

Theoretical identification of the lowest energy Si_xL_y clusters using Genetic Algorithms

John D. Head¹ and Yingbin Ge²

Department of Chemistry,
University of Hawaii,
2545 The Mall,
Honolulu, Hawaii 96822, USA

Received 8 July, 2005

Abstract: An overview of a strategy for theoretically finding the lowest energy structure of Si_xL_y nanoclusters using a genetic algorithm will be presented. The ab initio global minima identified for various Si_xH_y and Si_xF_y clusters will be discussed.

Keywords: Global optimization, genetic algorithms, Si_xH_y clusters, Si_xF_y clusters, ab initio calculations, semiempirical calculations, electronic structure of silicon nanoclusters.

Mathematics Subject Classification: Here must be added the AMS-MOS or PACS Numbers

PACS: Here must be added the AMS-MOS or PACS Numbers

1 Introduction

Nanometer-sized silicon clusters are of considerable interest because they exhibit a novel bright photoluminescence which might eventually be developed into a practical optoelectronic device. Several groups have performed quantum mechanical calculations on different Si_xL_y clusters with assumed structures where L serves as a passivating ligand. One potential problem with the calculations is that experimentally it is very difficult to determine the geometry of an individual cluster or even if the cluster has the anticipated stoichiometry. In this presentation we will describe the strategy we have been developing using genetic algorithms (GA) to globally optimize Si_xL_y clusters [1, 2, 3, 4, 5] so that cluster structure responsible for the bright photoluminescence might be identified. The presentation will consist of three main parts. An overview of the computational strategy will be given first. This will be followed by a discussion of the structures we have obtained for Si_xH_y clusters. In a practical optoelectronic device, H is not going to be a very stable passivating ligands. The last part of the talk will describe our work on Si_xF_y clusters and how we plan to extend our calculations to clusters with more inert passivating ligands.

2 Computational Strategy

The cluster global minimum search (CGA) is performed using a genetic algorithm which works directly on the cartesian coordinates of the atoms composing the clusters. An initial population of typically 100 clusters is randomly generated and locally optimized. The fitter, lower energy,

¹Corresponding author. E-mail: johnh@hawaii.edu

²Current address: Ames Lab, Iowa State University, Ames, Iowa 50011, USA.

clusters are then mated to produce an offspring population of locally optimized structures. The CGA effectively lets good structural features present in a cluster to be passed onto succeeding generations until the global minimum is found. In our initial approach we used the Deaven and Ho cut-and-paste mating method [6] along with some other relatively simple coordinate averaging mating operations [1, 2, 3]. The Deaven and Ho operator is a crossover method which cuts two parent clusters into halves along randomly orientated planes and recombines two halves from different parents into an offspring structure. The Deaven and Ho operator facilitates selecting low energy features present in an existing cluster structure whereas our coordinate averaging mating operations were intended to produce new structural features and enhance the diversity of the overall population.

While this initial CGA could find low energy and presumably the ab initio global minimum for various Si_xH_y clusters it was not able to find the $\text{Si}_{14}\text{H}_{20}$ global minimum [3]. Eventually we realized this was because our initial mating operators did not readily produce structures where a SiH_2 unit might be shifted between different parts of a cluster. This led to the development of a second CGA which in addition to Deaven and Ho cut-and-paste operator uses the new mating operators shown in figure 1 [4].

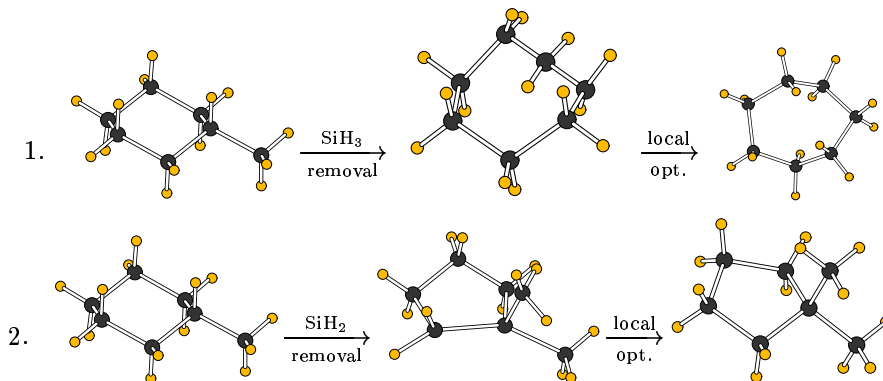


Figure 1: Examples illustrating two of the new mutation operators used in the cluster GA which act on a parent cluster to produce an offspring which is then locally optimized [4].

