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Stable bound states of $e^+ + \mathrm{Li}$ and $e^+ + \mathrm{Na}$

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Using model potentials to describe the ionic cores, we have approximated the $e^+ + \mathrm{Li}$ and $e^+ + \mathrm{Na}$ systems as quasi-three-body problems and performed adiabatic hyperspherical calculations to search for the existence of bound states. We have confirmed the existence of a bound state for $e^+ + \mathrm{Li}$ that was first predicted by Ryzhikh and Mitroy [Phys. Rev. Lett. **21**, 4124 (1997)] with a binding energy of 58 meV. Further, we predict the existence of a stable bound state for $e^+ + \mathrm{Na}$ with a binding energy of 7 meV and explain why bound states exist for these two systems but not for the $e^+ + \mathrm{H}$ system, despite the fact that H^- has a higher binding energy than either Li^- or Na^-. Based on this work, we find that it is unlikely that positrons can form stable bound states with any other of the alkali-metal atoms.
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Atomic and molecular negative ions in which an electron binds itself to a neutral atom or molecule are well known in nature. The question of whether a positron can bind itself to an atom or a molecule to form an electronically stable state is less well understood. For the simplest three-body system, an electron can form a stable bound state with atomic hydrogen with a binding energy of about 0.75 eV, but a positron and an atomic hydrogen cannot form a stable bound state. However, it has been shown recently by Ryzhikh and Mitroy [1] that a positron and a neutral Li atom can form a stable bound state, with a binding energy of about 59 meV. Their calculation was based on the stochastic variational method. In particular, they used Gaussian basis functions in which the nonlinear parameters were optimized using the stochastic technique of Varga and Suzuki [2]. Their prediction is in disagreement with the earlier negative results from the configuration-interaction-Hylleraas calculations of Clary [3] and from Yoshida and Miyako [4], who used the diffusion quantum Monte Carlo method.

One of the most powerful theoretical techniques for searching for stable bound states in few-body systems is the hyperspherical method within the adiabatic approximation. In this approach, the adiabatic hyperspherical potential is first calculated. If the potential curve is repulsive, there is no possibility for the existence of any bound states. If the potential curve is both attractive and deep enough, then stable bound states are expected. This method has been used to identify the existence of bound states and resonances in a variety of three-body and four-body systems. In this Rapid Communication, we report hyperspherical calculations for the $e^+ + \mathrm{Li}$ system, which supports the positive result of Ryzhikh and Mitroy [1]. In addition, we show that a similar bound state exists for the $e^+ + \mathrm{Na}$ system that has a binding energy of approximately 7 meV. In the past, the hyperspherical approach has been used to calculate the scattering cross sections of positrons with atoms to look for resonances [5,6], but has never been applied to Li and Na targets. The close-coupling approach has been used for e^+ collisions with Li, but no search for the bound states has been reported [7]. Although positrons are claimed to be capable of forming bound states with Mg, Zn, and other atoms from many-body calculations [8], this conclusion is not generally accepted.

In our calculation, we treat $e^+ + \mathrm{Li}$ as a three-body system, consisting of a Li^+ core, an electron, and a positron. The Li^+ core is represented by a model potential with the parameters adjusted to fit the Li bound-state energies. If r_+ (r_-) is the distance of the positron (electron) from the core, we define the hyperradius to be $R=\sqrt{r_+^2+r_-^2}$ and the hyperangle to be $\tan\phi = r_+/r_-$. In this paper we consider the $L=0$ case, which is most favorable for the existence of bound states. The wave function then is described by the three internal coordinates R, ϕ, and θ, where θ is defined to be the angle between the positron and the electron with respect to the Li^+ core. The Schrödinger equation is then given by (in atomic units) [9]

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial R^2} + \frac{\Lambda^2 - \frac{1}{4}}{2R^2} + V(R,\phi,\theta) \right)\psi = E\psi. \qquad (1)$$

Here, Λ is the grand angular-momentum operator and V is the potential among the three charged particles. Note that the wave function has been rescaled by a factor $R^{5/2}\sin\phi\cos\phi$ in order to eliminate first derivatives in R and ϕ. In the adiabatic approximation, the total wave function is approximated as $\psi(R,\phi,\theta) = F(R)\Phi(R;\phi,\theta)$, where the ''channel function'' $\Phi(R;\phi,\theta)$ is the solution of

$$\left(\frac{\Lambda^2 - \frac{1}{4}}{2R^2} + V \right)\Phi_\nu(R;\phi,\theta) = U_\nu(R)\Phi_\nu(R;\phi,\theta), \qquad (2)$$

