Tight-Binding Calculations of Si-H Clusters Using Genetic Algorithms and Related Techniques: Studies Using Differential Evolution

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A nonorthogonal tight-binding model has been developed for the system containing Si and H, where the energy functional included the contributions of both electronic and pairwise interaction between the atoms. In order to calculate the ground state structures of various clusters, energy minimization was carried out using Differential Evolution: a very recently developed biologically inspired computing technique, belonging, in general, to the family of Genetic Algorithms (GAs), but having a number of advantages over its conventional forms.

1. Introduction

Recent successes of calculating the structures of large carbon molecules[1–3] and various Si[3,4] and Si-H clusters,[5,6] by coupling the biologically inspired Genetic Algorithms (GAs)[7,8] with a tight-binding formulation[9] indeed have a far reaching consequence in the computational phase equilibria research. Tight-binding methodology has drastically simplified some of the computationally cumbersome features of the first principle *ab initio* formulation,[10] keeping its basic rigor intact—at least from the point of view of material design. Genetic Algorithms, on the other hand, have rendered the search for the ground state energy minimum a thorough and efficient process, showing an edge over a number of other techniques[11] that were used for such calculations in the past, making it worthy of further exploration.

The type of GAs that have been used in these studies is known as Simple Genetic Algorithms (SGA), which, by no means, is entirely free from shortcomings. Like all evolutionary computing techniques, SGA tends to mimic the basic processes of natural biology, and in order to do that, it requires mapping of all the system variables in a binary format. In the case of a large number of variables, this amounts to manipulating lengthy arrays containing 1’s and 0’s, often slowing down the computation to an unacceptable limit. Furthermore, binary arithmetic has an implicit disadvantage called the Hamming Cliff problem,[12] which often adversely affects the performance of SGA. In a Hamming Cliff situation, any small change in the real space requires a very large change in the corresponding binary, decelerating the progress of the solution and often making fine convergence impossible in a near optimal scenario.

Such problems can be easily overcome, if instead of a binary equivalent the genetic operations can be performed on the real-coded variables themselves. This has been successfully done in the recently proposed differential evolution (DE),[13] which is becoming increasingly popular in solving scientific problems of various disciplines,[14,15] but, to the best of our knowledge, has not yet been tested for any materials-related problems. In this study, we have successfully tested DE for calculating the ground state structures of a number of Si-H clusters. The system was chosen because hydrogenated amorphous silicon is a highly promising optoelectronic material and, during its formation through glow discharge of silane (SiH_4) gas, various assemblages of silicon and hydrogen are known to play a very important role.[16]

A brief overview of DE is provided below, since it is a newer concept and the materials community at large may not be familiar with some of its intricate features.

2. DE Fundamentals

Like its predecessor SGA, DE can also be used for optimizing any function with a number of constraints. Being an evolutionary optimization technique, DE works with a *population*, resorts to *natural selection*, based upon the *fitness* of its *individuals* and creates a new, and hopefully improved, *generation* by doing *crossover* and *mutation*. All these concepts have been explained in some earlier publications[5,17,18] in the context of SGA and are not repeated here. We, however, need to redefine all those operations here, because DE, unlike SGA, is a real-coded algorithm requiring no binary mapping of the variables, for which most of these operations are done in a different way.

In order to maximize a function $f(\mathbf{X})$, where $\mathbf{X}$ denotes the real coded variable vector $[x_1, x_2, \ldots x_n]$, DE resorts to the following procedure:

1. A random initial population is generated as in SGA. Each individual of the population is an array of all the n variables, and, unlike SGA, their real values are directly used.
2. Next, an individual $\Im_1$ is randomly picked up for mutation. Two additional random members of the population, $\Im_2$

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and $\Im_3$, are used for this purpose and the mutated vector $\Im_\mu$ is formed as

$$\Im_\mu = \Im_1 - \gamma(\Im_2 - \Im_3) \qquad \text{(Eq 1)}$$

where γ is the user-supplied mutation constant.[1]

3. The mutated vector is now crossed over with another random member of the population $\Im_4$. Here, the crossover operation involves swapping the variables between $\Im_4$ and $\Im_\mu$ probabilistically. Like SGA, a user supplied crossover probability is used for this purpose. In DE, it is always ensured that the offspring produced by the crossover operation, the so-called trial vector, inherits at least one variable from the mutated vector.
4. The fitness of the trial vector is then compared with $\Im_4$.[2] If the trial vector has a better fitness, it is selected for the next generation; otherwise, $\Im_4$ is selected instead.
5. This process is repeated until all the slots in the population are filled. The next generation thus formed is again subjected to the genetic operations described above. Calculations usually continue until a user-specified convergence criterion is met, or for some preassigned number of generations.

