JOURNAL OF CHEMICAL PHYSICS VOLUME 117, NUMBER 4 22 JULY 2002

Positron and positronium chemistry by quantum Monte Carlo. VI. The ground state of LiPs, NaPs, e^+Be, and e^+Mg

Massimo Mella[a] and Mosé Casalegno[b]
Dipartimento di Chimica Fisica ed Elettrochimica, Universita' degli Studi di Milano, via Golgi 19, 20133 Milano, Italy

Gabriele Morosi[c]
Dipartimento di Scienze Chimiche, Fisiche e Matematiche, Universita' dell'Insubria, via Lucini 3, 22100 Como, Italy

(Received 15 April 2002; accepted 26 April 2002)

The ground states of the positronic complexes LiPs, NaPs, e^+Be, e^+Mg, and of the parent ordinary-matter systems have been simulated by means of the all-electron fixed-node diffusion Monte Carlo (DMC) method. Positron affinities and positronium binding energies are computed by direct difference between the DMC energy results. LiPs was recomputed in order to test the possibility of approximating the electron–positron Coulomb potential with a model one that does not diverge for $r=0$, finding accurate agreement with previous DMC results. As to e^+Be, the effect due to the near degeneracy of the $1s^2 2s^2$ and $1s^2 2p^2$ configurations in Be is found to be relevant also for the positron affinity, and is discussed on the basis of the change in the ionization potential and the dipole polarizability. The DMC estimate of the positron affinity of Mg, a quantity still under debate, is 0.0168(14) hartree, in close agreement with the value 0.015 612 hartree computed by Mitroy and Ryzhihk [J. Phys. B. **34**, 2001 (2001)] using explicitly correlated Gaussians. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1486447]

I. INTRODUCTION

The ability of various atoms, ions, and neutral molecules to bind a positron or a positronium (Ps) atom is now well established by accurate theoretical calculations.[1] So far, the two most successful methods are represented by variational calculations employing explicitly correlated Gaussians (ECGs),[2] and by quantum Monte Carlo (QMC) techniques.[3] Recently, also *ab initio* configuration interaction (CI) calculations have attracted interest as a promising method for describing positron and positronium interaction with one and two valence electron atoms (see both Refs. 1 and 2 for a complete list of references). Conversely, for molecules its usefulness in computing bound states of positron complexes has still to be fully explored (e.g., see Ref. 4).

As often happens, each of these methods has advantages and shortcomings, so that we feel it important to consider them as complementary tools in studying positronic complexes. For instance, while the method based on ECGs is undoubtedly the most accurate one, the computational effort requested grows faster than for QMC upon increasing the number of active particles (electrons and positrons) in the system, therefore setting a practical upper bound to their maximum number. Up to now, no systems having more than five light active particles were computed. In principle, the limitation of ECG may be overcome by the CI approach, whose computational scaling with respect to the system size is more advantageous.

With the aim of obtaining information on the energetic and annihilation properties of positrons and positroniums interacting with molecules and in a condensed matter environment, the ongoing project in our group is to study positron and positronium physical chemistry applying QMC methods as flexible and predictive tools. These methods have the intriguing feature of recovering all the bosonic correlation energy, and therefore they are expected to consistently deliver accurate results for the energy component of the electron–positron interaction. In order to reach our goal, we believe it is mandatory to gain expertise on the largest variety of ‘‘model’’ systems before to dealing with more complicated ones. Here, the word ‘‘model’’ is just meant to indicate a real system for which it is possible to obtain accurate results employing different methods in order to make comparisons, rather than ‘‘toy’’ systems whose Hamiltonian has been completely invented. So far, the QMC methods, and especially the DMC method, have been applied to Ps-containing systems[5–7] on which they perform quite well, and on molecules having a large dipole moment that can bind a positron.[8–10] However, neither second row atoms and molecules, nor systems composed by a neutral polarizable fragment and a positron, have been investigated. In this work, we specifically address this deficiency, investigating the performance of the all-electron fixed node DMC (FN-DMC) on the title systems LiPs, NaPs, e^+Be, and e^+Mg.

Among the reasons for selecting these systems we indicate that, although positron affinity (PA) and positronium binding energy (BE) have been computed for all of them by either all-electron ECG or frozen-core ECG methods[11] by means of the stochastic variational method (SVM), an inde-

---

[a] Electronic mail: massimo.mella@unimi.it

[b] Electronic mail: mose.casalegno@unimi.it

[c] Electronic mail: gabriele.morosi@uninsubria.it

pendent confirmation of these results has not been given yet. Moreover, NaPs and e$^+$Mg have been studied only employing model potentials to eliminate core electrons, and therefore it is interesting to compare those results with all-electron calculations. To complicate the picture, for e$^+$Mg a discrepancy exists between the frozen-core SVM (FCSVM)[11] and the many body perturbation theory (MBPT)[12] positron affinity (PA) that requires scrutiny.

