EMBEDDING BY PSEUDO ATOMS, AND THE TOPOLOGICALLY DETERMINED ONE-ELECTRONIC ENERGY LEVELS

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Abstract

It is shown that the embedding of covalent clusters with the help of pseudo atoms and the *fullerene* π electronic structure of amorphous carbon can be studied by the same formalism. Tight-binding model calculations were done for silicon clusters. It was found that the covalent clusters often have topologically determined energy levels that are cleared out from the spectrum in the presence of embedding.

1. Introduction

Embedding of carbon and silicon clusters can be divided into two classes. In the present paper, we call these two classes Embedding 1 (EM1) and Embedding 2 (EM2). In the first case, EM1, we are interested in the embedding of the whole cluster into the bulk [1–10]. In the second case, EM2, the usual embedding is followed by a σ-*fullerene* π ($\sigma-F\pi$) separation [11,12]. The $\sigma-F\pi$ separation is very similar to the $\sigma-\pi$ separation. An example for EM1 is the calculation where the silicon or carbon surface is examined by a cluster that is embedded into the bulk [3,4]. One can find examples for EM2 in the study of amorphous carbon [11,12]. In an amorphous carbon structure, there are diamond-like and graphite-like atoms. The diamond-like atoms are fourfold coordinated and the graphite-like atoms are threefold coordinated. Graphite-like atoms form three localized σ states plus a delocalized π state. As the graphite-like atoms and their neighbors are not in a plane, special care must be taken for the study of these atoms [13–16]. Kroto [14] proposed the name of fullerene for the class of all closed carbon cages that are composed of threefold-coordinated carbon atoms. We call the π states of these threefold-coordinated atoms *fullerene* π ($F\pi$) states.

One of the greatest problems of embedding of covalent clusters is the boundary condition. There are periodic [17–24] and non-periodic [1–10,25–27] boundary conditions. In the present paper, we are dealing with non-periodic boundary conditions. In EM1, the dangling bonds are saturated by hydrogen atoms [1–10] or by pseudo atoms [3,4,25–27]. There are methods where the influence of the bulk is taken into account by a perturbation potential [6]. Theoretical calculations [3,4] and experimental results [28,29] show that the hydrogen atom is not an appropriate boundary condition

for silicon clusters. In EM2, there is no problem for the boundary conditions, and the motion of *fullerene* π electrons is described by an effective model Hamiltonian.

The purpose of this paper is to show that the two kinds of embeddings, EM1 and EM2, can be described by the same formalism using hybrid orbitals. These hybrid orbitals are associated to pseudo atoms. It will also be demonstrated by numerical calculations that the covalent clusters have topologically determined energy levels. The embedding procedure clears out these levels from the one electronic energy spectrum. Using a tight-binding method and first-neighbor interactions, the topologically determined levels are independent of the actual position of the atoms. They are determined by the topological arrangement of the atoms. The influence of pseudo atoms on the one-electron energy levels of the clusters will also be discussed.

2. Embedding by pseudo atoms

Let us suppose that our system of atoms is described by the effective Hamiltonian H. This Hamiltonian can be the Hückel Hamiltonian in the Hückel theory, the tight-binding Hamiltonian in a tight-binding approximation and the corresponding Fockian in any other method. In our LCAO calculation, $\varphi_1, \varphi_2, \ldots, \varphi_n$ are the atomic orbitals. We change this basis with the help of the following T and O transformations:

$$\varphi_k^T = \sum_{i=1}^{n} \varphi_i T_{ik}, \tag{1}$$

$$\varphi_k^{TO} = \sum_{i=1}^{n} \varphi_i^T O_{ik}, \tag{2}$$

where T_{ik} is the matrix of the transformation T in the basis φ_i and O_{ik} is the matrix of the transformation O in the basis φ_i^T. Since the transformation T is a hybridization transformation, the orbitals φ_i^T are atomic orbitals. The transformation O is an ordering transformation. It changes only the order of the orbitals φ_i^T. The O is defined in such a way that the transformed Hamiltonian

$$H^{TO} = O^{-1} T^{-1} H T O \tag{3}$$

has the following hypermatrix form in the basis φ_i^{TO}:

$$H^{TO} = \begin{pmatrix} H_{II} & H_{IP} & H_{IE} \\ H_{PI} & H_{PP} & H_{PE} \\ H_{EI} & H_{EP} & H_{EE} \end{pmatrix}. \tag{4}$$

Here, H_{II}, H_{PP} and H_{EE} are the Hamiltonian matrices for the internal orbitals, pseudo orbitals and external orbitals, respectively. The other submatrices of H^{TO} are the Hamiltonian matrices between the corresponding orbitals. The internal and

pseudo orbitals are centered on the cluster under study, while the external orbitals describe the environment. The problem of embedding is solved if the Hamiltonian

$$H^C = \begin{pmatrix} H_{II} & H_{IP} \\ H_{PI} & H_{PP} \end{pmatrix} \tag{5}$$

can be used for the study of the embedded cluster. In the framework of Löwdin's partitioning technique [40,41], H^C is the unperturbed Hamiltonian, and the neglected interaction matrices represent the perturbation.

