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Localization properties of the nonbonding π states at the Fermi level in amorphous carbon

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The π-electronic structure of graphitelike clusters of amorphous carbon (a-C) containing nonbonding states ($\varepsilon = E_F$) is studied in the tight-binding approximation. The localization characteristics of the eigenstates, especially around the Fermi level, are analyzed. These π orbitals were found to be more localized than in aromatic molecules. The nonbonding states are concentrated on surface atoms of the clusters, which implies that the additional hydrogen atoms removing the midgap states link probably to the circumference of the graphitelike regions of a-C.

In the last few years intense research has been devoted to the experimental[1-4] and theoretical[5-11] study of amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C:H). In a-C fourfold-coordinated (diamondlike) and threefold-coordinated (graphitelike) atoms are present at the same time. Graphitelike atoms form clusters with three localized sp^2 hybrid states per atom (σ bonds) and π states remaining delocalized.[5,7] These clusters are slightly distorted planar islands inside the a-C separated by one-dimensional internal surfaces from the bulk material. The extra π electrons form bands close to E_F and there exists a pseudogap around the Fermi level with some localized midgap states due to defects.[5,7,11] The density of states (DOS) at the Fermi level and the localization properties of the midgap states dominate the hopping conductivity of a-C.[1,7] It was also found that a-C:H has a wider gap around E_F than a-C, because the addition of hydrogen removes the π states from the gap[1-3,6,7,10,11] or, in the inverse process, the extraction of hydrogen lowers the gap.[4] It is still an open question as to where the additional hydrogen atoms saturating the midgap states bind to the cluster of graphitelike atoms.

Therefore the study of the π-electronic structure (especially around E_F) is essential in order to derive information on the electronic properties of a-C and a-C:H. These defect states have been investigated by means of band-structure calculations[6] and also using quantum-chemical cluster calculations based mainly on the Hückel theory,[5,7,8,11] which is the equivalent version of the tight-binding method for finite systems. Since the latter method retains only first-neighbor interactions between the atoms, the π-electronic structure obtained in this approximation reflects directly the topological arrangement of the atoms.

Hence in this work we have used the Hückel theory for graphitelike clusters in order to get details of the localization properties of the midgap states, which may give some insight into the problem of how the saturation of these states by hydrogen possibly takes place.

In constructing the mathematical model applied, we have considered the following facts. The graphitelike islands have separated confined π-electronic structures embedded in a σ-bonded diamondlike matrix. Therefore we impose free boundary condition for the eigenfunctions, however in the effective Hamiltonian we must incorporate the influence of the infinite atomic network. This requirement can be satisfied by choosing uniform on-site and interaction parameters over the whole graphitelike cluster, i.e., no distinction is made between bulk and surface atoms at the dynamical level. Hence within the Hückel theory the effective Hamiltonian reads as[12]

$$\underline{H} = \alpha \underline{I} + \beta \underline{A} \ , \tag{1}$$

where $\underline{I}$ is the unit matrix and $\underline{A}$ is the adjacency matrix of the graph of the finite cluster due to the topological structure. Matrix $\underline{A}$ is defined the following way:

$$\underline{A}_{ij} = \begin{cases} 1 & \text{if atoms } i \text{ and } j \text{ are first neighbors,} \\ 0 & \text{otherwise.} \end{cases} \tag{2}$$

Parameters α and β in Eq. (1) simply fix the zero level and unit of the energy scale. We will use $\alpha = 0$ and $\beta = 1$ without any loss of generality, i.e., we measure the energy in units of β and $\alpha = E_F = 0$. This way the eigenvalue problem of the Hamiltonian $H\psi = \varepsilon\psi$ is equivalent to the same problem of the adjacency matrix. The eigenvectors of the adjacency matrix $\underline{A}$ are called the topological states of the system.[12] The states corresponding to $\varepsilon < 0$, $\varepsilon = 0$, and $\varepsilon > 0$ are bonding, nonbonding, and antibonding states, respectively. Hereby we focus our attention mainly on the so-called nonbonding states with $\varepsilon = E_F = 0$. Based on graph-theoretical arguments, Kugler and László have shown that the existence of states at E_F may be predicted by analyzing the adjacency matrix of the cluster.[11]

The clusters under consideration have been chosen from the model C1120 (with 1120 atoms) of Beeman *et al.*[9] This model consists of the Cartesian coordinates of the atoms and the σ bonds connecting first neighbors are given as well.

