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Cluster morphology of silicon nanoparticles

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Abstract. It is proposed to use silicon polyhedral atomic clusters (ACs) in the study of nanoparticles. A scheme of the parametrized density functional theory for calculations of the atomic and electronic structures of these clusters is presented. The accuracy of the method is illustrated by the results of calculations for Si-ACs with different sizes.

Keywords: silicon, polyhedral atomic cluster, atomic and electronic structures, nanoparticle.

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In recent years, the optical properties of silicon nanostructures (Si-NS) have been the subject of intense investigations, because the quantum confinement of electrons and holes leads to linear and non-linear optical properties much different from those of bulk crystals. Since Canham's discovery of visible light emission from porous Si (see [1]), a great deal of efforts has been devoted to investigation of the optical properties of Si-NS. There are the direct experiments on the geometry of Si-NS [2, 3].

In addition, the optical data [4] indicated the existence of atomic clusters (ACs) in films and were mediated by the localized electronic states associated with clusters. In particular, the peculiar Raman spectra in Si-SiO₂ systems, being different from those of bulk c-Si, a-Si, and microcrystalline Si, but very similar to the density-of-state spectra of Si₃₃ and Si₄₅ [3], were observed. The experimental data strongly suggest that these films are the systems of ACs much smaller than about 2 nm embedded in SiO_x matrices. Although the size and the size distribution of the clusters are not known, the introduction of clusters with various sizes randomly into SiO₂ thin films may generate localized electronic states. If these previous results are taken into account, it is rather straightforward to attribute the presently observed $\ln \sigma$ (σ – conductivity) versus $T^{-1/4}$ (T – temperature) behaviour to the VRH (variable range hopping) conduction through the localized electronic states associated with C, Si, and Ge clusters [5, 6]. As the Si concentration increases, the slopes (B) of $\ln \sigma$ versus $T^{-1/4}$ straight lines decrease. Since the increase in the Si concentration leads to the increases in the size and/or number of Si clusters, the decrease in B may be

attributed to the increase in the size and/or number of Si clusters. Thus, the optical data indicate the existence of clusters in the films, and the present VRH conduction is thought to be mediated by the localized electronic states associated with clusters.

On the other hand, the small silicon clusters of atoms (Si-ACs) are the subjects of the intense study in the hope for that their properties can provide a new insight to the physical and chemical behaviour of the nanodimensional materials [7-11]. Probably, the Si-NS consist from Si-AC structures. The large surface-to-volume ratio and the large step and defect density allow one to expect that small Si-ACs will be highly reactive. Moreover, the flexibility afforded by the small number of atoms could give rise to novel structures, which can possibly lead to the synthesis of artificial materials with uncommon properties.

In the present paper, a new approach to the study of Si-NS consisting of small and intermediate-size Si-ACs is proposed.

Some calculations [7, 12, 13] predict that Si-ACs in this size range have tetrahedral bonded network structures whereas others predict more compact structures. Taking the above-said into consideration, we based on the following premises. First, for small Si-ACs ($n < 10$), it is possible to construct a tree with core of fourfold-coordinate atoms, similar to bulk Si (for example, see [7]). Second, for larger Si-ACs ($10 < n < 100$), it is possible to construct a network containing a core of fourfold-coordinate atoms, similar to bulk Si, which are surrounded by a surface of atoms with optimal (threefold or fourfold) coordination, similar to Si surfaces (as [10]). Structures of exceptional

stability can be obtained when exactly all surface atoms participate in the surface reconstruction, and any change in the size (addition or removal of atoms) introduces "defects" similar to those on c-Si surfaces. To construct a real Si-NS, our model used: 1) a core of fourfold-coordinated atoms similar to bulk Si (complete Si-NS) or 2) 5-, 6-, and 7-membered Si-rings and their combinations for the construction of surface blocks (empty Si-NS).

