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Structures and relative stability of medium- and large-sized silicon clusters. VI. Fullerene cage motifs for low-lying clusters Si_{39} , Si_{40} , Si_{50} , Si_{60} , Si_{70} , and Si_{80}

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We performed a constrained search, combined with density-functional theory optimization, of low-energy geometric structures of silicon clusters Si_{39} , Si_{40} , Si_{50} , Si_{60} , Si_{70} , and Si_{80} . We used fullerene cages as structural motifs to construct initial configurations of endohedral fullerene structures. For Si_{39} , we examined six endohedral fullerene structures using all six homolog C_{34} fullerene isomers as cage motifs. We found that the Si_{39} constructed based on the $\text{C}_{34}(\text{C}_s:2)$ cage motif results in a new leading candidate for the lowest-energy structure whose energy is appreciably lower than that of the previously reported leading candidate obtained based on unbiased searches (combined with tight-binding optimization). The $\text{C}_{34}(\text{C}_s:2)$ cage motif also leads to a new candidate for the lowest-energy structure of Si_{40} whose energy is notably lower than that of the previously reported leading candidate with outer cage homolog to the $\text{C}_{34}(\text{C}_1:1)$. Low-lying structures of larger silicon clusters Si_{50} and Si_{60} are also obtained on the basis of preconstructed endohedral fullerene structures. For Si_{50} , Si_{60} , and Si_{80} , the obtained low-energy structures are all notably lower in energy than the lowest-energy silicon structures obtained based on an unbiased search with the empirical Stillinger–Weber potential of silicon. Additionally, we found that the binding energy per atom (or cohesive energy) increases typically >10 meV with addition of every ten Si atoms. This result may be used as an empirical criterion (or the minimal requirement) to identify low-lying silicon clusters with size larger than Si_{50} . © 2008 American Institute of Physics. [DOI: [10.1063/1.2841080](https://doi.org/10.1063/1.2841080)]

I. INTRODUCTION

The notion of endohedral silicon fullerenes was first put forward in the early 1990s.^{1–7} Over the past few years, medium-sized endohedral silicon fullerenes have received increasing attention^{8–22} largely because of the advancement of global optimization methods and their application to medium-sized silicon clusters.^{23–27} Numerous theoretical studies of lowest-energy structures of medium-sized clusters Si_N ($N=25–40$ and 45) have shown that beyond the size $N=29$, spherical-like compact structures are more stable than elongated structures^{9,13,15,16,20} and that the carbon fullerene cages are likely to be generic *cage motifs* for a class of low-lying spherical-like clusters.^{9,14,16–18,20,21} An empirical rule for determining optimal “stuffing@ cage” combination for endohedral silicon fullerenes has been proposed.^{9,12} Recently, exploration of low-lying endohedral silicon fullerenes has been extended to silicon clusters beyond the size $N=45$,^{20,21} such as Si_{60} ,^{10,20–22} for which a great deal of theoretical effort has been made due to its relevance to the “bucky silicon” Si_{60} .^{28–37}

In our previous study (Paper V in this series¹⁷), we have shown that candidates for the lowest-energy structures of silicon clusters Si_N ($N=31–40$) are all in the form of endohedral fullerenes except Si_{39} , whose outer cage contains a seven-member ring. In that study, we used an *unbiased* glo-

bal search method (the minima-hopping method³⁸) directly combined with the semiempirical density-functional based tight-binding (DFTB) model of silicon.³⁹ Since the number of possible low-lying isomers grows dramatically with increase of cluster size, it becomes impossible to locate the global minima on the potential energy surface (PES) for medium- to large-sized silicon clusters. The unconstrained (global) search combined with the DFTB model has also become increasingly computationally demanding. It will be desirable to obtain some candidates of low-lying isomers before launching such a computationally demanding unconstrained global search. The motif-based constrained search is an option to achieve representative low-lying clusters. On one hand, motif-based search is highly efficient since the selection of motif dramatically reduces the dimensions of the potential energy surface. On the other hand, this approach is capable of producing competitive candidates for the low-lying clusters, as has been demonstrated for smaller silicon clusters Si_N in the size range of $N=15–30$.^{13,17}

In view of several previous studies (using various unconstrained global search methods) confirming that fullerenes are viable structural motifs to build low-lying medium-sized silicon clusters, here, we further examine fullerene-based structural motifs for constructing medium- to large-sized low-lying silicon clusters. To this end, we have performed a series of constrained (biased) searches using carbon fullerenes as cage motifs to seek low-lying silicon clusters of Si_{50} , Si_{60} , Si_{70} , and Si_{80} . To validate this approach, we used

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Si_{39} and Si_{40} as testing bed. Interestingly, for Si_{39} , we have found that a number of endohedral fullerene structures are appreciably lower in energy than the nonfullerene Si_{39} structure reported by us in Paper V.¹⁷ For Si_{50} and Si_{60} , we have found new low-energy endohedral fullerene structures whose energies are notably lower than those previously reported in the literature.^{12,21,22} Finally, we obtain low-energy endohedral fullerene structures for Si_{70} and Si_{80} . The structures of Si_{50} , Si_{60} , and Si_{80} may be considered as low-lying structures because their energies are appreciably lower than those of the corresponding low-lying structures obtained based on the *unbiased* global search with the Stillinger–Weber potential of silicon.

