



Fast global optimization of Si_xH_y clusters: new mutation operators in the cluster genetic algorithm

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Abstract

An improved strategy for finding the ab initio global minimum of Si_xH_y clusters based on a cluster genetic algorithm (CGA) is presented. Four new mutation operators are introduced which better facilitate retention of desirable structural features between the different generations of clusters in the CGA. The new CGA generally finds global minima with fewer energy evaluations and is now able to find the problem global minima for $\text{Si}_{14}\text{H}_{20}$ and Si_6H_6 which were not as readily located by our previous CGA. The new CGA is used to find the global minima for the even larger $\text{Si}_{18}\text{H}_{24}$ and $\text{Si}_{18}\text{H}_{22}$ clusters.

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1. Introduction

Nanometer sized Si particles have promising optoelectronic properties which could be useful in various technological applications. Since Si only clusters are highly unstable due to dangling bonds on the surface Si atoms a practical device will most likely be fabricated from silicon clusters whose surfaces are passivated by some chemically inert ligand. For these reasons we have been theoretically determining the globally optimized structures of Si_xH_y clusters where the H atoms serve as a prototypical passivating ligand. This structural information is difficult to obtain experimentally and is needed to correctly model the optoelectronic properties of Si nanoparticles. To find the global minimum structure of Si_xH_y clusters at the ab initio level we have recently developed a cluster genetic algorithm (CGA) strategy [1–3]. In our first procedure we used the AM1 semiempirical method [4] as a fast computational tool for prescreening the energy of the different Si_xH_y structures before performing the more demanding ab initio

calculations [1]. We soon realized that for an effective CGA we needed better energy prescreening than provided by AM1. This led us to develop a second approach where we used an iterative strategy involving both a parametrization genetic algorithm (PGA) and a cluster genetic algorithm (CGA) [2]. The PGA reparametrized the AM1 method against ab initio data to produce the GA-optimized AM1 (GAM1) parameters for a specific Si_xH_y stoichiometry [2]. We obtained two different GAM1 parameter sets for the Si_6H_2 and Si_6H_6 clusters which significantly improved the energy ranking ability of the semiempirical method. This iterative strategy enabled us to find the Si_6H_2 global minimum structure at the ab initio level and three nearby low energy local minima which closely resemble the Si_6H_6 ab initio global minimum. In Fig. 1, we show the Si_6H_6 ab initio 1(a) global minimum and two low energy structures obtained by the CGA: structure 1(b) is the lowest MP2 energy cluster we obtained and 1(c) is one of the low energy structures with the same Si_6 core as the ab initio 1(a) global minimum but with a different H atom arrangement.

Obtaining specific GAM1 parameters for each stoichiometry soon becomes very computationally demanding and the coupled PGA/CGA procedure is impractical

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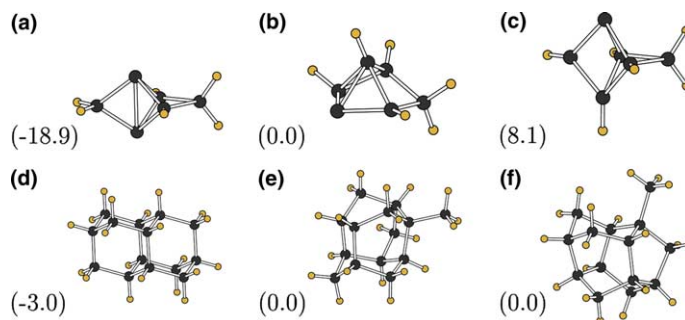


Fig. 1. The Si_6H_6 and $\text{Si}_{14}\text{H}_{20}$ low energy structures found in our earlier work. For Si_6H_6 : (a) MP2 global minimum, (b) the lowest MP2 energy cluster we obtained, and (c) one of the low energy structures from the CGA resembling (a) [2]. For $\text{Si}_{14}\text{H}_{20}$: (d) MP2 global minimum and (e) and (f) the two lowest MP2 energy structures found by the CGA [3]. The relative MP2 energies in kcal/mol for the different structures are given in parenthesis.