The nature of Si-NS and the reconstruction of Si-ACs in the range size $1 < n < 100$ (n is the number of atoms in AC) remain open to intense debate too. Si-ACs are a small piece of the nature in the range of nanometers, are not molecules, and cannot represent themselves as the bulk material as well. For example, J.R. Chelikowsky and J.C. Phillips [12] have suggested that the small Si-ACs are metallic rather than covalent in nature. This is due to of their physical size. Clusters of covalently bound non-metals usually have more open geometries that satisfy the specific highly directional bonding requirements of silicon and germanium. Si-ACs form prolate structures up to $n \approx 25-35$ [3, 5], but then they rearrange to more polyhedral morphologies [8, 9]. In fact, the Si-AC appears to be more closely related to the high-pressure metallic phases of bulk silicon than to the diamond structure [7, 12-14]. These works appear to define metallic clusters as those which have bond angles of 60° .

The absorption spectra from 0.94–5.58 eV are obtained for gas-phase neutral Si-ACs containing 18-41 atoms [6]. The spectra of all clusters are essentially identical. The optical signature of these clusters has much in common with that of c-Si. These spectra are unexpected: theoretical calculations predict a wide variation in structure over the size range, but, experimentally, a Si-AC has numerous strong sharp absorption lines which do not shift in energy over the Si-AC size range. Furthermore, the partial spectra of Si-AC are smaller than Si_{18} and larger than Si_{41} . The spectral signature common to Si_{18} – Si_{41} persists for sizes up to at least 70 atoms. This spectral similarity is completely unexpected. Because of the molecular point of view, these clusters span a sufficiently large size range to have structural differences which should show up in their optical spectra.

It follows from these data that Si-ACs in this size range are expected to undergo rapid structural changes because of the large surface/volume atom ratio. Nonetheless, major changes occur in the geometric structures of Si-ACs as a function of size below 50 atoms. Such changes are mirrored in the photoelectron spectra measured for Si-AC anions containing 3-12 atoms [8, 9]. Structural differences of Si-ACs (similar size range) for positively charged ACs have also been inferred from mobility and chemical reactivity data [4]. Thus, the electronic spectra of neutral Si-ACs larger than Si_{18} do not show any evidence for any structural changes. This allows us to conclude that all of these small silicon clusters share one or more common structural entities. One possibility is that a small Si-AC

shares a common bonding network which persists and extends as the cluster grows in size.

Yet, the absorption spectrum of crystalline silicon has much in common with the silicon cluster spectra. Strong absorption features at energies above 3 eV dominate in both Si-AC and c-Si spectra. The 800-K bulk spectrum, which is red shifted by the thermal expansion of the lattice, more closely corresponds to the cluster spectrum. Nonetheless, a number of discrepancies between the bulk and cluster spectra should still be explained. For instance, the cluster spectrum has six peaks between 3.0 and 5.6 eV, whereas the bulk spectrum contains only three features. Furthermore, the comparison with the 800-K bulk spectrum neglects the effects of lattice contraction and quantum confinement which are known for Si-NS, and these characteristics do not change as a function of the AC size range.

Given that Si-ACs containing only few tens of atoms are too small to have either band structures or bulk excitations, the similarity of their optical signature to crystalline silicon is unexpected. Moreover, these spectra are far more similar to the spectrum of the most stable crystalline form of Si than to the spectra of other Si forms.

Furthermore, optical spectra of small InP-ACs exhibit the absorption analogous to that of a-InP [13]. Other forms of more compact Si such as the β -tin and primitive hexagonal metallic phases [14] are also candidates for comparison in the light of theoretical calculations, which predict high coordination numbers in small Si-ACs. But none of these structures have optical properties which are as closely related to Si-AC spectra as c-Si. Moreover, Si-AC spectra cannot be easily compared to Si surface spectra [6].

In addition, it is reasonable to concentrate on models for experimentally observed sizes of exceptional stability [the so-called magic numbers (MNs) [15]]. A MN is observed and reflects differences in Si-ACs [11, 12]. The MN can be understood basing on structures predicted theoretically and observed experimentally. Si-ACs of somewhat larger size (for example, $10 < n < 100$) show the dramatic changes in their chemical reactivity, depending on the number of atoms in the cluster.

