

**Modified genetic algorithms to model cluster structures in medium-size silicon clusters**

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This paper presents the results obtained using a genetic algorithm (GA) to search for stable structures of medium size silicon clusters. In this work the GA uses a semiempirical energy function to find the best cluster structures, which are further optimized using density-functional theory. For small clusters our results agree well with previously reported structures, but for larger ones different structures appear. This is the case of  $\text{Si}_{36}$  where we report a different structure, with significant lower energy than those previously found using limited search approaches on common structural motifs. This demonstrates the need for global optimization schemes when searching for stable structures of medium-size silicon clusters.

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**I. INTRODUCTION**

The study of the structure and physical properties of atomic and molecular clusters is an extremely active area of research due to their importance, both in fundamental science and in applied technology [1].

Existing experimental methods for structural determination seldom can obtain the structure of atomic clusters directly. Therefore the calculation, using theoretical structures and comparison with experimental values of their physical and optical properties, is the most common way to obtain structural information of atomic clusters. While the prediction of the structures of clusters with a small number of atoms is well understood, the prediction of the structures and properties of medium-size (10–100 atoms) clusters is much less developed in spite of their critical importance in understanding the transition from microscopic to macroscopic behavior of nanomaterials and their possible technological applications.

The investigations on  $\text{Si}_n$  clusters [2–11] have been guided by the formidable developments in the field of carbon clusters during the last two decades. Differences and similarities between both series of atomic clusters have been pointed out in numerous publications [12]. For instance no fullerene-like structures have been identified for  $\text{Si}_n$  units, this is attributable to the  $sp^2$  characteristic hybridization in fullerenes, which is more favorable for  $\text{C}_n$  than for  $\text{Si}_n$  units [13], i.e., silicon clusters of five atoms form three-dimensional compact structures while pure carbon clusters with ten or less atoms show linear and planar structures.

Clusters with up to approximately ten atoms can be modeled using standard geometry optimization techniques in conjunction with quantum chemical methods, such as density-functional theory (DFT), second-order Møller-Plesset theory, coupled clusters, etc. Systematic, global ge-

ometry optimizations of larger clusters is complex and time consuming, due to the large number of possible structures [6], the time required for the calculation of their total energies, and the lack of effective methods to perform global searches. Nowadays, the global optimization of clusters with  $\sim 20$  atoms is almost an intractable problem and inconsistent results on the structures of  $\text{Si}_n$ ,  $10 \leq n \leq 30$  clusters have been reported in the literature [2–7, 11, 12, 14]. For these medium to large size clusters the option of using *ab initio* or DFT methods to calculate the cluster energies is limited to the study of a few plausible configurations. This is the case of the comprehensive study of one of the largest silicon clusters studied by *ab initio* methods:  $\text{Si}_{36}$  [12]. In this paper the authors locally optimized several plausible structures of  $\text{Si}_{36}$  that were constructed by introducing small modifications into several common structural motifs observed in nanostructures: cages, wires, and fullerenes. The high cost of the *ab initio* calculations precluded a more comprehensive study of the structural parameter space, leaving open the possibility that geometries quite different from those derived from the selected motifs may be valid candidates for stable isomers of this species.

In this paper, we report the use of a parallel genetic algorithm (PGA) to predict the structure of medium-size silicon clusters. This stochastic method was chosen because, in conjunction with basin-hopping Monte Carlo [15, 16] and simulated annealing [17], it is one of the best approaches to explore and find global and secondary minima of complex energy potential surfaces. Moreover, our recent research efforts have demonstrated the success of using parallel genetic algorithms [18, 19] to predict crystalline structures of organic compounds [20–22].

GAs are a family of search techniques rooted on the ideas of Darwinian biological evolution. The introductory sections of Refs. [23, 24] offer a very detailed description of the progress in the development of GA strategies to perform cluster optimizations in the last seven years. These methods are based in the principle of survival of the fittest, considering that each string or *genome* represents a trial solution candidate of the problem, and that at any generation the ge-

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nomes or “individuals” compete with each other in the population for survival and produce offsprings for the next generation by prescribed propagation rules. Operators analogous to crossover, mutation, and natural selection are employed to perform a search able to explore and learn the multidimensional parameter space and determine which regions of that space provide good solutions to the problem. One of the advantages of genetic algorithms is that they can provide not only global minima, but also information on other states with energies close to the minimum, an important property when analyzing atomic clusters.

