Ab initio quantum Monte Carlo study of the binding of a positron to alkali-metal hydrides

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Quantum Monte Carlo methods are used to investigate the binding of a positron to the alkali-metal hydrides, XH (X = Na and K). We obtain positron affinities for the NaH and KH molecules of 1.422(10) eV and 2.051(39) eV, respectively. These are considerably larger than the previous results of 1.035 eV and 1.273 eV obtained from multireference single- and double-excitation configuration interaction calculations. Together with our previous results for [LiH;e$^+$] [Y. Kita *et al.*, J. Chem. Phys. **131**, 134310 (2009)], our study confirms the strong correlation between the positron affinity and dipole moment of alkali-metal hydrides. © *2011 American Institute of Physics*. [doi:10.1063/1.3620151]

I. INTRODUCTION

The positron (e$^+$) is the anti-particle of the electron (e$^-$) and therefore has the same mass and spin, but the opposite charge. Positrons injected into a liquid or solid induce processes such as ionization or electronic excitation of atoms/molecules, the formation of a metastable bound state of a positron and an electron (positronium or Ps), and the formation of positronic compounds which are bound states of a positron and atoms or molecules, etc., before the positron undergoes pair-annihilation with an electron.[1,2] A number of positron annihilation experiments on molecular species have recently been reported by Surko and co-workers.[3–5] They have measured positron binding energies (positron affinity, PA) for many molecular species such as alkanes and aromatic molecules, etc., and have discussed the relationship between the positron binding and the properties of the parent molecule. However, since it is difficult to measure the properties of positronic compounds such as the electronic/positronic structures, the stable geometry, etc., theoretical calculations for positronic compounds have an important role to play.[6–15]

Theoretical analyses of positronic compounds have shown that an accurate description of correlation effects, especially electron-positron correlation, is indispensable for obtaining reliable values of the PA and other properties.[6–15] For example, Hartree-Fock theory gives too small a binding energy for Ps and too small a PA for even the simplest positronic compound, [H$^-$;e$^+$].[9] Conventional quantum chemical approaches based on *ab initio* molecular orbital methods such as many-body perturbation theory[10] and CI methods,[9] etc.,

are frequently used to describe correlation in positronic compounds. It is, however, desirable for the electronic and positronic wave functions to be constructed within a more sophisticated theoretical framework, because even full-CI calculations using H-centered Gaussian type basis functions have not given accurate results for the [H$^-$;e$^+$] system.[9]

Two accurate theoretical approaches are known for studying positronic compounds: variational calculations with explicitly correlated Gaussian (ECG) wave functions[11–13] and *ab initio* quantum Monte Carlo (QMC) calculations.[14,15] Although variational calculations with ECG wave functions have given the most accurate results obtained to date for small systems, this method cannot in practice be applied to large systems because the required computational effort grows very rapidly with the number of particles. Two types of QMC approach are typically used: the variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) methods.[16] The DMC method is also variational in the sense that the DMC energy is always higher than or equal to the exact energy and, in addition, it is always lower than or equal to the VMC energy calculated with the same trial wave function. The cost of *ab initio* QMC calculations grows much less rapidly with the number of particles than in CI and ECG methods, and they are therefore well suited for applications to positronic complexes.

Theoretical work by Crawford[17] suggests that a molecule with a dipole moment (DM) larger than a critical value of 1.625 D is able to bind either an e$^-$ or an e$^+$ in its electrostatic field. This estimate is based on the long-range form of the electrostatic potential of a dipole. Weakly bound positronic molecular states have large positronic orbitals and the short-range repulsion between the positron and nuclei does not necessarily prevent the formation of a positronic molecular complex. In a previous DMC study[18] we calculated the PA of the

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hydrogen cyanide (HCN) molecule, whose dipole moment of 3.312 D is about twice the critical value, finding it to be twice the value obtained in a previous CI calculation,[19] which gives strong support for the binding of a positron to a HCN molecule. Recently, Buenker *et al.* have analyzed positron binding to the alkali-metal hydrides, XH (X = Li, Na, K, etc.), using an *ab initio* multireference single- and double-excitation configuration interaction (MRD-CI) method.[20, 21] Although they obtained PAs for these molecules which are larger than the Hartree-Fock (HF) values and demonstrated the strong correlation between the PAs and dipole moments of the alkali-metal hydrides, the convergence of CI expansions is known to be slow.

