

# Global optimization of silicon nanoclusters

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## Abstract

A new method is presented for the computation of the lowest energy configurations of atomic clusters. It is based on recently developed set oriented numerical algorithms for the global optimization of nonlinear functions. Its underlying idea is to combine multilevel subdivision techniques for the computation of fixed points of dynamical systems with well known branch and bound methods. We describe how this method can be used to find global minima of silicon nanoclusters in the SCC-DFTB energy surface. Due to the insufficient experimental evidence of structures of silicon clusters, local minima that are near to the global minimum, are also important.

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## 1. Introduction:

The global optimization of any function with many degrees of freedom is one of the most difficult questions of current research both from the mathematical and the physical point of view. In applications in physics and chemistry, one is interested in all the minima of an interacting-potential surface for atomic structures (e.g. molecules, clusters, amorphous systems) with  $3N$  degrees of freedom, where  $N$  is the number of atoms. But there is a particular interest to find the global minimum of the energy function since the most likely growth behaviour and preferential growth forms can be realized from these atomic structures. There are two central problems of cluster geometry optimization: one is the almost exponential growth of the number of local minima with the cluster size, the other is that the details of the potential have a strong influence on the number and the conformation of local and global minima. Simulated annealing [1], genetic algorithms [2], basin-hopping [3], energy landscape paving (ELP) [4] are a couple of methods which are frequently used for geometry optimization of clusters. In [5, 6] a new global geometry

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optimization strategy has been proposed which is applied to the ab-initio potential surface. In this paper, we present a new set oriented numerical algorithm for global optimization [7] and how to apply it to the self-consistent-charge tight-binding-density-functional (SCC-DFTB) [8,9] energy function to obtain the lowest energy configurations of silicon nanoclusters. In contrast to the methods mentioned above, this approach is global in nature. That is, it directly and reliably finds the global minimum instead of jumping from one local minimum to the other in order to eventually reach the global one.

## 2. The Global Optimization Method:

The basic idea of this method is to view iteration schemes for local optimization – e.g. Newton’s method or conjugate gradient methods – as dynamical systems, and to compute coverings of their fixed points in phase space using set oriented methods for the computation of invariant sets of dynamical systems [10]. This idea has already been used in [11] and here it is combined with well-known branch and bound methods [12]. More concretely we obtain set coverings of the global minimizers of a given nonlinear objective function  $g : \mathbf{R}^n \rightarrow \mathbf{R}$  [7]. This approach will be used in Section 3 to find the global minimum of the quantum-mechanical SCC-DFTB energy hypersurface for silicon clusters.

We consider discrete dynamical systems of the form

$$x_{k+1} = f(x_k), k= 0, 1, 2, \dots$$

with  $f : \mathbf{R}^n \rightarrow \mathbf{R}^n$ .

For the purpose of global optimization,  $f$  is chosen to be an iteration scheme for local optimization, e.g.  $f(x) = x - \nabla^2 g(x)^{-1} \nabla g(x)$  in case of Newton’s method. Using the multilevel subdivision procedure described below set coverings of all those fixed points of  $f$  which correspond to the global minimizers of  $g$ , i.e. all points  $x \in \mathbf{R}^n$  with  $g(x) = \min_{y \in \mathbf{R}^n} g(y)$ , can be computed [7].

We start with an initial collection  $C_0$  consisting of a single rectangle  $B_0 = \{x \in \mathbf{R}^n : a_i < x_i < b_i, i = 1, \dots, n\} \subset \mathbf{R}^n$  (also called box in the sequel) in phase space. For  $k = 1, 2, 3, \dots$  successively refined collections  $C_k$  are inductively obtained from  $C_{k-1}$  in two steps:

### 1. Subdivision:

Construct a refined collection  $\overline{C}_k$  via bisection of all the boxes  $B \in C_{k-1}$  along the  $i$ -th coordinate direction, where  $i$  is varied cyclically with  $k$ , i.e.  $i = ((k-1) \bmod n) + 1$ , if  $n$  is the dimension of the phase space.

### 2. Selection:

Define the new collection  $C_k$  to contain only those boxes  $B$  of  $\overline{C}_k$  which fulfill the following two conditions:

- (a)  $f(B) \cap B \neq \emptyset$ . The boxes  $B$  in phase space with  $f(B) \cap B = \emptyset$  cannot contain fixed points of  $f$  and thus no local or global minimizers of  $g$ . These boxes have to be deleted from the covering. Since in general  $f(B)$  cannot be computed directly

this condition is usually discretized using a finite set of sample points within the box  $B$ . The selection criteria then reads:

$f(p) \in B$  for at least one point  $p$  of a set of sample points  $\{p_1, \dots, p_m\} \subset B$ .