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with R treated as a parameter. This equation is solved using the finite-element method [9]. The nth eigenstate for channel ν is then obtained by solving the one-dimensional hyperradial equation

$$\left(-\frac{1}{2}\frac{d^2}{dR^2} + U_\nu(R) + W_{\nu\nu}(R) \right) F_{\nu n}(R) = E_{\nu n} F_{\nu n}(R), \tag{3}$$

where $W_{\nu\nu}(R) = -\frac{1}{2}\langle \Phi_\nu | \, d^2/dR^2 \, | \Phi_\nu \rangle$ is the so-called second-order diagonal coupling term. If ν is the lowest channel, it can be shown that the lowest eigenenergy obtained from Eq. (3) gives an upper bound, while the eigenvalue obtained without the $W_{\nu\nu}$ term gives a lower bound [10].

The effective interaction among the three charged particles is given by $V = V_{12} + V_{13} + V_{23}$, where we use 1, 2, and 3 to denote the Li^+ core, the positron, and the electron, respectively. The e^--Li^+ interaction V_{13} is the sum of a static potential, a localized exchange potential [12], and an induced dipole polarization potential. The static potential is obtained from the two $1s$ wave functions obtained by performing Hartree-Fock self-consistent-field calculation for Li, which thus accounts for the relaxation of the core orbital. The polarization potential has the form $V_p(r) = -\alpha/2r^4 (1 - e^{-(r/r_c)^6})$, where $\alpha = 0.1923$ [13] is the dipole polarizability for Li^+ and r_c is the cutoff radius obtained by fitting so that the ground- and excited-state energies of Li are well reproduced ($r_c = 0.613$). For the interaction V_{12} between the Li^+ core and the positron, the static part of the potential is the same as in V_{13}, except of opposite sign; there is no exchange term, and the polarization potential is the same as in V_{13}. The potential V_{23} between the positron and the electron is

$$V_{23} = -\frac{1}{|\vec{r}_+ - \vec{r}_-|} + 2\cos\theta \sqrt{V_p(r_+) V_p(r_-)}, \tag{4}$$

where the second term is the so-called dielectronic correction to the polarization potential [14]. Note that this term, which is due to the polarization of the core, has the effect of reducing the interaction between the two ''bare'' charges.

We used the model potential described above to calculate the lowest few hyperspherical potential curves for the $e^+ + \mathrm{Li}$ system. In order to check the validity of the model potential and the adiabatic approximation used, we first performed the calculation for the Li^- system. Including the second-order nonadiabatic coupling term $W_{\nu\nu}$, the calculated Li^- ground-state energy is 0.0441 Ry, compared with the experimental result of 0.0458 Ry.

In Fig. 1 we show the adiabatic potential curves for $e^+ + \mathrm{Li}$ and $e^+ + \mathrm{Na}$ that asymptotically approach the ground state of Ps. The potential curves that approach the ground state of Li and of Na lie higher. From the $e^+ + \mathrm{Li}$ potential curve, we solved the one-dimensional eigenvalue problem, Eq. (3), and obtained a binding energy of 0.004 27 Ry, or 58.1 meV, which should be compared with the value 0.004 34 Ry (59 meV) obtained by Ryzhikh and Mitroy [1]. Thus, we confirm the existence of an electronically stable bound state for the $e^+ + \mathrm{Li}$ system. Note that its binding energy is much less than the binding energy of 623 meV for Li^-.

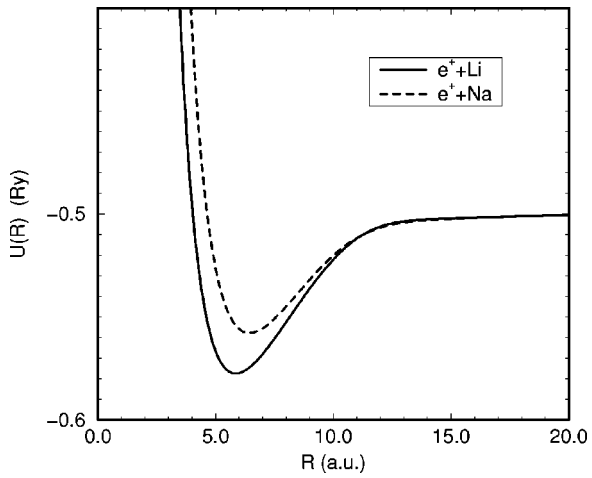

FIG. 1. The $L = 0$ adiabatic hyperspherical potential curve (including the diagonal coupling term) that supports the bound state for the $e^+ + \mathrm{Li}$ system (solid line) and for the $e^+ + \mathrm{Na}$ system (dashed line). Each curve approaches the Ps($1s$) limit asymptotically.

