

Nonorthogonal Tight-binding Study of the Geometries and Electronic Properties of G_e ($n= 2- 20$) Clusters*

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The universal-parameter nonorthogonal tight-binding scheme proposed by Menon and Subbaswamy was used to optimize the geometrical structures, binding energies and electron affinities of small germanium clusters G_e ($n= 2- 20$). A complete agreement with available *ab initio* results from the lowest-energy structures for $Ge_2- Ge_8$ was obtained and reasonable structures for these clusters were predicted and compared with those of corresponding silicon clusters in the range of $n= 7- 20$. The averaged discrepancy with experiments in binding energies for $n= 2- 7$ is about 6% and the calculated electron affinities agree well with the measured values in the range of $n= 2- 8$ as well.

Keywords Germanium cluster, Tight-binding study, Geometry, Electronic property

Introduction

Studies on clusters of group IV elements (C, Si, Ge, Sn and Pb) have received much attention in the last decade for their potential applications in material science. But most of the work has been done on carbon and silicon clusters, while much less theoretical and experimental researches have been performed on germanium and other heavier metal clusters^[1,2]. Recent experimental studies on G_e included photoelectron spectroscopies of negative ions^[3] and the injected ion drift tube measurements^[4,5]. Reliable theoretical predictions on G_e are limited to $n \leq 7$. Pacchioni and Koutecky^[6] predicted the geometries and energies of $Ge^-- Ge^7$ using a MO-LCAO/SCF-CI method which kept all the nearest bond lengths at one value. Most of the structures of $Ge_2- Ge_{14}$ in reference^[7] are unstable when checked with more accurate calculations^[1,6,8]. The most recent *ab initio* calculation by Lanza and co-workers^[8] optimized the structures of $Ge_2- G_e$ within the given symmetry constrains.

The universal-parameter nonorthogonal tight-binding scheme proposed by Menon and Subbaswamy^[9-11] has been successfully applied to both carbon (C_{60})^[10] and silicon clusters up to $n= 14$ ^[9,11,12]. In this work, we applied this method to optimizing the geometrical structures, binding energies and electron affinities of small G_e clusters ($n= 2- 20$).

Theoretical Method and Structural Optimization

In the nonorthogonal tight-binding scheme of Menon and Subbaswamy^[9,11] (referred to as

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M-S NTB model in this work), the total energy of an X_n cluster system is the sum of three terms:

$$U_T = U_{el} + U_{rep} + U_{bond} \quad (1)$$

where U_{el} is the sum of the one-electron energies for the occupied states:

$$U_{el} = \sum_k^{occ} \epsilon_k \quad (2)$$

and U_{rep} represents the classical repulsive two-body term contribution:

$$U_{rep} = \sum_i \sum_{j>i} i(r_{ij}) = \sum_i \sum_{j>i} i_0 \exp[-U(r_{ij} - d_0)] \quad (3)$$

where $U = 4/r_0$, $r_0 = 0.122$ nm, one-half of the dimer bond length^[13], d_0 is the nearest bond length in crystal germanium, and r_{ij} is the distance between two atoms. To prevent the collapse of cluster structures into physically unreasonable range during full structural optimization, we added a stiff wall $\exp[-50(r_{ij}/d_0 - 1.0)]$ (only when $r_{ij} < 0.8d_0$) in the repulsive part. The bond-counting term U_{bond} takes the following form:

$$U_{bond} = -N(a/b)^{1/N} \quad (4)$$

and

$$n_b = \sum_i \left[\exp\left(\frac{d_i - R_c}{\Delta}\right) + 1 \right]^{-1} \quad (5)$$

with $R_c = 0.350$ nm and $\Delta = 0.01$ nm, the same values as for silicon clusters^[9,11,12], a and b are fitting parameters which are chosen to reproduce the cohesive energies of several small Ge_n clusters in close agreement with the experimental values^[6].