In order to define the transformation T in the case of EM1, we introduce the oriented sp^n hybrid atomic orbital:

$$h = \left(\frac{1}{\sqrt{1+n}} \right)(s + \sqrt{n}\,(p_x \cos\alpha_x + p_y \cos\alpha_y + p_z \cos\alpha_z)), \tag{6}$$

where s, p_x, p_y and p_z are atomic orbitals, $\cos\alpha_x$, $\cos\alpha_y$ and $\cos\alpha_z$ are the direction cosines and n is the p character of the hybrid. In EM1, the transformation T changes only the boundary orbitals of the cluster. The other cluster orbitals and the bulk orbitals are not changed by T. The pseudo orbitals are boundary orbitals because they are centered on the boundary atoms. The other boundary orbitals and the orbitals centered on the bulk atoms are called external orbitals. The number of the pseudo orbitals is equal to the number of the neighboring cluster atoms of the given boundary atom. The pseudo orbitals are hybrid orbitals and are oriented to the neighboring cluster atoms. If a cluster orbital is not centered on a boundary atom, we call it an internal orbital. In our previous papers [3,4], we used sp^3 orbitals for the pseudo orbitals. An appropriate sp^n hybrid orbital may even be useful in a purely tetrahedral system as well [27]. A possible theoretical method to determine the best n value for the sp^n hybrid is the maximum localization rule [8]. The O ordering transformation orders the φ_i^T orbitals in such a way that it provides the H^{TO} Hamiltonian of eq. (4). The embedded cluster is described by the Hamiltonian H^C of eq. (5).

Now we turn to the EM2 case of embedding. In the study of amorphous carbon, we used the p orbital axis vector analysis (POAV) to define the *fullerne* π orbitals [16,30–33]. The embedded cluster of carbon atoms is composed of threefold-coordinated atoms. We associate three h hybrid orbitals to each cluster atom. These hybrids are oriented to the neighboring atoms. The orthogonality condition and the direction of the orbitals determine the value n in the sp^n hybridization. The *fullerne* π orbital h^π is orthogonal to the h hybrids of the given atom. This condition determines the direction and the n hybridization of the h^π hybrid [16,30–33]. We call these h^π orbitals pseudo orbitals. The other cluster and bulk orbitals are called external orbitals. Thus, we defined the transformation T. The transformation O is defined in the same way as was done for EM1. In EM2, there are no internal orbitals. The embedded cluster is described by the Hamiltonian

$$H^C = H_{PP}. \tag{7}$$

3.   Topologically determined energy levels

In this section, we shall study the influence of the embedding procedure on the topologically determined electronic energy levels. In order to characterize the topology of the cluster, we use first-neighbor interaction. In our previous papers, we have demonstrated the existence of topologically determined, usually degenerate energy levels [12, 34, 35]. We used graph-theoretical methods [12, 34–37] to describe the topology. We do not go into details for the EM2 case, which deals with *fullerene* π orbitals. We mention here only that the metallic behavior of amorphous carbon clusters can be explained by the topological arrangement of the threefold-coordinated carbon atoms [12].

As an example for the EM1 case, we take the embedding problem of Si_5, Si_{17} and Si_{29} clusters of the diamond structure. These clusters are the smallest spherical clusters of the diamond structure. In the present paper, we use the Slater–Koster tight-binding parameters [38] of Papaconstantopoulos [39]. The diagonal parameters of the Hamiltonian are $H_{ss} = E_s = -5.19278$ eV and $H_{pp} = E_p = 1.05825$ eV. The topological structures of the clusters under study are presented in figs. 1–3.