- (b)  $\beta(B) \leq \alpha_k$ , where the quantities  $\beta(B)$  and  $\alpha_k$  have to be chosen as follows:  $\beta(B)$  must be a lower bound on the possible function values of  $g$  for points in  $B$ , i.e.  $\beta(B) \leq \inf\{g(p) : p \in B\}$ . The values  $\alpha_k$ ,  $k=1,2,\dots$  have to form a nonincreasing sequence of upper bounds on the global minimum of  $g$ . For the determination of  $\alpha_k$  the values of the objective function obtained during the test point iteration for condition (a) can be used.  $\alpha_k$  is then given by the lowest objective value found so far. Boxes with  $\beta(B) > \alpha_k$  cannot contain a global minimizer and are no longer taken into account.

As indicated in Fig. 1. this algorithm produces a sequence of successively refined collections of boxes. During the course of the iteration more and more parts of the initial box, which cannot contain the global minimizers, are removed and only a small number of tiny boxes remain. Under reasonable assumptions on the bounds  $\beta(B)$  and  $\alpha_k$  it can be shown that the computed coverings converge to the set of global minimizers of  $g$  for  $k \rightarrow \infty$  [7]. In applications, however, the subdivision procedure is stopped when the boxes have reached a prescribed size. The exact locations of the global minimizers can then easily be found using local optimization methods for a few initial points per box.

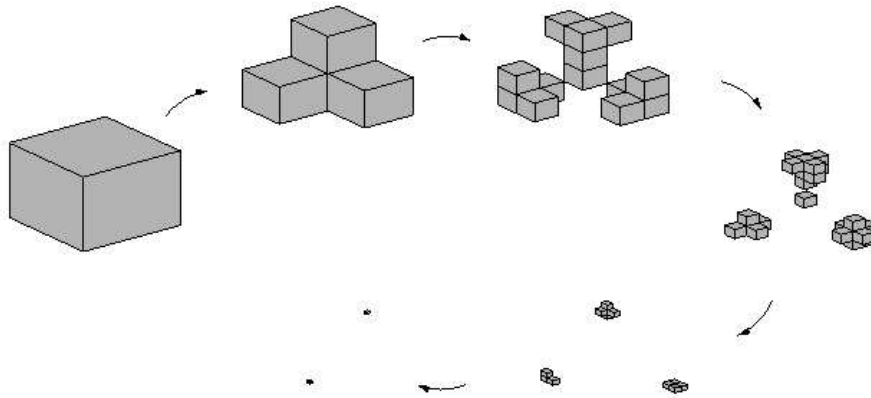


Fig. 1. Schematic description of the subdivision algorithm for global optimization of nonlinear functions.

### 3. Application to cluster optimization

This set oriented new method is used to obtain the global minima of silicon nanoclusters. In our scenario the SCC-DFTB energy function is the objective function for the new branch and bound method. SCC-DFTB is a two-center tight-binding like approximation to the density functional theory. The Kohn-Sham [13] energy is transformed by decomposing the electron density into a sum of a reference density and a density fluctuation and by further expanding the exchange correlation energy around the reference density to second order in the density fluctuation. Then the expression of SCC-DFTB energy is

$$E_{SCC}^{DFTB} = \sum_i^{occ} \langle \psi_i | \hat{H}_0 | \psi_i \rangle + \frac{1}{2} \sum_{A,B}^N \gamma_{AB} \Delta q_A \Delta q_B + E_{rep}$$

The first term depends on the reference density and within a LCAO approach the corresponding matrix element of the Hamiltonian can be calculated under two-centre approximation. The second term represents the charge fluctuations, which are not included in a classical tight-binding scheme.  $\gamma_{AB}$  is an algebraic function which depends only on the distance between nuclei of two atoms  $A$  and  $B$ .  $\Delta q_A = q_{Mulliken} - q_0$  is the difference between the Mulliken population of the respective atom with the core charge  $q_0$ . The third term is the pairwise repulsive potential energy which is calculated as the difference between the DFT (density functional theory) total energy and the band-structure energy in SCC-DFTB as a function of interatomic distance. In the new set oriented method (Section 2), the choice of proper phase space, initial box, iteration scheme ( $f$ ) and the computation of lower bounds ( $\beta(B)$ ) are essential to reach the global minimum of this energy hypersurface.

