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Stability of light positronic atoms: Quantum Monte Carlo studies

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We present accurate ground-state energies for the positronium atom in a Coulomb field of point charge Z (X^ZPs), for the positronium hydrogen (HPs) and positronium lithium (LiPs) atoms. Calculations are done using the diffusion quantum Monte Carlo (DQMC) method. For X^ZPs, the critical value of Z for binding is examined. While HPs is stable, the results show that LiPs is unstable against dissociation to a lithium atom and a positronium. [S1050-2947(96)04512-X]

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I. INTRODUCTION

Among other spectroscopies, positron annihilation stands out for its unique capability to monitor electronic structure changes produced by impurities and defects in several materials [1]. In order to extract detailed information from the experimental data, computational methods for calculating electron-positron correlation are needed [2,3]. A bound positron in the vicinity of a defect is a problem more directly related to current positron annihilation experiments (see for instance [4]), and has been treated [5,6] within the two-component density-functional theory [7]. However, the quantitative accuracy is limited by the local-density approximation (LDA). Finding the bound state of a positronium (Ps) in finite atomic systems is an easier related problem that could be useful for developing functionals of higher accuracy to describe the electron-positron correlation. Moreover, the stability of finite Coulomb systems formed by particles with various constituent masses and charges is a challenging open question in theoretical physics and chemistry [8]. At first glance, it is surprising to notice that three-particle systems as different as H^-, H_2^+, or Ps^- are stable against dissociation, whereas the positron-hydrogen system is unbound. Rigorous properties of the stability domain can be extracted [8], but in most cases an accurate numerical calculation is needed to confirm the stability.

The quantum Monte Carlo (QMC) methods are attractive tools for studying small electron-positron bound systems, where the electron-positron correlations are crucial. Accurate calculations using the QMC have already been performed for the Ps_2 [9] and for the positronium halides [10,11]. In this work, we perform total energy QMC calculations for the X^ZPs system where Z is a massive point charge ($0.5 \leqslant Z < 1$), and for HPs and LiPs. We compare the results for X^ZPs and HPs with the variational Hylleraas calculations [12,13]. We improve significantly the level of accuracy for the X^ZPs case. Our results for the HPs are in good agreement with the previous accurate results.

For the LiPs atom, we have performed both a model potential [14] and an all-electron calculation. The electron affinity of the lithium atom is well described by both methods, but the results for the LiPs atom differ in an important way. The total energy from the model potential calculation is below the total energy of both $Li^- + e^+$ and Li + Ps and would thus predict the stability of the LiPs system. However, for the all-electron calculation, the total energy is below the energy of $Li^- + e^+$ but not the energy of Li + Ps. We conclude that LiPs is unstable.

II. METHOD

The use of imaginary time converts the Schrödinger equation to a diffusion equation (in atomic units)

$$\frac{\partial \Psi}{\partial t} = \frac{1}{2}\nabla^2\Psi - V\Psi, \tag{1}$$

which can be solved by a random-walk method first suggested by Fermi and described by Anderson [15]. The diffusion quantum Monte Carlo (DQMC) method is based on a simulation where random walkers are made to diffuse and to multiply or disappear. The scheme can fail when the potential V is unbounded, but there is a simple cure discovered by Kalos, Levesque, and Verlet [16] for the Green's function QMC, but equally applicable to the DQMC [17–19]. The improved scheme is obtained by multiplying Eq. (1) by a trial function Ψ_T and considering the equation for $f = \Psi\Psi_T$ given by

$$\frac{\partial f}{\partial t} = \frac{1}{2}\nabla^2 f - \nabla[f\nabla \ln(\Psi_T)] - \frac{H\Psi_T}{\Psi_T} f, \tag{2}$$

where H is the Hamiltonian operator. Equation (2) has the terms on the right-hand side corresponding to diffusion, drift in a ''fluid velocity'' $\nabla \ln(\Psi_T)$ and birth or death of the walkers with a first-order constant given by the local energy $E_{loc} = H\Psi_T/\Psi_T$ of the trial wave function. The eigenvalue is given by an average value of E_{loc} at steady-state conditions. When the trial wave function Ψ_T approximates the true wave function the local energy is nearly constant and the variance in the computed value of E is reduced. The variational QMC (VQMC) as presented by Umrigar, Wilson, and Wilkins [20] is a very useful procedure to obtain optimized trial wave functions by minimizing the variance of the local energy. The trial wave function Ψ_T is chosen in the Jastrow-Slater form

