao and Green predicted the Positronium BE to be less than 1.5 eV (0.055 hartree), and a rough estimate gave a value of 1.3 eV (0.048 hartree) for this quantity. Few workers have tried to compute accurately the Positronium BE for OH: Kao and Cade,[31] using the SCF method, predicted a PA of 0.176 hartree and BE of −0.006; Tachikawa *et al.*[32] obtained a PA of 0.180 hartree and a BE of −0.004 hartree using second order Moeller–Plesset theory to introduce correlation between particles; Yoshida *et al.*,[14] exploiting FN-DMC, computed a PA of 0.205(5) hartree and a BE of 0.027(5) hartree. This work is the only one where EA was computed as an independent check of the accuracy of the method, while in the works by Kao and Cade,[31] and by Tachikawa *et al.*[32] experimental values for the EA were used to compute Positronium BE by means of a Born–Haber cycle.

Our PA and BE for [OH,Ps] are both positive and larger than the previous *ab initio*[31,32] calculations. This outcome is easily explained since our method is able to recover almost completely the correlation energy, especially the positron–electron one. In contrast, it is not an easy task to explain the difference between our values and the Yoshida *et al.*[14] DMC results. While our lower total energies for OH and OH^- [Yoshida *et al.* computed −75.6286(37) hartree for OH and −75.6973(38) hartree for OH^-] might be due to different and better nodal surfaces of our trial wave functions, the same claim cannot be made for the difference between the energy of OH and [OH,Ps] unless their nodal surfaces for OH^- are much worse than the nodal surfaces of OH. This does not seem to be the case, since they were able to compute the EA of OH to a good accuracy. To be sure that our result for [OH,Ps] is not plagued by the time step bias we carried out an additional calculation using a time step of 0.0005 hartree^{-1}, finding statistical agreement with the calculation done employing a time step of 0.001 hartree^{-1}. This simulation was carried out using 2000 walkers and was divided into 250 blocks, each 500 steps long: this means a total number of 250,000,000 configurations and pretty well converged results. If we rule out the possibility of an error in the

TABLE III. Variational and diffusion Monte Carlo Positron Affinity (PA) and Positronium Binding Energy (BE) for the complexes. FN-DMC and experimental Electronic Affinity (EA) for the molecules OH, CH and NH_2. Energies are in hartrees.

	PA_{VMC}	PA_{DMC}	BE_{VMC}	BE_{DMC}	EA_{DMC}	EA_{exp}[a]
$[OH,Ps]\ ^{2,1}\Sigma^+$	0.0040(36)	0.1941(10)	−0.172(3)	0.0102(12)	0.0661(9)	0.0673
$[CH,Ps]\ ^{2,3}\Sigma^-$	0.1529(9)	0.2200(4)	0.0959(6)	0.0161(6)	0.0461(5)	0.0456
$[NH_2,Ps]\ ^{2,1}A_1$	0.2064(35)	0.2277(7)	−0.0646(34)	0.0056(9)	0.0279(9)	0.0272

[a]Reference 29.

Yoshida *et al.* code,[14] we are left with the possibility that their calculation on [OH,Ps] might be not well converged. This idea is supported by our experience on similar complexes: many Ps containing systems have a leptonic structure that can be described with good approximation as composed by a neutral fragment plus a polarized and slightly bound Ps, most notably LiPs (in preparation). This situation requests FN-DMC to sample a very large zone in configuration space before one collects enough data to be sure the simulation is ergodic, and before one can trust the statistical result. Since we have not the details of the simulations carried out by Yoshida *et al.*[14] to test this hypothesis, we hope to solve this matter in the future using better trial wave functions based on our explicitly correlated *ansatz*,[33] for both OH^- and [OH,Ps].

As to $[NH_2,Ps]$ Tao and Green, in the same work cited above,[30] proposed that its BE ''should approach zero.'' To test their hypothesis we carried out the VMC and FN-DMC simulation for all the relevant systems. The molecular geometries for the NH_2 and NH_2^- systems were obtained by MP2 optimization using a 6-31G** basis set. Our results show that $[NH_2,Ps]$ is bound, even if only slightly, when the NH_2^- geometry is employed in the calculation. Due to the small value of the Positronium BE the stability of this complex cannot be said to be completely established: we think one should meaningfully compare total energies corrected by the zero point motion. Roughly speaking, on the basis of our FN-DMC simulation, the leptonic structure of $[NH_2,Ps]$ can be thought to be composed by the NH_2 fragment plus a polarized Ps, so one can expect both species to have nearly the same zero point motion, resulting in a global stability of the positronic complex.

As far as [CH,Ps] is concerned, this complex has not been previously studied. The only calculation carried out on similar systems was the one by Saito *et al.*[34] using an MP2 and DMC calculation on $[CH_3,Ps]$. Nevertheless, this complex might play an important role in discussing the fragmentation pattern of large organic molecules as discussed by Hullet *et al.*[1] and Passner *et al.*[2] and Glish *et al.*[3] in their seminal works. Due to the large EA (see Table III), CH appears as the most favorable candidate to bind a Ps during a fragmentation process, and indeed this is what our results show. Since [CH,Ps] is a neutral complex, there are few chances that direct proof of its existence might be experimentally found during fragmentation, but its appearance could only be inferred by the mass spectrum obtained from the process.

V. CONCLUSION

In this work we have computed accurate energy differences between M, M^- and [M,Ps] systems, where $M = OH, CH, NH_2$, using VMC and DMC methods. From these results, vertical Positron Affinities and adiabatic Positronium Binding Energy were calculated. These results show [OH,Ps] and [CH,Ps] to be stable, while the stability of $[NH_2,Ps]$ has been only qualitatively discussed since zero point motion could reverse the energetic order of the relevant species. Our results appear superior in accuracy than previously published values due the ability of DMC to recover the correlation between electrons and the positron. We hope these results will be useful to the experimentalists to gain a better understanding of the energetic in a matter–antimatter interaction, of the fragmentation dynamics of organic molecules and of the chemical reactions in an aqueous solution.

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