Estimation of Relativistic Effects on Loosely Bound States of Positronic Alkali Atoms

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Lithium and sodium atoms can interact with positronium to from a positronic alkali atom in which the ion core of the alkali atom loosely binds to positronium. The systems are suitable to investigate mechanisms of positron binding to atoms because the systems can be described with a three-body model and atomic interactions are included in a model potential between the ion core and the valence electron in the atoms. In order to clarify the details of the loosely bound states, we estimated relativistic effects by reconstructing the model potential. A major contribution to the relativistic effects on the binding energy are ascribed to the electron in the alkali atomic orbital whose contribution to the total wavefunction is small. It was found that the relativistic effects appear largely in the binding energy and geometry of $LiPs^+$ and $NaPs^+$ compared with those of Li and Na atoms.

1.   Introduction

Interaction between a positron (e^+) and an atom is of importance not only in atomic physics but in every field utilizing positron annihilation in matter. Because of the difference in sign of the charge the interaction differs from that between an electron (e^-) and an atom. This makes positrons an alternative probe to investigate Coulombic few-body systems. Some atoms and atomic ions can bind a positron [1, 2]. In the case of an alkali atom (A), the valence electron transfers to the positron and forms a positronium (Ps) because the ionization energies of alkali atoms are smaller than the binding energy of Ps. The residual ion core (A^+) polarizes the Ps and forms a loosely bound state of the positronic alkali atom ($APs^+ = A^+ + Ps$). The structure of the positronic alkali atom has been regarded as a Ps atom orbiting the alkali ion, which is described by the Ps-alkali ion channel. Previously, we pointed out that the fraction having the alternative positron-alkali atom configuration was small but played an indispensable role for the loosely bound system [3]. Since a three-body model consisting of a positron, a valence electron and a residual ion core is a good approximation for the positronic alkali atom, the mechanism can be investigated in detail by high-precision three-body calculations. Many theoretical works have been reported for positronic alkali atoms [2–10]. In the present paper, we estimate relativistic corrections for the loosely bound states. The Pauli approximation is used for the valence electron and positron. Atomic units (a.u.; $m_e = \hbar = e = 1$) are used throughout this paper except where mentioned otherwise.

2.   Theory

2.1   Two-body system

The two-body Hamiltonian for an alkali atom ion core and the valence electron is given as

$$H_{2body} = -\frac{1}{2}\nabla^2_{r_e} + V_e(r_e) \tag{1}$$

where V_{e} is a model potential as a function of the distance between the ion core and valence electron. The model potential given by Albright, Bartschat, and Flicek [11] is written as

$$V_{\mathrm{e}}(r_{\mathrm{e}}) = V_{\mathrm{st}}(r_{\mathrm{e}}) + V_{\mathrm{pol}}(r_{\mathrm{e}}) + V_{\mathrm{exc}}(r_{\mathrm{e}}), \tag{2}$$

where $V_{\mathrm{st}}(r_{\mathrm{e}})$ is a static potential given by a standard Hartree potential [12], $V_{\mathrm{exc}}(r_{\mathrm{e}})$ a local exchange potential by Furness and McCarthy [13] and $V_{\mathrm{pol}}(r_{\mathrm{e}})$ a polarization potential. The polarization potential $V_{\mathrm{pol}}(r_{\mathrm{e}})$ is written as

$$V_{\mathrm{pol}}(r_{\mathrm{e}}) = -\frac{\alpha_{\mathrm{d}}}{2r_{\mathrm{e}}^4}\left[1 - \exp\left\{-\left(\frac{r_{\mathrm{e}}}{r_{\mathrm{c}}}\right)^6\right\}\right], \tag{3}$$

where α_{d} and r_{c} are a dipole polarizability and a cut-off radius, respectively. The dipole polarizability and cut-off radius are optimized so as to reproduce the observed atomic energy levels E_{ns}^{obs} with a computer based calculation [11, 14]. The parameters $\alpha_{\mathrm{d}} = 0.531$ (1.412) a.u., $r_{\mathrm{c}} = 1.645$ (1.717) a.u. for a Li (Na) atom reproduce the observed energy levels up to the 6s (7s) state to an accuracy of 0.000 002 (0.000 002) a.u. [3].

