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Actinide Element and Germanium: A First-principles Density Functional Theory Investigation on the electronic and magnetic properties of ApGe (Ap=Ac-Lr) Diatoms

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Abstract

Geometries, electronic and magnetic properties of the ApGe (Ap=Ac-Lr) diatoms are studied by first-principles density functional theory with relativistic effect being taken into accounts. The calculated natural populations of ApGe (Ap=Ac-Lr) diatoms show that the electronic charges are transferred mainly from Ap to Ge, and most of Ap 5*f* subshell in ApGe is inert and without involving chemical bonding. The calculated highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps of ApGe (Ap=Ac-Lr) diatoms exhibit oscillating behaviors from AcGe to BkGe and slight increasing from CfGe to NoGe. The calculated magnetic moments of ApGe (Ap=Ac-Lr) showed that the total magnetic moments mainly depend on the 5*f* electrons of Ap in ApGe diatoms which generate the magnetic properties. Our calculated results are in good agreement with available theoretical and experimental data.

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1 Introduction

In order to develop new germanium based nanomaterials with tunable properties, the germanium clusters have been extensively investigated both *by* computational and experimental methods [1]. However, pure germanium clusters are unsuitable for the building blocks because they are chemically reactive due to the existence of dangling bonds. Transition metal or actinide atom-doped germanium clusters, on the other hand, may interact with germanium to form more stable geometries with new chemical and physical properties.[2-10]

The rare earth lanthanide (Ln) atoms can retain significant portions of their magnetic moments due to their localized *f*-electrons even when they are enclosed by a silicon or germanium cage. Among them, the Ln-doped silicon clusters have attracted wide interests and been extensively investigated [4-9]. In a way, actinide elements (Aps) are special transition metals, possessing the important optical and magnetic properties. Although there are some studies on the properties of Ap-doped silicon clusters [11], surely no systematic computational investigation on the ApGe (Ap=Ac-Lr) diatoms has been reported so far. In order to explore the properties of the ApGe diatoms, in this study, by including the relativistic effects, we carried a detailed study on their relative stabilities, structural and magnetic properties.

In order to reveal the unusual properties of the Ap-doped germanium clusters, the main objective of this research, therefore, is to provide a detailed investigation of equilibrium geometries, electronic structure properties, HOMO-LUMO gaps, and magnetic properties of all ApGe (Ap=Ac-Lr) diatoms.

This paper is organized as follows: in the second section, we briefly describe the theoretical method, particularly, the challenges to include the relativistic effect of the Ap due to its complicated 5*f* electrons. In the third section we show our results on ApGe diatoms and compare them with other available reports, and in the last section we summarize our conclusions.

2 Computational details

The explicit treatment of all the electrons in a cluster including actinide elements constitutes a demanding computational task because of having large number of electrons. One of the best ways to surmount this difficulty is to use relativistic electron core potentials (RECP) approach, also known as relativistic pseudopotentials [12] In this way, only the valence electrons are explicitly treated. Our previous results showed that the RECP calculations can actually provide accurate results for both homo- and heteronuclear clusters bearing actinide elements and germanium atoms [11]. Here, we demonstrate that the combination of density functional theory (DFT) methods with RECP also can provide a feasible and accurate approach to the electronic structure study of the ApGe (Ap =Ac-Lr) diatoms as shown in the following sections.

Present calculations are done at the level of the DFT with the hybrid exchange and correlation (mPW3PBE) functional in combination with the 6-31G* basis sets for Ge atom and Large-core Stuttgart quasi-relativistic effective core potentials (ECP60MWB) for describing Ac-Lr elements [12] as implemented in the Gaussian 09 package [13]. By considering with relativistic effect into calculations, geometries of the ApGe (Ap=Ac-Lr) diatoms are systematically optimized with the evaluation of their harmonic vibrational frequencies in order to attest the stabilities of diatoms. Different spin-polarizations for the ApGe (Ap=Ac-Lr) diatoms are taken into accounts during calculations.

3 Results and Discussions

3.1 Stabilities of ApGe (Ap=Ac-Lr) diatoms

The calculated bond lengths, spins, magnetic moments, frequencies, and total energies of the ApGe (Ap=Ac-Lr) diatoms are tabulated in Table 1. According to the calculated data of the ApGe diatoms, one can find that the calculated Ap-Ge bond lengths in the ApGe (Ap=Ac-Lr) diatoms range from 2.5 to 2.90 Å, and their corresponding frequencies are approximately in the range of 130 to 241 cm^{-1}.

For the AcGe diatom, at the mPW3PBE level in combination with the 6-31G* basis sets for Ge atom and ECP60MWB ECP for Ac element, the calculated bond length and vibrational frequency of AcGe are 2.568 Å and 209.9 cm^{-1} respectively. The obtained electronic state of the most stable doublet AcGe diatom with relativistic effect considered is $^2\Sigma$. The quartet and sextet spin states are 0.243 and 0.6 eV higher than the doublet spin state. In addition, the obtained magnetic moment of the AcGe is $1\mu_B$. Based upon the calculated atomic natural populations as listed in Table 2, among ApGe diatoms, the AcGe has the largest charge-transfer of 0.56*e* from Ac atom to Ge atom, reflecting that the AcGe is formed by both ionic and covalent bonding.

