Diffusion quantum Monte Carlo calculation of the binding energy of positronium hydroxide

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Using the diffusion quantum Monte Carlo method, the binding energy of positronium hydroxide (alternatively, the positronium affinity of the hydroxyl radical) has been calculated at a new level of accuracy and found to be 0.63 ± 0.15 eV. Using the same methods, we also calculate the electron affinity of the hydroxyl radical to be 1.86 ± 0.14 eV, which is in agreement with the experimental value. To the authors' knowledge, this is the only calculation of these quantities for which this essential consistency is demonstrated. [S1050-2947(96)03406-3]

I. INTRODUCTION

There is a long history of quantum-mechanical studies of systems containing positronium (Ps) bound to a *koino* atom or molecule [1,2], and a large variety of methods have been employed. There are several reviews of this literature [3,4]. Owing to the difficulty of adequately treating the correlation of attractive light particles [5], only a few calculations have given binding energies that are precise and reliable. Until the present work, all these have been atomic systems: positronium hydride (PsH) [6] and the positronium halides [7,8]. Experimental determinations are even more difficult, owing to the short lifetimes of these compounds ($\sim 5 \times 10^{-10}$ sec, the spin-averaged lifetime of positronium) and the problem of accumulating enough positrons to do an experiment [9]. Only one measurement has been reported [10]: a rough measurement on the atomic system PsH. Nevertheless, positrons play a significant role in several areas of applied chemistry, physics, and material science [11], so a knowledge of their basic energetics and existence would seem to be useful. Several compounds containing positronium have been definitely observed [10,12,13] and many more have been postulated in order to explain experimental results [14–21]. Approximate calculations suggest that a great many more such compounds exist [22–24].

Positronium hydroxide (PsOH) is a diatomic molecule, with the positron occupying its own molecular orbital, such as it can be defined in the presence of strong correlation effects with the electrons of the molecule. We assume the positron orbital has σ symmetry, giving the ground state of PsOH the term symbol $^{2,1}\Sigma^+$. The spin degeneracies, given here as the presuperscript 2,1, reflect the fact that the total lepton spin and total electron spin are both good quantum numbers [5]. This exotic molecule is important because (i) it possibly forms in several kinds of experiments, e.g., when high-energy positrons thermalize in water or when low-energy positrons emit from surfaces of solids on which water is adsorbed; and (ii) the high demands that the positron

places on quantum-chemical methods for treating light particle correlation make it a stringent and useful test of such methods. Furthermore, a determination of its binding energy is now possible with modern quantum-mechanical methods and will probably soon be carried out experimentally in a crossed-beam experiment [9].

The prior literature on PsOH is inclusive. In an early contribution to positronium solution chemistry, an attempt was made to infer positronium binding energies to *koino* atoms and molecules in water from the lifetimes of positrons in solutions of various electrolytes [25]. The dependence of the intensities of various lifetimes with concentration was interpreted with the aid of the "hot radical" model, which is controversial [26]. The bond strength of PsOH was given as an overestimate: < 1.5 eV. Hydration effects were ignored.

About ten years ago, Kao and Cade performed a Slater-type orbital (STO) restricted Hartree-Fock (RHF) calculation on PsOH and several other positronium compounds [27]. They obtained 4.802 eV for the positron affinity of OH^-, which, they point out, is an underestimate because it does not include the effect of electron-positron correlation. Using this value and the equation

$$E_B(\text{PsOH}) = A_E(\text{OH}) + A_P(\text{OH}^-) - 6.805 \text{ eV}, \quad (1)$$

they obtain -0.17 eV as the binding energy of PsOH; i.e., it is predicted to be unstable to dissociation. The symbols above mean binding energy, electron affinity [28], and positron affinity, respectively of the indicated species. The last term on the right-hand side above is the binding energy of positronium. Kao and Cade state the following: "It is possible that correlation effects will produce a positive $[E_B]$." Their total calculated energy for PsOH is $-75.587\,64$ a.u., which they state has converged to within 0.006 a.u. of the RHF limit. The near-limit RHF energy of OH^- is $-75.417\,54$ a.u [29] and of OH, $-75.420\,83$ a.u. [30]. Calculating the electron affinity of OH as the difference of the last two energies gives the wrong sign. It is our contention

TABLE I. Positronic molecular orbital used in the importance function. The orbital has the form $\Sigma_i c_i \varphi_i$, where φ is a normalized STO with an exponential argument $-\zeta r$. The p_z functions point at each other.

STO	ζ	c
$3p_z(O)$	0.936	-1.0
$3s(O)$	0.936	2.8
$2p_z(H)$	0.281	-0.6
$2s(H)$	0.281	1.5

TABLE II. Calculated energies, in atomic units. Uncertainties are calculated in the same way as in Refs. [7] and [8].

