

# Positron chemistry by quantum Monte Carlo. II. Ground-state of positron-polar molecule complexes

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The stability of the ground-state of positron-polar molecule complexes  $[M, e^+]$  has been explored for  $M = \text{LiH}, \text{HF}, \text{H}_2\text{O}, \text{BeO}, \text{LiF}$  using variational and diffusion Monte Carlo techniques. Our simulations show that the ground-state of the complexes  $[\text{LiH}, e^+]^{2,1}\Sigma^+$ ,  $[\text{BeO}, e^+]^{2,1}\Sigma^+$ , and  $[\text{LiF}, e^+]^{2,1}\Sigma^+$  is stable against the dissociation either in the two fragments  $M$  and  $e^+$  or in the other two fragments  $M^+$  and  $\text{Ps} = [e^+, e^-]$ , while the ground-state of  $[\text{H}_2\text{O}, e^+]^{2,1}A_1$ , and of  $[\text{HF}, e^+]^{2,1}\Sigma^+$  has an energy equal to the dissociation threshold,  $M$  and  $e^+$ . We also compare the predicted vertical positron affinity (PA) with high quality vertical electron affinity (EA) and discuss the relevant difference between the two values. © 1998 American Institute of Physics. [S0021-9606(98)01929-1]

## I. INTRODUCTION

The possibility to easily obtain slow positrons in gaseous and liquid phases has renewed the theoretical and experimental interest on the stability and annihilation of systems containing a positron, as shown by the growing mass of work done on them,<sup>1</sup> and by the fact that in some cases the existence of these systems has been postulated to explain experimental results.<sup>2</sup> In many cases both these problems were shown to represent a challenge for the standard methods of quantum chemistry (e.g., SCF, CI, CC, MBPT) (Refs. 3–7) that are not able to include electron–positron distances explicitly, hence to correctly reproduce the local behavior of the exact wave function. It is now clear that cusp properties of the trial wave function are one of the key ingredients needed to obtain qualitatively correct results. The goal to compute quantitatively accurate values for these systems, i.e., binding energy (BE) and annihilation properties, using analytical calculations with explicitly correlated wave functions, is hindered by the difficulty to obtain the values of the integrals needed in the optimization of the trial wave function. Moreover, the explicitly correlated trial wave functions used in previous works<sup>8,9</sup> that give analytically computable integrals are plagued by a slow convergence to the exact results, even for really small systems. Other routes have been taken to cope with these problems: in density functional theory (DFT) one indirectly introduces a correlation between the leptons using ad hoc “pseudo”-potentials<sup>10–13</sup> and corrects for the inability to describe the positron–electron cusp condition by means of a pair correlation correction;<sup>12</sup> however this appears to be more of a heuristic approach rather than something founded on sound theoretical bases.

So far, only few attempts were carried out to obtain positron affinities for two and three atom molecules<sup>5,6,14–16</sup> usually containing first row atoms, and only in one case<sup>6</sup> a correlation has been introduced by means of a CI technique. This last calculation showed the necessity to introduce the correlation in the description of the  $[\text{LiH}, e^+]$  system, but did not discuss the convergence behavior of the CI expansion.

Quantum Monte Carlo (QMC) techniques<sup>17</sup> have been tested for a long time, and the obtained results showed them to be flexible and powerful methods to solve the Schrödinger equation for small atoms and molecules, even if they contain exotic particles like positrons or muons,<sup>18–26</sup> or if one is interested in observables different from the energy.<sup>27,28</sup> These techniques were developed to avoid the necessity to compute the integrals used to optimize the trial wave function: this fact allows one to use any analytical form that can be appropriated, usually obtaining quite good results for all the properties of the system. This paper is the second in an ongoing project of our group to investigate atomic and molecular complexes with positron and positronium.

In this work we present a numerical study of the ground-states of the complexes  $[M, e^+]$  and of the molecules  $M$ , where  $M = \text{LiH}, \text{HF}, \text{H}_2\text{O}, \text{BeO}, \text{LiF}$ , by means of variational Monte Carlo<sup>17</sup> (VMC) and fixed node diffusion Monte Carlo<sup>17</sup> (FN-DMC) methods. The aim of this work is to compute accurate and reliable energetic quantities, in order to discuss their stability and the effect generated by the introduction of the correlation between electron pairs and between the positron and electrons. Moreover, we compare our numerical results for the ground-state of the  $[M, e^+]$  systems with the energy of an electron in a finite dipole field.<sup>29</sup> This is relevant to assess the ability of this model to describe the bound states of  $[M, e^+]$  in the adiabatic approximation, and to explore the possibility to use it as a model for the scattering of positrons by polar molecules.