The electron configuration of Th is [Rn]$7s^2 6d^2$. The ThGe diatom with different spin states is optimized, and the obtained most stable quintet ThGe isomer has electronic state of $^5\Pi$. The calculated bond length and frequency of the neutral quintet ThGe diatom are 2.785 Å and 208.8 cm^{-1} respectively. In addition, the 5*f* and 6*d* orbitals of Th atom obtain electronic charges (0.16e and 0.32e, respectively) from its 7*s* orbitals. Obviously, the 5*f* orbitals of Th slightly involve into the chemical bonding with Ge.

As far as the PaGe diatom is concerned, the electron configuration of Pa is [Rn]$7s^2 5f^2 6d^1$. The PaGe isomer with sextet spin state is optimized to be the most stable state. It should be pointed out that the doublet and quartet spin states of PaGe isomer are only 0.186 and 0.091 eV higher than the sextet spin state (Table 1). The calculated Pa-Ge bond length and vibrational frequency of the most stable neutral PaGe isomer are respective 2.817 Å and 194.4 cm^{-1}. From Table 2, it can be seen that the variation of natural population of Pd 5*f* orbitals is very small with a value of 0.05e. Hence, in PaGe isomer, the Pa 5*f* orbitals mainly keep inert.

In the literature, there are few studied on U-Ge related system. As a dualism of the 5*f* electrons of ferromagnetic superconductor, UGe_2 has been widely investigated recently [14,15]. The obtained data pointed out the dual behavior of the 5*f* electrons in

UGe_2 possessing simultaneously local and itinerant characters in two substates.[15] The valence state of uranium in this compound was confirmed as U^{5+} by X-ray photoelectron spectroscopy and electron paramagnetic resonance.[15] However, the calculated frequency and U-Ge bond length of the septet UGe diatom with electronic state being $^7\Sigma$ are 241.3 cm^{-1} and 2.606 Å, respectively. The calculated U-Ge bond length in the UGe is shorter than U-Ge bond lengths (2.96,2.94, and 2.91 Å) of UGe_2 and U-U bond length in UGe_2[15]. As can be seen from Table 2, the calculated HOMO-LUMO gap of UGe cluster is not the smallest one, reflecting that the HOMO-LUMO gap of UGe diatom is different that of USi diatom [11]. Our calculated results indicate that the U 5*f* orbitals involve in chemical bonding slightly with Ge and make the properties of U-contained compounds more complicated.

By evaluating the total energies of NpGe diatom with different spin states, the most stable spin state is identified as S=7/2. The calculated Np-Ge bond length and frequency in the neutral NpGe isomer are 2.799 Å and 174.4 cm^{-1}, respectively. Furthermore, the NpGe diatom has the magnetic moment of $7\mu_B$, reflecting that the unfilled 5*f* orbitals of Np mainly contributes to the high spin state. The actinide element compounds are nice magnetic material because the electrons residing in the more localized 5*f* orbitals of actinide atoms are hardly responsible for bonding. Consequently, the magnetic properties of actinide element doped Ge_n clusters can often be observed significantly. In addition, the sextet spin state is slightly higher in energy than the octet spin state. As one can see from Table 2, the calculated natural populations of Np 5*f* orbitals in NpGe is larger than those of U in UGe, reflecting that the 5*f* orbitals of Np in NpGe are more active and involved in the chemical interactions, whereas the U- contained compounds have complicated electronic properties.

Among the actinide elements, plutonium is unique in its physicochemical complexities by virtue of its position where the 5*f* electrons are at the border between delocalized (not associated with a single atom) and localized (associated with a single atom) behavior, and it is considered to be one of the most complex elements. Plutonium sits near the juncture where the actinide series transitions from main *d*-block element chemistry to rare earth like behavior as a result of the actinide contraction. Because of its importance and complexity, plutonium has been one of the most intensely investigated elements. Employing DFT, Baizaee and Pourghazi explored the structural stability, electronic structure and *f* hybridization of PuM_3 and Pu_3M (M=Ge, Sn, Pd) intermetallic compounds[16]. Their obtained results indicated that the Pu_3M structures are more stable than PuM_3 and there is a strong hybridization between M 5*p* with Pu 5*f* and Pu 6*d* orbitals in both PuM_3 and Pu_3M compounds. The Pu atom may provide high magnetic moments, owing to its electronic configuration ($7s^2 5f^6$). In addition, the Pu atom is the last element in actinide series in which the 5*f* electrons still have some contributions to the chemical bonding. Under the interaction of Ge with Pu atom, the most stable PuGe diatom consequently shows nonet spin state with the stronger magnetic moment. As can be seen from Table 1, the total magnetic moment of the most stable PuGe diatom is $8\mu_B$. Additionally, the quintet spin state of PuGe diatom is 0.004 eV higher in energy than the nonet spin state, the quintet and nonet spin states are degenerated. According to the calculated natural population, it is obvious that the varied natural population of 5*f* orbitals of Pu is 0.27e which contributes to the chemical bonding. The 6*d* subshell in Pu atom obtains 0.44e from 5*f* and 7*s* orbitals of Pu atom. The calculated Pu-Ge vibrational frequency and bond length in the PuGe isomer with spin *nonet* electronic state are 164.2 cm^{-1} and 2.821 Å, respectively.

