LETTER TO THE EDITOR

Electronic spectral dimension of a fractal aggregate taking account of hybridization

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Abstract. We have built fractal aggregates with tunable fractal dimension on a hexagonal lattice to represent the carbon atoms in the sp^2 hybridization. A random walk was performed on these aggregates, which takes account of the hybridization via the modified Hückel method. We obtain results for the σ hybridization for the spectral dimension calculations, which are the same as those obtained with a simple random walk on a quadratic lattice.

Over the past few years, fractal structures have been the subject of much attention [1, 2]. Fractal geometry has provided us with many well-defined structures which can be used either to represent real objects or to investigate the properties of well-known methods in physics. Recent experimental works have shown that fractal structures can be formed during the first stage of thin film growth [3, 4]. The fractal morphology observed for the growth of clusters and aggregates is usually a consequence of a non-equilibrium process in a system. Moreover, the properties of fractal carbon clusters are very useful as regards understanding the chemical processes in the atmosphere since carbon is the most frequently occurring element after hydrogen and helium.

The dynamical properties of fractal structures have been studied for a long time. Dyson [8] was able to obtain an exact solution for a special distribution of the ratio of the force constants to the masses in a random harmonic chain. Later it was shown that Dyson's case relates directly to what is now called off-diagonal disorder for a random one-dimensional tight binding electron band. The density of states of a fractal structure was studied for the first time by Alexander and Orbach [5] in 1982; they took the scaling properties of the mass and the connectivity into account. From these investigations, it is known that the vibrational density of states varies as a power $d_s - 1$ of the frequency above a phonon-to-fracton crossover frequency, ω_c, where d_s is the spectral dimension.

In this letter, we will study the electronic spectral dimension of a fractal aggregate of carbon atoms in the sp^2 hybridization. We have used a program written by Thouy and Jullien [9] to build aggregates of tunable fractal dimension. The aggregate that we will use has been built on a hexagonal lattice to represent the carbon atoms in the sp^2 hybridization (see figure 1). To build this hexagonal lattice, we have modified the original program. We studied aggregates with fractal dimension $D = 1.2, 1.5$ and 1.8. The aim of our work is to show the influence of the lattice pattern used and the influence of the hybridization on the electronic spectral dimension.
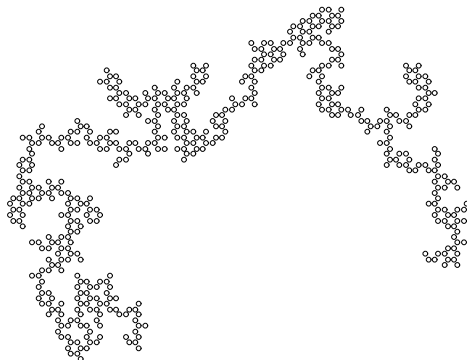
Figure 1. Representation of a fractal aggregate of 512 particles with a fractal dimension $D = 1.5$. The aggregate has been constructed on a hexagonal lattice to represent the sp^2 hybridizided carbon.

We will use a model built in the Hückel (tight-binding) approximation, but since carbon belongs to the IV–B group, we have to take hybridization into account; it is derived from the Friedel–Lannoo model [6] for the bulk, which has been made suitable by Leleyter *et al* [7] for microclusters of pure IV–B elements. We then used two Hamiltonians, the σ and π Hamiltonians, which can be treated separately in the Hückel theory. Since it is a one-electron approximation, the σ and π energy levels are calculated by diagonalizing the corresponding operators in the hybridization sp^2 and the total electronic energy E of the cluster is derived by filling in the levels with the total number of valence electrons (the origin of the energies is taken at the vacuum level). So, the Hamiltonian of the σ bonds becomes

$$H_\sigma = E_m \sum_{i,J} |i, J\rangle\langle i, J| + \Delta_\sigma \sum_{i,J,J'\neq J} |i, J\rangle\langle i, J'| + \beta_\sigma \sum_{i,i'\neq i,J} |i, J\rangle\langle i', J| \tag{1}$$

where E_m is the average energy $(E_s + 2 * E_p)|3$, β_σ is the usual hopping or resonance integral in Hückel theory, and Δ_σ is a promotion integral (transfer between hybrid orbitals on the same site). E_s and E_p are the atomic level energies, and $|i, J\rangle$ is the hybrid sp^2 orbital which points from site i along the bond J. The Hamiltonian of the π bonds becomes

$$H_\pi = E_p \sum_i |i\rangle\langle i| + \beta_\pi \sum_{i,i'\neq i} |i\rangle\langle i'| \tag{2}$$

where $|i\rangle$ is the π orbital centred on atom i and β_π is the hopping integral for π levels.