The CGA clearly requires a very large number of cluster energy calculations. After consideration of a number of fast energy methods we selected the AM1 semiempirical procedure for prescreening the relative energies of the Si_xH_y clusters prior to performing any ab initio calculations [1]. The AM1 method has a Hartree-Fock basis and has the capability to track the different type of bonding situations which might occur as the Si_x cluster core is surrounded by greater numbers of ligands L. For instance, since it was not clear how many H atoms might be needed to passivate the Si core, when there are excess H atoms the AM1 calculation automatically allows H₂ loss and the resulting $\text{Si}_x\text{H}_{y-2}$ cluster is globally optimized.

Although the AM1 method proved to be a useful fast energy method we soon found that the AM1 ranking of the various possible cluster structures differed significantly from the ab initio ranking. This led us to the idea of reoptimizing the AM1 parameters using data obtained from ab initio calculations on several low energy Si_xH_y clusters [2, 3]. As described below, the resulting GAM1 parameters produced cluster energy rankings more consistent with the ab initio calculations thereby facilitating a more reliable search for the Si_xH_y global minimum.

3 Global minima for Si_xH_y clusters

The initial CGA strategy enabled us to find low energy cluster structures at the ab initio level for both low and fully H passivated silicon clusters [1]. The CGA successfully found cluster global minima for the AM1 parameters but these were significantly different to the ab initio global minima which we expect to agree better with chemical reality. For instance, the ab initio $\text{Si}_{10}\text{H}_{16}$ global minimum was the tenth lowest AM1 energy structure. Using the GAM1 method, where the the AM1 parameters were reoptimized using a Si_7H_{14} training set, greatly improved the cluster structure energy prescreening with semiempirical calculations [3]. The same $\text{Si}_{10}\text{H}_{16}$ global minimum structure was obtained by both the GAM1 and ab initio calculations. Coupling GAM1 energy prescreening with the revised CGA operators in figure 1 lead to finding the global minima shown in figure 2.

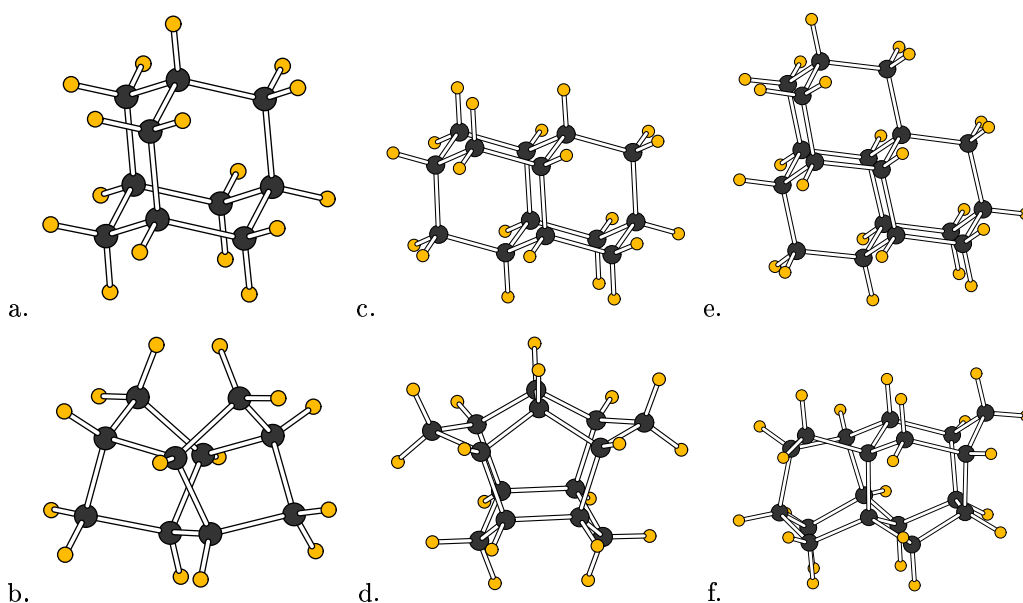


Figure 2: *Ab initio* global minima determined for: (a) $\text{Si}_{10}\text{H}_{16}$, (b) $\text{Si}_{10}\text{H}_{14}$, (c) $\text{Si}_{14}\text{H}_{20}$, (d) $\text{Si}_{14}\text{H}_{18}$, (e) $\text{Si}_{18}\text{H}_{24}$ and (f) $\text{Si}_{18}\text{H}_{22}$ [4].

