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ATOMIC STRUCTURE AND ELECTRONIC DENSITY OF STATES AROUND THE FERMI LEVEL
IN AMORPHOUS CARBON MODELS

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There are topologically determined energy levels concentrated around the Fermi level. Graph theory is used to estimate the density of states near the Fermi level (E_F) of amorphous carbon (*a*-C) structure. Within the *ab initio* Hartree–Fock calculations these states have lower energies than E_F , but they remain the highest occupied states in the electronic density of states.

Keywords: A. disordered systems, D. electronic band structure.

THE PROBLEM of the midgap electronic structure of amorphous carbon has received considerable attention in the last few years [1–5]. Usually the peak of the density of states (DOS) at the Fermi level E_F is attributed to isolated sp^2 sites or isolated linear C_3 chains of carbon atoms in sp^2 hybrid states. Sometimes it is mentioned that there are some other arrangements of sp^2 atomic sites as well which give electronic states around the Fermi level, but these structures have not been described so far in the literature. In our previous papers we used graph theory to derive the structures which give peaks at E_F [6–8]. In this paper we present a simple rule within tight-binding approximation in order to describe the topology of sp^2 network providing states around the Fermi level. Using the more realistic HF *ab initio* method we controlled the results.

In *a*-C the central and the three first-neighbor carbon atoms are only nearly planar in structure so it is better to say that the central atom is in a fullerene π ($F\pi$) state. To analyze DOS of the π - or ($F\pi$)-electron network, we applied previously the Hückel theory with the usual α and β parameters for the diagonal and first neighbor interactions [6]. We demonstrated that the existence or non-existence of states around the Fermi level was closely related to the topological arrangement of threefold-coordinated carbon atoms. We described this topological arrangement by means of a graph. The vertices of this graph represent the threefold-coordinated atoms and the

edges correspond to the bonds between first neighbors. Explained simply, this graph is the picture of the cluster of threefold-coordinated carbon atoms. We call it ($F\pi$) network referring to the fact that the threefold-coordinated atoms are in fullerene states. In [6], we found that the Hückel Hamiltonian has an eigenvalue of $\varepsilon = \alpha$ if the graph of the π -electron network does not have Sachs graph. (A Sachs graph is such a subgraph of graphite-like atomic structure which has only isolated edge- and/or ring-type components [6, 10].) To interpret the peak at E_F one must know the multiplicity of $\varepsilon = \alpha$ states. With the help of graph theory we proved the following Theorem [11].

The multiplicity of the $\varepsilon = \alpha$ eigenvalue of a ($F\pi$) network is at least $(m - n)$, if the N carbon atom of this network can be partitioned into three disjoint sets S_1 , S_2 and S_3 with the following properties:

1. There are not two carbon atoms in set S_1 which are neighbors. The number of atoms in set S_1 is m and all of them have the same α parameter.
2. Set S_2 contains all of the atoms that are neighbors of atoms in set S_1 . The number of atoms in set S_2 is n , ($n < m$).
3. The set S_3 contains those atoms that belong neither to set S_1 nor to set S_2 . Set S_3 is very often the empty set \emptyset .

In [11–13] this theorem is presented in a more general way and it is not restricted to the one orbital one site approximation. We draw attention to the fact,

that the number of degenerate states at $\varepsilon = \alpha$ does not depend on the non-zero off-diagonal matrix elements of the Hamiltonian of the $(F\pi)$ -electronic network. On the base of the above-mentioned Theorem we can derive the exact number of degenerate $\varepsilon = \alpha$ eigenvalues in a tight binding calculation, where the β off-diagonal matrix elements depend on the first neighbor atomic distances [13]. In practical applications, however, the diagonal matrix elements of the atoms in set S_1 are not exactly equal to the same value of α . In this case the $(m - n)$ degenerate eigenvalues are split up in the vicinity of the Fermi level. Using this rule it is easy to draw clusters providing electronic states at Fermi level.

In order to confirm the tight-binding results, *ab initio* Hartree-Fock calculations have been carried out on some clusters of carbon atoms. The smallest cluster contained 4 atoms while the biggest one has 64 carbon atoms in the $(F\pi)$ state. GAMESS *ab initio* program package was used for investigations. The standard STO-3G minimal basis set was applied for the calculation. The dangling bonds at the cluster boundaries were saturated by hydrogen atoms and carbon atoms in sp^3 states. Two of the calculations are presented here.