The characteristic equation of the system possesses the form

$$(H_{ij} - \epsilon_k S_{ij}) C^k = 0 \quad (6)$$

where $H_{ij} = \int \phi_i^* \hat{H} \phi_j d^3r$, $S_{ij} = \int \phi_i^* \phi_j d^3r$, both constructed from the universal orthogonal tight-binding parameters V_{ij} of Harrison^[14]

$$S_{ij} = \frac{2V_{ij}}{K(X_+ + X_-)} \quad (7)$$

$$H_{ij} = V_{ij} \left[1 + \frac{1}{K} - S_2^2 \right] \quad (8)$$

where

$$S_2 = \frac{S_{ss}^e - 2\sqrt{3}S_{sp}^e - 3S_{pp}^e}{4} \quad (9)$$

describes the nonorthogonality between two sp^3 bonding orbitals. The universal parameters V_{ij} are calculated by means of scaling Slater-Koster parameters $V_{\lambda\lambda'}$:

$$V_{\lambda\lambda'}(r_{ij}) = V_{\lambda\lambda'}(d_0) \exp[-T(r_{ij} - d_0)] \quad (10)$$

where $T = 1/r_0$.

The overlap parameter K and the coefficient i_0 in eq. (3) are fitted to reproduce the force constant and bond length for Ge_2 ^[1,13]. All the parameters used in this work are listed in Table 1.

Table 1 Parameters in the M-S NTB scheme used for Ge_n in this work*

$-X_0/eV$	$-X_1/eV$	$-V_{ss}^e/eV$	V_{sp}^e/eV	V_{pp}^e/eV	$-V_{pp}^c/eV$	K	i_0/eV	a/eV	b/eV	R_c/nm	Δ/nm
14.38	6.36	1.70	2.30	4.07	1.05	1.469	0.078	-0.313	-1.250	0.350	0.010

* X_0 , X_1 and $V_{\lambda\lambda'}$ were from ref. [14].

The optimization of the geometrical structures of a cluster X_n is, except for small n , a nontrivial task, owing to the high dimensionality of the problem. The most commonly used

strategies include the molecular dynamics (MD) and the Monte Carlo (MC) annealing simulations. In this work, we adopted the following procedure (1) For small clusters ($n \leq 9$), we employed a DFP variable metric minimization routine^[15] which minimizes the total energies of X_n starting from randomly constructed initial structures by treating the $3N - 3$ coordinates as independent variables. All the results for $n \leq 9$ were checked with an MC-based routine and the DFP full optimization method was found faster and more accurate. (2) For larger clusters ($n \geq 10$), either fragments of bulk cubic structures (*sc*, *bcc*, *fcc*, and diamond lattices) or specified high symmetry geometries (like a T_d structures for Ge_0) are generated as the starting geometries of the optimization process as described in (1). Most of these high symmetry structures were found unstable and distorted to the global or local minima. Considering the fact that germanium and silicon are similar in both bulk and microcluster forms, we also "borrowed" the optimized structures for silicon clusters with comparable size obtained by other authors^[9, 10, 12, 16, 17] as the initial geometries of the structural optimization. The strategy described above originates from that adopted for the structural optimization of silicon clusters based on a parameterized many-body potential^[18].

Geometrical Structures of Ge($n = 2 - 20$) Clusters

The optimized structures and binding energies per atom E_b obtained with the procedure described above are listed in Table 2, compared with available experimental and other electronic structure calculation results. Some of the optimized geometries are illustrated in Fig. 1. The second differences of cluster energies defined as $\Delta^2 E = E(n+1) + E(n-1) - 2E(n)$ ^[21], which are sensitive to indicate the relative stabilities of clusters, are shown in Fig. 2 for $n = 3 - 13$.

Table 2 The optimized geometries and binding energies per atom E_b (eV) obtained in this work compared with experimental and other electronic structure calculation results^[6, 8]

Ge_n	Struc.	Symm.	M-SNTB	Exper.	<i>Ab initio</i>	SCF-CI	Ge_n	Struc.	Symm.	M-SNTB	Exper.	<i>Ab initio</i>	SCF-CI
Ge ₂		$D_{\infty h}$	1.238	1.32	1.06	0.91	Ge ₉	XI	C_0	2.918			
Ge ₃	I	C_{2v}	2.032	2.24	1.49	1.28	Ge ₁₀	XII	D_{4d}	2.924			
	II	D_{3h}	2.013					XII	C_{3v}	2.907			
	III	C_{2v}	2.007				Ge ₁₁	XVI	C_{3v}	2.913			
Ge ₄	IV	D_{2h}	2.594	2.61	1.90	1.57	Ge ₁₂	XV	I_h	2.928			
Ge ₅	V	D_{3h}	2.715	2.74	1.97	1.40	Ge ₁₃	XVI	C_{3v}	2.896			
Ge ₆	VI	C_{2v}	2.838	2.98	2.12	1.47		XVII	C_{3v}	2.823			
	VII	C_{2v}	2.836				Ge ₁₄	XVIII	C_1	2.830			
Ge ₇	VIII	D_{3h}	2.911	3.04		1.60		XIX	C_0	2.825			
Ge ₈	IX	C_0	2.884				Ge ₂₀	XX	I_h	2.869			
	X	C_{2h}	2.866										