The Si_xH_y global minima we have obtained so far suggest that the low H passivated clusters, such as Si_6H_2 , Si_6H_6 and Si_{10}H_y , $y = 4, 8$ favor forming structures with compact Si cores somewhat analogous to elemental Si clusters where many of the Si atoms cannot achieve tetrahedral coordination [1]. For the higher H passivated we obtain global minimum of the type shown in figure 2. When there are enough H atoms, as with the $\text{Si}_{10}\text{H}_{16}$, $\text{Si}_{14}\text{H}_{20}$ and $\text{Si}_{18}\text{H}_{24}$ stoichiometries the Si core does favor forming a fragment of the bulk Si diamond lattice. However, for the slightly under passivated clusters $\text{Si}_{10}\text{H}_{14}$, $\text{Si}_{14}\text{H}_{18}$ and $\text{Si}_{18}\text{H}_{22}$ the global minima are more difficult to predict by using chemical intuition alone. Figure 2 shows that the $\text{Si}_{10}\text{H}_{14}$, $\text{Si}_{14}\text{H}_{18}$ and $\text{Si}_{18}\text{H}_{22}$ global minima do not have 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. One important conclusion from these studies is that the lowest energy distorted lattice structure in $\text{Si}_x\text{H}_{y-2}$ cannot be simply computed by removing two H atoms from the diamond-lattice like Si_xH_y global minimum and then performing a local geometry optimization.

4 Extending the Si_xL_y GM search to other ligands

Air inert Si nanoclusters for use in a real world optoelectronic device will require some other passivating ligand besides H. One of difficulties of going beyond H as the ligand L is that the semiempirical energy prescreening calculation becomes much slower. In the presentation we will describe our progress at developing faster prescreening methods for the heavier and more chemically inert ligands. Improved prescreening is clearly important as indicated by our preliminary calculations, illustrated in figure 3, which show that the global minima for Si_xF_y have structures very different to the corresponding Si_xH_y global minimum [5]. It appears the H atoms in low-energy well H-passivated Si clusters prefer to be fairly evenly distributed over the Si_x core enabling five- and six-membered Si rings to be formed. In contrast, the low-energy well F-passivated clusters like to form structures containing one or more trifluorosilyl groups at the expense of forming highly strained four- and even three-membered Si rings.

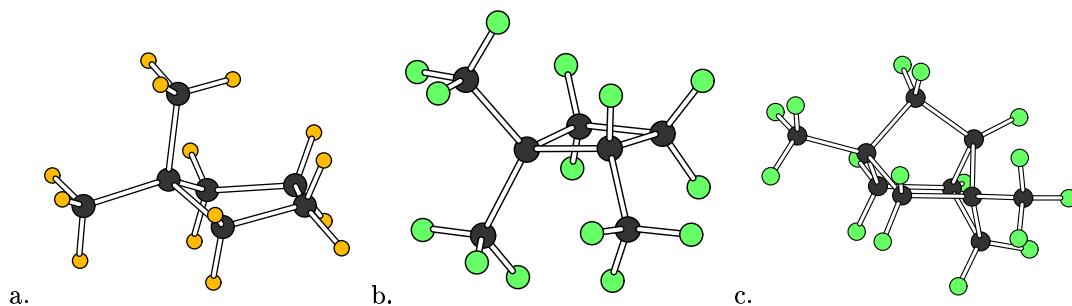


Figure 3: Example B3LYP Si_xF_y global minima: (a) Si_7H_{14} , (b) Si_7F_{14} and (c) $\text{Si}_{10}\text{F}_{16}$ [5].

Acknowledgment

We are grateful for the generous supply of computer time provided by the Maui High Performance Computing Center.

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