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LETTER TO THE EDITOR

## Structural properties of the endohedral complex $\text{Na}^+ @ \text{C}_{60}$

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**Abstract.** We have studied the electronic and structural properties of the so-called endohedral complex  $\text{Na}^+ @ \text{C}_{60}$  which consists of a  $\text{C}_{60}$  molecule with a sodium ion trapped inside. Based on the Su–Schrieffer–Heeger (SSH) model and the analysis of physical pictures of this kind of complex, we have introduced two reasonable terms into the Hamiltonian to describe the interaction between the ion and the  $\text{C}_{60}$  cage. Using the simplex optimization method, we have calculated the lattice distortion and its effect on the energy potential curve. Our results show that this effect, which has been neglected by other first-principles calculations, is very large and important. We discuss the physical meaning of our results.

Among many special aspects of research into  $\text{C}_{60}$ , the properties of the so-called endohedral complex, consisting of a fullerene cage with an atom or ion inside, are very interesting. Recently, much intensive experimental and theoretical work on this aspect has been carried out [1–7].

From first-principles calculations on  $\text{Na}^+ @ \text{C}_{60}$  based on a linear combination of Gaussian-type orbitals (LCGTO) local density functional (LDF) method, and other *ab initio* calculations, it has been found that at the centre the sodium ion is at a local maximum point and can gain about 0.12 eV upon being displaced about 0.7 Å from the centre along a fivefold axis [3–5]. Furthermore, to fit the calculated LDF potential-energy curve, an analytic functional form was proposed and the spectrum of the sodium ion vibrations in  $\text{C}_{60}$  and other properties were calculated [5,6]. Besides  $\text{C}_{60}$ , other kinds of endohedral complex have also been studied [7].

However, the first-principles LDF calculations have not considered the effect of the lattice distortion of carbon atoms on the cage. The lattice distortions, or so-called polarons in pristine  $\text{C}_{60}$  when it is doped with electrons, have been investigated by the extended Su–Schrieffer–Heeger (SSH) model [8–10]. However, no studies on the problem of lattice distortions of endohedral complex have been found. In this letter, we study this problem.

We proposed a tight-binding-type model which is based on the SSH model to study this endohedral complex. The Hamiltonian can be expressed as

$$H = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{i,j} [-t_0 + \alpha (l_{ij} - a_0)] (c_i^\dagger c_j + \text{HC}) + \frac{1}{2} K \sum_{i,j} (l_{ij} - a_0)^2 + \sum_i V_{0i}. \quad (1)$$

Let us consider this Hamiltonian. There are four terms. Without the first term and the last term, this is the SSH model which is widely and successfully used to study the properties of the  $\text{C}_{60}$  cluster [9–11]. Here,  $l_{ij}$  is the bond length of the bond connecting sites  $i$  and  $j$ ,  $K$  is the ‘spring’ constant,  $t$  is the hopping matrix element,  $c^\dagger$  and  $c$  are fermion creation and annihilation operators, and  $\alpha$  is the electron–phonon coupling constant.

When we study the case with a metal ion or atom inside the  $C_{60}$  cluster which is so-called endohedral complex, we need to consider the additional interactions between the inner metal ion and the cage. The first term in the Hamiltonian is the orbital energy of  $\pi$  electrons.

$$\varepsilon_i = \varepsilon_0 - \frac{e}{r_{0i}} \quad (2)$$

Here  $\varepsilon_0$  is the p orbital energy of carbon atom, which is  $-8.97$  eV. The second term on the right-hand side is the additional Coulomb interaction between the sodium ion and the  $\pi$  electrons on the cage.  $r_{0i} = |r_0 - r_i|$  is the distance from the sodium ion to each carbon atom at site  $i$  on the cage. When the sodium ion is at the centre of the  $C_{60}$  cage, all 60  $r_{0i}$  are equal; when the sodium ion deviates from the centre, the additional Coulomb term will break the high  $I_h$  symmetry, and result in changes of the electronic and cluster structures. This term and the second term in the Hamiltonian describe the electronic part, and are expressed in second quantization form and should be treated quantum mechanically.

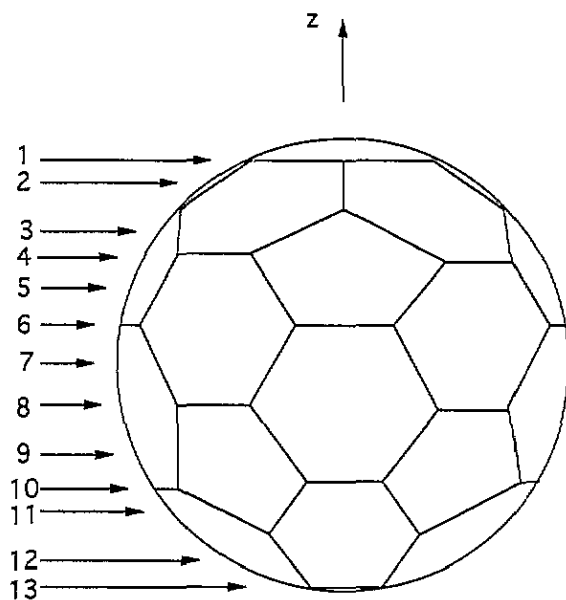


Figure 1. The fivefold axis  $z$ , and the 13 layers along it.

