Multireference configuration interaction calculation incorporating core-electron effects for positronium-rubidium atom complex

Saito Shiro L.

Abstract

Multireference singly and doubly excited configuration interaction (MRSDCI) calculations considering excitations from core-electrons $4s^2 4p^6$ for positronium-rubidium atom complex (PsRb) are performed, and the positronium (Ps) binding energy of PsRb is presented. The energy contributions due to many-body and higher angular momentum effects were estimated using extrapolation techniques and added to the MRSDCI energy to obtain the final energy. The resulting Ps binding energy is 0.043 eV.

1. INTRODUCTION

Our previous multireference singly and doubly excited configuration interaction (MRSDCI) study has revealed the stability of positronium-rubidium atom complex (PsRb). [1] The positronium (Ps) binding energy obtained is 0.093 eV. The Ps binding energy (E_B) is calculated as

$$E_B = E_{Ps} + E_{Rb} - E_{PsRb} , \tag{1}$$

where E_{Ps}, E_{Rb}, and E_{PsRb} are the energies of Ps, Rb, and PsRb, respectively. In our MRSDCI study, E_{PsRb} was the total energy given from the MRSDCI calculation dealing only with the valence shell $5s^2 1s^1_+$. The subscript '+' means a positronic orbital. E_{Rb} was the Hartree-Fock energy of Rb.

The Ps binding energy is also calculated as

$$E_B = E_{EA} + E_{PI} + E_{Ps} , \tag{2}$$

where E_{EA} and E_{PI} are the electron affinity of Rb and the positron ionization energy of PsRb,

respectively. Since the experimental value for the electron affinity of Rb exists, it is possible to analyze accuracy of the Ps binding energy using Eq. (2). To this end, the electron affinity of Rb was calculated. Rb^- was calculated using the singly and doubly excited configuration interaction (SDCI) method dealing only with the valence shell $5s^2$. The electron affinity of Rb obtained from this calculation is 0.475 eV, which is 0.011 eV less than the experimental value of 0.485916 eV [2]. This difference significantly affects the Ps binding energy because the Ps binding energy of PsRb is 0.093 eV.

We have also obtained the electron affinity of Rb from MRSDCI calculations incorporating the excitations from $4s^24p^6$.[3] The resulting electron affinity is 0.4861 eV, in excellent agreement with the experimental value. This shows the importance of considering the core-electron effects, i.e., core-core and core-valence correlation effects. Hence, the MRSDCI calculation incorporating excitations from $4s^24p^6$ for PsRb must be carried out.

In this work, we performed MRSDCI calculations with the core-electron effects for PsRb and obtained the Ps binding energy of PsRb. That is, MRSDCI wave functions constructed in the configurations excited from $4s^24p^65s^21s^1_+$ were calculated. The correlating orbitals used were the natural orbitals (NOs) obtained from a series of MRSDCI calculations. All atomic orbitals were expanded with B-splines. The B-spline set[4,5] 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 many-body and higher angular momentum effects are very important in the calculation of the positronium-atom complex. Unfortunately, it is infeasible to fully incorporate those effects. Hence, the full configuration interaction (FCI) energy limit and the energy contribution from higher angular momentum orbitals (the higher λ effect) were estimated using extrapolation techniques.

Details of the B-splines and MRSDCI calculations are described in the next section. Section 3 shows and discusses the results. Accuracy of the Ps binding energy is also analyzed using the electron affinity of Rb.

2. COMPUTATIONAL DETAILS

The present basis set 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:

$$0, R_1, R_1\,(1+\beta), R_1\,(1+\beta+\beta^2), \cdots, R\,, \tag{3}$$

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:

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

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. This work adopted $N = 40$, $R = 60$, $K = 9$. β was optimized by the Hartree-Fock (HF) calculation. Those 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 PsRb are listed in Table 1. *spdf*-NOs were obtained from the first MRSDCI calculations with HF orbitals. 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.

