

Electronic structures and stability of Si_{60} and $\text{C}_{60}@\text{Si}_{60}$ clusters

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The electronic structure and stability of a fullerenelike Si_{60} cluster have been studied by the density functional theory with the local density approximation. Our results suggest that the icosahedral structure of Si_{60} is an energy minimum, and the electronic structure near the Fermi level is similar to that of a C_{60} cluster. We have found that the C_{60} cluster is a good candidate to stabilize the Si_{60} cluster.

The discovery of fullerene C_{60} has aroused a great deal of research interest in the past few years for physicists and chemists. The intensive studies show that the C_{60} cluster and C_{60} solid have many interesting physical properties, for instance, C_{60} solid doped with some alkali-metal atoms exhibits superconductivity.¹ The fullerene C_{60} cluster has a very stable structure and also has a closed electronic shell, which makes it kinetically stable. Silicon and carbon are isovalent. It is clear that the structures of the clusters of carbon and silicon are quite different, the silicon clusters have multicoordinate structures with the maximum coordinate number up to six,² and experiments show that the structures of silicon clusters with more than 27 atoms are spherelike.³ Carbon clusters have linear or ring structures and fullerene structures.⁴ It is natural to ask if the fullerene Si_{60} cluster is stable. At least up to now, the fullerene Si_{60} is not observed in the experiment. Recently, the determination of the ground state of the Si_{60} cluster has been the subject of some theoretical work. By using the Harrison's parameters, Menon and Subbaswamy⁵ have used generalized tight-binding molecular dynamics to study the structure of the fullerene Si_{60} cluster; they found that icosahedral Si_{60} has metallic character with a partially filled fivefold level as the highest occupied molecular orbit (HOMO), consequently, the Jahn-Teller distortion changed the icosahedral structure to a lower symmetry structure with no changes of the threefold coordination. Piqueras *et al.*⁶ and Nagase and Kobayashi⁷ have reported the electronic structure of icosahedral Si_{60} , respectively. Based on the symmetry-restricted optimization, they found icosahedral Si_{60} to be an energy minimum, the fivefold HOMO is completely filled, which is different from the results obtained by parameter dependent tight-binding molecular dynamics,⁴ but clearly they find the gap between the HOMO and the lowest unoccupied molecular orbit (LUMO) to be too large, up to 6.69 eV for the fullerene C_{60} and 4.62 eV for the icosahedral Si_{60} . To further understand the electronic properties and the stability of the Si_{60} cluster, we have performed the density functional studies on the icosahedral Si_{60} . In agreement with results of Refs. 6 and 7, we have found the icosahedral Si_{60} to be an energy minimum with two distinct bond lengths, the HOMO is completely filled with a HOMO-LUMO gap up to 0.32 eV, which is much smaller than 1.72 eV for fullerene C_{60} obtained by the same method. Because the

size of the silicon atom is much larger than the size of carbon atom, the bonding in fullerene Si_{60} cluster is weaker than that in C_{60} . The smaller binding energy, compared to the binding energies of smaller silicon clusters, indicates that the icosahedral Si_{60} may be just a metastable structure. So we have studied the possibility of putting a stable C_{60} into the cage of Si_{60} to stabilize the Si_{60} cluster.

Our calculations are based on the density functional theory with the local density functional approximation,⁸ the wave functions of molecular orbits are expanded in symmetrized atomic wave functions. The Hamiltonian matrix elements are calculated in the scheme of discrete variational method.⁹ The Kohn-Sham equation is solved self-consistently. The total binding energy of the cluster is defined by $E_b = E_{\text{ref}} - E_t$, where E_t is the total energy and E_{ref} is the sum of total energies of individual atoms in the cluster.

For Si_{60} cluster, we start at a perfect icosahedral structure with only one bond length. By calculating the binding energy, we have optimized the atomic distances and arrived at two distinct bond lengths. The essential feature of the obtained structure is similar to the fullerene C_{60} , in agreement with what was obtained by Piqueras *et al.*⁶ and Nagase and Kobayashi,⁷ some obtained results are shown in Table I. The radius of the Si_{60} cage is about 1.53 times larger than that of the C_{60} cage, both clusters have two different bond lengths. The electronic structures of the Si_{60} and the C_{60} cages near the Fermi level are similar. The HOMO of the Si_{60} cluster is a completely filled fivefold H_u state too, this is different from the results of the tight-binding molecular dynamics studies in which the HOMO is not completely filled, but consistent with results of Refs. 6 and 7. The orbital energies and the symmetry species are shown in Table II.