Current computational limitations make it unfeasible to use *ab initio* methods in extensive GA searches, therefore in this paper we have adopted a compromise by using a semiempirical molecular orbital program, MSINDO [25–27] to evaluate the energy of the clusters in the global search using the GA, while using a DFT method to refine those more promising ones by performing a local optimization of the best structures found by the GA. To perform the calculations reported here, we have extended the computational package modified genetic algorithm for crystal and cluster structures (MGAC) [21] to add semiempirical methods as one of the possible options to calculate the energy.

Here we present two sets of results: one on small silicon clusters  $\text{Si}_n$  ( $n=4$ –14 and 16) to demonstrate the validity of the method in silicon clusters with structures that are well characterized using DFT methods [4,28–31], and a second set on  $\text{Si}_{36}$ , one of the largest silicon clusters previously studied by *ab initio* methods, to demonstrate the effectiveness of our method in larger clusters.

## II. METHODOLOGY

In any GA implementation it is necessary to define a genome with enough information to calculate the associated fitness function. For the case of atomic clusters, the genome is quite simple because there are no symmetry or periodicity relationships that constrain the parameters in the genome. The genome is given as an array containing the coordinates of the atoms. This array has dimension  $3N$ , where  $N$  is the number of atoms in the cluster. Moreover, any genetic operator, mating, crossover, mutation, etc., applied to this genome produces a valid individual, i.e., a possible structure for the desired cluster size.

The first population, of size  $N_{pop}$ , is constructed by generating a set of atomic coordinates using random numbers. These random numbers, used to define the atomic positions in the cluster, belong to specific intervals selected according to the expected dimensions of the cluster; these restrictions have been included to avoid sampling in nonphysical configurations. The distances between any pair of atoms is calculated and compared with a set of rules that guarantees that they are within the normal values for silicon interatomic distances, otherwise the structure is rejected. This set of rules is designated to eliminate from the initial population all those structures that are evidently unphysical. There are basically two rules: the first states that if any pair of atoms is closer than a minimal distance ( $r_1$ ) the structure will be rejected; the second rule states that if any atom is at a distance larger

than  $r_2$  to any other atom in the cluster the structure also will be rejected.

The GA operations of mating, mutation, and selection are used to evolve one generation into the next. In addition, for  $\text{Si}_{36}$  we have augmented these operations on the genome by using the real space “cut and split” operator introduced by Johnston and Roberts [32]. The population replacement is done through the steady-state genetic algorithm, which typically replaces only a portion of the individuals in each generation [33–35]. This technique is also known as elitism, because the best individuals among the population, 50% in our case, are copied directly into the next generation. The criteria for fitness probability, selection of the individuals and mutation are discussed in detail in Ref. [21]. Like any stochastic minimization procedure the GA should be run several times to guarantee that the resulting structures are independent of the initial population and statistically significant.

The MGAC package has been implemented in C++ language using parallel techniques, making it very portable as well as easy to maintain and upgrade. Our parallel MGAC implementation of the GA (PGA) is particularly efficient [36].

Using the information contained in the genomes the energy of each individual was evaluated and its structure relaxed to its local minimum. All the energy calculations for the GA optimizations were done using the MSINDO code. The optimizations used  $\approx 20$  individuals for clusters with less than ten silicon atoms, while the number of individuals was increased for larger clusters reaching 40 individuals for  $\text{Si}_{36}$ . In general the number of individuals was taken  $\approx \frac{1}{2}$  the number of free parameters in the optimization. For the small clusters the GA converged in  $\sim 30$  generations, while for  $\text{Si}_{36}$  the GA optimization required more than 200 generations to converge. The GA procedure was repeated several times employing different initial populations to confirm that the final selection of isomers was independent from the initial population. Populations were considered converged when the standard deviation of the energies in the population reaches 0.1 eV. The structures in the final population were manually classified selecting a set of structures with significant diversity for further refinement. All the structures in the population with significantly different features were considered for further analysis. The geometry of these isomers was locally optimized using density-functional methods with the B3PW91 exchange-correlation functional using the Stuttgart pseudopotential and basis set [37] augmented with the most diffuse *s* and *p* functions and one of the *d*-polarization functions of Sadlej’s basis set [38]. The DFT calculations in  $\text{Si}_{36}$  were done using the same principles, but to reduce the computational cost associated with this larger cluster the smaller LanL2DZ basis set and Los Alamos pseudopotential [39] were used. Additional calculations using the local spin-density approximation (LSDA) [40] exchange-correlation functional were performed to verify the sensitivity of the results with the selection of the exchange-correlation functional. Vibrational frequencies were calculated for the optimized structures to check that no imaginary frequencies are present, confirming that the isomers presented here correspond to true minima of the potential energy. All the calculations are done using the Gaussian package of programs [41].

