

Complexes of positronium and atoms with ns^2np^{1-4} valence shells

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Abstract

Multireference configuration interaction calculations for complexes of positronium (Ps) and atoms with ns^2np^{1-4} valence shells, PsAl, PsSi, PsP, PsS, PsGa, PsGe, PsAs, and PsSe, are carried out, and their positron ionization energies and Ps binding energies are presented. It is revealed that PsSi, PsS, PsGe, and PsSe are energetically stable. The electron affinities of Al, Si, P, S, Ga, Ge, As, and Se are also calculated, and accuracy of the Ps binding energies is analyzed.

1. INTRODUCTION

A positron forms positronium (Ps), a hydrogen-like atom, with an electron. Theoretical studies with quantum mechanical calculations have shown that positronium can form bound states with various atoms.¹⁻⁸ Experiments have confirmed the existence of positronium hydride (PsH)⁹ and positronium halides (PsCl, PsBr, and PsI)¹⁰. Theoretical studies of the bound states of positronium and atoms have preceded experimental studies. Hereafter the bound state of positronium and atom is referred to as the positronium-atom complex.

Quantum mechanical calculations have been performed for various positronium-atom complexes, most of which have closed electron shells. Quantum mechanical studies of positronium-atom complexes with open electron shells have been carried out only for PsB, PsC, PsN, and PsO.⁶⁻⁸ Those theoretical studies have revealed that PsC and PsO are energetically stable. It has been concluded that this is due to the large electron affinity of C and O.^{6,7} Thus, complexes of positronium and atoms with the large electron affinity may be energetically stable.

The present work studied the energetic stability of the complexes of positronium and the second row and third row atoms with valence shells ns^2np^{1-4} : Al (2P), Si (3P), P (4S), S (3P), Ga (2P),

Ge (3P), As (4S), and Se (3P). To this end, the multireference singly and doubly excited configuration interaction (MRSDCI) method was applied to $[\text{core}]3s^23p^{2-5}1s_+^1$ for PsAl ($^{2,3}P$), PsSi ($^{3,4}S$), PsP ($^{2,3}P$), and PsS ($^{1,2}P$), and $[\text{core}]4s^24p^{2-5}1s_+^1$ for PsGa ($^{2,3}P$), PsGe ($^{3,4}S$), PsAs ($^{2,3}P$), and PsSe ($^{1,2}P$). Here, the subscript '+' means a positronic orbital.

In the present MRSDCI calculation, all orbitals were expanded with B -splines^{11,12}. The B -splines of order K $\{B_{i,K}\}$ are piecewise polynomials of degree $K - 1$ on a knot sequence in a cavity of radius R . The knot sequence $\{t_i\}$ is a set of points defined on an interval $[0, R]$. $B_{i,K}$ is nonzero in the interval $[t_i, t_{i+K})$. The advantage of B -splines is that they are very flexible and are relatively free from computational linear dependence. Thus, it is possible to apply a common B -spline set to all atoms, irrespective of orbital symmetry, without loss of accuracy. We have shown that the atomic Hartree-Fock-Roothaan method using the B -spline set gives highly accurate energies.^{13,14} Hence, the B -spline set should accurately expand atomic orbitals.

The many-body and angular correlation effects are known to be very important for the positronium-atom complex. Unfortunately, the MRSDCI wave function is very slow to converge with respect to incorporating those effects. The MRSDCI method often gives unsatisfactory results owing to such slow convergence. It would nevertheless be possible to obtain good results with the help of appropriate extrapolation procedures. In the present work, the energy contributions due to the many-body and angular correlation effects were estimated using extrapolation techniques.

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

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

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:

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

From Eq. (2), one can see that accurate electron affinity and positron ionization energy are required, to calculate the accurate Ps binding energy. Accuracy of the Ps binding energy can be analyzed by accuracy of the electron affinity of A at least. To analyze accuracy of the Ps binding energy, the electron affinities of the corresponding neutral atoms were also calculated.

The next section explains the B -splines used and details of MRSDCI calculations. The third section summarizes the Ps binding energies and the positron ionization energies for PsAl, PsSi, PsP, PsS, PsGa, PsGe, PsAs, and PsSe. Accuracy of the Ps binding energies is also analyzed by calculating the

electron affinities of the corresponding neutral atoms.

