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

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

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We performed a constrained search, combined with density-functional theory optimization, of low-energy geometric structures of silicon clusters \( \text{Si}_{39}, \text{Si}_{40}, \text{Si}_{50}, \text{Si}_{60}, \text{Si}_{70}, \text{and Si}_{80} \). We used fullerene cages as structural motifs to construct initial configurations of endohedral fullerene structures. For \( \text{Si}_{39} \), we examined six endohedral fullerene structures using all six homolog \( \text{C}_{34} \) fullerene isomers as cage motifs. We found that the \( \text{Si}_{39} \) constructed based on the \( \text{C}_{34}(C;2) \) 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 \( \text{C}_{34}(C;2) \) cage motif also leads to a new candidate for the lowest-energy structure of \( \text{Si}_{40} \) whose energy is notably lower than that of the previously reported leading candidate with outer cage homolog to the \( \text{C}_{34}(C;1) \). Low-lying structures of larger silicon clusters \( \text{Si}_{60} \) and \( \text{Si}_{80} \) are also obtained on the basis of preconstructed endohedral fullerene structures. For \( \text{Si}_{50}, \text{Si}_{60}, \text{and Si}_{80} \), 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 \( \text{Si}_{50} \). © 2008 American Institute of Physics. [DOI: 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 \( \text{Si}_N \) (\( N=25–40 \) 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 \( \text{Si}_{40} \), for which a great deal of theoretical effort has been made due to its relevance to the “bucky silicon” \( \text{Si}_{60} \).\(^28–37\)

In our previous study (Paper V in this series\(^17\)), we have shown that candidates for the lowest-energy structures of silicon clusters \( \text{Si}_N \) (\( N=31–40 \)) are all in the form of endohedral fullerenes except \( \text{Si}_{39} \), whose outer cage contains a seven-member ring. In that study, we used an unbiased global search method (the minima-hopping method\(^38\)) 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 \( \text{Si}_N \) 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 \( \text{Si}_{50}, \text{Si}_{60}, \text{Si}_{70}, \) and \( \text{Si}_{80} \). 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. 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. 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 correlation (BLYP) and the Perdew–Burke–Ernzerhof (PBE) functional, both implemented in the CPMD program. 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 technique combined with the PWP-DFT optimization to search for low-energy clusters. The BH method essentially converts the potential energy surface ($\tilde{E}$) of a cluster to a multidimensional “staircase” via the mapping $\tilde{E}(X) = \min(E(X))$, where $X$ denotes the nuclear coordinates of the cluster and “min” refers to the energy minimization performed starting from $X$. 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.

In previous studies of small-sized clusters Si$_N$ ($N =7$–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. 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 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. Specifically, the $\text{Si}_{m+3}/\text{Si}_m$ ($m=1, 2, \ldots$) 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 Si$_8@$Si$_{13}$ whereas Si$_8@$Si$_{13}$ or Si$_4@$Si$_{15}$ combination may be slightly “overstuffing” or “understuffing” according to the empirical rule.

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

In Paper V, 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. 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 C$_{34}(C_2:2)$ in Fowler–Manolopoulos fullerene notation (where $C_2$ refers to the point-group symmetry and 2 refers to the Fowler–Manolopoulos label).

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 C$_{34}(C_2:2)$ and C$_{34}(C_2:5)$, respectively. Both si39-1a and si39-1b are notably lower in energy than those reported previously. si39-1a has a binding energy per atom of 3.959 eV (PBE calculation), about 0.4 eV lower 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$_{38}$. 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
currently the new leading candidate for the lowest-energy structure of Si_{39}. This structure can be used in the future study of the chemical reactivity of Si_{39} with small chemical molecules such as C_2H_2 and NO_2.\(^{50}\)