TABLE I. The obtained results for Si_{60} , C_{60} , and $\text{C}_{60}@\text{Si}_{60}$, equilibrium bond lengths d_1 and d_2 in atomic unit. Energy is in eV and the Fermi energy is shifted to be zero.

Clusters	E_b	d_1	d_2	E_g
Si_{60}	3.92	4.70	4.40	0.32
C_{60}	8.05	2.80	2.71	1.72
$\text{C}_{60}@\text{Si}_{60}$	6.31	4.69 (2.95)	4.39 (2.83)	0.27

TABLE II. The orbital energies and symmetry species of Si_{60} , C_{60} , and $\text{C}_{60}@\text{Si}_{60}$. Energy is in eV and the Fermi energy is shifted to be zero.

$\text{C}_{60}@\text{Si}_{60}$	Si_{60}	C_{60}	
$0.6345T_{1g}$	$0.583T_{2u}$	$2.945H_g$	
$0.5036G_u$	$0.398T_{1u}$	$1.693T_{2g}$	
$0.1298T_{1u}$	$0.163G_u$	$0.831T_{1u}$	LUMO
$-0.1348H_u$	$-0.156H_u$	$-0.829H_u$	HOMO
$-0.3738G_g$	$-0.602G_g$	$-1.762G_g$	
$-0.9338H_g$	$-0.642G_g$	$-1.826G_g$	

We can see that, the symmetries of the occupied states near the Fermi level are the same for both C_{60} and Si_{60} clusters. But there are some differences in the unoccupied orbits, the LUMO of the Si_{60} cluster is a fourfold state, instead of a T_{1u} state in the C_{60} cluster. There is a HOMO-LUMO gap, but it is much smaller than the gap of 1.72 eV in the C_{60} cluster obtained in the same method. The smaller HOMO-LUMO gap of the Si_{60} cluster may be attributed to the much weaker covalent bonds, accordingly the binding energy per atom would be small. As shown in Table I, we obtained only 3.92 eV/atom for the binding energy of the Si_{60} cluster, which is only about the half of the binding energy of the C_{60} cluster. In Fig. 1, we have presented the charge density of Si_{60} cluster. The covalent bonds between the nearest neighbors can be observed and it is quite similar to the result of the C_{60} cage.

All those results indicate that the icosahedral structure of the Si_{60} cluster could be an energy minimum. Since the binding energy is small and the multicoordinate smaller clusters may have larger binding energies,¹⁰ the icosahedral Si_{60} cluster may only be a metastable structure, and there might exist a more stable structure with a larger coordination number as found in the smaller clusters ($N \sim 30$). It is worth performing an accurate dynamical calculation on the stability of the Si_{60} cluster studying the transformation from the icosahedral structure to a more stable structure, but this is not the aim of the present paper. Instead, we are seeking a possibility to stabilize the

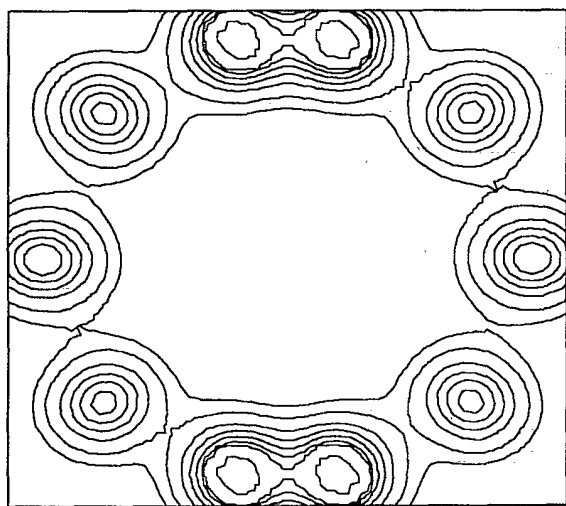


FIG. 1. The charge density of the Si_{60} cluster.

