

Multireference configuration interaction study of positronium-alkali atom complexes

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Abstract

Positronium (Ps) binding energies of positronium-alkali atom complexes, PsLi, PsNa, PsK, and PsRb, which were calculated by multireference configuration interaction (MRCI) method and extrapolation procedures are presented. In this work, a frozen-core approximation is applied. The Ps binding energies of PsLi and PsNa are in good agreement with accurate values given from the stochastic variational method (SVM) with explicitly correlated Gaussian function. The Ps binding energy of PsK is larger than the SVM value. For PsRb, the Ps binding energy of 0.093 eV is obtained. To analyze accuracy of the Ps binding energies, electron affinities for Li, Na, K, and Rb are also calculated.

1. INTRODUCTION

Positronium (Ps) is a bound state of one electron (e^-) and one positron (e^+). The positronium forms bound states with various atoms. These are called positronium-atom complexes. There are many quantum mechanical studies for various positronium-atom complexes.¹⁻²² It is revealed from those studies that several positronium-atom complexes are energetically stable. Quantum mechanical calculations for positronium-atom complexes require explicitly correlated functions, e.g., Hylleraas-type function or explicitly correlated Gaussian (ECG) function. Calculation methods with the explicitly correlated functions give very accurate results. Unfortunately, such methods are unsuitable for application to many-electronic systems because many-electron integrals appear. Therefore, the explicitly correlated functions are applied to only few-body systems.

Configuration interaction (CI) methods are extensively applied to quantum mechanical calculations for many-electronic systems. To obtain accurate CI wave functions, orbitals having high angular momentum are required for construction of CI wave functions. However, orbitals having

angular momentum less than ~ 10 are actually used because CI wave functions become very large. CI calculations of positronium-atom complexes require orbitals having quite high angular momentum. Hence, the energy contribution from orbitals having higher angular momentum has to be estimated with the help of an extrapolation procedure. Moreover, consideration of many-body effect is also important. In our previous works, we have performed multireference singly and doubly excited configuration interaction (MRSDCI) calculations for positronium hydride^{7,19}, positronium halide^{17,18,20}, positronium-carbon atom¹⁹, and so on.

Mitroy and co-workers have applied the stochastic variational method (SVM) with ECG to several positronium-atom complexes which have two valence electrons using a model potential.¹⁶ Their model potential is considered polarization effects. Their calculation method is called FCSVM_{pol}. Positronium-atom complexes calculated by them are positronium hydride, positronium-alkali atoms, positronium-copper atom, and so on.¹⁶ Mitroy and co-workers have given highly accurate Ps binding energies for those systems.

In this work, we performed MRSDCI calculations for positronium-alkali atom complexes, PsLi, PsNa, PsK, and PsRb, and estimated the full CI (FCI) energy limits and higher angular momentum effect using extrapolation procedures. The Ps binding energies of PsLi, PsNa, and PsK given from our calculation method are compared with those by Mitroy and co-workers.¹⁶

The Ps binding energy (E_B) of positronium-atom complexes (PsA) is calculated by

$$E_B = E_{Ps} + E_A - E_{PsA} \quad (1)$$

where E_{Ps} , E_A , and E_{PsA} are the total energies of Ps, A, and PsA, respectively. The Ps binding energy can also be calculated using the electron affinity (E_{EA}) of A and the positron ionization energy (E_{PI}) of PsA as follows:

$$E_B = E_{Ps} + E_{EA} + E_{PI} \quad (2)$$

From Eq.(2), one can see that accurate electron affinities and positron ionization energies are required, to calculate accurate Ps binding energy. Accuracy of the Ps binding energy can be analyzed by accuracy of the electron affinity of A at least, because there are experimental values of the electron affinity for various atoms. To analyze accuracy of Ps binding energy, we calculated the electron affinities and the positron ionization energies of PsA.

