Effects of core-electrons for the electron affinity of rubidium atom

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Abstract

The electron affinity of rubidium atom (Rb) given from multireference singly and doubly excited configuration interaction (MRSDCI) calculations considering excitations from core-electrons $4s^2 4p^6$ is presented. The resulting electron affinity 0.4861 eV is in excellent agreement with the experimental value 0.485916 eV. The electron affinity obtained from our previous MRSDCI calculations which treated only 5s-valence electrons is 0.475 eV. The core-electron effects are shown to be important in the calculation of the electron affinity of Rb.

1. INTRODUCTION

The accurate calculation of the electron affinity of atoms is very important for the theoretical research of energetical stability of positronium-atom complexes. The positronium (Ps) binding energy (E_B) of the complex PsA is written as $E_B = E_{EA} + E_{PI} + E_{Ps}$, where E_{EA}, E_{PI}, and E_{Ps} are respectively the electron affinity of atom A, the positron ionization energy of PsA, and the energy of Ps (–0.25 hartree). To analyze accuracy of the Ps binding energies, the accurate electron affinity of atom is required.

Our previous work[1] has obtained the Ps binding energy of positronium-alkali atom complexes, PsLi, PsNa, PsK, and PsRb, from the multireference singly and doubly excited configuration interaction (MRSDCI) calculations considering only the valence shells $ns^2 1s_+^1$. The electron affinities of Li, Na, K, and Rb have been also calculated considering only ns valence-electrons. The obtained electron affinities of Li, Na, and K have errors of ~0.005 eV compared to the experimental values[2], which is in good agreement with the experimental values except for Rb. The error for the electron affinity of Rb is 0.011 eV. This difference significantly affects the calculation of the Ps binding energy

of PsRb because its Ps binding energy is 0.093 eV. The error in the electron affinity of Rb may be due to the neglect of the relativistic effect and the core-electron effects, i.e., core-core and core-valence electron correlation effects. Calculations incorporating relativistic effects were performed with the third order Douglas-Kroll method[3] and yielded almost the same results as the non-relativistic calculations. Therefore, the core-electron effects are important for the calculation of the electron affinity of Rb. The calculation of PsRb must also include the core-electron effects.

In this work, we performed MRSDCI calculations with the core-electron effects for Rb and Rb$^-$ and obtained the electron affinity of Rb. Namely, excitations from $4s^2 4p^6 5s^1$ for Rb and $4s^2 4p^6 5s^2$ for Rb$^-$ were considered. Computational details are given in the next section. Section 3 shows and discusses the results.

2. COMPUTATIONAL ASPECT

In this work, all the atomic orbitals were expanded with B-splines[4,5]. The B-spline set is one of piecewise polynomials and is very flexible. Hence, all atomic orbitals of each system can be expanded using a common B-spline set regardless of the symmetry of the atomic orbitals. The B-spline set used consists of N Kth-order B-splines on a knot sequence defined on an interval $[0, R]$, where is in bohr. A knot sequence was used with endpoints of K-fold multiplicity:

$$0, R_1, R_1 (1+\beta), R_1 (1 + \beta + \beta^2), \cdots, R, \tag{1}$$

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:

$$R = R_1 (1 + \beta + \beta^2 + \cdots + \beta^{N-K+2}), \qquad (\beta \geq 1). \tag{2}$$

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. This work adopted $N = 40$, $R = 60$, $K = 9$. β was optimized by Hartree-Fock (HF) calculations. The parameters are the same as those used in the calculations dealing only with valence electrons[1].

Our MRSDCI calculations used the natural orbitals (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 configuration interaction wave function (a 'minimal reference space'). The minimal reference configurations of Rb and Rb$^-$ are listed in Table 1.

Let us explain construction of NOs. First, MRSDCI calculations were carried out with the HF

Table 1   Minimal reference configurations of Rb and Rb⁻

Rb	Rb⁻
$4s^2 4p^6 5s^1$	$4s^2 4p^6 5s^2$
$4s^2 4p^4 4d^2 5s^1$	$4s^2 4p^6 6s^2$
	$4s^2 4p^6 5p^2$
	$4s^2 4p^4 4d^2 5s^2$

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^{-6} were truncated at each step.

The full configuration interaction (FCI) energy limits and the energy contributions to the total energies from higher angular momentum orbitals (the higher λ effect) were estimated. To this end, 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 function. Those calculations were continued until $w_{\text{ref}} \approx 0.99$, where w_{ref} is the weight of reference space. The reference space finally extended is referred to as a 'maximum reference space'.

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.[6–8] All CI calculations were performed by the program ATOMCI [9,10].

3. RESULTS AND DISCUSSION

Table 2 summarizes the results of the MRSDCI calculations with the minimal reference space and the maximum reference space for Rb and Rb⁻. The loses of the MRSDCI energies due to the NO truncation (ε) are very small: the difference of ε for Rb and Rb⁻ is 0.000013 hartree (~0.00035 eV). ε may affect the electron affinity. Assuming additivity of energy, ε was added to the MRSDCI energy.

