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Transition from *exo*- to *endo*- Cu absorption in CuSi_n clusters: A Genetic Algorithms Density Functional Theory (DFT) Study

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Abstract

The characterization and prediction of the structures of metal silicon clusters is important for nanotechnology research because these clusters can be used as building blocks for nano devices, integrated circuits and solar cells. Several authors have postulated that there is a transition between *exo* to *endo* absorption of Cu in Si_n clusters and showed that for n larger than 9 it is possible to find endohedral clusters. Unfortunately, no global searchers have confirmed this observation, which is based on local optimizations of plausible structures. Here we use parallel Genetic Algorithms (GA), as implemented in our MGAC software, directly coupled with DFT energy calculations to show that the global search of CuSi_n cluster structures does not find endohedral clusters for $n < 8$ but finds them for $n \geq 10$.

Keywords

copper-silicon clusters; genetic algorithms; global optimization

Introduction

Silicon is the most important element in design of microelectronic components; therefore Si clusters have been studied from the experimental [1,2,3] and theoretical [4,5,6] points of view. These clusters are considered potential candidates as building blocks for well-controlled nanostructures. The basis to build clusters-assembled nanostructures is to define building blocks that are chemically stable and weakly interacting among them. Pure silicon clusters are chemically reactive, [7] but better stability can be reached by positioning a metal atom into the Si_n clusters.

Many researches [8,9] have studied the growth behavior of transition metal (TM) silicon clusters and showed that TM-encapsulated cage-like clusters are always the *magic clusters*, *i.e.* the more stable ones, as the number of silicon atoms increases. During the last years the focus has been placed in better understanding TM doped silicon cage-like clusters, both experimentally [10,11,12] and computationally. [13,14,15,16] The TM atom has been found to be a good stabilizing factor for MSi_n clusters because of their size and *d*-band filling behavior. Beck [17] observed stable clusters TM- Si_n ($n=16-18$, TM=Cr, Mo, W, Cu) of

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medium size. The mass spectra of CuSi_n show the most intense peak for CuSi_{10} ; no reactions between copper and silicon have been observed in the products with less than six silicon atoms and all products show only one copper atom.¹⁸ Another interesting discovery reported by Andriotis *et al.*, [19] shows that silicon nanotubes might be stabilized by insertion of a linear chain of TM atoms. K. Koyasu *et al.* [20] generated endohedral MSi_n clusters ($M = \text{Sc, Y, Lu, Ti, Zr, Hf, V, Nb}$ and Ta) by double laser vaporization, and analyzed the MSi_n^- photoelectric spectra, HOMO-LUMO gaps, and vertical detachment energies (VDE) in order to analyze their stability. Their results show that Si_n is less reacting than the doping atom and that the M reactivity is sensitive to its placement in the cluster, a peripheral metal atom is more reactive than an encapsulated one. So, a transition to low reactivity of MSi_n clusters would be an indication of cage like MSi_n encapsulated clusters, which therefore will be preferable for using as nano structural building blocks. Several authors have [21,22,23,24] investigated MSi_n clusters with 4, 6, 8, 10 and 12 silicon atoms using computational means. Both the computational and experimental results lead to several authors [20,18] to postulate that there is a transition from *exo to endo* in the absorption of a copper atom in a silicon clusters and showed that endohedric clusters appear only for $n > 9$. Unfortunately, no global searchers have confirmed this observation, which is based on calculations for plausible structures. In this paper we report the global search for the structures of CuSi_n employing our Modified Genetic Algorithms (MGAC) package, [25,26,27] which uses the Parallel implementation of Genetic Algorithms (GA), [28,29] directly coupled with DFT energy calculations.

Methods

In order to determine the most stable isomers, a stochastic method which uses a parallel genetic algorithm (GA) has been used. GA methods are based in the principle of survival of the fittest, considering that each string or genome represents a set of trial solutions candidate that at any generation compete with each other in the population for survival and produce offspring for the next generation by prescribed propagation rules. The clusters are represented by a genome of dimension $3N$, where N is the number of atoms in the cluster, the genetic operators, mating, crossover, mutation, *etc.*, have been constructed in such way that when they are applied to the a genome they produce a valid individual, *i.e.*, a possible structure for the desired cluster size. The GA operations of mating, crossover, mutation and the “cut and slice” operator introduced by Johnston and Roberts [30] were used here to evolve one generation into the next one. The best individuals among the population, 50 % , are directly copied into the next generation, and the other 50 % are replaced applying the genetic operators. This technique is also known as elitism. The criteria for fitness probability, selection of the individuals and genetic operators are discussed in detail in Ref. [27]. The GA procedure was run several times to guarantee that the resulting structures are independent of the initial population. We ran the MGAC about five times per CuSi_n system, employing from 15 to 200 generations with about 10 individuals. The number of generations needed to achieve convergence was between 15 and 200 and the total number of computer processors employed ranges from 49 to 98. As shown in Table 1 the computational resources needed for these calculations are significant, therefore for the case of $n=12$ only limited runs could be performed due to the limitations in the computer resources available.