In this work, we carried out Hartree-Fock (HF) calculations for the ground state (2S) of neutral alkali atoms Li, Na, K, and Rb, the ground state (1S) of anions of the alkali atom Li^- , Na^- , K^- , and Rb^- , and the ground state (2,1S) of the positronium-alkali atom complexes PsLi, PsNa, PsK, and PsRb. MRSDCI calculations with a frozen-core approximation were carried out for Li^- , Na^- , K^- , Rb^- , PsLi, PsNa, PsK, and PsRb using the natural orbitals (NOs). Hence, the reference configurations of the

MRSDCI calculation are $[\text{core}]ns^2$ and $[\text{core}]ns^2 1s_+^1$ for A^- and PsA , respectively. Here, the subscript ‘+’ means positronic orbital.

The next section explains basis functions, NO construction procedures, and extrapolation procedures. The third section summarizes the Ps binding energies and the positron ionization energies for PsLi , PsNa , PsK , and PsRb , and discusses them in comparison with the works of other researchers. The accuracy of the Ps binding energies is also analyzed by calculating the electron affinities for Li , Na , K , and Rb .

2. COMPUTATIONAL ASPECT

The basis set used is B -splines described below. The B -spline set is one of piecewise polynomials, because this set is free from computational linear dependence and is very flexible.^{23,24} Therefore, all atomic orbitals of each system can be expanded using a common B -spline set regardless of the symmetry of the atomic orbitals. The present basis set consists of N K th-order B -splines on a knot sequence defined on an interval $[0, R]$. A knot sequence was used with endpoints of K -fold multiplicity:

$$0, R_1, R_1(1 + \beta), R_1(1 + \beta + \beta^2), \dots, R, \quad (3)$$

where R_1 is the initial interval and β is the parameter characterizing the distribution of the knots. Here β is decided to satisfy the following condition:

$$R = R_1(1 + \beta + \beta^2 + \dots + \beta^{N-K+2}), \quad (\beta \geq 1). \quad (4)$$

Since the first and last terms of the B -splines with K -fold multiplicity are nonzero at $r=0$ and $r=R$, respectively, the N -term B -spline set was constructed omitting them. We adopted $N=40$, $R=60$ (bohr), $K=9$. β was optimized by HF calculations for each system individually.

Our MRSDCI calculations used the NOs with angular momentum λ up to 8 (i.e. l -symmetry). The NOs were generated by a series of MRSDCI calculations with reference spaces consisting of principal configurations of a single reference SDCI wave function (a ‘minimal reference space’). The minimal reference configurations of PsA are listed in Table 1.

Let us now explain the generating procedure for NOs. First, MRSDCI calculations were carried out with the HF orbitals, to obtain *spdf*-NOs. Subsequently, g -NOs were generated by MRSDCI calculations with the *spdf*-NOs. The NOs with higher λ than g were generated in the same way, step by step. Those NOs whose occupation number was less than 10^{-7} were truncated at each step because a wave function constructed with non-truncated NOs is very large.

To estimate the FCI energy limits and the higher λ effects for the total energies, a further series

of MRSDCI calculations was carried out using obtained NOs, increasing the reference configurations which were selected for the largest weight in the previous MRSDCI wave functions. These calculations were continued until $w_{\text{ref}} \approx 0.99$, where w_{ref} is the weight of reference configurations. We refer the reference space finally constructed as a ‘maximum reference space’.

Table 1. Minimal reference configurations of PsLi, PsNa, PsK, and PsRb.

PsLi	PsNa	PsK	PsRb
$2s^2 1s_+$	$3s^2 1s_+$	$4s^2 1s_+$	$5s^2 1s_+$
$2s3s2s_+$	$3s4s2s_+$	$4s5s2s_+$	$5s6s2s_+$
$2s2p2p_+$	$3s3p2p_+$	$4s4p2p_+$	$5s5p2p_+$
$2s3p3p_+$	$3s4p3p_+$	$4s5p3p_+$	$5s6p3p_+$
$2s3d3d_+$	$3s3d3d_+$	$4s3d3d_+$	$5s4d3d_+$
$2s4d4d_+$	$3s4d4d_+$	$4s4d4d_+$	$5s5d4d_+$
$2s4f4f_+$	$3s4f4f_+$	$4s4f4f_+$	$5s4f4f_+$

The FCI limits of the MRSDCI energies (E_{CI}) were estimated by extrapolating E_{CI} to $w_{\text{ref}}=1$. To this end, the convergence pattern of E_{CI} , $E_{\text{CI+Q}}$, and E_{AV} were analyzed with respect to w_{ref} . $E_{\text{CI+Q}}$ is E_{CI} plus the Davidson correction²⁰. E_{AV} is the average of E_{CI} and $E_{\text{CI+Q}}$.

