Electronic structure of small icosahedral silicon clusters

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Abstract. The electronic structure of small icosahedral (I_h) silicon clusters has been studied using the discrete variational method within the local density functional theory. The I_h Si_{13} cluster is not a closed-shell structure, in contrast to the predictions of empirical calculations. The Si_{13}^{2+} cluster is found to be stable, with an exceptionally large LUMO–HOMO gap.

Investigating the physical and chemical properties of atomic clusters of metallic, non-metallic and semiconductor elements is currently one of the most exciting areas in physics and chemistry, especially after the discovery of the stable C_{60} molecule and solid [1]. Recently, covalently bonded Si and Ge microclusters have attracted considerable attention, and extensive studies have been conducted both experimentally and theoretically.

Experimental work on semiconductors includes photoelectron spectroscopy [2], collision-induced dissociation [3], photofragmentation [4, 5] and chemical reactivity [6–8]. Chemical reactivity studies of C_2H_4, O_2 and D_2O with positive silicon cluster ions has showed that the 13-atom cluster is generally unreactive to these reagents, while other *magic* silicon clusters assumed by some authors [7], such as 33-, 39- and 45-atom clusters, were found only to be unreactive to particular reagents only. It is likely, therefore, that the 13-atom silicon cluster has a unique geometrical and electronic structure different from its neighbours.

First principles quantum mechanical calculations have successfully predicted the structure and properties of Si_n clusters for $n \leqslant 10$ [9]. Small silicon clusters prefer regular or distorted polyhedral structures which are close packed and which do not follow the structure of the bulk of the silicon crystal. Many atoms in these small clusters have a coordination number greater than four, and the chemical bonding between two atoms in the cluster never reaches sp^3 hybridization. For clusters with more than ten atoms, it is difficult to perform a global optimization on their geometrical structure by high-level *ab initio* calculations.

Chelikowsky and Phillips [10] have used a classical potential to model silicon clusters with up to 25 atoms. According to their model, the 13-atom cluster is icosahedral with a 1–5–1–5–1 layer structure. This provides a plausible way to account for the unreactivity of the Si_{13}^+ cluster. Rantala *et al* [11] have also predicted that the icosahedral Si_{13} cluster is a closed shell, using the empirical tight-binding method. It is interesting to note that the equilibrium structure of the Si_7 cluster determined by many groups has a 1–5–1 D_{5h} structure [9], and thus the icosahedral Si_{13} cluster could be viewed as a double Si_7 cluster. On the whole, there is some argument for the I_h Si_{13} cluster structure, both from experiments and empirical theoretical investigations. However, the icosahedral structure has been found only in inert gases or some metallic clusters [12], and no clear experimental evidence supports the I_h Si_{13} structure. Recently, Röthlisberger *et al* [13] reported Car–Parrinello molecular dynamical studies on the geometries of Na, Mg, Al and Si 13-atom clusters. They found

that the equilibrium structure of the Si_{13} cluster is a trigonal antiprism (TAP) with six caps on the three-fold faces and one six-fold coordinated additional cap. However, they did not give the electronic structure of the cluster.

The electronic structure of I_h 13-atom clusters is of great interest in cluster chemistry and physics. Many authors have reported studies on Al_{13} [14], Be_{13} [15] and B_{13} [16] clusters. We have also performed self-consistent-field spin-polarized studies on the Co_{13} cluster [17]. All these studies show that I_h clusters have many special properties due to their non-crystalline symmetry. Although Röthlisberger *et al* found that the I_h Al_{13} cluster is not a stable structure, Khanna and Jena [18] considered that if the central Al atom in the I_h Al_{13} cluster were replaced by an Si atom, the $Al_{12}Si$ cluster would be exceptionally stable, so being an ideal building block for assembling cluster materials.

In this paper, we have used the well-developped discrete variational method (DVM) [19] within the local density functional theory [20] to calculate the electronic structure of small icosahedral silicon clusters. This method has been successfully used in condensed matter physics and chemistry [21, 22]. Recent calculations on C_{60} obtained excellent results compared with experiments [23]. The computational procedure has been documented in detail elsewhere, and we only give a brief description. In the one-particle Kohn–Sham equation, the non-local Hartree–Fock exchange potential is replaced by an exchange–correlation potential depending only on the local density $\rho(r)$. The Kohn–Sham form for exchange–correlation potential [20] was used in the calculations. The matrix elements of the Hamiltonian and overlap are obtained by a weighted summation over a set of discrete sample Diophantine points [20]. 900 points were used for each atom in this study.