The localization properties of the eigenstates $|\mu\rangle$ are calculated using the linear combination of atomic orbitals (LCAO) expansion coefficients $c_{i\mu}$ over an orthonormal atomic basis set $\{|i\rangle\}$. Since in the following consideration we will be dealing with a given state $|\mu\rangle$, index μ will be dropped where this cannot cause any confusion. The square modulus of these coefficients give the charge of the eigenstate $|\mu\rangle$ on site-atom i: $Q_i=|c_i|^2$. Due to normalization we have $\sum_i^N Q_i=1$ (N is the number of atoms). In order to characterize the eigenvectors we define the following quantities:[13-17]

$$D^{-1}=\sum_{i=1}^{N} Q_i^2 \ , \tag{3a}$$

$$S=-\sum_{i=1}^{N} Q_i \ln Q_i \ , \tag{3b}$$

where D, called the delocalization measure[13] or the participation ratio,[14] practically gives the number of sites the eigenstate extends to, and S is the information entropy[15-18] which characterizes the shape of $|\mu\rangle$. We have shown[13] that for an orthonormal atomic basis-set relation,

$$1 \le D \le N \tag{4}$$

generally holds. Moreover, we may normalize this quantity to the system size in order to compare states in different systems defining the filling factor $q=D/N$, with $1/N \le q \le 1$. Defining the mean filling factor $\bar{q}$ for arbitrary M states as

$$\bar{q}^{\,-1}=\frac{1}{M}\sum_{\mu=1}^{M} q_\mu^{-1} \ , \tag{5}$$

it is possible to show that if M degenerate eigenstates are mixed with unitary transformations a maximum delocalization, i.e., filling factor ($q_{\max}$) exists,[13] which depends only on the total charge distribution.

The information entropy can be given as a sum of two physically different terms: the structural entropy ($S_{\rm st}$) and the extension entropy ($S_{\rm ex}$).[16,17] The most simple state is a steplike function which possesses extension only with no further structure. This state extends over D atoms and has equal ($Q_i=1/D$) charge on these atoms and $Q_i=0$ on the other $N-D$ ones. Hence the entropy of such charge distribution is given as $S_{\rm ex}=\ln D$ [see Eq. (3b)]. Therefore any structure in the charge distribution will show up in the deviation from this value. We have shown that $S-\ln D$ is a non-negative quantity[16] and we may call it the structural entropy $S_{\rm st}$. Furthermore, using a continuous lattice model, we have shown that there is a scale invariant functional relation between $S_{\rm st}$ and q, and this relation depends only on the form of the decay function $f(r)$ of the charge distribution and the dimension of the system.[16] In Fig. 1, the solid curves show some examples of this relation for various decay forms:[17] quadratic decay $f(r)=(1+r)^{-2}$, exponential decay $f(r)=\exp(-r)$, and Gaussian decay $f(r)=\exp(-r^2)$. The first application of this approach has been presented on some aromatic molecules and conjugated hydrocarbons.[17]

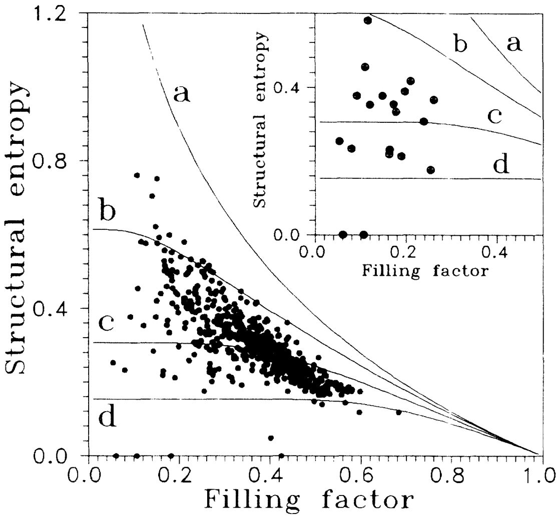

FIG. 1. Structural entropy $S_{\rm st}=S-\ln D$ vs filling factor $q=D/N$. Curve labeled a is for quadratic decay in two dimensions ($d=2$), b for exponential decay in $d=2$, c for Gaussian decay in $d=2$ and exponential in $d=1$, and d for Gaussian decay in $d=1$. Solid circles represent the results of our calculation. Inset shows the nonbonding orbitals on the Fermi level.

In our present calculation we have used 11 topologically inequivalent clusters ($C_1,\ldots,C_{11}$) of 47 to 68 atoms taken from the C1120 model of Beeman *et al.*[9] We have selected those atomic configurations that satisfy the topological requirement given in Ref. 11 in order to assure the appearance of nonbonding states ($\varepsilon=0$). These clusters contain altogether 592 atoms, mostly in threefold-coordinated configuration. The bordering atoms with two neighbors or one single neighbor are considered to be the surface atoms.

We have diagonalized the Hückel Hamiltonian (1) for each cluster and calculated the filling factor $q=D/N$ and structural entropy $S_{\rm st}=S-\ln D$ of the eigenvectors according to Eqs. (3a) and (3b). In Fig. 1 we have plotted the related $S_{\rm st}$ versus q values for all of the eigenfunctions obtained from various cluster configurations. The localization properties of the nonbonding states are shown separately also in the inset. Considering the q values, one can see that the π-electronic states of these structures are not very much extended, their filling factor is mainly in the range of $0.1 \le q \le 0.6$, which is lower than in aromatic molecules ($0.3 \le q \le 0.8$).[17] The mean filling factor (5) of all of the states was found to be low, $\bar{q}=0.32$. From the inset we can deduce that the nonbonding states are strongly localized ($\bar{q}=0.12$). For verification, we have also calculated the maximum filling factor ($q_{\max}$) for clusters with degenerate nonbonding states, and found that for these states $q_{\max}$ is always considerably lower than $\bar{q}$ for the total π-electronic structure.

