

Theoretical Investigation of Stable Structures of Ge₆ Clusters with Various Negative Charges

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Nine isomers of Ge₆, Ge₆²⁻, Ge₆⁴⁻, and Ge₆⁶⁻ have been searched for by the MP2/6-31+G(d), B3LYP/6-311+G(d), and B3LYP/LANL2DZ electronic structure calculations. Totally 16 isomers are found: six Ge₆, three Ge₆²⁻, five Ge₆⁴⁻, and two Ge₆⁶⁻. We discovered that the predicted stable shapes of Ge₆²⁻, Ge₆⁴⁻, and Ge₆⁶⁻ are octahedral, pentagonal pyramidal, and hexagonal, respectively, which agrees well with the Wade rule. It is concluded that the electron counting rule governs the structural preference in Ge anion clusters as well as in Si anion clusters. [doi:10.2320/matertrans.47.2624]

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1. Introduction

Semiconductor clusters have been intensively studied due to their scientific and technological importance. Structures of clusters are different from those of bulk materials and affect physical and chemical properties. There have been a number of experimental and theoretical studies on small germanium clusters including determinations of geometries, dissociation energies, electronic structures, and electron affinities.^{1,2)} In 1954, Ge_n (*n* = 2–8) clusters were first experimentally studied by Kohl.³⁾ Gingerich *et al.* investigated Au-Ge-Cu system by high temperature mass spectrometric technique and determined the stabilities of Ge_n (*n* = 2–5) clusters with higher accuracy.⁴⁾ Since then, Ge clusters have been studied by various experimental methods such as laser photo fragmentation,⁵⁾ mass spectrometry,⁶⁾ and photoelectron spectroscopy.⁷⁾

We found in our previous study⁸⁾ that an anionic silicon cluster (Si[−])₆, which is isoelectronic with (SiH)₆, forms a planar six-membered ring similar to benzene (CH)₆, although neutral (SiH)₆, the silicon analog of (CH)₆, takes a non-planar chair form.^{9–11)} The planar hexagon is aromatic with *D*_{6h} symmetry and we described it as “silicon benzene”.¹²⁾ Since germanium is adjacent to silicon in the periodic table, Ge clusters are expected to show similar structures and properties to the corresponding Si clusters. It is known that neutral (GeH)₆ forms a non-planar six-membered ring,¹³⁾ and it has been desired to investigate the stable structure of the germanium anion cluster. Experimentally, a dianion cluster consisting of six germanium atoms with organometallic protective groups was obtained in matrix and the structure of Ge₆ moiety was revealed to be octahedron.¹⁴⁾ In this paper, we study all the equilibrium structures of Ge₆^Z (*Z* = 0, 2-, 4-, 6-) and compare them with silicon clusters. We discuss structural preferences according to the Wade rule that relates the number of electrons in B_nH_m and the analogous systems to the stable structures.^{15,16)}

2. Theoretical Methods

Nine types of structures (planar hexagon, benzvalene, Dewar benzene, triangular prismane, bicyclopropenyl, octahedron, chair form, twist boat form, pentagonal pyramidal) were used as initial structures for calculations of Ge₆^z (*z* = 0, 2-, 4-, 6-) clusters. The first six are topologically possible valence isomers of (CH)₆.^{17–22)} Two non-planar and one planar six-membered rings are theoretically found ones in P₆²³⁾ and in anionic silicon clusters,⁸⁾ respectively.

Ab initio molecular orbital and density functional theory (DFT) calculations were performed using the Gaussian03 software package.²⁴⁾ We used Beck's hybrid three-parameter functional with the LYP correlation functional (B3LYP) in

