Questioning the existence of a unique ground state structure for Si clusters

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Density functional and quantum Monte Carlo calculations challenge the existence of a unique ground state structure for certain Si clusters. For Si clusters with more than a dozen atoms the lowest ten isomers are close in energy and for some clusters entropic effects can change the energetic ordering of the configurations. Isotope pure configurations with rotational symmetry and symmetric configurations containing one additional isotope are disfavored by these effects. Comparisons with experiment are thus difficult since a mixture of configurations is to be expected at thermal equilibrium.

The determination of the structure of clusters is a difficult task. The standard experimental techniques such as X-ray diffraction and NMR methods that allow to determine the atomic positions in crystals and molecules are not applicable to clusters. The main source of experimental information, ion mobility measurements, gives only crude information about the overall shape of a cluster. The exact atomic positions of all the atoms forming the cluster remain unknown. For this reason computational simulations provide a viable alternative to the experimental approach, which has been widely used for silicon clusters. From the theoretical point of view the ground state structure of a solid state system is determined by the global minimum of the Born-Oppenheimer potential energy surface. Finding the global minimum requires global optimization algorithms. Two problems arise in this context. First, most global optimization algorithms give no guarantee for finding the global minimum within a finite amount of computer time. Second, the Born-Oppenheimer energy surface has to be calculated with very high precision.

Concerning the first point there is now a large amount of agreement between different methods for medium size clusters containing up to 19 atoms. Genetic algorithms, the big-bang method, the basin hopping method and the minima hopping method give typically similar or even identical results. The discrepancies are rather due to different exchange-correlation functionals in different investigations.

The existence of a well defined ground state structure is generally taken to be granted for silicon clusters. Silicon clusters are, however, very different from bulk silicon where the second lowest configuration (a fourfold coordinated defect) is 2.4 eV higher than the crystalline ground state. Clusters are frustrated systems, where most of the atoms cannot adopt their favorite fourfold coordination. This can lead to small energy differences between different configurations. The significant deviations of the clusters bond lengths from the crystalline bond lengths shown in Fig. 1 illustrate this frustration.

In this work we did not only search for the ground state configurations of silicon clusters with up to 19 atoms, but for a large number of low energy configurations. This is possible with the dual minima hopping method (DMHM), which has the property that it explores higher and higher energy configurations after having found the global minimum. Fig. 2 shows the first major result of our investigation, the energies of the 10 lowest configurations of silicon clusters containing 7 to 19 atoms. The energy difference between the global minimum and the second lowest minimum is 0.8 mHa for Si₁₁, 0.9 mHa for Si₁₃, 2.1 mHa for Si₁₄, 3.1 mHa for Si₁₇ and 3.2 mHa for Si₁₉. For Si₁₃ and Si₁₇ the 10 lowest configurations are in an interval of roughly 10 mHa. Since room temperature corresponds to ~1 mHa, entropic effects play an important role for these clusters.

The results of Fig. 2 were obtained with the PBE functional. Even though this functional is considered to be among the most accurate ones, its accuracy is clearly insufficient to determine unambiguously the energetic ordering of the configurations. For this reason we have performed the most accurate electronic structure calculations that are feasible for these systems, namely quan-
tum Monte Carlo (QMC) simulations. The QMC calculations are performed using the CHAMP code developed by Umrigar and Filippi. The 1s, 2s and 2p electrons of Si are eliminated using a relativistic Hartree-Fock pseudopotential [22]. A Slater-Jastrow type wave function is used as the trial wave function. The orbitals of the Slater determinant are taken from a DFT calculation with the GAMESS [23] code using the B3LYP functional. The parameters of the Jastrow function describing electron-electron, electron-nuclear and electron-electron-nuclear correlations are optimized in variational Monte Carlo using energy minimization [24]. Diffusion Monte Carlo method calculates the final energies, which are presented in Table I. The corresponding configurations are shown in Table II. The QMC energies have error bars of the order of 1 mHa which is just enough to discriminate between the different energies. Even though the Monte Carlo results change the energetic ordering of the PBE results, the central feature remains. Different configurations have energies that are nearly identical. Table II also shows that the various high quality basis sets used by different electronic structure programs give slightly different answers that might change the energetic ordering.

The new low-lying structures Si₁₆₈, Si₁₆₆, Si₁₇₆, Si₁₇₈, Si₁₈₈ and Si₁₉₈, which were found with DMHM and the reference structures Si₁₆ [11], Si₁₇ [12], Si₁₈ [13] and Si₁₉ [14] were already presented in [15]. The structure Si₁₃ was found by Ho et al. [15]. The rotationally symmetric Si₁₃d structure was recently proposed by Hartke [25], Si₁₃f by Röthlisberger et al. [26] and Si₁₃g by Jeong et al. [27]. Using DMHM we found new low-lying structures Si₁₃a, Si₁₃b, Si₁₃c and Si₁₃e. From the QMC results in Table I, we conclude that the Si₁₃d and Si₁₃e configurations are the lowest energy structures. The new Si₁₃a structure found with DMHM contains the stable Si₆ subunit [28].