As to LiPs, the recently improved estimates of its BE by Mitroy and Ryhzikh[11] appear to be unquestionable: their accuracy is roughly 1% or better with respect to the exact value, so that there is no fundamental reason to recompute its ground state. Nevertheless, due the small number of electrons, LiPs represents an optimal playground to test any method or approximation devised to deal with the ground state of Ps complexes. For many of these systems, we do not expect their electronic structure to be much different from the one of the parent atom or molecule plus a Ps atom weakly bound by means of dispersion forces. If this were the case, one should expect only a minor change in the Ps BE to a neutral atom or molecule upon changing the electron–positron interaction potential close to the coalescence point. This would be due simply to the fact that the average distance of the positron from the parent system electrons is larger than from the electron in the Ps moiety. In this work, we exploited this idea approximating the correct Coulomb potential between the electrons and the positron with a model one that follows closely the $-1/r$ behavior for large r, while it converges to a finite value for $r=0$. It is important to stress that this substitution has the practical effect of ‘‘smoothing out’’ the Coulomb divergence in the electron–positron interaction, therefore allowing one to get rid of the explicit electron–positron correlation factors that are needed to avoid the possible blowup of the walker population during the branching step due to the local energy divergence. This fate is always lurking beneath any ergodic DMC simulation where potentials diverging towards $-\infty$ are employed. The similar problem for the electron–nucleus interaction is circumvented by using HF-quality electronic wave functions having the correct cusp conditions.

Besides the aforementioned reasons, we also stress the fact that the study of the ground state of all these complexes is a mandatory first step before applying DMC to the calculation of scattering observable[13,14] for Ps and e$^+$ as projectiles. In this respect, we point out that, recently, various models have been used by Sinha *et al.*,[15] in the framework of the close-coupling approximation (CCA) and of the static exchange approximation, to estimate the threshold cross section in the elastic scattering of o-Ps off Na. In order to get an insight on the accuracy of the various models, they made an attempt to compute the NaPs binding energy obtaining the three values 0.0042, 0.0044, and 0.0052 hartree depending on the CCA model employed. Although in some agreement with an earlier prediction of this quantity by Ryzhikh and Mitroy,[16] namely 0.005 892 hartree, their estimates based on the CCA models are quite different from the improved frozen-core value 0.008 419 hartree, by the same two authors.[11]

II. METHODS AND RESULTS

Since QMC methods are well described in the literature,[17] we only summarize the main points relevant to this work. DMC 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 the antisymmetrized wave function, so that our $\Psi_0(\mathbf{R})$ is the ground state wave function of the system with the constrain of having the same nodal surface of the trial wave function $\Psi_T(\mathbf{R})$. If the ground state has no nodes, or $\Psi_T(\mathbf{R})$ has the exact nodal structure, this method gives the exact ground state energy, otherwise one only obtains an upper bound. Usually, more than 90% of the correlation energy for first row atoms and molecules is recovered using this approach. The fixed node approximation, the major source of inaccuracy in the DMC method, is amenable of improvement by means either of nodal release[18] or of increasing the accuracy of the electronic part of the $\Psi_T(\mathbf{R})$ using, instead of a SCF wave function, a short linear combination of determinants[19] or explicitly correlated functions.[7,20] However, in this work we confine ourselves to deal only with fixed node results and, mainly, with trial wave functions built with a single determinant. Other sources of inaccuracy in DMC are represented by the time step error, due to the Trotter's splitting of the exact propagator, and to the stochastic noise of the simulation. Both are easily kept under control by reducing the time step size and running longer simulations in order to obtain more independent samples.

Besides confining the simulation in its nodal boundaries, the trial function $\Psi_T(\mathbf{R})$ is employed to guide the displacement of the set of points in configurational space and to compute the total energy of the systems by means of the mixed estimator

$$E_0 \simeq \frac{1}{N}\sum_{i=1}^{N} E_{\mathrm{eloc}}(\mathbf{R}_i) \simeq \frac{1}{N}\sum_{i=1}^{N} \frac{H\Psi_T(\mathbf{R}_i)}{\Psi_T(\mathbf{R}_i)}. \tag{1}$$

In our calculations the trial wave function Ψ_T is

$$\Psi_T = \mathrm{Det}|\phi_\alpha|\mathrm{Det}|\phi_\beta| e^{U(r_{\mu\nu})}\Omega(\mathbf{r}_p, r_{p\nu}), \tag{2}$$

$\phi_{\alpha,\beta}$ 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.[21,22] Also, $\Omega(\mathbf{r}_p, r_{p\nu})$ is the positron part of the trial wave function and is explicitly dependent on the positron–electron distances. We refer to our previous works[5,6,8] for the complete form of our trial wave functions.

As far as the electronic part of the wave function is concerned, we chose the Hartree–Fock quality orbitals by Clementi and Roetti.[23] For Li, Li$^-$, Be$^+$, and Be, the electronic correlation factor U is the ‘‘standard’’ variance optimized nine-term Jastrow form by Schmidt and Moskowitz.[21,22] Instead, for Na, Na$^-$, Mg$^+$, and Mg, we optimized the same Jastrow model, minimizing the energy by means of the procedure described by Lin, Zhang, and Rappe.[24] The electronic parameters for Mg and Na$^-$ were also employed in the simulation of NaPs and e$^+$Mg.