2. COMPUTATIONAL ASPECT

The present basis set consists of N K th-order B -splines on a knot sequence defined on an interval $[0, R]$, where R is in bohr. A knot sequence was used with endpoints of K -fold multiplicity:

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

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. The parameters $N = 40$, $R = 40$, and $K = 9$ were adopted. β was optimized by Hartree-Fock (HF) calculations for each system individually.

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’). In the first step of NO generation, MRSDCI calculations were carried out with the HF orbitals and obtain *spd*-NOs for PsAl, PsSi, PsGa, PsGe, and PsAs. For PsP, PsS, and PsSe, *spd*-NOs were obtained. Subsequently, the NOs with higher λ were generated, step by step. Those NOs whose occupation number was less than 10^{-6} were truncated at each step. For the neutral atoms and their negative ions, *spd*-NOs were constructed, and the NOs with higher λ was sequentially obtained in the same way.

Since the convergence of the MRSDCI function is very slow, the full configuration interaction (FCI) energy limits and the contributions to the total energies from higher angular momentum orbitals (the higher λ effect) were estimated using extrapolation techniques. To this end, a further series of MRSDCI calculations was carried out using obtained NOs for each system, increasing the reference configurations which were selected for the largest weight in the previous MRSDCI wave function. Those calculations were continued as long as the storage allowed. 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.¹³⁻¹⁵ All MRSDCI calculations were performed by the program ATOMCI^{16,17} modified for atomic systems containing positrons.

3. RESULTS AND DISCUSSION

Table 1 summarizes the results of the MRSDCI calculations with the minimal reference space for PsA, A, and A⁻. The weights of the reference space (w_{ref}) of MRSDCI wave functions for PsA are smaller than those for A and A⁻, even though the dimension of the MRSDCI wave function (N_{CI}) for PsA is very large. This indicates that the MRSDCI wave functions of PsA converge very slowly. The losses of the MRSDCI energies due to the NO truncation (ϵ) are slightly larger for PsA than for A and A⁻. Assuming additivity of energy, ϵ was added to the MRSDCI energies.

The FCI wave function is the MRSDCI wave function with $w_{\text{ref}} = 1$. The FCI energy limits were estimated by extrapolating MRSDCI energy (E_{CI}) to $w_{\text{ref}} = 1$. To this end, the convergence pattern of E_{CI} , $E_{\text{CI+Q}}$, and E_{AV} was analyzed with respect to w_{ref} . $E_{\text{CI+Q}}$ is E_{CI} plus the Davidson correction¹⁸. E_{AV} is the average of E_{CI} and $E_{\text{CI+Q}}$. Although E_{AV} has no physical meaning, it is useful for this extrapolation. Fig. 1 and 2 show the convergence pattern of E_{CI} , $E_{\text{CI+Q}}$, and E_{AV} for PsA against w_{ref} . One can see from Fig. 1 and 2 that the total energy of PsA converges very slowly. Thus, this extrapolation is very difficult, and ambiguity of extrapolated total energies may be large. The FCI

Table 1 Results of MRSDCI with minimal 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 (in hartree), and loss of total energies due to the NO truncation procedure (in $\mu\text{hartree}$)

	N_{CI}	w_{ref}	E_{CI}	ϵ		N_{CI}	w_{ref}	E_{CI}	ϵ
PsAl	119,513	0.801	-242.148803	-166	PsGa	144,611	0.822	-1923.527017	-154
Al ⁻	4,991	0.957	-241.951593	-63	Ga ⁻	5,226	0.960	-1923.327837	-57
Al	811	0.981	-241.935106	-35	Ga	736	0.983	-1923.314301	-59
PsSi	51,680	0.873	-289.181338	-201	PsGe	53,640	0.874	-2075.673202	-162
Si ⁻	3,895	0.965	-288.991751	-83	Ge ⁻	3,735	0.969	-2075.485069	-73
Si	2,550	0.975	-288.939895	-85	Ge	2,347	0.978	-2075.434215	-78
PsP	237,172	0.839	-341.048683	-255	PsAs	254,191	0.834	-2234.551852	-194
P ⁻	44,664	0.955	-340.857045	-136	As ⁻	28,903	0.942	-2234.359426	-101
P	2,175	0.978	-340.831385	-140	As	2,002	0.980	-2234.334451	-111
PsS	323,340	0.899	-397.938166	-317	PsSe	324,536	0.895	-2400.272581	-250
S ⁻	70,555	0.956	-397.748323	-174	Se ⁻	70,392	0.956	-2400.086923	-117
S	23,205	0.968	-397.672855	-195	Se	20,934	0.968	-2400.011343	-121

energy limits are listed in Table 2.