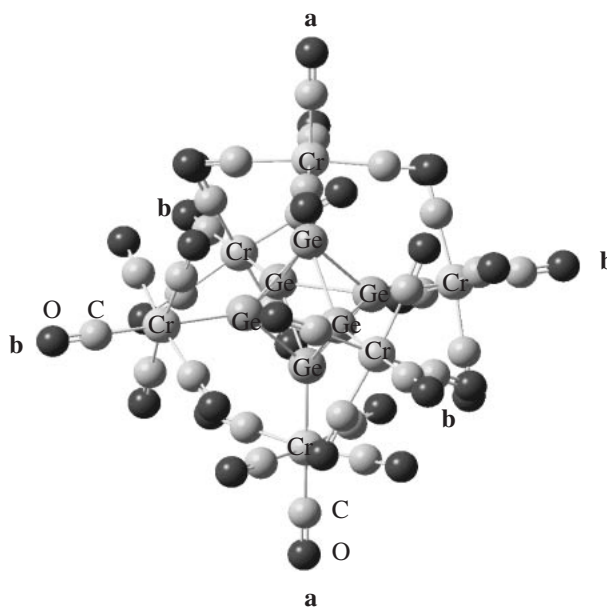


Fig. 1 The optimized structure of [(CO)₅Cr]₆Ge₆]²⁻ at the B3LYP/3-21G(d) and B3LYP/LANL2DZ levels. Selected distances [pm] and angles [°]: Gea-Cra 242.6, Geb-Crb 239.5, Gea-Geb 254.1, Geb-Geb 252.5; Geb-Gea-Cra 134.64, Gea-Geb-Crb 135.36, Geb-Geb-Crb 135.00 (experiment, *D*_{4h}). Ge-Cr 230.5, Ge-Ge 247.3; Ge-Ge-Cr 135.00 (B3LYP/3-21G(d), *O_h*). Ge-Cr 252.8, Ge-Ge 269.8; Ge-Ge-Cr 135.00 (B3LYP/LANL2DZ, *O_h*). **a** and **b** indicate apical and basal positions.

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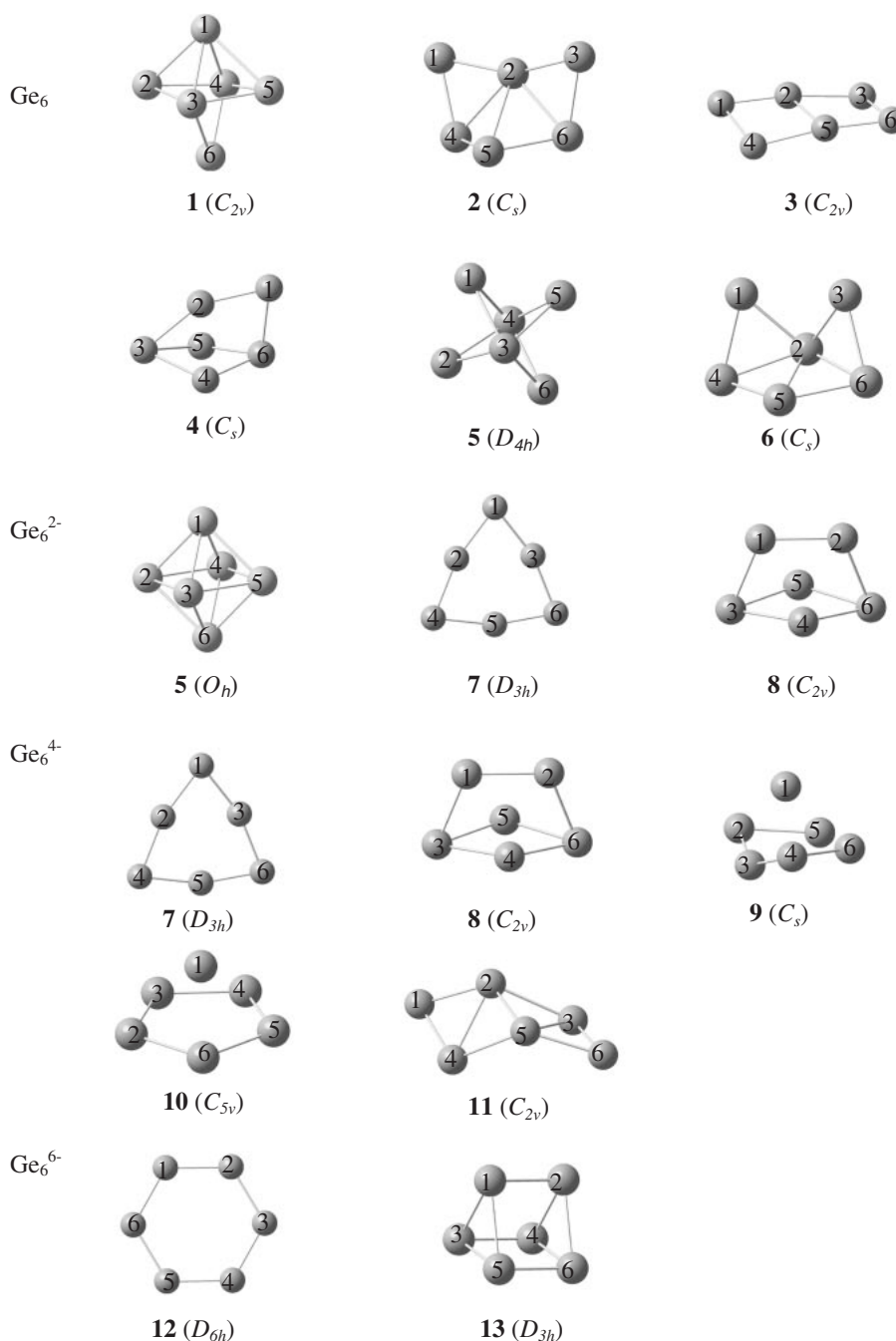


