

# High-precision calculation of loosely bound states of $\text{LiPs}^+$ and $\text{NaPs}^+$

Takuma Yamashita and Yasushi Kino\*

Department of Chemistry, Tohoku University, Sendai, 980-8578, Japan

E-mail: \*y.k@m.tohoku.ac.jp

**Abstract.** A positronic alkali atom would be the first step to investigate behavior of a positronium (Ps) in an external field from atoms/molecules because the system can be regarded as a simple three-body system using model potentials reflecting electron orbitals of the ion core. In order to precisely determine binding energies and structures of positronic alkali atoms ( $\text{LiPs}^+$  and  $\text{NaPs}^+$ ), we improve the model potential so as to reproduce highly excited atomic energy levels of alkali atoms (Li and Na). The polarization potential included by the model potential is expanded in terms of Gaussian functions to finely determine a short range part of the potential which has been assumed to be a simple form. We find better reproducibility not only of atomic levels of the alkali atoms but also of the dipole polarizability of the core ion than previous works. We construct a model potential between a positron and an ion core based on the model potential between the valence electron and ion core. Binding energies associated with a dissociation of the alkali ion core and positronium, and interparticle distances are recalculated. Our results show slightly deeper bound than other previous studies.

## 1. Introduction

Behavior of a positron ( $e^+$ ) in atoms/molecules is quite different from that of an electron because of its difference in charge. In particular, positronium (Ps; a bound state of a positron and an electron) formation is of importance. The Ps lifetime depends on the surrounded atoms/molecules and annihilation  $\gamma$ -rays of Ps reflect electronic states of atoms/molecules. The Ps lifetime spectrometry has been applied to investigate nano-structure of materials such as defects of metal and free volumes of polymer. Recently, high-precision experiments have been done such as a precise test of QED for Ps in *i*- $\text{C}_4\text{H}_{10}$  gas [1]. Therefore, effects given to a Ps by an external field from atoms/molecules have become more and more important.

A positronic alkali atom ( $\text{APs}^+$ ; “A” means an alkali atom), which is a bound state of an alkali ion core ( $\text{Li}^+$  or  $\text{Na}^+$ ) and a Ps, is a good testing ground to investigate the effects of external fields to a Ps. We can treat the  $\text{APs}^+$  as a simple three-body system composed of an alkali ion core, a valence electron and a positron by introducing model potentials which consists of a static and polarization potential. The static potential reflects core electron orbital without excitation and is calculated from Hartree-Fock wavefunctions. The polarization potential reflects virtual excitation of the orbitals and consists of short range part and well-known long-range part which is the lowest polarization potential. The short range part reflects higher order of the excitations, but it is usually assumed to be a simple function which only avoids a divergence at the origin. For the availability of precise calculations, a lot of calculations have been done [2–13]. When an alkali atom binds a positron, the valence electron transfers to the positron and forms a Ps halo. Since the Ps is a neutral particle, this state is a loosely bound state and has a large fraction of the Ps-alkali ion configuration. Kubota and Kino [11] have pointed out that the fraction



having the positron-alkali atom configuration is small but plays an indispensable role for the weakly bound system. In this mechanism, the polarization of the alkali ion core by the valence electron and the positron is of importance. The polarization potential consists of a short and long range parts whose asymptotic form is  $r^{-4}$ . Contribution of the short range part of the polarization potential should be small because the Coulomb interaction from the nucleus is highly dominant in that region. The short range part, therefore, can not be determined within a single particle approximation. The small binding energy of  $\text{APs}^+$  depends on the model potential strongly [10, 12].

In this work, we introduce a more flexible polarization potential having a larger parameter space than other previous studies in which a simple empirical function was used for the inner part of the potential. Binding energies and structures of  $\text{LiPs}^+$  and  $\text{NaPs}^+$  are recalculated by a high-precision three-body calculation, based on one of the most accurate calculation [11]. Atomic units (a.u.;  $m_e = \hbar = e = 1$ ) are used throughout this paper except where mentioned otherwise.