In this study, we have investigated the positron binding to the alkali-metal hydrides XH (X = Na and K) using *ab initio* DMC methods to evaluate accurate PAs.

II. COMPUTATIONAL DETAILS

We performed all-electron+positron VMC and DMC for NaH and KH positronic complexes, which contain 13 and 21 quantum particles, respectively. Slater-Jastrow trial wave functions were used with orbitals generated at the HF level of multi-component molecular orbital (MC_MO) theory,[10] in which electronic and positronic molecular orbitals are solved simultaneously using conventional self-consistent-field procedures. The calculations were performed using the optimized inter-nuclear separations obtained from the MRD-CI calculations by Buenker *et al.*,[20] that is, 1.887 Å for NaH, 2.167 Å for [NaH;e$^+$], 2.247 Å for KH, and 2.678 Å for [KH;e$^+$]. Gaussian type functions (GTFs) of 6-311++g($3d2f$, $3p2d$) and [$15s15p6d2f$] quality were employed for the electronic and positronic basis sets, respectively. Note that we have not included the diffuse positronic functions in the electronic basis in the present calculations contrary to the previous MRD-CI calculations.[20] The exponents of the positronic GTFs were chosen to form even-tempered sets. The smallest exponents for the s-, p-, d- and f-type positronic GTFs were 0.00010, 0.00010, 0.001, and 0.001 a.u., respectively, because very diffuse-type GTFs are required to represent the weakly bound positron orbital. The Jastrow factor contained two- and three-body terms, that is, electron-electron, electron-nucleus, electron-positron, positron-nucleus, and electron-electron-nucleus terms.[22] Three-body electron-nucleus-nucleus terms were not used as they are normally unimportant. The wave function contained 85 optimizable parameters for NaH, 136 for [NaH;e$^+$], 73 for KH, and 124 for [KH;e$^+$]. The parameters in the Jastrow factors were optimized by minimizing either the reweighted[23, 24] or the un-reweighted[25] variances of the energy.

We performed DMC calculations with four time steps $\Delta\tau$ ranging from 0.001 to 0.007 a.u. for [NaH;e$^+$], and from 0.002 to 0.008 a.u. for [KH;e$^+$]. The target population of walkers was chosen to be 5000 for the [NaH;e$^+$] system and 8000 for [KH;e$^+$]. These numbers are sufficient to make the population control error completely negligible. We have used the CASINO code[26] for all of our QMC calculations.
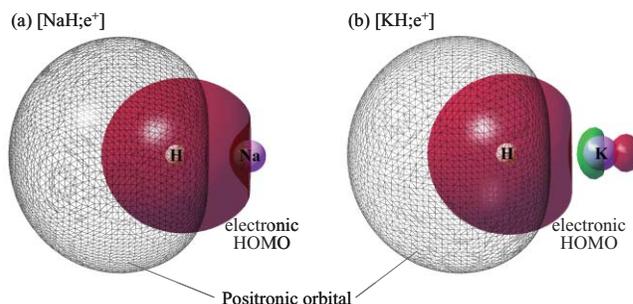
FIG. 1. The electronic and positronic molecular orbitals of (a) [NaH;e$^+$] and (b) [KH;e$^+$], obtained at the Hartree-Fock level using the MC_MO method. Contours of isovalue 0.015 are drawn. The meshed region denotes the contour of the positronic orbital, while the red and green regions denote contours of the positive and negative parts of the electronic HOMO, respectively. The percentages of the positron charge within the meshed region are 63.3% for [NaH;e$^+$] and 75.3% for [KH;e$^+$].

III. RESULTS AND DISCUSSION

Figure 1 shows the electronic and positronic molecular orbitals of [NaH;e$^+$] and [KH;e$^+$] obtained at the Hartree-Fock level using the MC_MO method. The positronic orbitals in both systems are much more diffuse than the highest-occupied electronic molecular orbital (HOMO) due to the strong repulsion between the nuclei and the positron. In agreement with our previous calculations for [LiH;e$^+$],[18] the positronic orbitals of [NaH;e$^+$] and [KH;e$^+$] are also situated at the H-end of the molecule due to the negative charge on the hydrogen atom.