Like our previous work,[5] here, the fitness value was taken as the negative of the energy functional. The computational task of the DE algorithm was to locate the atomic coordinates corresponding to the minimum energy value. The tight-binding formulation provided the description of energy in this case. Further details are provided below.

3. Modeling of Energy Functional Using a Nonorthogonal Tight-Binding Approximation

The tight binding approximation is now very widely used for studying covalently bonded material. It assumes that the system consists of ionic cores and electron gas and tends to calculate the total energy functional for the entire system (E^{total}) by summing up the one particle eigenvalues and the individual pair potential terms, such that

$$E^{\text{total}} = U_0 + E^{el} + E^{\text{pair}} \qquad \text{(Eq 2)}$$

where the constant U_0 shifts the cohesive energy as needed, E^{el} denotes the energy associated with the occupied eigenvalues of the electronic system, and E^{pair} is the sum of pair potential terms arising due to repulsion between the ionic cores.

Denoting the occupancy of the kth eigenstate as g_k and N^{occ} as the number of occupied orbitals, the electronic contribution to the total energy is expressed as

$$E^{el} = \sum_{k=1}^{N^{\text{occ}}} g_k \varepsilon_k \qquad \text{(Eq 3)}$$

Furthermore, summing up the pair potential terms related to repulsion between the ionic cores, E^{pair} is obtained as

$$E^{\text{pair}} = \sum_{i<j} \chi(r_{ij}) \qquad \text{(Eq 4)}$$

Using this basic definition for total energy, the wave functions of these eigenstates are given in terms of nonorthogonal basis as

$$|\psi_n\rangle = \sum_i C_i^n \cdot |\phi^i\rangle \qquad \text{(Eq 5)}$$

where the $|\phi^i\rangle$ values are the basis functions. In the nonorthogonal tight binding theory employed here, the basis functions are localized on each atom resembling its atomic orbital, and spherical harmonic functions (Y_{lm}) are used to describe their angular parts. The characteristic equation is then expressed as

$$\sum_i (H_{ij} - \varepsilon_{ij} S_{ij}) C_j^{ij} = 0 \qquad \text{(Eq 6)}$$

where H_{ij} denotes the Hamiltonian matrix elements between the ith and jth orbitals, such that

$$H_{ij} = \langle \phi^i | H | \phi^j \rangle \qquad \text{(Eq 7)}$$

The overlap matrix elements between them are expressed as

$$S_{ij} = \langle \phi^i \| \phi^j \rangle \qquad \text{(Eq 8)}$$

Further details of calculating the Hamiltonian and the overlap elements are provided elsewhere.[19,20]

4. Computational

A Cartesian coordinate system was adopted in this case for simplicity, and a DE-based search was conducted for the atomic coordinates of the ground state structure, in a cubic search space of 5 Å each side. Out of the infinite atomic arrangements possible in this solution domain, the task of DE was to locate the one corresponding to the ground state with minimum energy, which it could perform quite satisfactorily. During this study, we have written our own DE code based upon the prescriptions available in the literature,[13] which was also tested in other problems.[17,21] A population size of 10 times the number of variables appeared to be adequate in most cases, and a scheme for adjusting the mutation constant and crossover probability was evolved through systematic trial and error. For a number of clusters, DE reached the near-optimal range rather quickly compared to the SGA-based studies performed before.[5] The effect was more pronounced in some of the larger clusters; Si_6H, for example, was computed within just 350 generations. In general, however, a few hundred to over a thousand generations

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[1] The readers familiar with Evolutionary Algorithms will immediately realize that here the mutation is *self adjusting* in nature, because the second term in Eq 1 tends to become smaller as the population proceeds toward convergence.

[2] DE defines fitness in the same fashion as SGA, which has been detailed in Ref 2.

