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# Electronic structure of a fractal cluster of carbon atoms in the $sp^2$ hybridization calculated by the Hückel method

N Olivi-Tran and M Leleyter

Groupe de Simulation Numérique en Physique des Agrégats, Faculté des Sciences, 33 rue Saint-Leu, 80039 Amiens Cédex, France

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**Abstract.** The electronic structure of a fractal aggregate of carbon atoms in the  $sp^2$  hybridization is calculated by the Hückel method. We have first constructed a fractal cluster of carbon atoms which has a fractal dimension  $D$ . To determine the electronic structure of this cluster, we have used two methods: the direct diagonalization, and a method based on the decomposition of the Hückel matrix. We got finally the density of states (DOS) which has properties of similarity for different sizes of the clusters.

## 1. Introduction

Fractal geometry has provided us with many new well defined structures which can be used either to represent real objects or to investigate the properties of well known methods in physics in a new context [1, 2]. We can find fractal structures of carbon in soot, but generally these structures are mostly on the mesoscopic or even macroscopic scale, i.e. the lower cut-off of the fractal domain in these structures is of the size of a particle of a few ångströms [3, 4, 5, 6]. These structures are currently being studied on the basis of light scattering properties.

The following study could allow us to detect in soot small molecules of carbon atoms via the properties of their electronic structure.

The fractal morphology observed for the growth of clusters and aggregates is usually a consequence of a non-equilibrium process in a system. Gao *et al* [7] have shown that the formation of thin films begins first with the formation of several fractal clusters, which at the end of the process cover all of the plane.

Moreover, the properties of fractal carbon clusters are very useful as regards understanding the chemical processes in the atmosphere and in the interstellar environment, since carbon is the most frequently occurring element after hydrogen and helium.

The study of the electronic levels of fractal structures is of wide interest, and has been under way for a few years. So far, the methods which have been used most frequently are the renormalization group method [8, 9, 10, 11], and the iteration method within the renormalization group method [9], which produce good results. Tremblay *et al* [12, 13] have also studied the electronic density of states of a fractal aggregate using the renormalization group method with the Green functions corresponding to the electronic Hamiltonian. Here we will present a very simple analysis of the problem based on the Hückel method. In section 2, we give a brief summary of the Hückel method. In section 3, we present our calculation method which is based essentially on the properties of matrices and determinants.

Finally, in section 4, the numerical results are reported, and a discussion of them and of our method is given.

## 2. The Hückel method

We will use a tight-binding Hückel model modified in order to take hybridization into account since carbon belongs to the IV-B group. It is derived from the Friedel–Lannoo model [14] for the bulk, which has been made suitable for microclusters of pure IV-B elements by Leleyter and Joyes [15]. Since the tight-binding approximation is a one-particle theory, the Hamiltonian can be split into two parts:  $\sigma$  (or  $\sigma$ -) and  $\pi$ -Hamiltonians. The  $\sigma$  and  $\pi$  energy levels are calculated then by diagonalizing the corresponding operators, and the total electronic energy  $E$  of the cluster is derived by filling the levels with the total number of valence electrons (the origin of the energies is taken at the vacuum level). The Hamiltonian of the  $\sigma$ -bonds is written as follows:

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

where  $E_m$  is the average energy  $(E_s + 2E_p)/3$  (in the case of  $sp^2$  hybridization),  $\beta_\sigma$  is the usual hopping or resonance integral in Hückel theory, and  $\Delta_\sigma$  is a promotion integral (for transfer between hybrid orbitals on the same site).  $E_s$  and  $E_p$  are the carbon atomic level energies, and  $|i, J\rangle$  is the hybrid  $sp^2$  orbital which points from site  $i$  along the bond  $J$ .

On the other hand, the Hamiltonian of the  $\pi$ -bonds reads

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

where  $|i\rangle$  is the  $\pi$ -orbital centred on atom  $i$ , and  $\beta_\pi$  is the hopping integral for  $\pi$ -levels.