Although the calculation is carried out based on the non-relativistic Schrödinger equation, the atomic energy levels E_{ns}^{obs} include relativistic effects. As a result, the model potential given in Eq. (2) automatically includes the relativistic effects. In order to evaluate the relativistic effect on the binding energies, we divide the model potential (Eq. (2)) into two, namely, a non-relativistic part and a relativistic part,

$$V_{\mathrm{e}}(r_{\mathrm{e}}) = V_{\mathrm{e}}^{\mathrm{nr}}(r_{\mathrm{e}}) + V_{\mathrm{e}}^{\mathrm{rel}}(r_{\mathrm{e}}). \tag{4}$$

The total two-body Hamiltonian is written as

$$H_{\mathrm{2body}}^{\mathrm{tot}} = H_{\mathrm{2body}}^{\mathrm{nr}} + H_{\mathrm{2body}}^{\mathrm{rel}} \tag{5}$$

with

$$H_{\mathrm{2body}}^{\mathrm{nr}} = -\frac{1}{2}\nabla_{r_{\mathrm{e}}}^2 + V_{\mathrm{e}}^{\mathrm{nr}}(r_{\mathrm{e}}), \tag{6}$$

and

$$H_{\mathrm{2body}}^{\mathrm{rel}} = \alpha^2\left(-\frac{\mathbf{p}_{\mathrm{e}}^4}{8} + \frac{1}{8}\nabla_{r_{\mathrm{e}}}^2 V_{\mathrm{e}}^{\mathrm{nr}}(r_{\mathrm{e}})\right), \tag{7}$$

where α ($\alpha^{-1} = c \approx 137$; c is the speed of light) is the fine structure constant and $\mathbf{p}_{\mathrm{e}}$ the momentum vector of the electron. The relativistic part of the Hamiltonian $H_{\mathrm{2body}}^{\mathrm{rel}}$ is derived from the Dirac equation with the Pauli approximation.

To calculate the $V_{\mathrm{e}}^{\mathrm{nr}}$, the model potential is rewritten as a sum of a long range Coulomb potential and a short range part which is expanded in terms of Gaussian basis functions,

$$V_{\mathrm{e}}(r_{\mathrm{e}}) = -\frac{1}{r_{\mathrm{e}}} - \frac{1}{r_{\mathrm{e}}}\sum_{j=1}^{j_{\max}} B_j \exp(-b_j r_{\mathrm{e}}^2), \tag{8}$$

where b_j and B_j are Gaussian range parameters and expansion coefficients, respectively. Since $V_{\mathrm{e}}^{\mathrm{rel}}$ is much smaller than $V_{\mathrm{e}}^{\mathrm{nr}}$, we construct the $V_{\mathrm{e}}^{\mathrm{nr}}$ by changing the short range part of the V_{e} slightly,

$$V_{\mathrm{e}}^{\mathrm{nr}}(r_{\mathrm{e}}) = -\frac{1}{r_{\mathrm{e}}} - \frac{1}{r_{\mathrm{e}}}\sum_{j=1}^{j_{\max}} (B_j + \delta_j) \exp(-b_j r_{\mathrm{e}}^2). \tag{9}$$

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Here, the expansion coefficients B_j and δ_j satisfy the boundary condition,

$$\lim_{r_e \to 0} V_e^{nr}(r_e) = -\frac{Z}{r_e}, \tag{10}$$

where Z is the nuclear charge.

