

Connection between topology and π -electron structure in amorphous carbon

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The π -electron structure of amorphous carbon has been studied within the framework of a tight-binding approximation. Graph theory is used to estimate the density of states near the Fermi level.

Amorphous carbon (*a*-C) has been studied by means of a quantum-chemical cluster calculation in order to determine the density of states (DOS) around the Fermi level E_F . Different methods¹⁻⁵ suggest an optical gap of 0.4-0.7 eV in *a*-C and 1.6-2.7 eV of *a*-C:H; furthermore, the weakly bonded π electrons form both the valence- and conduction-band states in *a*-C and in *a*-C:H. Based on topological disorder a theoretical prediction will be reported concerning the π -electron states. Graph theory^{6,7} is applied to study the topological structures.

Structural investigations^{8,9} show different percentages of fourfold- and threefold-coordinated atoms in *a*-C. The neighbors of diamondlike atoms are tetrahedrally coordinated, allowing the construction of four sp^3 hybrid orbitals on each of them. Graphitelike atoms form three localized σ states (sp^2 hybrid) plus a delocalized π state near E_F . To analyze the DOS of the π -electron network we applied the Hückel theory. For the Hückel Hamiltonian H we have

$$H_{ij} = \begin{cases} \alpha & \text{if } i=j \\ \beta & \text{if } j \text{ is the first neighbor of } i \\ 0 & \text{otherwise,} \end{cases} \quad (1)$$

where α and β are the interaction parameters. The subset (the cluster) of graphitelike atoms in *a*-C structure can be described by a graph where each atom is a vertex of graph and each bond represents an edge. In this case one can rewrite the above Hamiltonian in the following form:

$$H = \alpha I + \beta A, \quad (2)$$

where I is the unit matrix and A is the adjacency matrix of graph G due to the topological structure. The matrix A is defined in the following way:

$$A_{ij} = \begin{cases} 1 & \text{if the vertices } i \text{ and } j \text{ are adjacent} \\ 0 & \text{otherwise.} \end{cases} \quad (3)$$

Thus the secular equation $\det|H - \epsilon I| = 0$ can be written as

$$\det|xI - A| = 0, \quad (4)$$

where the relation between eigenvalues of H and A is the following:

$$\epsilon = \alpha + x\beta. \quad (5)$$

If $P_G(x)$ is the characteristic polynomial of matrix A , then

$$P_G(x) = \det|xI - A| = \sum_{n=0}^N a_n x^{N-n}, \quad (6)$$

where N is the number of vertices in graph G . According to the theory of Sachs^{6,7} the a_n coefficients are

$$a_n = \begin{cases} \sum_{S \in S_n} (-1)^{C(S)} 2^{r(S)} & \text{if } 0 < n \leq N \text{ and } S_n \neq \emptyset \\ 0 & \text{if } 0 < n \leq N \text{ and } S_n = \emptyset \\ 1 & \text{if } n = 0. \end{cases} \quad (7)$$

Here each S (a Sachs graph) is such a subgraph of graph G which has only edge- and/or ring-type isolated components. S_n is the set of all Sachs graphs with n vertices. $C(S)$ and $r(S)$ denote the number of all components and of ring components in S , respectively. As an example let us apply Eq. (7) for a simple cluster (see Fig. 1): $a_0 = 1$, $a_1 = 0$, $a_2 = (-1)^1 2^0 + (-1)^1 2^0 + (-1)^1 2^0 + (-1)^1 2^0 = -4$, $a_3 = 0$, $a_4 = (-1)^2 2^0 + (-1)^2 2^0 + (-1)^1 2^1 = 0$, and thus $P_G(x) = x^4 - 4x^2$.

By setting $P_G(x)$ to zero one can get the x eigenvalue spectra. If

$$a_N = a_{N-1} = a_{N-2} = \dots = a_{N-\nu+1} = 0, \quad (8)$$

then $x=0$ is a ν -fold-degenerate eigenvalue. There are two different ways to get $a_n=0$: S_n is not an empty set and the sum in Eq. (7) equals zero or S_n is an empty set. In the present work we have used the more trivial second case to find a connection between topology and DOS near E_F . Figure 2 shows a graph G of *a*-C model containing 64 sp^2 type atoms. The geometry was taken from a completely three-coordinated model of Beeman *et al.*⁴ Looking for S_n set of Sachs graphs there are four critical vertices of topology preventing us from constructing Sachs graphs with $n=64, 63, 62$, and 61 vertices. It leads to the equations $S_{64} = S_{63} = S_{62} = S_{61} = \emptyset$ and from Eq. (7) it follows that $a_{64} = a_{63} = a_{62} = a_{61} = 0$. The characteristic polynomial has four $x=0$ roots. If we ignore the presence of these topological degeneracies we are able to construct Sachs graph $S \in S_{60}$ and thus a_{60} is probably not equal to zero.

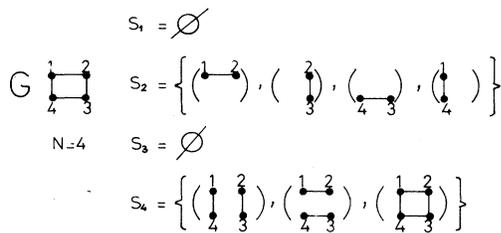


FIG. 1. Sachs graph construction.