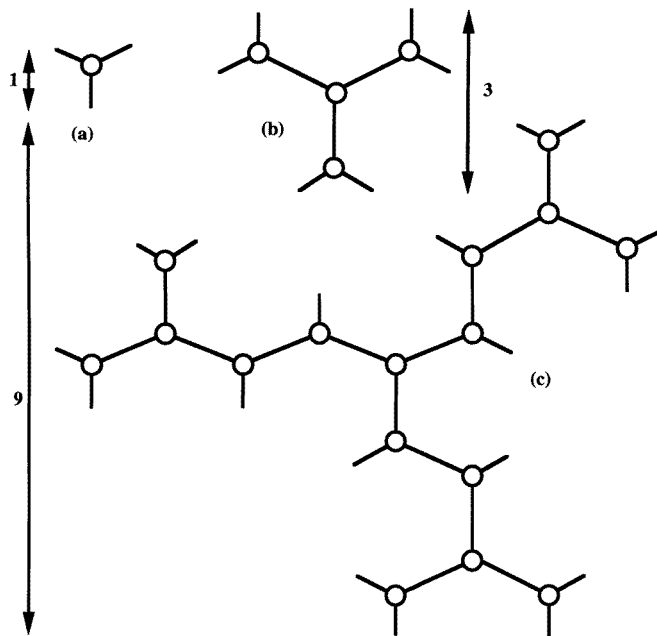
So there are only three parameters:  $\beta_\sigma$ ,  $\beta_\pi$ , and  $\Delta_\sigma$ . The parameters  $\beta_\sigma = -7.5$  eV,  $\beta_\pi = -3.01$  eV, and  $\Delta_\sigma = -2.903$  eV are obtained by fitting Hückel calculation results with data obtained from *ab initio* computations [16]. As the eigenstates in a fractal are localized [17, 18], and can be considered as non-interacting, we have used them even for large clusters. Furthermore, neither the repulsion between the nuclei nor the dielectronic correlations are taken into account.

Now we are going to explain (section 3) how we can derive the energy levels from the Hückel framework.

## 3. Method and model

We propose here a model of fractal clusters of carbon atoms. It would be interesting to analyse the electronic structure of a carbon atom cluster in the  $sp^2$  hybridization because this is a planar problem. This cluster may be a precursor during the constitution of graphite planes, for example during the growing of thin films. So we have constructed a fractal cluster of carbon atoms. The initial pattern is a cluster of four carbon atoms, one in the centre and the three others connected to the first one. We have thus obtained an equilateral triangle with one atom at its centre. In the second iteration, we put one of the initial patterns at the centre and we attach three others around it, every second link—and so on. The scheme of this construction is represented in figure 1. The mass fractal dimension  $D$  of this cluster can be calculated, as we know that in iteration  $n$ , the mass grows as  $4^n$  and the linear dimension varies as  $3^n$ . So, the fractal dimension becomes

$$D = \frac{\log 4}{\log 3}. \quad (3)$$



**Figure 1.** Representations of the cluster in three stages of iteration. (a) represents the monatomic cluster (iteration  $n = 0$ ), (b) represents the cluster composed of four atoms (iteration  $n = 1$ ), and finally (c) represents a cluster at iteration  $n = 2$  with  $4^2$  atoms.

To determine the electronic energy levels of these fractal clusters in each iteration, we have used the Hückel method.