Our previous study on CuSi_n clusters [31] clearly demonstrated that when transition metals are included in the calculations it is necessary to directly couple the GA global optimization with the DFT method used for the energy calculations. [32,33] All the energy calculations were done using the CPMD code. [34] The isomers selected by MGAC/CPMD calculations were analyzed, and their vibration frequencies evaluated to discriminate transition states (TS) from stable structures.

In this study we used the Goedecker *et al.* [35] pseudopotential, the PBE (Perdew-Burke-Ernzerhof) [36] exchange correlation functional with an energy cutoff (Ecut) of 100 Ry, and a cell length of 4 Å plus the largest dimension of the cluster. The pseudopotential was selected after comparing the rms (root mean square) between experimental and predicted bond lengths, binding energies, and vibrational frequencies, for Si₂, Cu₂, and SiCu, employing different density functional methods implemented in the CPMD code and several all electron methods, which include electron correlation. The results of this comparison are presented in Table 2, which shows that the selected combination, PBE/GO, is as good or better than any other DFT approach and better than most of the all electron approaches considered here.

In this paper we have also evaluated the spin-density, the static dipole polarizabilities, inertial moments, and frequencies for each final CuSi_n structure, at the B3LYP/6-31+G* level of theory. All the DFT calculations have been done using the Gaussian package of programs. [37]

Results and Discussion

CuSi₆ and CuSi₈

Figures 1(a) and 1(b) show the structures of the six lowest energy isomers of CuSi₆ and CuSi₈, respectively. Structures CuSi₆-d, CuSi₆-f and CuSi₈-a correspond to transition states, but several structures in the figures have not been previously reported; only CuSi₆-a, CuSi₆-b and CuSi₈-a have been reported previously in the literature.[21] The CuSi₆ isomers produced by MGAC/CPMD, show the building block of Si₆-a or Si₆-b from Ref. [38] with one copper atom attached on their periphery. The CuSi₈ isomers can be thought as the product of the substitution of one silicon atom on Si₉-a or Si₉-b [38] by one Cu atom or the addition of one Cu atom on Si₈-a.[38] CuSi₆-e and CuSi₆-f are mirror images, and CuSi₆-b is similar to the structure of CuSi₆⁺ reported by Gruene *et al.* [39] Relaxation of CuSi₈-a to the corresponding stable state changes its atomic binding energy from 4.671 to 4.661 eV.

From Figures 1(a) and 1(b) it is apparent that all the low energy structures predicted here have the Cu atom in the periphery of the cluster, because the MGAC/CPMD performs a global search over all possible cluster configurations, this is a very strong evidence that endohedral configurations are not energetically favorable for these clusters. Moreover due to the relatively modest size of the calculations required for n=6 and n=8 we were able to perform several searches confirming these findings.

The vibration spectra corresponding to structures CuSi₆-b and CuSi₈-b are depicted in Figures 2 and 3, respectively. Our predicted vibration spectra for CuSi₆-b with the principal vibration mode of about 450 cm⁻¹, is close to the corresponding principal vibration mode, about 430 cm⁻¹ predicted for the CuSi₆ cation. [39] Our predicted vibration spectra for CuSi₈-b are very similar to the experimental spectra reported on reference [39] for CuSi₈⁺. The four predicted and experimental modes are, 250 cm⁻¹, 310 cm⁻¹, 360 cm⁻¹ and 440 cm⁻¹; and 275 cm⁻¹, 325 cm⁻¹, 350 cm⁻¹, 400-450 cm⁻¹, respectively. Gruene *et al.* [39] showed a theoretical structure different from CuSi₈-b. In fact, we are reporting a new structure, CuSi₈-b, whose theoretical spectrum reproduces better the experimental spectrum than that predicted by Gruene *et al.* [39] for CuSi₈⁺.