The bond length $r = 0.2445$ nm and binding energy $E_b = 1.238$ eV obtained for Ge₂ are in close agreement with experimental results ($r = 0.2439$ nm, $E_b = 1.32$ eV)^[1, 6, 8]. The lowest-energy structures found for Ge₃ is an isosceles triangle (I, C_{2v}) with a bond length $r = 0.2462$ nm and the apex angle $\theta = 95^\circ$, while the equilateral triangle (II, D_{3h}) with $r = 0.2514$ nm lies only 0.06 eV higher in energy. The other local minimum with C_{2v} symmetry (III) has a shorter bond length $r = 0.2428$ nm and smaller apex angle $\theta = 76^\circ$. The linear Ge₃ is much less stable and is not a minimum on the potential-energy surface. These parameters are comparable with MRSDCI $^1A_2 C_{2v}$ ground state ($r = 0.232$ nm, $\theta = 83.3^\circ$)^[19] and the ECP-DZP $^1A_2 D_{3h}$ ground state ($r = 0.2473$ nm)^[8]. It is of interest to note that Si₃ also has two

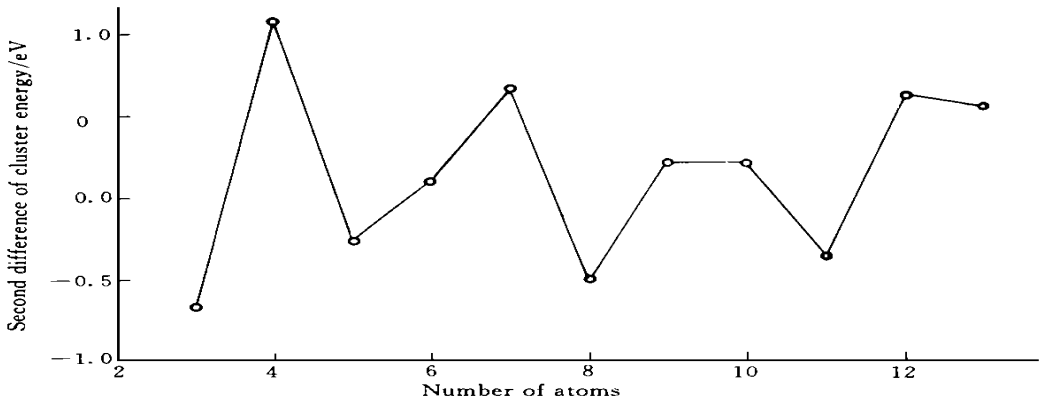


Fig. 1 The low-energy geometrical structures of Ge_3^- – Ge_{20} obtained with the M-S NTB scheme.

isosceles triangles as minima on the potential energy surface which have been related with a Jahn-Teller distortion^[1]. A planar rhombus (IV, D_{2h}) was found to be the lowest-energy structure for Ge_4 with $r_{1-2} = 0.2520$ nm and $r_{1-3} = 0.2653$ nm, in close agreement with the *ab initio* result ($r_{1-2} = 0.2457$ nm, $r_{1-3} = 0.2622$ nm)^[8]. The ground state structure obtained for Ge_5 is a severely compressed trigonal bipyramid (V, D_{3h}) ($r_{1-2} = 0.257$ nm, $r_{2-3} = 0.372$ nm, $r_{1-5} = 0.281$ nm), also in line with the *ab initio* result ($r_{1-2} = 0.2472$ nm, $r_{2-3} = 0.3379$ nm, $r_{1-5} = 0.3037$ nm)^[8]. The two minima with C_{2v} symmetry were found for Ge_6 (VI and VII) with the edge-capped trigonal bipyramid (VI) 0.012 eV lower in energy than the face-