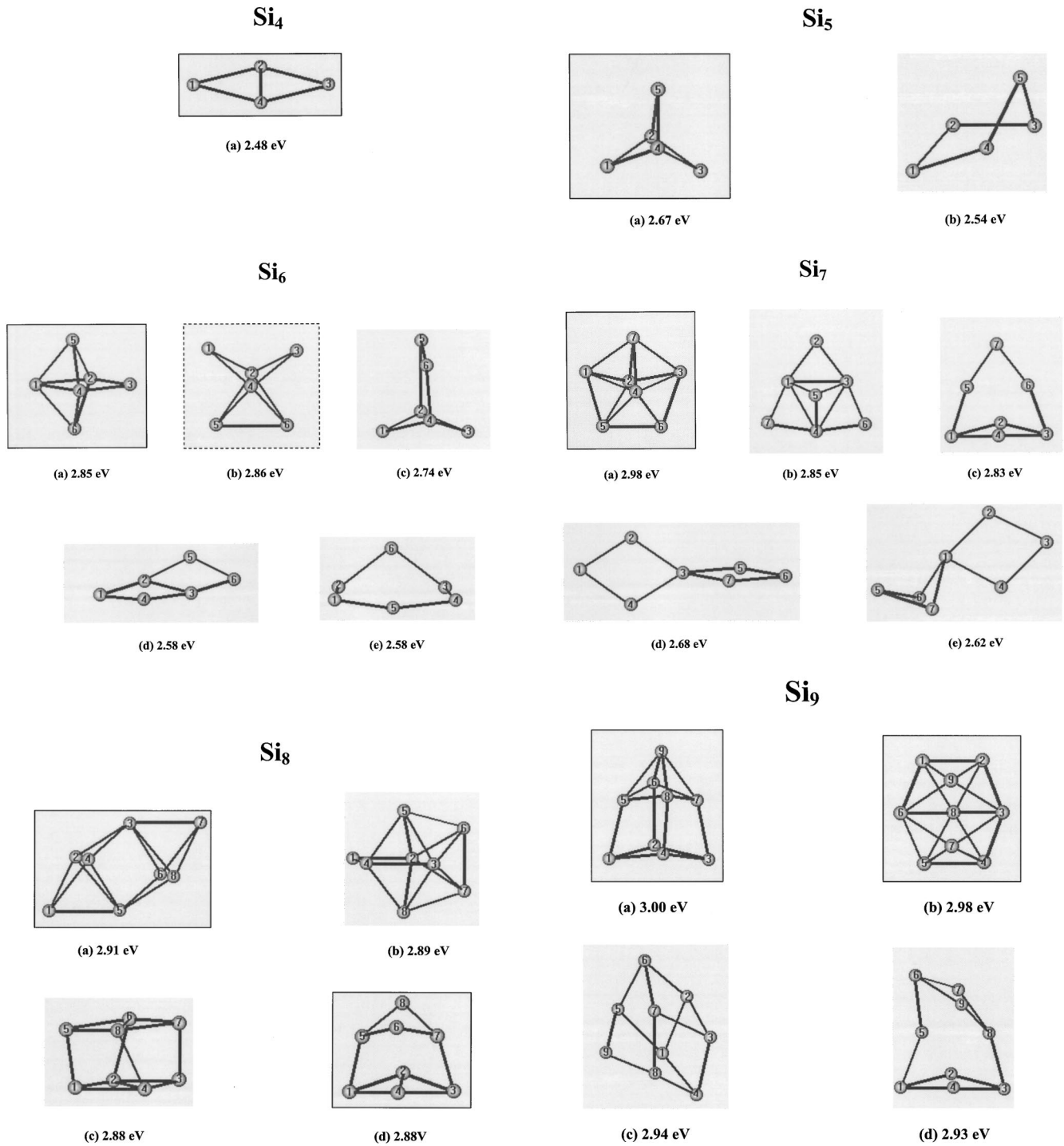


FIG. 1. Optimized structures and binding energies per atom for Si<sub>n</sub>, n=4–14 and 16 clusters. All energies in eV based on a Si atomic energies of -102.449 eV.