The higher λ effect for the total energies was also estimated by extrapolating the energy contributions due to the respective λ -NOs to $\lambda \rightarrow \infty$. To treat the systems on equal footing, we extrapolated the total energies to $\lambda \rightarrow \infty$ using E_{CI} with $w_{\text{ref}} \approx 0.99$. The energy contribution ΔE_λ was plotted on a log-log scale, and it was fitted by the following relation with four parameters α , β , γ , and ε ²⁶:

$$-\Delta E_\lambda = \begin{cases} 10^{-\alpha \{\log_{10}(\lambda + \frac{1}{2})\}^\beta + \gamma}, & \text{for } \lambda \leq \lambda_c \\ \varepsilon \left(\lambda + \frac{1}{2}\right)^{-4}, & \text{for } \lambda \geq \lambda_c \end{cases} \quad (5)$$

where λ_c is the point at which the derivatives of the two functions (5) $\left(\frac{d \log_{10}(-\Delta E_\lambda)}{d \log_{10} \lambda}\right)$ are equal, and is expressed as

$$\lambda_c = 10^{\{4(\alpha\beta)^{-1}\}(\beta-1)^{-1}} - \frac{1}{2}. \quad (6)$$

The first function of Eq.(5) is equal to the second function of Eq.(5) in case of $\alpha=4$, $\beta=1$, and $\gamma=\log_{10}\varepsilon$. The contribution from the NOs having λ greater than 8 ($E_{\lambda>8}$) was estimated as

$$E_{\lambda>8} = \sum_{\lambda=9}^{\infty} \Delta E_\lambda. \quad (7)$$

We finally obtained the FCI limits including the higher λ effect.

The HF calculations with the B -spline set were carried out using our atomic self-consistent field program code based on the algorithm of Roothaan and Bagus.^{27,28} All CI calculations were performed by the program ATOMCI^{29,30} modified for atomic systems containing positrons.

3. RESULTS AND DISCUSSIONS

Table 2 summarizes the results of the MRSDCI calculations with the minimal reference space and the maximum reference space for PsLi, PsNa, PsK, and PsRb. The losses of the MRSDCI energies due to the NO truncation are very small: the maximum lose is 0.00002 hartree (~ 0.0005 eV). The energy losses may not affect the positron ionization energies and the Ps binding energies. The weights of the MRSDCI wave function with the maximum reference configuration are very close to 1.

Table 2. Results of MRSDCI with minimal and maximum reference spaces. $\Delta\varepsilon$ is loss of total energies due to the NO truncation procedure and N_{CI} is the number of terms of MRSDCI wave function.

	Reference spaces	N_{CI}	w_{ref}	E_{CI} (hartree)	$\Delta\varepsilon$ (hartree)
PsLi	minimal	26515	0.897407	-7.683650	0.000020
	maximum	144581	0.991153	-7.683797	
PsNa	minimal	24728	0.884815	-162.103970	0.000016
	maximum	138796	0.991190	-162.104139	
PsK	minimal	22175	0.845244	-599.402598	0.000009
	maximum	118264	0.988084	-599.402879	
PsRb	minimal	21298	0.829349	-2938.592397	0.000008
	maximum	116153	0.987129	-2938.592728	

Table 3 lists the weights of principal configurations of the MRSDCI wave functions with the maximum reference space for PsLi, PsNa, PsK, and PsRb. The weight of [core] ns^21s_+ configuration for all the systems is quite small: it is less than 0.5. The weights of npn^+p_+ and ndn^+d_+ excited configurations are large. For PsRb, the weight of $5p2p_+$ excited configuration is almost same as that of [core] $5s^21s_+$ configuration. This shows that PsRb has larger the diatomic molecule-like structure Ps-Rb than the atomic structure $e^+-\text{Rb}^-$. The structure of the positronium-alkali atom complexes mainly is the diatomic molecule-like character. This situation is larger with an increase of the atomic number for the alkali atoms.