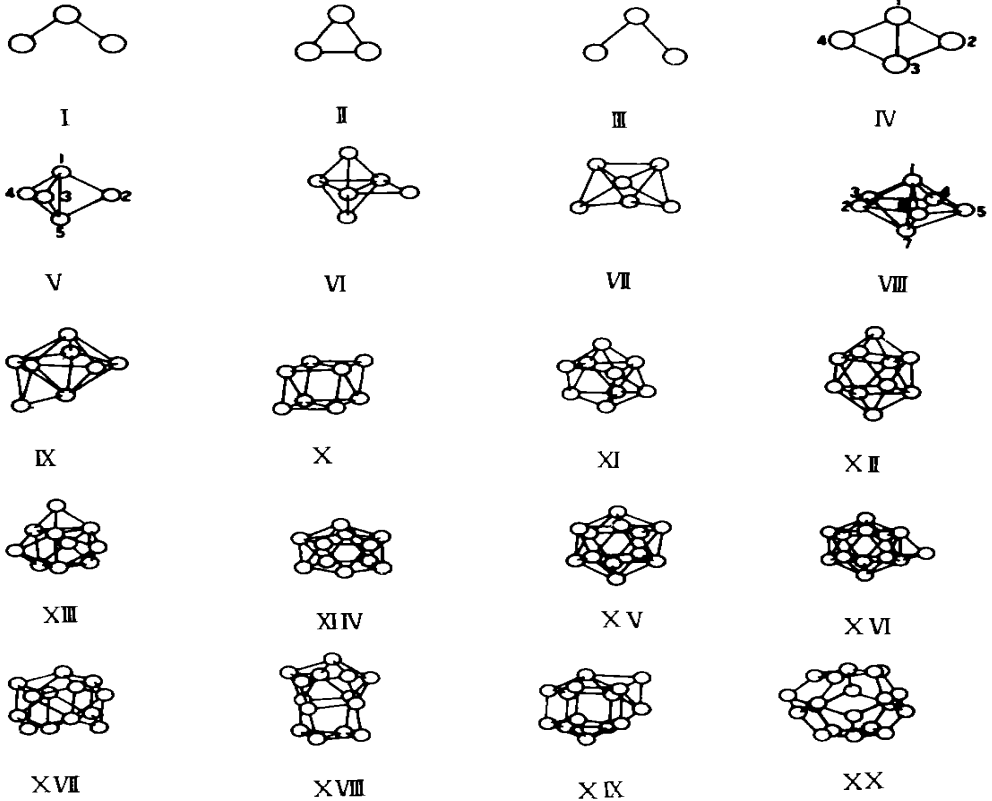


Fig. 2 The second differences of clusters energies for Ge_3^- – Ge_{13} .

capped one(VII), agreeing well with the relative stability and energy difference ($\Delta E = 0.01$ eV) obtained for the two structures in ref. [8] as well.

A pentagonal bipyramid(VIII) was found to be the optimum structure for Ge^7 ($r_{1-2} = 0.266$ nm, $r_{2-3} = 0.263$ nm and $r_{1-7} = 0.425$ nm), in line with that of the SCF-CI prediction with the nearest bond length of $r = 0.284$ nm^[11]. There is no electronic structure calculation result available for Ge^n when $n \geq 8$. A face-capped pentagonal bipyramid(IX) was found slightly lower in energy (0.14 eV) than the distorted bicapped octahedron(X) for Ge^8 . In fact, the small energy difference between the two structures is within the accuracy of the NTB method. By comparison with Si^8 , which has a distorted bicapped octahedron(X) as its ground-state structure^[1,10], this result is satisfactory. The bicapped pentagonal bipyramid Ge^9 (XI) is a natural derivation of Ge^7 and Ge^8 . This structure can also be viewed as a capped anti-prism. Extensive searching produces no structures with lower energies. Two low-energy isomers for Ge^{10} have been found, of which the bicapped anti-prism(X) is 0.17 eV lower in energy than the tetracapped trigonal prism(X). The results for Ge^{10} are comparable with the *ab initio* structures of Si^{10} , which has a tetracapped trigonal-prism as its optimum geometry(X)^[1,16]. Starting from a perfect icosahedron, a slightly distorted icosahedron(X) were found favorable in energy for Ge^{12} compared with other structures, similar to Si^{12} ^[12]. Removing one cap in Ge^{12} produces the lowest-energy structure of Ge^{11} (X) while Ge^{13} (X) can be constructed by adding one cap on one face of the icosahedron Ge^{12} . This capped Ge^{13} is more stable than the capped 6:6 two-layer structure(X). But for Ge^{14} , a bicapped icosahedron(X) is less stable than a 4:4:4 three-layer structure with two adjacent face caps(X I). This is also true for Si^{14} ^[12]. A slightly distorted dodecahedron fullerene structure(X) is favored for Ge^{20} in this model compared with an elongated bicapped 6:6:6 three-layer structure defined in Ref.^[16]. Similar structures of fullerene Si^{20} and its derivatives have been the object of theoretical calculation^[17].