for Si_xH_y clusters with more than 10 Si atoms. Therefore, in our most recent work, we investigated under what conditions the GAM1 parameters from a small Si_xH_y cluster can be applied to a larger cluster so that only the CGA global search need be performed [3]. We choose Si_7H_{14} as the starting stoichiometry since it can adopt various possible structures which model a Si_7 core completely passivated by H atoms. We found that the GAM1 parameters obtained by fitting to the MP2 optimized structures and energies for a Si_7H_{14} training set were transferable to larger clusters such as the $\text{Si}_{14}\text{H}_{20}$ clusters providing there was a comparable level of H passivation. Calculations using the Si_7H_{14} GAM1 parameters and the MP2 method both rank the $\text{Si}_{10}\text{H}_{16}$ and $\text{Si}_{14}\text{H}_{20}$ clusters, where the fully H passivated Si core have bulk Si diamond-lattice like structures, as the global minima. We also found the Si_7H_{14} GAM1 parameters reproduced the MP2 energy ranking for stoichiometries corresponding to slightly lower levels of H passivation, such as in the $\text{Si}_{10}\text{H}_{14}$ and $\text{Si}_{14}\text{H}_{18}$ clusters, but the quality of the GAM1 energy ranking deteriorated for stoichiometries where the Si_x core is only partially H passivated [3].

In contrast to our initial work [1], the Si_7H_{14} GAM1 parameters now enabled the CGA to correctly identify the global minimum of $\text{Si}_{10}\text{H}_{16}$, $\text{Si}_{10}\text{H}_{14}$ and $\text{Si}_{14}\text{H}_{18}$ clusters [3]. Unfortunately, the CGA was still not able to find the 1(d) $\text{Si}_{14}\text{H}_{20}$ global minimum, and instead the lowest energy structures such as 1(e) and 1(f) shown in Fig. 1 were obtained. We take the diamond-lattice like structure to be the global minimum since the CGA never generated another $\text{Si}_{14}\text{H}_{20}$ structure which has a lower ab initio or GAM1 semiempirical energy. Many of the low energy $\text{Si}_{14}\text{H}_{20}$ structures found by the CGA, such as 1(e) and 1(f) closely resemble the 1(d) global minimum but have one of the SiH_2 units present in one of the six-membered Si rings moved to form a SiH_3 group on the cluster surface. The CGA is unable to rapidly find the $\text{Si}_{14}\text{H}_{20}$ global minimum because none of the three mating methods used in the CGA readily create off-

spring where the surface SiH_3 is recombined back into Si_{x-1} core. We have a similar problem due to the mating operations not generating different H atom arrangements while maintaining the same Si_6 core structure when we globally optimize the Si_6H_6 cluster.

Three different mating operators were used in our previous CGA [1–3]. The most important mating operator is the cut-and-paste method first proposed by Deaven and Ho [5] in a GA for global optimization of atomic clusters. The method cuts two parent clusters into halves along randomly orientated planes and recombines two halves from different parents into a offspring structure: a more fit offspring inherits desirable partial structures from the parents. The other two mating operators were really designed to cause mutations and introduce additional structural diversity into the cluster population. The coordinate averaging method takes the mathematical mean of the cartesian coordinates for two parent cluster geometries to produce cartesian coordinates of the offspring cluster. The fragment mixing operator replaces a fragment of the Si core from one parent structure by a Si fragment from the other parent and also replaces a fragment of the H shell of one parent structure by a fragment of the H shell from the other parent. Although both operators introduce structural diversity to the CGA they often result in unphysical starting cluster geometries which causes many of the local geometry optimizations to fail. The goal of this Letter is to describe four new mutation operators which replace the coordinate averaging and fragment mixing operators in our previous CGA. We show this new CGA is now able to find the global minima for Si_6H_6 and $\text{Si}_{14}\text{H}_{20}$. In addition, there is an overall reduction in the number of energy evaluations needed before finding the Si_xH_y global minimum with the new CGA.