**B. Si_{40} (Si_{6} @ Si_{34} or Si_{8} @ Si_{36})**

In Ref. 12, we reported a low-lying endohedral fullerene structure of Si_{40} 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 Si_{40} which has a binding energy per atom (3.372 eV) in BLYP calculation. The homolog fullerene cage of the former Si_{40} structure is C_{34}(C_{3h}:6), whereas that of the latter is C_{36}(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 Si_{40}. They used the “compressing-liquid-silicon” strategy together with the stuffed-fullerene approach.\(^{21}\) The outer cage of the new Si_{40} structure is homolog to a C_{34} 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 Si_{40} with lower energies. Again, we used all six isomers of fullerene C_{34} as cage motifs to construct initial endohedral fullerene configurations of Si_{40}. Expectedly, two new endohedral fullerene structures of Si_{40} 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 C_{34}(C_{3h}:2) as si39-1a while si40-1b possesses the same homolog fullerene cage C_{34}(C_{2h}:5) as si39-1b, suggesting that the fullerene cages C_{34}(C_{3h}:2) and C_{34}(C_{2h}:5) are the two best cage motifs to generate lower-lying Si_{39} and Si_{40}. Note also that the leading candidate for the lowest-energy structure of Si_{38} (Paper V, Ref. 17) also possesses the homolog C_{34}(C_{2h}:5) cage. In summary, si40-1a and si40-1b are new leading candidates for the lowest-energy structure of Si_{40} 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 C_{36}(D_{3h}:13).

**C. Si_{50} (Si_{6} @ Si_{42} or Si_{8} @ Si_{44})**

According to the empirical rule illustrated previously, an optimal core-filling@cage combination for endohedral fullerene Si_{50} is Si_{6} @ Si_{42} or Si_{8} @ Si_{44}. In the previous study,\(^{12}\) we performed an unbiased search for the global minimum of Si_{50} 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 Si_{50} is an endohedral fullerene whose outer cage is homolog to C_{42}(C_{1h}: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 Si_{39} and Si_{40}. In this sense, this Si_{50} structure may no longer be considered as a low-lying structure. Zhou and Pan reported another low-energy structure of Si_{50} using the compressing-liquid-silicon approach.\(^{21}\) The outer cage of that Si_{50} is homolog to a C_{40} 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 Si_{10} @ Si_{40} combination is slightly overstuffed for Si_{50}.

Here, we constructed two initial configurations of endohedral fullerene Si_{50} using the lowest-energy carbon fullerene C_{42}(D_{3h}:45) and C_{44}(D_{7h}:75) as cage motifs.\(^{17}\) 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 Si_{40}, the newly obtained si50-1a may be qualified as a good candidate for the low-lying cluster of Si_{50}, 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 Si60 and Si70 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).

<table>
<thead>
<tr>
<th>Optimal core-filling@cage combination</th>
<th>Binding energy (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[homolog fullerene cage]</td>
<td>PBE</td>
</tr>
<tr>
<td>si39-1a</td>
<td>Si6@Si34 [C34(C5:2)]</td>
</tr>
<tr>
<td>si39-1b</td>
<td>Si6@Si34 [C34(C5:5)]</td>
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<tr>
<td>si39-1c</td>
<td>Si6@Si34 [C34(C5:6)]</td>
</tr>
<tr>
<td>si39-1d</td>
<td>Si6@Si34 [C34(C5:3)]</td>
</tr>
<tr>
<td>si39-1e</td>
<td>Si6@Si34 [C34(C5:4)]</td>
</tr>
<tr>
<td>si39-1f</td>
<td>Si6@Si34 [C34(C5:1)]</td>
</tr>
<tr>
<td>si39 (Ref. 18)</td>
<td>Si6@Si34 [C34(C5:2)]</td>
</tr>
<tr>
<td>si39 (Ref. 17)</td>
<td>Si6@Si34 (C34 has a seven-member ring)</td>
</tr>
<tr>
<td>si40-1a</td>
<td>Si6@Si40 [C34(C5:2)]</td>
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<tr>
<td>si40-1b</td>
<td>Si6@Si40 [C34(C5:5)]</td>
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<tr>
<td>si40-1c</td>
<td>Si6@Si40 [C34(C5:4)]</td>
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<tr>
<td>si40-1d</td>
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<td>Si6@Si40 [C34(C5:1)]</td>
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<td>si40 (Ref. 21)</td>
<td>Si6@Si40 (C34 has a seven-member ring)</td>
</tr>
<tr>
<td>si40 (Ref. 12)</td>
<td>Si6@Si40 [C34(C5:6)]</td>
</tr>
<tr>
<td>si40-1a‘ (Ref. 17)</td>
<td>Si6@Si56 [C34(D3h:131)]</td>
</tr>
</tbody>
</table>

