ELSEVIER

Topologically determined midgap states in amorphous carbon: five- and sevenfold rings

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Abstract

Using ab initio quantum chemical calculations, it was shown that the topologically determined energy levels decrease the energy gap at E_F. It was demonstrated in examples that the presence or lack of five- and sevenfold rings are not sufficient for the existence or non-existence of electronic states at the Fermi level within tight binding approximation.

1. Introduction

There is a growing interest in the understanding of the electronic and geometrical structure of amorphous carbon. Especially the electronic density of states (DOS) around the Fermi level, E_F, has received considerable attention in the last decade [1–10]. In the framework of tight-binding (TB) models the peaks at E_F are usually attributed to isolated sp^2 sites or to isolated linear three atomic carbon chains in sp^2 hybrid states [1–3]. In the case of ab initio calculations, however, the metallic features of amorphous carbon disappear [6]. The results are controversial.

As already pointed out [8,10] within Hückel approach the so-called Sachs graphs play an important role in the derivation of DOS at E_F. A Sachs graph is such a subgraph of an atomic structure which has only isolated edge- and/or ring-type components (see Fig. 1). If the graph of a model cluster does not have Sachs graph, topologically determined midgap states at E_F appear. In our previous papers we described some arrangements of carbon atoms of sp^2 sites which yield topologically determined electronic energy levels at E_F if tight binding calculations are performed [8,10,12]. In the present paper it will be shown that these states of the TB model result the decrease of gap in ab initio calculations.

2. Methods

The ab initio calculations were carried out using the GAMESS program package [14]. The standard STO-3G minimal basis set was applied in the calculations. The electronic density of states curve was obtained from the calculated one electron energies with a Gaussian line broadening method, using $\sigma = 0.03$ a.u. In our previous work [13] we have investigated the influence of the ab initio basis set on DOS around the Fermi level. We have found that the use of other basis sets (e.g., STO-6G or 3-21G) results in practically no changes in DOS. Similarly, small geometrical changes within the same topological arrangement have no influence on the DOS curves.

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The dangling bonds at the cluster boundaries were saturated by hydrogen or by carbon atoms in sp^3 state, if the neighbouring hydrogen atoms were too close to each other. We have studied several cluster structures of carbon atoms in π states that provide topologically determined energy levels at E_F. These structures are the following: (a) isolated atoms; (b) linear chain of odd number of atoms; (c) alternating structures with odd number of atoms; (d) some alternating structures with even number of atoms. Two examples of them are presented here.

3. Results

First, we consider models containing a five- and a sevenfold ring. These clusters can be seen in Fig. 1. Calculations were performed on three models. Model (a) contains only two rings. One can draw the Sachs graph of the cluster. Model (b) was obtained from Model (a) by adding a carbon atom of sp^2 site to the sevenfold ring so, that it still has a Sachs graph. Model (c) was created from Model (a). It does not have a Sachs graph, so TB approach yields one electronic state at the Fermi level. These calculations provide a good evidence for the fact, that the existence of five- and sevenfold rings in itself is not enough for the appearance of electronic states around the Fermi level.

Ab initio Hartree–Fock calculations have been performed on these models. The DOS of Model (a) and Model (b) is undistinguishable, therefore the DOS of Model (a) is not shown here. The calculated

Fig. 2. The density of states obtained for the models of Fig. 1. The solid line curve displays the DOS of Model (b); the dashed line curve represents the DOS curve of Model (c).

DOS curves of Model (b) (solid line) and (c) (dashed line) are displayed in Fig. 2. According to the graph theory, we expect, that Model (c) has a midgap state. Fig. 2 shows that this state is shifted, i.e. the energy gets lower, but it remains the highest occupied electronic state. The gap decreases (dashed line curve) where the cluster does not have a Sachs graph.