In Section 2, we describe the new mating operators now utilized by the CGA along with other general computational details. The improved performance of the new CGA is presented in Section 3, and we also describe

testing the new CGA to globally optimize the larger $\text{Si}_{18}\text{H}_{24}$ and $\text{Si}_{18}\text{H}_{22}$ stoichiometries. Concluding remarks are given in Section 4.

2. Computation methods

We use the same basic CGA as used in our earlier work [3] but have modified the genetic operators which produce new offspring from the parent clusters. We keep our original cut-and-paste mating method and now add the four new mutation operations which are shown in Fig. 2. The first three of these operations can be thought of as analogues to the add/etch operations which Wolf and Landman [6] used in their global optimization studies of large Lennard–Jones clusters. The covalent bonding network ubiquitous to Si_xH_y clusters makes implementing the add/etch operations more difficult and requires that each Si atom be assigned a functional group identification which we simply determine through connectivity information obtained from the internuclear separation matrix. For each Si atom in a cluster we determine it to be connected to another either H or Si atom when their internuclear separations are less than 120% of the usual Si–H and Si–Si bond length (1.48 and 2.35 Å), respectively. Thus a SiH_3 group consists of a Si atom connected to 3 H atoms and a SiH_2 group has a Si atom connected to 2 H atoms.

The first new mutation operation, shown in Fig. 2, removes a peripheral SiH_3 group and replaces it with a single H atom and inserts a SiH_2 group between two randomly selected neighboring Si atoms to produce

either a longer Si chain or an expanded Si ring. The second mutation operation is just the reverse procedure of the first one: it removes a SiH_2 group from the cluster and then a randomly chosen H atom is replaced by a SiH_3 group. To reduce making a drastic geometry change the two Si atoms which were neighboring the SiH_2 group are pulled slightly towards each other to induce the formation of a new Si–Si bond. The third mutation operation is a H shift operator which simply shifts a H atom from one Si atom to another. It is only applied to clusters which contain incompletely passivated Si atoms as illustrated for the Si_6H_6 cluster in Fig. 2. The last operator, a piece-rotation mutation method, is a single-parent cut-and-paste operator and is similar to the operator used by Rata et al. [7] for the global optimization of Si-only clusters. The Si_xH_y clusters is randomly cut into two parts and then one-half of the cluster is randomly rotated relative to the other half. When applying the CGA to well H passivated Si_xH_y clusters we use the cut-and-paste, SiH_3 removal, SiH_2 removal and piece-rotation operators with equal probability; whereas in the global optimization of low-passivated Si clusters the cut-and-paste, piece-rotation and H-shift genetic operators are selected with 25%, 25% and 50% probabilities, respectively.

The global optimization starts from 120 randomly generated locally optimized structures as the ancestor population. The fitness value of an individual is taken as the absolute value of the GAM1 energy of the locally optimized cluster. Tournament selection is used to select the parents needed to produce offspring. The calculations are performed on either a 16 or a 32 processor

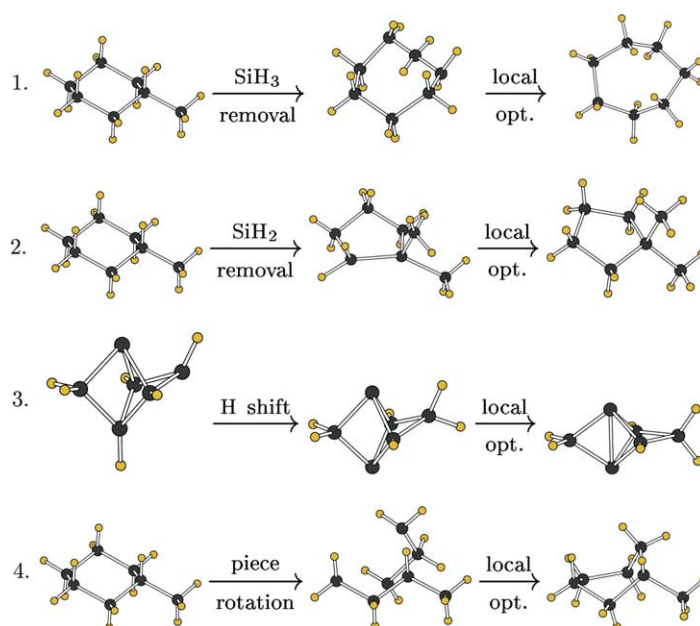


Fig. 2. Examples showing the four new mutation operators acting on a parent cluster to produce an offspring which is then locally optimized.