We demonstrated [34, 35] that if a cluster of carbon or silicon atoms (or of any other atoms with only s and p atomic orbitals) has the partial topological structure of fig. 4, then the multiplicity of the $\varepsilon = E_p$ one-electron level is at least ν ($\nu > 1$). Since this property is additive, the multiplicities of the $\varepsilon = E_p$ energy level in the clusters Si_5 and Si_{17} are at least 4 and 12, respectively. This multiplicity is exact in the first-neighbor approximation and it does not depend on the actual positions of the atoms, even if the non-diagonal elements are dependent on the positions of the atoms. In numerical calculations, we have found that the multiplicity of the $\varepsilon = E_p$ energy levels in the clusters Si_5, Si_{17} and Si_{29} are, respectively, 8, 23 and 0. We changed randomly the coordinates of the atoms and the before-mentioned degeneracies did not change. The calculated degeneracies for the clusters Si_5, Si_{17} are larger than was expected, because the structure of fig. 4 means only a sufficient condition for the existence of the $\varepsilon = E_p$ energy level. We mention here that the cluster Si_{29} contains neither the structure of fig. 4 nor the one-electronic eigenvalue $\varepsilon = E_p$. Naturally, the second and third neighbor interactions split up the degeneracies but, in this case too, more than half of these levels are concentrated in a range width of 0.5 eV around the value of the E_p level.

We call the one-electron energy levels that are cleared out from the spectrum by embedding boundary levels (E_b). The calculated average boundary levels $\overline{E}_b$ are 0.04 eV, 0.06 eV and 0.08 eV, respectively, for the clusters Si_5, Si_{17} and Si_{29}. For the clusters under study, the following approximate numerical relation holds:

$$\overline{E}_b = E_{sp^3} + (E_p - E_{sp^3})\left(\frac{1}{3}\right), \tag{8}$$
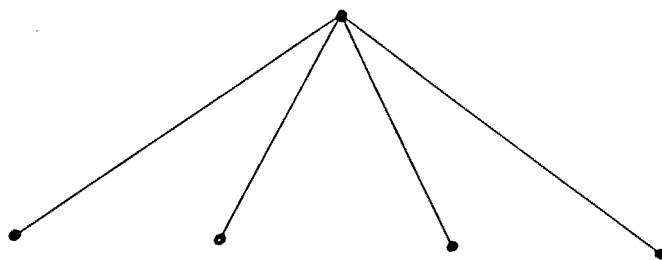
where

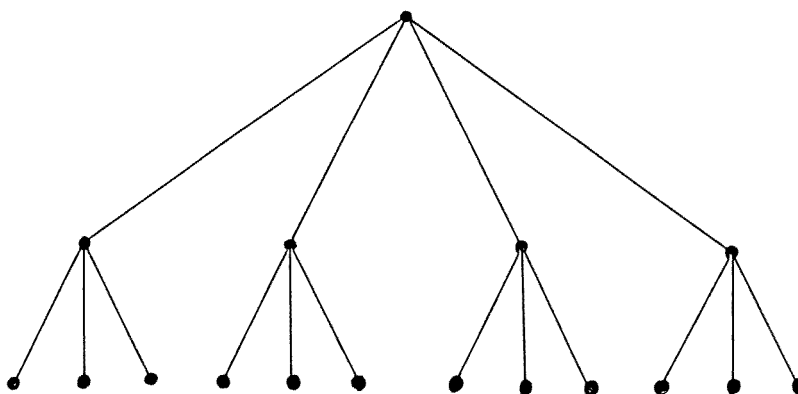Fig. 1. The topological structure of the Si_5 clusters under study.

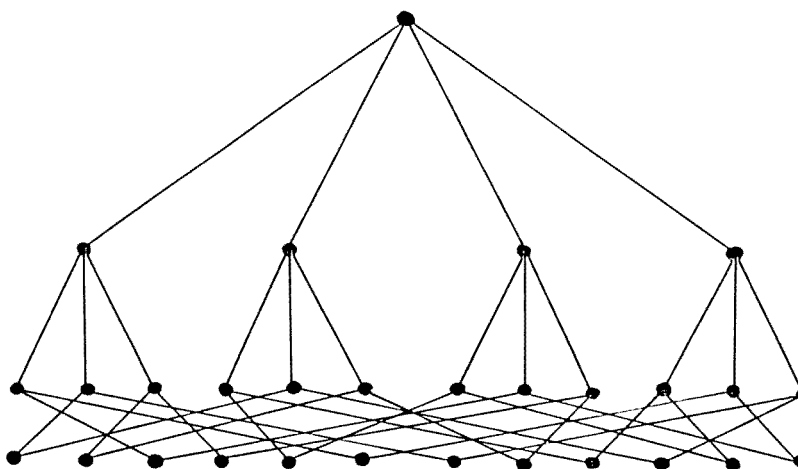Fig. 2. The topological structure of the Si_{17} clusters under study.