First, we considered the DOS for a compact cluster of fused benzene rings containing 22 carbon atoms (see Fig. 1). If we neglect the σ states and use the simple nearest-neighbor Hückel approximation the Sach graph theory provides two topologically determined midgap states at the Fermi level ($m - n = 2$). The results of *ab initio* calculations are shown in Fig. 2(a). The DOS curve was obtained by smoothing the one electron energies with Gaussian line broadening ($\alpha = 0.03$ a.u.). Occupied π and unoccupied π^* states are present within the gap. The

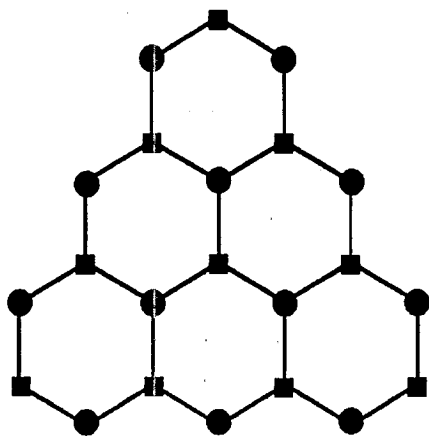


Fig. 1. Fused benzene rings where solid circles and solid squares are carbon atoms in sets S_1 and S_2 , respectively ($m = 12$, $n = 10$).

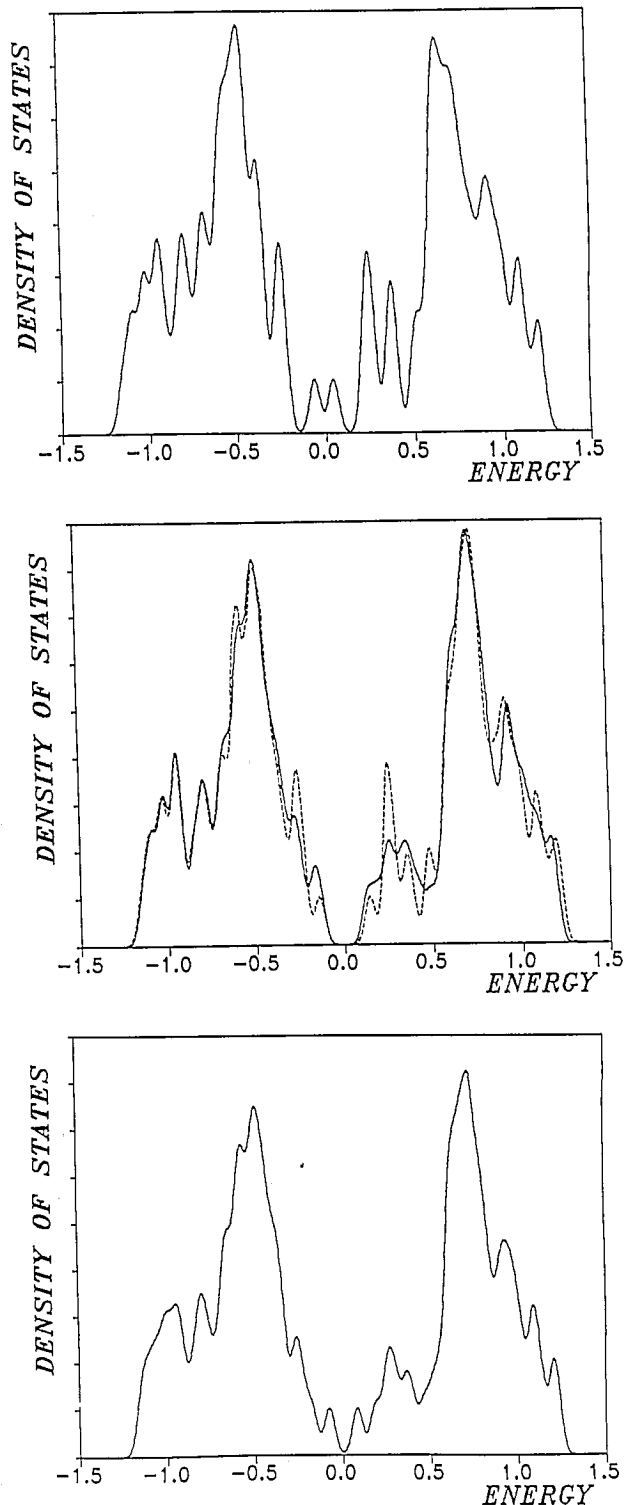


Fig. 2. Three examples of density of states. (a) Fused benzene rings. (b) Saturation of two carbon atoms belonging to the set S_1 of Fig. 1. Solid and dashed lines show the two different case of saturation. In both cases the midgap states are disappeared. (c) One of the saturated carbon atoms belongs to the set S_1 while the other belongs to the set S_2 of Fig. 1. Now the number of midgap states did not change.