The second model we considered was a 64-atom cluster. This is a larger model in which five- and sevenfold rings are embedded. It was cut out from the C1120 model of Beeman et al. [11] and was investigated earlier by TB method [8]. It has no Sachs graph. Removing four convenient atoms from the sp^2 network, one can draw the Sachs graph. Saturating these four carbon atoms of sp^2 state to sp^3 state a modified model having Sachs graph was
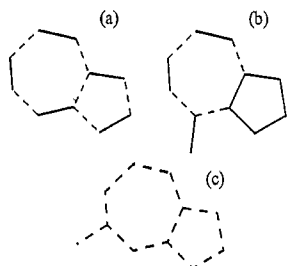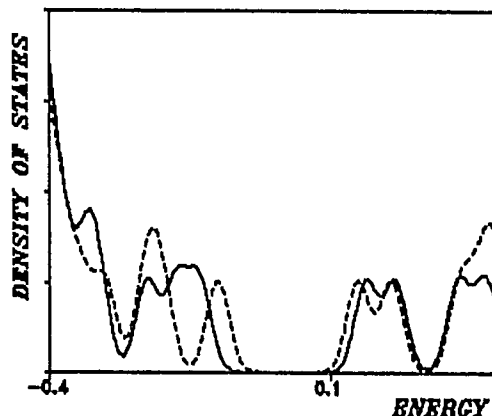

Fig. 1. Model clusters for ab initio HF calculations. The Sachs graphs of the models are denoted by solid lines. (a) Fused five- and sevenfold rings, (b) Model (a) plus an additional carbon atom of sp^2 state, (c) similar to Model (b). The position of the additional atom is different. This model does not have a Sachs graph. (See Refs. [12,13].)
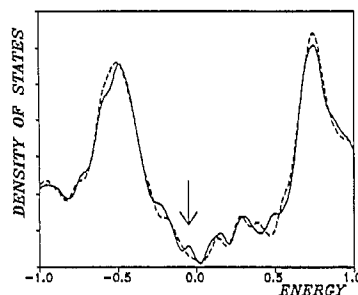

Fig. 3. DOS curves of the 64-atom cluster. The dashed line curve displays the electronic states of the original cluster, while the solid line curve represents the DOS of saturated cluster. The small peak near the Fermi level, which disappears on the modified model's curve, is denoted by an arrow.
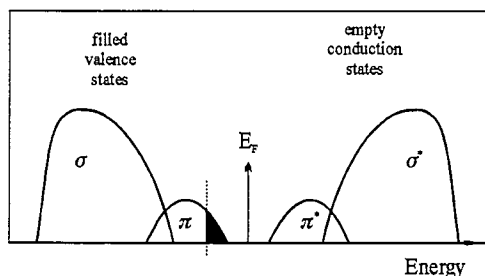
Fig. 4. σ and π bands of amorphous carbon. The topologically determined states appear at higher energies of the π band (shaded).

created. Fig. 3 displays two DOS curves. The dashed line curve belongs to the original model having a small peak near the Fermi level. The solid line curve represents the DOS obtained for a modified cluster obtained from the original one by saturating four convenient carbon atoms to sp^3 state. According to the Sachs graph theory this change results in, that four midgap states are removed. The small peak near the Fermi level is disappeared on the modified model's curve. Removing not convenient atoms so, that it is impossible to draw the Sachs graph, the midgap states remain.

The σ and π states are displayed in Fig. 4. This is a conventional representation of the DOS [7]. The topologically determined states, which appear at the Fermi level in TB approximation, are shifted to the π band in ab initio level calculations. So the π band can be divided into two parts: topologically determined states appear at higher energies, and the other π levels can be found below this interval. This result is confirmed by the ab initio calculations on the other types of carbon clusters mentioned above.

4. Conclusions

Within TB approach, using the Sachs graph theory the existence of the midgap states can be predicted. We gave a clear evidence that the number of electronic states around the Fermi level is determined by the global structure of the π network and it is independent of the number of five- and seven-fold ring groups. HF ab initio calculations show that these topologically determined states have energies lower than E_F, but they remain the highest occupied states in the electronic density of states and they decrease the gap.

Acknowledgements

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