II. COMPUTATIONAL METHOD

Geometric optimization for all clusters was carried out using the plane-wave-pseudopotential density-functional theory (PWP-DFT) within generalized-gradient approximation (GGA). Two GGA functionals were employed (see reason below), the Becke exchange and Lee–Yang–Parr correlation⁴⁰ (BLYP) and the Perdew–Burke–Ernzerhof (PBE) functional,⁴¹ both implemented in the CPMD program.⁴² In the PWP-DFT calculations, we used an energy cutoff of 30 Ry for plane-wave expansion and a supercell size of 25 Å in dimension.

We employed the basin-hopping (BH) global optimization technique⁴³ combined with the PWP-DFT optimization to search for low-energy clusters.²⁷ The BH method essentially converts the potential energy surface ($\tilde{E}$) of a cluster to a multidimensional “staircase” via the mapping $\tilde{E}(\mathbf{X}) = \min\{E(\mathbf{X})\}$, where $\mathbf{X}$ denotes the nuclear coordinates of the cluster and “min” refers to the energy minimization performed starting from $\mathbf{X}$.⁴³ Specifically, the canonical Monte Carlo (MC) sampling method was used to sample the transformed potential energy surface $\tilde{E}$ at a fixed temperature. With each MC move in the BH search, coordinates of all core atoms are randomly displaced while those of the outer-cage atoms are constrained, followed by a geometry optimization using the PWP-DFT methods. In the BH search, we used a smaller energy cutoff (12 Ry) for plane-wave expansion and a smaller supercell size (15 Å). For the purpose of comparison, we also used the unbiased BH global optimization method to locate the lowest-energy clusters of Si_{39} , Si_{40} , and Si_{50} based on an empirical Stillinger–Weber (SW) potential of silicon.^{44,45}

In previous studies of small-sized clusters Si_N ($N = 7\text{--}20$) (Papers I–III, Refs. 13, 46, and 47), we used *ab initio* molecular-orbital methods at the MP2/6-31G(*d*) level of theory for geometry optimization and the coupled-cluster theory for total-energy calculation. However, for medium- to large-sized silicon clusters, geometry optimization at the MP2/6-31G(*d*) level is computationally very demanding, and the total-energy calculation at the coupled-cluster level of theory is impractical. Therefore the calculation of binding energies per atom and determination of the energy ranking among isomers of silicon clusters are all based on density-functional level of theory. Since DFT entails a larger error bar in total-energy calculation compared to the MP2 or

coupled-cluster methods, we thus view those isomers with binding energy differences less than 4 meV as isoenergetic. It is known that the energy ranking among isomers with very close energy can be sensitive to the functional selected in the DFT calculation. Moreover, we have found that the PBE functional favors more compact silicon clusters (in terms of energy ranking) whereas the BLYP functional favors clusters having less core-filling atoms.^{13,17} We thus present results of binding energies based on the two functionals, namely, the PBE and BLYP.

III. RESULTS AND DISCUSSIONS

Initial configurations of endohedral fullerene clusters were constructed using carbon fullerenes^{48,49} as cage motifs, in which a certain number of core-filling silicon atoms were added randomly. The selection of the number of core-filling atoms and the associated fullerene cage motif was guided based on an empirical rule derived previously to achieve optimal core-filling@cage combination.⁹ Specifically, the $\text{Si}_{m+3}/\text{Si}_m$ ($m = 1, 2, \dots$) is an upper/lower limit for the number of core-filling atoms to fit in a Si_{26+2m} fullerene cage. For example, to construct an endohedral fullerene cluster Si_{40} , an optimal core-filling@cage combination is $\text{Si}_6 @ \text{Si}_{34}$ whereas $\text{Si}_8 @ \text{Si}_{32}$ or $\text{Si}_4 @ \text{Si}_{36}$ combination may be slightly “overstuffing” or “understuffing” according to the empirical rule.

A. Si_{39} ($\text{Si}_5 @ \text{Si}_{34}$)

In Paper V,¹⁷ we reported a low-lying Si_{39} cluster with an outer cage of Si_{34} . However, the outer cage Si_{34} contains a seven-membered ring, and thus is not a classical fullerene. Moreover, the cluster has less binding energy per atom than its neighbor low-lying clusters Si_{38} and Si_{40} , indicating that Si_{39} cluster is not the best candidate for the lowest-energy cluster. Later, Ma *et al.*¹⁸ reported an endohedral fullerene the Si_{39} structure with a slightly larger binding energy per atom in DFT-PBE calculation than that reported in Ref. 17. The homolog carbon cage of this endohedral fullerene Si_{39} structure is $\text{C}_{34}(\text{C}_s:2)$ in Fowler–Manolopoulos fullerene notation (where C_s refers to the point-group symmetry and 2 refers to the Fowler–Manolopoulos label).⁴⁸