## 2. Theory

### 2.1. Improvement of model potential

A model potential between the ion core and valence electron  $V_e(r_e)$  is composed of static, exchange and polarization potentials, namely,

$$V_e(r_e) = V_{\text{st}}(r_e) + V_{\text{exch}}(r_e) + V_{\text{pol}}(r_e), \quad (1)$$

where the  $r_e$  is a distance between the ion core and valence electron. The static potential  $V_{\text{st}}(r_e)$  and the local exchange potential  $V_{\text{exch}}(r_e)$  [14] are given by a standard Hartree calculation [15, 16] by a computer program [17, 18] written by Albright *et al.* A polarization potential is written as

$$V_{\text{pol}}(r_e) = -\frac{\alpha_d}{2r_e^4} [1 - f(r_e)], \quad (2)$$

where  $\alpha_d$  is a dipole polarizability,  $\alpha_d = 0.192$  for Li and  $\alpha_d = 0.923$  for Na given by Gien [19]. The  $f(r_e)$  is a short range function determined numerically and has boundary conditions of  $f(r_e \rightarrow 0) = 1$  and  $f(r_e \rightarrow \infty) = 0$ . Usually, the  $1 - f(r_e)$  is written in an exponential form [18] or a polynomial form [20, 21]. In this work, we expand the polarization potential by Gaussian functions and increase flexibility:

$$V_{\text{pol}}(r_e) = \sum_{i=1}^N C_i r_e^2 e^{-a_i r_e^2}, \quad (3)$$

where  $C_i$  and  $a_i$  are optimization parameters. Although the Gaussian function decreases rapidly, a linear combination of Gaussian functions with small  $0.0001 < a_i < 0.1$  can effectively reproduce the asymptotic form of the polarization potential.

The Schrödinger equation about the valence electron can be written as

$$H_A \psi_{nl} = \varepsilon_{nl} \psi_{nl}, \quad (4)$$

with

$$H_A = -\frac{1}{2} \left\{ \frac{1}{r_e} \frac{d^2}{dr_e^2} r_e - \frac{l(l+1)}{r_e^2} \right\} + V_e(r_e), \quad (5)$$

where  $\psi_{nl}$  is a wavefunction of the alkali atom,  $\varepsilon_{nl}$  the eigenenergy of  $\psi_{nl}$ ,  $n$  the principal quantum number ( $n \geq 2$  for Li and  $n \geq 3$  for Na) and  $l$  the orbital angular momentum quantum number. We determine the parameters  $C_i$  and  $a_i$  in (3) so that the calculated energy levels  $\varepsilon_{nl}$  can reproduce experimental energy levels [22] of the alkali atom within the boundary conditions.

According to literature calculations [2, 3], the model potential between the ion core and positron is given by

$$V_p(r_p) = -V_{st}(r_p) + V_{pol}(r_p), \quad (6)$$

where the  $r_p$  is a distance between the ion core and the positron. The polarization potential between the ion core and positron is attractive and has the same form as the potential (3) because the polarization effect is quadratic in charge of the projectile [23].

## 2.2. Precise calculation of $APs^+$ systems

In order to solve the  $APs^+$  three-body system precisely, we employ a Gaussian expansion method (GEM) which has been applied to a variety of few-body systems (see the review article [24] and references therein). In our previous work, precision of the three-body calculation is ensured by a test calculation using the same Peach potential as in Refs. [20, 21]. Total Hamiltonian  $H_{APs^+}$  and the three-body wavefunction  $\Psi_{APs^+}$  are given in our previous study [11] and satisfy the Schrödinger equation:

$$H_{APs^+} \Psi_{APs^+} = E_{APs^+} \Psi_{APs^+}. \quad (7)$$

The binding energy associated with the dissociation of  $A^+ + Ps$  is given by a subtraction of the free Ps energy ( $-0.25$  a.u.) from the three-body energy  $E_{APs^+}$ .