As to the positronic part of the trial wave function, this was obtained in a different way than before. In the case of

TABLE I. VMC and DMC energy and EA for the alkali atoms. All values in atomic units.

	^{2}S Li	^{1}S Li$^-$	^{2}S Na	^{1}S Na$^-$
$\langle E\rangle_{\mathrm{HF}}$[a]	-7.4184	-7.4282	-161.8589	-161.8547
$\langle E\rangle_{\mathrm{VMC}}$	$-7.4731(6)$[b]	$-7.4813(2)$[d]	$-162.0592(8)$	$-162.115(1)$
$\langle E\rangle_{\mathrm{DMC}}$	$-7.47802(4)$[c]	$-7.4985(2)$	$-162.2388(12)$	$-162.2579(9)$
$\mathrm{EA}_{\mathrm{VMC}}$	0.0082(6)[d]		0.056(1)	
$\mathrm{EA}_{\mathrm{DMC}}$	0.0205(2)		0.0191(15)	
$\mathrm{EA}_{\mathrm{exp}}$	0.023[e]		0.020 07(18)[e]	

[a] Reference 23.
[b] Reference 21.
[c] Reference 34.
[d] Reference 22.
[e] Reference 35.

LiPs and NaPs, we used the electronic density given by the SCF wave functions by Clementi and Roetti[23] for Li$^-$ and Na$^-$ to generate a frozen effective potential, built as the sum of the positron interaction with the nucleus and with the frozen electron density, in which the positron moves. The radial Schrödinger equation for e$^+$ was then solved using the grid method proposed by Tobin and Hinze,[25] and the numerical wave function was successively fitted with the model $\phi(r_+)=[1+(Z+a)r_+]e^{-ar_+}$, where Z is the nuclear charge and a is a fitting parameter. This simple model has the advantage to exactly fulfill the positron–nucleus cusp condition. As to the electron–positron correlation factor in $\Omega(\mathbf{r}_p, r_{p\nu})$,[8] for NaPs this was taken as the simple Jastrow $\exp[-0.5r_{+-}/(1+br_{+-})]$ with the correct cusp condition, and the parameter b was roughly optimized minimizing the fluctuation of the energy in short variational Monte Carlo (VMC) runs. No electron–positron correlation factor was introduced in the LiPs wave function. The functions $\phi(r_+)$ for e$^+$Be and e$^+$Mg were obtained using a similar procedure, with the only difference that the effective potential was built adding the polarization potential parametrized by Mitroy *et al.*[2] to the frozen potential obtained by the SCF wave functions.

The trial wave functions so obtained were successively employed to guide the DMC simulations. These were done using a population of 5000 configurations, and time steps ranging from 0.002 to 0.0003 hartree^{-1} depending on the system. Once again, we found that longer simulation time is needed for positronic complexes than for the parent systems in order to fully converge our results. We believe this outcome to be due to the necessity of sampling a larger volume of configurational space, and to wait for a time long enough to allow all the relevant electron density changes to take place.

A. Li, Li$^-$, Na, Na$^-$, Be$^+$, Be, Mg$^+$, and Mg

The VMC and DMC energy results for the parent Li,[34] Li$^-$, Na, and Na$^-$ systems are shown in Table I, and those for Be, Be$^+$, Mg$^+$, and Mg in Table II, together with the electron affinities (EA)[35] and ionization potentials (IP).[36] Since in this work we are mainly concerned with computing energy differences (i.e., PA and BE), we choose not to discuss absolute energies for these systems, but to concentrate only on EAs and IPs.

TABLE II. VMC and DMC energy and IP for the alkali-earth atoms. All values in atomic units.

	^{2}S Be$^+$	^{1}S Be	^{2}S Mg$^+$	^{1}S Mg
$\langle E\rangle_{\mathrm{HF}}$[a]	-14.2774	-14.5567	-199.3715	-199.6146
$\langle E\rangle_{\mathrm{VMC}}$	$-14.3191(2)$[b]	$-14.6332(8)$[c]	$-199.6828(7)$	$-199.9145(16)$
$\langle E\rangle_{\mathrm{DMC}}$	$-14.3248(1)$	$-14.6579(2)$	$-199.7555(7)$	$-200.0319(10)$
		$-14.6670(1)$[d]		
$\mathrm{IP}_{\mathrm{VMC}}$		0.3141(8)		0.2317(16)
$\mathrm{IP}_{\mathrm{DMC}}$		0.3331(2)		0.2764(12)
		0.3422(2)[d]		
$\mathrm{IP}_{\mathrm{exp}}$		0.3425[e]		0.2810[e]

[a] Reference 23.
[b] Reference 22.
[c] Reference 21.
[d] Two configuration trial wave function: $\Psi_T=c_1|1s^22s^2|+c_2(|1s^22p_x^2|+|1s^22p_y^2|+|1s^22p_z^2|)$.
[e] Reference 36.