Fig. 2 Equilibrium structures of neutral and anionic clusters.

the DFT calculations.²⁵⁾ The basis sets used were polarized basis sets supplemented by diffuse functions (6-31+G(d) and 6-311+G(d)) and LANL2DZ with effective core potentials by Hay and Wadt.²⁶⁾ Stationary points were confirmed to be minimum by harmonic vibrational frequency analysis at each level. 3-21G(d) basis was used for large clusters. We checked the RHF-UHF instability of wavefunction for all equilibrium structures.

3. Results and Discussion

Since experimentally observed X-ray crystal structure is available for comparison, we first calculate $[(\text{CO})_5\text{-Cr}]_6\text{Ge}_6]^{2-}$ that includes octahedral Ge₆.¹⁴⁾ The optimized

molecular structure at the B3LYP/3-21G(d) and B3LYP/LANL2DZ levels are shown in Fig. 1. The computationally optimized molecular structure has O_h symmetry at both calculation levels, while experimentally observed anion cluster has lower D_{4h} symmetry probably due to crystal packing effect. Geometric parameters at equilibrium are similar at both levels of calculations. Comparing with experimental values, the Ge-Ge (Ge-Cr) distances decreases approximately 3% (5%) at the B3LYP/3-21G(d) level and increases approximately 7% (5%) at the B3LYP/LANL2DZ level.

Next, we calculate a model system of charged germanium clusters. Six Ge₆, three Ge₆²⁻, five Ge₆⁴⁻, and two Ge₆⁶⁻ are obtained as equilibrium (no imaginary vibrational frequen-

Table 1 Optimal geometric parameters of Ge_6 , Ge_6^{2-} , Ge_6^{4-} , and Ge_6^{6-} isomers at the B3LYP/6-311+G(d), B3LYP/LANL2DZ, and MP2/6-31+G(d) levels.