CuSi₁₀

Figure 4 depicts the structures of the twelve lowest energy isomers for CuSi₁₀ with their binding energies. Most of the MGAC/CPMD isomers show a Si₁₀-a cluster from Ref. 21 as building block with a Cu atom attached on its periphery, or a Si₁₁ cluster from Ref. 21 with a substitution of one silicon atom by one copper atom. However MGAC/CPMD has found

two cages like structures with endohedral copper and with binding energies in the order of 0.04 eV lower than the best isomer, Si₁₀Cu-a in Figure 4.

To compare our results with those from Ref. [40] the two cage structures, Cu@Si₁₀-h and Cu@Si₁₀-l were re-optimized using the B3LYP exchange correlation functional and the 6-31+G* basis set. Cu@Si₁₀-l energy resulted only 0.049 eV lower than Cu@Si₁₀-h energy, in agreement with the previous results by Hossain *et. al.* [23] Both of these isomers are TS for GO/PBE, but stable ones for B3LYP /6-31+G*. To verify that the structure Cu@Si₁₀-h is a new structure that has not been reported before by King, [40] we tried a local optimization of the structure of Cu@Si₁₀-h enforcing the D_{4d} symmetry, as it was suggested by the topological model proposed in Ref. [40], but the optimization did not reach convergence for the model. This provides strong evidence that Cu@Si₁₀-h is a truly new structure that has not been reported previously.

Figure 5 depicts the spin density for Cu@Si₁₀-h and Cu@Si₁₀-l. In Cu@Si₁₀-l, the density is mostly localized in the three silicon atoms at the top and bottom of the cage, whereas in Cu@Si₁₀-h the delocalization extends to the Cu atom.

In agreement with previous reports, the MGAC/CPMD method is able to find endohedral structures for CuSi₁₀, but in contrast with previous studies these structures are not postulated *a priori* and locally optimized, but are found automatically by the GA search.

CuSi₁₂

Due to the very large computer time required, only two independent GA optimizations using two different seeds were performed for CuSi₁₂. The optimizations were run for 30 and 14 generations respectively. The structures with the best energies are depicted in Figure 6, along with two cage type structures (Cu@Si₁₂-a and Cu@Si₁₂-h) that were constructed manually and locally optimized. The most stable isomer found by MGAC/CPMD, is 0.370 eV less stable than the best cage compound Cu@Si₁₂-a, but many of the MGAC/CPMD isomers are more stable than the other cage configuration reported in the literature Cu@Si₁₂-h.[22] Several of the isomers found by the MGAC/CPMD method show incipient cage features (for instance Cu@Si₁₂-e and Cu@Si₁₂-g), but clearly the number of generations used for these calculations are insufficient to find the best cage isomer (Cu@Si₁₂-a). From these results it is apparent that our DFT method can predict cages structures as low energy ones like, Cu@Si₁₂-a, but it appears that these structures are quite difficult to find using global optimization procedures, because they were not found by the limited MGAC/CPMD calculations performed here. Unfortunately more exhaustive calculations were not possible due to the limitations in the computer resources available.

Energetics and structure of Cu@Si_n

The energetic parameters of the CuSi_n clusters depicted in Figures 1, 4, and 6 are reported in Table 3. Those parameters are the embedding energy, $EE = E[Si_n] + E[Cu] - E[CuSi_n]$, where $E[Si_n]$ is the energy of the most stable silicon cluster (Si₆ and Si₈ from Ref. [38] and Si₁₀ and Si₁₂ from Ref.[21], and $E[Cu]$, is the energy of a copper atom. EE represents the energy necessary to add (or remove) a copper atom to a Si_n to form a CuSi_n cluster. The vertical ionization potential (VIP) and vertical electron affinity (VEA), and the HOMO-LUMO gaps for α and β electrons, ϵ_α and ϵ_β are also reported in the Table. EE and VEA show the same trend, because the electronic configuration of copper is Ar [3d¹⁰4s¹], with one electron in the outer shell. EE is smaller for CuSi₆, CuSi₁₀, and CuSi₁₂ than for CuSi₈, by about 0.8 eV, 1.3 eV, and 0.6 eV respectively, which is an indication of the efficient elimination of the Cu atom on those systems. This is in agreement with the experimental

observations from Jaeguer *et al.* [12], who detected abundance of Si_6^+ and Si_{10}^+ in the photo dissociation of CuSi_6^+ and CuSi_{10}^+ .