As to the two alkali atoms, whereas the statistical error bar of the EA for Na nicely overlaps with the experimental value, the EA for Li is smaller by 0.0025(2) hartree. A similar behavior, i.e., a more accurate result for the larger system, is present also for the IP of Be and Mg, the errors being respectively 0.0094(2) and 0.0046(12) hartree. These findings can be rationalized recalling the near degeneracy of the ns^2 and np^2 configurations for the two valence electron systems, i.e., that the ground state requires a two-configuration wave function in order to be described qualitatively in a correct way. This is well known both in the field of *ab initio* calculations and of the QMC ones. As far as DMC is concerned, it is now established that for these systems, although the net effect varies from one to another, a single configuration wave function may generate poor nodal surfaces, while a two-configuration one has nodal surfaces closer to the exact ones. To show that this is just the case, Table II also contains the total energy and the IP for Be computed by means of a DMC simulation where the two-configuration state function $\Psi_T=c_1|1s^22s^2|+c_2(|1s^22p_x^2|+|1s^22p_y^2|+|1s^22p_z^2|)$ was used as trial function. This was obtained by means of a MC-SCF calculation on the Be atom (c_1/c_2 being 5.557), and its DMC energy ($-14.6670(1)$ hartree) compares favorably with the accurate ECG result by Komasa *et al.*, $-14.667\,355\,021$ hartree.[26] Using this DMC result, the nodal error in the computed IP decreases from 0.0094(2) to 0.0003(1) hartree, therefore indicating the strong multiconfigurational character of the Be ground state. Also, to check if it were possible to improve on this estimate, we ran a few more simulations slightly changing the c_1/c_2 ratio without seeing any statistically meaningful change in the total energy.

From Tables I and II, it can be inferred that the net effect of using a single determinant wave function is to artificially raise the DMC energy for Li$^-$, Be, and Mg, with respect to the parent Li, Be$^+$, and Mg$^+$, and therefore to decrease both EA and IP.

Besides, it is known that for these systems a single configuration wave function gives a much larger polarizability than the exact one, an effect that is rationalized on the basis of the second-order perturbation theory as deriving from a

TABLE III. Energy, positron affinity, and positronium binding energy for LiPs, NaPs, e^+Be, and e^+Mg. All quantities in atomic units.

	$\langle E\rangle$	P*A*	BE
	LiPs		
DMC one-conf V_{lb}[a]	$-7.7368(5)$	0.2385(6)	0.0093(5)
DMC one-conf V_C[b]	$-7.7376(8)$		0.0096(8)
DMC Jastrow[c]	$-7.73959(6)$		0.011 53(6)
SVM[d]	-7.740208		0.012 148
FCSVM[d]			0.012 341
	NaPs		
DMC one-conf [a]	$-162.498(1)$	0.240(1)	0.009(1)
FCSVM[d]			0.008 419
	e^+Be		
DMC one-conf [a]	$-14.6609(3)$	0.0037(2)	
SVM[d]	-14.669042	0.001 687	
FCSVM[d]		0.003 147	
Extrapolated CI[e]		0.003 083	
	e^+Mg		
DMC one-conf [a]	$-200.0486(9)$	0.0168(14)	
FCSVM[d]		0.015 612	
MBPT [f]		0.0362	
Extrapolated CI[g]		0.01615	

[a] This work.
[b] Reference 5.
[c] Reference 7.
[d] Reference 11.
[e] Reference 28.
[f] Reference 12.
[g] Reference 29.

reduced energy difference between the *S* state described by the wave function and the first excited *P* state.

These two artificial effects, i.e., the rise of the ground state energy of the parent system due to the wrong nodal surface of the single determinant trial wave function and the larger polarizability, are expected to play a role in defining the overall accuracy of DMC calculations on these positronic complexes as suggested by the model system results presented in Ref. 27.

B. LiPs and NaPs

Turning now to the positronium complexes, Table III shows the numerical results obtained by the DMC simulations, together with recent results.[11,12,28,29]

As already discussed in the Introduction, the leptonic structure and BE of many Ps complexes should be fairly insensitive to the analytical form of the positron–electron interaction close to the coalescence point. To check if this hypothesis is correct, in the LiPs complex we substituted the positron-electron Coulomb potential $V_C(r_{+-})$ with the lower bounded $V_{lb}(r_{+-})$,

$$V_C(r_{+-})\simeq V_{lb}(r_{+-})=-\frac{[1-\exp(-\gamma r_{+-})]}{r_{+-}}, \tag{3}$$

where γ is an adjustable parameter upon which the accuracy of our approximation is dependent. Whereas V_{lb} behaves as $-1/r$ for large r, therefore mimicking the Coulomb interaction, close to $r=0$ it follows $-\gamma(1-\gamma r/2)$. The effect of this substitution on the total energy of Ps can be estimated by means of the first-order perturbation theory to be $E_0^1(\gamma)=(1+\gamma)^{-2}/2$, showing that it can be reduced at will simply increasing γ. The second-order correction coming from an excited *S* state is estimated to be much smaller and to behave asymptotically like γ^{-4}.