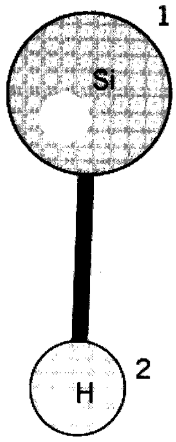

Fig. 1 The ground state structure of SiH cluster

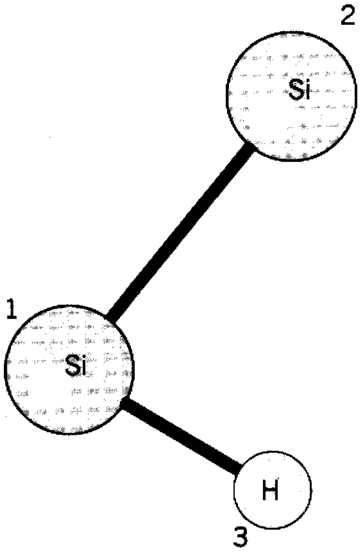

Fig. 2 The ground state structure of Si_2H cluster

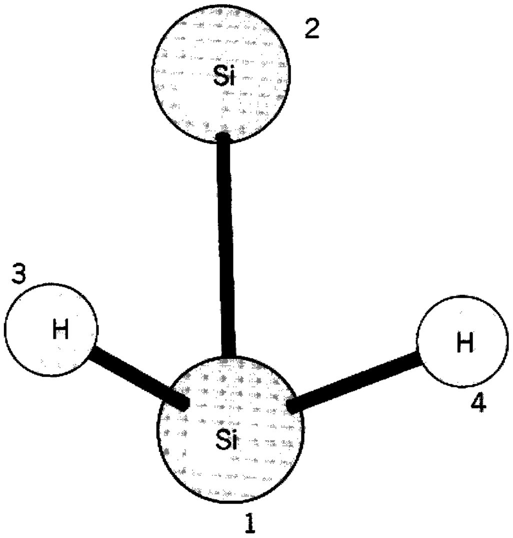

Fig. 3 The ground state structure of Si_2H_2 cluster

were necessary to resolve a structure, and, often, the computation for larger assemblages took a lesser amount of time compared to some of the smaller assemblages.

All the calculations were performed in a local area network of a number of Silicon Graphics (Mountain View, CA) workstations of SG 200 Origin series.

5. Results and Discussions

A total of 12 clusters were calculated during this study. Further details of each of them are provided below.

Si-H: This simplest possible configuration (Fig. 1) readily yielded to DE computations, resulting in a cohesive energy of −2.97 eV and a bond length of 1.52 Å, which, as expected, are suggestive of a typical covalent coupling.

Si_2H: Like the previous studies using simulated annealing (SA)[19,20] and SGA,[5] the present calculations using DE have also determined this structure as an asymmetric planar structure (Fig. 2) with the hydrogen atom located closer to one silicon atom than the other. The ground state cohesive energy is determined as −6.56 eV, that is, very similar to the values obtained in earlier calculations.[5,19,20] Although the cohesive energy calculated through DE is actually identical to what was obtained earlier through SGA,[5] the bond lengths are now slightly altered. Here, the two Si-H bond lengths are calculated as 1.62 and 2.12 Å, respectively, as against 1.51 and 2.71 Å calculated through SGA. The Si-Si bond length is now calculated as 2.33 Å, which was earlier determined as 2.34 Å.[5] Because of its high asymmetry, calculation of this structure was a bit cumbersome. We needed to run our DE code for about 400 generations to obtain complete convergence.

Si_2H_2: In Si_2H_2 (Fig. 3), the two silicon atoms are bound to each other with their bond length comparable to that in Si_2H. This is a symmetrical structure where both the hydrogen atoms are bonded strongly to a silicon atom as mirror images of each other. The Si-H bond length is calculated as 1.54 Å. The calculated value of cohesive energy is 10.14 eV, which is in excellent agreement with the earlier work.[19,20]

The DE was able to resolve this structure approximately within 500 generations, and, in fact, a near-optimal situation was reached much earlier. A variable mutation constant between 0.02 and 0.3 and variable crossover probability between 0.5 and 0.9 were judiciously used over a population size of 120. The mechanisms of probability variation were evolved through a systematic trial and error.

Si_2H_3: Although the structure calculated by DE (Fig. 4) is qualitatively similar to what was obtained by SGA and SA,[5,19,20] by some quarks of computing, the DE predicted the cohesive energy as −7.04 eV, as opposed to the −12.87 eV computed earlier. In fact, this is the only case where DE failed to reach the correct convergence and performed in an inferior way compared to both SGA and SA. We ran the code for about 900 generations varying the mutation constant between 0.0001 and 0.2 and the crossover probability between 0.5 and 0.99, and decided not to proceed further. The reasons for the poor performance of DE in this case are not clearly understood. However, it can be taken as a very rare exception rather than a rule, and we left the matter at that.