We have also performed similar calculations for the $e^+ + \mathrm{Na}$ system. The model potentials between each pair of particles are generated in the same fashion as for $e^+ + \mathrm{Li}$. The dipole polarizability is $\alpha = 0.9448$ [13] and the fitted cutoff radius is $r_c = 1.05$. We first checked the results for Na^- where the adiabatic hyperspherical method obtains a binding energy of 0.0393 Ry, to be compared with the experimental value of 0.0402 Ry. For the $e^+ + \mathrm{Na}$ system, the potential curve shown in Fig. 1 gives a binding energy of 0.000 51 Ry, or about 7 meV. Even though this is a small value, we believe that the bound state does indeed exist, since we expect the calculated binding energy to be an upper bound for a given model potential. (The upper bound is not rigorous here since the potential curve shown is not the lowest one in the present model calculation. There are three unphysical curves that approach the $1s$, $2s$, and $2p$ orbitals of Na^+ asymptotically, but they are well separated from the present curve of interest.) Furthermore, as stated above, the equivalent calculation for Na^- gives a bound state at -0.0393 Ry, which is above the experimental value of -0.0402 Ry. In other words, the binding energy for the $e^+ + \mathrm{Na}$ system is likely to be somewhat larger than 7 meV. We mention that the hyperspherical approach has no difficulty finding bound states that are very close to the threshold. For states that are near the threshold, the wave functions extend over the large-R region where the asymptotic potentials are well known. Thus the small error in the potential curve in the small-R region has less effect on the calculated energies for these diffuse bound states. For instance, the two weakly bound states in the $^4He_3$ trimer have been accurately obtained using this method [9].

To explore the sensitivity of the calculated binding energy for the $e^+ + \mathrm{Na}$ system on the model potential used, we arbitrarily altered the cutoff radius parameter r_c from 1.05 to 1.5. The resulting binding energies in rydbergs for the two models and from the experiment are (0.377 81, 0.373 32, 0.377 71) for $3s$, (0.143 37, 0.142 35, 0.143 15) for $4s$, (0.225 94, 0.224 36, 0.223 09) for $3p$, and (0.111 89, 0.111 85, 0.111 87) for $3d$, respectively; i.e., the new potential is not as attractive as the fitted one. With the new r_c

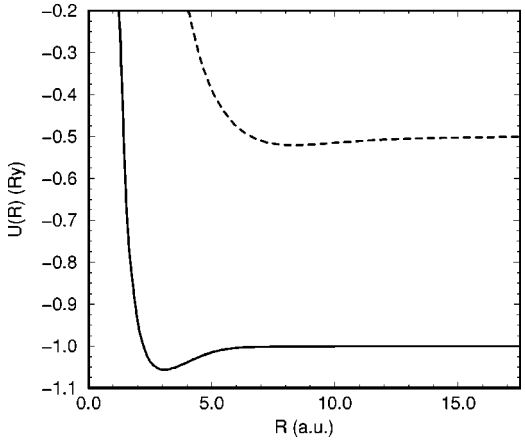

FIG. 2. The two lowest $L=0$ adiabatic hyperspherical potential curves for the $e^+ + \mathrm{H}$ system.

$=1.5$, the calculated binding energy for the $e^+ + \mathrm{Na}$ system is 4.2 meV. We emphasize that the second term in Eq. (4) is needed. If this term is neglected then the calculated binding energy for the $e^+ + \mathrm{Na}$ system is 14 meV. (Recently, Ryzhikh *et al.* [11] have calculated the binding energy for this system to be at 4.8 meV. They also used the model potential approach, and the resulting three-body system was solved using the stochastic variational method. Their model potential between the electron and the Na^+ core differs somewhat from ours. Their binding energies for $3s$, $4s$, $3p$, and $3d$ are 0.363 62, 0.140 15, 0.219 26, and 0.111 47 Ry, respectively.)

The above calculation clearly confirms the existence of a stable bound state for the $e^+ + \mathrm{Li}$ system for $L=0$, as predicted by Ryzhikh and Mitroy [1]. We have also predicted the existence of a bound state for the $e^+ + \mathrm{Na}$ system. On the other hand, the existence of such bound states is quite unexpected since it is known that there are no bound states for the $e^+ + \mathrm{H}$ system, despite the fact that H^- has a larger binding energy (0.75 eV) than either Li^- or Na^- (binding energies of 0.623 eV and 0.547 eV, respectively). Thus, one of the remaining issues is to understand why a positron cannot bind itself to H but can to Li and Na.