Using the thermodynamic force field, the equilibrium structures of Si-ACs ($n = 11-25$) were calculated in [12]. The following interesting results about the structure of these clusters were obtained. Since a Si-AC containing 7 atoms (and $n = 13$ or $n = 19$), clusters have a pentagonal pattern (or icosahedral plus the associated face capping). These results are fully consistent with MNs found in the reaction rates for the addition of first C_2H_4 molecules to Si_n^+ clusters.

These experimental and theoretical data showing the spectral regularity of Si-ACs challenge all known theoretical models which are used for the construction of space structures in the size range $10 < n < 100$. This leads to the intriguing conclusion that silicon clusters containing tens of atoms are derived from a common structural entity. We do not know the nature of this

entity, but its spectral similarities to the bulk crystalline spectrum provide a firm ground for further theoretical investigations. However, this is not the optimal practical procedure for clusters with larger sizes: for a system with many degrees of freedom, the problem of identifying the lowest-energy configuration becomes computationally difficult and depends on the sizes of clusters. A Si-AC with size range $10 < n < 100$ requires to search for the possible new calculation schemes. In addition to this, in order to elucidate the properties of ACs, the development of different specific models has great importance.

These facts became the motivation of our computer researches. To attack this problem, we investigated the electronic and geometric structures of Si-ACs theoretically using the parametrized density-functional theory (PDFT).

To study the dynamics of clusters, we offer an approximate calculation scheme. This is the density-functional theory (DFT) in the realization of Kohn and Sham (KS), using a few empirical parameters. This method, which is named parametrized DFT-PDFT, is based on the Hartree-Fock scheme plus a proper treatment of the electron correlation [16-18]. The use of only a few parameters minimizes the effort for the determination of the parameters, and it yields a close relation to full *ab initio* DFT schemes (for example, GAMESS [16]). This is a guarantee of the good “transferability” of the parameters, while going from one system to another. On the other hand, the use of some approximations in connection with a few empirical parameters makes the scheme of computations to be extremely fast. PDFT allows also the study of dynamical processes through the coupling with molecular dynamics (MD).

The method is based on the LCAO ansatz for the KS wave functions:

$$\Psi(\vec{r}) = \sum_{\mu} C_{\mu} \zeta_{\mu}(\vec{r} - \vec{R}_j). \quad (1)$$

Here, ζ_{μ} – the atomic orbital which will be utilized as basic wave functions (BWF) in the form [10, 11]:

$$\zeta_{\mu} = N_{\mu} r^{n^*-1} e^{-\alpha_{\mu} r} Y_{lm}, \quad (2)$$

where N_{μ} is constant; α_{μ} is the Slater’s parameter which is defined by an algorithm [11]; Y_{lm} are spherical harmonic functions, and n^* is the effective quantum number. The LCAO ansatz leads to the secular problem. The matrix elements of the Hamiltonian $H_{\mu\nu}$ and the overlap matrix elements $S_{\mu\nu}$ are defined as

$$H_{\mu\nu} \equiv \langle \xi_{\mu} | \hat{H} | \xi_{\nu} \rangle, \quad S_{\mu\nu} \equiv \langle \xi_{\mu} | \xi_{\nu} \rangle. \quad (3)$$

In the offered method of PDFT, the Hamiltonian of the system looks as

$$\hat{H} = \hat{T} + V_{\text{eff}}(\vec{r}), \quad (4)$$

where \hat{T} is the operator of kinetic energy, and $V_{\text{eff}}(\vec{r})$ is the effective KS potential. It is approximated as a simple superposition of the potentials of neutral atoms V_j^0 :

$$V_{\text{eff}}(\vec{r}) = \sum_j V_j^0(\vec{r}_j), \quad (5)$$

where $r_j \equiv |\vec{r} - \vec{R}_j|$. Such an approximation for the potential is consistent with the following approximations in the matrix elements of the Hamiltonian:

$$H_{\mu\nu} \begin{cases} \langle \xi_{\mu} | T + V_j + V_k | \xi_{\nu} \rangle, \mu \cap \nu \in \{j, k\} \\ 0 \end{cases}. \quad (6)$$

Thus, only two-center terms in the Hamiltonian matrix are considered, but all two-center terms $H_{\mu\nu}, S_{\mu\nu}$ are calculated exactly.