The Hückel matrix for the  $\sigma$ -levels for one atom of carbon is

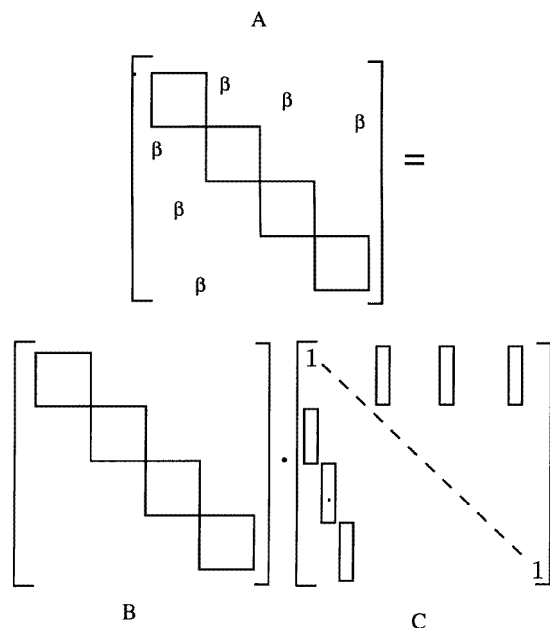
$$\begin{pmatrix} 0 & \Delta_\sigma & \Delta_\sigma \\ \Delta_\sigma & 0 & \Delta_\sigma \\ \Delta_\sigma & \Delta_\sigma & 0 \end{pmatrix} \quad (4)$$

i.e. for iteration  $n = 0$ . There is no  $\pi$ -matrix for this iteration. The  $\pi$ -matrix for iteration  $n = 1$  is the following:

$$\begin{pmatrix} 0 & \beta_s & \beta_s & \beta_s \\ \beta_s & 0 & 0 & 0 \\ \beta_s & 0 & 0 & 0 \\ \beta_s & 0 & 0 & 0 \end{pmatrix}. \quad (5)$$

In the following, we will present our recursion method for the  $\sigma$ -levels; the method used for the  $\pi$ -levels is the same, and the transposition is easy.

The Hückel matrix for the  $\sigma$ -levels which is obtained at iteration  $n$  for our fractal cluster is represented in figure 2. The matrix can easily be factorized and expressed as the product of two matrices  $B_n$  and  $C_n$  as shown in figure 2. For comparison, we have represented in figure 3 the Hückel matrix and its decomposition for a tridimensional Sierpinski web (see [11]). In this case, the carbon atoms are in  $sp^3$  hybridization and there is no  $\pi$ -matrix. One can clearly see that the columns in the corresponding  $C$ -matrix are related to the connectivity of the previous iteration patterns.



**Figure 2.** The Hückel matrix for our fractal cluster representing either the  $\pi$ -matrix or the  $\sigma$ -matrix, decomposed into two matrices  $B$  and  $C$ . In the case of  $\sigma$ -matrix, the squares have dimension  $3 \times 4^n$ . In the case of matrix  $\pi$ , the squares have dimension  $4^n$ . The columns of matrix  $C$  have the same vertical dimension as the corresponding squares. Following each case,  $\beta$  equals  $\beta_\sigma$  or  $\beta_\pi$ .

The advantage of this decomposition into two matrices is that the determinant of matrix  $A_n$  is the product of the determinant of matrix  $B_n$  and the determinant of matrix  $C_n$ . The determinant of matrix  $B_n$  in iteration  $n$  is simply the determinant of  $A_{n-1}$  in iteration  $n-1$  to the power 4: indeed, matrix  $B_n$  is square diagonal, the squares being equal to those of matrix  $A_{n-1}$  in iteration  $n-1$ . The determinant of matrix  $C_n$  can be easily computed. We remark that the Hückel matrix is self-similar: the squares in the matrix in iteration  $n$  can be replaced by the whole matrix itself but in iteration  $n-1$ .

$\text{Det}(C_n)$  reduces to a very simple form in every iteration:

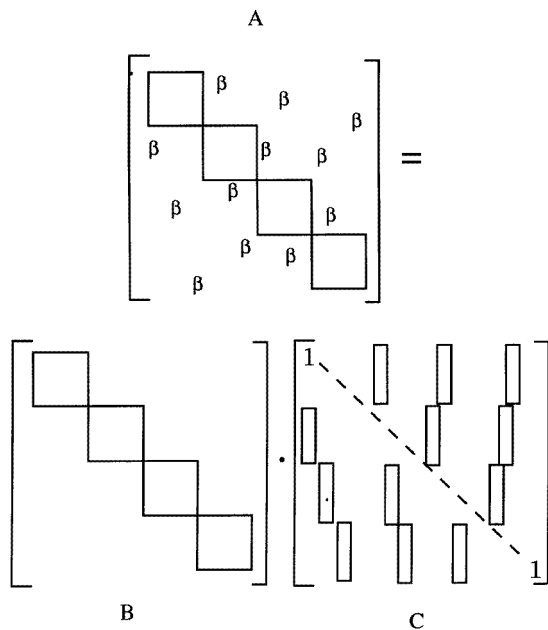
$$\text{Det}(C_n) = (1 - F_n^2)(1 - E_n^2)(1 - D_n^2). \quad (6)$$