Table I gives the total energies of NaH and [NaH;e$^+$] obtained from our QMC calculations. The values from the MRD-CI calculations of Buenker *et al.*[20] are also given. For both systems, our VMC energies are substantially lower than both the Hartree-Fock and MRD-CI energies, where a frozen core approximation was employed for the Na 1s electrons in the MRD-CI calculations. DMC calculations use a short-time approximation and the energies should be extrapolated to zero time step. The variation of the DMC energy with time step is smooth and the extrapolation is well-behaved. The DMC energies of NaH and [NaH;e$^+$] at a time step of $\Delta\tau = 0.001$ are, respectively, 0.0013(2) and 0.0009(4) a.u. lower than the values extrapolated to zero time step (see Table I). These energy differences are comparable with the scale of interest but, as explained below, the time step dependence of the difference

TABLE I. Total energies of NaH and [NaH;e$^+$] from various calculations. The PAs are also given.

Method		Total energy (a.u.)		
		NaH	[NaH;e$^+$]	PA (eV)
HF		−162.380271	−162.389916	0.262
VMC		−162.721(2)	−162.751(2)	0.80(7)
FN-DMC	$\Delta\tau = 0.001$	−162.809260(89)	−162.86113(17)	1.412(5)
	extrapolated	−162.80798(18)	−162.86025(35)	1.422(10)[a]
MRD-CI	(Ref. 20)	−162.5653	−162.60332	1.035

[a]The extrapolated PA and its uncertainty due to time step bias are estimated from a quadratic fit to the time step data shown in Fig. 2.
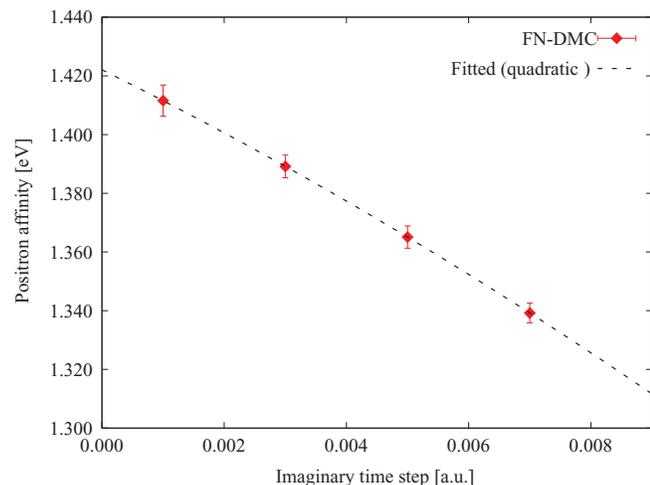
FIG. 2. Time step dependence of the PA of the NaH molecule ($PA_{NaH} = E_{NaH} - E_{[NaH;e^+]}$). The standard error of each DMC energy is shown and the dashed line is a quadratic fit to the DMC data.

between the energies of NaH and [NaH;e$^+$], which gives the PA, is much smaller.

To compare the accuracy of our DMC calculation for NaH with the MRD-CI calculation of Buenker et al.,[20] we estimated the percentages of the correlation energies retrieved. We used an accurate value of the non-relativistic energy of the Na atom of -162.2546 a.u.,[27] the experimental dissociation energy of the NaH molecule of 0.07206 a.u.,[28] the HF energy of a Na atom of -161.8587 a.u.,[27] and the HF energy of the NaH molecule of -162.3923 a.u.[29] Using this data we deduce that our DMC calculation for NaH retrieves 95.7% of the total correlation energy, which is considerably larger than the 39.8% retrieved in the MRD-CI calculation. We note that this large difference is mainly due to the frozen core approximation used for the Na 1s electrons in the MRD-CI calculations.