The approximation formulated above leads to the same structure of the secular equations as in the (non-orthogonal) tight-binding (TB) or Iterative Extended Huckel (IEHT) [11] schemes, but it has the important advantage that all matrix elements are calculated, and none of them is handled as an empirical parameter. P. Blaudeck and co-workers [18] showed that the quality of results, especially those concerning the binding energies, can be improved distinctly by using basis functions and potentials from slightly “compressed atoms,” rather than from free atoms. This “compression” is achieved by the introduction of an artificial additional repulsive potential of the form $(r/r_0)^k$ in the atomic calculations. The authors of works [16, 17] originally developed such a potential for the optimization of LCAO-LDA band structure calculations. The main effect of this term is a damping of the long-range part of basis functions. Practically, it optimizes the basis functions concerning the approximations, mainly by neglecting the 3-center terms.

The total energy $E[\rho(\vec{r})]$ can be written in a form using the KS eigenvalues ε_i as

$$E[\rho(\vec{r})] = \sum_i^{\text{occ}} \varepsilon_i - \frac{1}{2} \left[\int d^3 r V_{\text{eff}} \rho - \int d^3 r V_{\text{ext}} \rho \right] + E_{XC} - \frac{1}{2} \int d^3 r V_{XC} \rho + E_N. \quad (7)$$

The external potential V_{ext} is the electron-nucleus potential, E_{XC} is the exchange-correlation energy, V_{XC} is the corresponding potential, and E_N stands for the nuclear repulsion energy. The representation of the density and the potential as a superposition of atomic-like contributions, i.e., $\rho = \sum_i \rho_i$, $V = \sum_i V_i$, allows us to write the total energy as

$$\begin{aligned}
 E[\rho(\vec{r})] = & \sum_i^{occ} \varepsilon_i - \frac{1}{2} \sum_j \sum_{j'} \int d^3r V_j \rho_{j'} - \\
 & - \frac{1}{2} \sum_j \sum_{j'} \int d^3r \frac{Z_j \rho_{j'}}{r_j} + \\
 & + \frac{1}{2} \sum_j \sum_{j'} \int d^3r \tilde{V}_{XCj} \rho_{j'} + \frac{1}{2} \sum_{j \neq j'} \int d^3r \frac{Z_j Z_{j'}}{R_{jj'}},
 \end{aligned} \quad (8)$$

where $R_{jj'}$ is the distance between nuclei:

$R_{jj'} = |\vec{R}_j - \vec{R}_{j'}|$, Z_j is the charge of the j -th atom, ρ_j is the electronic density localized on the j -th atom, and ε_i is the one-electron energy.

For large internuclear distances, the electron-nucleus energy compensates strongly the nuclear repulsion energy, and the two-center terms with the potential vanish also: $\int d^3r V_j \rho_{j'} = 0$, $j \neq j'$, due to the screening of the potential. Assuming additionally that $\int d^3r \tilde{V}_{XCj} \rho_{j'} = 0$ and writing the total energy $E[\rho(\vec{r})]$ of a single atom in the corresponding form as (8), one can evaluate the binding energy approximately by the KS eigenvalues ε_B and the KS energies ε_{n_j} of the atomic orbital n_j :

$$\varepsilon_B \equiv E - \sum_j E_j \approx \sum_i^{occ} \varepsilon_i - \sum_j \sum_{n_j} \varepsilon_{n_j}. \quad (9)$$

The binding energy calculated in this way and the binding energy from the full SCF-LDA calculation, by using algorithm GAMESS [16] ($\Delta E \equiv \varepsilon_B - E_B^{GAMESS}$) for the Si-AC, are in good agreement, as it was illustrated in [8, 9]. The differences between these energies increase with decrease in the internuclear distance (r). However, this increase is rather smooth, and the difference practically vanishes already at distances about $3/2 r_0$.