Different from Ac-Np, Am has the electron configuration of $[Rn]7s^2 5f^7$. Its empty 6*d* orbitals do not directly play roles in the chemical bonding while its 5*f* electrons retract from bonding and become localized. The degree of itinerancy of the 5*f* electrons is quite sensitive to small variations in the chemical environment. In order to study the electronic properties of the AmGe diatom, the AmGe cluster is optimized, and the obtained Am-Ge vibrational frequency and bond length in AmGe cluster are 152.9 cm^{-1} and 2.877 Å, respectively. The obtained electronic spin of the AmGe diatom is

9/2, and the total magnetic moment of the most stable AmGe diatom is 9μ_B. Based on the calculated natural populations of AmGe diatom, the Am 5*f* electrons are less sensitive to bind with germanium atom because the variation of $5f^{6.96}$ electrons is very small from the $5f^7$ configuration in pure Am. Obviously, the Am 5*f* electrons in AmGe with half-filled configuration is stable and can achieve higher spin state. In addition, the calculated HOMO-LUMO gap of the AmGe diatom is 2.180 eV.

Cm element possesses the electron configuration of $[Rn]7s^25f^76d^1$. Different from Am, its 6*d* orbital has one electron. By calculating the total energies of CmGe diatom with different spin states at the mPW3PBE level, the most stable spin state of CmGe is identified as S=5 (Table 1). The calculated Cm-Ge vibrationalfrequency and bond length in this configuration are 185.8 cm^{-1} and 2.772 Å, respectively. Furthermore, the calculated total magnetic moment is 10μ_B, which is the biggest among all ApGe (Ap=Ac-Lr) diatoms. Such results indicate that the Cm-doped germanium clusters can be used as new stronger magnetic material because the Cm atom can generate the strongest magnetic property compared to other actinide elements. In addition, the spin state stability of the CmGe diatom is mainly attributed to the half-filled $5f^7$ electron shell configuration ($[Rn]7s^25f^76d^1$) of Cm atom in CmGe.

Berkelium with electronic configuration of $[Rn]7s^25f^9$ is the first member of the second half of the actinide series. Studying the physicochemical properties of this element enables more accurate extrapolations to the behavior of the heavier elements. In order to explore the properties of Bk doped germanium material, BkGe diatom is calculated by considering different spin states. The obtained results showed that the most stable BkGe has S=7/2. The calculated Bk-Ge vibrational frequency and bond length in this configuration are 138.9 cm^{-1} and 2.809 Å, respectively. According to the calculated natural populations of Bk atom, the natural population variation of 5*f* electrons is very small (0.08e), in other words, different from its 6d orbitals, the Bk 5*f* electrons are not sensitive to bind with germanium atom and hence do not involve in chemical bonding.

Californium with electronic configuration of [Rn]$7s^2 5f^{10}$ is among the second half of the actinide series where their *f* electrons are further removed or shielded from the valence electrons in comparison with those lighter actinides. By considering with relativistic effect into calculations, the CfGe isomer is optimized. We found that the most stable CfGe is a septet configuration with electronic spin S=3. The calculated frequency, magnetic moment, and Cf-Ge bond length are 144.5 cm^{-1}, $6\mu_B$, and 2.859 Å, respectively. According to the calculated HOMO and LUMO values of the CfGe, it is found that the CfGe has the larger HOMO-LUMO gap and indicates the CfGe is formed manly by covalent bonding.

By optimizing EsGe diatom with different spin states, the obtained results show that its most stable state has S=5/2. The calculated Es-Ge vibrational frequency and bond length ine EsGe are 140.2 cm^{-1} and 2.854 Å, respectively. In addition, the calculated total magnetic moment of EsGe diatom is 5.0 μ_B.

Similarly, the calculated Fm-Ge bond length, and vibrational frequency in FmGe are 2.862 Å and 138.0 cm^{-1}, respectively. The spin state of FmGe is $^5\Sigma$ with total magnetic moment of 4.0 μ_B .

By considering relativistic effect into our calculation, the obtained Md-Ge bond length and vibrational frequency in MdGe diatom are respective 2.867 Å and 135.7 cm^{-1}. The most stable MdGe diatom has quartet spin state of S=3/2 with total magnetic moment of $3\mu_B$. The results show that there are the larger charge-transfer between Md and Ge atom.

In the case of NoGe diatom, the calculated No-Ge bond length and vibrational frequency of the triplet NoGe with relativistic affect being considered are 2.874 Å and 132.1 cm^{-1}, respectively. In addition, its corresponding magnetic moment is $2\mu_B$.