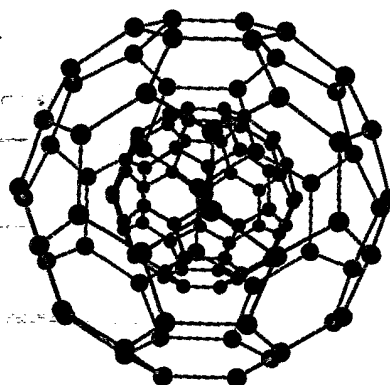


FIG. 2. The structure of the $\text{C}_{60}@\text{Si}_{60}$ cluster. The outer shell represents Si_{60} and the inner shell C_{60} .

icosahedral Si_{60} by doping an endohedral superatom into the Si_{60} cluster, like what has been done for Al_n clusters and smaller silicon clusters.^{11,12} Because the radius of the hollow Si_{60} cage is about 5.91 Å, a single atom is too small to fill the hollow space in the cage. In fact, the stable C_{60} cluster, which has a proper size, can be a very good candidate to fill the hollow space of Si_{60} cluster. There are many ways to arrange the C_{60} cluster in the Si_{60} cage with different relative orientations. For simplicity, we have chosen the highest final icosahedral symmetry, and fixed the ratio of short bond length to long bond length, and optimized the radius of the Si_{60} cage and radius of the C_{60} cage. The structure of $\text{C}_{60}@\text{Si}_{60}$ cluster is shown in Fig. 2. The obtained bond lengths are listed in Table I. We can see that the changes in bond lengths are very small. Unsurprisingly, the $\text{C}_{60}@\text{Si}_{60}$ cluster has a similar electronic structure near the Fermi level compared to the isolated Si_{60} and C_{60} clusters, and the HOMO is still a fivefold H_u level, mainly contributed by C_{60} and Si_{60} cages. In Fig. 3, we show a contour plot of wave function of the HOMO, it is clear that the HOMO is a p- π bonding state between the Si_{60} cage and the C_{60} cage. The LUMO is a threefold T_u level contributed by

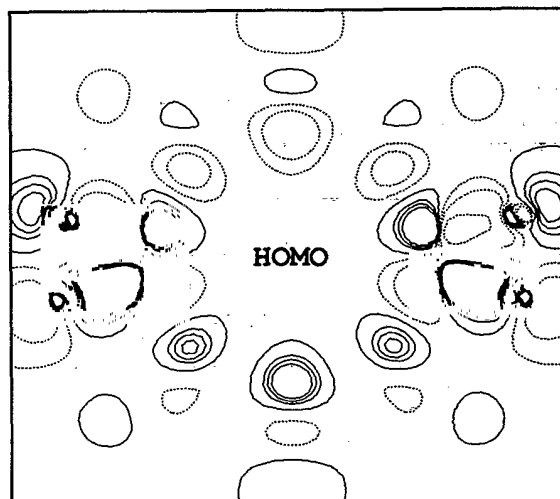


FIG. 3. The contour plot of the wave function of the highest occupied state in the $\text{C}_{60}@\text{Si}_{60}$ cluster. The solid lines denote the positive value, the dashed lines denote the negative value.

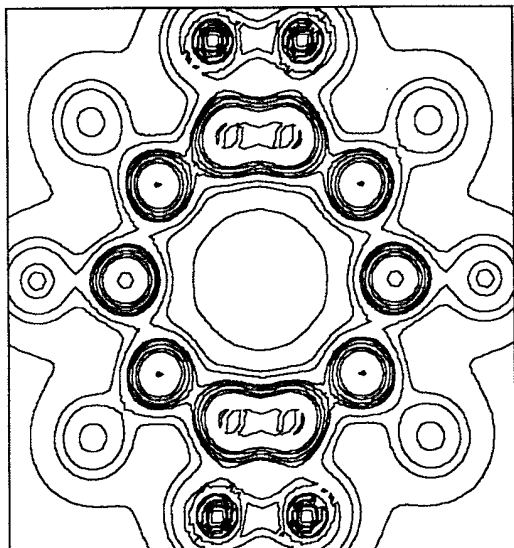


FIG. 4. The total charge density of the $C_{60}@Si_{60}$ cluster.