Within the PDFT approximation, the forces acting on the atoms (F_m) can be calculated easily using the LCAO coefficients ($C_{i\mu}$) and the derivatives of the Hamilton and overlap matrices $\left(\frac{\partial H_{\mu\nu}}{\partial x_j}, \frac{\partial S_{\mu\nu}}{\partial x_j} \right)$, respectively:

$$\begin{aligned}
 F_m = & \sum_i^{occ} \sum_{\mu} \sum_{\nu} C_{i\mu} C_{i\nu} \left[-\frac{\partial H_{\mu\nu}}{\partial x_j} + E_i \frac{\partial S_{\mu\nu}}{\partial x_j} \right] + \\
 & + \sum_{j \neq j'} \frac{\Delta E_{jj'}}{\partial x_j}.
 \end{aligned} \quad (10)$$

Having the forces, MD simulations can be easily performed (see, e.g. [19]). In order to obtain the relaxed atomic geometries for the models described below, we have performed extensive energy-minimization calculations. The PDFT Si-AC database includes the total

energies of clusters, energy fragmentation, the overlap integral matrix, charges on atoms, etc.

We have tested a new PDFT approach to calculations of the total energy for a complicated atomic geometry, which has included the electron-electron interaction in a self-consistent manner.

We start with a bulk-like Si-AC size of 4 atoms and examine the cluster-size dependence of electronic states for Si up to 60 atoms. The AC-size dependence of the calculated energy levels, local densities of states, and charge distributions are examined for Si-AC, it is found that a 10-atom cluster, which had three possible space configurations was good enough for the AC-core to be identified and to study the optical spectra [10]. To study the regularity of the behaviour of big ACs (including ACs with $n = 18-41$), it is very important to define the properties of a Si-AC with 10 atoms. The PDFT method (with different basis sets: STO-3G and HF/3-21G) was utilized for the analysis of the geometry and electronic structures of Si-ACs with the size range $1 < n \leq 60$.

In addition, the surface elementary Si-AC models are investigated. The PDFT method is applied to the isolated 5-, 6-, and 7- atomic rings reconstructed as a fragment of the Si(111)2×1 surfaces of materials crystallizing in the diamond structure. In Fig. 1, an example of the simulation of a 5-atom silicon ring is presented. We researched the possibility to derive a planar Si-cyclic 5-AC structure. The energy transition is present in Fig. 1. The displacements of the 1st, 4th, and 5th atoms are equal to $\Delta R_{kj} = 0.11 \text{ \AA}$; for the 2nd and 3rd atoms $-\Delta R_{kj} = 0.18 \text{ \AA}$. We note that, as the surface Si-atom is moved inward, the hybridization of the local orbitals on the surface atom is changed to keep them orthogonal. Therefore, we are forced to study the dehybridization of Si-atomic sp^3 -orbitals from the equivalent form in terms of the relative positions of Si-atoms.

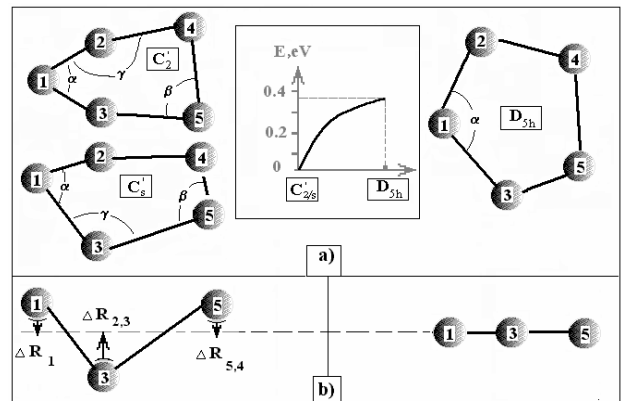


Fig. 1. The illustration of the possible space orientation of a 5-membered cyclic Si-AC and the transition energy E (a), and the direction of a displacement of Si-atom for obtaining the planar AC (b).