Si_2H_4: With just an additional hydrogen atom, DE, however,

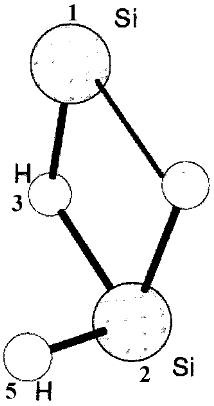

Fig. 4 The ground state structure of Si_2H_3 cluster

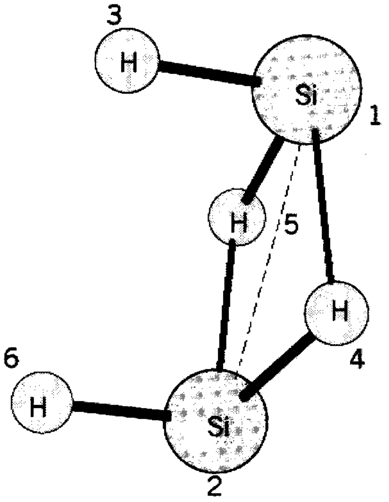

Fig. 5 The ground state structure of Si_2H_4 cluster

produced a structure energetically superior to the structures obtained through both SA and SGA.[5,19–20] The structure shown in Fig. 5 corresponds to a cohesive energy of −17.02 eV, where the values computed through SA and SGA were −16.93 and −17.01 eV, respectively. The structure looks similar to what has been obtained through SGA,[5] but in variance with the structure determined through SA.[19,20] Here, the hydrogen atoms 3 and 6 (Fig. 5) are located at the same side of the corresponding silicon atoms at a distance of 1.5 Å, while the SA calculations had predicted them to be at the opposite sides of the Si-Si axis. The remaining two hydrogen atoms (4 and 5) are symmetrically bonded with the Si atoms; the bond lengths are of the order of 1.8 Å.

To ensure stability of the structure, we ran the calculations for about 1300 generations. A mutation constant of 0.2 was mostly used along with a crossover probability of 0.8.

SiH_2: This small cluster is essentially planar and highly symmetrical (Fig. 6). Its cohesive energy was calculated as −7.04 eV, irrespective of the technique used. The DE was able to resolve its structure well within 400 generations, using a mutation constant of 0.4 and a crossover probability of 0.8.

SiH_3: This is a simple pyramidal structure (Fig. 7). The distance between the Si and H atoms is approximately 1.5 Å, resembling the covalent bond length. The DE was able to predict this structure within approximately 550 generations. The mutation constant was varied between 0.001 and 0.25, while the probability of crossover was varied between 0.5 and 0.9. The cohesive energy of this structure was calculated as −8.90 eV, which was in excellent agreement with the earlier predictions.[5,19,20]

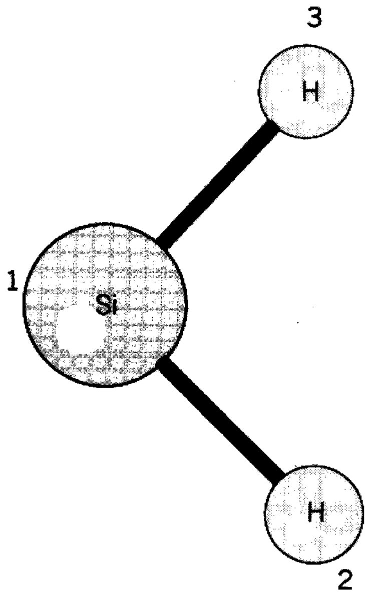

Fig. 6 The ground state structure of SiH_2 cluster

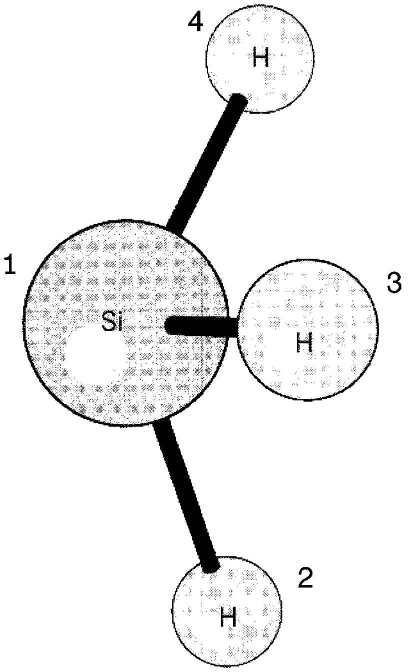

Fig. 7 The ground state structure of SiH_3 cluster

SiH_4: This is the only cluster in the present investigation here that exists independently as a molecule. The highly symmetrical silane structure (Fig. 8) was resolved through GA after running the code for 750 generations with a varying mutation constant between 0.001 and 0.2, along with a variable crossover probability between 0.5 and 0.99. In this study, the