$$\Psi_T = F\prod_s \det_s|\phi_i(r_j)|, \tag{3}$$

where s runs over the different species of particles (spin-up electrons, spin-down electrons, spin-up positrons, spin-down positrons), ϕ are the one-body wave functions, and $F=\exp(\Sigma_{i<j}u_{ij})$ is the product of the two-body correlation factors. In a good trial function the singularities in the local kinetic energy must cancel those of the potential. For the Coulomb potential this leads to the Kato cusp condition [21] of the two-body correlation factor

$$\frac{du_{ij}(0)}{dr}=\frac{\mu_{ij}q_iq_j}{(k+1)}, \tag{4}$$

where q_i and q_j are the constituent charges, $\mu_{ij}=m_im_j/(m_i+m_j)$ is the reduced mass, and k is the angular momentum of the two-particle subsystem, i.e., 0 for unlike spins and unlike particles and 1 for like spins. For u we have used the form

$$u_{ij}=\frac{\mu_{ij}q_iq_j}{(k+1)}\frac{r}{1+b_{ij}r}, \tag{5}$$

where the b_{ij} are variational parameters. The one-body wave functions ϕ can be expressed as linear combinations of Slater functions $r^m\exp(-\zeta r)$ that fulfill the Kato cusp condition at the nuclei.

In our DQMC runs, we have evaluated the error estimates using the standard formula of the statistical analysis

$$\Delta E=\sigma_E\left(\frac{L_c}{N}\right)^{1/2}, \tag{6}$$

where σ_E is the standard deviation of the energy from a single DQMC run, N is the number of time steps taken after the transient, and L_c is the correlation length (in the same units as N). L_c is the value where the autocorrelation function of the energy is less than 10% [22]. The transient is determined from the plot of energy as a function of time.

One disadvantage of the DQMC is the systematic error due to a finite time step Δt. In practice one must repeat the calculation with different Δt in order to extrapolate to the $\Delta t\to 0$ limit. We have done the extrapolation using second-order polynomials and a least-squares fit.

Another problem for the DQMC can be posed by the antisymmetry in the case of the Fermi statistics [23]. As a matter of fact, the interpretation of the Schrödinger equation in imaginary time as a generalized diffusion equation rests on the interpretation of the wave function as a probability density represented by the concentration of diffusing particles (the walkers). The ground state with different particle species or with identical bosons can be described with a real positive distribution (in the absence of magnetic fields). In the case of identical fermions, the wave function is negative as often as positive. The stochastic approach can still be used to solve the Schrödinger equation if the diffusion process is confined within a subdomain bounded by the nodal surface. In the fixed-node (FN) approximation, one forbids moves in which the sign of the trial function changes. However, the resulting energy will be an upper bound of the exact ground-state energy [24]. In this work, the FN approximation is implemented so that the configurations that cross the nodal boundary are discarded. The number of walkers used in this work is around 200 and the walkers are propagated for around 10^4 steps.

III. RESULTS

A. The X^ZPs system

Positron states in ionic crystals can have properties resembling a Ps atom [26]. Boev and Arefiev [12] proposed a simple model considering the Ps-like states in ionic crystals as a positron-electron pair bound states in the Coulomb field of the charge Z less than unity. In addition, the behavior of the system as Z is varied, is rich and illustrative for the study of both positron, and positronium binding. The Hamiltonian for this system is

$$H=-\frac{1}{2}(\nabla_1^2+\nabla_2^2)-\frac{Z}{r_1}+\frac{Z}{r_2}-\frac{1}{r_{12}}, \tag{7}$$

where index 1 refers to the electron, index 2 to the positron and r_{12} is the distance of electron and the positron. The mass of the point charge Z is taken to be infinite. We will assume that the positron is repulsed by the point charge $(Z>0)$, but the interchange of indices 1 and 2 is equivalent to the opposite charge Z. To be stable, the energy of the system should lie below its lowest dissociation threshold, which corresponds to the less negative of the Ps and the hydrogenlike atom (X^Ze^-) total energies. In atomic units, the Ps total energy is $-\frac{1}{4}$ and that of X^Ze^- is $-\frac{1}{2}Z^2$. These are equal when $Z=\sqrt{1/2}$.

A simple qualitative description of the X^ZPs is the *onion model*, which is exact for $Z\to 1$. One considers the electron localized close to the point charge and the positron surrounding the hydrogenlike atom (X^Ze^-), feeling only an effective charge of $Z-1$. Thus the electron and positron shells have some similarity to the onion shells. The total energy of the system in this model is given by

$$E\cong-\tfrac{1}{2}Z^2-\tfrac{1}{2}(Z-1)^2. \tag{8}$$

According to this model, for $Z=1$ the system becomes unstable and the positron escapes away. On the other hand, for $Z<\frac{1}{2}$ the system becomes more stable if Z is reduced. Therefore in this region of Z one can expect that the Ps escapes from the point charge. However, the onion model is not accurate in this region due to the overlap of the electron and positron wave functions and we need a more careful investigation. This is easily done using the DQMC.