the Si_{60} cage. The HOMO-LUMO gap in the Si_{60} cluster remains. The binding energy is 6.31 eV/atom, the energy gain upon the doping of the C_{60} into the Si_{60} is about 38.4 eV. Since the atom on the C_{60} cage has only one neighbor at the Si_{60} cage, the binding energy for one Si-C pair is approximately 0.64 eV, and this amount of energy is much smaller than the binding energy of Si-C covalent bond. These results suggest the interaction between the Si_{60} cage and the C_{60} cage is not very strong, because the distance of 2.10 Å between the C and Si is large. This bonding behavior can also be confirmed by the total charge density of the $C_{60}@Si_{60}$ cluster, which is shown in Fig. 4. We can clearly see that the bond charge still exists between the nearest neighbors of carbon, and also between the nearest neighbors of silicon, but charge density between Si and C is very small. From the Mulliken population analysis, we get 1.55 and 1.45 electrons occupied at 3s and 3p orbits, respectively, for Si_{60} cluster. In the $C_{60}@Si_{60}$ cluster, the occupation numbers almost remain the same.

From the results presented above, we can see that the s - p hybridization in the cage is not changed. Since the strong covalent bonds of the C_{60} cage remain unchanged and the C_{60} is still very stable, the existence of the C_{60} in the Si_{60} cage prohibits the structure changes for the Si_{60} cluster from the fullerenelike to a more compact structure. So, we can expect that the $C_{60}@Si_{60}$ cluster would be stable. In Fig. 5, we have presented the density of states of the $C_{60}@Si_{60}$ cluster, and the partial density of states for C_{60} and Si_{60} at the equilibrium bond length, obtained by the Lorentz expanding of the eigenvalues.

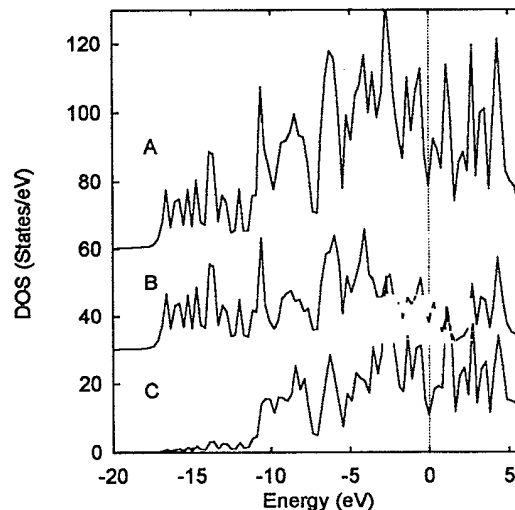


FIG. 5. The density of states of the $C_{60}@Si_{60}$ cluster. Line A is for total density of states, line B for partial density of states for C_{60} , and line C is for partial density of states for Si_{60} .

Although the small gap is smeared out by the Lorentz expansion, we can still see that the Fermi level is at a small valley, which suggests that both clusters should be kinetically stable. The large peak near -15 eV is contributed by carbon 2s states, and the peak near -9 eV is from the silicon 3s states. The interaction between the carbon 2s and the silicon is very small. The states near the Fermi level have p - π character from carbon 2p and silicon 3p.

In summary, we have studied the electronic properties of the icosahedral Si_{60} cluster. We have found that it has a small HOMO-LUMO gap with two distinct bond lengths, and it has a similar electronic structure near the Fermi level to the C_{60} cluster. Since the icosahedral Si_{60} cluster has a quite large size cage, and has a small binding energy, it can be a meta-stable structure and may collapse into a more compact structure as the smaller silicon cluster does. We have tried to stabilize the icosahedral Si_{60} by doping with a stable C_{60} cluster, and found that the $C_{60}@Si_{60}$ cluster can be stable with a completely filled HOMO and a sizable gap at the Fermi level; the covalent bonding between Si_{60} cage and C_{60} cage is weak, and the bonding character in the cage almost remains. Because of the existence of the C_{60} inside the Si_{60} cage, the Si_{60} cage will not collapse.

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