The FCI wave function is the MRSDCI wave function with $w_{\text{ref}} = 1$. The FCI limits of the MRSDCI

Table 2   Results of MRSDCI with minimal and maximum reference spaces. N_{CI}, w_{ref}, E_{CI}, and ε respectively denote the dimension of the MRSDCI wave function, weight of reference space, total energy, and loss of total energy due to the NO truncation procedure

	Reference space	N_{CI}	w_{ref}	E_{CI} (hartree)	ε (hartree)
Rb	minimal	39,798	0.965306	–2938.604332	–0.000029
	maximum	561,515	0.990258	–2938.609003	
Rb⁻	minimal	41,993	0.959980	–2938.619986	–0.000016
	maximum	2,435,727	0.987818	–2938.626857	

energies (E_{CI}) were estimated by extrapolating E_{CI} to w_{ref} = 1. To this end, the convergence pattern of E_{CI}, E_{CI+Q}, and E_{AV} was analyzed with respect to w_{ref}. E_{CI+Q} is E_{CI} plus the Davidson correction[11]. E_{AV} is the average of E_{CI} and E_{CI+Q}. Although E_{AV} has no physical meaning, it is useful for this extrapolation. Fig. 1 shows the convergence pattern of E_{CI}, E_{CI+Q}, and E_{AV} for Rb and Rb⁻ against w_{ref}. Extrapolating E_{CI} to w_{ref} = 1 produced the FCI limits –2938.60930 hartree and –2938.62717 hartree for Rb and Rb⁻, respectively.

The higher λ effect for the total energies was estimated by extrapolating the energy contributions due to the respective λ-NOs to $\lambda \to \infty$. To treat with the same accuracy, we extrapolated the total energies to $\lambda \to \infty$ using MRSDCI energies with $w_{ref} \approx 0.99$. Fig. 2 shows the energy contributions from the respective λ-NOs (ΔE_λ), on a log-log scale. The energy contribution converges linearly. Hence, ΔE_λ was fitted by the following relation with two parameters α and β :

$$-\Delta E_\lambda = \alpha\lambda^{-\beta}. \tag{3}$$

The energy contribution from the NOs having λ greater than 8 ($E_{\lambda>8}$) was estimated as

$$E_{\lambda>8} = \sum_{\lambda=9}^{\infty} \Delta E_\lambda. \tag{4}$$

We finally obtained the FCI energy limits including the higher λ effect. The energy contribution
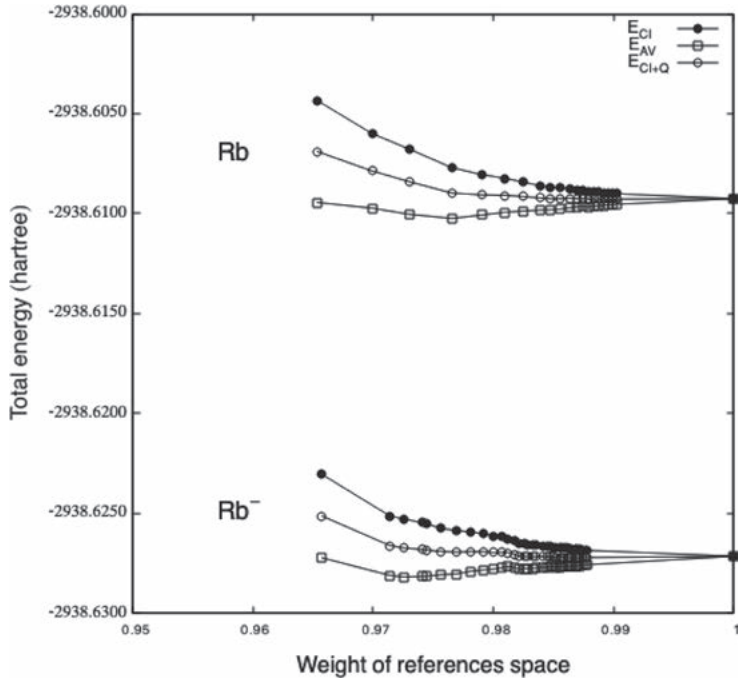

Fig. 1　Convergence of CI energies for Rb and Rb⁻ with respect to the weight of the reference space

due to the higher λ effect is –0.000841 hartree and –0.000839 hartree for Rb and Rb⁻, respectively. The difference of the energy contribution is very small value –0.000002 hartree (–0.000054 eV). Therefore, the higher λ effect can be neglected.

Table 3 summarizes the electron affinity of Rb with our previous and the experimental values. Our final electron affinity of Rb is 0.4861 eV, which is an improvement over our previous calculation result that treated only valence electrons. The difference from the experimental value is 0.0002 eV, which is in excellent agreement with the experimental value.