So there are only three parameters, β_σ, β_π and Δ_σ, with values $\beta_\sigma = -7.5$ eV, $\beta_\pi = -3.01$ eV and $\Delta_\sigma = -2.903$ eV. Furthermore, neither the repulsion between the nuclei nor the dielectronic correlations are taken into account.

An alternative way to determine the spectral dimension is to study random walks on the same fractal aggregates.

The fundamental property of the random walks in which we are interested is the variation of the mean square displacement from the origin at time t (t being here the number of steps performed on the aggregate). An exponent ν is introduced to describe the asymptotic behaviour [5]:

$$\langle R^2(t)\rangle \propto t^{2\nu} \tag{3}$$

for large t.

Interaction between two orbitals sigma of different atoms

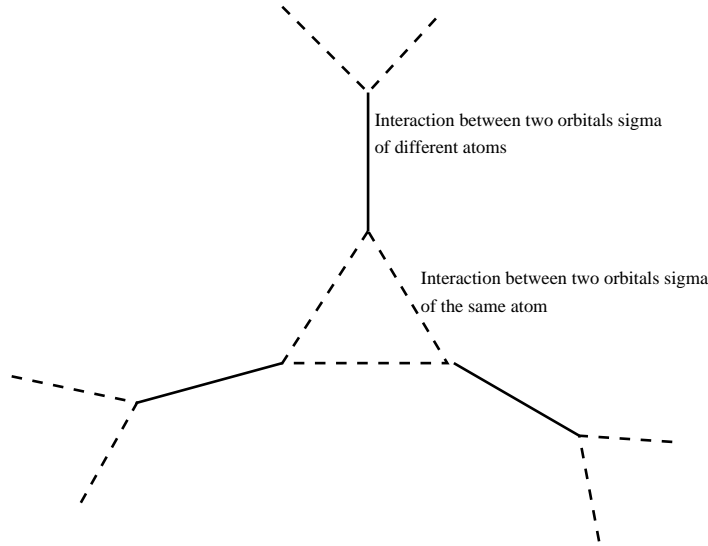Interaction between two orbitals sigma of the same atom

Figure 2. Representation of the orbitals constructed for the random walk.

With scaling arguments, it is shown that, on a fractal structure [5]

$$\nu = \frac{d_s}{2D} \tag{4}$$

where d_s is the spectral dimension and D is the fractal dimension. In a Euclidean space of dimension d, it is well known that $\nu = 1/2$. As it should be, the standard value $1/2$ is recovered on a Euclidean lattice, where $d_s = D$. With (4), relation (3) becomes:

$$\langle R^2(t) \rangle \propto t^{d_s/D} \tag{5}$$

when $t \to \infty$.

The return probability for a simple random walk i.e. for the π hybridization, is

$$P_{x,0}(t+1) = P_{x,0}(t) + \sum_{y(x)} (w_{x,y} P_{y,0}(t) - w_{y,x} P_{x,0}(t)) \tag{6}$$

where $P_{x,0}(t)$ is the probability density of being at site x at time t having started from site 0 at the initial time $t_0 = 0$. The notation $y(x)$ means that the sum is restricted to the nearest neighbours y of x. $w_{x,y}$ is the inverse of the coordination number at each site.

To relate the random walk to the Hückel method i.e. the hybridization, the return probability taking account of hybridization is

$$P_{x,0}(t+1) = P_{x,0}(t) + \frac{\Delta_\sigma}{\Delta_\sigma + 2\beta_\sigma} \sum_{y(x)_\Delta} (P_{y,0}(t) - P_{x,0}(t))$$

$$+ \frac{\beta_\sigma}{\Delta_\sigma + 2\beta_\sigma} \sum_{y(x)_\beta} (P_{y,0}(t) - P_{x,0}(t)) \tag{7}$$