Table 3. Weights of principal configurations of wave functions for PsLi, PsNa, PsK, and PsRb.

PsLi		PsNa		PsK		PsRb	
weight	configuration	weight	configuration	weight	configuration	weight	configuration
0.419	$2s^21s_+$	0.386	$3s^21s_+$	0.299	$4s^21s_+$	0.274	$5s^21s_+$
0.282	$2s2p2p_+$	0.279	$3s3p2p_+$	0.285	$4s4p2p_+$	0.280	$5s5p2p_+$
0.102	$2s3d3d_+$	0.117	$3s3d3d_+$	0.143	$4s3d3d_+$	0.153	$5s4d3d_+$
0.039	$2s4f4f_+$	0.048	$3s4f4f_+$	0.062	$4s4f4f_+$	0.068	$5s4f4f_+$
0.024	$2s3p3p_+$	0.023	$3s4p3p_+$	0.028	$4s5g5g_+$	0.031	$5s5g5g_+$
0.016	$2s5g5g_+$	0.020	$3s5g5g_+$	0.022	$4s5p3p_+$	0.021	$5s6p3p_+$

We estimated FCI limits of E_{CI} by extrapolating E_{CI} to $w_{ref}=1$. Fig. 1 shows the convergence pattern of E_{CI} , E_{CI+Q} , and E_{AV} against the weight for PsLi, PsNa, PsK, and PsRb. E_{CI} for all the systems have no change at $w_{ref}\approx 0.99$. Hence, all the FCI limits can be regarded as the total energy given from the MRSDCI calculations with the maximum reference configuration.

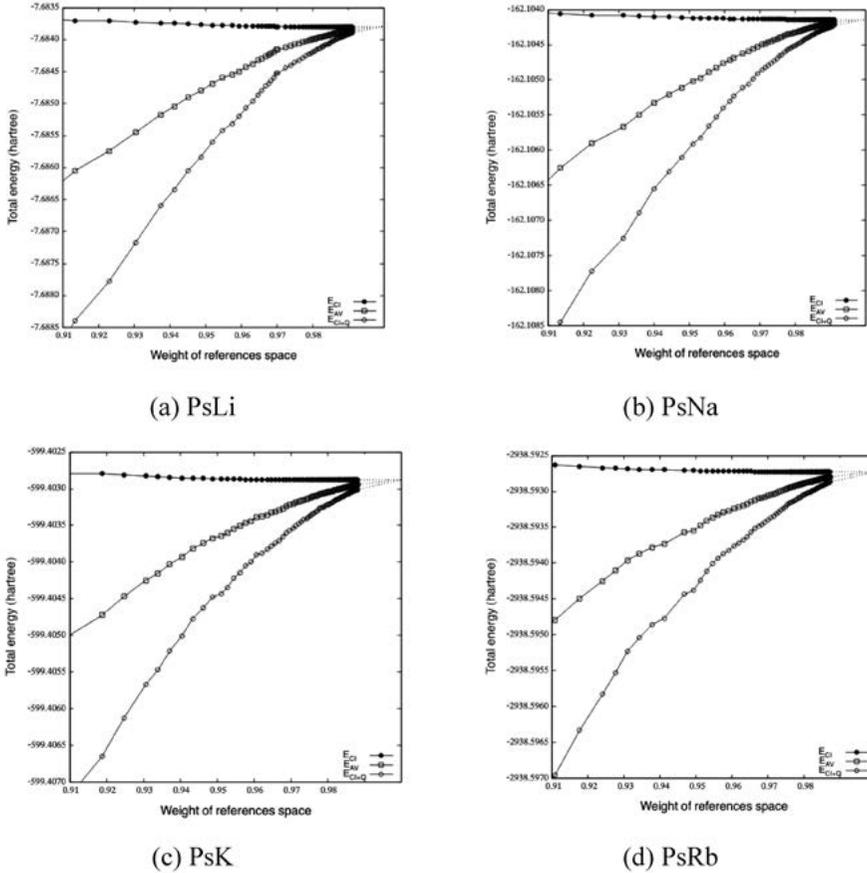


Fig. 1. Convergence of CI energies for the positronium-alkali atom complexes with respect to the weight of the reference space.