The relativistic corrections ΔE_{ns} is calculated with the use of the first-order perturbation theory,

$$\Delta E_{ns} = \langle \phi_{ns}^{nr}(r_e) | H_{2body}^{rel} | \phi_{ns}^{nr}(r_e) \rangle, \tag{11}$$

where $\phi_{ns}^{nr}(r_e)$ is the non-relativistic wavefunction calculated from the Schödinger equation,

$$H_{2body}^{nr} \phi_{ns}^{nr}(r_e) = E_{ns}^{nr} \phi_{ns}^{nr}(r_e). \tag{12}$$

The calculated energy levels E_{nl} are given by a sum of the non-relativistic energies and relativistic corrections, namely,

$$E_{ns} = E_{ns}^{nr} + \Delta E_{ns}. \tag{13}$$

We iteratively calculate the Eqs. (6), (9), (11), and (12) with $\delta_j = 0$, namely $V_e^{nr}(r_e) = V_e(r_e)$, as an initial value so as to conform E_{ns} to observed energy levels E_{ns}^{obs}. The iterative calculation converges quickly.

Figure 1 shows the relative difference between the model potential and its relativistic part plotted as a function of r_e. The contribution of the relativistic effect is small and is significant only inside the ion core. In the positronic atom three-body system, therefore, the relativistic effect appears in between the valence electron and ion core and in the positronium component. The relativistic effect on the positron and ion core component does not appear because of repulsive Coulombic interaction between them.
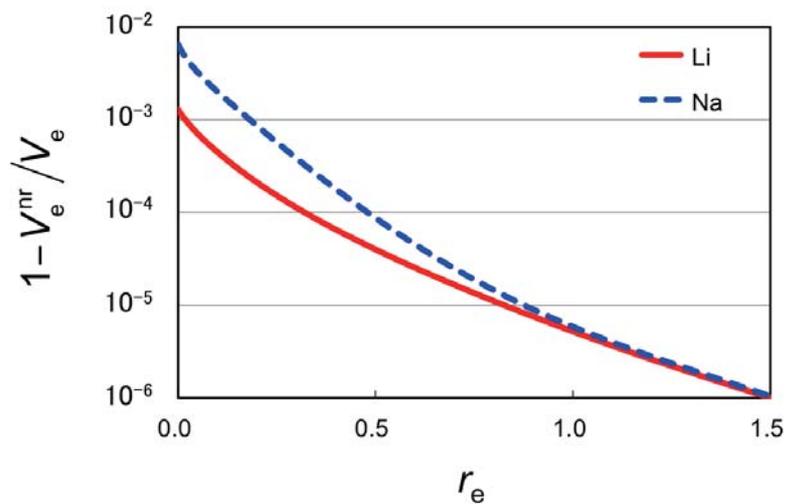

Fig. 1. The relative difference between the model potential $V_e(r_e)$ and its non-relativistic part $V_e^{nr}(r_e)$ plotted as a function of r_e.

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2.2 Three-body system

In order to accurately calculate the loosely bound states, we employ the Gaussian Expansion Method (GEM) [15] which has been applied to a variety of few-body systems (see Ref. [15] and references therein). We introduce two sets of coordinates $(\mathbf{r}, \mathbf{R})$ and $(\mathbf{r}_e, \mathbf{r}_p)$ of rearrangement channels ($c = 1$ and 2) illustrated in Fig. 2, and inter-particle correlations can be directly taken into account.

A total three-body wavefunction in the S state Ψ_0 is described as a sum of amplitudes of the two channels

$$\Psi_0 = \Phi_0^1(\mathbf{r}, \mathbf{R}) + \Phi_0^2(\mathbf{r}_e, \mathbf{r}_p). \tag{14}$$

Each amplitude is expanded in terms of Gaussian basis functions,

$$\Phi_0^c(\mathbf{x}_c, \mathbf{y}_c) = \sum_{nNl_c} A_{nNl_c}^c x_c^{l_c} y_c^{l_c} \exp(-\mu_n x_c^2 - \nu_N y_c^2) \mathrm{P}_{l_c}(\hat{\mathbf{x}}_c \cdot \hat{\mathbf{y}}_c), \tag{15}$$