where Δ_σ and β_σ are the parameters deduced from the modified Hückel method. The sum over $y(x)_\Delta$ means that the probabilities are valid for the nearest-neighbour orbitals which are on another atom and the sum over $y(x)_\beta$ means that the probabilities are valid for the nearest-neighbour orbitals which are on the atom where the random walker is located at time t.
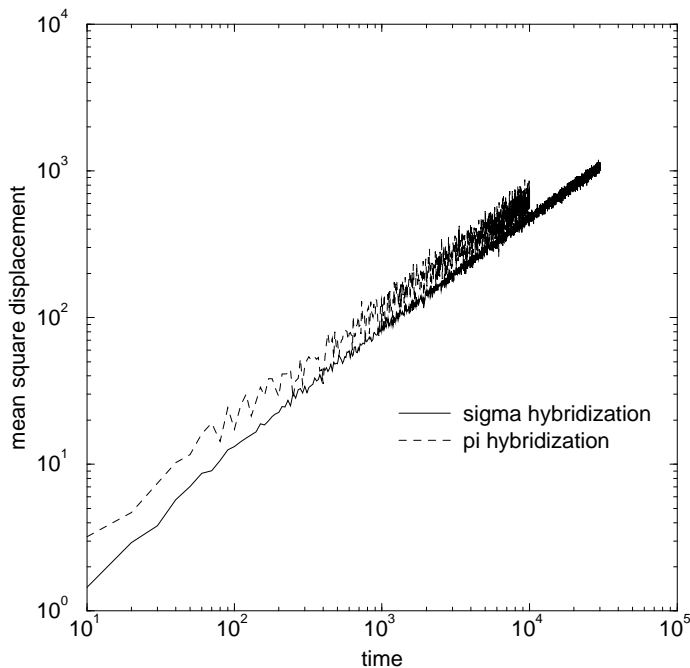
Figure 3. Log–log plot of R^2 (mean square displacement) versus the time t for aggregates of fractal dimension $D = 1.5$. The upper curve is the result for the π hybridization and the lower curve is that for the σ hybridization.

To model the σ hybridization, we have replaced each atom by a triangle, so each σ orbital is in relation with the two other σ orbitals on each atom, and one orbital is linked to one of another atom (see figure 2).

So, in accordance with (6) and (7), we have performed random walks on aggregates of $N = 1024$ particles, for 1000 steps (π hybridization) and for 3000 steps (σ hybridization), averaged over 100 different starting sites. Each starting site is chosen randomly in a small square box, containing the centre of mass of the aggregate. We have also averaged over 10 different samples in order to minimize fluctuations. Figure 3 presents one example of a plot obtained with the diffusion method: a log–log plot of $\langle R^2(t) \rangle$ versus t for an aggregate with fractal dimension $D = 1.5$ for π and σ hybridization.

Table 1. The spectral dimensions for the three fractal dimension ($D = 1.2, 1.5, 1.8$) and for the π and the σ hybridization.

D	1.2	1.5	1.8
d_s for σ	0.95	1.13	1.34
d_s for π	0.94	1.12	1.34

In table 1, we report the different results for the spectral dimension of the three fractal dimensions $D = 1.2, 1.5$ and 1.8. We don't have an evident difference between the spectral dimension for the π and σ hybridizations, but the spectral dimensions for the three fractal dimensions are different. The electronic spectral dimension for fractal dimension $D = 1.5$ is the same as that found in the literature [10]. So we can conclude that the pattern of our

lattice on which the aggregate has been built has no influence on the random walk even if the connectivity on a hexagonal lattice is not the same as on a square lattice. In fact, the electronic spectral dimension depends on the fractal dimension D and on the connectivity of the lattice. If we consider the aggregate built to compute the spectral dimension for the σ hybridization, each triangle which represents the interaction between orbitals of the same atom has the same connectivity as the atom itself. For the fractal dimensions $D = 1.2$ and 1.8 there are no references in the literature, so we cannot compare our results to others.

So there are no evident differences between the two hybridizations. That can be explained by the fact that, even if we take account of the hybridization, by constructing the orbitals on the fractal aggregate, the fractal dimension of such aggregate is the same as that of the 'π' aggregate. Furthermore, when replacing each triangle representing the interaction between orbitals of the same atom by one site, we obtain the same aggregate as that for the π hybridization. So, the results are thus the same for the two hybridization, for the spectral dimension.

In conclusion, we can say that the scaling properties of the σ density of states and the π density of states are the same. We find in fact the same result as in our previous paper, where we demonstrated that the π and σ densities of states follow the same rule for a regular fractal aggregate [11].

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