

Structural and electronic properties of small silicon clusters

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Abstract. The atomic structure and electronic spectrum of silicon nanoclusters (Si-ncs) Si₇, Si₁₀, Si₁₀H₁₆ and Si₁₀H₂₀ are calculated using the evolutionary algorithm with total energy computed within density functional theory and generalized gradient approximation (DFT-GGA). When analysing the low-energy structures, we pay significant attention to their symmetry and interatomic bond geometry. The candidate structures arising in the process of evolutionary algorithm convergence are also considered and classified by their topology and grouping near local energy minima. Possible ways to improve the convergence of evolutionary computation are discussed. Addressing qualitative criteria for the ground-state atomic structure of Si-ncs, we consider correlations between the density of electronic states and the total energetics of clusters in the ground state and low-energy-isomer configurations.

1. Introduction

It is well known that due to reduced dimensionality, nanoclusters demonstrate properties essentially different from those of bulk material. These differences, often very unusual, underlie a vast area of applications, both existing and potential. This area covers optics, nanoelectronics, nanophotonics, solar energetics, biology and medicine [1, 2, 3]. For example, silicon nanoclusters (Si-ncs), which are the point of interest in this article, show bright visible photoluminescence [4], whereas in bulk silicon the radiative transitions are suppressed due to indirect band gap.

The origins of these differences lie in the quantum confinement and the significant surface effects. The share of surface atoms grows as the cluster size decreases. Being on the surface, an atom forms less bonds compared to the 'inner' atoms. In turn, this affects the contribution of the atom to the total energy. Moreover, if a cluster is small enough (~ 1 nm), the distinction between core and shell atoms becomes vague. So, when trying to make any conclusions regarding the cluster characteristics, one has to take into account its exact atomic structure.

The existing structural analysis technique has been developed aimed mostly to analyse crystal lattice. Therefore, when it comes to nanoscale objects, the experimental structure determining faces several difficulties [5]. The structures of very small clusters can be obtained using indirect methods such as DFT analysis of IR multiple-photon dissociation spectra, allowing to reconstruct structures for $N \leq 10$ (N is a number of atoms) [6]. Yet, in general, the experimental data on



cluster structures are rather scarce. Thus, at the present time theoretical predictions grow in importance.

The structure prediction is clearly an attractive field for many theorists. Not only for the prediction itself, but also because it implies methods of new materials design. At the dawn of the global structure optimization studies, the unbiased *ab initio* global minimum search seemed unrealizable [7]. So, different researches compared the energies of structures, that were built either with application of predetermined symmetries [8], or using 'cutting' from the bulk lattice, or applying some other tricks. In any case, these techniques contained prescriptions concerning the structure sought. With increasing computer performance many promising computational methods emerged, which involved direct energy calculation. Of course, they are not strictly unbiased, because otherwise they are reduced to random search. First of all, the dimensionality of search space ($d = 3N + 3$, where N is the number of atoms per unit cell for crystals, or $d = 3N$ for clusters) is reduced because these algorithms operate not with all possible atomic positions, but on the manifold of locally optimized (relaxed) structures. Even the random search method, combined with local optimization delivers correct solutions – though for small systems ($N < 8 - 10$) [9]. And second, these methods rule out absurd structures in advance, such as those with two atoms on the same spot. Except for these two points, these methods contained no other mandatory constraints. The advanced methods include simulated annealing [10], basin hopping [11], minima hopping [12], metadynamics [13] and evolutionary algorithms [14]. Many of these methods rely on the fact that low energy structures share some similarities i.e. they are close to each other in configurational space. This assumption, used by chemists for a long time, is now proved right for many real systems [15].

In this article we study geometry and electronic structure of small bare silicon and hydrogen passivated silicon nanoclusters. This choice was dictated by several reasons. First, as is mentioned above, silicon clusters exhibit properties that can be useful for future technological applications. Second, their structures are simple enough to study them systematically by means of *ab initio* methods. And third, despite the simplicity we can trace trends of cluster forming and reveal correlations between electronic and atomic structures. For the global structure optimization we chose the evolutionary algorithm as implemented in USPEX code. A set of blind tests showed this method to be one of the most effective [16]. Using topology analysis and intermediate evaluations of evolutionary algorithm we investigate cluster isomerism. Comparing isomers for several atomic compositions we explore dependence of electronic structure details on number and locations of atoms.