On the other hand, the structural entropy $S_{\rm st}$ shows that almost all states have faster decay than two-dimensional (2D) exponential but slower than 1D Gaussian. Some states exhibit steplike behavior ($S_{\rm st}=0$).

Based on the above properties the following question arises: where are the nonbonding states localized? In order to answer this question we have divided all clusters to surface and bulk atoms according to the definition given above. Since the total charge belonging to a given state is unity ($Q_{\rm surf}+Q_{\rm bulk}=1$), the portion of the charge accumulated on surface atoms $Q_{\rm surf}$ has been calculated and plotted in Fig. 2(a) versus energy. Figure 2(b), shows the

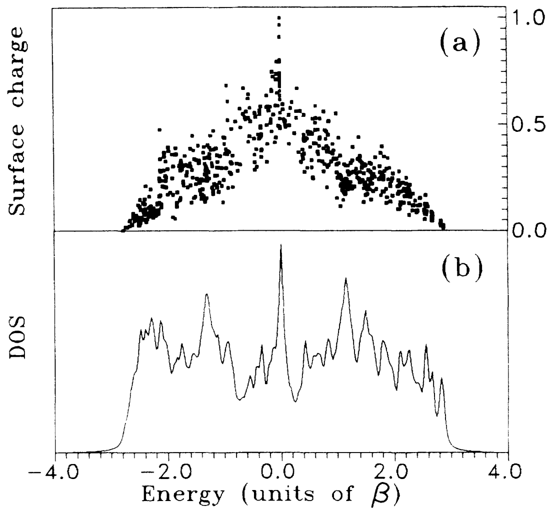

FIG. 2. (a) Total charge of the π-electronic states on the surface atoms. (b) Cumulative density of states of the π-electronic states of the topologically inequivalent clusters of the C1120 model using Hückel theory. The broadening parameter of the Lorentzian curves is $\delta=0.04$. The energy is measured in units of β, the off-diagonal element of the Hamiltonian. The Fermi energy is shifted to $E_F=0$. The large peak at $E=0$ is due to the nonbonding orbitals, which also produce a peak in the surface charge vs energy.

TABLE I. Localization properties (filling factor, structural entropy, surface charge) of the 20 nonbonding states ($\varepsilon=0$) obtained by Hückel theory based on clusters ($C_1, \ldots, C_{11}$) of the model C1120 of Beeman *et al.* (Ref. 9).

Cluster	$q=D/N$	$S_{st}=S-\ln D$	Q_{surf}
C_1	0.1484	0.3776	0.7487
	0.1729	0.3554	0.6885
	0.1784	0.3348	0.7088
	0.0539	0.2532	0.9679
C_2	0.0924	0.3778	0.8000
	0.2101	0.4175	0.5348
C_3	0.0606	0.0000	1.0000
C_4	0.0797	0.2335	0.7273
C_5	0.2541	0.1766	0.5629
	0.1214	0.3538	0.6918
	0.1631	0.2191	0.6454
C_6	0.1064	0.0000	1.0000
	0.1064	0.0000	1.0000
C_7	0.2611	0.3669	0.4889
C_8	0.1905	0.2130	0.6250
C_9	0.1170	0.5808	0.7319
C_{10}	0.1641	0.2312	0.6667
C_{11}	0.1976	0.3896	0.8075
	0.2393	0.3084	0.7372
	0.1095	0.4549	0.9134

calculated density of states obtained by the diagonalization of the Hamiltonian given in Eq. (1). The Hückel one-electron energies have been smoothed with Lorentzian line broadening of $\delta=0.04$. The large thin peak at $\varepsilon=0$ accounts for the nonbonding states. Comparing Figs. 2(a) and 2(b) it is clear that approaching the Fermi level the surface charge is increasing with a maximum at $\varepsilon=0$. Thus the midgap states are most likely localized on the surface atoms. The detailed analysis of the localization properties of the nonbonding states is given in Table I. The data of Table I indicate that a considerable amount of the total charge of the nonbonding states is located on the surface atoms.

In the hydrogenation process the additional hydrogen atom binds to an sp^2 carbon of the graphitelike cluster causing the formation of an sp^3 bond and changing the adjacency matrix this way. Kugler and László have shown furthermore that this change removes one of the nonbonding states from the gap.[11] In the above study we have located the nonbonding states to the surface of the clusters indicating that hydrogen atoms probably link to the bordering atoms of the graphitelike islands in *a*-C. Considering recent experimental evidences,[1–4] this property may be essential in the electronic structure and transport properties of *a*-C. Deeper understanding of this process deserves further investigations.

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