computer and as a consequence we do not explicitly treat separate generations. Usually in GA procedures which are run on a single processor, the offspring individuals are not produced until the fitness of all the individuals in the parent generation has been evaluated. In the present GA most of the computer time is spent locally optimizing cluster structures. Waiting for a complete generation of optimized individuals would cause several of the available processors to become idle owing to a wide range of convergence times for the different local optimizations. Therefore, instead of determining the fitness for the complete generation of individuals, we let the CGA running on multiple processors perform parent selection, the mating/mutation process and generate a new trial offspring structure as soon as the local geometry optimization of a parent cluster is finished on a processor. To avoid identical structures dominating the population new offspring which already exist in the current population are discarded. The clusters with lowest GAM1 energies obtained from CGA are locally optimized at the MP2 ab initio level.

All of the ab initio and semiempirical calculations were performed using the GAMESS program [8]. Since we are finding the global minimum of fairly large Si_xH_y clusters the ab initio calculations were performed with the MP2 method [9] and the LanL2dz(d) scheme consisting of the Hay–Wadt effective core potential (ECP) and valence basis set for Si [10] augmented with a d function ($\zeta = 0.45$) [11] and the Dunning–Hay basis for H [12]. For the completely H passivated Si_xH_y clusters new H and Si GAM1 parameters listed in Table 1 were derived using the same Si_7H_{14} training set and PGA described previously [3] but now fitted to the LanL2dz(d) ab initio

calculations. The Si GAM1 parameters for Si_6H_6 are also listed in Table 1 [2].

3. Results and discussion

We have repeated the CGA runs using both the new Si_7H_{14} GAM1 parameters and the new mutation operators to globally optimize the $\text{Si}_{10}\text{H}_{16}$, $\text{Si}_{10}\text{H}_{14}$, $\text{Si}_{14}\text{H}_{20}$ and $\text{Si}_{14}\text{H}_{18}$. We performed five CGA runs on each stoichiometry and obtained not only the same global minimum structures for the $\text{Si}_{10}\text{H}_{16}$, $\text{Si}_{10}\text{H}_{14}$ and $\text{Si}_{14}\text{H}_{18}$ stoichiometries as before, but the CGA now produces the diamond-like lattice structure as the GAM1 global minimum of the $\text{Si}_{14}\text{H}_{20}$ cluster. The final global minimum structures for each stoichiometry are illustrated in Fig. 3. To check that the semiempirical method correctly ranks the low energy structures we locally optimize the clusters with the 20 lowest GAM1 energies at the MP2/LanL2dz(d) level. So far none of these MP2/LanL2dz(d) local geometry optimizations have resulted in a cluster with an energy ranking significantly different from the GAM1 ranking. The new mutation methods dramatically improve the efficiency of the CGA. Originally it took 560 ± 242 , 1170 ± 1041 and 3170 ± 2826 local optimizations to locate the global minimum of the $\text{Si}_{10}\text{H}_{14}$, $\text{Si}_{10}\text{H}_{16}$ and $\text{Si}_{14}\text{H}_{18}$ clusters [3], in the new CGA these numbers drop to 438 ± 300 , 841 ± 241 and 1448 ± 518 , respectively. Most importantly, we located the diamond-lattice like $\text{Si}_{14}\text{H}_{20}$ structure as the GAM1 global minimum in three out of five CGA runs using only 3000 local optimizations whereas before the global minimum was not located in any of the three CGA runs where 9000 local optimizations were performed per CGA [3].