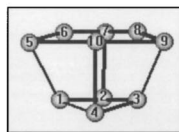
### III. RESULTS AND DISCUSSION

Figure 1 shows the structures obtained for the isomers with up to 16 silicon atoms and their corresponding binding energy per atom. These binding energies are based on a calculated silicon atomic energy of -102.449 eV. The isomers enclosed into frames are those that have been previously reported in the literature [11]. Those enclosed by dashed lines correspond to structures that have been reported in the litera-

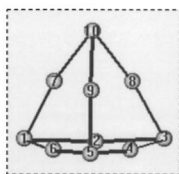
ture and that were also found by the MGAC/MSINDO search, but for which at least one of the calculated vibrational frequencies is imaginary when the structure is further optimized by DFT.

Comparing the results in the figure with those from the literature we observe that our approach was able to find most of the stable isomers previously reported in the literature. For all but Si<sub>12</sub> and Si<sub>16</sub> the most stable isomer found here coin-

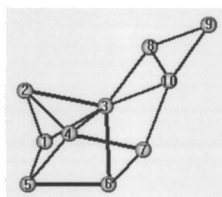
**Si<sub>10</sub>**



(a) 3.02 eV

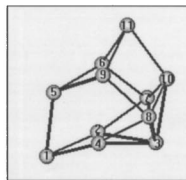


(b) 3.02 eV

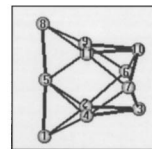


(c) 2.87 eV

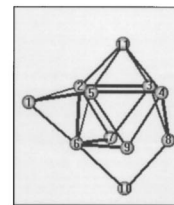
**Si<sub>11</sub>**



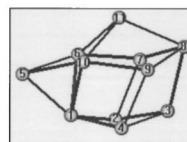
(a) 3.04 eV



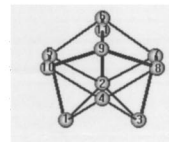
(b) 3.03 eV



(c) 3.02 eV

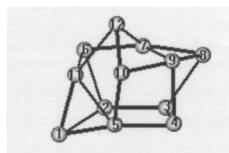


(d) 3.00 eV

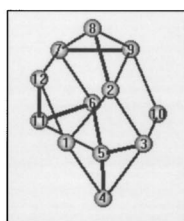


(e) 2.99 eV

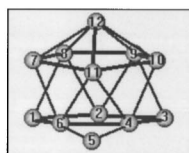
**Si<sub>12</sub>**



(a) 3.02 eV

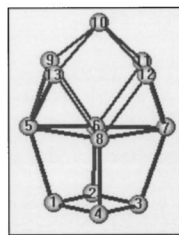


(b) 3.00 eV

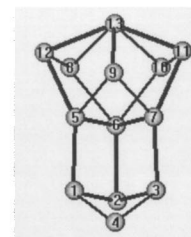


(c) 2.99 eV

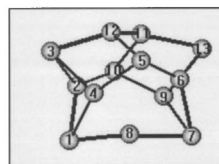
**Si<sub>13</sub>**



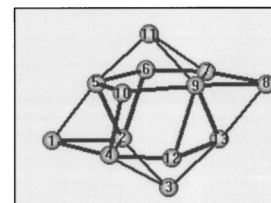
(a) 3.06 eV



(b) 3.03 eV

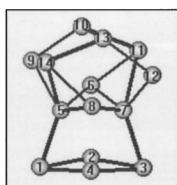


(c) 3.02 eV

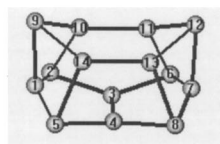


(d) 2.98 eV

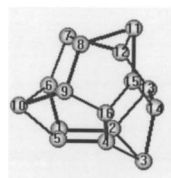
**Si<sub>14</sub>**



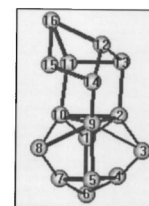
(a) 3.11 eV



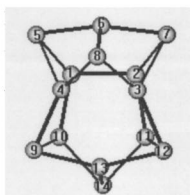
(b) 3.10 eV



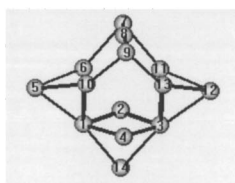
(a) 3.02 eV



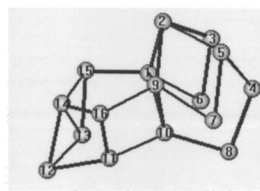
(b) 3.01 eV



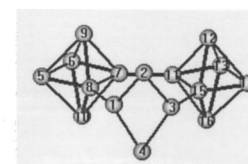
(c) 3.08 eV



(d) 3.05 eV



(c) 3.00 eV



(d) 2.91 eV

**Si<sub>16</sub>**

FIG. 1. (Continued).