Lawrencium with electronic configuration of [Rn]$7s^2 5f^{14} 6d^1$ behaves differently from dipositive nobelium and more like the tripositive elements earlier in the actinide series. From the calculated results of LrGe diatom, one can find that the Lr-Ge bond length and vibrational frequency in its most stable state are 2.804 Å and 155.6 cm^{-1}, respectively. Furthermore, the magnetic moment of LrGe is $3\mu_B$. As can be seen from Table 2, the $5f$ subshell of Lr is filled with 14 electrons and does not involve in chemical bonding with Ge atom.

3.2 Charge-Transfer

The calculated natural populations and natural orbital configurations of actinide elements in ApGe diatoms are tabulated in Table 2 and shown Figure 1. According to the calculated results, it can be seen that the natural populations of all actinide elements are positive, which means that the electronic charges are transferred from actinide elements to germanium atom. This finding is different from those of transition metal (TM) doped silicon clusters in which the electrons transferred from Si to TM.[4,10,18] As shown in Table 2, it is obvious that the ThGe and CmGe diatoms have smaller charge-transfer while the AcGe diatom has larger charge–transfer (Figure 1). The largest charge-transfer is observed in the AcGe diatom while the smallest charge-transfer is predicted in the ThGe diatom.

As can be seen from Table 2, it is apparent that the contributions of $7p$ orbitals of actinide atoms to charge-transfer maintain nearly invariable except for Lr(0.14) in LrGe. it should be pointed out that the contribution of the $7p$ orbitals of actinide atom to charge-transfer is very small and the electronic charges are mainly transferred from the $6s$ orbitals of Ap (Ap=Ac-Lr) to the $7p$ orbitals of Ap (Ap=Ac-Lr); furthermore, the $5f$ orbitals of Ap in the ApGe (Ap=Ac, Pa, Am-Lr) involve slightly charge-transfers, especially for U, Th, Np, and Pu in respective UGe, ThGe, NpGe, and PuGe having larger charge-transfer relatively. Generally, the $5f$ orbitals of Ap (Ap=Am-Lr) maintain their original electronic configurations, and do not involve chemical bonding. The main charge-transfer involves in the 7s and 6d orbitals of

ApGe (Ap=Ac-Lr) (Table 2). Furthermore, the charge-transfer is oscillating increased from ThGe to BkGe.

3.3 HOMO-LUMO gaps

The HOMO and LUMO energies as well as the corresponding HOMO-LUMO gaps of the ApGe diatoms are tabulated in Table 1, meanwhile the HOMO-LUMO gaps of the ApGe diatoms are shown in Figure 2. It is remarkable that the ThGe and PaGe diatoms have smaller HOMO-LUMO gaps than other isomers. Among them, the ThGe has the smallest HOMO-LUMO gap, which indicates that the ThGe is a softest molecule and has strong chemical reactivity. However, the HOMO-LUMO gaps of AcGe, UGe, PuGe, LrGe, and CmGe are bigger than other isomers, and the LrGe has the biggest HOMO-LUMO gap, exhibiting that the LrGe has the strongest chemical hardness and dramatically enhanced chemical stability. In addition, the HOMO-LUMO gaps of ApGe diatoms exhibit oscillating behaviors from AcGe to BkGe and show invariable behaviors from BkGe to NoGe.

Based upon the contour maps of the HOMO for the most stable ApGe diatoms in Figure 2a, one can find that the most stable UGe,NpGe, PuGe, CmGe, and LrGe diatoms are formed by σ-bonding type while the most stable AnGe (An=Ac,Am, Bk-No) diatoms are formed by π-bonding type. Furthermore, the most stable ThGe and PaGe are formed mainly by δ-bonding type. Consequently, the main bonding types of ApGe (Ap=Ac-Lr) diatoms are different due to the different Ap in each ApGe diatom having different electron configuration.

3.4 Magnetic moments

The calculated magnetic moments of the ApGe (Ap=Ac-Lr) are listed in Table 1 and shown in Figure 3. Interestingly, the total magnetic moments of the ApGe (Ap=Ac-Lr) increase gradually from AcGe to CmGe alone with the electrons of 5*f* subshell in actinide atom being increased from $5f^0$ in Ac to $5f^7$ in Cm, and generally decrease from CmGe to LrGe alone with the electrons in 5*f* subshell of actinide atom being increased from $5f^7$ of Cm to $5f^{14}$ of Lr. The unfilled $5f$ subshell gives rise to strong magnetism because the magnetic effects of electrons in the incomplete $5f$ subshell do not cancel each other as they do in a completed subshell. The CmGe has the biggest total magnetic moment because Cm atom has $5f^7 6d^1 7s^2$ electronic configuration. Furthermore, our results show that the behavior of magnetic moment in the ApGe (Ap=Ac-No) is similar to those in the LnSi (Ln=La-Lu) and ApSi (Ap=Ac-No) diatom systems.[11,17]