To approximate the molecular density $\rho(r)$ we used a variational density expansion method, as described by Delley and Ellis [24]. In this method the approximate charge density $\rho(r)$ is cast into a multicentre-overlapping multipolar form,

$$\rho(r) = \sum_j d_j \rho_j(r). \tag{1}$$

The density function $\rho_j(r)$ has been divided into two sets. The first set consists of atomic spherical charge densities, calculated from the wavefunction variational basis set. In what is called the self-consistent charge (SCC) procedure, only this set of functions is used to represent the electron density. The second set is a totally symmetric combination of spherical harmonics, $l \leqslant 1$ in this calculation, centred on the symmetry-related atoms of the molecule. The coefficients d_j are determined self-consistently by a global least-squares fit to the molecular charge density. This self-consistent multipolar (SCM) scheme gives a better representation of the details of the molecular charge distribution than the SCC procedure based on the Mulliken analysis [25], especially for covalent materials.

According to the standard local density approximation [20], the binding energy can be evaluated as

$$E_b = E_t - E_{ref} = \sum_j f_j \epsilon_j - \frac{1}{2} \int \int \frac{\rho(r')\rho(r)}{|r - r'|} \, d^3r \, d^3r'$$
$$+ \int \rho(r)[E_{xc}(r) - V_{xc}] \, d^3r + \frac{1}{2} \sum_{\mu,\nu}^{'} \frac{z_\mu z_\nu}{R_{\mu\nu}} - E_{ref} \tag{2}$$

where E_{ref} is the energy of dissociated atoms in the cluster, and ϵ_j, f_j are the eigenvalue and occupation of the molecular orbital, respectively.

The 3s, 3p and 4s atomic numerical functions of Si were used as variational valence orbitals, while the inner orbitals were kept frozen in the calculations. To satisfy ourselves

that the choice of the basis functions and the numerical procedure are reliable, we calculated the bond length, binding energy and ground-state configuration of the Si dimer, for which both experimental results and previous calculations are available. We find that Si_2 has a $^3\Sigma_g^-$ state with a bond length of 2.28 Å and a binding energy of 3.09 eV. This is in very good agreement with the experimental values of 2.24 Å and 3.0 eV, respectively.

The bond lengths of Si_{13} and Si_{12} clusters have been relaxed by calculating the binding energy minima, while maintaining the I_h symmetry. The calculated binding energy and bond length for the Si_{13} cluster are 3.80 eV and 4.75 au, respectively, and for the Si_{12} cluster 3.76 eV and 4.70 au.

The electron levels for Si_{13}^+, Si_{13} and Si_{12} clusters are shown in figure 1. The highest occupied molecular orbital (HOMO) for the Si_{13}^+ cluster is a four-fold degenerate G_g orbital, but with only one-electron occupation. Therefore, the I_h symmetry Si_{13}^+ cluster is not a closed-shell structure and will be distorted by the Jahn–Teller effect. In order to achieve reliable accuracy, we used a extended basis set including 3d and 4p orbitals, and changed the exchange–correlation function as well as the discrete sample points for integration. We found that the choice of different exchange–correlation and discrete points has a negligible effect, but that the extended basis set expanded the valence band. However, the open electronic structure of the I_h Si_{13} cluster remained unchanged, in good agreement with recent Car–Parrinello calculations [13].
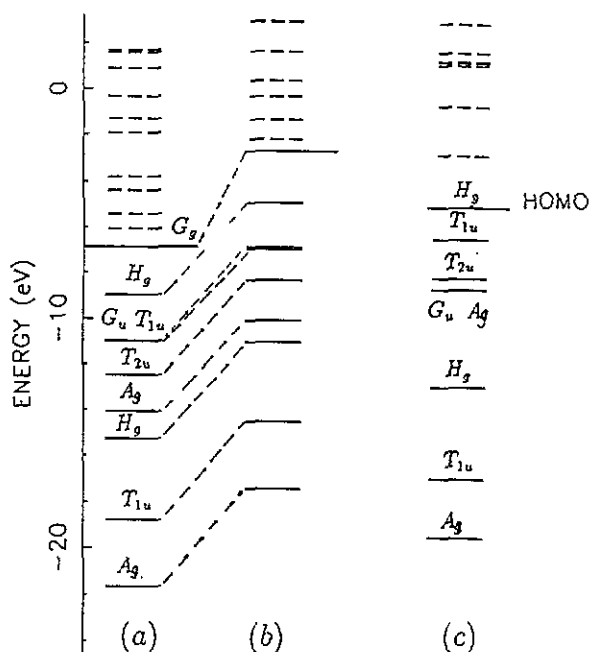

Figure 1. Electronic levels of (a) Si_{13}^+, (b) Si_{13} and (c) Si_{12} clusters.