The parameters  $D_n$ ,  $F_n$ , and  $E_n$  are solutions of the square system of  $3 \times 4n$  equations with  $A_{n-1}$  as the first member and a column vector with zeros everywhere except one element which is equal to  $\beta_F$  (or  $\beta_D$  or  $\beta_E$ , correspondingly) as the second member. The non-linear recursion relations for the electronic energy levels relating iteration  $n$  to iteration  $n-1$  are then

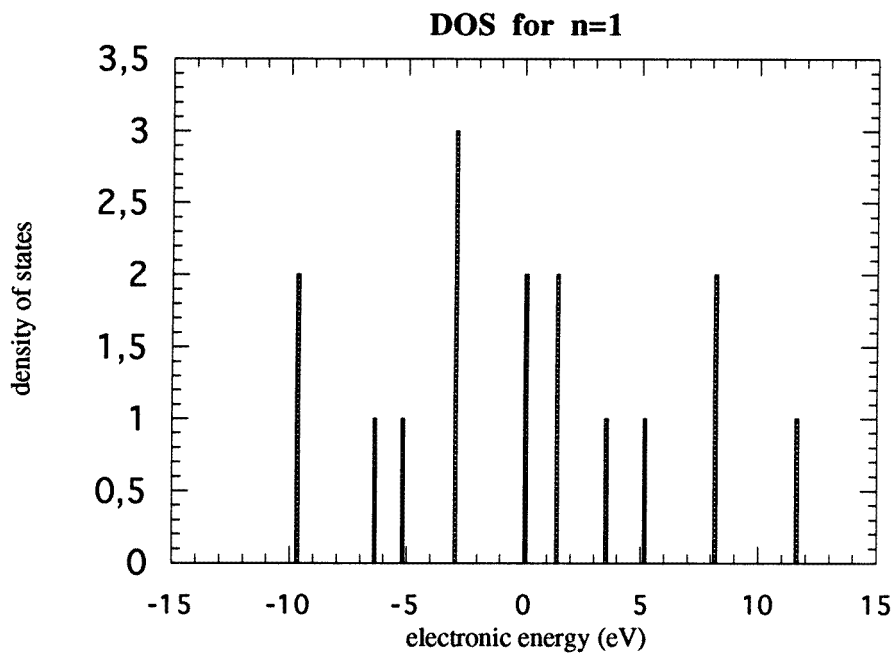
$$\text{Det}(A_n) = (\text{Det}(A_{n-1}))^4 (1 - F_n^2)(1 - E_n^2)(1 - D_n^2). \quad (7)$$

To simplify this equation, we use the well-known method of taking the codeterminant (coDet). So all of these parameters are similar to

$$D_n = \frac{\text{coDet}(\beta_D)}{\text{Det}(A_{n-1})} \quad (8)$$



**Figure 3.** The Hückel matrix and its decomposition for the tridimensional Sierpinski web composed of carbon atoms in the  $sp^3$  hybridization.