2. Methods

The problem of structure optimization is mathematically formulated as the search for the global minimum on a very irregular multidimensional surface determined by potential energy (potential energy surface, PES). Of course, there's no general recipe to solve this problem. All of the global optimization tools are essentially heuristic. The practice, however, shows that situation is more optimistic. Among others mentioned above, USPEX code developed by Oganov's group, shows very good results in structure prediction of crystalline materials, molecular crystals, clusters and surfaces [14, 21].

The underlying evolutionary algorithm of the USPEX code is based on the principles of natural selection. By applying evolutionary operations to the generations of structures and ruling out the least fit ones, we progressively obtain better and better species. The algorithm consecutive steps can be shortly described as follows. The first step is the choice of an adequate representation of the problem, i.e. a one-to-one correspondence between a point in the search space and a set of numbers. Then goes the initialization of the first generation – a set of points in the search space which satisfy some constraints. After that, the algorithm determines the fitness of each member of the population and chooses some of them as parents of the next generation.

These parents undergo specially designed evolution operators that produce offspring. The next generation is evaluated and the procedure of new generation creation and evolution repeats. This loop is stopped once some halting criteria are achieved.

We would like to emphasize the importance of step 1 – the representation choice. The mathematical representation of the species, the evolution operators and the fitness of the species are basically what distinguishes one evolutionary algorithm from another. Unlike standard use of binary strings in genetic algorithms, the USPEX code has physically meaningful representation of both objects and operators. The code uses real numbers for the lattice vectors and atomic positions representation. On the one hand it increases the difficulty of the problem, but on the other hand it allows to construct physically meaningful evolution operators.

The evolutionary operators in USPEX can be divided into two major groups: heredity, that uses a few parent solutions to product one offspring solution, and mutation, where a single parent is used to build a single child. Heredity operators are the essential part of any evolutionary algorithm. They allow to utilize the information gathered during algorithm execution. Since the properties of the crystal are determined by the arrangement of atoms, the most physically meaningful way to implement heredity is to use a combination of pieces cut from two or more parent structures. In this case, the lattice of the child is in some way the average of its parent structures. As for mutation, here we have the diversity of operations including atomic permutation, random distortion, soft-mode mutation, etc.

Once the code has generated another set of the offspring structures, each structure is tested for correspondence with a number of constraints, and if it satisfies all of them, it undergoes a local optimization procedure. Constraints provide the feasibility of candidate structures, and include the following conditions. First, the distance between atoms cannot be less than some user-defined limit. Second, no lattice vector could be shorter than some threshold length, determined by e.g. the biggest atomic diameter. The third condition concerns the angles between lattice vectors. It guarantees that a unit cell is not too flat.

Local optimization means the relaxation of the candidate structures to a local minimum. This step allows to find the lowest free energy structures in the current generation. Candidate structures are relaxed using *ab initio* methods, thus, this part is the most computationally expensive. The USPEX code has a great flexibility concerning the choice of relaxation procedures. We used the generalized gradient approximation (GGA) [18] of density functional theory, as implemented in the Quantum Espresso code [17] for cluster structure relaxation. The pseudopotential is Troullier-Martins-type[19] norm-conserving pseudopotential with GGA exchange-correlation functional, generated by fhi98PP code [20]. Self-consistent electronic structure is calculated for given atomic positions of the candidate structure. Then atoms are moved to decrease system energy and electronic structure is calculated again. This procedure repeats until the energy convergence is achieved. USPEX code allows to improve relaxation parameters step by step: first relaxation of a given structure could be done roughly, then the precision of further relaxations is improved until required accuracy is achieved. Such strategy results in a notable performance improvement. For the numerical optimization during structure relaxation the BFGS algorithm (iterative quasi-Newton method) was implemented.