Time step	0.005	0.0025
PsOH	-75.9003 ± 0.0046	-75.9024 ± 0.0042
OH$^-$	-75.6949 ± 0.0043	-75.6973 ± 0.0038
OH	-75.6258 ± 0.0040	-75.6286 ± 0.0037

Kalia [38] for diatomic positronium (Ps$_2$).

that, for a method to be considered credible for calculating positronium affinities, it must give a good account of electron affinities.

Very recently another calculation on PsOH was reported [31]. Using a 6-31G Gaussian expansion and a second-order Møller-Plesset (MP) perturbation estimation of lepton correlation, Tachikawa *et al.* obtained 4.9 eV as the positron binding energy of OH$^-$, very close to that found by Kao and Cade in 1984. Unfortunately, Tachikawa *et al.* used 2.6 eV for the electron affinity of OH to deduce the binding energy of PsOH, which they thus found to be stable. However, if the experimental value [28] of the electron affinity is used in Eq. (1) with Tachikawa's value of $A_P(OH^-)$, a binding energy of -0.1 eV is found; i.e., the opposite conclusion is reached. The electron affinity of OH was not calculated by Tachikawa *et al.*, so that test of the credibility of their method cannot be made.

II. APPROPRIATE QUANTUM MECHANICS

Each state of a positronium compound is in reality a resonance embedded in a continuum of states of a system with two fewer leptons and two more photons and annihilation is the transition from the resonance to the continuum. It is easily shown that the coupling of the resonance and the continuum is weak. The energy shift due to this coupling has been calculated for the ground $1s$ state of positronium and it amounts to only 3.6×10^{-4} eV [32–35]. It is undoubtedly also a small quantity for positronium compounds. The lifetimes of these compounds, about 5×10^{-10} sec, amount to $\sim 10^7$ a. u. of time, so they live long enough to map out their wave functions to a high degree of precision. The finite lifetimes imply an uncertainty in the binding energies of only ~ 1 μeV, so they also are well defined. It follows that nonrelativistic Schrödinger wave mechanics can be used to calculate accurately the wave functions and energies of positronium compounds and the continuum coupling can be treated in first order to give the annihilation rate. This conclusion was reached a long time ago by Lee [36]. The full technology of modern quantum chemistry is immediately applicable to the zeroth-order problem, provided that symmetry and spin coupling are properly treated [5,37]. The diffusion quantum Monte Carlo method seems ideal for atoms and molecules that contain a positron because the often crucial electron-positron correlation, so difficult to treat with more conventional methods (as the work of Tachikawa *et al.* illustrates), is treated more or less automatically. The efficacy of the quantum Monte Carlo method for dealing with this kind of correlation has been demonstrated by Lee, Vashishta, and

III. PRESENT WORK AND RESULTS

We perform diffusion quantum Monte Carlo calculations on the species PsOH, OH$^-$, and OH, using a method of calculation similar to that used in our previous studies of PsF, PsCl, and PsBr [7,8], except that the core electrons are treated explicitly here rather than with a model potential as in previous work. The important functions for OH$^-$ and OH are taken to be simple approximate RHF wave functions calculated with GAUSSIAN 92 at the STO-3G level and are expressed in our calculations as minimal STO expansions. For PsOH, the OH$^-$ function, determined as just described, is multiplied by a positronic orbital inferred by fitting a short STO expansion to a figure in the paper by Kao and Cade, which gives their calculated positronic probability density. We assume the positronic orbital to be nodeless. Our positronic orbital is given in Table I.

We perform our calculations at the experimentally determined internuclear distances of OH and OH$^-$, which are 0.970 Å and 0.964 Å, respectively. The latter is used also for PsOH, based on our assumption that the positron, being located almost entirely on the exterior of the molecule [27], has little effect on the bonding of O and H. For each of the three systems, calculations are performed for time steps of 0.0025 and 0.005 and extrapolations to zero time are made, assuming that the calculated energies converge linearly with the time step [39].

The calculated energies are given in Table II. These energies are 4–5 eV below those recently reported for the 6-31G+MP2 calculations [31], and 6–9 eV below the older STO RHF energies [27,30]. Our results indicate an electron affinity of OH of 1.86 ± 0.14 eV, a positron affinity of OH$^-$ of 5.57 ± 0.15 eV, and a positronium affinity of OH of 0.63 ± 0.15 eV. The extrapolations to zero time step are trivial because these results are found to be independent of the time step within statistical uncertainty.

The demonstrated consistency with the experimental value for the electron affinity of OH, not achieved in previous work, strongly suggests the adequacy of our treatment. Our results provide reliable evidence of the stability of a chemical bond between positronium and a molecule.

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