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, we extrapolated the total energies to $\lambda \rightarrow \infty$ using MRSDCI energies with the almost same w_{ref} . Fig. 3 and 4 show the energy contributions from the respective λ -NOs (ΔE_λ), on a log-log scale. The energy contribution converges linearly. Hence, the energy contribution was fitted by the following relation with two parameters α and β :

$$-\Delta E_\lambda = \alpha \lambda^{-\beta}. \quad (5)$$

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

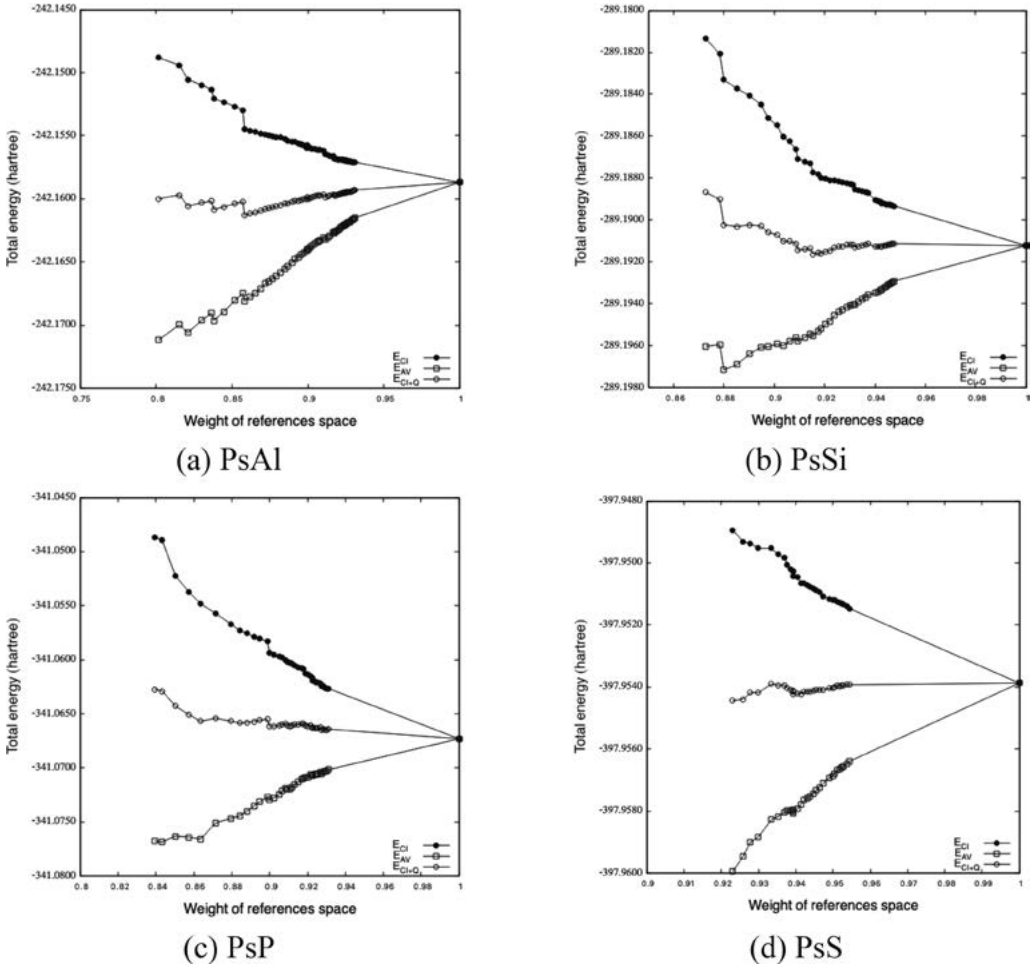


Fig. 1 Convergence of CI energies for PsAl, PsSi, PsP, and PsS with respect to the weight of the reference space