where $(\mathbf{x}_1, \mathbf{y}_1) = (\mathbf{r}, \mathbf{R})$, $(\mathbf{x}_2, \mathbf{y}_2) = (\mathbf{r}_e, \mathbf{r}_p)$, $(\hat{\mathbf{x}}_c, \hat{\mathbf{y}}_c) = (\mathbf{x}_c/x_c, \mathbf{y}_c/y_c)$ and $\mathrm{P}_{l_c}(\hat{\mathbf{x}}_c \cdot \hat{\mathbf{y}}_c)$ is the Legendre polynomial. The Gauss range parameters μ_n and ν_N are given according to the geometrical progression to describe both short-range correlation and long-range tail behavior. Here, we consider the positronic alkali atom is in the s-state. The internal angular momentum l_c is restricted to $0 \le l_c \le l_{\max}$. Eigenenergies E_0 and coefficients $A_{nNl_c}^c$ are determined by the Rayleigh-Ritz variational principle. Employing the GEM where the positronium channel (A^+−Ps) and alkali atom channel (A−e^+) are explicitly introduced, we calculate energies and wavefunctions of bound states of positronic alkali atoms.

We produce the model potential between the ion core and positron by referring the V_e in Eq. (2) and it is given by

$$
\begin{aligned}
V_p(r_p) &= -V_{st}(r_p) + V_{pol}(r_p) \\
&= -V_e(r_p) + 2V_{pol}(r_p) + V_{exc}(r_p),
\end{aligned} \tag{16}
$$

and

$$V_p^{nr}(r_p) = -V_e^{nr}(r_p) + 2V_{pol}(r_p) + V_{exc}(r_p). \tag{17}$$

The non-relativistic three-body Hamiltonian is given as

$$H_{3body}^{nr} = -\frac{1}{2}\nabla_{r_e}^2 - \frac{1}{2}\nabla_{r_p}^2 + V_e^{nr}(r_e) + V_p^{nr}(r_p) - \frac{1}{r} + V_{2pol}(\mathbf{r}_e, \mathbf{r}_p) + \lambda \sum_i \left|\phi_i^{core}\right\rangle\left\langle\phi_i^{core}\right|, \tag{18}$$
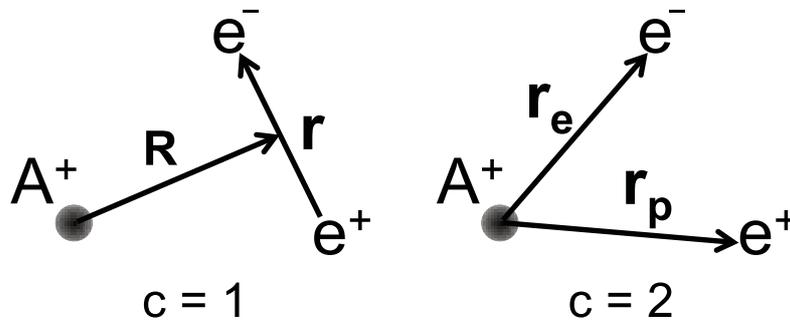

Fig. 2. Two sets of rearrangement coordinates of a positronic alkali atom system. The first channel ($c = 1$) is suited to describe the A^+−Ps configuration. The second channel ($c = 2$) is suited to describe the A−e^+ configuration.

where $V_{2\text{pol}}$ is a two-body correction to the polarization potentials for the electron and positron. The $V_{2\text{pol}}(\mathbf{r}_e, \mathbf{r}_p)$ [16] was given by Norcross and Seaton, and is written as

$$V_{2\text{pol}}(\mathbf{r}_e, \mathbf{r}_p) = 2\,\hat{\mathbf{r}}_e \cdot \hat{\mathbf{r}}_p \sqrt{V_{\text{pol}}(r_e)V_{\text{pol}}(r_p)}. \tag{19}$$

The last term of the Hamiltonian is introduced to remove pseudo-states where the electron occupies core orbital ϕ_i^{core} from the total wavefunction [17]. The relativistic three-body Hamiltonian is

$$H_{3\text{body}}^{\text{rel}} = -\frac{1}{2}\nabla_{r_e}^2 - \frac{1}{2}\nabla_{r_p}^2 + V_e(r_e) + V_p(r_p) - \frac{1}{r} + V_{2\text{pol}}(\mathbf{r}_e, \mathbf{r}_p) + \lambda \sum_i \left|\phi_i^{\text{core}}\right\rangle\!\left\langle\phi_i^{\text{core}}\right| + H_{\text{Ps}}^{\text{BP}} + H_{\text{Ps}}^{\text{A}}. \tag{20}$$