The result for the DMC simulation carried out with the modified potential and $\gamma=30$ is reported in Table III, together with the values computed in Refs. 5 and 7. Here, the $\gamma=30$ value was chosen on the basis of the first-order difference estimate in order to have its value smaller than the statistical error bar of the result reported in Ref. 5. The agreement with the DMC total energy from Ref. 5, computed using the Coulomb potential and the same electronic part of the wave function, is quite good. Their difference, 0.0008(9) hartree, is inside the combined statistical error and overlaps with the first-order estimate $E_0^1(30)=0.000\,52$ hartree for the change in the Ps energy. The same is also true for the DMC BE estimates shown in Table III when the first-order corrected Ps energy (i.e., $-0.249\,48$ hartree) is used as reference. Conversely, the approximate total energy is higher than the one from Ref. 7, $-7.739\,59(6)$ hartree, where a different trial wave function was used to define the nodal surfaces. The difference between the two trial functions fully accounts for the difference in total energy, the lower one being the most accurate one, and in BE [0.0093(5) and 0.01153(6) hartree[7]]. It is interesting to notice that the difference between the two BEs, 0.0022(5) hartree, is statistically equal to the error in the EA, namely 0.0025(2) hartree, suggesting this last quantity to be responsible for the difference in total energy.

The comparison between the results obtained using the same nodal surfaces indicates that the proposed approximation for the positron–electrom potential may be useful to compute Ps BE to neutral open shell systems without the necessity of devising and optimizing complicated analytical wave functions, but simply letting the DMC to do the ‘‘dirty’’ work. Here, it is worth to mention that such an approximation may degrade in performance in the case of Ps containing complexes for which the EA of the parent system is quite large, e.g., PsF, PsCl, and PsBr. These exotic compounds are more correctly described by the superposition between the aforementioned van der Waals (A plus Ps) picture and an ionic one (A^- plus e^+) in which the positron is orbiting around a compact anion, as suggested by the large BE obtained in Refs. 5 and 30.

As to NaPs, this is the first all-electron estimate of its energy and related quantities. This calculation has two main goals: testing whether DMC could deal with second row positronic complexes, as well as delivering an independent estimate of its Ps BE without the frozen core approximation. Not surprisingly, our DMC estimate for BE, 0.009(1) hartree, nicely contains within its error bar the frozen core stochastic variational minimization (FCSVM) one by Mitroy and Ryzhikh,[11] 0.008 419 hartree. Having previously shown that a single determinant trial function allows us to compute EA in good agreement with the experiment, and being the binding mechanism of Ps to Na primarily driven by the Ps polarization due to the atomic field, we believe our NaPs result to be statistically exact and to be a direct indication of the accuracy of the frozen core approach in computing BE. Specifically, the weakest part of the FCSVM method, i.e., the core polarization potential, seems to be an accurate approximation, at least for the level of accuracy we can get at present.

C. e^+Be and e^+Mg

Our estimate of the PA result for Be (see Table III), obtained using a single configuration function for the electronic part, appears to be in fairly good agreement with the latest result by Mitroy and Ryhzhik[11] computed using the frozen core approximation. However, as already pointed out for the IP of Be, the error on the PA due to the near degeneracy of the $2s^2$ and $2p^2$ configurations might be of some importance. To check, we ran a similar simulation using the two configuration state function for the electronic part already used for the Be ground state. The total energy and the PA results, respectively $-14.6682(4)$ and $0.0012(4)$ hartree, do indicate that the effect is quite pronounced, accounting for a 68% decrease of the PA with respect to the single configuration result. This value is less than half of the PA estimated by the FCSVM method, while it is in agreement with the older all-electron SVM estimate, namely 0.001 687. However, this last value is far from being converged, as clearly stated by the authors,[11] so that in our opinion this agreement is fortuitous. The FCSVM result for the PA is supported by the extensive CI calculations presented in Ref. 28. They display a similar, although magnified, effect on going from a (basically) single reference (i.e., Hartree–Fock type) to a multireference description of the electronic part.

Even if it has a somehow unexpected magnitude, the change in the DMC PA on going from a single- to a multireference trial wave function can be rationalized on the basis of the changes in both the IP and the polarizability. As well clarified by calculations on simple models,[27] for a system having an IP larger than 0.25 hartree, the PA is expected to decrease when the IP increases or the polarizability decreases due to the competition between the nucleus and the positron in binding the valence electrons. This idea also explains the difference in magnitude of the PA changes found in DMC and CI calculations: the DMC calculation using only one determinant gives an IP value closer to the experimental one than the HF wave function. After introducing the double excitations in the electronic part of the CI, the computed PA drops to a value in much better agreement with the extrapolated full CI result.

Since for e^+Be we used the c_1/c_2 ratio of the electronic wave function of Be, in order to explore the dependence of the DMC energy on the relative weight of the two configurations, we ran other DMC simulations for e^+Be with the ratio c_1/c_2 in the range [5.001,16.671]. The total energy results, together with the PAs computed using the two-configuration DMC energy from Table II, are presented in Table IV. The results computed with c_1/c_2 in the range [5.001,6.668] are statistically indistinguishable, showing therefore a scarce sensitivity of the total energy to this parameter and to the change in the nodal location. For $c_1/c_2 > 6.668$, the total energy increases as expected, due to the larger single configurational character, therefore decreasing the computed PA values.