### D. Si60 (Si12 @ Si48 or Si10 @ Si50)

As pointed out in the Introduction, Si60 is of particular interest because of its relevance to previous studies of bucky silicon Si60. According to the empirical rule, the optimal core-filling@cage combination for endohedral fullerene Si60 is Si12 @ Si48 or Si10 @ Si50. Recently, Zhao et al. reported a low-lying endohedral fullerene structure of Si60 whose outer cage is homolog to C48. This carbon fullerene is the lowest-energy structure among the 199 fullerene isomers of C48. Zhou et al. also found that endohedral fullerenes in the form of Si14 @ Si46 combination generally give much higher energies than Si10 @ Si50 combination. Zhou and Pan utilized the compressing-liquid-silicon approach and independently confirmed that the preferred structure for Si60 is endohedral fullerene. Interestingly, the reported low-energy Si60 also has a Si48 outer cage which is homolog to C48(D3h:169). The latter is the tenth lowest-energy structure among the 199 fullerene isomers of C48.

The Si60 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 Si60. Because the Si60 structure of Zhao et al. was built based on the lowest-energy C48 cage, we just performed a direct constrained BH search based on this Si60 and obtained an improved structure, si60-1a [Fig. 2b]. 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 I). We performed another BH search using an initial configuration constructed based on C48(C5:2), which is the second lowest-energy structure among the 199 fullerene isomers of C48. The obtained structure is si60-1b [Fig. 2b], whose binding energy per atom (PBE calculation) is nearly the same as that of si60-1a (Table I).

Additionally, we performed a BH search starting from an initial configuration of endohedral fullerene Si60 whose outer cage is homolog to carbon fullerene C50(D3h:270). Note that C50(D3h:270) is the lowest-energy structure among the 271 fullerene isomers of C50. The resulting low-energy structure is named si60-1a‘ [Fig. 2b]. 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 Si48 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 Si60 since their binding energies per atom are at least 10 meV greater than those of si50-1a.

### E. Si70 (Si14 @ Si56 or Si12 @ Si58)

Li et al. studied an endohedral fullerene Si70 whose outer cage is homolog to the bucky ball C60(I1). They found that the endohedral fullerene cluster is much lower in energy than the fullerene cage Si70. On the other hand, according to the empirical rule, the optimal core-filling@cage combination for endohedral fullerene Si70 is Si14 @ Si56 or Si12 @ Si58, rather than Si10 @ Si60.

Here, we constructed two initial configurations of endohedral fullerene Si70 using the lowest-energy carbon fullerene cages C56(D3h:916) and C58(C1v:1205), respectively. We then performed the BH search and obtained two low-energy structures, si70-1a and si70-1a‘ [Fig. 2c]. 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...
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, respectively, as well as those based on C54 and C60.

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.
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. \textbf{Si}_{50} (\textbf{Si}_{18} @ \textbf{Si}_{62} \text{ or } \textbf{Si}_{16} @ \textbf{Si}_{64})

For large-sized cluster \textbf{Si}_{50}, the empirical rule suggests that the optimal core-filling@cage combination is \textbf{Si}_{18} @ \textbf{Si}_{62} or \textbf{Si}_{16} @ \textbf{Si}_{64}. We thus constructed two initial configurations of endohedral fullerene \textbf{Si}_{50} using the lowest-energy carbon fullerene cage of \textbf{C}_{62}(C_{2v}; 1994) and \textbf{C}_{64}(D_{2h}; 1988), respectively.\textsuperscript{47} We then performed the BH search and obtained two structures, \textbf{si}_{50}-1a and \textbf{si}_{50}-1a’ [Fig. 2(c)]. Both \textbf{si}_{50}-1a and \textbf{si}_{50}-1a’ have nearly the same binding energy per atom in PBE and BLYP calculation and both low-lying isomers are obtained based on the \textbf{C}_{64}(D_{2h}; 1988) cage motif. Interestingly, the low-lying isomer obtained based on \textbf{C}_{62}(D_{2h}; 1994) cage motif is slightly higher in energy than \textbf{si}_{50}-1a (PBE calculation), even though \textbf{si}_{50}-1a has less core filling \textbf{Si} atoms (16). It is worthy to mention that the 16 core-filling \textbf{Si} atoms in \textbf{si}_{50}-1a [blue atoms in Fig. 2(c)] also forms a cage-like structure. Thus, \textbf{si}_{50}-1a may be viewed as a cage-in-cage or doubleshell structure.