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Since our trial wave functions contain positron-electron distances explicitly, our approach could also allow one to compute the rate of two gamma photons annihilation in these compounds.<sup>30</sup> At present we are exploring this possibility for atomic and molecular systems containing up to four electrons,<sup>31</sup> using more accurate analytical forms for the trial wave function than the ones adopted in this work.

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

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

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

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

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

between the charged 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. In this work we deal only with systems where  $N = \sum_{n=1}^{N_{\text{nuc}}} Z_n$ , i.e., with the complexes of a neutral molecule and a positron.

To approximate the wave functions of the different states for the  $[M, e^+]$  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,

$$\Psi_T = \text{Det}[\phi_{\alpha}] \text{Det}[\phi_{\beta}] e^{U(r_{\mu\nu})} \Omega(\mathbf{r}_p, r_{p\nu}). \quad (3)$$

$\phi_{\alpha, \beta}$  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.<sup>32,33</sup> In Eq. (3),

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

where<sup>26,30,34</sup>

$$\Phi_i(\mathbf{r}_p, r_{p\nu}) = f_i(\mathbf{r}_p) e^{k_i \sum_{\nu=1}^N r_{p\nu} - \sum_{n=1}^{N_{\text{nuc}}} k_{i,n} + 1 r_{p,n}}. \quad (5)$$

In this equation  $f_i(\mathbf{r}_p)$  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  $N_{\text{nuc}}$  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 condition usually accelerates the convergence of the wave function<sup>35</sup> 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)

$$\text{PA}_{[M, e^+]} = E_M - E_{[M, e^+]}, \quad (6)$$

accurate energy values for the neutral molecules and the positron complexes are needed. In this work we computed both VMC and DMC energies for both systems, to exploit as much as possible the cancellation of the systematic error in DMC simulations due to the nonexact nodal surface location. These methods have been found to be quite effective by Lüchow and Anderson<sup>36</sup> in computing first-row hydride binding energies, and by ourselves in obtaining accurate values for positronium binding energy of first-row atoms.<sup>37</sup>

The chosen form for the trial wave function  $\Psi_T$  [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<sup>17</sup> is well suited for this goal since it requires only the evaluation of the wave function, its gradient, and its Laplacian. Since VMC and other Monte Carlo methods are well described in the literature,<sup>17</sup> 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

$$\langle \mathcal{O} \rangle_{\text{VMC}} = \frac{\int \Psi_T^2(\mathbf{R}) \mathcal{O}_{\text{loc}}(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^2(\mathbf{R}) d\mathbf{R}}, \quad (7)$$

where

$$\mathcal{O}_{\text{loc}}(\mathbf{R}) = \frac{\mathcal{O} \Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}. \quad (8)$$

Here,  $\Psi_T^2(\mathbf{R})$  is interpreted as a probability distribution and it is sampled using Metropolis or Langevin algorithms.<sup>17</sup> As an explicit example, the expectation value of the Hamiltonian is written as

$$\langle \mathcal{H} \rangle_{\text{VMC}} = \frac{\int \Psi_T^2(\mathbf{R}) \mathcal{H}_{\text{loc}}(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^2(\mathbf{R}) d\mathbf{R}}, \quad (9)$$

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

To optimize the nonlinear parameters in the trial wave function we minimized the function

$$\mu^2(E_r) = \frac{1}{N_{\text{conf}}} \sum_{j=1}^{N_{\text{conf}}} [\mathcal{H}_{\text{loc}}(\mathbf{R}_j) - E_r]^2, \quad (10)$$

$\{\mathbf{R}_j, j=1, N_{\text{conf}}\}$  being a set of  $N_{\text{conf}}$  fixed configurations sampled from  $\Psi_T^2$ , and  $E_r$  is an approximation to the true

TABLE I. Ground state experimental equilibrium geometry and dipole moment, VMC and DMC energies (hartree) of the neutral molecules.