Table 4 shows the adiabatic and vertical IPs and EAs for the most stable isomer of the series CuSi_n and Si_n . Only the adiabatic EA shows the same trend for CuSi_n and their corresponding Si_n clusters, as it was observed in Ref. [21]. Kishi *et al.* [41] studied sodium doped silicon clusters produced by laser vaporization techniques and found a parallelism between IPs of Si_nNa ($n=4-11$) and EAs of their corresponding Si_n cluster. They considered that it was consistent with the fact that the structure of Si_nNa clusters keeps the frame of the corresponding Si_n cluster unchanged, and that the electronic structure of Si_nNa is similar to that of the corresponding negative ion Si_n^- . This parallelism is not observed in Table 4 for the CuSi_n clusters. The reason could be that the interaction Na-Si has ionic character while the interaction Cu-Si is ionic-covalent, as it was remarked by Xiao *et al.* [42].

Polarizabilities and structure of Cu@Si_n

When the number of atoms in a cluster increases there are many clusters in a narrow range of energies, so the calculation of properties like dipole polarizability, may be useful to be compared with the experimental data. [43] It is also known that the HOMO-LUMO gap correlates well with the polarizability of a system, being easier to polarize those systems with a smaller HOMO-LUMO gap. [44] However, this correlation is not verified in medium size clusters, unless that the shape of the clusters is not too different among them. [45] Pouchan *et al.* [45] found a correlation between polarizability of Si_n ($n=3-10$) and the size of the energy gap between symmetry-compatible bonding and antibonding molecular orbital, that is the “allowed gap”, instead the HOMO-LUMO gap, related to the preference of the cluster to adopt oblate, prolate or compact structure. Jackson *et al.* [46] computed polarizabilities for compact and prolate structures of Si_n clusters ($n=20-28$, and $n=50$) and found that the charge density show a *metallic-like* response of the clusters to an external field, and the calculated polarizabilities, are reproduced by the prediction of jellium-models for spheres and cylinders, suggesting a metallic-like character for these medium-size clusters. It is easiest to polarize a prolate cluster than a compact one. If the principal axis of the structure of one isomer are labeled a, b, and c, it is compact if the components of inertial moment verify $I_a \approx I_b \approx I_c$. Instead the structure is prolate if $I_a \ll I_b \approx I_c$, and oblate if $I_a \approx I_b \ll I_c$. The relation between the absolute value of the inertial moment and its largest component, $|I|/I_c$, discriminates compact from oblates structures. Table 5 reports atomic polarizability, the relation $|I|/I_c$, and bonding distance (Si-Si, Si-Cu) for each isomer in the CuSi_n series produced by MGAC/CPMD methodology. The atomic polarizability of the most prolated clusters, $\text{CuSi}_6\text{-a}$ and $\text{CuSi}_{12}\text{-a}$, with $|I|/I_c$ 1.352, and 1.454, respectively, is larger (34.184 au. and 34.032 au.) than the corresponding values for the less prolated isomers, $\text{CuSi}_8\text{-a}$ and $\text{CuSi}_{10}\text{-a}$. The structures are considered perfectly prolated if $|I|/I_c = 1.414$. Furthermore the cage structure $\text{Cu@Si}_{10}\text{-h}$ shows the lowest atomic polarizability and $|I|/I_c = 1.677$. The present study does not show a relation between stability and HOMO-LUMO gap for the series CuSi_n , but there is an evident relation between the size extension of the cluster and the polarizability.

Reactivity of CuSi_n clusters

As discussed in the introduction, structures of low reactivity can be used as building blocks for cluster-assembled materials. In order to identify these building blocks, Hiura *et al.* [47] noted that the growth rate $W\text{Si}_n\text{H}_x^+$ decreased as n increased. In particular, $W\text{Si}_n\text{H}_x^+$ grows very slowly with $n \geq 10$, and the cluster is rarely found if $n > 12$, even at the long reaction time. This behavior means that clusters lose reactivity with molecules of silane (SiH_4) when n reaches 12. Lightstone *et al.* [48] found that the adsorption energy for sequential adsorption of $n\text{CO}$ molecules to the $M_4S_6^+$ ($M=\text{Mo}, \text{W}$) cluster are consistent with the

experimental mass spectra (with $n = 4$ being energetically the most favorable product consistent with the preferential formation). The increment of relative abundance implies greater adsorption energy and that means that the cluster is more reactive.