Table I gives the PA of the NaH molecule and Fig. 2 shows the time step dependence of the PA. The VMC value of the PA of 0.80(7) eV is slightly smaller than the MRD-CI value of 1.035 eV and is further from the DMC result, even though VMC gives a lower variational energy than MRD-CI. Such a result is typical of VMC calculations as the inherent bias due to the choice of trial wave function can be substantial. DMC energies are much less sensitive to the trial wave function. The time-step-extrapolated DMC value of the PA of 1.422(10) eV is substantially larger than the VMC value of 0.80(7) eV. Even at the largest time step used of $\Delta\tau = 0.007$ the DMC value of the PA of the NaH molecule is 1.339(4) eV, which is close to the extrapolated value. The PA increases by only 0.00037(4) a.u. (0.01 eV) on going from the value for $\Delta\tau = 0.001$ to the extrapolated value, see Fig. 2. This cancellation of time step errors in the NaH molecule and positronic complex occurs because of the similarity of the two systems and because the time step error arises mainly from the core orbitals, which vary rapidly in space but are very similar in the molecule and positronic complex. We conclude that the time step error in our extrapolated DMC value of the PA of NaH is smaller than 0.01 eV.

TABLE II. Total energies of KH and [KH;e$^+$] from various calculations. The PAs are also given.

| Method | | Total energy (a.u.) | | PA (eV) |
		KH	[KH;e$^+$]	
HF		-599.680525	-599.703078	0.614
VMC		$-600.072(3)$	$-600.130(3)$	1.6(1)
FN-DMC	$\Delta\tau = 0.002$	$-600.43605(11)$	$-600.51044(17)$	2.024(6)
	extrapolated	$-600.40028(39)$	$-600.47638(57)$	2.051(39)[a]
MRD-CI	(Ref. [20])	-600.069358	-600.116143	1.273

[a]The value of the PA is taken to be the average of those from the linear and quadratic fits at zero time step shown in Fig. 3. The uncertainty in the PA due to time step bias is estimated from the difference between the values of the PA obtained from the two extrapolations.

When the ionization potential (IP) of the parent molecule is greater than the formation energy of positronium (Ps) of 6.8 eV, the structure of the [NaH;e$^+$] system is closer to the configuration of NaH $\cdots$ e$^+$ rather than NaH$^+$ $\cdots$ Ps, due to the strong attraction of the electron to the parent molecule. The first IP of NaH is estimated to be 7.037 eV, which is a little larger than 6.8 eV. To estimate the total energy of NaH$^+$ we used the accurate total energy of the Na atom,[27] the IP of the Na atom of 5.139 eV, and the binding energy of NaH$^+$ of 0.061 eV reported by Melius et al.[30] The energy of infinitely separated NaH + e$^+$ is -162.8266 a.u., which is lower than the energy of NaH$^+$ + Ps of -162.81798 a.u. We also found another feasible dissociation channel of [NaH;e$^+$] to Na$^+$ + [H$^-$;e$^+$], which has an energy of -162.85494 a.u.[13] Therefore the lowest-energy channel for dissociation of [NaH;e$^+$] is to Na$^+$ + [H$^-$;e$^+$] rather than NaH + e$^+$ or NaH$^+$ + Ps. The zero-point vibration of NaH$^+$ and NaH molecules does not change the order of the energies of these dissociation channels, because the zero-point energy (ZPE) of NaH$^+$ can be neglected and that of NaH is very small (0.072 eV).[21] The lowest-energy dissociation channel for [LiH;e$^+$] system is also to form Li$^+$ + [H$^-$;e$^+$], but LiH + e$^+$ is less stable
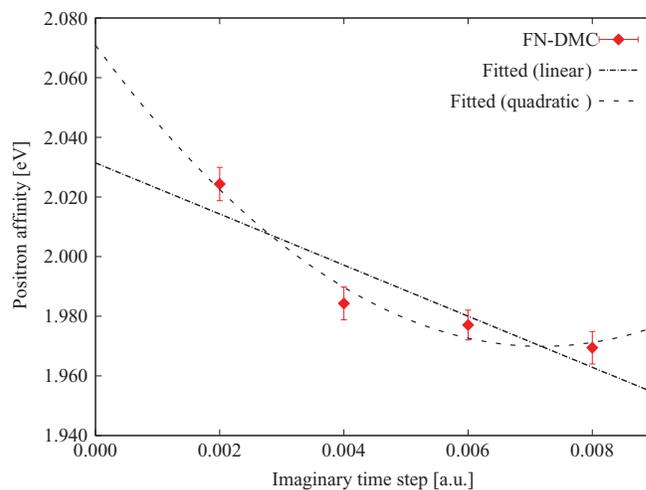
FIG. 3. Time step dependence of the PA of the KH molecule ($PA_{KH} = E_{KH} - E_{[KH;e^+]}$). The standard error of each DMC energy is shown. The dashed-dotted line is a linear fit to the DMC data, while the dashed line is a quadratic fit.
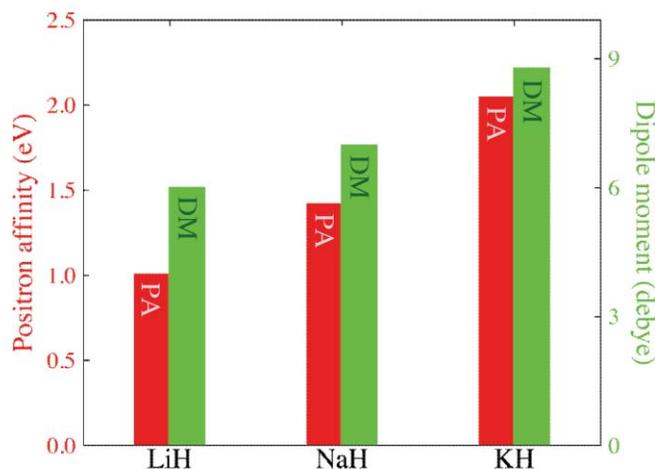
FIG. 4. PAs and DMs of LiH, NaH, and KH. The PAs and DMs are estimated using DMC and CCSD(T)/6-311++G($3d2f$, $3p2d$) calculations, respectively.