To explore the effectiveness of the H-shift mutation method, we performed five CGA runs to globally optimize the Si_6H_6 clusters using the Si_6H_6 GAM1 parameters. Each CGA was allowed to perform a maximum of 1000 local optimizations. The previous CGA found several low energy structures with the same Si_6 core as in the global minimum structure, but the new H-shift mutation method now enables us to also find the preferred H atom locations. The Si_6H_6 global minimum structure 1(a) was found in four of the CGA runs after only 142, 459, 776 and 950 local optimization.

To further test the new CGA we have applied it to the $\text{Si}_{18}\text{H}_{24}$ and $\text{Si}_{18}\text{H}_{22}$ clusters. We choose the $\text{Si}_{18}\text{H}_{24}$ cluster because it can adopt a global minimum corresponding to another diamond-lattice like structure shown in the Fig. 3. We performed five CGA runs utilizing 15000 local optimizations for both the $\text{Si}_{18}\text{H}_{24}$ and $\text{Si}_{18}\text{H}_{22}$ stoichiometries. Only one of the CGA runs, after 11280 local geometry optimizations, finds the $\text{Si}_{18}\text{H}_{24}$ diamond-lattice like structure which we take to be the GAM1 and MP2 global minimum. The four

Table 1
Si and H GAM1 parameters

Parameters	GAM1 ^a		GAM1 ^b
	H	Si	Si
U_{ss} (eV)	-11.356885	-33.723108	-32.918202
U_{pp} (eV)		-29.628321	-26.183913
ζ_s (a.u.)	1.049572	1.578831	1.685995
ζ_p (a.u.)		1.327590	1.300521
β_s (eV)	-5.900161	-3.716276	-3.282843
β_p (eV)		-1.893157	-3.040449
α (\AA^{-1})	2.751108	2.336323	2.141541
K_1	0.119580	0.231462	0.183072
K_2	0.005199	0.062800	0.114281
K_3	-0.017641	0.019162	0.021690
L_1	4.932948	9.739164	5.598440
L_2	5.089244	5.347795	6.848934
L_3	1.929803	4.490209	3.091319
M_1	1.028925	0.858012	0.919845
M_2	1.816682	1.885485	1.608310
M_3	2.452170	2.946521	8.058081

^a Si and H parameters for fully H passivated Si_xH_y clusters obtained from the Si_7H_{14} training set [3] and MP2/LanL2dz(d) calculations.

^b Si parameters from the Si_6H_6 training set [2].

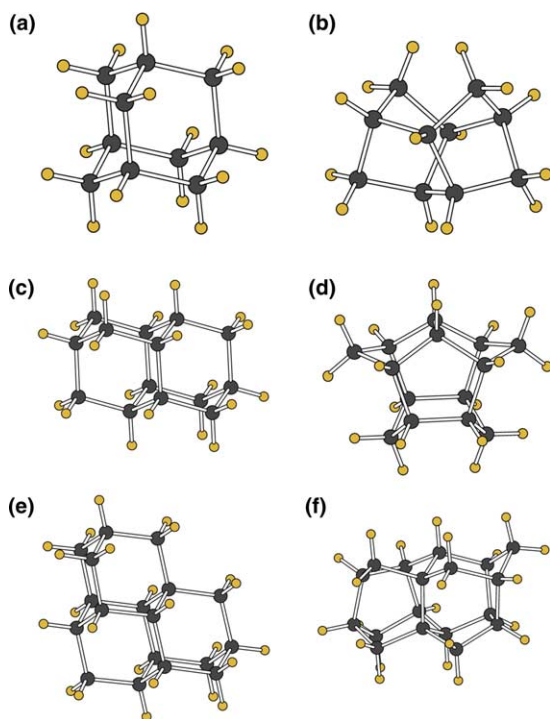


Fig. 3. The Si_xH_y MP2/LanL2dz(d) global minima: (a) $\text{Si}_{10}\text{H}_{16}$; (b) $\text{Si}_{10}\text{H}_{14}$; (c) $\text{Si}_{14}\text{H}_{20}$; (d) $\text{Si}_{14}\text{H}_{18}$; (e) $\text{Si}_{18}\text{H}_{24}$; (f) $\text{Si}_{18}\text{H}_{22}$.