To estimate the FCI energy limit and the higher λ effect, 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. The final MRSDCI calculation is denoted as 'MRSDCI(max)'.

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] modified for atomic systems containing positrons.

Table 1 Minimal reference configurations of PsRb

$4s^2 4p^6 5s^2 1s_+^1$
$+5s^1 1s_+^1 \rightarrow 5p^1 2p_+^1$
$+5s^1 1s_+^1 \rightarrow 4d^1 3d_+^1$
$+5s^1 1s_+^1 \rightarrow 5d^1 3d_+^1$
$+5s^1 1s_+^1 \rightarrow 4f^1 4f_+^1$
$+4p^2 \rightarrow 5d^2$
$+4p^2 \rightarrow 4d^1 5d^1$

3. RESULTS AND DISCUSSION

Table 2 summarizes the results of the MRSDCI calculations with the minimal reference space for PsRb. The weight of the reference space (w_{ref}) is smaller as the maximum λ of NOs (λ_{max}) is larger. This shows the importance of the excited configurations with NOs having higher λ. The loses of the MRSDCI energies due to the NO truncation (ε) are larger than those for Rb. The total ε for PsRb is –0.000419 hartree. The total ε may affect the Ps binding energy. Assuming additivity of energy, the total ε was added to the MRSDCI energy.

We estimated the FCI energy limit using an extrapolation. The FCI wave function is the MRSDCI wave function with w_{ref}=1. The FCI limits of the MRSDCI energies (E_{CI}) were estimated by extrapolating E_{CI} to w_{ref}=1. To this end, the convergence pattern of E_{CI}, $E_{\mathrm{CI+Q}}$, and E_{AV} was analyzed with respect to w_{ref}. $E_{\mathrm{CI+Q}}$ is E_{CI} plus the Davidson correction[11]. E_{AV} is the average of E_{CI} and $E_{\mathrm{CI+Q}}$. Although E_{AV} has no physical meaning, it is useful for this extrapolation. Fig. 1 shows the convergence pattern of E_{CI}, $E_{\mathrm{CI+Q}}$, and E_{AV} against w_{ref}. Extrapolating E_{CI} to w_{ref} = 1 produced the FCI energy limits –2938.84872 hartree.

The higher λ effect for the total energies was estimated by extrapolating the energy contributions due to the respective λ-NOs to $\lambda \rightarrow \infty$. To treat with the same accuracy, the extrapolation was performed using MRSDCI energies with $w_{\mathrm{ref}} \approx 0.92$. 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 :

$$-\Delta E_{\lambda} = \alpha \lambda^{-\beta}. \tag{5}$$

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

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

λ_{max}	N_{CI}	w_{ref}	E_{CI} (hartree)	ε (hartree)
f	182,521	0.920969	–2938.754632	–0.000223
g	254,276	0.905446	–2938.784324	–0.000056
h	319,833	0.894532	–2938.796978	–0.000033
i	384,666	0.886293	–2938.804136	–0.000025
k	441,337	0.880044	–2938.808698	–0.000049
l	495,202	0.875298	–2938.811804	–0.000033