To achieve an improved endohedral fullerene cluster of Si_{39} , we examined all six isomers of fullerene C_{34} as cage motifs for initial configurations. We performed BH search based on the six initial endohedral fullerene structures. The obtained six low-energy structures are labeled as si39-1a to si39-1f (Fig. 1), in the rank of decreasing binding energy per atom (Table I). Among the six Si_{39} isomers, the homolog fullerene cage of si39-1a and si39-1b is $\text{C}_{34}(\text{C}_s:2)$ and $\text{C}_{34}(\text{C}_2:5)$, respectively. Both si39-1a and si39-1b are notably lower in energy than those reported previously.^{17,18} si39-1a has a binding energy per atom of 3.959 eV (PBE calculation), about 10 meV greater than that of si39-1b. More importantly, si39-1a has a greater binding energy per atom (PBE) than that (3.948 eV) of the leading low-lying structure of Si_{38} .¹⁷ si39-1a also has a binding energy per atom of 3.364 eV (BLYP calculation), which is nearly the same as that reported in Ref. 17 (3.365 eV). In summary, si39-1a is definitely qualified as a low-lying cluster and is

FIG. 1. (Color) Geometries of low-lying endohedral silicon fullerene clusters Si₃₉ and Si₄₀. The core-filling atoms are in blue and the outer cage atoms are in yellow. The corresponding homolog carbon fullerene cages (gray) are also displayed.

currently the new leading candidate for the lowest-energy structure of Si₃₉. This structure can be used in the future study of the chemical reactivity of Si₃₉ with small chemical molecules such as C₂H₂ and NO₂.⁵⁰

B. Si₄₀ (Si₆@Si₃₄ or Si₄@Si₃₆)

In Ref. 12, we reported a low-lying endohedral fullerene structure of Si₄₀ which has a binding energy per atom of 3.943 eV (PBE calculation, Table I). In Ref. 17, we reported another low-lying endohedral fullerene structure of Si₄₀ which has a binding energy per atom (3.372 eV) in BLYP calculation. The homolog fullerene cage of the former Si₄₀ structure is C₃₄(C_{3v}:6), whereas that of the latter is C₃₆(D_{3h}:13) (Table I). As shown in previous studies,^{13,17} the PBE functional favors more compact clusters, whereas the BLYP functional favors clusters having a larger fullerene cage and less core-filling atoms.

Zhou and Pan recently reported a new low-lying structure of Si₄₀. They used the “compressing-liquid-silicon” strategy together with the stuffed-fullerene approach.²¹ The outer cage of the new Si₄₀ structure is homolog to a C₃₄ cage having a seven-member ring. However, the binding energy per atom (in PBE calculation) is 3.955 eV, appreciably larger than that reported in Ref. 12. We have tested whether the fullerene cage motifs can outperform the nonfullerene cage motifs to obtain new Si₄₀ with lower energies. Again, we used all six isomers of fullerene C₃₄ as cage motifs to con-

struct initial endohedral fullerene configurations of Si₄₀. Expectedly, two new endohedral fullerene structures of Si₄₀ are obtained, namely, si40-1a and si40-1b (Fig. 1). Both si40-1a and si40-1b have binding energy per atom (3.966 and 3.962 eV in PBE calculation or 3.364 and 3.365 eV in BLYP calculation; see Table I) notably greater than the best candidate (3.955 eV in PBE binding energy) reported previously.²¹ Interestingly, si40-1a possesses the same homolog fullerene cage C₃₄(C_s:2) as si39-1a while si40-1b possesses the same homolog fullerene cage C₃₄(C₂:5) as si39-1b, suggesting that the fullerene cages C₃₄(C_s:2) and C₃₄(C₂:5) are the two best cage motifs to generate lower-lying Si₃₉ and Si₄₀. Note also that the leading candidate for the lowest-energy structure of Si₃₈ (Paper V, Ref. 17) also possesses the homolog C₃₄(C₂:5) cage. In summary, si40-1a and si40-1b are new leading candidates for the lowest-energy structure of Si₄₀ based on PBE calculation, whereas si40-1a' (Table I)¹⁷ remains to be the leading candidate based on BLYP calculation. si40-1a' possesses an outer cage homolog to C₃₆(D_{3h}:13).