Note that the binding energy per atom of \textbf{si}_{80}-1a is 4.025 eV (PBE calculation), about 14 meV/atom greater than that of \textbf{si}_{170}-1a, and the binding energy per atom of \textbf{si}_{80}-1a’ is 3.452 eV (BLYP calculation), about 22 meV/atom greater than that of \textbf{si}_{170}-1a’. Therefore, both \textbf{si}_{80}-1a and \textbf{si}_{80}-1a’ structures meet the minimal requirement to be considered as low-lying structures of \textbf{Si}_{80}.

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

In a previous study,\textsuperscript{45} we performed an unbiased global search for the global minima of silicon clusters up to \textbf{Si}_{30} by using three empirical potential models of silicon. In general, for small-sized silicon clusters (e.g., \textbf{Si}_{9}–\textbf{Si}_{18}), 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,\textsuperscript{44} which is fitted to reproduce bulk properties of silicon, predicts the onset of endohedral spherical-like lowest-energy structures at \textbf{Si}_{27}. Although, in reality, the onset of endohedral spherical-like lowest-energy structures occurs in the size range of \textbf{Si}_{27}–\textbf{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 \textbf{Si}_{39}, \textbf{Si}_{40}, \textbf{Si}_{50}, \textbf{Si}_{60}, \textbf{Si}_{70}, and \textbf{Si}_{80}. Details of the method have been published in Ref. 45. For \textbf{Si}_{39}, \textbf{Si}_{40}, and \textbf{Si}_{50}, we were able to locate the global minima starting from three independent random structures, typically within 50 000 MC steps. However, for \textbf{Si}_{60}, \textbf{Si}_{70}, and \textbf{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 II. Optimal core-filling@cage combinations for low-lying endohedral fullerene clusters \textbf{Si}_{50}, \textbf{Si}_{60}, \textbf{Si}_{70}, and \textbf{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).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Core-filling@cage combination</th>
<th>PBE</th>
<th>BLYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>si50-1a</td>
<td>\textbf{Si}<em>{18} @ \textbf{Si}</em>{62} [C_{62}(D_{2h}; 1994)]</td>
<td>3.988</td>
<td>3.393</td>
</tr>
<tr>
<td>si50-1a’</td>
<td>\textbf{Si}<em>{18} @ \textbf{Si}</em>{62} [C_{62}(D_{2h}; 1994)]</td>
<td>3.950</td>
<td>3.361</td>
</tr>
</tbody>
</table>

### TABLE III. Lowest-lying or low-lying isomers obtained from BH global search on the basis of the SW potential model. \textbf{Si}_{39}, \textbf{Si}_{40}, and \textbf{Si}_{50} are the predicted global minima, whereas \textbf{Si}_{60}, \textbf{Si}_{70}, and \textbf{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 \textbf{Si}_{50}.