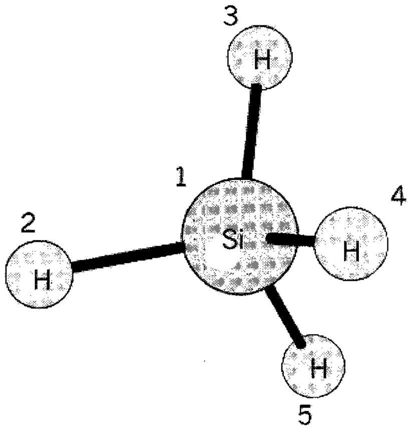

Fig. 8 The ground state structure of SiH_4 cluster

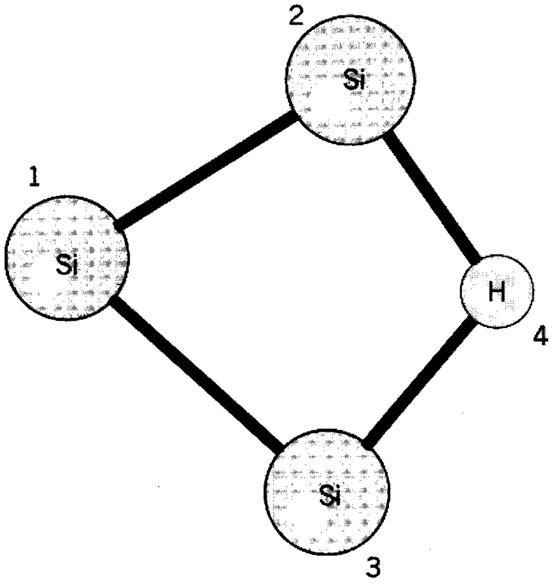

Fig. 9 The ground state structure of Si_3H cluster

cohesive energy was calculated as −13.42 eV, as compared to −13.41 eV predicted earlier both through SGA and SA,[5,19,20] leading to a slightly more stable configuration.

Si_3H: In the Si_3H structure (Fig. 9), the Si atoms 1 and 2 are situated symmetrically with respect to the third. The lone hydrogen atom is situated equidistantly from the Si atoms 1 and 2. It is a planar structure with Si-H bond distance being of the order of 1.8 Å, which is greater than that existing in the SiH cluster. The DE determined the cohesive energy of the ground state structure as −10.61 eV, which is well in accord with the earlier predictions.[5,19,20] We ran our DE calculation with a mutation constant of 0.25 and a crossover probability of 0.8 for approximately 100 generations for obtaining this structure.

Si_4H: The ground state structure of this cluster (Fig. 10) is quite similar to that of Si_4 reported earlier.[22] The presence of hydrogen causes some distortion in the structure, retaining however the essential geometric features of Si_4. We ran the DE calculations for it for about 2000 generations with a mutation constant 0.3 and a crossover probability of 0.8. The cohesive energy for the ground state structure was calculated as −14.81 eV, based upon the earlier findings,[5,19,20] which appears to be quite acceptable.