Table 4 lists the weights of the principal configurations in the MRSDCI wave function with the maximum reference space. The main configuration of the Rb wave function is $4s^2 4p^6 5s^1$, and the weights of the $4p^2 \rightarrow 4d^2$, $4s^1 4p^1 \rightarrow 4d^1 4f^1$, and $4p^1 5s^1 \rightarrow 4d^1 5p^1$ excited configurations are large. For
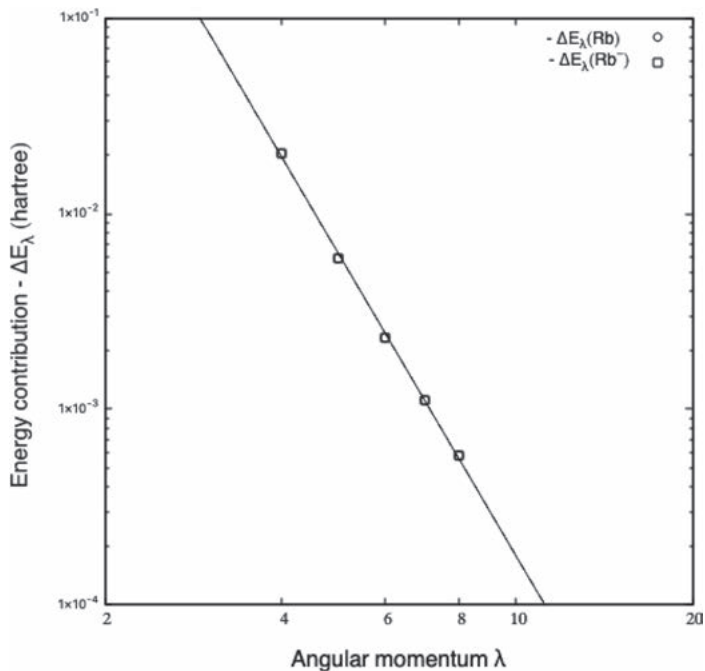

Fig. 2 Contributions to the total energies from the respective λ orbitals

Table 3 Electron affinity (EA) of Rb

Method	Reference	EA (eV)
MRSDCI	This work	0.4858
MRSDCI + ε	This work	0.4855
FCI limit	This work	0.4862
FCI limit + higher λ	This work	0.4861
FCI limit + higher λ	Ref. 1	0.475
Experiment	Ref. 2	0.485916

Table 4   Weights of principal configurations of MRSDCI wave function for Rb and Rb⁻

Rb		Rb⁻	
weight	configuration	weight	configuration
0.923	$4s^24p^65s^1$	0.825	$4s^24p^65s^2$
0.037	$4s^24p^44d^25s^1$	0.079	$4s^24p^65p^2$
0.006	$4s^14p^54d^14f^15s^1$	0.033	$4s^24p^44d^25s^2$
0.005	$4s^24p^54d^15p^1$	0.009	$4s^24p^66s^2$
0.004	$4s^24p^45s^15p^2$	0.005	$4s^14p^54d^14f^15s^2$

Rb⁻, the weights of the $5s^2 \rightarrow 5p^2$, $6s^2$ excited configurations are large, followed by the weights of the $4p^2 \rightarrow 4d^2$ and $4s^14p^1 \rightarrow 4d^14f^1$ excited configurations as Rb. The core-electron effects are large for both and are non-negligible. Therefore, the core-electron effects must be considered when calculating the electron affinity of Rb.

In summary, the calculation of the electron affinity of Rb should incorporate the core-electron effects. Therefore, MRSDCI calculations must be performed for PsRb as well, incorporating the core-electron effects.

REFERENCES

[1] S.L. Saito, Chukyo Univ. Bulletin of the Faculty of Liberal Arts and Sciences, 3(2), 1 (2023).

[2] T. Andersen, H.K. Haugen, and H. Hotop, J. Phys. Chem. Ref. Data 28, 1511 (1999).

[3] M. Douglas and N.M. Kroll, Ann. Phys., 82, 89 (1974).

[4] C. de Boor, *A practical guide to splines*, (Springer, Berlin, Heidelberg, New York, 2001).

[5] J. Sapirstein and W.R. Johnson, J. Phys. B 29, 5213 (1996).

[6] C.C.J. Roothaan and P.S. Bagus, Meth. Comput. Phys. 2, 47 (1963).

[7] S.L. Saito, Theor. Chem. Acc. 109, 326 (2003).

[8] S.L. Saito, At. Data Nucl. Data Tables, 95, 836 (2009).

[9] F. Sasaki, Int. Quantum Chem. 8, 605 (1974).

[10] F. Sasaki, M. Sekiya, T. Noro, K. Ohtsuki, and Y. Osanai, In: E. Clementi (ed) *Modern techniques in computational chemistry*, p.181 (MOTECC. ESCOM, Leiden, 1990).

[11] S.R. Langhoff and E.R. Davidson, Int. J. Quantum Chem. 8, 61 (1974).