**Figure 4.** The density of states of the cluster in iteration  $n = 1$ .

where  $\beta_D$  is the number  $\beta$  corresponding to the calculation of  $D_n$ . Also, we can simplify equation (7).  $\text{coDet}(\beta_D)$  is a determinant of dimension  $3 \times 4^{n-1}$ . Finally, to obtain the

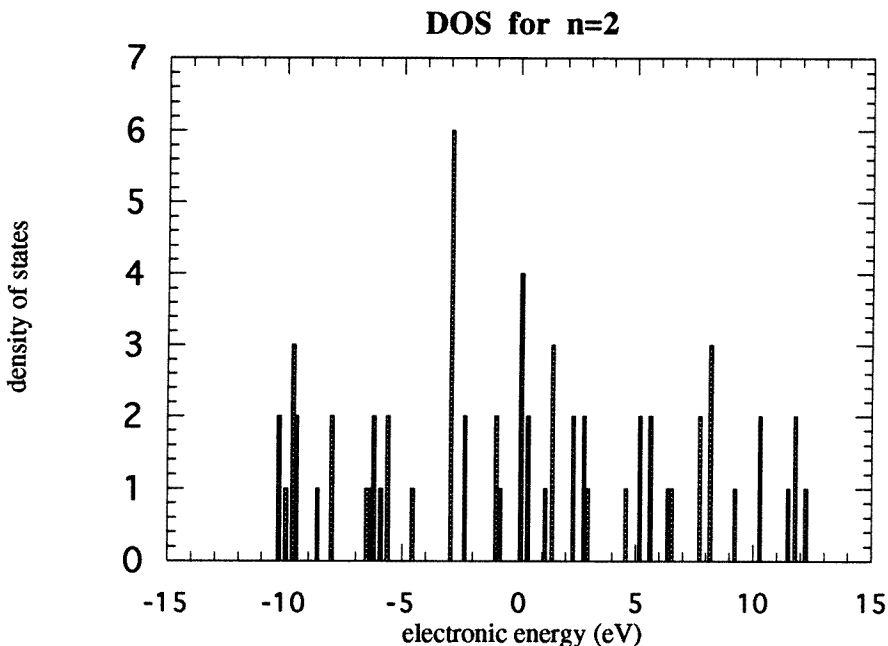


Figure 5. The density of states of the cluster in iteration  $n = 2$ .

energy levels in iteration  $n$ , and after simplification, one has to solve

$$\left( \prod_{i=D,E,F} (\text{Det}(A_{n-1}) - \text{coDet}(\beta_i))(\text{Det}(A_{n-1}) + \text{coDet}(\beta_i)) \right) / \text{Det}(A_{n-1})^2 = 0. \quad (9)$$

Equation (9) can be simplified in order to remove the numerator. Furthermore, equation (9) removes degeneracy from the remaining roots, and this explains the splitting of the energy levels between stage  $n - 1$  and stage  $n$ .

Hence the excitation spectrum at stage  $n$  can be exactly computed if one knows the form of the Hückel matrix in iteration  $n - 1$ . At each step, one has to solve for the determinant of  $C_n$  which depends in fact on the determinant of  $A_{n-1}$ . Thus, taking account of the determinant in the previous step  $n - 1$ , one obtains the energy levels at the stage  $n$ .

We have computed the energy levels following two methods: direct diagonalization of the Hückel matrix obtained as recalled in section 2, and the method which is described in this section. The direct diagonalization has been performed by the Jacobi method. We get exactly (within the numerical precision of our computer) the same results for the two methods. In order to get the DOS, we have simply computed the numbers of each of the energy levels and we have represented these numbers as a function of the energy levels.

#### 4. Results and discussion

In figures 4, 5, and 6, we have represented the electronic DOS for iterations  $n = 1$ ,  $n = 2$ , and  $n = 3$ . We can see that there is similarity among the three densities of states: the densities of states are self-similar if we normalize them to the number of atoms at each iteration stage. The property of self-similarity becomes more exact as the number of