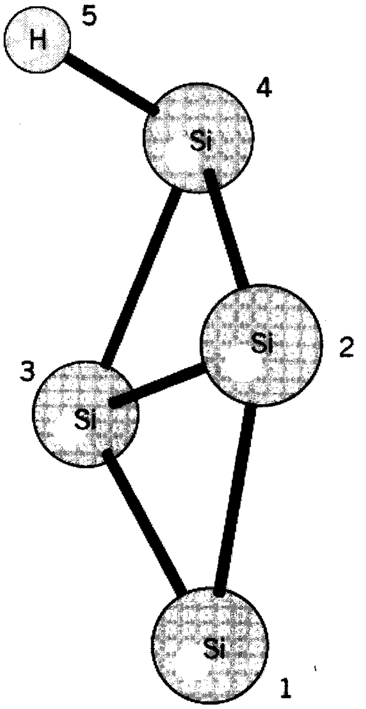

Fig. 10 The ground state structure of Si_4H cluster

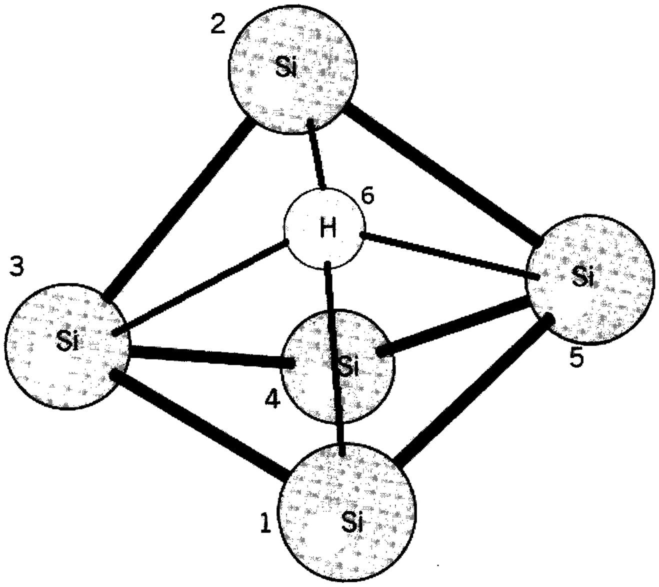

Fig. 11 The ground state structure of Si_5H cluster

Si_5H: The ground state structure of Si_5H is shown in Fig. 11. Here, the three Si atoms 3, 4, and 5 are situated on the same plane as the lone hydrogen atom. The structure is symmetric along this plane with Si atoms 1 and 2 symmetrically placed on the two sides of it. This structure is quite deviant from the reported structure of Si_5,[22] and, in fact, it is more like the reported structure of Si_6.[22] The hydrogen therefore causes a very large distortion to the Si_5 structure, which was also observed in the earlier studies.[5,19,20] The cohesive energy

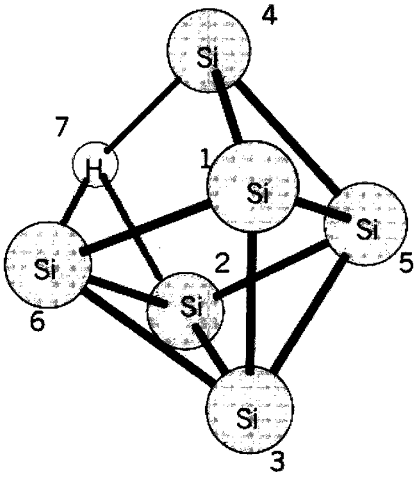

Fig. 12 The ground state structure of Si_6H cluster

was calculated as −23.90 eV, and, with variable mutation constants within 0.1 and 0.3 and the corresponding crossover probabilities between 0.5 and 0.85, DE was able to obtain this relatively large structure just within 600 generations.

Si_6H: This relatively large cluster was very efficiently resolved by DE. The ground state configuration shown in Fig. 12 was obtained just within 350 generations with a mutation constant of 0.2 and a crossover probability of 0.9. The cohesive energy was calculated as −23.90 eV, which is identical to what was obtained through SA[19,20] and better than the prediction through SGA.[23]

The ground state structure of Si_6H appears to be a slightly distorted bicapped tetrahedron. The distortion is caused by the presence of hydrogen in the lattice, which shifts the Si atoms in its immediate neighborhood.

In general, we have observed in this study and also in its predecessors[5,6,19,20,23] that even a lone hydrogen atom can very significantly alter the geometry of silicon cluster. A close examination of the hydrogenated clusters studied here shows that the hydrogen atoms tend to occupy positions either outside or at the surface of the clusters. In no case was hydrogen found to reside inside the clusters. This appears to be quite interesting; however, how far this can be generalized is still an open question. Hydrogen also seems to form multicentered bonds with two or more Si atoms, where it is not strongly attached to any particular one of them. The Si-H bonding distances in these cases generally varied between 1.5 and 1.8 Å. Such findings may have a far-reaching consequence in material selection for the opto-electronic devices such as light sensors, thin film transistors, light emitting diodes, *etc.*, where hydrogenated amorphous silicon is currently emerging to be a strong candidate.[16]

6. Concluding Remarks

This study has conclusively shown that the recently developed DE[13] can be very efficiently used for determining the ground state configurations of a large number of hydrogenated silicon clusters. The success of a DE usage demonstrated here could be of immense significance to the computational materials scientists at large, as this technique can be easily tried out for a large number of hitherto unsolved problems. The new vista of materials research opened through the recent applications of GA in materials problems[1–5,24] can now be further enriched through the adoption of DE, and being a highly efficient optimizer, its increasing presence in phase equilibria and other related research is expected to be seen in the very near future.

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