				Parameter
Ge_6	1	B3LYP/6-311+G(d)	Bond length/pm	$r_{12}/280.2, r_{14}/259.5, r_{24}/256.2, r_{46}/252.1$
			Bond angle/degree	$a_{142}/65.83, a_{246}/75.01$
		B3LYP/LANL2DZ	Bond length/pm	$r_{12}/278.0, r_{14}/278.2, r_{24}/271.8, r_{46}/260.1$
			Bond angle/degree	$a_{142}/60.71, a_{246}/80.38$
	2	B3LYP/6-311+G(d)	Bond length/pm	$r_{12}/245.1, r_{14}/245.1, r_{24}/271.1, r_{25}/288.0, r_{45}/248.9$
			Bond angle/degree	$a_{123}/155.14, a_{214}/67.16, a_{142}/56.43, a_{254}/60.14, a_{245}/67.11$
		B3LYP/LANL2DZ	Bond length/pm	$r_{12}/251.5, r_{14}/253.8, r_{24}/290.5, r_{25}/314.6, r_{45}/256.0$
			Bond angle/degree	$a_{123}/161.76, a_{214}/70.19, a_{142}/54.53, a_{254}/60.19, a_{245}/69.97$
	3	B3LYP/6-311+G(d)	Bond length/pm	$r_{12}/237.0, r_{14}/251.0, r_{25}/257.6, r_{45}/260.4$
			Bond angle/degree	$a_{123}/170.86, a_{145}/112.20, a_{125}/118.22, a_{214}/66.18$
		MP2/6-31+G(d)	Bond length/pm	$r_{12}/240.8, r_{14}/250.7, r_{25}/257.0, r_{45}/251.2$
			Bond angle/degree	$a_{123}/162.76, a_{145}/112.20, a_{125}/113.60, a_{214}/65.13$
		B3LYP/LANL2DZ	Bond length/pm	$r_{12}/243.5, r_{14}/261.3, r_{25}/266.2, r_{45}/269.2$
			Bond angle/degree	$a_{123}/173.18, a_{145}/110.89, a_{125}/117.97, a_{214}/67.37$
		4 MP2/6-31+G(d)	Bond length/pm	$r_{12}/242.8, r_{23}/261.0, r_{16}/250.8, r_{34}/256.3, r_{46}/247.9$
			Bond angle/degree	$a_{216}/70.93, a_{164}/101.46, a_{465}/71.05, a_{346}/107.20$
	5	B3LYP/LANL2DZ	Bond length/pm	$r_{12}/251.4, r_{23}/271.0, r_{16}/261.9, r_{34}/269.3, r_{46}/261.3$
			Bond angle/degree	$a_{216}/71.46, a_{164}/103.70, a_{465}/72.95, a_{346}/103.82$
		MP2/6-31+G(d)	Bond length/pm	$r_{13}/253.8$
			Bond angle/degree	$a_{132}/70.81$
	6	MP2/6-31+G(d)	Bond length/pm	$r_{12}/248.9, r_{14}/256.6, r_{24}/259.8, r_{25}/251.7, r_{45}/254.4$
			Bond angle/degree	$a_{214}/61.82, a_{142}/57.64, a_{254}/61.78, a_{245}/58.60, a_{456}/122.84$
Ge_6^{2-}	5	B3LYP/6-311+G(d)	Bond length/pm	$r_{12}/267.4$
		MP2/6-31+G(d)	Bond length/pm	$r_{12}/264.3$
		B3LYP/LANL2DZ	Bond length/pm	$r_{12}/281.0$
		B3LYP/6-311+G(d)	Bond length/pm	$r_{12}/241.4$
	7	B3LYP/6-311+G(d)	Bond angle/degree	$a_{213}/76.11, a_{124}/163.89$
			Bond length/pm	$r_{12}/240.4$
		MP2/6-31+G(d)	Bond angle/degree	$a_{213}/74.72, a_{124}/165.30$
			Bond length/pm	$r_{12}/247.2$
	8	B3LYP/LANL2DZ	Bond angle/degree	$a_{213}/79.49, a_{124}/160.53$
			Bond length/pm	$r_{12}/257.0, r_{13}/258.3, r_{34}/257.5$
		B3LYP/6-311+G(d)	Bond angle/degree	$a_{126}/110.46, a_{134}/68.87, a_{435}/63.05$
			Bond length/pm	$r_{12}/259.8, r_{13}/263.4, r_{34}/255.8$
		MP2/6-31+G(d)	Bond angle/degree	$a_{126}/108.53, a_{134}/63.99, a_{435}/62.57$
			Bond length/pm	$r_{12}/266.7, r_{13}/264.8, r_{34}/267.7$
		B3LYP/LANL2DZ	Bond length/pm	$r_{12}/266.7, r_{13}/264.8, r_{34}/267.7$
			Bond angle/degree	$a_{126}/110.64, a_{134}/73.45, a_{435}/64.27$
Ge_6^{4-}	7	B3LYP/6-311+G(d)	Bond length/pm	$r_{12}/245.5$
			Bond angle/degree	$a_{213}/72.09, a_{124}/167.91$
		MP2/6-31+G(d)	Bond length/pm	$r_{12}/245.6$
			Bond angle/degree	$a_{213}/69.14, a_{124}/170.64$
	8	MP2/6-31+G(d)	Bond length/pm	$r_{12}/259.1, r_{13}/263.6, r_{34}/262.5$
			Bond angle/degree	$a_{126}/109.28, a_{134}/63.91, a_{435}/62.43$
		B3LYP/LANL2DZ	Bond length/pm	$r_{12}/275.3, r_{13}/265.3, r_{34}/279.0$
			Bond angle/degree	$a_{126}/104.27, a_{134}/69.90, a_{435}/83.28$
	9	B3LYP/6-311+G(d)	Bond length/pm	$r_{15}/278.9, r_{23}/246.8, r_{25}/269.7, r_{56}/260.9$
			Bond angle/degree	$a_{156}/62.10, a_{325}/78.62, a_{256}/113.66, a_{234}/139.45$
	10	B3LYP/6-311+G(d)	Bond length/pm	$r_{12}/283.3, r_{23}/254.0$
			Bond angle/degree	$a_{213}/53.28$
		MP2/6-31+G(d)	Bond length/pm	$r_{12}/277.1, r_{23}/252.1$
			Bond angle/degree	$a_{213}/54.11$
	11	B3LYP/LANL2DZ	Bond length/pm	$r_{12}/293.8, r_{23}/264.0$
			Bond angle/degree	$a_{213}/53.40$
		B3LYP/6-311+G(d)	Bond length/pm	$r_{12}/259.0, r_{23}/290.0, r_{14}/239.6, r_{25}/249.5, r_{24}/271.2$
			Bond angle/degree	$a_{123}/126.64, a_{214}/65.78, a_{142}/60.55, a_{245}/52.66, a_{254}/59.80$
Ge_6^{6-}	12	MP2/6-31+G(d)	Bond length/pm	$r_{12}/246.2$
	13	B3LYP/6-311+G(d)	Bond length/pm	$r_{12}/245.9, r_{13}/267.6$
		B3LYP/LANL2DZ	Bond length/pm	$r_{12}/288.7, r_{13}/284.8$

