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Stability of Si_{70} cage structures

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Abstract. We have performed calculations on the cage structures with and without inner atoms, a stacked structure for Si_{70} cluster by using FP-LMTO-MD method. It is found that the Si_{70} perfect cages, including its ionic cages, would distort into puckered hollow balls. But the distorted hollow ball is still less stable than a stacked structure. Further calculations suggest that a distorted cage structure with inner atoms, resulting from Si_{60} perfect cages by inserting 10 inner atoms, is much more stable than the distorted hollow cage and the stacked structure of Si_{70}.

PACS. 36.40.-c Atomic and molecular clusters – 71.10.-w Theories and models of many-electron systems – 71.20.-b Electron density of states and band structure of crystalline solids – 31.15.-p Calculations and mathematical techniques in atomic and molecular physics (excluding electron correlation calculations)

Fullerene cages are important structures for carbon clusters. Among the cages, C_{60} and C_{70} cages show special stability [1]. Although there are numerous possible C_{60} and C_{70} cage isomers, the most stable cages are the C_{60} cage with I_h, and C_{70} cage with D_{5h}, respectively. The cages have extensively stimulated a variety of studies on their physical and chemical properties. Similarly, the corresponding Si_{60} and Si_{70} fullerene cages to the C_{60} and C_{70} cages have been also investigated by different methods [2–9]. For Si_{60} cluster, two different results have been proposed. Semi-empirical calculations at AM1 level suggest that the perfect cage is the most stable [4–6]. Tight-binding molecular dynamics method shows that the Si_{60} perfect cage is not stable and relaxes into a structure resembling a puckered ball [8,9]. Using FP-LMTO-MD method, we have also investigated the Si_{60} perfect cage. Our result indicates that the Si_{60} perfect cage distorts into a puckered ball with lower T_h symmetry [10]. In addition, their atomic arrangement tends toward tetrahedral geometry [10]. Compared to one stacked structure built from tricapped trigonal prism (TTP) subunits, the distorted structure is still not stable [11]. For Si_{70} cluster, Khan et al. have investigated the stability of its cage structure using tight-binding molecular dynamics [8]. They have found that the Si_{70} unrelaxed cage structure has different bond lengths. But after relaxation, all the bonds become approximately 2.37 Å.

In this paper, we have performed calculations on three different structures of Si_{70} cluster by using more sophisticated FP-LMTO-MD method. Our principal aim is to investigate the stability of the Si_{70} cages.

The FP-LMTO method [12–15] is a self-consistent implementation of the Kohn-Sham equations in the local-density approximation. More ten years ago, Methfessel et al. had applied the method to clusters. The method has been improved many times. At present, it has been used successfully to find the ground state structures for small and medium-size silicon clusters [16]. We have further improved the method to investigate the stable structures for silicon ionic clusters. Some satisfied results have been obtained [17]. In this method, space is divided into two parts: non-overlapping muffin-tin (MT) spheres centered at the nuclei and the remaining interstitial region. The electron wave functions are expanded in terms of muffin-tin orbitals [18]. The LMTO's are augmented Hankel functions, and are augmented only inside the MT spheres rather than in the interstitial region [18–20]. All MT sphere radii for Si are taken as 2.0 a.u. The LMTO basis sets include s, p, and d functions on all spheres. Its potential and density are expressed as a linear combination of Hankel functions. The details of how the molecular dynamics can be performed are described in references [12–15,18–20]. The method is suited for investigating the cluster structures. In order to test the accuracy of this method, we present our results for Si_2-Si_7 clusters in Tables 1 and 2, and compare them with those obtained by some ab initio (HF/6-31 G* and MP4/6-31 G*) calculations [21]. In the method compared, the ground state structures were optimized with the standard 6-31G* basis set. The method with the 6-31G* basis set has been used widely in the

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Table 1. Optimized molecular geometries (in Å) for Si_2−Si_7 clusters by the Hartree-Fock (HF) level of theory with the polarized 6-31G* basis sets and FP-LMTO-MD method. The entries under "Bond length, or bond angle" correspond to Figure 2 of reference [29]. The HF/6-31G* values are cited from reference [21].