TABLE IV. Energy of e^+Be and PA for various two configuration trial functions. Total energy of Be is taken as the two configuration DMC result from Table II. All quantities in atomic units.

c_1/c_2	$\langle E\rangle_{DMC}$	PA
5.001	−14.6681(5)	0.0011(5)
5.279	−14.6677(4)	0.0007(4)
5.557	−14.6682(4)	0.0012(4)
5.835	−14.6682(6)	0.0012(6)
6.668	−14.6688(4)	0.0016(4)
8.336	−14.6676(4)	0.0006(4)
16.671	−14.6658(5)	−0.0012(5)

In conclusion, we feel hard-pressed at the present time to explain the difference between our DMC results and the FCSVM one,[11] unless some residual inaccuracy in the nodal surfaces for DMC, or a major effect due to the core polarization potential for FCSVM are present. The last possibility could be safely discarded if one notices that the difference between the FCSVM PAs computed in Ref. 31 with and without the polarization potential is only 0.000 067 hartree. Conversely, the CI results[28] show that the PA depends largely on the quality of the electronic part of the wave function. In fact, introducing the possibility of a double electronic excitation to *d* orbitals allowed the authors of Ref. 28 to increase the CI PA by roughly 20%! In order to clarify this issue, we are currently planning to run a Green's function Monte Carlo simulation employing the nodal release technique and a more accurate trial wave function, and to project the sampled electron density matrix of the system in order to study its natural orbital CI expansion.

Turning to e^+Mg, our total energy result, $-200.0486(9)$ hartree, allows us to compute a PA of 0.0168(14) hartree. This value is in agreement with the FCSVM result (0.015 612 hartree),[11] and with a recent CI estimate by Bromley and Mitroy, namely 0.016 15 hartree.[29] On the contrary, it is less than half the MBPT one, 0.0362 hartree.[12] However, our calculation was carried out using a single determinant wave function to define the nodal surfaces, so that, according to our Be findings, one might suspect the DMC PA to be slightly larger than the exact one. Being the e^+Mg simulation computationally expensive, we address this issue on the basis of the detailed CI PA results by Bromley and Mitroy,[29] as well as of the model alkali atom results presented in Ref. 27. Similarly to e^+Be, in the CI calculations on e^+Mg the PA shows a net decrease (from 0.026 68 to 0.013 885 hartree) upon introducing double excitations. Parallel, steep changes in value of both Mg IP (from 0.2512 to 0.2803 hartree) and dipole polarizability (from 98.417 to 70.232 a.u.) are observed substituting the trial HF wave function with the $L_{int}=1$ CI expansion (i.e., the first containing the excitation to the $3p^2$ configuration). Here, L_{int} is a parameter used to control the length of the CI expansion by constraining the possible electronic excitation to follow the rule $\min(l_1,l_2)\leqslant L_{int}$, where l_1 and l_2 are the electronic orbital angular momenta. These results support a strong correlation between PA and IP or polarizability.[27]

From the tables of Ref. 29, we computed the $L_{int}=0$ and $L_{int}=3$ IPs to be 0.251 267 and 0.280 314 hartree and the

PAs to be 0.026 680 and 0.014 509 hartree. The energies for Mg and e^+Mg were computed by the same wave function for the electronic part. Assuming for Mg a linear dependence of PA on IP, the slope of the stright line is computed to be −0.4176. Multiplying the result for the slope (−0.4176) by the difference between the DMC IP and the experimental value, namely 0.0046(12) hartree, we obtain 0.0019(5) hartree as estimate of the DMC PA error. There are two possible sources of error in this estimate, namely the nonlinearity of PA versus IP (for instance see Ref. 27) and the incomplete recovering of the positron–electron correlation energy due the finite number of positron–electron double excitations in the CI expansion for a chosen L_{int}. As to the behavior of PA versus IP, the data from Ref. 29 for $L_{\mathrm{int}}=1$ and $L_{\mathrm{int}}=2$ show that PA(IP) has a positive second derivative: so, a straight line connecting $[\mathrm{IP}_1,\mathrm{PA}(\mathrm{IP}_1)]$ to $[\mathrm{IP}_2,\mathrm{PA}(\mathrm{IP}_2)]$ will always overestimate the PA value inside the $[\mathrm{IP}_1,\mathrm{IP}_2]$ interval (see also Ref. 32). Conversely, it is much more difficult to draw conclusions about how the error in the positron–electron correlation energy changes upon changing the IP of the electronic models. We believe it is roughly correct to expect the error to be larger (both in absolute and relative value) for the single configuration model than for the multireference one, so that the computed slope is probably an underestimate, although not a large one. Concluding, we feel safe indicating a possible error of the e^+Mg PA similar to the quoted statistical error bars, although these two quantities are completely uncorrelated. In turn, this conclusion appears to definitively indicate the MBPT PA to be too large. A detailed account of the possible reasons for such a result was already given.[11]