Here we analyzed the reactivity of the most stable isomers of CuSi_6 , CuSi_8 , CuSi_{10} and CuSi_{12} , and cage structures $\text{Cu@Si}_{10}\text{-h}$, $\text{Cu@Si}_{10}\text{-l}$, $\text{Cu@Si}_{12}\text{-a}$ and $\text{Cu@Si}_{12}\text{-h}$ at the B3LYP/6-31+G* level of theory: i) with an analysis of natural charges, ii) with an analysis of adsorption energy $E_{\text{ads}} = E(\text{CuSi}_n\text{H}^+) - E(\text{CuSi}_n)$, defined as the energy absorbed by CuSi_n cluster by adding of a proton (H^+) performed for $\text{CuSi}_{10}\text{-a}$, $\text{Cu@Si}_{10}\text{-h}$, $\text{Cu@Si}_{10}\text{-l}$, and $\text{Cu@Si}_{12}\text{-a}$ clusters.

Figure 7 and 8 show the natural charges evaluated at the B3LYP/6-31+G* level of theory, for the best isomers $\text{CuSi}_6\text{-a}$, $\text{CuSi}_8\text{-a}$, $\text{CuSi}_{10}\text{-a}$, $\text{CuSi}_{12}\text{-b}$, and $\text{CuSi}_{12}\text{-c}$, characterized by the placement of the Cu atom in the periphery of the cluster, and the cage like structures $\text{Cu@Si}_{10}\text{-h}$, $\text{Cu@Si}_{10}\text{-l}$, $\text{Cu@Si}_{12}\text{-a}$ and $\text{Cu@Si}_{12}\text{-h}$ with an endohedral metal atom. The Cu atom has a positive charge, and it is surrounded by negative charges for $\text{CuSi}_6\text{-a}$, $\text{CuSi}_8\text{-a}$, $\text{CuSi}_{10}\text{-a}$, $\text{CuSi}_{12}\text{-b}$, and $\text{CuSi}_{12}\text{-c}$, this is consistent with the observation that the copper atom is electron withdrawing. [21] Isomer $\text{Cu@Si}_{10}\text{-l}$ shows also negative charges in the periphery, but they are very small (compare with $\text{CuSi}_{10}\text{-a}$ in the same figure). Instead, the $\text{Cu@Si}_{10}\text{-h}$ cage-like isomer shows a negative charge on copper, and positive charges in the periphery. These charge distributions indicate that it is easier to adsorb a proton (H^+) if it approaches surface of negative charges, than if it approaches a surface with positive charges. Because of that, the cage-like structures with an endohedral copper atom, are less reactive than those with the metal in their periphery. $\text{Cu@Si}_{12}\text{-a}$ and $\text{Cu@Si}_{12}\text{-h}$ show positive charges on copper but the negative charges in the periphery are very small, especially for the cage $\text{Cu@Si}_{12}\text{-a}$. We observed in Figure 9 that the absorption energy of a peripheral proton, (H^+), is 9.72 eV for $\text{CuSi}_{10}\text{-a}$, 9.22 eV for $\text{Cu@Si}_{10}\text{-l}$, only 8.57 eV for $\text{Cu@Si}_{10}\text{-h}$, and 9.23 for $\text{Cu@Si}_{12}\text{-a}$, an evidence of the lowest reactivity of these cage-like structure. Then $\text{Cu@Si}_{10}\text{-h}$ would work as better building block than $\text{Cu@Si}_{10}\text{-l}$, and $\text{Cu@Si}_{12}\text{-a}$ would be an excellent building block.

Conclusions

Using the MGAC/CPMD method with the GO/PBE approach to calculate the energy we have shown that the GA search does not find any endohedral cluster for CuSi_n clusters with $n < 8$, but it is able to find them for $n = 10$ and $n = 12$. This has been previously postulated but the MGAC/CPMD method is able to find these structures without any *a priori* information on the approximate conformation of the clusters.

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Figure 1.

(a) CuSi_6 and (b) CuSi_8 structures obtained by the MGAC/CPMD, and their binding energy per atom. All energies in eV based on a Si atomic energies of -101.319 eV and Cu atomic energies of -1289.34 eV. Isomers marked with * are transition states (TS) presenting one imaginary frequency.

Figure 2. Vibration spectra of $\text{CuSi}_6\text{-b}$ at B3LYP/6-31+G* level of theory. On the top right is the experimental spectra reported on Ref. [39] for CuSi_6^+ .