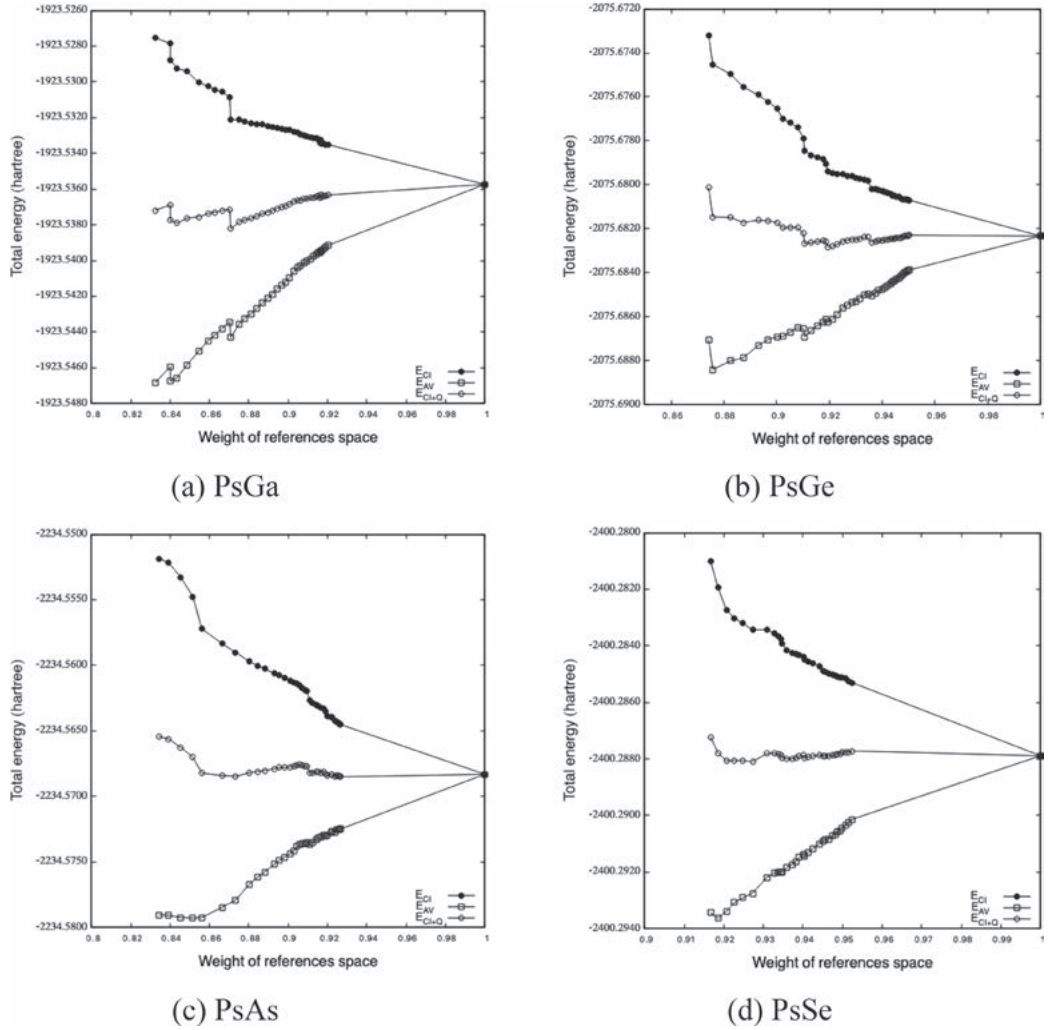


Fig. 2 Convergence of CI energies for PsGa, PsGe, PsAs, and PsSe with respect to the weight of the reference space

$$E_{\lambda>8} = \sum_{\lambda=9}^{\infty} \Delta E_{\lambda}. \quad (6)$$

We finally obtained the FCI energy limits including the higher λ effect. Table 3 summarizes the energy contribution due to the higher λ effect ($E_{\lambda>8}$) for PsA, A, and A⁻. $E_{\lambda>8}$ for PsA are all considerably larger than for A and A⁻. The energy of PsA converges slowly with respect to λ , indicating that the higher λ orbitals are needed to calculate PsA wave functions.