Usually for systems consisting of about tens of atoms and more, the total number of trial structures is of the order of 10^3 . Therefore, in order to save time, the maximum precision used in each relaxation is lowered and is often not sufficient for quantitative analysis. In this case it is worthwhile to pick out a number of lowest-lying topologically different structures obtained during the whole evolutionary computation and re-compute them with more precise accuracy. The refinement can even result in the interchange of the isomers, though only those very close in energy. The procedure of classification is described in the next section.

3. Structure classification and cluster geometry

In this section we explore the process of global search with the evolutionary algorithm and consider its intermediate and final results, which give rich information about the lowest energy (ground-state) structure and first isomer configuration of clusters. Examining the trial structures geometry may be useful to find possible routes to speed-up the search of the optimal cluster structures.

As we have noted above, not only the final result but also execution process of the algorithm might provide useful information. The subject of interest is the geometry and the total energy distribution of numerous trial structures, which lie energetically slightly above the ground state. Many of these structures have a similar arrangement of atoms and, probably, relate to the same local minimum of energy. Their occurrence in evolutionary searching is caused by imperfect atomic relaxation and a possible existence of soft modes in atomic displacements. The removal of such structures from the process of searching may save much computational time and resources. For this reason a proper classification of trial atomic structures is highly important for the search of the ground state atomic configuration.

Of course, the term 'similar arrangement of atoms' demands exact mathematical definition, and numerous measures have been proposed. Probably the most natural way is to classify the trial structures by their relationship with the representative isomer. It is well known, that the isomers are divided into two major groups: structural isomers and stereoisomers. The structural isomers are distinguished by bond topology, while stereoisomers differ only in spatial orientation of bonds. Structural isomers can be filtered using method based on graph theory [22]. Using this technique we sorted the total structural data array into groups, each of which corresponds to a distinct structural isomer.

The objects of our consideration are two bare Si-ncs (Si_7 and Si_{10}) and two Si-ncs passivated by hydrogen ($\text{Si}_{10}\text{H}_{16}$ and $\text{Si}_{10}\text{H}_{20}$). We chose Si_7 and Si_{10} clusters for their structures have been studied in detail both experimentally and theoretically. Cluster $\text{Si}_{10}\text{H}_{16}$ is one of the widely used model systems for cluster-related studies, as its structure is a highly symmetrical result of cutting-from-bulk procedure. Cluster $\text{Si}_{10}\text{H}_{20}$ is notable for a high number of low energy isomers. In Figure 1 we present results of topology analysis applied to evolutionary procedure carried out for Si_7 , Si_{10} , $\text{Si}_{10}\text{H}_{16}$ and $\text{Si}_{10}\text{H}_{20}$ clusters. The first thing we note here is that during its execution the algorithm tends to produce numerous structures close to the global minimum. Comparing results for Si_7 and $\text{Si}_{10}\text{H}_{20}$ we also see that the distance between structural isomers decreases when we go from smaller systems to larger ones. Most likely this is caused by the increasing of the total number of degrees of freedom. More total degrees of freedom means more 'soft' degrees of freedom, which provide small energy differences in the total energy.

The optimal (ground state) structures and the first structural isomers are shown in Figure 2. Our results, given by evolutionary algorithm for bare clusters are in perfect agreement with the experimental study [6]. The Si_7 and Si_{10} have 5-fold and 3-fold symmetry axes respectively. It is important to note, that the coordination numbers of atoms in both of these clusters do not correspond to the common silicon valency of 4. This means that the bonding in these clusters differs from four σ -bonds and sp^3 -hybridization inherent in the diamond crystal lattice. This fact affects the cluster stability and spectrum details. Below we discuss the relation between this difference and energetic characteristics.

The ground state structure of $\text{Si}_{10}\text{H}_{16}$ indeed coincides with a fragment of the diamond crystal lattice having broken bonds saturated by hydrogen. The structure has tetrahedral symmetry. Looking at its first isomer and the structures of $\text{Si}_{10}\text{H}_{20}$ we see that bigger systems are not necessarily highly symmetrical, which once again emphasizes that the global search should be unbiased.