C. Si₅₀ (Si₈@Si₄₂ or Si₆@Si₄₄)

According to the empirical rule illustrated previously, an optimal core-filling@cage combination for endohedral fullerene Si₅₀ is Si₈@Si₄₂ or Si₆@Si₄₄. In the previous study,¹² we performed an unbiased search for the global minimum of Si₅₀ using the generic algorithm method combined with the nonorthogonal tight-binding model for silicon.⁵¹ Interestingly, the unbiased search showed that the lowest-energy structure of Si₅₀ is an endohedral fullerene whose outer cage is homolog to C₄₂(C₁:39) [Fig. 2(a)]. The binding energy per atom is 3.954 eV (PBE calculation; Table II), less than that of the low-lying structures of Si₃₉ and Si₄₀. In this sense, this Si₅₀ structure may no longer be considered as a low-lying structure. Zhou and Pan reported another low-energy structure of Si₅₀ using the compressing-liquid-silicon approach.²¹ The outer cage of that Si₅₀ is homolog to a C₄₀ cage containing a seven-member ring. Its binding energy per atom is 3.950 eV (PBE calculation; Table II), less than that reported in Ref. 12. Thus, it seems that the Si₁₀@Si₄₀ combination is slightly overstuffing for Si₅₀.

Here, we constructed two initial configurations of endohedral fullerene Si₅₀ using the lowest-energy carbon fullerene C₄₂(D₃:45) and C₄₄(D₂:75) as cage motifs.⁴⁷ We then performed a BH search combined with the DFT/PBE optimization for the former and with the DFT/BLYP optimization for the latter. Both BH searches give two markedly improved endohedral fullerene structures, namely, si50-1a and si50-1a' [Fig. 2(a)]. The si50-1a is particularly noteworthy since its binding energy in PBE calculation is 22 meV/atom greater than that of si40-1a, while its binding energy in BLYP calculation is 21 meV/atom greater than that of si40-1a' (Table II). Given that si40-1a and si40-1a' are the leading candidates for the lowest-energy clusters of Si₄₀, the newly obtained si50-1a may be qualified as a good candidate for the low-lying cluster of Si₅₀, and thus may be used as a prototype model for study chemical reaction with small chemical molecules.

TABLE I. Optimal core-filling@cage combinations for low-lying endohedral fullerene clusters Si_{39} and Si_{40} shown in Fig. 1. The binding energy per atom was calculated at the PWP-DFT level of theory with two GGA functionals. The boldface denotes the lowest-energy isomer (isomers whose binding energy is within 4 meV/atom from the lowest-energy isomer are also highlighted in bold).

	Optimal core-filling@cage combination [homolog fullerene cage]	Binding energy (eV/atom)	
		PBE	BLYP
si39-1a	$\text{Si}_5@ \text{Si}_{34} [\text{C}_{34}(\text{C}_s; 2)]$	3.959	3.364
si39-1b	$\text{Si}_5@ \text{Si}_{34} [\text{C}_{34}(\text{C}_2; 5)]$	3.950	3.357
si39-1c	$\text{Si}_5@ \text{Si}_{34} [\text{C}_{34}(\text{C}_{3v}; 6)]$	3.942	3.366
si39-1d	$\text{Si}_5@ \text{Si}_{34} [\text{C}_{34}(\text{C}_s; 3)]$	3.938	3.358
si39-1e	$\text{Si}_5@ \text{Si}_{34} [\text{C}_{34}(\text{C}_2; 4)]$	3.938	3.350
si39-1f	$\text{Si}_5@ \text{Si}_{34} [\text{C}_{34}(\text{C}_2; 1)]$	3.929	3.359
si39 (Ref. 18)	$\text{Si}_5@ \text{Si}_{34} [\text{C}_{34}(\text{C}_s; 2)]$	3.941	3.362
si39 (Ref. 17)	$\text{Si}_5@ \text{Si}_{34}$ (C_{34} has a seven-member ring)	3.939	3.365
si40-1a	$\text{Si}_6@ \text{Si}_{34} [\text{C}_{34}(\text{C}_s; 2)]$	3.966	3.364
si40-1b	$\text{Si}_6@ \text{Si}_{34} [\text{C}_{34}(\text{C}_2; 5)]$	3.962	3.365
si40-1c	$\text{Si}_6@ \text{Si}_{34} [\text{C}_{34}(\text{C}_2; 4)]$	3.949	3.356
si40-1d	$\text{Si}_6@ \text{Si}_{34} [\text{C}_{34}(\text{C}_s; 3)]$	3.946	3.357
si40-1e	$\text{Si}_6@ \text{Si}_{34} [\text{C}_{34}(\text{C}_{3v}; 6)]$	3.944	3.349
si40-1f	$\text{Si}_6@ \text{Si}_{34} [\text{C}_{34}(\text{C}_2; 1)]$	3.938	3.350
si40 (Ref. 21)	$\text{Si}_6@ \text{Si}_{34}$ (C_{34} has a seven-member ring)	3.955	3.353
si40 (Ref. 12)	$\text{Si}_6@ \text{Si}_{34} [\text{C}_{34}(\text{C}_{3v}; 6)]$	3.943	3.359
si40-1a' (Ref. 17)	$\text{Si}_4@ \text{Si}_{36} [\text{C}_{36}(\text{D}_{3h}; 13)]$	3.928	3.372