Figure 3. Vibrational spectra of CuSi₈-b at B3LYP/6-31+G* level of theory. On the top right is the experimental spectra reported on Ref. [39] for CuSi₈⁺.

Figure 4.

CuSi₁₀ structures obtained by the MGAC/CPMD and their binding energy per atom. All energies in eV based on a Si atomic energies of -101.319 eV and Cu atomic energies of -1289.34 eV. Isomers marked with * are transition states (TS) presenting one imaginary frequency.

Figure 5. Spin density of Cu@Si₁₀-h (right) and Cu@Si₁₀-l (left) clusters obtained at B3LYP/6-31+G* level of theory. The isovalue of the contour map is at 0.001.

Figure 6.

CuSi_{12} structures obtained by the MGAC/CPMD and their binding energy per atom. All energies in eV based on a Si atomic energies of -101.319 eV and Cu atomic energies of -1289.34 eV. Isomer (f) marked with * is a transition state (TS) presenting one imaginary frequency. Isomers marked with ** have two imaginary frequencies.

Figure 7. Natural charges for the most stable isomers of CuSi_6 , CuSi_8 and CuSi_{10} , and the cage like structures $\text{Cu@Si}_{10}\text{-h}$ and $\text{Cu@Si}_{10}\text{-l}$, at the B3LYP/6-31+G* level of theory.

Figure 8.

Natural charges for some isomers of CuSi_{12} , including cage like structures Cu@Si₁₂-a and Cu@Si₁₂-h, at the B3LYP/6-31+G* level of theory.

Figure 9. Absolute value of the absorption energy of H^+ on $\text{CuSi}_{10}\text{-a}$, $\text{Cu@Si}_{10}\text{-h}$, $\text{Cu@Si}_{10}\text{-l}$ y $\text{Cu@Si}_{12}\text{-a}$ at the B3LYP/6-31+G* level of theory.

Computational and timing parameters used in the calculation of the structures of CuSi₆, CuSi₈, CuSi₁₀ and CuSi₁₂ atomic clusters using the MGAC method for global search and the CPMD method for the local optimization and energy calculations. The calculations were done using an energy cutoff of 100 Ry.

Table 1

System	Individuals in the population	Number of computer processors ^a			Elapsed time per generation ^b	Number of generations
		Level 1	Level 2	Total		
CuSi ₆	14	7	7	49	24.00	15
CuSi ₈	14	7	14	98	28.52	22
CuSi ₁₀	10	5	16	80	9.00	200
CuSi ₁₂	8	4	20	80	36.00	30

^aLevel 2 of parallelization corresponds to the number of processors used for each CPMD calculation, while Level 1 is the number of ways in which the populations is divided.

^bThe elapsed time is given in hours. The total execution time of the search is the time per generation times the number of generations needed to achieve convergence.

Table 2

rms between experimental and calculated geometry parameters (R_e), binding energy (E_b), and vibrational frequencies (Freq) for Si_2 , Cu_2 and $SiCu$ systems with $E_{cut}=100$ Ry.

Method	R_e [Å]	E_b [eV]	Freq [cm ⁻¹]
PBE/GO	0.070	0.301	53
BP/GO	0.070	0.277	56
LDA/GO	0.098	0.547	62
B3LYP/GEN	0.040	0.162	16
LCGTO-LSD	0.020	0.520	49
LCGTO-GGA	0.050	0.180	60
All electron calculation			
B3LYP/6-311+G(d)	0.043	0.217	19
MP4(6s,5p,3d,1f)	0.019	0.149	2
QCISD/6-311+G(d)	0.038	0.420	16
QCISD(T)/6-311+G(d)	0.045	0.463	5
CASSCF/CASPT2	0.010	0.265	56
CASSCF/CASPT2+DK	0.081	0.058	64

Table 3

Calculated embedding energies (**EE**), the vertical ionization potential (**VIP**), the vertical electron affinity (**VEA**) and α and β energy gaps for the Si_nCu clusters found by the MGAC-CPMD method. Their structures are given in Figs. 1, 2 and 3. The italicized entries correspond to those found by the MGAC-CPMD method that were not previously reported in the literature [21].