The situation with stereoisomers is more complicated. Given two topologically identical structures we cannot tell for sure whether they are related to the same local minimum or to

the different ones. Let us consider two pairs of $\text{Si}_{10}\text{H}_{20}$ structures corresponding to different topologies (Figure 3). After high-precision atomic relaxation, the structures A1 and A2 retain their different atomic arrangements. The situation with the structures B1 and B2 is opposed. We note that even at first glance the shape of B2 structure suggests the existence of a local energy maximum, but not a minimum. To check this assumption, we used a small structure distortion with subsequent high-precision relaxation. Indeed, B2 eventually relaxed to B1, which confirms our assumption. This shows, that B1 and B2 are related to one stereoisomer, while A1 and A2 are related to two different stereoisomers. However, to distinguish between two topologically identical structures in general case, one should trace several intermediate configurations between them to find whether these structures are separated by a potential barrier.

4. Correlation between the Kohn-Sham electron spectrum and cluster stability

The density of electronic states (DOS) $N(E)$ is the standard characteristic of electronic structure in a material. While DOS determines directly only one contribution to the total energy - the sum of one-electron energies, it may provide useful information on the total energetics of a material. For example, in metals a high value of $N(E_F)$ (E_F is the Fermi energy) is an indication of possible low stability or even instability of the system with respect to lattice distortions or spin polarization. For this reason, when studying the most stable atomic structures of Si-ncs, we paid attention to their DOS in order not to miss possible correlations between the behavior of $N(E)$ and the total energetics of clusters.

Figures 4 – 7 show the calculated dependencies $N(E)$ (smoothed with the Gaussian of 0.1 eV width) for the ground state structures and the lowest-energy structural isomers in the clusters Si_7 , Si_{10} , $\text{Si}_{10}\text{H}_{16}$, and $\text{Si}_{10}\text{H}_{20}$. One can see in these figures that the DOS of the ground state structure is similar to that of all presented isomers with the same chemical composition. Except for small DOS variations between the atomic configurations of the same composition, we did not find any regular distinctions in their $N(E)$ dependencies. At the same time, the comparison of bare Si-ncs (Si_7 and Si_{10}) with Si-ncs passivated by hydrogen ($\text{Si}_{10}\text{H}_{16}$ and $\text{Si}_{10}\text{H}_{20}$) reveals