The detailed algorithm to carry out the estimations of a hybridization degree is described in [1]. Clearly, this is consistent with the intuitive consideration that, upon the relaxation (to the planar position), the dangling-orbital becomes more p_z -like and the back-bonds become more s -like tending toward the trigonal sp^2 form. The dangling-orbitals on the raised atoms become s -like, while those on the lowered atoms become more p_z -like. The calculated lengths of Si-Si bonds (r_{kj}) and angles between chemical bonds (α, β, γ) for the most probable space configurations are given in Table 1.

Altogether, the theoretical Si-AC structure seems to be somewhat less strained than the experimental ones. The bond lengths obtained from the total energy minimization vary in the interval 2.34–2.215 Å. The bond angle variation around the ideal tetrahedron value of 109.5° increases. These values indicate a slightly higher strain in the same sequence.

The π -bonded chain structure with the 7- and 5-atomic Si-clusters includes two critical bond angles. They are remarkably smaller than the ideal tetrahedron bond angle of 109.5° due to the adaptation of the 7-atomic ring and the 5-atomic ring. From the chemical point of view, such bond angles, $< 90^\circ$, cannot occur since the underlying structures are not stable.

The calculated geometry of the clusters is in good agreement with results from the corresponding DFT *ab initio* calculations, provided using the GAMESS algorithm [15]. The nearest neighbour distances in the Si lattice are obtained correctly. The energetic positions and the equilibrium distances of high-pressure modifications of silicon are described rather well.

In the next step, the Si-NS was constructed. For the interaction of Si-polyhedral clusters (Si-PCs), the pairwise additive approximation (PAA) [9] was used. The calculation analysis of Si-PCs, which have spherical symmetry, was performed. Formally, the total energy of an ensemble of N Si-ACs can be written as:

$$E_N = \sum_{i < j}^N E_{ij}(r_{ij}, \Omega_{ij}) + \sum_{i < j < k}^N E_{ijk}(r_{ij}, r_{jk}, \Omega_{ijk}) + \dots + \dots \sum_{i < j < k < l}^N E_{ijkl}(r_{ij}, r_{ik}, r_{il}, r_{jk}, r_{jl}, r_{lk}, \Omega_{ijkl}) + \dots \quad (11)$$

Table 1. Bond lengths r_{kj} (in Å) and bond angles α, β, γ (in degrees) for 5-membered Si-ACs with different symmetries (C_2, C_s, D_{5h}). The basis set is STO-3G (or HF/3-21G).

Si-AC	r_{kj} , Å			α	β	γ
	k	j	r_{kj}			
C_2	1	3	2.234	110.0° (110.2°)	103.5° (103.3°)	103.6° (103.6°)
	3	5	2.271			
	5	4	2.269			
C_s	1	3	2.234	108.5° (109.0°)	108.0° (108.0°)	101.0° (101.0°)
	2	4	2.271			
	5	4	2.269			
D_{5h}	1	3	2.215	108.0° (108.0°)	108.0° (108.0°)	108.0° (108.0°)
	3	5	2.215			
	5	4	2.215			




structure	geometry	calculation scheme
NDSP particle		PAA
NS surface structure		
Polyhedral Si-AC		MD PDFT MIEHT- α

Fig. 2. Atomic cluster as a block of the nanodimensional structure.

where the first term is the sum of all two-body (E_{ij}) interactions (each as a function of the separation r_{ij} and the relative orientation Ω_{ij} of the two “balls”). The three-body term E_{ijk} provides the difference between the actual energy for a trio of Si-PCs in a given orientation and the sum of the three pair potential terms; similarly, E_{ijkl} is the corresponding correction to give the correct energy for a quartet of “balls”; etc. For the system which consist of Si-PCs, we used the pairwise additive approximation, by taking only the first term in the above-presented expansion. The NS consists of Si-PCs with average diameter d (as shown in Fig. 2). For the choice of a potential (E_{ij}, E_{ijkl}), the stick-and-ball model may be recommended.