In Fig. 2 we show the two lowest $L=0$ potential curves for the $e^+ + \mathrm{H}$ system. The first curve has a minimum at $R=3$ a.u. and approaches the $\mathrm{H}(1s)$ limit asymptotically, while the second curve has a minimum at $R=8$ a.u. and approaches the $\mathrm{Ps}(1s)$ limit asymptotically. In Figs. 3(a) and 3(b) we show the probability densities of the channel functions Φ_ν at their potential minima, $R=3$ and 8 a.u., respectively. For comparison, the density for $e^+ + \mathrm{Li}$ at the minimum ($R=6$ a.u.) of the potential curve in Fig. 1 is also shown in Fig. 3(c). In order to understand these figures, it is useful to recall the definition of the hyperspherical coordinates above. If the positron is farther away from the nucleus than the electron, then ϕ is between $\pi/4$ and $\pi/2$. If the electron and positron form a pair, with nearly equal distance from the ion, then ϕ is close to $\pi/4$. Recall also that the angle θ is between the electron and the positron with respect to the ion. For $e^+ + \mathrm{H}$, from Fig. 3(a), the density is distributed over the range of ϕ between $\pi/4$ and $\pi/2$; i.e., the positron in general is farther away from the nucleus than the electron. At the same time, the probability density ranges in θ from 0 to

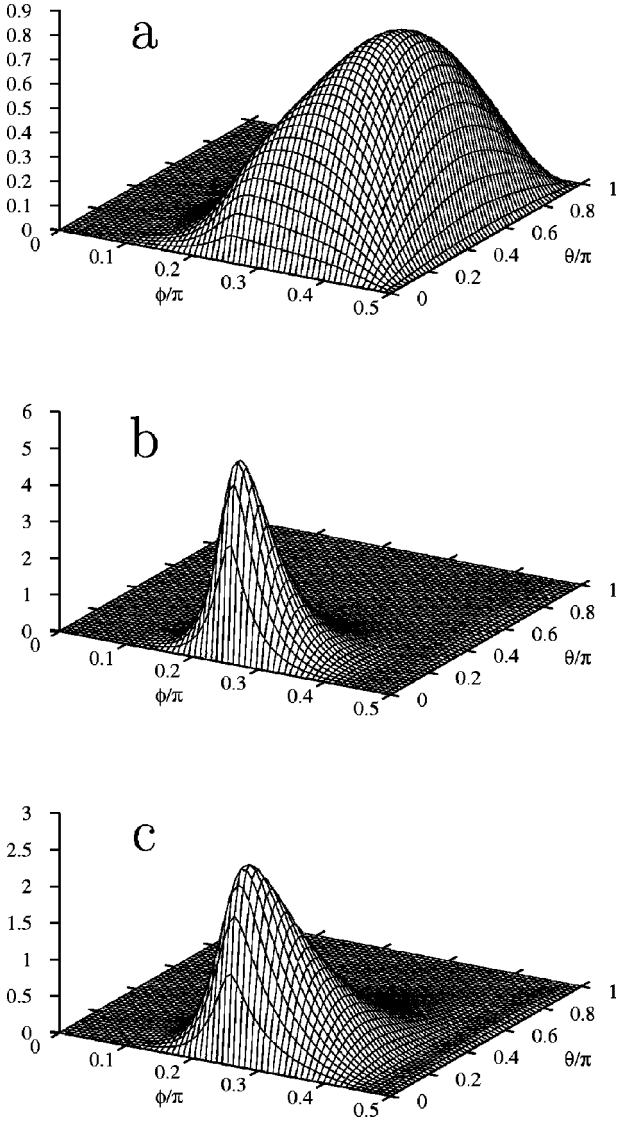

FIG. 3. Density plots of the channel wave functions in the (ϕ,θ) plane. For the $e^+ + \mathrm{H}$ system: (a) the first channel at $R=3$ a.u.; (b) the second channel at $R=8$ a.u.; (c) similar plots for the $e^+ + \mathrm{Li}$ system at $R=6$ a.u.