The last two terms of the three-body Hamiltonian are the relativistic corrections for the Ps coordinate as the leading correction for the Breit-Pauli perturbation [18] and annihilation channel correction [19], respectively, and are given by

$$H_{\text{Ps}}^{\text{BP}} = \alpha^2 \left[-\frac{\mathbf{p}^4}{4} + \pi\delta(\mathbf{r}) - \frac{\mathbf{p}\cdot\mathbf{p}}{2r} - \frac{(\mathbf{p}\cdot\mathbf{r})(\mathbf{p}\cdot\mathbf{r})}{2r^3} + \frac{4\pi}{3}\left\{S(S+1) - \frac{3}{2}\right\}\delta(\mathbf{r}) \right], \tag{21}$$

and

$$H_{\text{Ps}}^{\text{A}} = \alpha^2 \pi S(S+1)\delta(\mathbf{r}), \tag{22}$$

where $\mathbf{p}$ is the corresponding momentum vector of $\mathbf{r}$, and S is total spin angular quantum number of the electron and positron pair. Since the correction is sufficiently smaller than the total three-body energy, we use the first order perturbation approximation for the last two terms of the relativistic three-body Hamiltonian. The lowest break-up threshold is the ground state of Ps and ion core. A binding energy of the three-body system is calculated by subtracting the energy of the ground state of Ps from the total three-body energy.

3. Results and discussion

In Table I, binding energies and expectation values of inter-particle distance are listed with relative errors. The non-relativistic binding energy E^{nr} associated with Ps(1s) + A$^+$ threshold $E_{\text{Ps}}^{\text{nr}}$ is given as

$$-E^{\text{nr}} = E_0^{\text{nr}} - E_{\text{Ps}}^{\text{nr}}, \tag{23}$$

where the eigenenergy E_0^{nr} is calculated with the non-relativistic Hamiltonian of Eq. (18). The expectation value $\langle r_e \rangle^{\text{nr}}$ is

$$\langle r_e \rangle^{\text{nr}} = \langle \Psi_0^{\text{nr}} \mid r_e \mid \Psi_0^{\text{nr}} \rangle, \tag{24}$$

where the Ψ_0^{nr} is the non-relativistic three-body wavefunction. On the other hand, the relativistic binding energy E^{rel} associated with Ps(1s) + A$^+$ threshold $E_{\text{Ps}}^{\text{rel}}$ is

$$-E^{\text{rel}} = E_0^{\text{rel}} + \langle \Psi_0^{\text{rel}} \mid H^{\text{BP}} + H^{\text{A}} \mid \Psi_0^{\text{rel}} \rangle - E_{\text{Ps}}^{\text{rel}}, \tag{25}$$

where the E_0^{rel} and Ψ_0^{rel}, which are calculated with the unperturbed Hamiltonian of Eq. (20), represent a relativistic eigenenergy and three-body wavefunction respectively. The threshold $E_{\text{Ps}}^{\text{rel}}$ is

$$E_{\text{Ps}}^{\text{rel}} = E_{\text{Ps}}^{\text{nr}} + \langle \phi_{\text{Ps}}^{\text{nr}} \mid H^{\text{BP}} + H^{\text{A}} \mid \phi_{\text{Ps}}^{\text{nr}} \rangle, \tag{26}$$

where the $\phi_{\mathrm{Ps}}^{\mathrm{nr}}$ is a non-relativistic two-body wavefunction of Ps(1s). Using the Ψ_0^{rel}, the expectation value of the inter-particle distance $\langle r_{\mathrm{e}} \rangle^{\mathrm{rel}}$ is

$$\langle r_{\mathrm{e}} \rangle^{\mathrm{rel}} = \langle \Psi_0^{\mathrm{rel}} \mid r_{\mathrm{e}} \mid \Psi_0^{\mathrm{rel}} \rangle. \tag{27}$$

The relative errors are given by $\Delta_E = 1 - E^{\mathrm{nr}}/E^{\mathrm{rel}}$ and $\Delta_r = 1 - \langle r_{\mathrm{e}} \rangle^{\mathrm{nr}}/\langle r_{\mathrm{e}} \rangle^{\mathrm{rel}}$.