In conclusion, we present the results of PDFT-calculations for nanometer-size particles of silicon. The geometric characteristics of Si_{60} , having symmetry I_h , are listed in Table 2. “Si-ball” is constructed from twelve 5-atom Si-rings (5-Si-AC) and twenty 6-Si-ACs. Using PDFT, we have estimated the diameter d of such a Si-PC.

As seen from Table 2, the Si-Si interatomic distances in 6- and 5- AC rings are reduced. These distances are designated as \bar{r}_{66} and \bar{r}_{65} , respectively. The calculated bond lengths and the diameter of Si-AC are given together with errors. These data are in a quite good agreement with

Table 2. Geometric characteristics of $I_h - Si_{60}$ Si-ACs.

\bar{r}_{66} , Å	\bar{r}_{65} , Å	Δr , Å	d , Å	Method and basis set
2.189	2.226	0.037	123 ± 0.4	MIEHT- α [11]
2.062 ± 0.04	2.152 ± 0.04	0.085 ± 0.01	11.4 ± 0.4	STO-3G PDFT
2.213 ± 0.04	2.301 ± 0.04	0.088 ± 0.01	11.6 ± 0.4	HF/3-21G PDFT

the other results (see [8, 9]). The Si-Si bond length was generally overestimated by about 2 %, and the diameter of Si-PC was calculated to within 3.5 %.

We have analyzed other polyhedral ACs of silicon as well. Among them, we separate the following ones: 1) Si₅₀ (*D*_{5h}) – $\Delta E = 0.0868$ eV; 2) Si₃₀ (*C*_{2v}) – $\Delta E = 0.252$ eV; 3) Si₂₄ (*D*₃) – $\Delta E = 0.404$ eV. Here, ΔE denotes the difference between the total energies of PCs Si₆₀ and Si₅₀ (Si₃₀, Si₂₄). The 60-atomic Si-structure has appeared more stable than 50, 30, 24 Si-ACs. The given fact testifies that the probability of the synthesis for such stable structures as AC *I*_h – Si₆₀ is extremely high. Therefore, polyhedral silicon structures took part in the creation of the Si-NS and were identified experimentally [1, 2, 4].

Summary. We have tested the modified DFT scheme in calculations of the total energy for a complicated atomic geometry which included some useful simplicity. Due to both the neglect of all three-center integrals and the use of a short-range repulsive interaction potential in calculations of the energies, the method is computationally extremely fast. It gives reliable results for the geometries, binding energies, and vibration frequencies of different ACs. The method is applied to the building of the Si-PC from the Si-surface “blocks” reconstructed as planar. The bond lengths and the angles are obtained with errors less than 5 %.

Three important reconstruction steps have been considered: 1) the isolated Si-cyclic ACs (with 5-, 6- and 7-atoms), 2) the Si-PC which consists of Si-cyclic ACs, and 3) the cluster model of Si-NS. We have found a reasonable agreement of the different structures for the *i*-fold Si-AC rings on the elementary cell surface. However, there are also the characteristic discrepancies with respect to the order of magnitude for several effects and quantities: the buckling amplitude and the bond length in a chain, relaxation in the first and second atomic layers, bond angles. But these problems will be considered in the following publications.

The PDFT scheme may be viewed as a “hybrid” between the pure *ab initio* method – based on DFT – and the use of purely empirical potentials. It has the advantage over the latter in overcoming the “transferability” problem, and it requires much less computational efforts than full *ab initio* methods. Even in comparison with the traditional TB schemes which are computationally as fast as our method, the transferability is much better, since few parameters are used, and their determination is straightforward.

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