Fig. 3. The topological structure of the Si_{29} clusters under study.
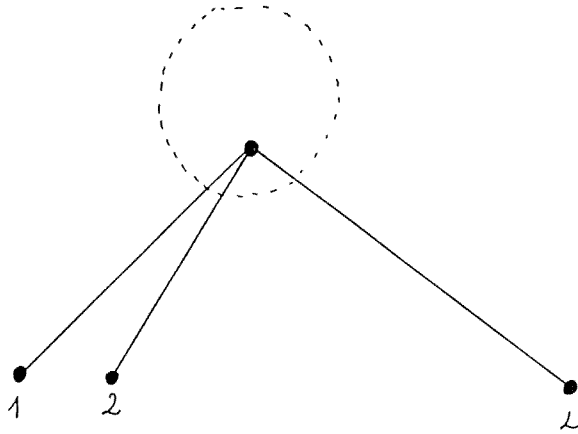
Fig. 4. A special cluster of atoms containing s and p atomic orbitals. In this cluster, the multiplicity of the electronic eigenvalue $\varepsilon = E_p$ is at least v ($v > 1$), if we use first-neighbor interactions in a tight-binding calculation. The dashed lines symbolize arbitrary connections between the atoms of the cluster.
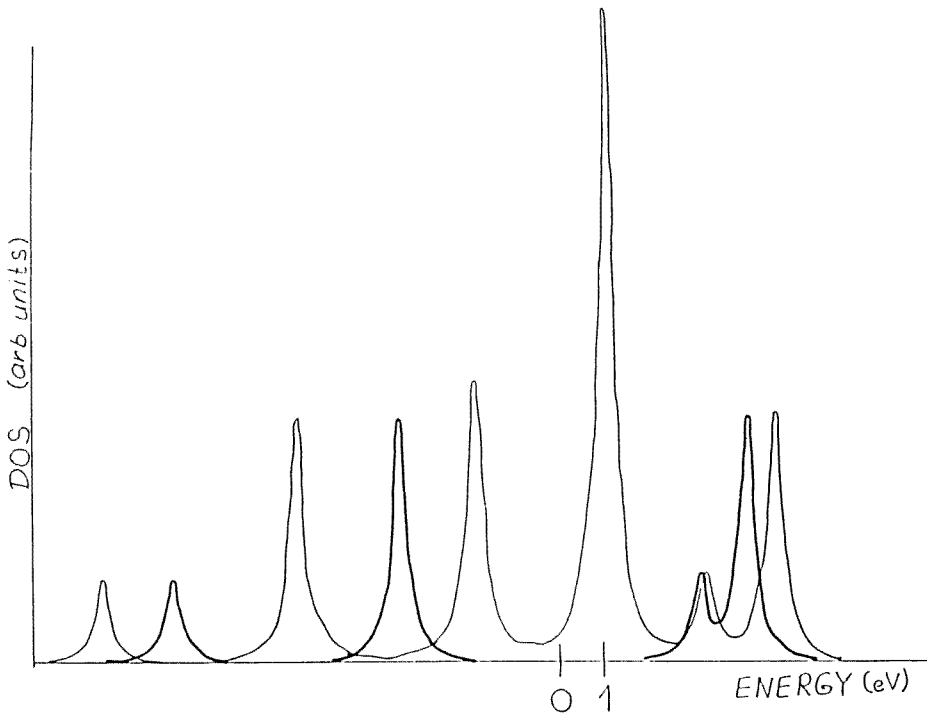