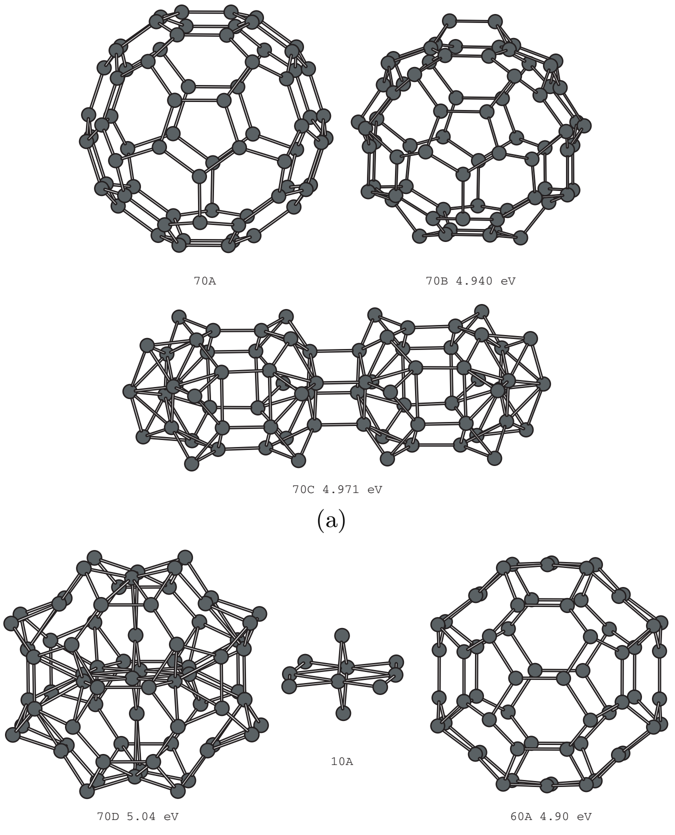
cluster	symmetry	bond length, or bond angle	HF/6-31G*	FP-LMTO-MD
Si_2	D_{2h}	Si−Si	2.23	2.18
Si_3	C_{2v}	d_{1-3}	2.17	2.17
		θ_{132}	77.8°	80.0°
Si_4	D_{2h}	d_{1-3}	2.30	2.31
		d_{3-4}	2.40	2.39
Si_5	D_{3h}	d_{1-4}	2.34	2.30
		d_{1-2}	2.78	2.96
Si_6	D_{4h}	d_{1-3}	2.35	2.35
		d_{3-5}	2.71	2.72
Si_7	D_{5h}	d_{1-4}	2.47	2.47
		d_{1-6}	2.48	2.45

Table 2. Calculated total binding energy (E_b, in eV), binding energy per atom (E_a, in eV), scaled binding energy per atom (E_s, in eV), and the measured binding energy per atom (E_{exp}, in eV) by Knudsen mass spectrometers. The HF/6-31G* and MP4/6-31G* calculations are cited from reference [21]. The experiment results are quoted from references [30–36].

cluster	Si_2	Si_3	Si_4	Si_5	Si_6	Si_7
E_b (HF/6-31G*)	1.47	2.96	5.90	7.24	9.90	12.08
E_b (MP3/6-31G*)	2.60	6.34	10.57	13.74	18.02	22.16
E_b (FP-LMTO-MD)	4.05	9.97	15.81	21.30	26.97	32.61
E_a (MP3/6-31G*)	1.30	2.11	2.64	2.75	3.00	3.17
E_a (FP-LMTO-MD)	2.02	3.32	3.95	4.26	4.50	4.66
E_s (MP3/6-31G*)	1.56	2.54	3.17	3.30	3.60	3.80
E_s (FP-LMTO-MD)	1.56	2.54	3.05	3.28	3.47	3.59
E_{exp}	1.66	2.44	2.99	3.24	3.43	3.53