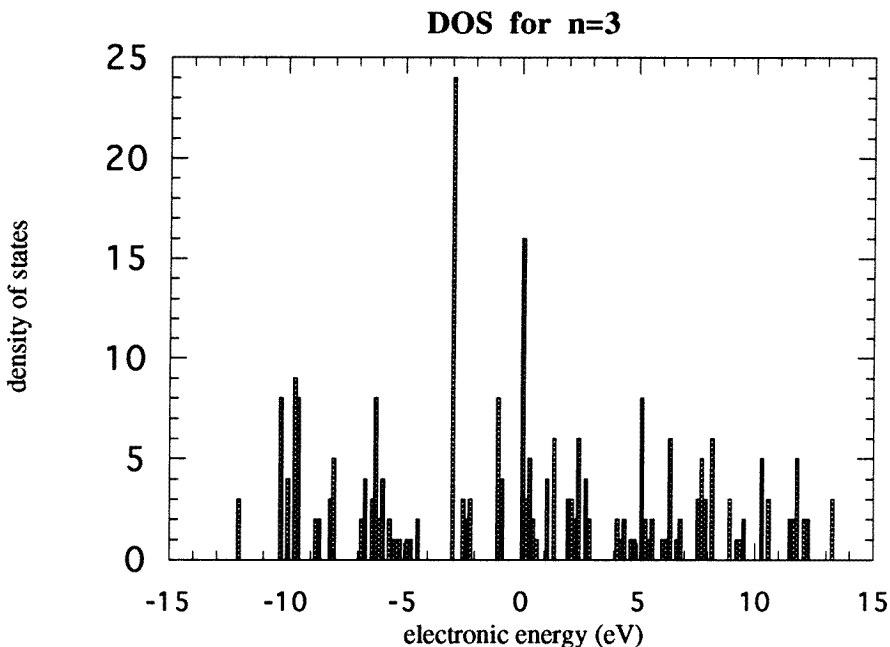


Figure 6. The density of states of the cluster in iteration  $n = 3$ .

iterations grows: for low numbers of iterations, there are finite-size effects.

For the electronic levels, one can see that the densities of states after different numbers of iterations are very similar: the peaks at  $E = 0$  eV and  $E = -2.903$  eV remain in each iteration. The peak at  $E = -2.903$  eV is the value of  $\Delta_\sigma$ . The relative height of this peak becomes larger as the iteration number grows. For the case where  $E = -2.903$  eV, the peak arises from the existence of dangling bonds on ‘surface’ atoms [15]. But the peak at 0 eV can be explained by the fact that there is a pseudo-confinement effect.

Confinement effects are usually taken to indicate the presence of topologically disconnected carbon clusters in the matrix. Electron eigenstates are mostly not extended ones, being either localized or critical; this will cause a pseudo-confinement effect even though the matrix is fully connected. This can explain the fact that we have a DOS which is composed of several peaks instead of being continuous.

However, the matrix  $C$  removes degeneracy for almost all levels except the two for which we obtain two large peaks. There is a process of subband splitting in each iteration [19].

Finally, the method used here to find the electronic levels can be extended to all regular fractal clusters composed of atoms in any hybridization. Indeed, there always exists a matrix similar to matrix  $C$  which allows one to compute the electronic levels of the next iteration in the construction of the cluster. The only parameter which changes with the geometry of the (regular) fractal is the number of  $\beta$ s in matrices  $C$  and  $A$ , regardless of their dimensions.

We have presented an ideal model for a fractal cluster of carbon atoms in the  $sp^2$  hybridization. At the structural level, one can say that such regular clusters do not exist—the carbon atom clusters in nature are certainly less regular. Regular fractals are used as models in physics. Furthermore, the surface sites would be more likely to be occupied



by other atoms, such as hydrogen atoms. The modification of these clusters to statistical fractal clusters of carbon atoms would transform this problem, which is exactly soluble, to a problem which would only be computable by a numerical method.

We have emphasized that the method employed here can be applied to the computation of the DOS of a regular fractal in any hybridization. This method would also be applicable for the calculation of the spectral density of states. As a conclusion we can say that we have developed in this paper a method which is very simple to use and which allows one to go further in the determination of eigenvalues of one kind of matrix (self-similar matrices). This method is complementary to the renormalization group methods: it allows one to calculate the DOS for fractal clusters where finite-size effects occur and where scaling is not exact. Hence, the properties of the DOS such as multifractality and corrections to scaling may be studied in an analytical way.

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