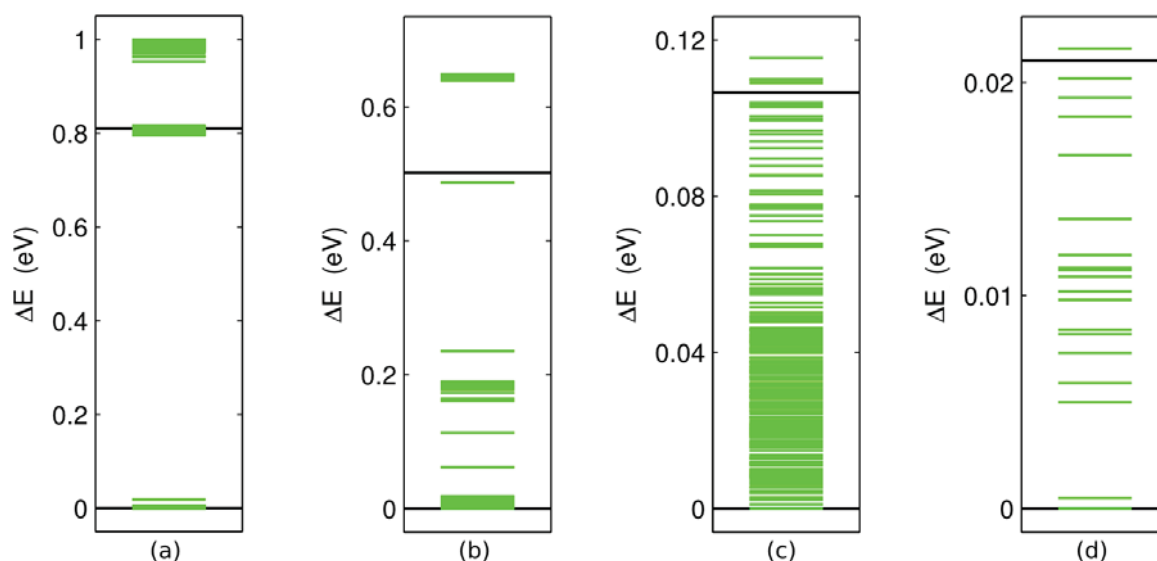


Figure 1. Energies of clusters (a) Si_7 , (b) Si_{10} , (c) $\text{Si}_{10}\text{H}_{16}$ and (d) $\text{Si}_{10}\text{H}_{20}$: Energies of all candidate structures are shown by short green dashes, while ground state and first structural isomer structures are shown by long black lines. Notice that energy scales on the graphs are very different.

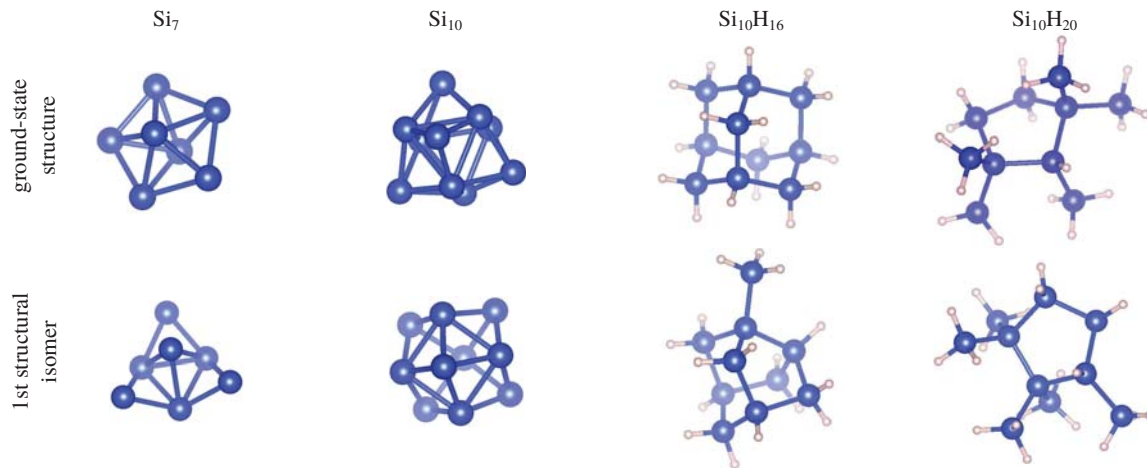


Figure 2. The ground-state and first structural isomers of Si_7 , Si_{10} , $\text{Si}_{10}\text{H}_{16}$ and $\text{Si}_{10}\text{H}_{20}$.

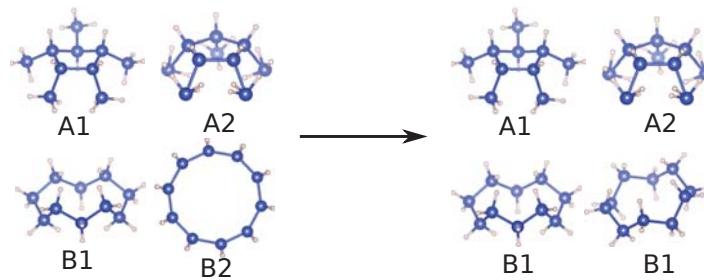


Figure 3. Two pairs of stereoisomers (A1, A2 and B1, B2) related to different topologies (A and B), before (left-hand) and after (right-hand) relaxation with preliminary small random distortion. B2 relaxes to B1, showing that the B2 structure corresponds to a local maximum of the total energy

evident differences in their DOS – the HOMO-LUMO gap is narrower and the valence band is wider in bare Si-ncs than in passivated ones. To quantify this observation using an integral characteristic appropriate for comparison, we defined the valence band width by the formula:

$$W_{\text{val}} = 2\sqrt{3} \left\{ \frac{\int dE \theta(E_F - E) N(E) (E - \bar{E})}{\int dE \theta(E_F - E) N(E)} \right\}^{1/2}, \quad (1)$$

where the factor $2\sqrt{3}$ is fitted to reproduce exactly a rectangular DOS width. In this equation