<table>
<thead>
<tr>
<th>\textbf{Si}_{n}</th>
<th>Point group</th>
<th>( V/n ) DFT/PBE</th>
<th>( V/n ) DFT/BLYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{Si}<em>{39} (\textbf{Si}</em>{18} @ \textbf{Si}_{62})</td>
<td>( C_1 )</td>
<td>-1.6079</td>
<td>3.919</td>
</tr>
<tr>
<td>\textbf{Si}<em>{40} (\textbf{Si}</em>{18} @ \textbf{Si}_{62})</td>
<td>( C_2v )</td>
<td>-1.6104</td>
<td>3.921</td>
</tr>
<tr>
<td>\textbf{Si}<em>{50} (\textbf{Si}</em>{18} @ \textbf{Si}_{62})</td>
<td>( C_3 )</td>
<td>-1.6408</td>
<td>3.961</td>
</tr>
<tr>
<td>\textbf{Si}<em>{50} (\textbf{Si}</em>{16} @ \textbf{Si}_{64})</td>
<td>( C_1 )</td>
<td>-1.6584</td>
<td>3.979</td>
</tr>
<tr>
<td>\textbf{Si}<em>{50} (\textbf{Si}</em>{16} @ \textbf{Si}_{64})</td>
<td>( C_1 )</td>
<td>-1.6715</td>
<td>4.011</td>
</tr>
<tr>
<td>\textbf{Si}<em>{50} (\textbf{Si}</em>{16} @ \textbf{Si}_{64})</td>
<td>( C_1 )</td>
<td>-1.6860</td>
<td>4.002</td>
</tr>
</tbody>
</table>
size all exhibit spherical-like endohedral structures. Except SW Si_{40}, 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 atom are also shown in Table III. It can be seen that, with the exception of SW Si_{70}, 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 Si_{70} 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 si_{70-1a} and si_{70-1a}', respectively. Hence, SW Si_{70} can be viewed as a low-lying cluster. Note that the homolog carbon cage of SW Si_{70} is also C_{66} 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 (Si_{14}@Si_{56}) as the empirical rule predicts. This result suggests that the SW potential becomes increasingly reasonable in predicting large-sized low-energy silicon clusters.

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 Si_{40}, 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 Si_{50}.

Jarrold and Honea have reported cohesive energies (or binding energies per atom) of cluster ions in the range of Si_{6}–Si_{70}.\(^{53}\) 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 Si_{50}–Si_{70}. We estimated the slope of the dotted line (Fig. 6 in Ref. 53) for the large-sized clusters (e.g., Si_{63}–Si_{70}), which is about

| TABLE IV . Calculated HOMO-LUMO gaps for low-lying endohedral fullerene clusters Si_{40}, Si_{50}, Si_{60}, Si_{70}, and Si_{80}. 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) |     |
| Si_{40}-1a      | 1.25 |
| Si_{40}-1a'     | 0.90 |
| Si_{50}-1a      | 1.42 |
| si_{50}-1a'     | 1.36 |
| Si_{60}-1a      | 1.12 |
| Si_{60}-1a'     | 1.36 |
| Si_{70}-1a      | 0.84 |
| Si_{70}-1a'     | 1.25 |
| Si_{80}-1a      | 0.74 |
| Si_{80}-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 \( N \approx 400 \), suggesting that the core of the endohedral silicon cluster could be crystallinelike at the size of the cluster approaching \( N = 400 \).\(^{54,55}\)

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.\(^{59}\) 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., \( \text{si}40-1a \) and \( \text{si}50-1a \)) exhibit a larger HOMO-LUMO gap than the less compact isomers with less core-filling atoms (e.g., \( \text{si}40-1a' \) and \( \text{si}50-1a' \)), whereas for \( N \approx 60 \), the less compact clusters (e.g., \( \text{si}60-1a' \), \( \text{si}70-1a' \), and \( \text{si}80-1a' \)) possess larger energy gaps than the compact clusters (e.g., \( \text{si}60-1a \), \( \text{si}70-1a \), and \( \text{si}80-1a \)).

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 \( \text{Si}_{39} \), \( \text{Si}_{40} \), and \( \text{Si}_{50} \), 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 \( \text{Si}_{50} \) and possibly up to \( \text{Si}_{60} \). For \( \text{Si}_{70} \), 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 (\( \text{Si}_{14}@\text{Si}_{58} \)) 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 \( \text{Si}_{50} \) and \( \text{Si}_{60} \) and possibly \( \text{Si}_{70} \) and \( \text{Si}_{80} \) can be useful as prototype structural models to study size-dependent properties.

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