4 Conclusions

Employing first-principles density functional theory with the hybrid exchange and correlation (mPW3PBE) functional in combination with the 6-31G* for Ge atom and Large-core Stuttgart quasi-relativistic effective core potentials (ECP60MWB) used to describe Ac-Lr elements, in this study, we systematically investigated the electronic and magnetic properties of ApGe (Ap=Ac-Lr) diatoms. The obtained Ap-Ge bond lengths, vibrational frequencies, HOMO-LUMO gaps, and magnetic properties of the neutral ApGe (Ap=Ac-Lr) diatoms are in good agreement with available experimental and theoretical data. Based on the calculated total energies, ground state with electronic state and spin is determined for each ApGe diatom. The calculated natural populations of ApGe (Ap=Ac-Lr) clusters exhibit that the charges are transferred from Ap to Ge and most of $5f$ subshell of Ap in ApGe diatoms is inert without involving chemical bonding. The calculated HOMO-LUMO gaps of ApGe showed that the HOMO-LUMO gaps exhibit oscillating behaviors from AcGe to BkGe, meanwhile, the HOMO-LUMO gap of the LrGe has the largest value of 3.06 eV. The obtained magnetic moments of the ApGe (Ap=Ac-Lr) diatoms indicate that the total magnetic moments depend on the electrons filled in Ap $5f$ subshell which generates the magnetic properties of the ApGe diatoms. Among ApGe, the CmGe possesses a largest magnetic moment of $10\mu_B$.

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Table 1, Bond lengths (Bond, Å), spin(S), vibrational frequencies (Freq, cm^{-1}), magnetic moments ($\mu_{T,}$ μ_B), electronic configuration, energy difference △E(eV) and total energies (E_{tot}, hartree) of the ApGe(Ap=Ac-Lr) diatoms at the mPW3PBE level.

System	State	S	M	Ap-Ge	Freq	E_{gap}	E_T	EXP[a)]	△E	electronic configuration
			μ_b	Å	cm^{-1}	eV	Hartree		eV	
AcGe	$^2\Sigma$	1/2	1	2.568	209.9	2.592	-2450.252590		**0.00**	**$\pi^2\sigma^1$**
	$^4\Sigma$	3/2					-2450.243666		0.243	
	$^6\Sigma$	5/2					-2450.230537		0.600	
ThGe	$^5\Sigma$	2	4	2.785	208.8	1.953	-2482.222694		0.00	**$\pi^2\sigma^2$**
	$^1\Sigma$	0					-2482.188385		0.934	
	$^3\Sigma$	1					-2482.210041		0.344	
	$^7\Sigma$	3					-2482.158679		1.742	
PaGe	$^6\Sigma$	5/2	5	2.817	194.4	2.009	-2515.917154		0.00	**$\pi^2\sigma^1\delta^2$**
	$^2\Sigma$	1/2					-2515.910331		0.186	
	$^4\Sigma$	3/2					-2515.913799		0.091	
	$^8\Sigma$	7/2					-2515.902412		0.401	
	$^{10}\Sigma$	9/2					-2515.614437		8.237	
UGe	$^7\Sigma$	3	6	2.606	241.3	2.379	-2551.491658	2.9 Å	0.00	**$\pi^2\sigma^1\delta^2\sigma^1$**
	$^1\Sigma$	0					-2551.412798		2.146	
	$^3\Sigma$	1					-2551.456322		0.962	
	$^5\Sigma$	2					-2551.465769		0.704	
	$^9\Sigma$	4					-2551.475624		0.436	
NpGe	$^8\Sigma$	7/2	7	2.799	174.4	2.125	-2589.031611		0.00	**$\pi^2\sigma^2\delta^2\sigma^1\pi^2$**
	$^2\Sigma$	1/2					-2589.008786		0.621	
	$^4\Sigma$	3/2					-2588.968581		1.715	
	$^6\Sigma$	5/2					-2589.030343		0.035	
	$^{10}\Sigma$	9/2					-2589.016210		0.419	
PuGe	$^9\Sigma$	4	8	2.821	164.2	2.281	-2628.559074		0.00	**$\pi^2\delta^2\sigma^1\pi^2\sigma^1$**
	$^1\Sigma$	0					-2628.356581		5.510	
	$^3\Sigma$	1					-2628.521824		1.014	
	$^5\Sigma$	2					-2628.558930		0.004	
	$^7\Sigma$	3					-2628.546279		0.348	
	$^{11}\Sigma$	5					-2628.549354		0.264	
AmGe	$^{10}\Sigma$	9/2	9	2.877	152.9	2.180	-2670.153363		0.00	**$\pi^2\sigma^1\varphi^2\delta^2\sigma^1\pi^2\sigma^1$**
	$^2\Sigma$	1/2					-2670.022318		3.566	
	$^4\Sigma$	3/2					-2670.070004		2.268	
	$^6\Sigma$	5/2					-2670.152255		0.030	
	$^8\Sigma$	7/2					-2670.142162		0.305	
	$^{12}\Sigma$	11/2					-2670.142868		0.286	
CmGe	$^{11}\Sigma$	5	10	2.772	185.8	2.421	-2713.746694		0.00	**$\varphi^2\delta^2\pi^2\sigma^1\sigma^1\pi^2\sigma^1\sigma^1$**
	$^1\Sigma$	0					-2713.439898		8.348	
	$^3\Sigma$	1					-2713.680887		1.791	
	$^5\Sigma$	2					-2713.733842		0.350	
	$^7\Sigma$	3					-2713.730669		0.436	
	$^9\Sigma$	4					-2713.732632		0.383	
BkGe	$^8\Sigma$	7/2	7	2.809	138.9	2.249	-2759.463138		0.00	**$\varphi^2\delta^2\sigma^1\pi^2\sigma^1\pi^2\sigma^1\pi^2$**
	$^2\Sigma$	1/2					-2759.381102		2.232	
	$^4\Sigma$	3/2					-2759.462998		0.004	
	$^6\Sigma$	5/2					-2759.4506428		0.340	
	$^{10}\Sigma$	9/2					-2759.442905		0.551	
CfGe	$^7\Sigma$	3	6	2.859	144.5	2.261	-2807.816048		0.00	**$\varphi^2\delta^2\pi^2\sigma^1\sigma^2\pi^2\sigma^1$**
	$^1\Sigma$	0					-2807.641810		4.741	
	$^3\Sigma$	1					-2807.800501		0.423	
	$^5\Sigma$	2					-2807.804571		0.312	
	$^9\Sigma$	4					-2807.792690		0.636	
EsGe	$^6\Sigma$	5/2	5	2.854	140.2	2.254	-2858.439614		0.00	**$\delta^2\pi^2\sigma^2\pi^2\sigma^1\sigma^1\pi^2$**
	$^4\Sigma$	3/2					-2858.434834		0.130	