Table 4 summarizes the Ps binding energies (E_B) and the positron ionization energies of PsA (E_{PI}). All the Ps binding energies obtained from HF calculations are negative. The Ps binding energies obtained from the estimated FCI energies incorporating the higher λ effect are improved and are

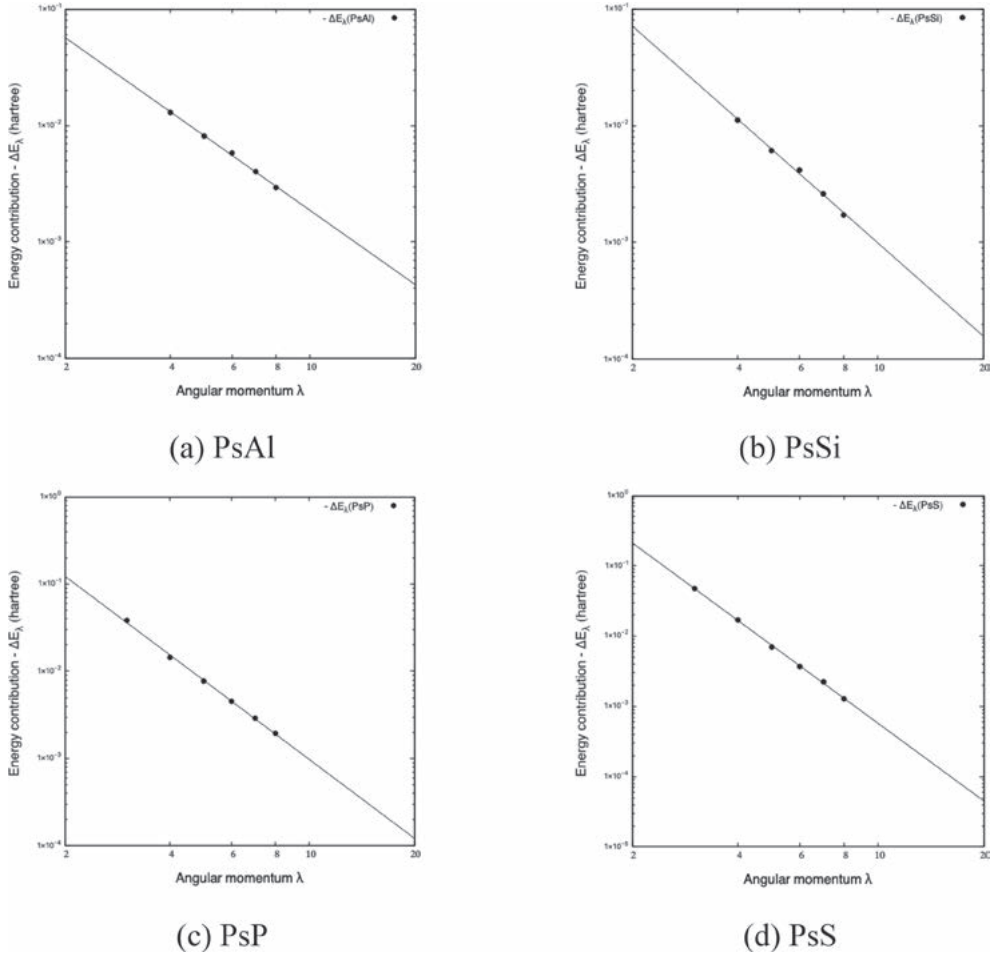
Table 2 Total energies (E_{CI}) and weights of reference space (w_{ref}) of MRSDCI(max) and full CI energy limits (E_{FCI}) for total energies (in hartree)

	MRSDCI (max)				MRSDCI (max)		
	w_{ref}	E_{CI}	E_{FCI}		w_{ref}	E_{CI}	E_{FCI}
P _s Al	0.931	-242.157085	-242.15868	P _s Ga	0.920	-1923.533514	-1923.53574
Al ⁻	0.992	-241.951978	-241.95201	Ga ⁻	0.993	-1923.328194	-1923.32821
Al	0.997	-241.935185	-241.93519	Ga	0.993	-1923.314384	-1923.31438
P _s Si	0.948	-289.189325	-289.19122	P _s Ge	0.950	-2075.680705	-2075.68233
Si ⁻	0.994	-288.992688	-288.99273	Ge ⁻	0.995	-2075.485836	-2075.48586
Si	0.996	-288.940313	-288.94031	Ge	0.994	-2075.434556	-2075.43457
P _s P	0.931	-341.062672	-341.06730	P _s As	0.927	-2234.564531	-2234.56831
P ⁻	0.990	-340.859247	-340.85938	As ⁻	0.988	-2234.363575	-2234.36375
P	0.989	-340.832095	-340.83217	As	0.988	-2234.334973	-2234.33508
P _s S	0.954	-397.951463	-397.95387	P _s Se	0.952	-2400.285299	-2400.28789
S ⁻	0.988	-397.751117	-397.75138	Se ⁻	0.989	-2400.089541	-2400.08973
S	0.993	-397.675166	-397.67525	Se	0.993	-2400.013261	-2400.01343