D. Si_{60} ($\text{Si}_{12}@ \text{Si}_{48}$ or $\text{Si}_{10}@ \text{Si}_{50}$)

As pointed out in the Introduction, Si_{60} is of particular interest because of its relevance to previous studies of bucky silicon Si_{60} .^{28–37} According to the empirical rule, the optimal core-filling@cage combination for endohedral fullerene Si_{60} is $\text{Si}_{12}@ \text{Si}_{48}$ or $\text{Si}_{10}@ \text{Si}_{50}$. Recently, Zhao *et al.* reported a low-lying endohedral fullerene structure of Si_{60} whose outer cage is homolog to $\text{C}_{48}(\text{C}_2; 199)$. This carbon fullerene is the lowest-energy structure among the 199 fullerene isomers of C_{48} .⁴⁷ Zhou *et al.* also found that endohedral fullerenes in the form of $\text{Si}_{14}@ \text{Si}_{46}$ combination generally give much higher energies than $\text{Si}_{12}@ \text{Si}_{48}$ combination. Zhou and Pan²¹ utilized the compressing-liquid-silicon approach and independently confirmed that the preferred structure for Si_{60} is endohedral fullerene. Interestingly, the reported low-energy Si_{60} also has a Si_{48} outer cage which is homolog to $\text{C}_{48}(\text{D}_2; 169)$. The latter is the tenth lowest-energy structure among the 199 fullerene isomers of C_{48} .⁴⁷

The Si_{60} structure reported by Zhao *et al.* has a binding energy per atom of 3.993 eV (PBE calculation), 5 meV/atom greater than that of si50-1a. Thus, it may be viewed as a candidate for the low-lying cluster of Si_{60} . Because the Si_{60} structure of Zhao *et al.* was built based on the lowest-energy C_{48} cage,²² we just performed a direct constrained BH search based on this Si_{60} and obtained an improved structure, si60-1a [Fig. 2(b)]. Note that the binding energy per atom (PBE calculation) of si60-1a is 3.998 eV, 10 meV/atom greater than that of si50-1a (Table II). We performed another BH search using an initial configuration constructed based on $\text{C}_{48}(\text{C}_2; 171)$, which is the second lowest-energy structure among the 199 fullerene isomers of C_{48} .⁴⁷ The obtained structure is si60-1b [Fig. 2(b)], whose binding energy per atom (PBE calculation) is nearly the same as that of si60-1a (Table II).

Additionally, we performed a BH search starting from an initial configuration of endohedral fullerene Si_{60} whose outer cage is homolog to carbon fullerene $\text{C}_{50}(\text{D}_3; 270)$. Note that $\text{C}_{50}(\text{D}_3; 270)$ is the lowest-energy structure among the 271 fullerene isomers of C_{50} .⁴⁷ The resulting low-energy structure is named si60-1a' [Fig. 2(b)]. Its binding energy per atom is 3.977 eV (PBE calculation; Table II). Moreover, si60-1a' has the greatest binding energy per atom, 3.421 eV, in BLYP calculation, compared to other isomers with Si_{48} cages. This result confirms again that the BLYP functional favors clusters with a larger fullerene cage and less core-filling atoms. In summary, si60-1a and si60-1a' may be considered as the low-lying structures of Si_{60} , since their binding energies per atom are at least 10 meV greater than those of si50-1a.

E. Si_{70} ($\text{Si}_{14}@ \text{Si}_{56}$ or $\text{Si}_{12}@ \text{Si}_{58}$)

Li *et al.*⁵² studied an endohedral fullerene Si_{70} whose outer cage is homolog to the bucky ball $\text{C}_{60}(\text{I}_h)$. They found that the endohedral fullerene cluster is much lower in energy than the fullerene cage Si_{70} . On the other hand, according to the empirical rule, the optimal core-filling@cage combination for endohedral fullerene Si_{70} is $\text{Si}_{14}@ \text{Si}_{56}$ or $\text{Si}_{12}@ \text{Si}_{58}$, rather than $\text{Si}_{10}@ \text{Si}_{60}$.

Here, we constructed two initial configurations of endohedral fullerene Si_{70} using the lowest-energy carbon fullerene cages $\text{C}_{56}(\text{D}_2; 916)$ and $\text{C}_{58}(\text{C}_{3v}; 1205)$, respectively.⁴⁷ We then performed the BH search and obtained two low-energy structures, si70-1a and si70-1a' [Fig. 2(c)]. Both si70-1a and si70-1a' have nearly the same binding energy per atom in PBE calculation, as well as nearly degenerate binding energy per atom in BLYP calculation (Table II). Note that the binding energy per atom of si70-1a

FIG. 2. (Color) Geometries of low-lying endohedral silicon fullerene clusters (a) Si₅₀, (b) Si₆₀, and (c) Si₇₀ and Si₈₀. The core-filling atoms are in blue and the outer cage atoms are in yellow. The corresponding homolog carbon fullerene cages (gray) are also displayed.

is 4.011 eV (PBE calculation), about 13 meV/atom greater than that of si60-1a, whereas the binding energy per atom of si70-1a' is 3.430 eV (BLYP calculation), about 9 meV/atom greater than that of si60-1a'. Hence, si70-1a meets the minimal requirement (at least 10 meV/atom greater) to be considered as low-lying structures of Si₇₀.