Fig. 2 shows the energy contributions from the respective λ -NOs, on a log-log scale. The parameters of Eq.(5) were decided by fitting $-\Delta E_\lambda$ with Eq.(5). The energy contributions from the NOs having λ greater than 8 ($E_{\lambda>8}$) were estimated as Eq.(7). The resulting FCI limits and the higher λ contributions for the total energies are summarized in Table 4. As can be seen in Fig. 2, as the atomic number of the alkali atoms is larger, $-\Delta E_\lambda$ is larger. The functional form is similar to each other.

Table 4. Full CI limits (E_{FCI}) and higher λ contributions ($E_{L>8}$) for total energies (in hartree).

	E_{FCI}	$E_{L>8}$	$E_{\text{FCI}}+E_{L>8}$
Li ⁻	-7.455360	-0.000001	-7.455361
P sLi	-7.683797	-0.010299	-7.694096
Na ⁻	-161.878906	-0.000001	-161.878907
P sNa	-162.104139	-0.012369	-162.116508
K ⁻	-599.183042	-0.000002	-599.183044
P sK	-599.402879	-0.016533	-599.419412
Rb ⁻	-2938.374897	-0.000006	-2938.374903
P sRb	-2938.592728	-0.018142	-2938.610870

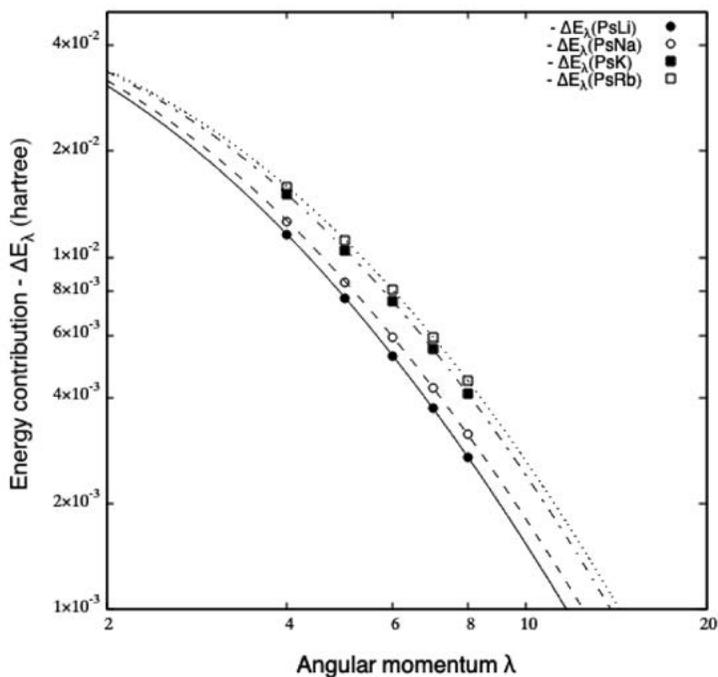


Fig. 2. Contributions to the total energies from the respective λ orbitals.

Table 5 summarizes the positron ionization energies and the Ps binding energies for PsLi, PsNa, PsK, and PsRb, together with the works of other researchers. The most accurate Ps binding energies are given from FCSVM_{pol} calculations presently. PsLi has been calculated by several methods. However, their Ps binding energies are no good agreement with the FCSVM_{pol} values except for diffusion Monte Carlo (DMC) performed by Bressanini et al.¹⁰ The second-order variational perturbation theory (VPT) calculation⁸ slightly improves the HF value. However, the Ps binding energy given from VPT is negative value. The Ps binding energies given from density functional theory (DFT) calculation performed by Harrison³ are almost same as the HF value. DFT performed by Kanhere et al.⁴ gives the Ps binding energies which are inconsistent with the FCSVM_{pol} value. Our Ps binding energy of PsLi are good agreement with the FCSVM_{pol} value. The higher λ effect greatly increases the Ps binding energy for PsLi. This situation is similar for the Ps binding energies of the other positronium-alkali atom complexes.