The bound states are located just below the Ps(1s) + A$^+$ threshold energy. Since the probabilities of finding the 1s state of Ps in the total three-body wavefunction are 0.871 for LiPs$^+$ and 0.953 for NaPs$^+$ [3], the relativistic corrections for the Ps component almost cancel out in the subtraction of the Ps energy consequently. Therefore, in loosely bound states such as LiPs$^+$ and NaPs$^+$, relativistic effects of the binding energy mainly come from the valence electron motion. In addition, the positron located far away from the nucleus does not affect the correction. For these reasons, the binding energy of positronic alkali atoms should be compared with that of the alkali atoms.

The relative error Δ_E of the binding energy of LiPs$^+$ is about 10 times larger than that of Li(2s) and the error of NaPs$^+$ is about 29 times larger than that of Na(3s). The A$^+$ loosely binds the Ps in APs$^+$ and the A$^+$ tightly binds the valence electron in A. The binding energies of APs$^+$ are two or three orders of magnitude smaller than those of A. Thus, the relative errors of APs$^+$ become larger than those in A, though the relativistic corrections in APs$^+$ are one order of magnitude smaller than those in A.

The relativistic effects attract electrons and electron clouds shrink. In the loosely bound states, the potential energy changes slowly at large distance. The binding energy, therefore, increases and the expectation value of the inter-particle distance between the ion core and valence electron decreases by -0.04 % for LiPs$^+$ and -1.64 % for NaPs$^+$ compared with non-relativistic bound states.

In the present calculation using an approximative relativistic potential, it becomes clear that the relativistic effects contribute largely to the loosely binding states of LiPs$^+$ and NaPs$^+$. A more accurate calculation based on the Breit equation is in progress [20].

Table I. Binding energies (E^{rel}, E^{nr}), expectation values of inter-particle distance ($\langle r_{\mathrm{e}} \rangle^{\mathrm{rel}}$, $\langle r_{\mathrm{e}} \rangle^{\mathrm{nr}}$) and relative errors($\Delta_E$, Δ_r) of the ground state of positronic atoms and corresponding atoms. The binding energies of the two-body systems, namely Li and Na, are given as $E^{\mathrm{rel}} = E_{nl}^{\mathrm{nr}} + \Delta E_{nl}$ and $E^{\mathrm{nr}} = E_{nl}^{\mathrm{nr}}$ which are appeared in Eq. (13).

	LiPs$^+$	Li(2s)	NaPs$^+$	Na(3s)
E^{rel}	0.002 615	0.198 136	0.000401	0.188 859
E^{nr}	0.002 612	0.198 113	0.000377	0.188 476
Δ_E	0.11 %	0.011 %	5.8 %	0.20 %
$\langle r_{\mathrm{e}} \rangle^{\mathrm{rel}}$	8.950	3.84	17.87	4.10
$\langle r_{\mathrm{e}} \rangle^{\mathrm{nr}}$	8.953	3.84	18.16	4.10
Δ_r	-0.04 %	0.0 %	-1.64 %	0.0 %

4. Conclusion

For a detailed understanding of the loosely bound states of positronic alkali atoms, we estimate relativistic effects by reconstructing a model potential between the ion core and valence electron in the atoms. It was found that the relativistic effects appear largely in the binding energy and geometry of the LiPs$^+$ and NaPs$^+$ compared with those of corresponding atoms. Although the positron-alkali atom configuration component is small in the bound states, it mainly contributes to the relativistic cor-

rections on the binding energy. Relativistic effects play an indispensable role to verify such loosely bound states, LiPs$^+$ and NaPs$^+$.

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