	$^{8}\Sigma$	7/2					-2858.367622	1.959	
	$^{8}\Sigma$	9/2					-2858.321145	3.224	
FmGe	$^{5}\Sigma$	2	4	2.862	138.0	2.241	-2911.394515	0.00	**$\varphi^{2}\sigma^{1}\pi^{2}\delta^{2}\sigma^{1}\pi^{2}\delta^{2}\sigma^{2}\pi^{2}$**
	$^{1}\Sigma$	0					-2911.299952	2.573	
	$^{3}\Sigma$	1					-2911.339428	1.499	
	$^{7}\Sigma$	3					-2911.364406	0.819	
	$^{9}\Sigma$	4					-2911.244991	4.069	
MdGe	$^{4}\Sigma$	3/2	3	2.867	135.7	2.254	-2966.046304	0.00	**$\pi^{2}\sigma^{1}\delta^{2}\sigma^{1}\pi^{2}\sigma^{1}\sigma^{2}\pi^{2}$**
	$^{2}\Sigma$	1/2					-2966.008704	1.023	
	$^{6}\Sigma$	5/2					-2966.002579	1.190	
	$^{8}\Sigma$	7/2					-2965.849340	5.360	
NoGe	$^{3}\Sigma$	1	2	2.874	132.1	2.274	-3023.333921	0.00	**$\varphi^{2}\pi^{2}\delta^{2}\varphi^{2}\delta^{2}\sigma^{1}\pi^{2}\sigma^{2}\sigma^{1}\pi^{2}$**
	$^{1}\Sigma$	0					-3023.293248	1.107	
	$^{5}\Sigma$	2					-3023.293791	1.092	
	$^{7}\Sigma$	3					-3023.085637	6.756	
LrGe	$^{4}\Sigma$	3/2	3	2.804	155.6	3.062	-3082.315620	0.00	**$\varphi^{2}\sigma^{1}\varphi^{2}\delta^{2}\sigma^{1}\pi^{2}\delta^{2}\pi^{2}\sigma^{2}\sigma^{1}\sigma^{2}\pi^{2}\sigma^{1}$**
	$^{2}\Sigma$	1/2					-3082.295981	0.534	
	$^{6}\Sigma$	5/2					-3082.218427	2.645	
	$^{8}\Sigma$	7/2					-3081.940385	10.211	

a) experimental value of U-Ge bond length in UGe_2 from Ref .15.

Table 2, Natural populations (Ap and Ge), and natural configurations of Ap in the ApGe (Ap=Ac-Lr) diatoms.

System	Ge	Ap	Ap natural orbital populations			
			5f	6d	7p	7s
AcGe	-0.56	0.56	0.06	1.15	0.09	1.17
ThGe	-0.22	0.22	0.16	2.32	0.07	1.25
PaGe	-0.35	0.35	1.95	1.21	0.06	1.45
UGe	-0.39	0.39	3.11	1.56	0.07	0.90
NpGe	-0.36	0.36	4.57	0.57	0.08	1.43
PuGe	-0.39	0.39	5.73	0.44	0.07	1.39
AmGe	-0.46	0.46	6.96	0.30	0.07	1.23
CmGe	-0.34	0.34	7.02	0.95	0.08	1.62
BkGe	-0.47	0.47	8.92	0.27	0.07	1.95
CfGe	-0.47	0.47	9.97	0.21	0.06	1.30
EsGe	-0.48	0.48	10.98	0.19	0.05	1.30
FmGe	-0.48	0.48	11.99	0.17	0.05	1.32
MdGe	-0.48	0.48	12.99	0.13	0.05	1.35
NoGe	-0.47	0.47	13.99	0.13	0.04	1.38
LrGe	-0.47	0.47	14.00	0.54	0.14	1.84