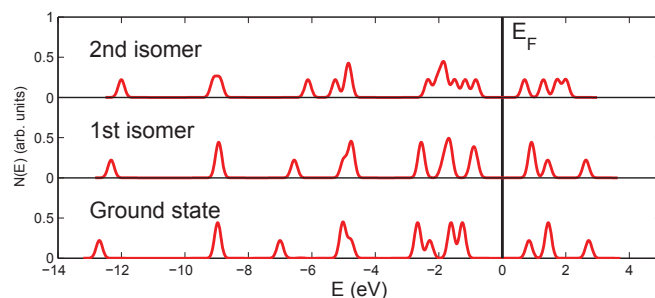


Figure 4. DOS of Si_7 cluster calculated for the lowest-energy structures.

the energy center of the valence band is:

$$\bar{E} = \frac{\int dE \theta(E_F - E) N(E) E}{\int dE \theta(E_F - E) N(E)}. \quad (2)$$

Table 1 presents the main parameters of electronic structure for the ground state geometry of the clusters Si₇, Si₁₀, Si₁₀H₁₆ and Si₁₀H₂₀ – the width of the HOMO-LUMO gap, the valence band width, the reaction energy (for clusters Si₁₀H_{2m} with $m = 0, 8, 10$) given by the formula $\varepsilon_R = E_{\text{tot}}(\text{Si}_{10}\text{H}_{2m}) - E_{\text{tot}}(\text{Si}_{10}) - mE_{\text{tot}}(\text{H}_2)$, and the energy distance of the first low-energy structural isomer from the ground state of a cluster. For clusters Si₁₀H₁₆ and Si₁₀H₂₀ stabilized by hydrogen (energy gain about 6.2 eV), the HOMO-LUMO gap is wider by 2.2 – 2.6 eV and the valence band width is narrower by 2.6 – 3.0 eV than for the bare silicon clusters Si₇ and Si₁₀. It is noticeable that the energy difference between the first structural isomer and the ground state structure is large for bare silicon clusters (about 0.5 eV) and is only 0.01 – 0.1 eV for Si-ncs passivated by hydrogen. In general, our results indicate that the HOMO-LUMO gap width and the valence band width correlate well with reaction energy and can be used for the qualitative estimate of cluster stability.

Table 1. The main parameters of electronic structure (in eV) for the clusters Si₇, Si₁₀, Si₁₀H₁₆ and Si₁₀H₂₀ – the HOMO-LUMO gap Δg , the valence band width W_{val} , the reaction energy ε_R , and the energy difference between the first structural isomer and the ground state, $E_1 - E_0$.

Cluster	Δg	W_{val}	ε_R	$E_1 - E_0$
Si ₇	2.10	11.8	–	0.81
Si ₁₀	2.10	11.8	0	0.50
Si ₁₀ H ₁₆	4.70	9.2	-6.21	0.11
Si ₁₀ H ₂₀	4.34	8.9	-6.26	0.02

5. Discussion and conclusions

In this paper, we presented our calculations of atomic structure and electronic spectra in silicon nanoclusters Si₇, Si₁₀, Si₁₀H₁₆ and Si₁₀H₂₀. Analysing them allowed to reveal several features of the global search process applied to semiconductor clusters. In searching for least-energy structure, we ran over most promising atomic configurations delivered by the evolutionary algorithm. A general observation is that the evolutionary algorithm realized in the USPEX code gives good convergence of trial configurations to a ground-state atomic structure. The convergence behavior is not the same for different clusters, but depends on cluster characteristics. For the clusters Si₇, Si₁₀, Si₁₀H₁₆ with the low-lying-isomer energy well above the ground state,

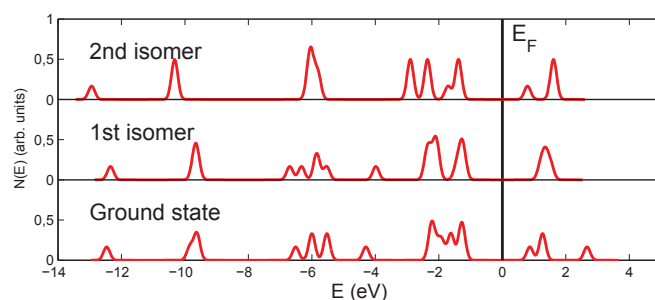


Figure 5. The same as in Figure 4, but for Si₁₀.

