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Diffusion quantum Monte Carlo calculations of positronium hydride and positron lithium

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The diffusion quantum Monte Carlo (QMC) method is applied to the calculations of the binding energies of the positronium hydride, ${}^{1,2}S[e^+\text{-H}^-]$, and the positron lithium, ${}^{2,1}S[e^+\text{-Li}]$. The QMC binding energy of the positronium hydride system is found to be in excellent agreement with the recent experimental value. The result of the energy of the positron-lithium system suggests that it is stable with respect to positron dissociation, but is probably unstable compared to separated Ps and Li^+. [S1050-2947(96)04811-1]

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Does an atom or a molecule form a stable state with a positron or a positronium? This is a question of great interest for theorists as well as for experimentalists of various fields such as surface study, radiation chemistry, mass spectrometry, etc. [1]. If the positron is fully exploited as a probe to study the electronic structures of molecules and solids, their properties will become much better understood than they are at present.

The diffusion quantum Monte Carlo (QMC) method, which solves the many-body Schrödinger equation through an appropriate diffusing random walk of particles, has been successfully utilized to calculate the physical quantities of various atoms and molecules [2]. Recently this approach has been applied to the computations of the binding energies of the positronium fluoride, $[e^+\text{-F}^-]$, positronium chloride, $[e^+\text{-Cl}^-]$, and positronium bromide, $[e^+\text{-Br}^-]$, in combination with *ab initio* core model potentials [3,4].

In the present paper we report the results of QMC calculations on the binding energies of the ${}^{1,2}S$ state of the positronium hydride, $[e^+\text{-H}^-]$ and the ${}^{2,1}S$ state of the positron lithium, $[e^+\text{-Li}]$. The present method is essentially identical to that previously used [3,4], although all particles were treated explicitly here.

TABLE I. Total energy of the positronium hydride. Statistical uncertainty is given in parentheses.

Author	Energy (hartree)
Goldanskii, Ivanova, and Prokopev [5]	0.6677
Lebeda and Schrader [6]	−0.7742
Houston and Drachman [7]	−0.7748
Page and Fraser [8]	−0.7868
Clary [9]	−0.7842
Ho [10]	−0.7889
This work	−0.7891(20)

The time-dependent Schrödinger equation can be transformed into

$$-\frac{\partial f(R,t)}{\partial t}=-D\nabla^2 f+[E_L(R)-E_T]f+D\boldsymbol{\nabla}[fF_Q(R)], \tag{1a}$$

$$f(R,t)=\Psi(R)\Phi(R,t), \tag{1b}$$

$$E_L(R)=H\Psi(R)/\Psi(R), \tag{1c}$$

$$F_Q(R)=\boldsymbol{\nabla}\ \ln|\Psi(R)|^2. \tag{1d}$$

Here t is an imaginary time, D is a diffusion coefficient, E_T is a constant shift in the zero of energy, and $\Psi\ (R)$ is an approximate trial wave function to guide the random walk, and $\Phi\ (R,t)$ is the exact wave function. The term $E_L(R)$ is called the ''local energy'' whose average is an estimator of energy, and $F_Q(R)$ is called the ''quantum force'' which represents the local drift velocity.

The transformed Schrödinger equation can be simulated by a process of diffusion, multiplication, and disappearance of configuration of particles.

TABLE II. Binding energy (BE) of the positronium hydride. Statistical uncertainty is given in parentheses.

Author	BE (eV)
Goldanskii, Ivanova, and Prokopev [5]	−2.24
Lebeda and Schrader [6]	0.66
Houston and Drachman [7]	0.67
Page and Fraser [8]	1.01
Clary [9]	0.93
Ho [10]	1.06
This work	1.06(5)
Experiment [11]	1.1

TABLE III. Total energy of the positron lithium. Statistical uncertainty is given in parentheses.

Author	Energy (hartree)
Clary [9]	-7.5094
This work	$-7.5203(48)$
Exact Li	-7.4780
Exact Ps+Li$^+$	-7.5299

We employed a Hartree-Fock (HF) single determinant composed of a single-ζ (SZ) quality basis to construct $\Psi(R)$, and an average ensemble size of 100 configurations for each QMC computation.

First, we carried out a QMC calculation on the $^{1,2}S$ state of the positronium hydride, $[e^+\text{-H}^-]$. As for the binding energy of the positronium hydride, there have been several rigorous calculations accounting for correlation and an experiment, in addition to the Hartree-Fock calculation of Goldanskii, Ivanova, and Prokopev [5]. Therefore this prototypical system can be used to check the accuracy of the present method.

Lebeda and Schrader [6], Houston and Drachman [7], and Page and Fraser [8] made extensive variational calculations with use of Hylleraas-type trial functions. Clary performed a Hylleraas configuration-interaction (HCI) calculation by use of the function containing 68 configurations consisting of antisymmetrized products of r_{ij}^{ν} (ν=0,1,2) coordinates with Slater-type orbitals (STO's) [9]. Ho yielded a very accurate binding energy using the 396-term trial wave function [10]. Schrader *et al.* performed an experiment of producing a positronium hydride using a positron beam to measure the binding energy of this compound [11].

It can be seen from Table I that the QMC energy of $^{1,2}S$ $[e^+\text{-H}^-]$ lies about 0.12 hartree below the HF energy, and is also superior to other variational calculations. The positronium affinities estimated from the total energies are shown in Table II, compared with the result recently obtained by the positron beam experiment [11]. One finds that the HF approximation provides an inaccurate result due to the lack of both electron-positron and electron-electron correlation effects.

The QMC positronium affinity is in excellent agreement with the experimental value as well as with Ho's result although our trial wave function using a SZ basis is much simpler than his 396-term function.

Second, we provide the result of the energy for the $^{2,1}[e^+\text{-Li}]$ system. The QMC energy obtained for the $^{2,1}S[e^+\text{-Li}]$ system is listed in Table III, in comparison with other computation results as well as the exact energies of the lithium atom and Ps+Li$^+$.

Clary [9] obtained the HCI result through the same procedure as that for the positronium hydride, with 84 configurjations to construct the trial wave function. It can be seen that the present result obtained with a simple SZ basis is about 0.01 hartree lower than the H-CI value. One also finds that the QMC energy as well as the H-CI result of the positron-lithium system is lower than the exact ground-state energy of the Li atom, but is not lower than that of Ps+Li$^+$.

Although there is still a possibility of the improvement of trial wave function yielding a lower energy, the present result is probably more accurate than any other reported so far.

In conclusion, the QMC result as well as the H-CI energy suggests that the $^{2,1}S[e^+\text{-Li}]$ system is stable with respect to dissociation into Li+e^+, but it is considered to be unstable compared to separated Ps and Li$^+$ at this stage.

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