		$R_e$ (bohr)	$E_{\text{VMC}}$	$E_{\text{DMC}}$	$\mu$ (debye)
LiH	$^1\Sigma^+$	3.015 <sup>a</sup>	-8.0603(6)	-8.0704(1)	5.88 <sup>a</sup>
HF	$^1\Sigma^+$	1.733 <sup>b</sup>	-100.2233(18)	-100.4429(11)	1.82 <sup>c</sup>
H <sub>2</sub> O	$^1A_1$	1.811, 104.95 <sup>c</sup>	-75.9051(8)	-76.4086(9)	1.84 <sup>c</sup>
BeO	$^1\Sigma^+$	2.51 <sup>a</sup>	-89.3173(25)	-89.7854(13)	6.26 <sup>a</sup>
LiF	$^1\Sigma^+$	2.955 <sup>a</sup>	-107.2015(15)	-107.4069(9)	6.33 <sup>a</sup>

<sup>a</sup>Reference 45.<sup>b</sup>Reference 16. Second entry for H<sub>2</sub>O is the HOH angle.<sup>c</sup>Reference 36

value of the energy for the system. This method, proposed by Frost<sup>38</sup> and Conroy,<sup>39</sup> was described in detail by Umrigar *et al.*<sup>40</sup> and by Mushinski and Nightingale<sup>41</sup> and has been proven 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<sup>28</sup> 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<sup>17,42</sup> is employed. This method samples the distribution  $f(\mathbf{R}) = \Psi_T(\mathbf{R})\Psi_0(\mathbf{R})$ , simulating the time-dependent Schrödinger equation in imaginary time as a diffusion equation having source and sink terms. We use the fixed node approximation to sample an antisymmetrized wave function. So,  $\Psi_0(\mathbf{R})$  is the ground state wave function of the system with the same nodal surface of the trial wave function. The value of the energy can be computed using the ‘‘mixed estimator’’

$$\langle \mathcal{H} \rangle_{\text{DMC}} = \frac{\int \Psi_T(\mathbf{R})\Psi_0(\mathbf{R})\mathcal{H}_{\text{loc}}(\mathbf{R})d\mathbf{R}}{\int \Psi_T(\mathbf{R})\Psi_0(\mathbf{R})d\mathbf{R}}. \quad (11)$$

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

### III. RESULTS

In this work the ground state energies of M and  $[M, e^+]$  systems, where M=LiH, HF, H<sub>2</sub>O, BeO, LiF, were computed by means of VMC and FN-DMC simulations. The VMC and DMC energies of the neutral molecular systems M are reported in Table I together with the experimental geometry used in the calculations and the experimental dipole moments. 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 lengths, and hence the quality, of the correlation factor  $U(r_{\mu\nu})$  used in this work differ for each molecule, depending on the computational time needed to optimize it. This task was accomplished minimizing Eq. (10). All our DMC results for the M systems were computed using a time step of 0.001 hartree<sup>-1</sup>, and their

TABLE II. Ground state VMC and DMC energies (hartree) of  $[M, e^+]$  complexes.

		$E_{\text{VMC}}$	$E_{\text{DMC}}$
[LiH, $e^+$ ]	$^2,1\Sigma^+$	-8.0658(2)	-8.1037(4)
[HF, $e^+$ ]	$^2,1\Sigma^+$	-100.2250(30)	-100.4445(12)
[H <sub>2</sub> O, $e^+$ ]	$^2,1A_1$	-75.9013(30)	-76.4070(10)
[BeO, $e^+$ ]	$^2,1\Sigma^+$	-89.3365(13)	-89.8134(12)
[LiF, $e^+$ ]	$^2,1\Sigma^+$	-107.2062(9)	-107.4243(10)

accuracy was checked employing smaller time steps and comparing the results, that were found to be in statistical agreement.

As to the  $[M, e^+]$  complexes, the calculations were performed at the same geometry as the neutral molecules, and the same set of parameters obtained by the optimization of the correlation factor for the neutral species was used to carry out the calculation of the complexes. The parameters of the positronic part of the trial wave function were optimized, again, minimizing  $\mu^2(E_r)$  given by Eq. (10), the  $\Omega$  function including  $N_{\text{terms}} \leq 3$  [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  $[M, e^+]$  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 neutral systems. In Table III we report the values for vertical PA computed in this work, together with previously published results. Except for the semiempirical CNDO calculations<sup>16</sup> whose parameters were rather approximate, all the *ab initio* calculations give conservative estimates of the positron affinity (PA), as the *ab initio* techniques exclude (in the case of SCF) or do not completely include (in the case of CI) the contribution of the correlation between electrons and the positron.

Since different approaches and approximations were used in the previous works, it is meaningless to compare energy absolute values: our discussion will be limited to PA's.