π. Thus, near the potential minimum the three-body system behaves like a positron *outside* a hydrogen atom. For the second curve, the density distribution peaks near $\phi=\pi/4$ [see Figs. 3(b)], indicating that the positron and the electron are at the same distance from the H^+ ion. Furthermore, the range of θ is limited, so that the three charged particles approximately form an isosceles triangle with the electron and the positron at the base and the H^+ ion at the top. Since the positron and the electron are separated by about 2 a.u. and the plot is for $R=8$ a.u., one can calculate that the distance from the proton to the electron (and positron) is about 6 a.u. At this distance, while H^+ can polarize Ps, it is too far for the polarization potential to form a bound state for the three particles. (A bound state belonging to this channel would actually be a resonance, since it can decay to the lower channel.)

We next examine Fig. 3(c) to see if we can find a plausible explanation for the existence of the calculated bound state for $e^+ + \mathrm{Li}$. This figure clearly shows that the $e^+ + \mathrm{Li}$ system has the shape of an isosceles triangle also, with e^+

and e^- at the base and Li^+ at the top. Since the electron and the positron have a mean distance of 2 a.u. and the potential curve has its minimum at $R = 6$ a.u., one can calculate that the distance between the electron (positron) and Li^+ is about 4.2 a.u.—about 30% smaller than the distance between the electron (positron) and H^+ in the $e^+ + H$ system. Thus, the isosceles triangle for the $e^+ + Li$ system is rather flat, as can be seen from the larger range of θ [by comparing the range of θ in Figs. 3(b) and 3(c)]. The proximity of Li^+ to the positronium results in a stronger attraction among the three particles so as to form a stable bound state. The same qualitative discussion can also be applied to $e^+ + Na$. The potential minimum for this system is at about $R = 6.5$ a.u., so that the distance from the electron (and positron) to Na^+ is about 4.6 a.u., and the calculation shows that a weakly bound state still exists. On the other hand, the binding energy has decreased significantly compared to $e^+ + Li$. We thus anticipate that a positron cannot bind itself to heavier alkali-metal atoms like K and Cs. Although the possible bound states will have the same shape of an isosceles triangle, the ion core will be too far from the Ps to achieve binding. In fact, the bound states found for Li and Na targets here are likely the exception rather than the norm.

We mention that there is a Feshbach resonance associated with the Ps($1s$) threshold for the $e^+ + He^+$ system that can be considered to be a bound state of $He^{2+} + Ps(1s)$. Calculations by Igarashi and Shimamura [6] show that the potential minimum occurs at R around 7 or 8 a.u. The existence of a bound state in this system despite this larger R is consistent with our explanation, since the positronium experiences a larger nuclear charge of 2.

In conclusion, we have performed adiabatic hyperspherical calculations on the $e^+ + Li$ and $e^+ + Na$ systems to search for the possible existence of bound states. For $e^+ + Li$ we confirmed the result of Ryzhikh and Mitroy [1] that a bound state exists at about 58 meV, and for $e^+ + Na$ we predicted a bound state with a binding energy of about 7 meV. We analyze the condition for the existence of such bound states and explain why such bound states occur in the present two systems, but not for the $e^+ + H$ system, in spite of the fact that H^- has a higher binding energy than the corresponding Li^- and Na^- ions. We also tentatively conclude that positrons cannot form bound states with other heavier alkali-metal atoms.

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[1] G. G. Ryzhikh and J. Mitroy, Phys. Rev. Lett. **79**, 4124 (1997).
[2] K. Varga and Y. Suzuki, Comput. Phys. Commun. **106**, 157 (1997).
[3] D. C. Clary, J. Phys. B **9**, 3115 (1976).
[4] T. Yoshida and G. Miyako, Phys. Rev. A **54**, 4571 (1996).
[5] Y. Zhou and C. D. Lin, J. Phys. B **27**, 5065 (1994).
[6] A. Igarashi and I. Shimamura, Phys. Rev. A **56**, 4733 (1997).
[7] A. A. Kernoghan, M. T. McAlinden, and H. R. J. Walters, J. Phys. B **27**, L625 (1994).
[8] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and W. A. King, Phys. Rev. A **52**, 4541 (1995).
[9] B. D. Esry, C. D. Lin, and C. H. Greene, Phys. Rev. A **54**, 394 (1996).
[10] M. G. Sucre, F. Goychman, and R. Lefebvre, Phys. Rev. A **2**, 1738 (1970).
[11] G. G. Ryzhikh, J. Mitroy, and K. Varga, J. Phys. B **31**, L265 (1998).
[12] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981), p. 189.
[13] M. Marinescu, H. R. Sadeghpour, and A. Dalgarno, Phys. Rev. A **49**, 982 (1994).
[14] D. W. Norcross and M. J. Seaton, J. Phys. B **9**, 2983 (1976).