In Fig. 1 we compare the DQMC with a variational Hylleraas basis calculation [12] and the onion model. The energies for the positronium and the hydrogenlike state X^Ze^- are shown, too. In the limit $Z\to 1$, the calculated energies approach the onion model and the hydrogenlike state. For $Z<\sqrt{1/2}$, the energy is closer to the energy of a Ps system than the X^Ze^- system. Among the points we have calculated, the point $Z=0.7$ gives the greatest stability, binding energy being 0.049 (a.u.). Table I gives a precise comparison of our DQMC results with the variational calculations [12]. We can see that the DQMC energies are lower. In the limit $Z\to 1$, both of the methods give almost the same energy, but they differ when Z is smaller. In this region the electron-positron

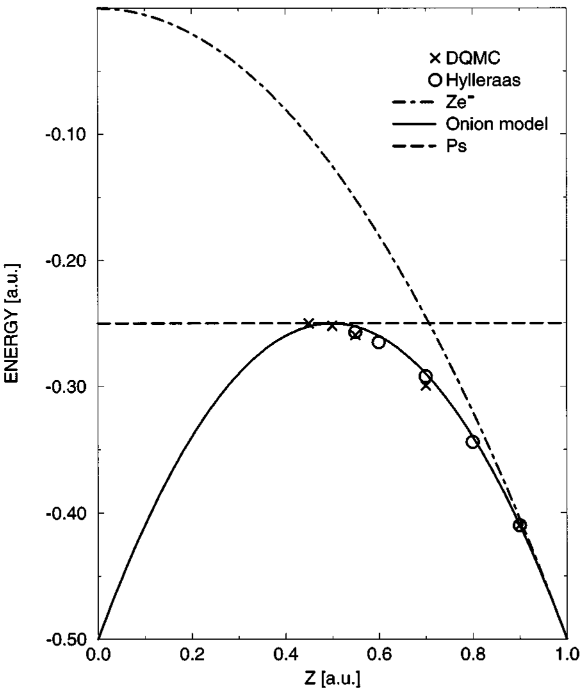

FIG. 1. The DQMC total energy of the X^ZPs system and the results of Boev and Arefiev [12] compared with the onion model and the energies of a free positronium and a hydrogenlike state $X^Z e^-$.

correlation is more important and the difference is due to the fact that DQMC is able to recover the correlation energy exactly. Moreover, the DQMC confirms the onion model prediction that the Ps escapes from the point charge at a critical charge Z_C. The inclusion of the correlation effects enlarge the range of stability and we find $Z_C \approx 0.45$.

B. The HPs and the LiPs systems

The hydrogen-positron system is unstable, but this is not the case for the HPs system [13]. We have performed the DQMC simulation for HPs using different time steps. The results are shown in Table II. The extrapolation to zero time step gives the total energy $E = -0.7885 \pm 0.0005$ (a.u.), which is very close to the value $E = -0.788\,945$ found by Ho [13]. This clearly shows the accuracy of our algorithm. From the total energies HPs is found stable by 0.039 (a.u.).

TABLE I. Total energy for the X^ZPs system (in a.u.) obtained by the DQMC simulations compared with the Hylleraas basis calculation by Boev and Arefiev [12]. The statistical error in the last digit is in the parentheses.

Z	DQMC	Hylleraas
0.45	−0.2502(5)	—
0.5	−0.252(1)	—
0.55	−0.2593(5)	−0.257
0.6	—	−0.265
0.7	−0.299 25(30)	−0.292
0.8	—	−0.344
0.9	−0.4100(2)	−0.410

TABLE II. The total energy for HPs system for various time steps (in a.u.) obtained by the DQMC method. The statistical error in the last digit is in the parentheses.

Time step	DQMC
0.2	−0.7980(2)
0.15	−0.7960(2)
0.1	−0.7938(3)
0.05	−0.7909(6)
0.03	−0.7898(9)
0.0	−0.7885(5)[a]

[a] Extrapolated.

In general, the straightforward method of calculating the binding energy of XPs or the Ps affinity of an atom X by subtracting the calculated total energy of XPs from the sum of that of Ps and X, is not the most reliable way. The reason is that an uncanceling error may result [10]. Another method [25] is to consider the positron affinity of the corresponding anion

$$A_{e^+}(X^-) = E(X^-) - E(X\mathrm{Ps}), \tag{9}$$

and the electron affinity

$$A_{e^-}(X) = E(X) - E(X^-). \tag{10}$$

Then the Ps affinity of atom X is

$$A_{\mathrm{Ps}}(X) = A_{e^-}(X) + A_{e^+}(X^-) - 1/4. \tag{11}$$

Thus $A_{\mathrm{Ps}}(X)$ is a delicate balance of the binding energy of Ps ($\frac{1}{4}$), the electron affinity of the atom and the positron affinity of the negative ion. All these quantities require high precision for the description of correlation.