Table 5. Positron ionization energies (E_{PI}) and Ps binding energies (E_B) (in eV).

	PsLi		PsNa		PsK		PsRb	
	E_{PI}	E_B	E_{PI}	E_B	E_{PI}	E_B	E_{PI}	E_B
This work								
HF	2.766	-4.159	2.618	-4.288	2.247	-4.634	2.135	-4.737
minimal MRSDCI	6.212	0.025	6.124	-0.134	5.974	-0.332	5.918	-0.410
FCI limit	6.216	0.029	6.129	-0.130	5.982	-0.324	5.927	-0.401
FCI limit + higher λ	6.496	0.309	6.465	0.207	6.432	0.126	6.421	0.093
Other works								
HF ^a	2.776	-4.163						
VPT ^b	3.990	-2.190						
DFT ^c	2.776	-4.027						
DFT ^d	8.844	2.667						
DMC ^e	6.97	0.78						
DMC ^f	6.506	0.261						
VMC ^f	0.160	-6.117						
FCSVM _{pol} ^g	6.517	0.336	6.487	0.229	6.399	0.089		

^a Patrick and Cade (Ref.2).

^b Saito (Ref.8).

^c Harrison (Ref.3).

^d Kanhere et al. (Ref.4).

^e Yoshida and Miyako (Ref.9).

^f Bressanini et al. (Ref.10).

^g Mitroy and Ryzhikh (Ref.16).

In comparison with the $\text{FCSVM}_{\text{pol}}$ values, our Ps binding energies for PsLi and PsNa are underestimated. However, our Ps binding energy for PsK is larger than that of $\text{FCSVM}_{\text{pol}}$: this difference is 0.037 eV. To analyze this difference, we calculated the electron affinity of K together with that of Li, Na, and Rb and list them in Table 6. Our electron affinities are in good agreement with the $\text{FCSVM}_{\text{pol}}$ ¹⁶ and experimental values³². Our electron affinity of K is larger than the $\text{FCSVM}_{\text{pol}}$ value by 0.005 eV. This difference may not affect the Ps binding energy for PsK. The higher λ effect makes the Ps binding energy of PsK higher than the $\text{FCSVM}_{\text{pol}}$ value. If the $\text{FCSVM}_{\text{pol}}$ value for PsK is correct, the energy contribution for $\lambda > 8$ must be a small value. Namely, the fitting curve of PsK in Fig. 2 must be steeper than that of PsLi and PsNa. The fitting curve form for PsK is similar to that of PsLi and PsNa. Therefore, our estimation of the higher λ effect could be correct. Conclusively, the $\text{FCSVM}_{\text{pol}}$ calculation of PsK is not convergent yet, and the Ps binding energy of PsK must be much larger.

Table 6. Electron affinities of alkali atoms (in eV).

	Li	Na	K	Rb
This work				
SDCI	0.616	0.544	0.497	0.475
Other works				
FCSVM _{pol}	0.619 ^a	0.545 ^a	0.492 ^b	
Experiment ^c	0.618	0.548	0.501	0.486

^a Mitroy and Ryzhikh (Ref.15).

^b Mitroy and Ryzhikh (Ref.31).

^c Hotop and Lineberger (Ref.32).

We obtained the Ps binding energy of PsRb 0.093 eV. The electron affinity of Rb which we calculated is smaller than the experimental value by 0.011 eV. Hence, our Ps binding energy of PsRb may be small by ~ 0.01 eV. To improve the Ps binding energy of PsRb, MRSDCI calculations considering the core-valence interaction have to be carried out.

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