III. DISCUSSION AND CONCLUSIONS

The diffusion Monte Carlo method has been used in this work to compute total energy, positron affinity, and positronium binding energy for the positronic systems LiPs, NaPs, e^+Be, and e^+Mg. While NaPs, e^+Be, and e^+Mg have been simulated in the well-known framework of the all-electron fixed-node approach, the additional approximation of substituting the positron–electron Coulomb potential with the one in Eq. (3) has been introduced in the LiPs case. As far as LiPs is concerned, the accurate agreement of our approximate result with the one previously presented in Ref. 5 seems to indicate that the substitution of the potential may represent a valid tool to tackle open shell Ps-containing systems without the burden of optimizing accurate and expensive trial wave functions. As promising candidates for the application of this approximation, we mention the Ps substituted alkanes, alkenes, and alkines (e.g., $PsCH_3$, PsC_2H_3, and PsC_2H).

As to NaPs, the good agreement between our FN-DMC EA result and the experimental one allows us to consider the DMC BE as having a total accuracy comparable to its statistical error bar. This is also supported by the good agreement with the frozen-core ECG result in Ref. 11. A similar statement could be made for the PA of e^+Mg, for which a value of roughly 0.016 hartree is getting a large consensus from completely different computational methods. As to the PA of e^+Be, there are still some discrepancies from our best energy PA value and the accurate frozen-core ECG result[11] that we feel deserve a more careful investigation. These findings strongly push towards a nodal release approach to tackle the issue. It is also worth noticing that a similar effect, although relatively less important, is present in the e^+Mg case.

Besides being interesting for themselves, the computed all-electron FN-DMC results allow us to speculate about the ground state properties of some small positron–molecule complexes. Recently,[33] we have proposed to study the ground state of some diatomic molecules, namely e^+Li_2 and e^+Be_2, in order to explore the possibility of seeing a behavior of the annihilation rate Γ versus R different from the e^+LiH case. More specifically, we suggested that there should be a range of nuclear distances where Γ is larger than the one of e^+Li or e^+Be due to the interaction of the positron with the electronic density of two atoms. Here, we offer an update with respect to the two positron–alkali systems e^+Li_2 and e^+Na_2, and we also add some other consideration on e^+Be_2 and e^+Mg_2.

In a previous work,[33] we implicitly assumed that the correct dissociation pattern for e^+A_2 ($A=$Li, Na) were e^+A plus A, while it is now shown to be APs plus A^+. Using the FCSVM BE's for APs shown in Table III together with the BE for e^+Li, 0.002 477 hartree, and for e^+Na, 0.000 473 hartree, from Ref. 2, it is easy to compute the energy difference ΔE between the two dissociation patterns as the energy released in the process

$$e^+A+A\rightarrow \mathrm{Ps}+A+A^+\rightarrow A\mathrm{Ps}+A^+ \tag{4}$$

simply using

$$\Delta E(A)=BE(A\mathrm{Ps})-BE(e^+A). \tag{5}$$

It turns out $\Delta E(\mathrm{Li})=0.009\,86$ hartree, and $\Delta E(\mathrm{Na})=0.007\,95$ hartree, indicating the e^+A_2 asymptotic breakup to be similar to the e^+LiH ones, namely PsH plus Li^+. From these results, one might be tempted to predict an asymptotic Γ versus R behavior for e^+A_2 where the polarization of APs, induced by A^+, decreases the Γ upon decreasing the nuclear distance R. However, this conclusion must be checked by numerical calculations since the two closest breakup patters, namely e^+Li plus Li, and Li plus Li^+ plus Ps, just lay few mhartrees above the lowest one.

Moreover, the finding that the LiPs plus Li^+ breakup has an energy below the one of Li_2 at the equilibrium distance (a DMC estimate at the nuclear distance 5.051 bohr is −14.9938(1) hartree as given in Ref. 37), also indicates the possibility of forming LiPs upon collision between a swarm of positrons and lithium dimer gas. However, since also other processes are energetically allowed, e.g., the formation of Li_2^+ plus Ps, a numerical calculation of the reactive cross sections must be carried out in order to explore if such a possibility is practically feasible.

Turning now to e^+Be_2 and e^+Mg_2, the overall picture for these two systems appears much less complicate than for e^+A_2 thanks to their larger IPs which make any ionic dissociation pattern much higher in energy than the e^+A plus A one.

Although we feel safe in indicating these systems to be bound with high probability, the mechanism responsible for the binding might be quite complicated, as suggested by the small binding energy of the two dimers, respectively

0.003 60 and 0.001 93 hartree for Be_2 (Ref. 38) and Mg_2.[39] Specifically, due to the fact that the atomic PA is of the same or larger order of magnitude of the dimer binding energy, one should not expect such a mechanism to be a simple sum of the different energetic contributions. Although we would expect a complicated dynamical interplay between nuclear and positronic motion, a semiquantitative prediction could, nevertheless, be obtained by accurately computing the interaction energy between, let us say, e^+Be and Be for various nuclear distances. We hope to see such an exploration carried out in the near future.