other CGA runs find other $\text{Si}_{18}\text{H}_{24}$ structures which are 0.01, 1.0, 1.5 and 3.2 kcal/mol higher in GAM1 energy and which after MP2 local optimization, respectively, still have energies of 4.1, 5.5, 3.6 and 7.5 kcal/mol greater than the diamond-lattice like global minimum. Fig. 3 also shows the MP2 global minimum for $\text{Si}_{18}\text{H}_{22}$ which was obtained after 1599 local optimizations in one of the CGA runs. The $\text{Si}_{18}\text{H}_{22}$ MP2 global minimum is the second lowest GAM1 energy cluster, the GAM1 global minimum located in the other four CGA runs has a 0.4 kcal/mol lower GAM1 energy but a 2.0 kcal/mol higher MP2 energy. The disagreement of the MP2 and GAM1 predicted global minimum structures may be starting to indicate the limit of applicability range of the Si_7H_{14} GAM1 parameters in the global minimum search of larger Si_xH_y clusters. Fig. 3 shows that the slightly under H passivated $\text{Si}_{10}\text{H}_{14}$, $\text{Si}_{14}\text{H}_{18}$ and $\text{Si}_{18}\text{H}_{22}$ stoichiometries have global minima which do not show any obvious structural similarities. The $\text{Si}_{18}\text{H}_{22}$ global minimum does appear to retain more of the diamond-lattice like structure than in the smaller $\text{Si}_{14}\text{H}_{18}$ and $\text{Si}_{10}\text{H}_{14}$ clusters. Perhaps as expected, this suggests that in larger under H passivated Si clusters more of the bulk Si structure will be retained, but in the region of the cluster with incomplete H passivation there will be a structure corresponding essentially to a Si lattice defect. Unfortunately, the CGA global optimization procedure shows that the lattice defect structure in $\text{Si}_x\text{H}_{y-2}$ cannot be simply derived by removing two H atoms from the diamond-lattice like Si_xH_y global

minimum and then performing a local geometry optimization.

4. Conclusion

We have developed a faster cluster genetic algorithm (CGA) for finding the global minimum of Si_xH_y clusters. The key components to the CGA are the genetic operators. We continue to use the cut-and-paste mating operator to produce an offspring from two parent clusters. We also introduce four new mutation operators: SiH_3 removal, SiH_2 removal, H shift and piece rotation. These new operators better retain good structural information between different generations in the CGA thereby enabling a global minimum structure to be found with fewer cluster energy evaluations. The SiH_3 and SiH_2 removal operators facilitate the CGA correctly locating the diamond-lattice like $\text{Si}_{14}\text{H}_{20}$ structure as the global minimum. For the low H passivated clusters, the H shift operator better explores different H arrangements allowing the Si_6H_6 global minimum to be found.

The improved rate of finding the global minimum was further demonstrated by using the new CGA to find the global minima for the $\text{Si}_{18}\text{H}_{24}$ and $\text{Si}_{18}\text{H}_{22}$ clusters. One out of the five runs with the new CGA succeeds at finding the expected diamond-lattice like lowest energy structure for $\text{Si}_{18}\text{H}_{24}$ and we take this as the global minimum since the CGA produces no other structures with lower MP2 energy. What we take as the $\text{Si}_{18}\text{H}_{22}$ MP2 global minimum is the second highest energy GAM1 structure. The global minima structures for $\text{Si}_{18}\text{H}_{24}$ and $\text{Si}_{18}\text{H}_{22}$ are consistent with our previous results that if the Si_xH_y cluster is fully H passivated then the Si_x core forms a diamond-lattice like structure, while the Si_x core in $\text{Si}_x\text{H}_{y-2}$ is significantly different from the diamond-lattice structure. Consequently, the new CGA has the important utility of the being able to locate the distinct global minima of clusters like $\text{Si}_{18}\text{H}_{24}$ and $\text{Si}_{18}\text{H}_{22}$.

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