Isomer	EE (eV)	VIP(eV)	VEA(eV)	ϵ_{α} gap (eV)	ϵ_{β} gap (eV)
CuSi₆-a	2.857	7.156	2.301	1.035	1.399
CuSi₆-b	2.824	6.922	2.094	1.207	1.392
<i>CuSi₆-c</i>	<i>2.757</i>	<i>6.929</i>	<i>2.142</i>	<i>1.194</i>	<i>1.174</i>
<i>CuSi₆-d</i>	<i>2.689</i>	<i>7.009</i>	<i>2.308</i>	<i>1.165</i>	<i>1.585</i>
<i>CuSi₆-e</i>	<i>2.595</i>	<i>6.943</i>	<i>2.281</i>	<i>1.218</i>	<i>1.490</i>
<i>CuSi₆-f</i>	<i>2.588</i>	<i>6.806</i>	<i>2.138</i>	<i>1.319</i>	<i>1.279</i>
CuSi₈-a	3.533	7.001	2.652	0.757	1.269
<i>CuSi₈-b</i>	<i>3.523</i>	<i>7.111</i>	<i>2.465</i>	<i>1.112</i>	<i>1.540</i>
<i>CuSi₈-c</i>	<i>3.443</i>	<i>6.887</i>	<i>2.427</i>	<i>0.696</i>	<i>1.336</i>
<i>CuSi₈-d</i>	<i>3.382</i>	<i>6.807</i>	<i>2.382</i>	<i>0.979</i>	<i>1.490</i>
<i>Si₈Cu-e</i>	<i>3.345</i>	<i>6.943</i>	<i>2.293</i>	<i>1.374</i>	<i>0.885</i>
<i>CuSi₈-f</i>	<i>3.279</i>	<i>6.893</i>	<i>2.498</i>	<i>0.897</i>	<i>0.956</i>
CuSi₁₀-a	2.269	6.557	2.338	1.395	1.377
<i>CuSi₁₀-b</i>	<i>2.120</i>	<i>6.385</i>	<i>2.358</i>	<i>1.298</i>	<i>0.965</i>
<i>CuSi₁₀-c</i>	<i>2.114</i>	<i>6.340</i>	<i>2.278</i>	<i>1.682</i>	<i>1.081</i>
<i>CuSi₁₀-d</i>	<i>2.057</i>	<i>6.203</i>	<i>2.060</i>	<i>1.982</i>	<i>0.754</i>
<i>CuSi₁₀-e</i>	2.044	6.172	2.187	1.777	0.798
<i>CuSi₁₀-f</i>	<i>2.035</i>	<i>6.701</i>	<i>2.265</i>	<i>1.445</i>	<i>1.217</i>
CuSi₁₀-g	2.031	6.729	2.379	1.346	1.211
<i>Cu@Si₁₀-h</i>	<i>1.977</i>	<i>6.570</i>	<i>2.321</i>	<i>1.938</i>	<i>0.780</i>
CuSi₁₀-i	1.976	6.256	2.179	1.719	0.830
<i>CuSi₁₀-j</i>	<i>1.858</i>	<i>6.958</i>	<i>2.753</i>	<i>0.895</i>	<i>1.392</i>
CuSi₁₀-k	1.812	6.545	2.516	0.909	1.171
Cu@Si₁₀-l	1.634	6.759	2.702	0.262	0.967
Cu@Si₁₂-a	2.899	6.700	2.889	0.274	1.490

Isomer	EE (eV)	VIP (eV)	VEA (eV)	ϵ_{agap} (eV)	ϵ_{pgap} (eV)
<i>CuSi₁₂-b</i>	2.529	6.819	2.879	0.896	1.248
<i>CuSi₁₂-c</i>	2.496	6.629	2.716	0.888	1.063
<i>CuSi₁₂-d</i>	2.361	6.551	2.726	0.868	0.911
<i>Cu@Si₁₂-e</i>	2.236	6.777	2.879	0.377	1.424
<i>CuSi₁₂-f</i>	2.194	6.316	2.510	1.171	0.760
<i>Cu@Si₁₂-g</i>	2.053	6.738	2.850	0.422	0.914
Cu@Si₁₂-h	1.509	6.996	3.052	0.477	1.056

Table 4

Calculated ionization potential and electron affinity, vertical and adiabatic for the most stable isomer of CuSi_n and Si_n .