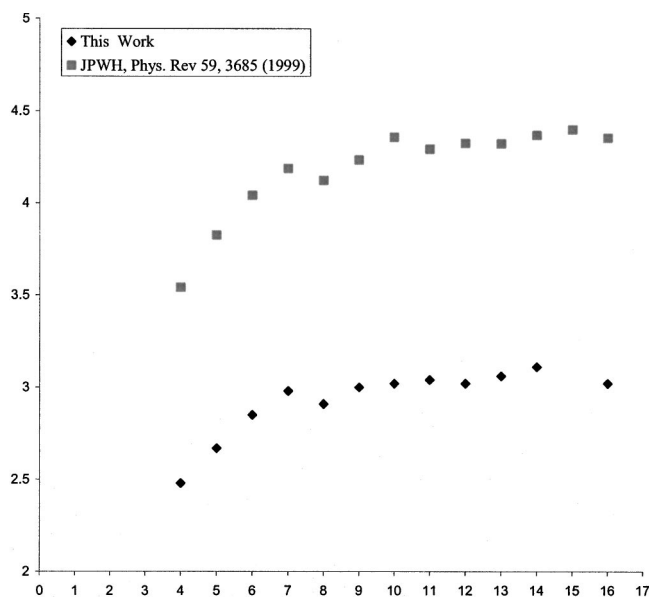


FIG. 2. Calculated binding energies per atom for  $Si_n$ ,  $n=4-16$  clusters. All values are in eV.

cides with those reported previously, while for these two clusters,  $Si_{12}$  and  $Si_{16}$ , our approach is able to find structures that are more stable than those previously known. For most cluster sizes, our approach is also able to find a larger number of stable structures, with higher energies than the lowest one, than previous approaches based on lattice replacements and local optimization of known structural motifs. It is very important to emphasize that for the smaller clusters in the series, our approach produces the same results than those found by less exhaustive searches, while as the size of the clusters grows our approach is able to locate different lower-energy configurations ( $Si_{12}$  and  $Si_{16}$ ) as well as other stable structures. This shows the clear advantage of our methodology that uses GA to perform a global search of the structural parameter space with respect to other approaches based on limited searches. Clearly these approaches are successful for the smaller structures but they are not able to fully explore that entire conformation space for larger clusters because this methodology privileges the presence of symmetry constraints in the final structures.

Figure 2 compares the calculated binding energies per atom, of the most stable cluster found in this work, as a function of the cluster size with existing results from the literature [5]. It is apparent from the figure that the method used here is able to reproduce the features observed by others in the smaller clusters.

$Si_{36}$  is one of the largest silicon clusters studied using first principles. In a recent paper [12] several structures derived from first-principles calculations were proposed; all of them were obtained by local optimizations of structures derived, by introducing small changes, of plausible structural motifs. This approach leaves open the possibility that more stable structures, which cannot be derived from these motifs, may exist. Using the method presented here, which as it was demonstrated above is able to find the correct structures of small silicon clusters; we found several different stable structures