However, this is inconsistent with the results of Chelikowsky and Phillips [10], who found that Si_{13} cluster has a stable icosahedral structure. Rantala *et al* [11] have also reported, using a tight-binding model, that the Si_{13} cluster is a closed-shell structure with a large energy gap between LUMO and HOMO of 2.8 eV. Therefore, the empirical potentials used in these studies may not be suitable for describing the directional bonding of silicon clusters, as has been pointed out by Andreoni and Pastor [26]. Khom and Broughton [27] have reported molecular-dynamics relaxation on icosahedral silicon clusters with more than

50 atoms, and found that these icosahedral Si clusters are not stable and that the relaxed clusters look like pocked balls, showing the difference between the silicon and carbon I_h microclusters. This is consistent with our calculations on Si_{13} and Si_{12} clusters. We have not attempted to relax those structures within the local density approximation because the calculations would be very long. However, at this stage some interesting results have been obtained.

The electronic structure of alkali and coinage metal clusters are well described in terms of the electronic shells of spherical jellium [28]. Microclusters of other metal elements are also described by this model [15]. It is interesting to ask if the electronic shell model is applicable to silicon clusters. We give the corresponding spherical shells along with the orbitals in I_h symmetry in table 1. From this table, we note that the electronic orbitals in the icosahedral structure can be classified according to the spherical shell model, despite the covalent nature of silicon. Discrepancies from the spherical shell model appear in the higher energy 1f and 1g orbitals. Therefore, the energy levels of the icosahedral silicon clusters are not predicted perfectly by the jellium model, despite the similarity between icosahedron and sphere.

Table 1. Orbital energy (in eV), occupations and percentage compositions for the occupied valence molecular orbitals of the Si_{13}^+ cluster. Si(1) and Si(2) represent the central and surface Si atoms, respectively.

Spherical shell representation	I_h orbital	Energy	Occupancy	Si(1)			Si(2)		
				3s	3p	4s	3s	3p	4s
1s	$1A_g$	−21.606	2	12			65	22	
1p	$1T_{1u}$	−18.746	6		11		76	9	
1d	$1H_g$	−15.202	10				77	22	
2s	$2A_g$	−14.022	2	62			29		8
1f	$1T_{2u}$	−12.386	6				99		
	$1G_u$	−10.944	8				100		
2p	$2T_{1u}$	−10.876	6		25		27	46	
1g	$2H_g$	−8.898	10				31	68	
	$1G_g$	−6.787	1					100	
	$3A_g$	−6.28		45				52	

The density of states (DOS) can be obtained by summing over Lorentzian lines of width σ, 0.27 eV in this calculation, centred at the molecular orbital energy ϵ_p,

$$D(E) = \sum_p \frac{\sigma/\pi}{(E - \epsilon_p)^2 + \sigma^2}.$$ (3)

Figure 2 shows the DOS of the Si_{13} cluster. Because there are only two electrons at the HOMO of the Si_{13} cluster, the Fermi level is close to the bottom of the HOMO where the DOS is lower. The HOMO of the Si_{12} cluster (see figure 3) is a five-fold H_g orbital occupied by eight electrons; this structure is also not shell-closing and the DOS at the HOMO level is higher than for the Si_{13}^+ cluster. It is interesting to note that the Si_{13}^{2+} cluster will be a stable cluster with a large LUMO–HOMO gap of about 2.0 eV. Kawai and Weare [16] recently reported that, although the B_{13} cluster is not a closed shell, the B_{13}^+ cluster is very stable with large energy gap of about 2.0 eV. These exceptionally stable clusters might be used as building blocks to form new nanomaterials, as reported in [18].