The calculations on HF and H<sub>2</sub>O were intended as a first step to explore the possible structure of the corresponding liquids containing a positron. However, as the results in Table III show, for these systems we found a statistically zero PA value, similarly to what was found for EA by means

TABLE III. Positron affinity (PA) (hartree).

PA	VMC <sup>a</sup>	DMC <sup>a</sup>	SCF <sup>b</sup>	CI <sup>c</sup>	CNDO <sup>d</sup>
LiH	0.0055(6)	0.0333(4)	0.0059	0.0170	0.0165
HF	0.0017(35)	0.0016(16)			-0.0308
H <sub>2</sub> O	0.0038(31)	0.0016(13)			0.0033
BeO	0.0191(28)	0.0280(18)	0.0110		-0.0400
LiF	0.0047(17)	0.0174(13)	0.0066		-0.0297

<sup>a</sup>This work.<sup>b</sup>Reference 15.<sup>c</sup>Reference 6.<sup>d</sup>Reference 16.

of *ab initio* calculations.<sup>43</sup> For water and hydrogen fluoride, the positron distribution at the end of the DMC simulation was much more diffuse than to the electron distribution, with quite large values for the powers of the distance of the positron from the center of mass of the molecules, much larger than the VMC results. The trial wave functions used in the VMC simulations were square-integrable, and these results raise the suspect that a complete dissociation of the positron from the molecules might happen if the simulations were carried out without using a square integrable trial wave function for the positronic part of the systems, and hence that the two complexes are not stable against their dissociation. This fact is consistent with our finding that DMC energies are statistically equal to the threshold energies. Although these facts are not complete proofs of the instability of  $[\text{HF}, e^+]$  and  $[\text{H}_2\text{O}, e^+]$ , they stress the overall quality of the simulations, showing DMC to be able to find the relevant dissociation channel for these complexes. As to the other dissociation channel  $M^+$  and Ps, for all the systems studied in this work the ionization potential can be computed with sufficient accuracy using Koopman's theorem: for HF and H<sub>2</sub>O it was found larger than 0.25 hartree, and this result rules out the possibility to have as relevant dissociation channel  $M^+$  and Ps. It is worth saying that, similarly to what happens for EA,<sup>43</sup> there are chances for the dimers of these two molecules to bind a positron; the dipole moment of the supermolecules might become large enough to electrostatically bind the positron, but it is not possible to exclude *a priori* a relevant contribution from the correlation between the leptons.

As to the molecules LiH, LiF and BeO, that are able to bind the positron, DMC gives larger PA than any other method. All the outcomes presented above can be easily explained by the ability of DMC to recover almost completely the correct description of the correlated motions between the leptons in the systems. The disagreement between DMC and SCF results<sup>15</sup> puts in evidence that the binding of the positron to the polar molecule cannot be explained using only mean-field models, as remarked in the case of LiH also by the comparison with the CI result. So, the contribution of the correlation between electrons and the positron plays a very important role in defining the PA of these systems. This fact contradicts Kurtz and Jordan's statement<sup>15</sup> that, since "the orbital occupied by the positron in  $[\text{LiH}, e^+]$  is much more diffuse than that occupied by the electron in  $\text{LiH}^-$ , one can expect a smaller contribution of correlation to the PA than to the EA." This statement could be extended to all the systems we dealt with in this work, since all the positron orbitals are extremely diffuse. Our results show that this is not the case, since it appears evident that correlation doubles the PA for BeO and LiF, which makes the PA for LiH six times the SCF value.

Previous calculations carried out on LiH (Ref. 6) put in evidence that the CI technique performs poorly for this system. We believe this difficulty to be due to the slow convergence to the exact wave function, whose local behavior is much more complicated to describe in the case of positron-electron coalescence than in the electron-electron one.

Comparing our results with CNDO calculations<sup>16</sup> re-

TABLE IV. Electron affinity (hartree) computed using Koopman's theorem and CCSD(T).