Table 2 Relative energies among Ge₆^Z (Z = 0, 2-, 4-, 6-) isomers in kJ/mol.^{a,b}

		B3LYP/6-311+G(d)	MP2/6-31+G(d)	B3LYP/LANL2DZ
Ge ₆	1	0.00		0.00
	2	132.61		75.47
	3	121.73	287.37	73.42
	4	46.88	123.28	25.95
	5	0.04	0.00	3.60
	6		285.19	
Ge ₆ ²⁻	5	0.00	0.00	0.00
	7	67.23	185.23	21.06
	8	46.51	64.84	32.53
Ge ₆ ⁴⁻	7	0.00	50.78	
	8		4.69	91.63
	9	19.84		
	10	20.01	0.00	0.00
	11	44.16		
Ge ₆ ⁶⁻	12	150.94	0.00	0.00
	13	0.00		291.30

^aEnergies include zero-point energy corrections.^bItalic face indicating a transition state.Table 3 Total energies (*E*) in kJ/mol and RHF-UHF instability of wavefunction (WF) for Ge₆^Z (Z = 0, 2-, 4-, 6-) isomers.^a

		B3LYP/6-311+G(d)		MP2/6-31+G(d)		B3LYP/LANL2DZ	
		<i>E</i>	WF	<i>E</i>	WF	<i>E</i>	WF
Ge ₆	1	-32735088.92	Stable			-59421.87	Stable
	2	-32734956.35	Stable			-59346.41	Stable
	3	-32734967.20	Stable	-32677316.55	Unstable	-59348.46	Stable
	4			-32677480.61	Unstable	-59395.95	Stable
	5			-32677603.91	Unstable		
	6			-32677318.70	Unstable		
Ge ₆ ²⁻	5	-32735131.77	Stable	-32677615.21	Stable	-59480.77	Stable
	7	-32735064.52	Stable	-32677429.97	Unstable	-59459.70	Stable
	8	-32735085.25	Stable	-32677550.35	Stable		
Ge ₆ ⁴⁻	7	-32733914.21	Unstable	-32676284.00	Unstable		
	8			-32676330.12	Unstable	-57779.73	Stable
	9	-32733894.35	Unstable				
	10	-32733894.20	Stable	-32676334.80	Unstable	-57871.35	Stable
	11	-32733870.03	Unstable				
Ge ₆ ⁶⁻	12			-32674017.89	Unstable		
	13	-32731911.89	Unstable			-54573.91	Stable

^aEnergies include zero-point energy corrections.

cies in the harmonic approximation). The optimized structure, selected geometric parameters, and relative energies among isomers are given in Fig. 2 and Tables 1–2. Two isomers (**9** and **11** of Ge₆⁴⁻) are obtained at the B3LYP/6-311+G(d) level and three isomers (**5** and **6** of Ge₆: **12** of Ge₆⁶⁻) are obtained at the MP2/6-31+G(d) level. In neutral Ge₆, deformed octahedral, **1** and **5**, are the most stable with comparable energies, Octahedral **5** of Ge₆²⁻ is the most stable at all levels of calculations studied here. The planar six-membered ring **12** of Ge₆⁶⁻ is obtained only at the MP2/6-31+G(d) level. Isomers of Ge₆ are more than those of Si₆, but isomers of Ge₆²⁻ and Ge₆⁴⁻ are less than those of Si₆²⁻ and

Si₆⁴⁻. It is interesting that **7** is obtained in Ge₆²⁻ and Ge₆⁴⁻ despite of the difference in the number of valence electrons. The more electrons are doped, the larger the molecular size is: the Ge-Ge bond length of **7** is 245.5 pm in Ge₆⁴⁻ and 241.4 pm in Ge₆²⁻ at the B3LYP/6-311+G(d) level.