Adiabatic		IP		EA	
n	Si_n	CuSi_n	Si_n	CuSi_n	
6	7.449	6.967	2.018	2.407	
8	7.084	6.815	2.226	2.814	
10	7.763	6.075	2.215	2.724	
12	6.976	6.486	2.257	3.064	

Vertical		IP		EA	
n	Si_n	CuSi_n	Si_n	CuSi_n	
6	7.146	7.156	1.922	2.301	
8	7.413	7.006	1.757	2.652	
10	7.856	6.557	1.971	2.338	
12	7.425	6.700	1.622	2.889	

Table 5

Calculated polarizabilities per atom (α/m), moment of total inertia I per its maximum component I_c (I/I_c) and average Si-Si bond lengths, Si-Cu bond lengths for the Si_nCu clusters found by the MGAC-CPMD method. Their structures are given in Figs. 1, 2 and 3. The italicized entries correspond to those found by the MGAC-CPMD method that were not previously reported in the literature [21].

Isomer	$\alpha/m[\text{au}]$	I/I_c	Bond Lengths	
			Si-Si[Å]	Si-Cu[Å]
CuSi ₆ -a	34.184	1.352	2.492	2.372
CuSi ₆ -b	35.069	1.430	2.439	2.323
CuSi ₆ -c	<i>35.122</i>	<i>1.540</i>	<i>2.475</i>	<i>2.399</i>
CuSi ₆ -d	<i>36.472</i>	<i>1.375</i>	<i>2.436</i>	<i>2.254</i>
CuSi ₆ -e	<i>36.261</i>	<i>1.375</i>	<i>2.448</i>	<i>2.452</i>
CuSi ₆ -f	<i>36.031</i>	<i>1.406</i>	<i>2.463</i>	<i>2.341</i>
CuSi ₈ -a	33.554	1.590	2.474	2.363
CuSi ₈ -b	<i>33.618</i>	<i>1.452</i>	<i>2.477</i>	<i>2.398</i>
CuSi ₈ -c	<i>34.041</i>	<i>1.390</i>	<i>2.504</i>	<i>2.352</i>
CuSi ₈ -d	<i>34.115</i>	<i>1.415</i>	<i>2.479</i>	<i>2.341</i>
CuSi ₈ -e	<i>34.208</i>	<i>1.534</i>	<i>2.472</i>	<i>2.432</i>
CuSi ₈ -f	<i>34.313</i>	<i>1.391</i>	<i>2.491</i>	<i>2.429</i>
CuSi ₁₀ -a	32.735	1.566	2.493	2.349
CuSi ₁₀ -b	<i>32.620</i>	<i>1.561</i>	<i>2.461</i>	<i>2.338</i>
CuSi ₁₀ -c	<i>32.698</i>	<i>1.578</i>	<i>2.447</i>	<i>2.317</i>
CuSi ₁₀ -d	<i>32.480</i>	<i>1.537</i>	<i>2.517</i>	<i>2.365</i>
CuSi ₁₀ -e	32.784	1.536	2.513	2.232
CuSi ₁₀ -f	<i>32.162</i>	<i>1.541</i>	<i>2.486</i>	<i>2.308</i>
CuSi ₁₀ -g	32.085	1.573	2.507	2.310
Cu@Si ₁₀ -h	<i>31.280</i>	<i>1.677</i>	<i>2.580</i>	<i>2.352</i>
CuSi ₁₀ -i	32.542	1.403	2.480	2.333
CuSi ₁₀ -j	<i>32.393</i>	<i>1.560</i>	<i>2.492</i>	<i>2.309</i>
CuSi ₁₀ -k	32.863	1.571	2.502	2.268
Cu@Si ₁₀ -l	33.780	1.568	2.475	2.440
Cu@Si ₁₂ -a	34.032	1.4538	2.420	2.455
CuSi ₁₂ -b	<i>33.029</i>	<i>1.5145</i>	<i>2.502</i>	<i>2.457</i>
CuSi ₁₂ -c	<i>32.689</i>	<i>1.3657</i>	<i>2.518</i>	<i>2.452</i>
CuSi ₁₂ -d	<i>32.454</i>	<i>1.5028</i>	<i>2.514</i>	<i>2.381</i>
Cu@Si ¹² -e	<i>31.910</i>	<i>1.5731</i>	<i>2.496</i>	<i>2.463</i>
CuSi ¹² -f	<i>33.078</i>	<i>1.4991</i>	<i>2.476</i>	<i>2.415</i>
Cu@Si ₁₂ -g	<i>32.641</i>	<i>1.4219</i>	<i>2.482</i>	<i>2.488</i>
Cu@Si ₁₂ -h	32.366	1.5826	2.589	2.552