There is still room to improve the endohedral fullerene structures of Si₇₀ to achieve even lower energy than that of si70-1a or si70-1a'. For example, one could in principle perform BH searches based on initial configurations constructed from all the 924 and 1205 isomers of C₅₆ and C₅₈ cage motifs,⁴⁷ respectively, as well as those based on C₅₄ and C₆₀

TABLE II. Optimal core-filling@ cage combinations for low-lying endohedral fullerene clusters Si_{50} , Si_{60} , Si_{70} , and Si_{80} shown in Fig. 2. The binding energy per atom was calculated at the PWP-DFT level of theory with two GGA functionals. The boldface denotes the lowest-energy isomer (isomers whose binding energy is within 4 meV/atom from the lowest-energy isomer are also highlighted in bold).

	Optimal stuffing cage combination [homologfullerene cage]	Binding energy (eV/atom)	
		PBE	BLYP
si50-1a	$\text{Si}_8@ \text{Si}_{42}$ [$\text{C}_{42}(\text{D}_3:45)$]	3.988	3.393
si50 (Ref. 12)	$\text{Si}_8@ \text{Si}_{42}$ [$\text{C}_{42}(\text{C}_1:39)$]	3.954	3.364
si50 (Ref. 21)	$\text{Si}_{10}@ \text{Si}_{40}$ (C_{40} has a seven-member ring)	3.950	3.361
si50-1a'	$\text{Si}_6@ \text{Si}_{44}$ [$\text{C}_{42}(\text{D}_2:75)$]	3.938	3.400
si60-1a	$\text{Si}_{12}@ \text{Si}_{48}$ [$\text{C}_{48}(\text{C}_2:199)$]	3.998	3.395
si60-1b	$\text{Si}_{12}@ \text{Si}_{48}$ [$\text{C}_{48}(\text{C}_2:171)$]	3.996	3.386
si60 (Ref. 22)	$\text{Si}_{12}@ \text{Si}_{48}$ [$\text{C}_{48}(\text{C}_2:199)$]	3.993	3.388
si60 (Ref. 21)	$\text{Si}_{12}@ \text{Si}_{48}$ [$\text{C}_{48}(\text{D}_2:169)$]	3.987	3.379
si60-1a'	$\text{Si}_{10}@ \text{Si}_{50}$ [$\text{C}_{50}(\text{D}_3:270)$]	3.977	3.421
si70-1a	$\text{Si}_{14}@ \text{Si}_{56}$ [$\text{C}_{56}(\text{D}_2:916)$]	4.011	3.427
si70-1a'	$\text{Si}_{12}@ \text{Si}_{58}$ [$\text{C}_{58}(\text{C}_{3v}:1205)$]	4.007	3.430
si80-1a	$\text{Si}_{16}@ \text{Si}_{64}$ [$\text{C}_{64}(\text{D}_2:1998)$]	4.025	3.451
si80-1a'	$\text{Si}_{16}@ \text{Si}_{64}$ [$\text{C}_{64}(\text{D}_2:1988)$]	4.024	3.452

cage motifs. However, the main goal of this study is not to locate a single global minimum for each medium- or large-sized silicon clusters but to obtain prototype low-lying clusters that can represent one class of low-lying endohedral silicon clusters in the considered size range (see Sec. IV and Fig. 3 below).

F. Si_{80} ($\text{Si}_{18}@ \text{Si}_{62}$ or $\text{Si}_{16}@ \text{Si}_{64}$)

For large-sized cluster Si_{80} , the empirical rule suggests that the optimal core-filling@cage combination is $\text{Si}_{18}@ \text{Si}_{62}$ or $\text{Si}_{16}@ \text{Si}_{64}$. We thus constructed two initial configurations of endohedral fullerene Si_{80} using the lowest-energy carbon fullerene cage of $\text{C}_{62}(\text{C}_2:1994)$ and $\text{C}_{64}(\text{D}_2:1988)$, respectively.⁴⁷ We then performed the BH search and obtained two structures, si80-1a and si80-1a' [Fig. 2(c)]. Both si80-1a and si80-1a' have nearly the same binding energy per atom in PBE and BLYP calculation and both low-lying isomers are obtained based on the $\text{C}_{64}(\text{D}_2:1988)$ cage motif. Interestingly, the low-lying isomer obtained based on $\text{C}_{62}(\text{D}_2:1994)$ cage motif is slightly higher in energy than si80-1a (PBE calculation), even though si80-1a has less core filling Si atoms (16). It is worthy to mention that the 16 core-filling Si atoms in si80-1a [blue atoms in Fig. 2(c)] also forms a cage-like structure. Thus, si80-1a may be viewed as a cage-in-cage or double-shell structure.

Note that the binding energy per atom of si80-1a is 4.025 eV (PBE calculation), about 14 meV/atom greater than that of si70-1a, and the binding energy per atom of si80-1a' is 3.452 eV (BLYP calculation), about 22 meV/atom greater than that of si70-1a'. Therefore, both si80-1a and si80-1a' structures meet the minimal requirement to be considered as low-lying structures of Si_{80} .