The Ge-Ge bond lengths are longer by 9.9–19.6 pm at the B3LYP/LANL2DZ level than those at the B3LYP/6-31G(d) level. In general, diffuse functions are important for anion systems. Actually, the characteristics of stationary points changes by adding diffuse function: 11 minima and 10 transition states are obtained at the B3LYP/6-31G(d) level, while 6 minima and 15 transition states at the B3LYP/6-

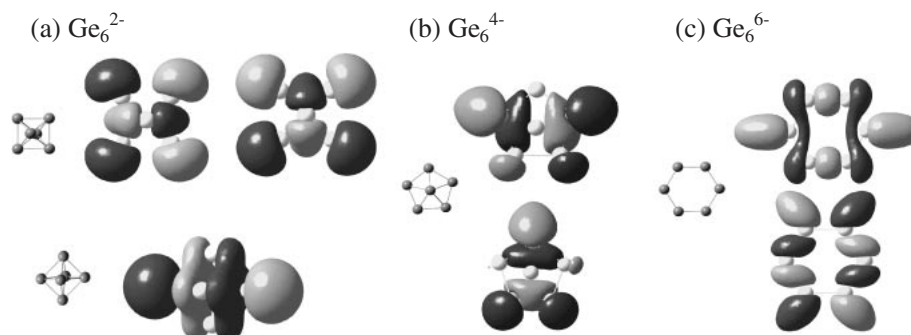


Fig. 3 Highest Occupied Molecular Orbital (HOMO) of the most stable structures (a) Ge_6^{2-} , (b) Ge_6^{4-} at the B3LYP/6-311+G(d) level and (c) Ge_6^{6-} at the MP2/6-31+G(d) level. All degenerated orbitals are shown.

31+G(d) level. No remarkable difference in the characteristics of stationary points and the geometric parameters is found between 6-31+G(d) and 6-311+G(d) basis sets using B3LYP method. We use 6-31+G(d) for MP2 method.

RHF-UHF instability is examined at equilibrium structures (Table 3). Many RHF-UHF instabilities of Hartree-Fock wave functions used for Møller-Plesset calculation and less instabilities of DFT wavefunction indicate that incorporation of electron correlations is quite substantial for the present system. It is noted that wave functions are always stable at B3LYP/LANL2DZ geometries. Energetics at the B3LYP/6-311+G(d) and B3LYP/LANL2DZ levels indicates that the most stable structures are octahedral **5** for Ge_6^{2-} and pentagonal pyramidal **10** for Ge_6^{4-} excluding the structures with unstable wave functions. Singlet-state **7** of Ge_6^{4-} gives unstable wave function, but triplet-state **7** of Ge_6^{4-} gives stable wave function. Total energy of optimized triplet-state **7** of Ge_6^{4-} is lower by 29.87 kJ/mol than that of the optimized singlet-state **7** of Ge_6^{4-} at the B3LYP/6-311+G(d) level. It is enumerated that the Wade rule comprise high predictability, but as the doped electron increases, the agreement with the Wade rule and the RHF-UHF stability of the wave functions become worse. No structure with stable wave function is obtained for Ge_6^{6-} at the B3LYP/6-311+G(d) level.

Natural bond orbitals of the most stable charged clusters predicted by the Wade rule are depicted in Fig. 3. It is shown that the HOMO of those structures mainly consists of lone electron-pair orbitals.

4. Conclusions

We have investigated the stable structures of germanium anion clusters. As the number of doped electrons increased, the agreement with the Wade rule and the RHF-UHF stability of the wave functions became worse. Common feature of anionic germanium clusters with Si clusters was that both anions have preferable structures according to the Wade rule. Difference was that the isomers of Ge_6 are more than those of Si_6 , but the isomers of Ge_6^{2-} and Ge_6^{4-} are less than those of Si_6^{2-} and Si_6^{4-} . The HOMO of the most stable charged clusters consisted mainly of the orbital of the lone-electron pair.

The present anionic system may seem to be hypothetical and unlikely ever to be synthesized. However, multiply

charged germanium systems are well established in crystals. More realistic model is a neutral molecule where a counter cation balances the negative charge of the anionic germanium system.

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