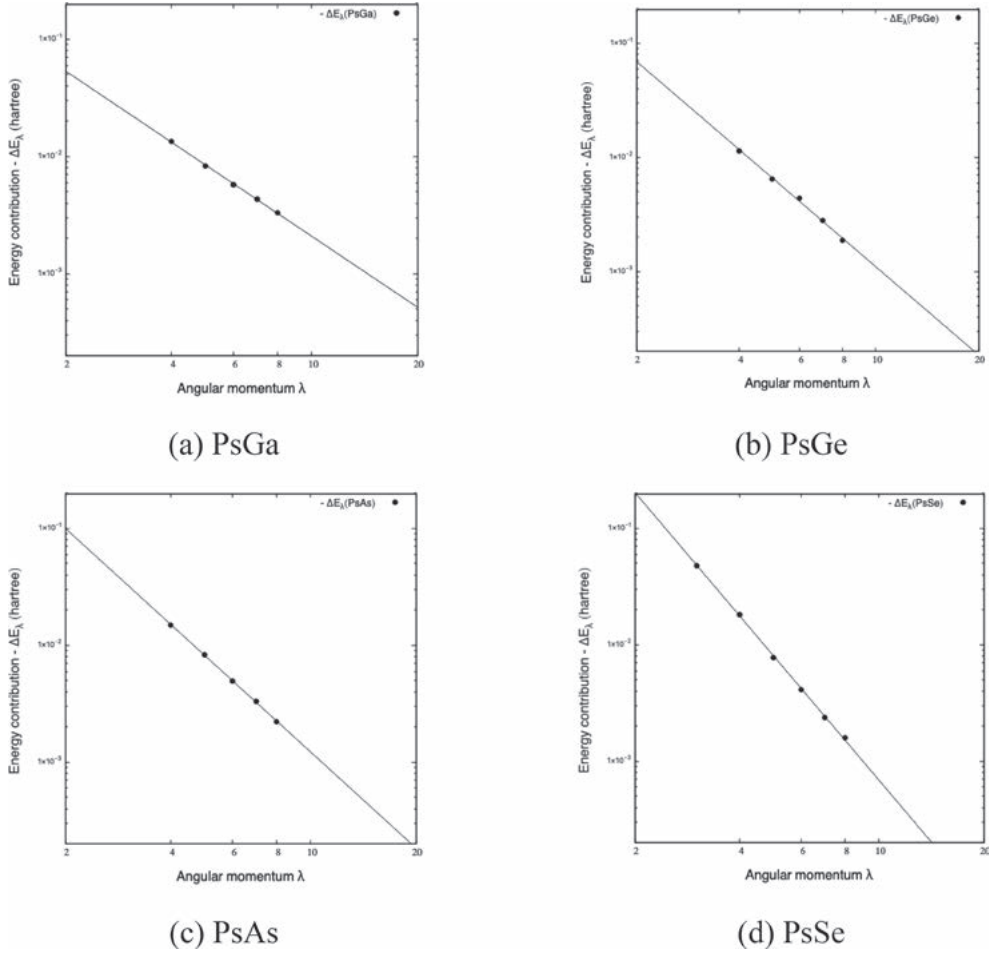
positive values except for PsAl, PsP, PsGa, and PsAs. The present work resulted that PsAl, PsP, PsGa, and PsAs are energetically unstable. Our previous work showed that PsB and PsN are unstable. Therefore, we conclude that the complexes of positronium and the group 13 and 15 atoms are unstable. Cheng et al. have estimated the Ps binding energies of various positronium-atom complexes using some atomic data.¹⁹ Our Ps binding energies are in good agreement with their results except for PsP and PsAs. They have reported that PsP and PsAs are energetically stable, in contrast to our results.

Table 5 summarizes the electron affinities of Al Si, P, S, Ga, Ge, As, and Se. The electron affinities obtained from the estimated FCI energies are largely improved. On the contrary, the higher λ effect has a small effect on the electron affinities. Comparing the experimental data²⁰ with the present results, the errors are large except for P and S, ranging from 0.034 eV to 0.163 eV. One possible reason is that only the valence electrons were treated. To improve the values, it may be necessary to incorporate core-electron effects. The largest error is for Ge, which is overestimated by 0.163 eV; a correct positron ionization energy of PsGe would result in a smaller Ps binding energy of PsGe.