energy of occupied π states are lower than E_F . If we saturate a pair of sp^2 carbon atoms belonging to set S_1 (represented by solid circles on Fig. 1) by hydrogen the Sachs graph theory predicts the absence of midgap states. Two different arrangements were constructed for the *ab initio* calculation and the results are shown in Fig. 2(b). The midgap states completely disappeared from the gap. The last modification of this finite cluster of fused six-fold rings was the following: a carbon atom from set S_1 and the other from set S_2 were saturated by hydrogen. The graph theory provides the same number of midgap states as are in the unsaturated case. The *ab initio* electronic DOS shown in Fig. 2(c) are in a very good correlation with the original density of states [see Fig. 2(a)]. Recently, we published a paper on an analysis of fused five- and sevenfold rings [15]. In conclusion, from these results we may state that the topologically determined states predicted by Sachs graph theory at the E_F exist but they are a little split up.

As a second step, a random network model of a 64 carbon cluster was considered. It was taken from the C1120 model of Beeman *et al.* [16] and it was investigated earlier [6]. It has four topologically determined electronic midgap states. Figure 3 displays two *ab initio* results. The solid line represents the DOS of original cluster. Saturating four atoms according to the Sachs graph theory we can remove these four mid-gap states. The dashed line shows the DOS of this modified cluster. The small peak below E_F disappeared.

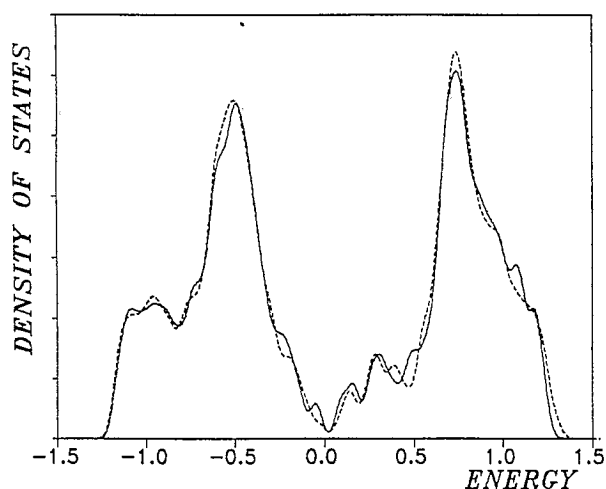


Fig. 3. Two DOSs of a cluster containing 64 carbon atoms. The solid line represents the density of states of the original cluster having small peak near the Fermi level while the dashed curve shows the DOS of saturated cluster. The number of states around E_F is lower in the case of saturation.

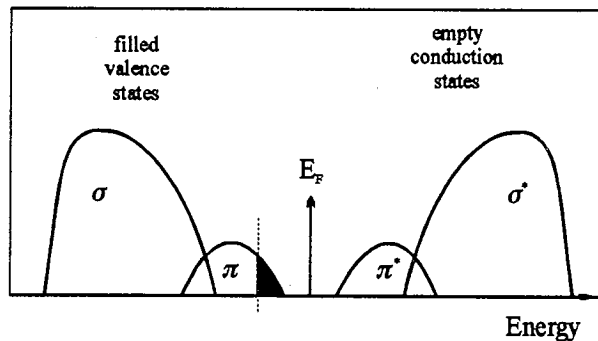


Fig. 4. σ and π bands of amorphous carbon. The topologically determined states appear at higher energies of the π band (shaded).

Finally, the conventional representation of σ and π state are displayed in Fig. 4. On the basis of our HF *ab initio* results we conclude that the topologically determined states, which appear at E_F in tight-binding approximation, are shifted to the π band in *ab initio* level calculations. So these topologically determined states have lower energies than E_F , but they still remain the highest occupied states in the electronic density of states and they decrease the gap. 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.

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