The last term represents the interaction between the sodium ion and the carbon atoms on the cage. When a plane of graphite is rolled into a fullerene cage, a little electron charge will be transferred from inside the cage to outside the cage, due to the higher density of electrons inside and the repulsive interactions between them. Therefore, the  $C_{60}$  cage can be viewed as a spherical double layer with a slight positive charge inside and a negative charge outside. Based on the physical picture, we take the positive screening dipole interaction form to describe the interaction between the sodium ion and the carbon atoms on the cage.

$$V_{0i} = A \frac{e^{-\beta r_{0i}}}{r_{0i}^2} \quad (3)$$

Here,  $A$  is the strength factor and  $\beta$  is the screening factor;  $1/\beta$  is the screening length. These two parameters can be determined by other results of first-principles calculation or

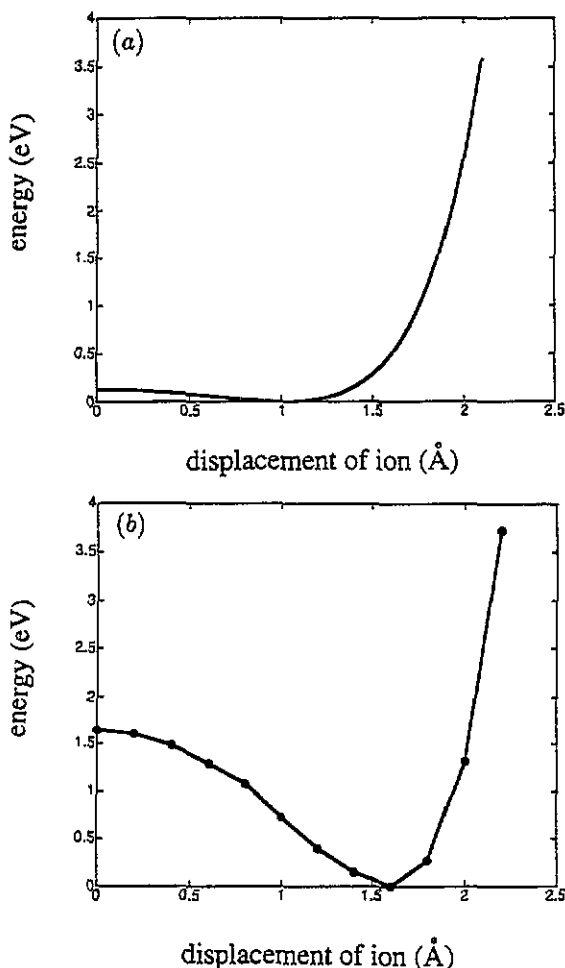


Figure 2. (a) The total energy versus the movement of the sodium ion along the  $z$  axis, when all the carbon atoms are stable. (b) The total energy versus the movement of the sodium ion along the  $z$  axis, when all the carbon atoms are relaxed.

experiments. This term and the third term in the Hamiltonian describe the interaction between atoms and ions-atoms, and can be treated classically.

We list all the parameters we used in our calculations:  $t_0 = 2.50$  eV,  $a_0 = 1.40$  Å,  $\alpha = 3.57$  eV Å<sup>-1</sup>,  $K = 28.4$  eV Å<sup>-2</sup>.  $A = 250$  eV,  $1/\beta = 0.44$  Å. The parameters in the SSH model are similar to those of other workers used to study C<sub>60</sub>. The last two parameters are proposed by us. We find that the results are sensitive to these two parameters.

First, let us compare the results with those of the first-principles calculations for the simplest case. We keep all carbon atoms stable on the C<sub>60</sub> cage and move the sodium ion along the fivefold axis, and use the model we proposed to calculate the total energy of this system. In figure 2 we plot the calculated total energy of this endohedral complex versus the displacement of the sodium ion from the centre of the cage along a fivefold axis. The results show that at the centre of the cage, the energy is a local maximum and the sodium ion is unstable; when it moves a certain distance (here about 1.0 Å) from the centre, it reaches a minimum point which is lower than the energy at the centre by 0.12 eV. When