due to the ZPE of the LiH molecule as discussed by Mitroy *et al.*[31] and Mella *et al.*[32]

Results for KH and [KH;e$^+$] are shown in Table II. The DMC energies are significantly lower than the MRD-CI ones. The DMC energies of KH and [KH;e$^+$] extrapolated to zero time step are $-600.40028(39)$ and $-600.47638(57)$ a.u., respectively. The time step dependence of the PA of KH is shown in Fig. 3. In this molecule the variation of the PA with time step is larger than for NaH as the quality of the wave function is poorer because electronic orbitals with very different energies are present. In addition, the time step error is not well-described by a linear form and therefore we have plotted both linear and quadratic fits in Fig. 3. We have estimated the extrapolated PA by averaging the values from the linear and quadratic fits and taking the error bar from the time step bias to equal the difference between the linear and quadratic extrapolations, giving a PA of 2.051(39) eV. Our DMC value of the PA is much larger than the MRD-CI value and the uncertainty in the time step error is small on the scale of the difference between them.

Figure 4 shows the PAs and dipole moments of LiH, NaH, and KH. The value of the PA of the LiH molecule was obtained from our earlier DMC calculation,[18] and is very close to the highly accurate ECG study.[11] We estimated the dipole moments of these molecules at the coupled cluster singles and doubles level augmented by a perturbative correction for connected triple excitations, CCSD(T), with a 6-311++G($3d2f$, $3p2d$) Gaussian basis sets. Figure 4 clearly shows that a polar molecule with a larger dipole moment binds a positron more strongly.

IV. CONCLUSIONS

We have applied *ab initio* quantum Monte Carlo methods to the positronic alkali-metal hydrides, [XH;e$^+$] (X = Na and K), for which accurate theoretical predictions have not previously been made. Our fixed-node DMC calculations for [NaH;e$^+$] and [KH;e$^+$] give the lowest variational energies obtained so far for both systems. The values of the

PAs obtained in our DMC calculations for the NaH and KH molecules are 1.422(10) eV and 2.070(18) eV, respectively. These values are considerably larger than those from MRD-CI calculations[20] of 1.035 eV and 1.273 eV, respectively. Along with our earlier result for [LiH;e$^+$], our DMC calculations confirm the strong correlation between the positron affinity and dipole moment of alkali-metal hydrides. The mechanism of positron binding in the molecular dipole field was investigated many years ago by Crawford,[17] and recent MRD-CI calculations[20] have yielded quantitative estimates of positron affinities. We believe, however, that our DMC positron affinities are substantially more accurate. The DMC method can provide an excellent description of the electron-electron and electron-positron correlation in positronic complexes. The present study shows that this accurate methodology can be applied to systems containing atoms with atomic numbers up to at least 19. The polynomial scaling of the algorithm should make it feasible to perform accurate DMC calculations for substantially larger positronic complexes.

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