In the present work, energetical stability of positronium-atom complexes with open electron shells, PsAl, PsSi, PsP, PsS, PsGa, PsGe PsAs, and PsSe, were investigated using the MRSDCI method. The MRSDCI wave functions of the complexes are very large because of the open shells. Hence, it is very

Fig. 3 Contributions to the total energies of PsAl, PsSi, PsP, and PsS from the respective λ orbitalsTable 3 Energy contributions ($E_{\lambda>8}$) due to higher λ effect (in hartree)

	$E_{\lambda>8}$	$E_{\text{FCI}}+E_{\lambda>8}$		$E_{\lambda>8}$	$E_{\text{FCI}}+E_{\lambda>8}$
PsAl	-0.015671	-242.17435	PsGa	-0.024341	-1923.56008
Al ⁻	-0.000017	-241.95203	Ga ⁻	-0.000021	-1923.32823
Al	-0.000012	-241.93520	Ga	-0.000020	-1923.31440
PsSi	-0.007852	-289.19907	PsGe	-0.009063	-2075.69139
Si ⁻	-0.000050	-288.99278	Ge ⁻	-0.000062	-2075.48592
Si	-0.000033	-288.94035	Ge	-0.000041	-2075.43461
PsP	-0.006741	-341.07404	PsAs	-0.009354	-2234.57766
P ⁻	-0.000150	-340.85953	As ⁻	-0.000164	-2234.36391
P	-0.000080	-340.83225	As	-0.000091	-2234.33517
PsS	-0.003294	-397.95716	PsSe	-0.004089	-2400.29198
S ⁻	-0.000365	-397.75175	Se ⁻	-0.000390	-2400.09012
S	-0.000235	-397.67549	Se	-0.000271	-2400.01362

Fig. 4 Contributions to the total energies of PsGa, PsGe, PsAs, and PsSe from the respective λ orbitalsTable 4 Ps binding energies (E_B) and positron ionization potentials (E_{PI}) for positronium-atom complexes (in eV)

	PsAl		PsSi		PsP		PsS	
	E_B	E_{PI}	E_B	E_{PI}	E_B	E_{PI}	E_B	E_{PI}
HF	-3.829	2.931	-2.566	3.276	-3.878	3.467	-2.210	3.680
MRSDCI	-0.696	5.622	0.112	5.421	-0.325	5.677	0.878	5.528
FCI limit	-0.721	5.624	0.025	5.401	-0.405	5.658	0.779	5.510
FCI limit + higher λ	-0.176	6.169	0.237	5.613	-0.223	5.837	0.862	5.590
Estimation ^a	-0.18		0.30		0.13		0.85	
	PsGa		PsGe		PsAs		PsSe	
	E_B	E_{PI}	E_B	E_{PI}	E_B	E_{PI}	E_B	E_{PI}
HF	-3.873	2.947	-2.632	3.219	-3.898	3.333	-2.316	3.477
MRSDCI	-0.790	5.715	-0.003	5.361	-0.406	5.631	0.729	5.398
FCI limit	-0.779	5.647	-0.061	5.346	-0.456	5.566	0.668	5.392
FCI limit + higher λ	-0.118	6.309	0.190	5.591	-0.204	5.816	0.772	5.493
Estimation ^a	-0.18		0.20		0.11		0.73	

^a Cheng et al. (Ref.19)

Table 5 Electron affinities of atoms (in eV)

	Al	Si	P	S	Ga	Ge	As	Se
HF	0.042	0.961	-0.542	0.913	-0.017	0.953	-0.428	1.010
MRSDCI (max)	0.485	1.495	0.800	2.153	0.298	1.439	0.766	2.134
FCI limit	0.458	1.426	0.740	2.072	0.376	1.396	0.780	2.078
FCI limit + higher λ	0.458	1.427	0.742	2.075	0.376	1.396	0.782	2.082
Experiment ^a	0.433	1.390	0.747	2.077	0.41	1.233	0.814	2.021

^a Andersen et al. (Ref.20)

difficult to obtain MRSDCI wave functions with sufficiently large w_{ref} . Highly accurate results for the complexes with open shells will not be available unless a breakthrough computational method is developed.

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