EA	KT <sup>a</sup>	CCSD(T) <sup>a</sup>
LiH	0.00763	0.01132
BeO	0.06396	0.07824
LiF	0.01045	0.01249

<sup>a</sup>Reference 45.

ported in Table III for all five systems studied here, one could infer that the parameters employed in the CNDO calculations were quite crude, and that a much better parametrization has to be found before one can expect even qualitatively correct results for polar molecules. We believe that this problem can be even worse for nonpolar molecules, where correlation effects must be really important to obtain a positive PA. In order to get some insight about the order of magnitude of the PA for nonpolar systems one can use  $[\text{Li}, e^+]$  as model system: using explicitly correlated Gaussians, Ryzhikh and Mitroy<sup>44</sup> obtained a PA of 0.054 hartree with respect to Li, and a binding energy of 0.00217 hartree with respect to  $\text{Li}^+$  and Ps. These numbers show that very high accuracy must be pursued to obtain qualitatively exact answers as it is proved by the slow convergency of the energy mean values reported in Ref. 44, and that every semi-empirical method has to be calibrated against *state of the art* experimental and theoretical results in order to prove its overall applicability.

As far as it concerns the binding mechanism of the positron to LiH, BeO and LiF molecules, more information can be obtained comparing the PA values computed in this work with the accurate EA values computed in Ref. 45 and reported in Table IV, and with the binding energies of a positron in a two point-charge dipole field.<sup>29</sup> The last ones, displayed in Fig. 1 together with the computed PA, show that the two point-charge approximation of the molecular dipole field is not really a good model of these systems, the actual

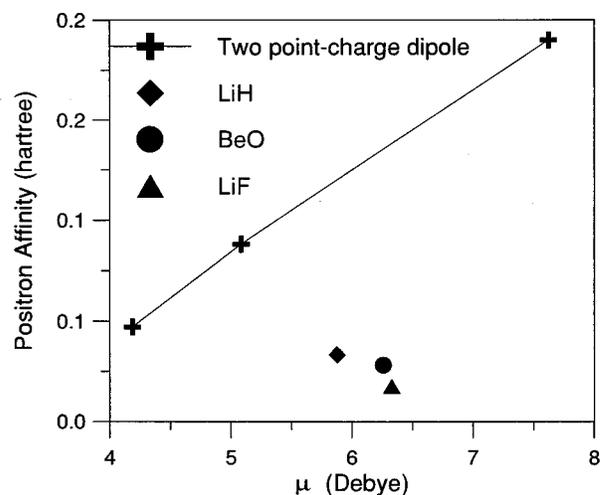


FIG. 1. LiH, BeO, LiF and two-point-charge dipole positron affinity as a function of the dipole moment.

distribution playing a major role in determining the binding energy. More precisely, the presence of the nucleus of the atom on the negative side of the dipole repels the positron since the nucleus is not completely shielded by the electron cloud. The EA's reported in Table IV for LiH and LiF, are smaller than the correspondent PA's; again, this can be due to the strong influence of the correlation of the motions between positron and electrons. In comparing the PA and EA of BeO one should keep in mind that, even if LiF and BeO are isoelectronic molecules, their electronic structure is quite different, due to the "strong bivalent" character of both Be and O. This difference is reflected even in calculations carried out using Koopman's theorem, EA for BeO being quite larger than for LiH and LiF.

It is our opinion that these systems deserve a more careful investigation of their potential energy surfaces, in order to better clarify this mechanism. In particular, LiH seems to be a good candidate since it has a small number of electrons and its relevant dissociation channel is, quite surprisingly,  $\text{Li}^+$  and  $\text{PsH}$ . This result can be easily obtained comparing the total energy of the two possible dissociation channels whose fragments are stable:  $-8.03208$  hartree for  $[\text{Li}, e^+]$  (Ref. 44) and H, and  $-8.069083$  hartree for  $\text{Li}^+$  (Ref. 46) and  $\text{PsH}$ .<sup>8</sup>

Moreover, the possibility to have some dipole bound excited state for these systems deserves an accurate investigation; unluckily, QMC is not the best tool to study excited states having the same symmetry as the ground state, while it can deal with states having different symmetries. For the systems we have presented, this means one has to work with  $\Pi$  and  $\Delta$  states, i.e., some nodal plane has to be located on the molecular axis, spreading outward the positronic distribution.

#### IV. CONCLUSIONS

In this work we have computed accurate energy differences between M and  $[\text{M}, e^+]$  systems, where  $\text{M}=\text{LiH}, \text{HF}, \text{H}_2\text{O}, \text{BeO}, \text{LiF}$ , using VMC and DMC methods. From these results, vertical positron affinities were calculated. Our results appear superior in accuracy than previously published values due to the ability of DMC to recover all the correlations between electrons and the positron. We hope these results will be useful to the experimentalists to gain a better understanding of the energetic in the matter-antimatter interaction, and to the theoreticians to improve the parametrization of the semiempirical methods like CNDO and related, and to formulate better models of the positron-matter interactions.

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