## 3. Results and Discussion

In table 1, calculated energy levels of Li and Na atom are shown together with experimental values. The model potential (1) obtained in this work reproduces observed energy levels of alkali atoms within  $|\varepsilon_{nl}^{theo} - \varepsilon_{nl}^{obs}| < 0.000\,004$ , where  $\varepsilon_{nl}^{theo}$  is calculated energy levels and  $\varepsilon_{nl}^{obs}$  experimental energy levels. This reproducibility is more a precise result than results of the other previous calculations. In our previous work [11], the dipole polarizability  $\alpha_d$  in (2) was a little different from experimental values. We numerically determine the inner empirical part of the polarization potential by the expansion of Gaussian functions (3) using experimental polarizabilities.

Then we show the results of three-body calculations. In table 2, the convergence of the ground state energy of  $APs^+$  is shown. We obtain the energies in 7-digit accuracy using more than 6000 basis functions. In table 3, the binding energy associated with the  $A^+ + Ps$  dissociation and the expectation values of interparticle distances are shown together with other theoretical results. The results in this work show slightly deeper bound and larger polarization of a bound Ps than previous results. Since the Ps component in  $APs^+$  is located far away from the ion and the long range parts of  $V_e(r_e)$  and  $V_p(r_p)$  cancel each other, small differences among the calculations are mainly caused by their short range parts. In the previous calculations listed in table 3, the short range part of the potentials has a simple analytical form having a few optimization parameters for theoretical convenience. In this work, we expand the part with sufficient number of functions with much more optimization parameters than previous calculations. Moreover some of previous calculations do not include the exchange potential which is effective only in the short range. Thus, we conclude the present result should be more accurate than previous results.

## 4. Summary

We improve the model polarization potential for precise calculation of loosely bound states of  $APs^+$  with a fine-tuned polarization potential. As a result, we get a good reproducibility up to highly excited states using polarizabilities based on experimental values. These flexible polarization potentials can be applied to other alkali atom systems and high-precision calculations of positron-alkali atom scattering.

The three-body calculation is carried out by GEM using the improved model potential. The binding energies are recalculated in 7-digit accuracy. The geometry of  $APs^+$  system shows slightly larger polarization and deeper bound of Ps but no contradiction with other previous works.

**Table 1.** Energy levels of Li and Na atoms calculated with various model potentials. The experimental values are taken from the NIST Atomic Spectra Database [22].

State	Theory			Experiment [22]
	Han <i>et al.</i> [10]	Kubota <i>et al.</i> [11]	This work	
Li	2s	−0.197 952	−0.198 136	−0.198 142
	3s	−0.074 224	−0.074 173	−0.074 182
	4s	−0.038 641	−0.038 613	−0.038 615
	5s		−0.023 636	−0.023 636
	6s		−0.015 945	−0.015 945
Na	3s	−0.188 855	−0.188 859	−0.188 858
	4s	−0.071 581	−0.071 586	−0.071 578
	5s		−0.037 588	−0.037 584
	6s		−0.023 134	−0.023 132
	7s		−0.015 664	−0.015 662

**Table 2.** Convergence of the energies of bound states as a function of the number of basis functions for  $\text{LiPs}^+$  and  $\text{NaPs}^+$ .

Number of basis functions	$\text{LiPs}^+$	Number of basis functions	$\text{NaPs}^+$
5216	−0.252 578 6	5216	−0.250 479 5
5691	−0.252 578 7	5660	−0.250 479 9
6159	−0.252 578 8	6128	−0.250 480 2
6651	−0.252 578 8	6620	−0.250 480 3

**Table 3.** Binding energies and expectation values of inter-particle distances  $\langle r_e \rangle$ ,  $\langle r_p \rangle$ ,  $\langle r_{ep} \rangle$  for the bound state of  $\text{LiPs}^+$  and  $\text{NaPs}^+$ . The  $r_{ep}$  is a distance between a positron and a valence electron.