ACKNOWLEDGMENTS

The authors would like to thank Jim Mitroy for many useful comments on positron systems, for the help in improving the manuscript, and for giving access to the CI results on e^+Mg before publication. Also, valuable discussions on reactive scattering with Rocco Martinazzo are acknowledged. Financial support by the Universita' degli Studi di Milano is gratefully acknowledged. The authors are indebted to the Istituto CNR per le Scienze e Tecnologie Molecolari (ISTM) for grants of computer time.

[1] D. M. Schrader, J. Moxom, and G. G. Ryzhikh, in *New Directions in Antimatter Chemistry and Physics*, edited by C. M. Surko and F. A. Gianturco (Kluwer Academic, Dordrecht, 2001), p. 263.
[2] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, in *New Directions in Antimatter Chemistry and Physics*, edited by C. M. Surko and F. A. Gianturco (Kluwer Academic, Dordrecht, 2001), p. 199.
[3] M. Mella, S. Chiesa, D. Bressanini, and G. Morosi, in *New Directions in Antimatter Chemistry and Physics*, edited by C. M. Surko and F. A. Gianturco (Kluwer Academic, Dordrecht, 2001), p. 235.
[4] K. Strasburger, Chem. Phys. Lett. **253**, 49 (1996).
[5] D. Bressanini, M. Mella, and G. Morosi, J. Chem. Phys. **108**, 4756 (1998).
[6] D. Bressanini, M. Mella, and G. Morosi, J. Chem. Phys. **109**, 5931 (1998).
[7] M. Mella, G. Morosi, and D. Bressanini, J. Chem. Phys. **111**, 108 (1999).
[8] D. Bressanini, M. Mella, and G. Morosi, J. Chem. Phys. **109**, 1716 (1998).
[9] M. Mella, G. Morosi, D. Bressanini, and S. Elli, J. Chem. Phys. **113**, 6154 (2000).
[10] M. Mella, D. Bressanini, and G. Morosi, J. Chem. Phys. **114**, 10579 (2001).
[11] J. Mitroy and G. G. Ryzhikh, J. Phys. B **34**, 2001 (2001).
[12] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and W. A. King, Phys. Rev. A **52**, 4541 (1995).
[13] S. Chiesa, M. Mella, and G. Morosi, Phys. Rev. A (submitted).
[14] S. Chiesa, M. Mella, and G. Morosi (unpublished).
[15] P. K. Sinha, P. Chaudhuri, and A. S. Ghosh, Phys. Rev. A **65**, 022509 (2002).
[16] G. G. Ryzhikh and J. Mitroy, J. Phys. B **31**, L401 (1998).
[17] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry*, 1st ed. (World Scientific, Singapore, 1994).
[18] D. M. Ceperley and B. J. Alder, J. Chem. Phys. **81**, 5833 (1984).
[19] A. Lüchow and R. F. Fink, J. Chem. Phys. **113**, 8457 (2000).
[20] M. Snajdr and S. M. Rothstein, J. Chem. Phys. **112**, 4935 (2000).
[21] K. E. Schmidt and J. W. Moskowitz, J. Chem. Phys. **93**, 4172 (1990).
[22] J. W. Moskowitz and K. E. Schmidt, J. Chem. Phys. **97**, 3382 (1992).
[23] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).
[24] X. Lin, H. K. Zhang, and A. M. Rappe, J. Chem. Phys. **112**, 2650 (2000).
[25] F. L. Tobin and J. Hinze, J. Chem. Phys. **63**, 1034 (1975).
[26] J. Komasa, W. Cencek, and J. Rychlewski, Phys. Rev. A **52**, 4500 (1995).
[27] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, J. Phys. B **32**, 2203 (1999).
[28] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **65**, 012505 (2002).
[29] M. W. J. Bromley and J. Mitroy, Phys. Rev. A (to be published).
[30] D. M. Schrader, T. Yoshida, and K. Iguchi, J. Chem. Phys. **98**, 7185 (1993).
[31] G. G. Ryzhikh, J. Mitroy, and K. Varga, J. Phys. B **31**, 3965 (1998).
[32] J. Mitroy, J. Phys. B **33**, 5307 (2000).
[33] M. Mella, S. Chiesa, and G. Morosi, J. Chem. Phys. **116**, 2852 (2002).
[34] A. Lüchow and J. B. Anderson, J. Chem. Phys. **105**, 7573 (1996).
[35] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, J. Phys. Chem. Ref. Data Suppl. **17**, 1 (1988).
[36] H. Hotop and W. C. Lindberg, J. Phys. Chem. Ref. Data **14**, 731 (1985).
[37] C. Filippi and C. Umrigar, J. Chem. Phys. **105**, 213 (1996).
[38] I. Cernusak, J. Noga, G. H. F. Diercksen, and A. J. Sadley, Chem. Phys. **125**, 255 (1988).
[39] E. Czuchaj, M. Krosnicki, and H. Stoll, Theor. Chem. Acc. **107**, 27 (2001).