After having discussed the limitations of computational approaches in determining the total energy of silicon clusters with the necessary accuracy let us discuss the physical effects that can change the energetic ordering. For the Si₁₃, Si₁₃ₐ and Si₁₃d clusters we have zero point energies of 24.0, 25.0 and 24.5 mHa. For the Si₁₉ and Si₁₉₈ we have 38.8 and 38.0 mHa. So the differences of the zero point energies are all of the order of mHa and thus not negligible, but do not change the energetic ordering for the clusters we studied. In order to study the entropic effects we calculated the rotational and vibrational free energy based on the harmonic frequencies obtained from density functional (PBE) calculations [29]. The translational free energy does not depend on the configuration and was therefore not considered. If one compares the sum of the rotational and vibrational free energy for non-symmetric configurations, one typically finds differences of about 0.5 mHa at room temperature and about 1 mHa close to the melting point of the clusters [30]. This might change the energetic ordering, but we did not find a case where it actually does.

The situation is different if one compares a symmetric with a non-symmetric configuration. Silicon occurs in nature mainly as ²⁸Si or ²⁹Si isotope. The predominant isotope for silicon ²⁸Si (abundance ~92% [31]) has mass 28 and no nuclear spin, the ²⁹Si isotope (abundance ~5% [31]) has mass 29 and nuclear spin 1/2. When studying configurations with rotational symmetry, we

![Figure 2: The dependence of the PBE energy interval for the lowest 10 configurations on the cluster size.](image)

| Cluster | B3LYP | PBE | PBE | PBE | DMC |
|---------|-------|-----|-----|-----|-----|
| Si₁₃    | 0.0   | 0.0 | 0.0 | 0.0 | 0.0 |
| Si₁₃ₐ   | 11.7  | 6.3 | 7.1 | 5.3 | 3.3±1.0 |
| Si₁₃b   | -1.4  | 9.5 | 13.2| 11.5| 5.7±1.0 |
| Si₁₃c   | 8.6   | 4.7 | 3.1 | 3.1 | 6.4±1.0 |
| Si₁₃d   | -6.7  | -2.9| 0.9 | 0.6 | -5.7±1.1 |
| Si₁₃f   | 3.6   | 3.9 | 4.1 | 4.2 | 6.1±1.0 |
| Si₁₃g   | 4.2   | 7.0 | 8.5 | 8.0 | 10.6±1.0 |
| Si₁₉    | -6.3  | -0.8| 2.6 | 2.3 | 0.0±1.1 |
| Si₁₆    | 0.0   | 0.0 | 0.0 | 0.0 | 0.0 |
| Si₁₆ₐ   | 24.0  | -0.2| -6.0| -3.7| 9.9±1.4 |
| Si₁₆₉   | 9.5   | 0.9 | 0.9 | 1.4 | 8.3±1.4 |
| Si₁₇    | 0.0   | 0.0 | 0.0 | 0.0 | 0.0 |
| Si₁₇ₐ   | 7.4   | 8.4 | 2.6 | 2.7 | 6.3±1.5 |
| Si₁₇₉   | 10.2  | 11.6| 8.4 | 8.4 | 13.2±1.7 |
| Si₁₈    | 0.0   | 0.0 | 0.0 | 0.0 | 0.0 |
| Si₁₈ₐ   | 31.3  | 17.1| 10.0| 10.2| 23.9±1.6 |
| Si₁₉ₐ   | 0.0   | 0.0 | 0.0 | 0.0 | 0.0 |
| Si₁₉₉   | 15.4  | -1.0| -4.2| -1.9| 2.1±1.7 |