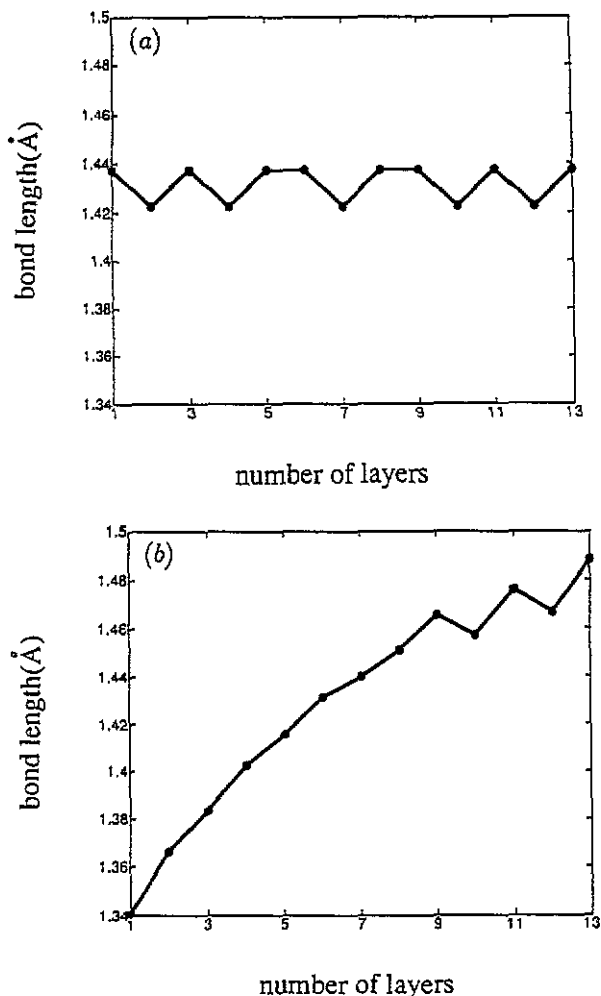


Figure 3. (a) The bond lengths of the 13 layers when the sodium ion is at the centre of the cage, that is  $z = 0$ . This is the dimerization state without lattice distortion. (b) The bond lengths of the 13 layers when the sodium ion moves a distance  $z = 1.6 \text{ \AA}$  from the centre.

the ion moves further towards the cage, the energy increases rapidly. This result is similar to the first-principles calculations. In fact, we adjusted the two parameters  $A$  and  $\beta$  to fit our result to the first-principles results [3].

From our simple model, we can give a clear physical explanation of this phenomenon: when the ion is close to the centre and far from the cage, the attractive long-range Coulomb interactions between the ion and the  $\pi$  electrons on the cage are dominant and reduce the energy; when the ion moves near the cage, the repulsive short-range dipole interaction between the ion and the carbon atoms on the cage becomes important. The competition between these two factors gives a minimum point at a certain distance.

Furthermore, when the ion moves, the lattice of the carbon atoms will move too, the cluster structure will be distorted, and the bond lengths will change. The first-principles calculations have not considered these important effect. How great is this effect and how do the bond lengths change? We have studied these problems using our model with the

determined parameters. When the ion moves, we take the coordinations of all carbon atoms as variable, that is, let all carbon atoms relax, and express the total energy calculated from the model as a functional of these variables, and then use the simplex optimization method to calculate the optimized coordinations of all carbon atoms, which give the structure distortion and bond length changes, and the total energy. In the practical procedure of the calculation, we use a  $C_{5v}$  symmetry and keep the radius constant when the ion moves along the fivefold axis to simplify the complicated optimization calculation.

In figure 2(b) we plot our results. We have found that the energy gain defined as the difference between the energies at the centre and at the minimum point is much larger than that in figure 2(a), which is the same as that of the first-principles calculations.

In figure 1 we explain the way we divided this cluster structure into 13 layers along the fivefold axis which we defined as the  $z$  axis. We keep the  $C_{5v}$  symmetry when the ion moves along the  $z$  axis, therefore, in each layer, the bond lengths are equivalent.

Figure 3(a) shows the bond length when the sodium ion is at the centre, that is the displacement of the ion  $z = 0$ . In fact, this figure gives the dimerization of the bonds, without lattice distortion.

Figure 3(b) shows the bond length changes when the sodium ion moves upwards at  $z = 1.6 \text{ \AA}$ , which is the minimum point of the potential energy curve.

From these figures we can analyse the physics of these results. When the sodium ion moves upwards, the bond lengths in upper layers become shorter, and the bonds in lower layers become longer. This is the optimized result, which means that such a kind of structure makes the energy of this system much lower than that of the stable cage structure; this is the reason why the energy gain of figure 2(b) is much larger than that of figure 2(a).

In summary, we have investigated the effect of the change of the cluster structure on the total energy when the sodium ion moves inside the endohedral complex  $Na^+@C_{60}$ . Our results have shown that with the movement of the sodium ion, the lattice of carbon atoms will be distorted: the bonds towards which the ion moves become shorter; on the other side, bonds become longer. These distortions make the energy of this system lower. Therefore, we have found from our calculated results that the energy gain, that is the energy difference between the state with the ion at the centre and that with the ion at the minimum point, is much larger than that of keeping all carbon atoms stable. This conclusion is important for further calculations which depend on the potential-energy curve, and comparison of that computed spectrum with experiments. The model we propose could also be applied to other endohedral complexes which consist of different kinds of atom or ion and different fullerenes. Our calculation on  $M@C_{70}$  is in development.

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