**Phase space and initial box ( $B_0$ ):** In our global optimization approach, first an appropriate initial box  $B_0$  has to be chosen. Since the SCC-DFTB energy function is invariant (i.e., it does not change its value) with respect to cluster rotation, translation and renumbering of the atoms, each particular cluster geometry with  $N$  atoms is represented by infinitely many points in the configuration space. Since the subdivision algorithm computes all global minimizers of  $g$  this has to be taken into account in order to avoid unnecessary computations. We therefore restrict ourselves to structures with the center of mass fixed to the origin. In addition, the phase space is chosen such that all cluster geometries, which differ only by rotation, are uniquely represented by a single point. Finally the atoms are numbered in such a way that their distances from the origin are always in descending order. One then ends up with only one point in phase space for each particular cluster geometry or at least with a finite number in the case when the numbering cannot be made unique.

The size of the initial box  $B_0$  is chosen such that all structures with a given maximal distance between the atoms are contained within this box. For this maximal distance we use the length of the linear chain of atoms since all low minima will have a more compact structure than this unfavourable state.

**Iteration scheme ( $f$ ):** The dynamical system  $f$  needed for the subdivision procedure is constructed using a small number of steps of a BFGS method with adaptive step size

applied to the silicon SCC-DFTB energy function in combination with a conversion between points in the chosen phase space.

**Lower bound ( $\beta(B)$ ):** The computation of a lower bound  $\beta(B)$  of the energy for all structures contained in a given box  $B$  is a difficult task. For this purpose, first the possible distances of all pairs of atoms for the structures contained in the box under consideration are determined. If for a pair of atoms, the range of possible distances overlaps the silicon bond range (the bulk silicon bond length  $\pm 15\%$ ) it is assumed that there exists a structure in the box with a bond between these two atoms. Since the bulk energy is the ground state energy of silicon it is used as a lower bound on the contribution of this pair of atoms to the total energy. If for a particular pair of atoms no bond is possible for all structures in the given box no contribution to the total energy is taken into account. Summation over all pairs of atoms then gives the desired energy bound for structures in the box  $B$ .

By using these proper parameters of the branch and bound method, we can reach the global minimum of the energy hypersurface. Since it is applied to silicon cluster optimization, some additional selection criteria can be used in the subdivision algorithm to delete boxes, which cannot contain the global minimizers. In this case, these criteria are evolved from the physical background of silicon and are as follows:

If the distance between two atoms in a cluster is too small (2.0 a.u.), it is physically unfavourable. Boxes containing only such structures are immediately deleted from the current collection without any further time consuming computations of bounds or test point iterations. Other unfavourable structures, which should not be considered, are those, which consist of several disjoint pieces of smaller clusters. For a given box  $B$  a graph is built with a node for each atom. There will be an edge between two nodes if there exists a structure within the box, which may form a bond between the corresponding atoms. Using graph algorithms it can be detected if this graph is disconnected which implies that the box  $B$  contains only disconnected structures. The above conditions are also checked for each particular structure during the evaluation of the iteration scheme  $f$  in order to avoid unnecessary computation of energy and forces by the SCC-DFTB method.

#### 4. Result:

We have tested the functionality of this new method by an application to a small number of atoms with the Lennard Jones potential. The global minima of clusters up to 15 atoms are computed and the results are in perfect agreement with the known minima. Then this method is applied to the more complicated SCC-DFTB potential. Since there exist both experimental [14,15] and theoretically [16-21] established structure information for silicon clusters up to 10 atoms, this new algorithm is used for structure optimization up to 15 atoms. Also here this new method reliably finds the structures (Fig. 2.), which are quite well-known for the SCC-DFTB method and for other methods. Since our approach is global in nature and we did not find any new lowest minima structures, we can assume that no lower energy structures are present in this energy hypersurface.