Fig. 5. Density of states (DOS) for the Si_5 clusters. The DOS of the free cluster is shown by a solid line. The thick solid line shows the DOS of the embedded cluster.
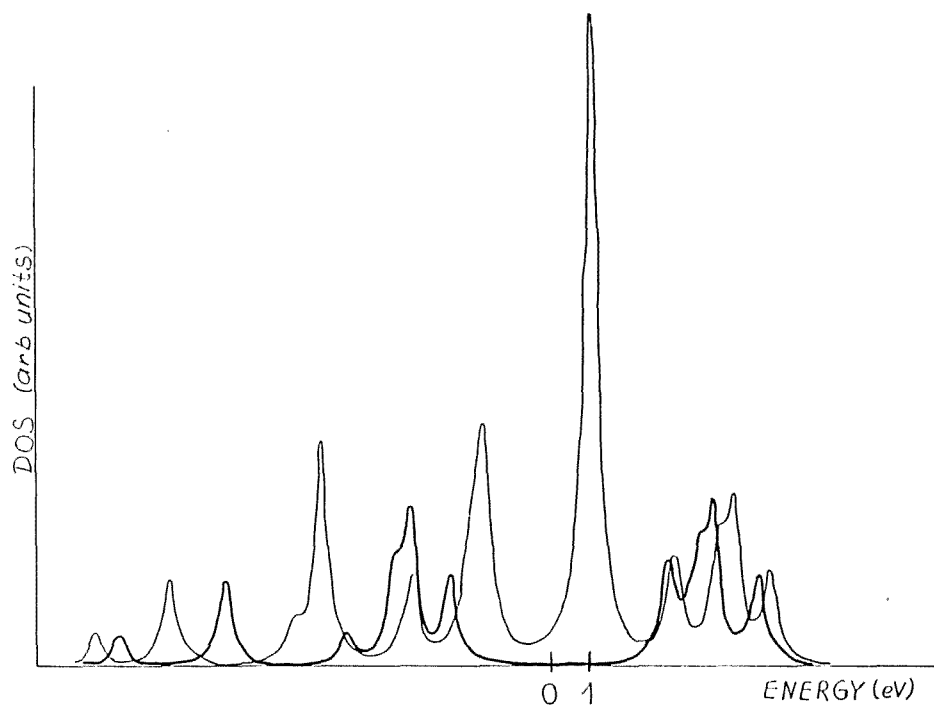
Fig. 6. Density of states (DOS) for the Si$_{17}$ clusters. The DOS of the free cluster is shown by a solid line. The thick solid line shows the DOS of the embedded cluster.
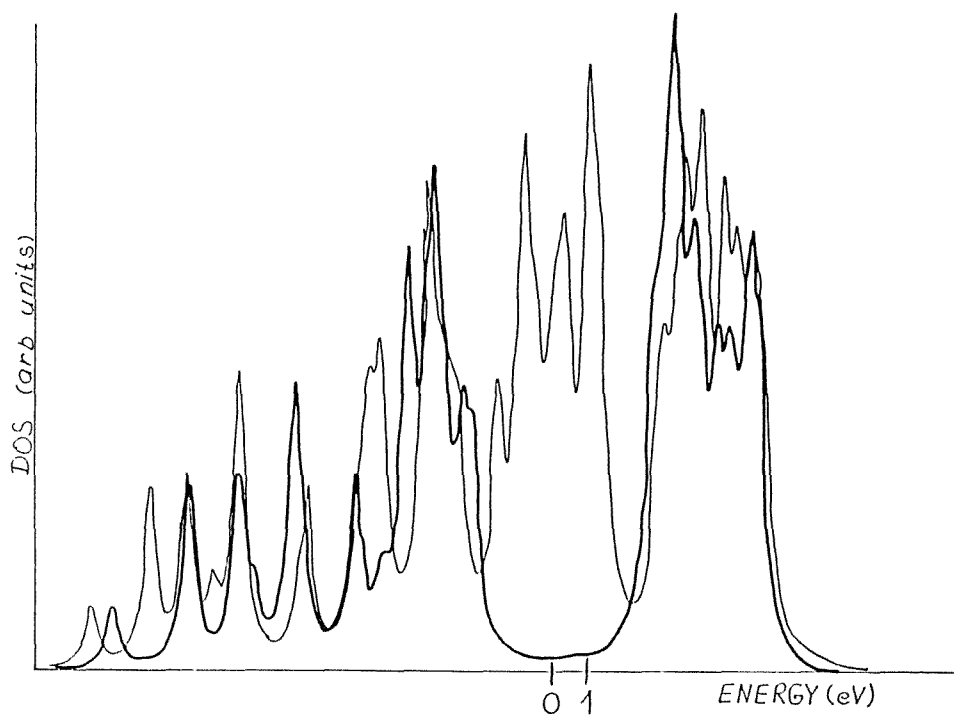

Fig. 7. Density of states (DOS) for the Si$_{29}$ clusters. The DOS of the free cluster is shown by a solid line. The thick solid line shows the DOS of the embedded cluster.

$$E_{sp^3} = (E_s + 3E_p)\left(\frac{1}{4}\right) \tag{9}$$

is the sp^3 hybrid one-electron energy. From eq. (8), it follows that the boundary levels are neither pure p states nor pure sp^3 hybrid states. The calculated density of states (DOS) of our Si clusters are presented in figs. 5–7. We used Gaussian line broadening that corresponds to the full width of 0.2 eV. From these figures, it is clear that the embedding by pseudo atoms provides a shift for the one-electron energy levels. The lower levels are shifted up and the higher levels are shifted down.

Summarizing our results for Si clusters, we can say that in the EM1 embedding procedure the topologically determined energy levels are cleared out from the spectrum and the average boundary energy level $\overline{E}_b$ is two times nearer to the sp^3 hybrid one-electron energy level than to the E_p p electronic level.

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