	Method	Binding energy	$\langle r_e \rangle$	$\langle r_p \rangle$	$\langle r_{ep} \rangle$
$\text{LiPs}^+$	This work	0.002 579	8.987	9.859	3.403
	GEM [11]	0.002 615	8.950	9.824	3.404
	FCSVM [6, 7]	0.002 478 9	9.110 1	9.967 8	3.396 7
	AHM [10]	0.002 455	9.135	9.991	3.393
	FEM [9]	0.002 37	9.01(10)	9.87(10)	3.40(5)
$\text{NaPs}^+$	This work	0.000 480	16.66	17.07	3.165
	GEM [11]	0.000 401	17.87	18.25	3.152
	FCSVM [4]	0.000 473	16.818	17.231	3.162
	AHM [10]	0.000 447	17.12	17.52	3.159
	FEM-ITM [12]	0.000 357	18.24	18.62	3.146

## Acknowledgments

This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. The computation was partially carried out on the supercomputers in Kyushu University and KEK.

## References

- [1] Ishida A, Namba T, Asai S, Kobayashi T, Saito H, Yoshida M, Tanaka K and Yamamoto A 2014 *Phys. Lett. B* **734** 338
- [2] Ryzhikh G and Mitroy J 1997 *Phys. Rev. Lett.* **79**(21) 4124
- [3] Ryzhikh G G, Mitroy J and Varga K 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 3965
- [4] Mitroy J and Ryzhikh G G 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** L621
- [5] Mitroy J, Bromley M W J and Ryzhikh G G 2002 *J. Phys. B: At. Mol. Opt. Phys.* **35** R81

- [6] Mitroy J 2004 *Phys. Rev. A* **70**(2) 024502
- [7] Mitroy J 2005 *Phys. Rev. Lett.* **94**(3) 033402
- [8] Le A T, Bromley M and Lin C D 2005 *Phys. Rev. A* **71**(3) 032713
- [9] Shertzer J and Ward S 2006 *Phys. Rev. A* **73**(2) 022504
- [10] Han H I, Li Y, Zhang X and Shi T 2008 *J. Chem. Phys.* **128** 244314
- [11] Kubota Y and Kino Y 2008 *New J. Phys.* **10** 023038
- [12] Shertzer J and Ward S 2010 *Phys. Rev. A* **81**(6) 064505
- [13] Yamashita T, Irisawa A and Kino Y 2014 *Jpn. J. Appl. Phys. Conf. Proc.* **011005** 2
- [14] Furness J B and McCarthy I E 1973 *J. Phys. B: At. Mol. Phys.* **6** 2280
- [15] Hartree D R 1928 *Proc. Camb. Phil. Soc.* **24** 111
- [16] Mitroy J 1983 Ph.D. thesis University of Melbourne
- [17] Bartschat K 1996 *Computational Atomic Physics Ch. 2* (Berlin: Springer) p 15
- [18] Albright B J, Bartschat K and Flicek P R 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** 337
- [19] Gien T 1987 *Phys. Rev. A* **35**(5) 2026
- [20] Peach G, Saraph H E and Seaton M J 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 3669
- [21] Peach G 1982 *Comments At. Mol. Phys.* **11** 101
- [22] Kramida A, Yu Ralchenko, Reader J and NIST ASD Team 2014 NIST Atomic Spectra Database (ver. 5.2) <http://physics.nist.gov/asd>. National Institute of Standards and Technology, Gaithersburg, MD.
- [23] Charlton M and Humberston J W 2001 *Positron Physics Ch.1* (Cambridge: Cambridge University) p 35
- [24] Hiyama E, Kino Y and Kamimura M 2003 *Prog. Part. Nucl. Phys.* **51** 223