Binding Energies and Electron Affinities

With adjustable parameters in the NTB method, especially b in eq. (4) which shifts the center of binding energy by Nb, the M-NTB binding energies fit with experimental results much better than the previously published electronic structure calculations^[6,8] for $\text{Ge}^z - \text{Ge}^{\theta}$ (see Table 2). Our averaged discrepancy with the experiment is about 6% in this range, while the SCF-CI method covers only 40% and the SDCI(Q) 70% of the corresponding measured values^[1,12,14]. The second differences of cluster energies in Fig. 2 show the peaks at $n = 4, 6, 7, 9, 10$, and 12, in accordance with the maxima in binding energies listed in Table 2, both roughly in agreement with the mass distribution of Ge^n positive ions^[1,21].

The electron affinities of Ge^n ions ($n = 2-10$) were calculated according to $E_A = E(4n) - E(4n-1)$ (here $4n$ stands for the number of valence electrons in neutral Ge^n)^[2], as show in Table 3. It should be pointed out that the bond lengths of anionic ions are generally shorter than that of the neutral species and in some cases the optimum structures may be different. For example, the optimum structure of Ge^3 is an equilateral triangle(D_{3h}) and that of Ge^4 is an off-plan rhombus(D_{2d}). Ge^5 is still a pentagonal bipyramid, but Ge^6 takes a flat octahedron as its optimum geometry. We chose the binding energies of the optimum structures in the calculation of E_A . The averaged deviation from the experimental values^[3] is about 10% and the three maxima at $n = 3, 5-6$, and $8-10$, and the three minima at $n = 2, 4$ and 7 observed in experiment are reproduced. The general trend agrees satisfactorily with

that of experiments^[3] except for Ge⁹ which has exceptionally a high E^A value.

Table 3 The calculated electron affinities of Ge ($n=2-10$) compared with experiments

Ge _n	Ge ₂	Ge ₃	Ge ₄	Ge ₅	Ge ₆	Ge ₇	Ge ₈	Ge ₉	Ge ₁₀
M-S NTB	1.930	2.448	1.804	2.135	2.358	2.114	2.200	2.205	2.290
Experiment ^[3]	2.07	2.23	1.81	2.51	2.06	1.80	2.41	2.86	2.41

Discussion and Conclusion

As described above, the binding energies of small Ge_n clusters have been included in the parameterization process and the M-S NTB scheme has reproduced a close agreement with experiments in binding energies as expected. But no structural information has been involved in the parameterization scheme. The complete agreement in structural predictions with *ab initio* results for $n=2-6$ and the satisfactory comparison with corresponding silicon clusters in the range of $n=7-20$ strongly suggest that the M-S NTB scheme reflects the main features of the covalent bonding in germanium clusters. The quantum-mechanic nature makes this method superior to other empirical potentials^[7] and the explicit incorporation of the nonorthogonality leads this parameterization scheme transferable from one coordination environment to another and is hence suitable to the study of semiconductor clusters, where great varieties of bonding coordination and compact configurations rather than tetrahedral structures occur. We conclude from the applications of this method to both silicon clusters in refs. [9, 10, 12] and germanium clusters in this work that the empirical M-S NTB scheme is reliable and accurate in the study of semiconductor clusters while keeping the computational task acceptably small.

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