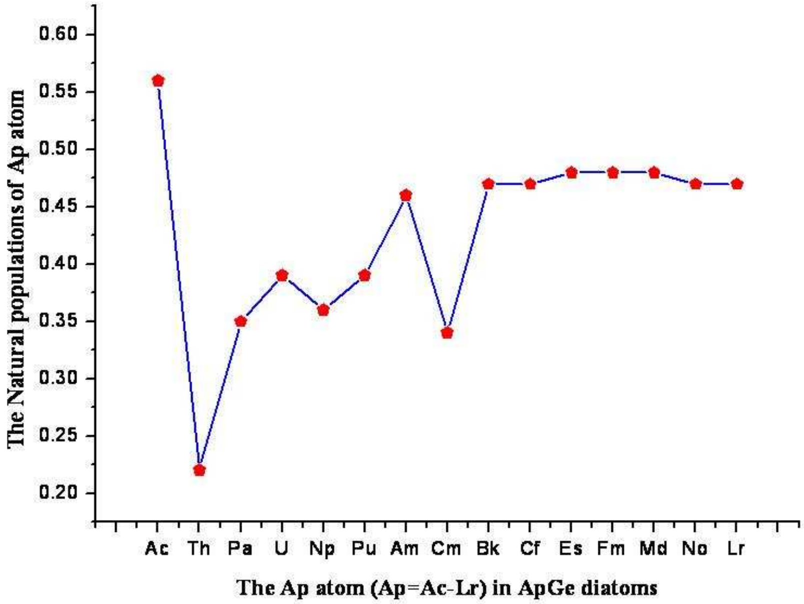


Figure 1, The natural populations of actinide atom in the ApGe (Ap=Ac-Lr) diatoms.

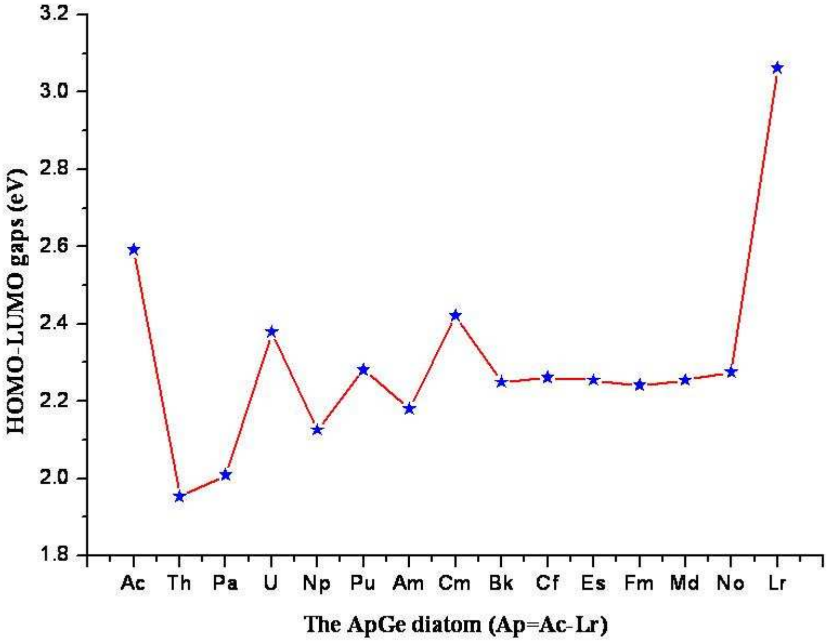
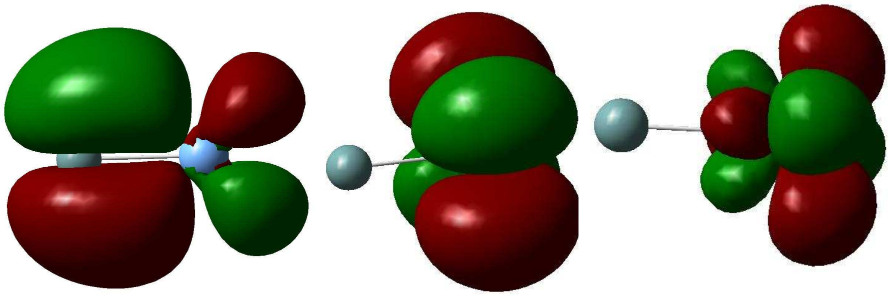
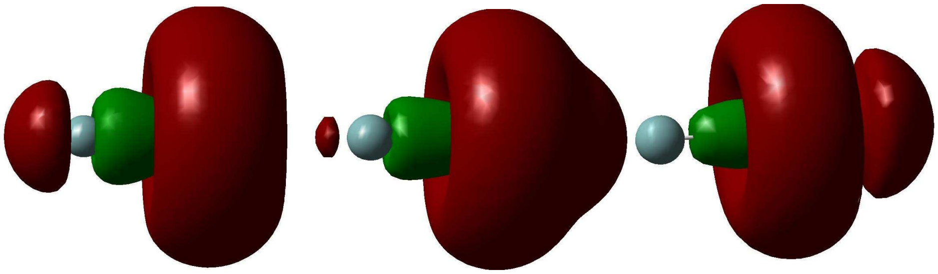