According to the Coulson-Rushbrooke theorem¹⁰ in an alternating hydrocarbon the molecular orbital energy levels are symmetrically paired about an appropriate zero ($\epsilon = \alpha$ for $x=0$) such that if $\epsilon_x = \alpha + x\beta$ is a root of the secular equations then $\epsilon_{-x} = \alpha - x\beta$ is also a root. Since $\alpha, \beta < 0$ and in the ground state only the lowest one-electron states are occupied, the $x=0$ eigenvalues ($\epsilon = \alpha$) are at the Fermi level in the case of the alternate hydrocarbon. For the majority of nonalternate clusters the $x=0$ eigenvalues are also near to the E_F .¹¹

Two different types of calculations were carried out on C356 model of Beeman *et al.*⁴ This *a*-C structure contains 356 atoms, of which about 50% are three coordinated. The π DOS curve, as obtained by smoothing the Hückel one-electron energies with Gaussian line broadening that corresponds to a full width of 0.2 eV at half maximum, is presented in Fig. 3. Saturating the topological degeneracies by hydrogen, the huge thin peak disappears. In the second case the π -orbital axis vector analysis¹² was applied to define the π states and the orbital orthogonality relationship was used to define the π -orbital hybridizations and directions. In this more realistic calculation a

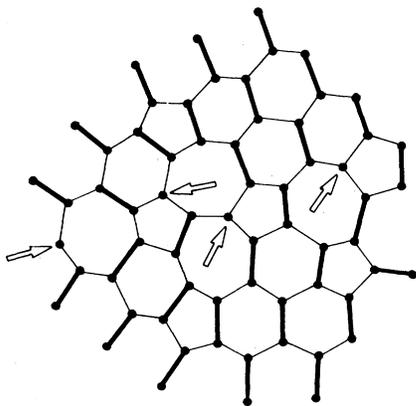


FIG. 2. Part of a model made by Beeman *et al.* (Ref. 4). Constructing S_n set of Sachs graphs (one of them represented by thick solid lines) there are four critical vertices of topology (marked by arrows). It leads to a fourfold degenerated $x=0$ eigenvalue. Usually the topology determines only the number of critical vertices without uniquely fixing their positions.

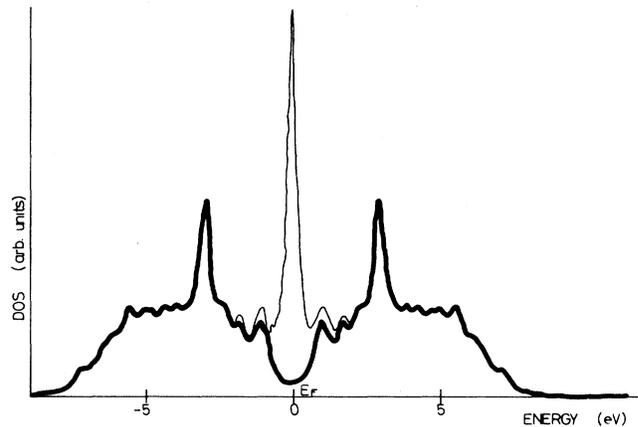


FIG. 3. π -band DOS of the C356 model (Ref. 4) (containing 40% sp^2 atoms) calculated by Hückel theory. There are some zero eigenvalues of the adjacency matrix causing a high sharp peak (solid line). The topological degeneracies are saturated by hydrogen (thick solid line). Two lines differ from each other only in the range of Fermi level.

similar large peak appears around the Fermi level and the previous saturational process eliminates this peak as well (see Fig. 4).

In conclusion we can say that as the Fermi level is nearly at the $x=0$ values, the metallic behavior of amorphous carbon clusters can be explained by the $x=0$ eigenvalues of the adjacency matrix of the structure defined by the three-coordinated carbon atoms. It means, based on topology, that one can estimate the π -band DOS at the Fermi level without any quantum-mechanical calculation and topological degeneracies play a more important

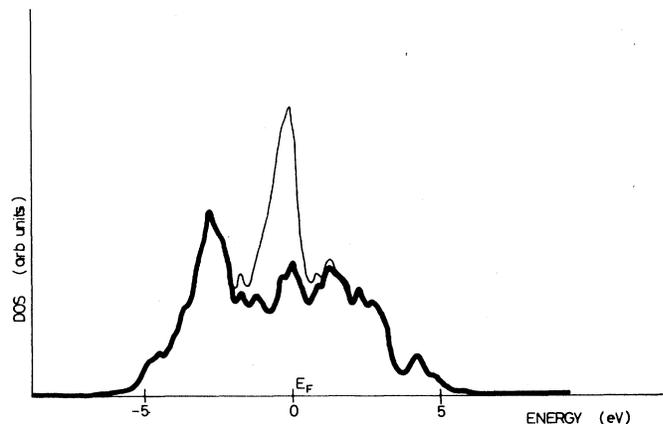


FIG. 4. π -band DOS of the C356 model (Ref. 4) using the π orbital axis vector analysis. Solid line displays the DOS of cluster containing some $x=0$ eigenvalues of the adjacency matrix. The zero eigenvalues of the adjacency matrix are saturated by hydrogen (thick solid line). Two lines differ from each other only around E_F .

role than angle distortion in amorphous systems containing π -electron islands. One can see in Fig. 2 that the position of critical vertices is not fixed in the structure. Almost every three-coordinated carbon atom can be critical vertex. As the hydrogen-carbon bond is σ bond we suppose that in a process of saturation the hydrogen atoms can transform three-coordinated carbons into four-coordinated carbons. In such a process the number of critical vertices decreases and states disappear around the Fermi level. This is in agreement to experimental results,

where it was found that the hydrogen increased the optical gap.¹⁻⁵

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