IV. COMPARISON WITH LOWEST-ENERGY STILLINGER-WEBER SILICON CLUSTERS

In a previous study,⁴⁵ we performed an unbiased global search for the global minima of silicon clusters up to Si_{30} by

using three empirical potential models of silicon. In general, for small-sized silicon clusters (e.g., Si_6 – Si_{20}), the global minima of empirical model silicon clusters differ markedly from the true global minima of silicon clusters. However, we found that the SW potential,⁴⁴ which is fitted to reproduce bulk properties of silicon, predicts the onset of endohedral spherical-like lowest-energy structures at Si_{20} . Although, in reality, the onset of endohedral spherical-like lowest-energy structures occurs in the size range of Si_{27} – Si_{30} , it is expected that the SW potential will predict better overall structures of silicon clusters as the size of the cluster increases. Therefore, for the purpose of comparison, we also carried out an unbiased BH search for the global minima of SW Si_{39} , Si_{40} , Si_{50} , Si_{60} , Si_{70} , and Si_{80} . Details of the method have been published in Ref. 45. For SW Si_{39} , Si_{40} , and Si_{50} , we were able to locate the global minima starting from three independent random structures, typically within 50 000 MC steps. However, for SW Si_{60} , Si_{70} , and Si_{80} , we only obtained a number of low-lying clusters after 100 000 MC steps. Results of the obtained lowest-lying or low-lying clusters of SW clusters are shown in Table III and Fig. 3. As expected, the lowest-lying or low-lying SW silicon clusters from medium to large

TABLE III. Lowest-lying or low-lying isomers obtained from BH global search on the basis of the SW potential model. SW Si_{39} , Si_{40} , and Si_{50} are the predicted global minima, whereas SW Si_{60} , Si_{70} , and Si_{80} are the best local minima obtained from this study. The (classical) potential energy per atom V/n is given in the dimensionless unit. We also reoptimized the isomers at the DFT-PBE and DFT-BLYP levels of theory and calculated the corresponding binding energy per atom (eV). The bold highlights the binding energies per atom of low-lying cluster of Si_{70} .

SW	Point group	V/n	DFT/PBE	DFT/BLYP
Si_{39} ($\text{Si}_5@ \text{Si}_{34}$)	C_1	-1.6079	3.919	3.352
Si_{40} ($\text{Si}_4@ \text{Si}_{36}$)	C_{2v}	-1.6104	3.921	3.363
Si_{50} ($\text{Si}_8@ \text{Si}_{42}$)	C_3	-1.6408	3.961	3.389
Si_{60} ($\text{Si}_{12}@ \text{Si}_{48}$)	C_1	-1.6584	3.979	3.382
Si_{70} ($\text{Si}_{14}@ \text{Si}_{56}$)	C_1	-1.6715	4.011	3.433
Si_{80} ($\text{Si}_{16}@ \text{Si}_{64}$)	C_1	-1.6860	4.002	3.428

FIG. 3. (Color) Geometries of lowest-lying SW silicon clusters SW Si₃₉, Si₄₀, and Si₅₀, as well as the low-lying SW Si₆₀, Si₇₀, and Si₈₀. The core-filling atoms are in blue and the outer cage atoms are in yellow. The corresponding homolog carbon fullerene cages (gray) are also displayed where the four, seven, and eight members are highlighted in red.

size all exhibit spherical-like endohedral structures. Except SW Si₄₀, the corresponding homolog carbon cages are generally nonfullerene cages. In Fig. 3, we highlight four-, seven-, and eight-membered rings on the outer cage of SW clusters.

To compare with the low-lying clusters obtained from the motif-based constrained search, we reoptimized the SW silicon clusters using the DFT-PBE and DFT-BLYP levels of theory. Results of the binding energy per atoms are also shown in Table III. It can be seen that, with the exception of SW Si₇₀, the binding energy per atom in PBE calculations is notably less (ranging from 14 to 45 meV/atom) than the obtained low-lying clusters shown in Tables I and II. Hence, most of these lowest-lying or low-lying SW clusters cannot be qualified as the true low-lying silicon clusters. On the other hand, SW Si₇₀ possesses binding energies per atom of 4.011 eV/atom (PBE calculation) and 3.433 eV/atom (BLYP calculation), which are comparable or slightly greater than those of si70-1a and si70-1a', respectively. Hence, SW Si₇₀ can be viewed as a low-lying cluster. Note that the homolog carbon cage of SW Si₇₀ is also C₅₆ but containing two seven-membered rings (Fig. 3). It is still remarkable to see that the unbiased search based on the SW potential also gives rise to the same optimal core-filling/cage combination (Si₁₄@Si₅₆) as the empirical rule predicts. This result suggests that the SW potential becomes increasingly reasonable in predicting large-sized low-energy silicon clusters.