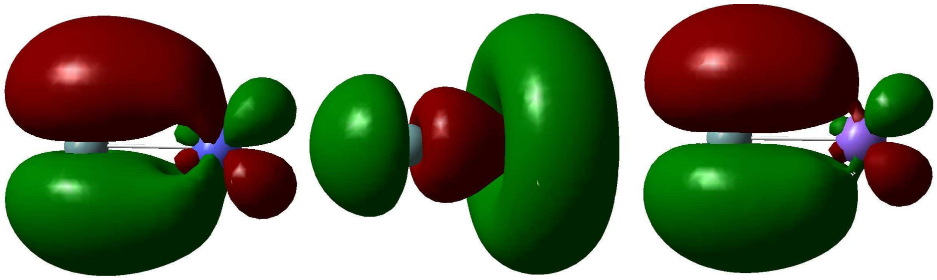
Figure 2, The HOMO-LUMO gaps of the ApGe (Ap=Ac-Lr) diatoms.



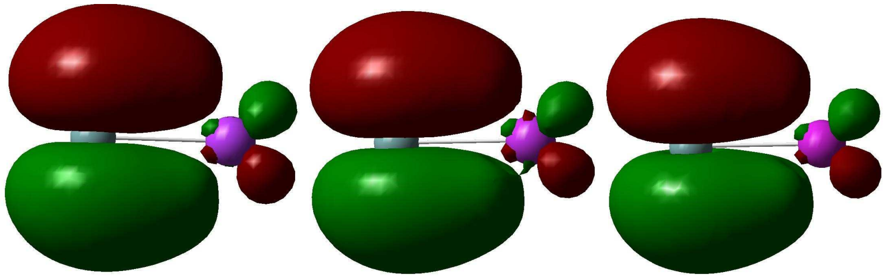
AcGe, π-bonding ThGe,δ-bonding PaGe, δ-bonding



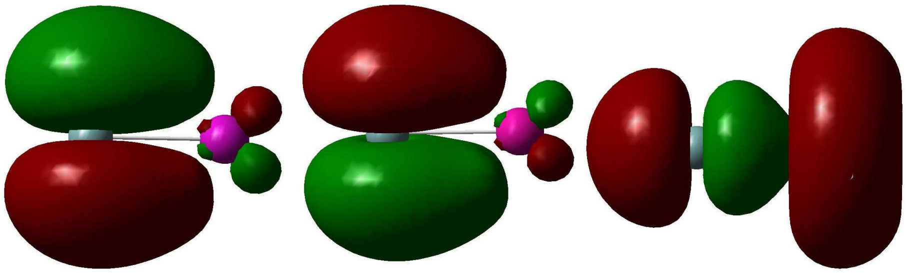
UGe,σ-bonding NpGe, σ bonding PuGe, σ-bonding



AmGe, π-bonding CmGe, σ-bonding BkGe, π-bonding



CfGe, π-bonding EsGe, π-bonding FmGe, π-bonding



MdGe, π-bonding NoGe,π-bonding LrGe, σ-bonding

Figure 2a, The contour maps of the HOMO for the most stable ApGe diatoms (The left atom in light blue is Ge while the Ap atom is on the right).

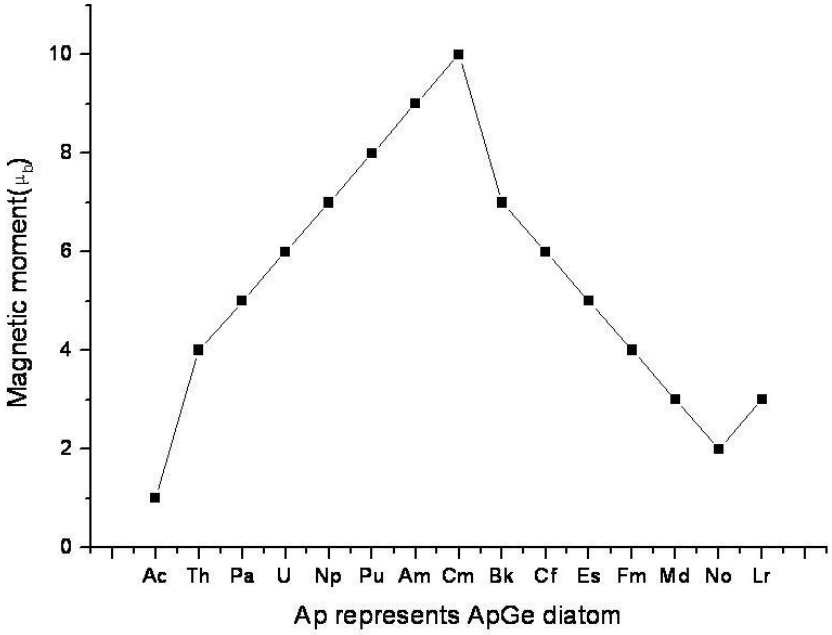


Figure 3, The calculated total magnetic moments of the ApGe (Ap=Ac-Lr) diatoms.