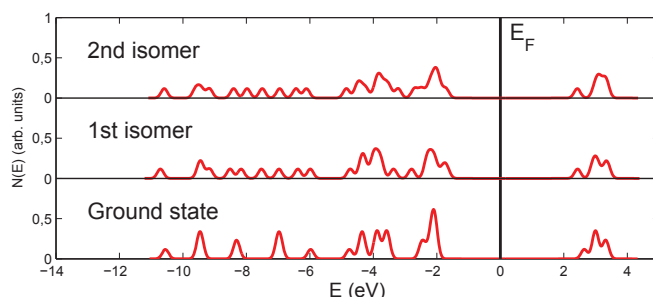


Figure 6. The same as in Figure 4, but for $\text{Si}_{10}\text{H}_{16}$.

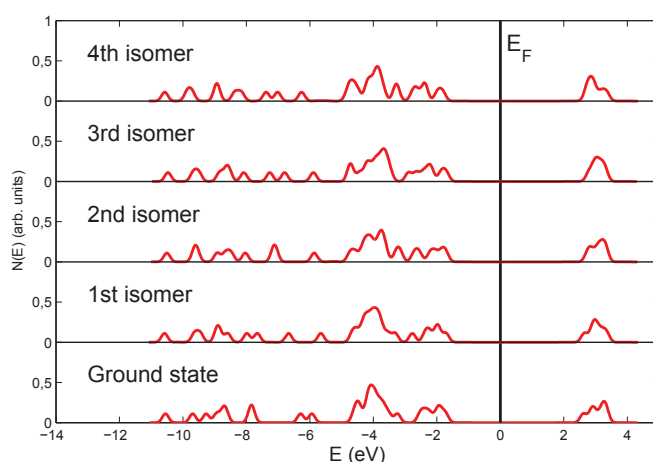


Figure 7. The same as in Figure 4, but for $\text{Si}_{10}\text{H}_{20}$.

the convergence is stable and fast. However, in the case of cluster $\text{Si}_{10}\text{H}_{20}$, which has several isomers separated from the ground state by $\Delta E_{\text{tot}} < 0.1$ eV, the convergence behavior is less stable, with a three times larger number of iterations needed.

The analysis of atomic configurations arising in these iterations shows (see Section 3) that both structural and stereoisomers emerge among them. As the atomic relaxation is in many cases incomplete, a number of slightly perturbed structures close to local energy minima also arise in the course of computations as independent candidates. The calculation of these perturbed structures provides no helpful information and only increases the amount of computation. For this reason, the removal of these structures from computation could significantly accelerate searching for the ground state atomic structure. It should be noted that the perturbed structures can be easily distinguished from structural isomers by the comparison of bond topologies using the graph theory methods [22]. The distinction between perturbed structures and stereoisomers is not so evident and generally requires additional laborious calculations. In this connection, a challenging problem is to define a measure for quantifying the similarity between different atomic structures. The use of such measure in combination with the evolutionary algorithm will assist further progress in atomic structure prediction.

The density of electronic states is a useful characteristic which can be a qualitative indication of a low stability or even instability of an investigated material. Our analysis of electronic DOS for nanoclusters of varied composition shows that a wider HOMO-LUMO gap and a smaller valence band width generally correlate with the cluster stability and energy gain from formation of clusters. The comparison between electronic DOS of ground state and that of low-lying isomer structures in the clusters of the same composition shows, however, no noticeable correlations with atomic structure stability. Our results presented in Figures 4 – 7 and Table 1 suggest that DOS is a rather rough qualitative characteristic of cluster stability, which is sufficient for the detection of large reaction energy changes $\Delta \epsilon_R \geq 1$ eV, but insensitive to small energy

differences $\Delta E_{\text{tot}} < 0.1$ eV between the low-energy isomers and ground-state structure, as well as between the low-energy isomers themselves.

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