determination of geometries for a variety of systems, and the calculated Si−Si bond lengths can be expected to be reliable to within 1−2% [21]. Their electron correlation effects were included by means of complete fourth order Moller-Plesset perturbation theory with the 6-31G* basis set (MP4/6-31G*). The theory has contributions from single, double, triple, and quadruple substitutions from the starting HF determinant and gives reliable binding energies for many systems. However, by comparison with the experimental values, the binding energies of Si_2 and Si_3 obtained by the MP4/6-31G* calculations suggests that about 80−85% of the true binding energy is obtained. A scale factor of 1.2 empirically corrects for the underestimations in Si_2 and Si_3, and yields binding energies in excellent agreement with experiment. If the scale factor is used for other Si clusters, the scaled binding energies per atom agree with experiment basically. We have also obtained the lowest energy structures for the small Si clusters by using the FP-LMTO-MD method. It is found that our calculated structures are also reliable. Although the calculated binding energies are larger than the corresponding experimental values, we find that a scale factor of 0.77 empirically corrects for the overestimations, and yields binding energies in excellent agreement with experiment. They are much closer to the experimental values than those obtained by MP4/6-31G*. The use of such a single uniform scale factor does not bias the relative comparisons of the different cluster [22]. The stable structures in this paper are obtained by performing FP-LMTO-MD optimization without any symmetry restrictions.

In this section, we will present three different stable structures of Si_{70} cluster. Because there are many isomers for Si_{70} cluster, it is very difficult to find its ground state structure. However, it is interesting to investigate the stability of its cage structures by selecting three representative structures. The first structure is the perfect icosahedral structure corresponding to C_{70} fullerene cage shown as 70A in Figure 1. It consists of 12 pentagons and 25 hexagons. Their bond lengths range between 2.22 Å and 2.27 Å. Starting from such a perfect geometrical configuration, we have performed calculation on it by using FP-LMTO-MD method. In each time step, the eigenvalue problem is solved exactly and the output density is admixed to the input density in the usual way. The nuclei are then moved according to the forces using the Verlet algorithm. We then decompose the mixed density, move each partial density along with its atom, and re-overlap at the new geometry. After many iterations, the process is stopped when the self-consistent condition meets. We find that the perfect initial configuration with D_{5h} symmetry is unstable, it would distort to a lower C_{2v} symmetrical geometry. Its final stable configuration is shown as 70B in Figure 1. It is obvious that the cage has severe structural distortion. 70B looks like a puckered hollow ball similar to Si_{60} cage [10]. The silicon atomic arrangement on the surface tends toward tetrahedral geometry. Some of the bond lengths become longer compared with those in 70A. Because some of the 70 vertices have approximate tetrahedral angle, the bond angles also change obviously. In addition, we have also performed calculations on the perfect anionic and cationic cages. It is found that they have similar structural distortions to the neutral



(a)

(b)

Fig. 1. Perfect cage 70A, distorted hollow cage 70B, stacked structure 70C and distorted solid cage 70D for Si_{70} cluster.

Table 3. The binding energy per atom E_a and energy gap E_g between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) of distorted cage and stacked structure of neutral, anionic and cationic Si_{70} cluster.

70B	E_a	E_g	70C	E_a	E_g	70D	E_a	E_g
neutral	4.93	0.11	neutral	4.97	0.36	neutral	5.04	0.12
anion	4.98	0.26	anion	5.01	0.66	anion	5.08	0.20
cation	4.86	0.14	cation	4.90	0.35	cation	4.97	0.12

cage. Their binding energies are listed in Table 3. Their energy gaps E_g between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) are also listed in Table 3.

70C is a stacked structure. The optimization calculation suggests that it is more stable than the distorted cage 70B. It lies 2.66 eV below 70B. The structure consists of four units. Its subunit includes 16 atoms. Three atoms cap the subunits on the two ends. Similarly, its two ionic structures, which correspond to 70C, are also more stable than two charged hollow cages, respectively.