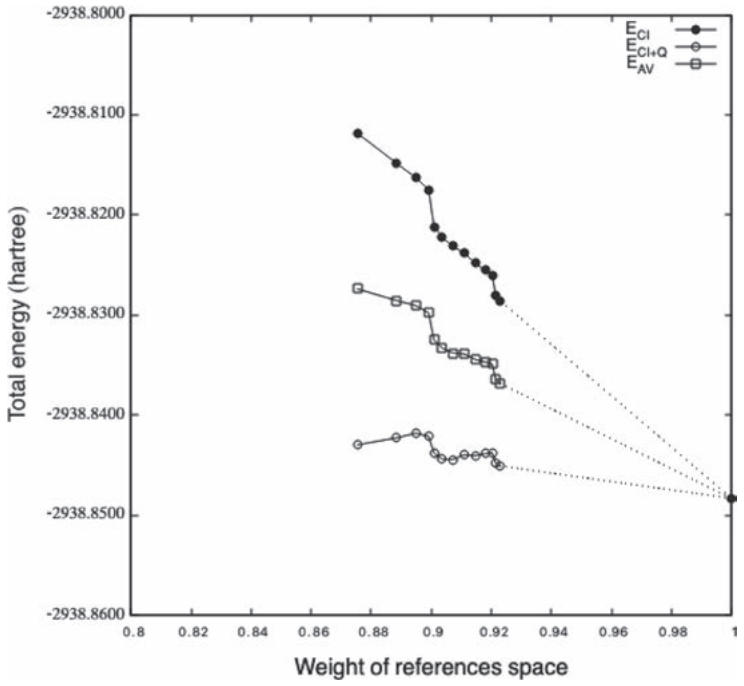

Fig. 1 Convergence of CI energies for Rb and Rb^- with respect to the weight of the reference space

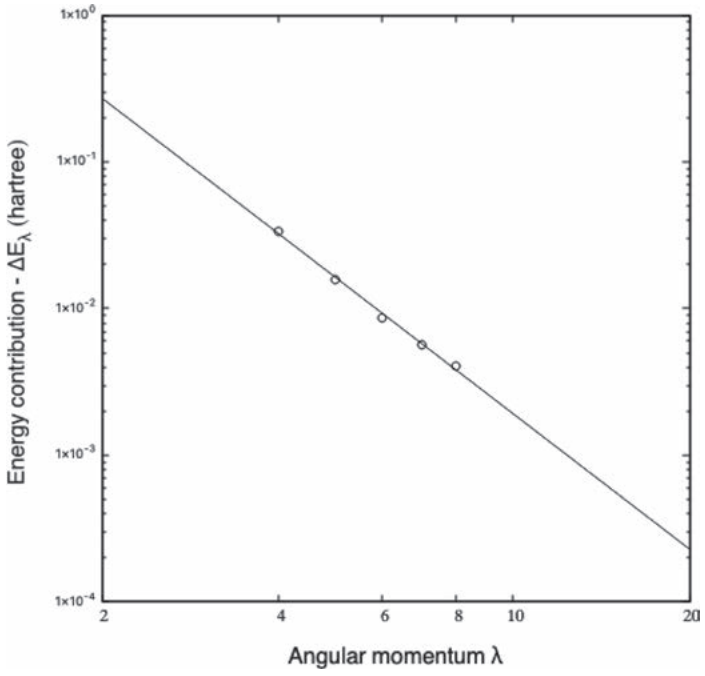

Fig. 2 Contributions to the total energies from the respective λ orbitals

$$E_{\lambda>8} = \sum_{\lambda=9}^{\infty} \Delta E_{\lambda} \,. \tag{6}$$

The FCI energy limit including the higher λ effect was obtained finally. The energy contribution due to the higher λ effect is –0.012969 hartree.

Table 3 summarizes the Ps binding energy of PsRb with our previous value. Our final Ps binding energy is 0.043 eV. The present value is smaller than our previous value by 0.050 eV. The result is unsatisfactory because the present calculation may include large ambiguity due to insufficient calculations. To obtain a reliable Ps binding energy, the reference space must be further extended and wave functions with large w_{ref} must be computed. Such calculations should remove ambiguity in the extrapolation of E_{CI} to $w_{\mathrm{ref}} = 1$ and in the estimation of the energy contribution due to the higher λ effect.

Table 3 Ps binding energy (E_{B}) and positron ionization energy (E_{PI}) of PsRb

Method	Reference	E_{B} (eV)	E_{PI} (eV)
MRSDCI(max)	This work	–0.332	6.285
FCI limit	This work	–0.287	6.029
FCI limit + higher λ	This work	0.043	6.343
FCI limit + higher λ	Ref. 1	0.093	6.421

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