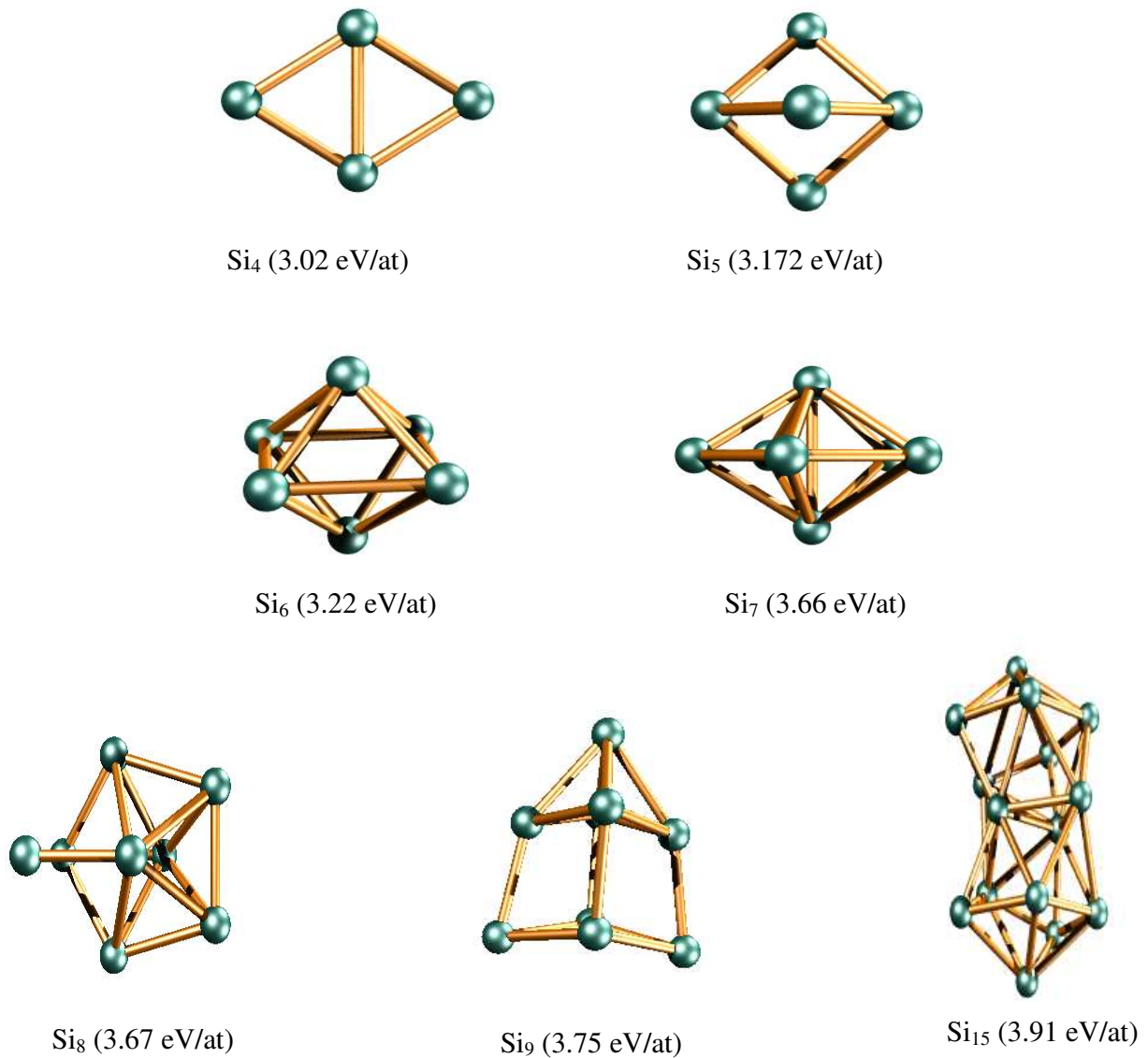


Fig.2. Binding energies with respect to spin polarized atoms in eV/atom

## 5. Conclusion:

This set oriented new method shows successful results for small silicon clusters to find the unique global minima in the multidimensional SCC-DFTB potential. Due to the insufficient experimental evidence of structures of silicon clusters, local minima, which are near to the global minimum, are also important and can be found using a slightly modified version of this method. While the branch and bound method is used for the DFTB potential, it is difficult to find good lower bounds. The ground state of the silicon represents the deepest energy state therefore the lower bound as defined here is certainly

robust. But it would be desirable to have a tighter bound, since the cluster configurations do not always correspond to the bond morphology of the ideal silicon crystal. The lower bound of the total energy can be further improved using the harmonic approximation. In an advanced stage of the branch and bound method, the boxes become so small that the certified connection length (bond-length) always corresponds to the minimum energy position. If the connection length differs slightly from the bond length corresponding to minimum energy, one can use the harmonic energy function to compute the lower bound. The optimal connection length of the cluster may deviate from the crystalline length. Therefore this approximation can give a better lower bound, which can help to reach the global minimum more rapidly.

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