FIG. 4. Binding energies per atom (eV/atom) of the lowest-energy endohedral silicon fullerenes highlighted (in bold) in Tables I and II. The squares represent PBE binding energies while the circles represent BLYP binding energies. The two horizontal dashed lines represent cohesive energies of the bulk silicon from PBE and BLYP calculations, respectively.

V. FURTHER DISCUSSIONS

In Fig. 4, we plot the binding energy per atom for the obtained low-lying clusters (highlighted in bold in Tables I and II). It can be seen that for clusters larger than Si₅₀, the binding energy per atom increases almost linearly with the size of the cluster, and the slope of the solid lines is $\sim 1-1.4$ meV/atom. In other words, with addition of one silicon atom to the cluster, the binding energy per atom (or cohesive energy) should gain at least 1 meV. We have considered this result as an empirical criterion (or the minimal requirement) to identify low-lying silicon clusters with size larger than Si₅₀.

Jarrold and Honea have reported cohesive energies (or binding energies per atom) of cluster ions in the range of Si₆–Si₇₀.⁵³ From their data (Fig. 6 in Ref. 53), it appears that the measured cohesive energies increase linearly with the size of the clusters in the range of Si₅₀–Si₇₀. We estimated the slope of the dotted line (Fig. 6 in Ref. 53) for the large-sized clusters (e.g., Si₆₃–Si₇₀), which is about

TABLE IV. Calculated HOMO-LUMO gaps for low-lying endohedral fullerene clusters Si₄₀, Si₅₀, Si₆₀, Si₇₀, and Si₈₀. The geometric optimization is performed at the PWP-DFT level of theory with the PBE functional. The HOMO-LUMO gaps are calculated based on the B3LYP/6-31G(d) single-point calculation.

HOMO-LUMO gap (eV)	
Si40-1a	1.25
Si40-1a'	0.90
Si50-1a	1.42
si50-1a'	1.36
Si60-1a	1.12
Si60-1a'	1.36
Si70-1a	0.84
Si70-1a'	1.25
Si80-1a	0.74
Si80-1a'	1.01

1.3 meV/atom. Hence, our theoretical result on the increase of cohesive energy with increasing the cluster size appears to be consistent with the measured result in the same size range, lending strong support on the empirical criterion (or minimal requirement) proposed here.

We also calculated the cohesive energy of the bulk silicon using the CPMD program, that is, 4.455 eV in PBE calculation and 3.880 eV in BLYP calculation (dashed lines in Fig. 4). If we assumed that the binding energy per atom increases linearly with increasing the cluster size, the two solid lines would intercept with the two dashed lines at about $N \sim 400$, suggesting that the core of the endohedral silicon cluster could be crystallinelike at the size of the cluster approaching $N \sim 400$.^{8,54,55}

As stated previously, the main goal of this study is to obtain a class of representative low-lying clusters that can be used for the study of chemical reaction with small chemical molecules, the growth pattern of the spherical-like silicon clusters, or the size-dependent electronic properties.^{50,54–57} For the latter, as an example, we have calculated highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gaps of the representative low-lying clusters (see Table IV). We used a hybrid density functional (B3LYP) with the 6-31G(*d*) basis set.⁵⁸ We find that for medium- to large-sized clusters, the HOMO-LUMO gaps are typically around 1 eV, and the gaps show a maximum at size $N=50$. Another interesting observation is that for $N \leq 50$, the compact clusters with more core-filling atoms (e.g., si40-1a and si50-1a) exhibit a larger HOMO-LUMO gap than the less compact isomers with less core-filling atoms (e.g., si40-1a' and si50-1a'), whereas for $N \geq 60$, the less compact clusters (e.g., si60-1a', si70-1a', and si80-1a') possess larger energy gaps than the compact clusters (e.g., si60-1a, si70-1a, and si80-1a).

VI. CONCLUSION

In conclusion, we have performed a constrained basin-hopping search for the low-lying endohedral silicon clusters in the medium-to-large size range. For Si₃₉, Si₄₀, and Si₅₀, the BH search indicates that clusters constructed based on the fullerene cage motifs consistently achieve lower energy than those based on nonfullerene cage motifs (previously obtained from *unconstrained* global search). Thus, this study further confirms that fullerene cages are promising cage motifs for building low-lying spherical-like clusters, at least up to Si₅₀ and possibly up to Si₆₀. For Si₇₀, we found two candidates of low-lying cluster, one with a fullerene cage and the best one with a nonfullerene cage containing two seven-membered rings. The latter isomer was obtained based on an unbiased search using the empirical Stillinger–Weber potential of silicon. Interestingly, the unbiased search based on the SW potential also gives rise to the same optimal core-filling@cage combination (Si₁₄@Si₅₆) as an empirical rule suggests. This result suggests that the SW potential becomes increasingly reasonable in predicting large-sized low-energy silicon clusters. Finally, we remark that the obtained low-lying silicon clusters Si₅₀ and Si₆₀ and possibly Si₇₀ and Si₈₀

can be useful as prototype structural models to study size-dependent properties.

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