One commonly thinks of hydrogen as a group I element, sitting above lithium and other alkali-metal elements. The main difference is that H has no core electrons. However, it can also appear in group VII along with the halogens, as H is just one electron short of having a closer outer shell. Therefore, the alkali elements and the halogens are the next good candidates for Ps binding. DQMC calculations for halogens [10,11] found FPs stable by 0.073 (a.u.), ClPs by 0.070 (a.u.), and BrPs by 0.042 (a.u.). These positronium binding calculations were done using a model potential [10,11]. In the same way, the alkali-negative ions and H^- can be treated using similar approaches [14]. In particular, the core electrons of Li could be frozen as their polarizability is very small. Therefore, it is justified to treat Li^- as a system composed only of two electrons in an external potential

$$V(r) = -\frac{1 + (Z-1)\exp(-\alpha_1 r) + \alpha_2 r\ \exp(-\alpha_3 r)}{r}, \tag{12}$$

where $Z = 3$, $\alpha_1 = 7.9$, $\alpha_2 = 10.31$, and $\alpha_3 = 3.898$. This potential has been parametrized by Klapisch (as quoted in Ref. [14]) to reproduce the experimental energy levels of Li [31] [its ground-state energy is $E(\mathrm{Li}) = -0.198$ (a.u.)]. For Li^-, our DQMC calculation gives $E(\mathrm{Li}^-) = -0.223$ (a.u.). Then, the corresponding electron affinity is 0.025 (a.u.), which is in

TABLE III. The total energy for LiPs vs time steps. The statistical error in the last digits is in the parentheses. All numbers are in atomic units.

Time step	Energy
0.3000	−7.772(5)
0.2000	−7.742(2)
0.1000	−7.712(2)
0.0750	−7.712(2)
0.0500	−7.712(2)
0.0300	−7.713(2)
0.0200	−7.708(2)
0.0000	−7.709(4) [a]

[a] Extrapolated.

good agreement with the experimental value [29]. We have performed DQMC simulations for LiPs using the model potential for the electrons and the Coulomb potential (with a frozen core) for the positron. Our optimized trial wave function for LiPs gives a variational energy $E=-0.4234\pm0.0003$, indicating an instability against dissociation to Li and Ps. However, our DQMC result gives a very small binding of 0.015 (a.u.). To improve this approach, we have also performed an all-electron DQMC calculation using the fixed-node approximation [24] and optimized VQMC the trial function Ψ_T. We have used a novel optimization method for both Jastrow and one-body wave functions [27]. The resulting total energies are $E(\mathrm{Li})=-7.470\pm0.002$ (a.u.), $E(\mathrm{Li}^-)=-7.487\pm0.004$ (a.u.), and $E(\mathrm{LiPs})=-7.709\pm0.004$ (a.u.). The total energy for the LiPs with various time steps is shown in Table III. The result for the neutral atom is only slightly higher than the ''exact,'' nonrelativistic, infinite mass energy $E(\mathrm{Li})=-7.478025$ (a.u.) [28]. This is due to the fixed-node error. The electron affinity $A_{e^-}(\mathrm{Li})=0.017\pm0.006$ (a.u.) is in good agreement with the experimental value of 0.0227 [29]. The energy for the LiPs system is higher by around 0.02 (a.u.) than the sum of the energies of Li and Ps systems. This indicates the instability of the system. Positronium escapes from the Li atom as it escapes from the point charge for $Z\leqslant0.45$. Clary has reported the stability of e^+Li against Li and e^+ dissociation but has suggested a similar instability against Li$^+$ and Ps [30]. Finally, we would like to emphasize the importance of optimizing both the Jastrow factor and the one-body orbitals, as done in the present work. As a matter of fact, we observed that the use of the same one-body orbitals for LiPs than for Li$^-$ leads to much higher instability of LiPs.

IV. CONCLUSION

We have used the DQMC in order to perform rigorous studies of the positron energetics in small system such as X^ZPs, HPs, and LiPs. For the X^ZPs, the electron-positron correlation effects are important when $Z\leqslant\sqrt{1/2}$. Using a model potential and a frozen core approximation LiPs is found weakly stable, but the all-electron calculation and the FN approximation shows the system to be unbound with respect to dissociation to Li and Ps.

The techniques for cooling and trapping positrons [32] point to the possibility of well-defined experimental studies of positrons and Ps interacting with a few atoms. This gives further impetus for developing and applying accurate calculation methods for these systems.

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