The main results for the Si_{13}^+ cluster are given in tables 1 and 2. It can be seen that most molecular orbitals are a combination of surface atomic orbitals, in particular the HOMO has the complete 3p character of the surface atom. The main characters of molecular orbitals
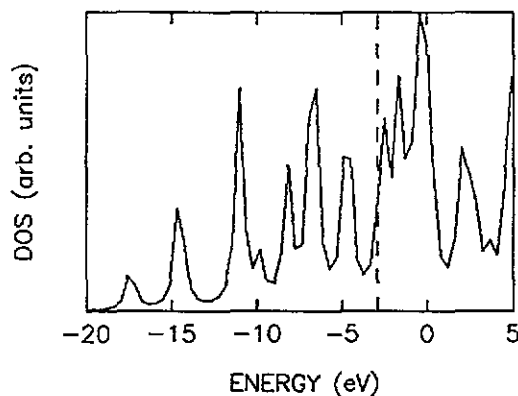
Figure 2. Density of states of the Si_{13} cluster. The broken line indicates the Fermi level, which is estimated according to the occupation of the HOMO level.
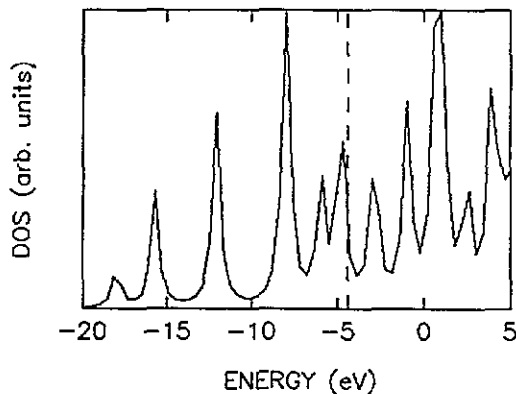
Figure 3. Density of states of (a) the Si_{12} cluster. Notation as in figure 2.

below -12 eV are 3s, while above -12 eV they are 3p. Simple Mulliken populations in table 2 show that the Si(1) atom is negatively charged and that the 3s electrons transfer to the 3p orbital, but that the surface Si(2) atoms are positively charged and nearly have the free-atom configuration s^2p^2. This is in line with *ab initio* calculations on small ($n < 10$) silicon clusters.

Table 2. Mulliken population of Si_{13}^+ and Si_{13} clusters.

	Si_{13}^+		Si_{13}	
	Si(1)	Si(2)	Si(1)	Si(2)
3s	0.959	1.918	0.864	1.888
3p	3.408	1.937	3.294	2.059
4s	0.173	0.128	0.197	0.023
Net	−0.540	0.128	−0.355	0.030

From figure 1 we found that the electron levels of the Si_{13}^+ cluster are evenly separated and that those of Si_{13} are only shifted upwards without great changes.

Recently, Jelski *et al* [29] have pointed out that the chemical reactivity of a cluster is not related to the stability, because the former is kinetic and the latter is thermodynamic. According to their point of view, the cluster reactivity is affected by the coordination number on the cluster surface and the electronic states near the Fermi level. As the coordination number on the cluster surface increases and the charge of the HOMO becomes mor evenly distributed, then the cluster may become more unreactive. According to this point of view, the chemical reactivity of the Si_{13}^+ cluster is expected to be low.

For metallic elements, a 25-atom cluster appears to be enough for bulk-like chemical and physical behaviours. However, experimental studies by Jarrold *et al* [3, 6] have revealed that silicon clusters with less than 70 atoms are much less reactive than the bulk silicon surface, which indicates that the geometry of these silicon clusters may be close packed with lower dangling bond density, rather than the bulk-like open structure. It has been commonly accepted that a variety of isomers exist for a given number Si cluster, these isomers being degenerate in energy, and it is impossible to isolate a single structure by experiments. Furthermore, for many metallic microclusters, the 13-atom cluster is preferentially of icosahedral structure [12]. Previous calculations have showed that the chemical bonding

of Si_n ($n \leqslant 10$) clusters is essentially metallic-like [9]. If such behaviour still holds for the Si_{13} cluster, the icosahedral Si_{13} cluster could exist under certain conditions, although it may not have the lowest energy and the chemical bonding in the cluster is unfavourable compared with the bulk structure.

In summary, we use a very accurate DV–SCM scheme from first principles local density theory and find that the icosahedral Si_{13}^+ cluster is not a closed-shell structure, and that the empirical potentials derived from the silicon crystal are not realistic for microclusters. However, Si_{13}^{2+} is a closed-shell cluster with large LUMO–HOMO gap.

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