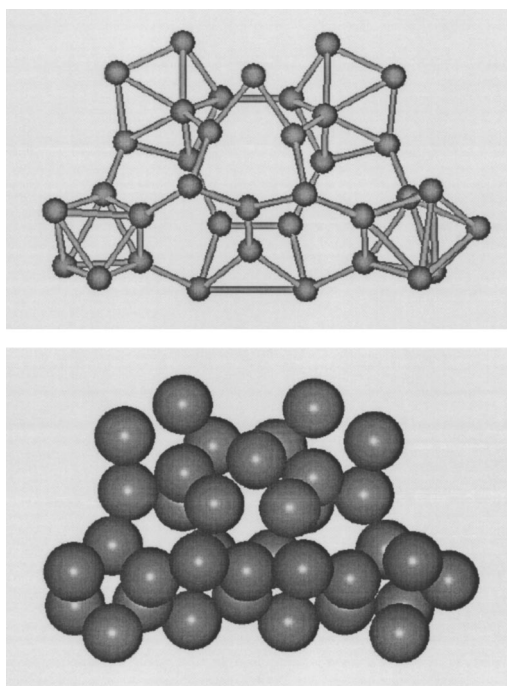


FIG. 3. Optimized structure of  $Si_{36}$  found by MGAC/MSINDO and local DFT Optimization (B3LPW91/LanL2DZ).

for  $Si_{36}$ . The most stable one found by the GA was subject to further refinement by performing a local optimization using the B3PW91 exchange-correlation function and the LanL2DZ basis set with the Los Alamos pseudopotential. The final optimized structure is presented in Fig. 3. This structure is quite different from any of those presented in Ref. [12], which were derived from cage, wire, and stuffed-fullerene motifs. In Table I we compare the binding energy per atom of our optimized structure with three representative structures from Ref. [12], each one corresponding to a different motif. The calculations of the energies of these structures were done using the Cage 2, Wire 2, and Stuff30-A structures from Ref. [12] and the LanL2DZ basis set. Calculations were performed for both the B3PW91 and LSDA exchange-correlation functionals. From the table it is appar-

TABLE I. Calculated binding energies per atom for  $Si_{36}$  isomers. All values in eV based on Si atomic energies of  $-102.155$  eV and  $-101.428$  eV for the LSDA and B3PW91 approaches, respectively.

Structure	LSDA <sup>a</sup>	B3PW91 <sup>a</sup>
Cage 2 <sup>b</sup>	4.79	3.93
Wire 2 <sup>b</sup>	4.95	4.18
Stuff30-A <sup>b</sup>	5.00	4.16
MGAC/MSINDO	5.13	4.41
MGAC/MSINDO plus local DFT optimization	5.19	4.46

<sup>a</sup>All calculations done using the LanL2DZ basis set with its respective Los Alamos pseudopotential.

<sup>b</sup>Geometries from Ref. [12].

ent that the structure found here using the MGAC/MSINDO followed by the local DFT optimization has a significant higher binding energy, therefore more stable than those obtained in Ref. [12]. The locally refined structure is slightly more stable than the MGAC/MSINDO structure, but clearly both are significantly more stable than the previously determined structures of  $\text{Si}_{36}$ . Local minimization of the second two lowest MGAC/MSINDO structures lead, after DFT (B3PW91) optimization, to two structures very similar to the one depicted in Fig. 3 with binding energies per atom of 4.46 eV and 4.45 eV. This shows that there are at least three structures of  $\text{Si}_{36}$  that have significant lower energy than those previously known in the literature. This finding clearly highlights the importance of exploring the complete configuration space when searching for atomic cluster.

#### IV. CONCLUSION

We have demonstrated a strategy to find stable isomers of silicon clusters. The principal advantage of the hybrid technique proposed here is that it does not need to make any assumptions on the symmetry or type of the cluster structures, allowing for a full exploration of the complete configuration space available for the cluster geometry. Moreover the use of GA for the exploration of the space allows for an efficient search into those regions of the configuration space that represent the desirable low-energy configurations. This global search was possible due to the use of a semiempirical

energy function because computational limitations still make these searches not feasible when using *ab initio* methods for medium-size clusters.

For small clusters our results agree well with previously reported structures, but for larger ones different structures appear. For  $\text{Si}_{36}$  it is clearly demonstrated that previous approaches, using local optimization of plausible structural motifs, may produce structures that are significantly higher in energy than those presented here. This demonstrates the need for global optimization schemes when searching for stable structures of medium-size Si clusters.

#### ACKNOWLEDGMENTS

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