For Si_{60} cluster, similar situation is found [10]. After structural optimization, the perfect cage would distort into a puckered hollow ball shown as 60A in Figure 1. Its binding energy per atom is 4.90 eV. If we insert 10 inner atoms into the perfect hollow cage for Si_{60} cluster, we can obtain an initial geometrical configuration of Si_{70} cluster. Structural optimization finds that it would undergo obvious distortion into a much more stable structure 70D with D_{2h} symmetry. Its binding energy per atom is up to 5.04 eV. It is found from observing 70D and 60A in Figure 1 that the cage of 70D has much severer structural distortion compared to that of 60A. 10 inner atom configuration is shown as 10A in Figure 1. It can be obtained by adding 4 edge atoms on the ground state structure (a tetragonal bipyramid) of Si_6 cluster. 70D is 7.70 eV more stable than 70B. Its two ionic structures have also larger binding energies. Obviously, the Si_{70} cage (70B) without interior atoms is difficult to find experimentally.

For small silicon clusters ($n = 5-13$), their ground state structures are polyhedrons, which are not pieces of silicon crystal. The configurations reduce the number of the hanging bonds on the surface atoms to minimum. As the atom number increases, the stacked prolate structures become more stable than other structures. There are not any inner atoms in the stacked structures between $n = 14$ and $n = 23$. In the range from 14 to 23, an inner atom inserted would form multi-bonds with the surrounding atoms. In general, the coordination number of the inner atom is larger than 6 because of narrow space in the stacked structures. It is well-known that there may be a saturation of coordination at 6, and further bonding may cause overcrowding and destabilization for silicon clusters [23]. The "prolate to spherical" structural transition begins at $n = 24$ in the experiment [24,25]. Starting from this size, the compacted structures with inner atoms begin to compete for the ground state structures with the prolate structures. For the silicon clusters in the range from 24 to 30, there is enough space for the inner atoms inserted. For larger silicon clusters ($n > 30$), only a few results have been reported up to now. Kaxiras proposed physical appealing structures to explain the exceptional chemical stability of Si_{33} and Si_{45} clusters reported by Elkind et al. [26,27]. In the Si_{45} cluster, Kaxiras's structure contains a central fourfold coordinated atoms, a surrounding shell of four atoms that are also fourfold coordinated, and 40 surface atoms arranged similar to the π-bonded chains believed to be responsible for the 2×1 reconstruction of the Si(111) surface [28]. For the larger silicon clusters, the inner atoms make the structures more compacted. At the same time, they become more stable because of some atoms fourfold coordinated and the surface reconstructed. At this stage, the clusters transit into crystal structure gradually as their sizes increase. It can be expected that 70D should have larger binding energy due to its structural characteristics as follows.

For C_{70} cluster, the perfect fullerene cage shows special stability due to sp^2 hybrid. However, the sp^3 hybrid of silicon results in the distortion of the cage, forming some tetrahedron-like configurations on its surface. Although the tetrahedron-like configurations strengthen the stability of the hollow cage, it is only a meta-stable structure because there is large interior space in its structure. However, the inner atoms inserted would make some atoms in the cage be fourfold coordinated and the structure more compacted. For example, further observation on 70D finds that many atoms are fourfold coordinated. The bond angles and bond lengths of some atoms are equal to those in silicon crystal approximately. This is the reason why 70D is more stable than 70B. As the atom number increases, more atoms are fourfold coordinated. The compacted structures with inner atoms appear preferable to other structures when they transfer into crystal.

It is found from Table 3 that the energy gaps E_g of 70D and its ionic structures approximate to those of 70B, whereas the E_gs of 70C are different. It appears that the E_gs are mainly determined by their surface structures instead of the inner configurations.

In summary, using full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO MD) method, we have performed calculations on three representative structures for the interesting Si_{70} cluster. Calculated results suggest that the stable structure of Si_{70} fullerene cage is a distorted puckered ball with C_{2v} symmetry. But it is not as stable as a stacked structure built from four subunits. If 10 atoms inserted into the perfect cage of Si_{60} cluster, structural optimization finds that the cage with inner atoms is much more stable than the hollow cage and stacked structure. As atom number increases, the preferred configurations in energy should be the compacted cages with inner atoms.

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