TABLE I: The energy differences in mHa between the lowest energy geometries Si₁₃ₐ, Si₁₃b, Si₁₃c, Si₁₃d, Si₁₃f, Si₁₆₈, Si₁₆₆, Si₁₇₆, Si₁₇₈, Si₁₈₈, Si₁₉₈ and the reference structures Si₁₃, Si₁₁₆, Si₁₁₇, Si₁₁₈ and Si₁₁₉, proposed earlier as global minima in DFT. The Gaussian [17] calculations used the 6-311G(2d) basis and the DMOl3 2005 [18, 19] calculations the extended basis set. The CPMD [20] calculations were performed with an accurate pseudopotential [21] with a 35 Ry plane wave cutoff and a 30 Å simulation cell.
will consider pure clusters consisting only of $^{28}\text{Si}$ atoms since the presence of a $^{29}\text{Si}$ atom would destroy the rotational symmetry. One can easily estimate from the abundancies of the isotopes that $\sim 34\%$ of $\text{Si}_{13}$ clusters will be pure clusters. For such a cluster with rotational symmetry, the order of the rotational subgroup enters into the formula for the rotational free energy. This leads to a weaker decrease of the free energy for symmetric configurations compared to non-symmetric configurations and thus favors non-symmetric structures. In Fig. 4 we present the free energy curves for the structures $\text{Si}_{13a}$ and $\text{Si}_{13d}$ as a function of temperature with the $\text{Si}_{13}$ free energy chosen as reference energy. The width of the bands for $\text{Si}_{13a}$ and $\text{Si}_{13d}$ represents the statistical errors in the QMC energies with respect to that of structure $\text{Si}_{13}$. For the symmetric $\text{Si}_{13a}$ configuration the order of the rotational subgroup is 3, for $\text{Si}_{13d}$ it is 2 and for $\text{Si}_{13}$ it is 1. This leads to a reversal of the energetic ordering of the structures $\text{Si}_{13}$ and $\text{Si}_{13a}$ in the interval between 250 and 650 K. Because of the entropic effect the $\text{Si}_{13}$ configuration, which is the highest at zero temperature, becomes the lowest at temperatures above 1000 K. At room temperature the $\text{Si}_{13a}$ and $\text{Si}_{13d}$ bands are separated by an energy gap in the range between $\sim 1.2\text{mHa}$ and $\sim 5.5\text{ mHa}$. This corresponds to a Boltzmann weight in the range between $0.7\%$ and $30\%$.

These considerations are only valid for clusters consisting purely of $^{28}\text{Si}$ atoms. The presence of a $^{29}\text{Si}$ isotope destroys the rotational symmetry. One can estimate from the abundancies of the isotopes that $\sim 24\%$ of $\text{Si}_{13}$ clusters will contain one $^{29}\text{Si}$ isotope. If one $^{28}\text{Si}$ atom with nuclear spin 0 is replaced by a $^{29}\text{Si}$ isotope which has spin $1/2$, the nuclear wave-function is a doublet and additional degeneracy comes from the fact that the isotope can replace any of the atoms. For a non-symmetric cluster with $N$ atoms the degeneracy is thus $2N$. For a symmetric cluster that has several equivalent atoms the degeneracy is however reduced. In the case of the $\text{Si}_{13a}$ structure there are for instance only 5 non-equivalent sites, $\text{Si}_{13d}$ has 6 and $\text{Si}_{13}$ has 9. The nuclear entropy thus favors $\text{Si}_{13}$ over $\text{Si}_{13d}$ by $-kT \ln(\frac{9}{6})$ which is $\sim 0.4\text{ mHa}$ at room temperature. In addition, the vibrational and rotational entropy contributions are slightly changed by the presence of an isotope leading to an effect of the same order of magnitude.

Up to now we have concentrated on the 10 lowest structures. Considering higher lying configurations, the energetic spacing between configurations decreases even further. This can be inferred from the fact that the configurational density of states, defined as the number of configurations per energy interval, increases strongly. This is shown in Fig. 5 for the $\text{Si}_{17}$ cluster.

Several simulations have shown that the lowest energy structures for Si clusters with less than 20 atoms are non-spherical whereas larger clusters prefer to be spherical [1, 8]. In these studies the non-spherical to spheri-
disfavors symmetric clusters \( S_{17} \) and energetic ordering of the lowest configurations. Entropy effects that are usually neglected can change the number of configurations for certain silicon clusters that are energetically extremely close to the ground state. As a consequence, measured properties of clusters can be sensitive to symmetry considerations might thus easily change the energy order of clusters with more than 19 atoms. Even if there is no reordering, different structures can be so close in free energy that a mixture of two or more configurations will be found at thermal equilibrium. As a consequence measured properties of clusters can be some average of the properties of several low-lying isomers.

In summary, we have shown that there exists a large number of configurations for certain silicon clusters that are energetically extremely close to the ground state. This feature was observed for \( S_{13} \) and \( S_{19} \) and it will presumably be even more important for larger cluster sizes that were not studied in this work. As a consequence, entropy effects that are usually neglected can change the energetic ordering of the lowest configurations. Entropy disfavors symmetric clusters \( S_n \) in the range \( 13 \leq n \leq 19 \) which contain in most cases no \( ^{29}\text{Si} \) isotope or one \( ^{29}\text{Si} \) isotope. Larger clusters will on average contain more than one \( ^{29}\text{Si} \) isotope and the symmetry related effects discussed above do not exist. However, for larger clusters the 10 lowest configurations can be expected to lie within an even smaller interval. The entropic effects not related to symmetry considerations might thus easily change the energy order of clusters with more than 19 atoms. Even if there is no reordering, different structures can be so close in free energy that a mixture of two or more configurations will be found at thermal equilibrium. As a consequence measured properties of clusters can be some average of the properties of several low-lying isomers.

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