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Existence of stable electronic energy levels in the presence of vibrational and off-diagonal disorder

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We have found that the topological arrangement of atoms can guarantee the existence of stable electronic eigenvalues. These levels are stable in the presence of vibrational and off-diagonal disorder. Graph theory is used to describe the topological structure of the Hamiltonian. The actual applications are presented in tight-binding approximation. It was found that graph theory can be used even if the atoms have more than one atomic orbital.

The Bloch theorem is a unifying mathematical principle that considerably helps theoretical study of ordered systems. The advantages come from the application of translational symmetry. There is no such unifying mathematical principle in the case of disordered systems.[1] As is demonstrated in this paper, there is a simple mathematical principle that can be used for the study of the electronic density of states (DOS) of disordered systems. As our statements will be expounded in a general way they can also be used in other problems concerning the eigenvalues of a finite matrix.

We consider a tight-binding Hamiltonian of the form

$$H = \sum_{i=1}^{N} |i\rangle H_{ii} \langle i| + \sum_{\substack{i,j=1 \\ i \neq j}}^{N} |i\rangle H_{ij} \langle j| , \qquad (1)$$

where N is the number of atomic orbitals. As N is finite, we call our system a cluster. This Hamiltonian can describe even a solid state, if N is sufficiently large.

We shall demonstrate that the topological arrangement of the atoms can guarantee the existence of some eigenvalues of the Hamiltonian. Very often these eigenvalues produce peaks in the DOS. These energy levels do not depend on the $H_{ij} \neq 0$ off-diagonal elements. In the present paper the topology of the Hamiltonian is described by fixing of the $H_{ij} = 0$ off-diagonal elements and by fixing of some H_{ii} diagonal elements. That is, the topology does not change by changing those H_{ij} elements that are not fixed. Thus the topology of the Hamiltonian is a consequence of the topological arrangement of the atoms.

In most applications the $H_{ij} = 0$ off-diagonal elements are determined if the first-neighbor interactions are taken into account in Eq. (1). The orthogonality of the atomic orbitals can give several other $H_{ij} = 0$ elements, too.[2,3] The actual eigenvalues of the above-mentioned energy levels are equal to some H_{ii} diagonal elements of H. These eigenvalues are topological invariants of the system and are not affected by the off diagonal and vibrational disorder. Graph theory[4–8] is applied to describe the eigenvalue spectrum of the clusters under study.

Our statements about graph theoretical theorems are either trivial or they will be proved in a longer publication. In any case the physical consequences can be verified very easily.

In a previous paper[8] we studied the π-electronic structure of amorphous carbon. We used the following effective Hamiltonian:

$$H_{ij} = \begin{cases} \alpha, & \text{if } i = j \\ \beta, & \text{if } j \text{ is the first neighbor of } i \\ 0, & \text{otherwise ,} \end{cases} \qquad (2)$$

where α and β are the interaction parameters. The more general standpoint of the present paper can be summarized as follows: (1) H_{ii} depends on i in the Hamiltonian of Eq. (1), but it does not depend on i in Eq. (2). (2) In the Hamiltonian of Eq. (1) we can use s, p_x, p_y, and p_z orbitals, whereas the Hamiltonian of Eq. (2) is restricted to the one-orbital one-site approximation. (3) There can be an off-diagonal disorder in the Hamiltonian of Eq. (1), whereas in the Hamiltonian of Eq. (2) H_{ij} is a constant value for the first neighbors.

Our discussion is concerned with weighted graphs of the Hamiltonian H, in which we assign to each edge, (v_i, v_j), joining vertices, v_i and v_j, an edge weighting, $H_{ij} = H_{ji}$. There is no edge between v_i and v_j if $H_{ij} = 0$. If $H_{ij} \neq H_{ji}$, directed weighted graphs are used, and there is little difference in the consequences. For the sake of simplicity, and because in the case of cluster tight-binding calculations the $H_{ij} = H_{ji}$ condition is valid, we deal here with undirected graphs. The loop (v_i, v_i) will be weighted by H_{ii}.

After Rigby, Mallion, and Day[7] we now define a mutation graph G^M of a graph, G, which has N vertices, as follows.

A mutation graph G^M is a subgraph of G, the com-

ponents of which can only be one or more of the following:

(i) the loop graph,[6] i.e., $\bigcirc$,

(ii) the complete graph of two vertices and one edge,[6] i.e., ●——● ,

(iii) any cyclic graph,[6] $3 \leq n \leq N$, i.e.,

$$n \quad \underset{n-1}{\diagdown} \quad 2$$
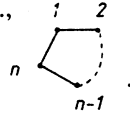
Here we mention that the terminology *Sachs graph* is often used for unweighted mutation graphs.[7]

The characteristic polynomial of the Hamiltonian of Eq. (1) reads as

$$D(\varepsilon) = \det|\varepsilon I - H| = \sum_{n=0}^{N} a_n \varepsilon^{N-n} . \tag{3}$$

It is demonstrated[7] that $a_n = 0$ if the graph G of Hamiltonian H does not have mutation graphs G^M with n vertices. So if there are not mutation graphs with N, $N-1, \ldots, N-v+1$ vertices, the following equations are valid:

$$a_N = a_{N-1} = a_{N-2} = \cdots = a_{N-v+1} = 0 .$$

Thus $\varepsilon = 0$ is a v-fold degenerated eigenvalue of the Hamiltonian. As the existence and nonexistence of the mutation graphs G^M does not depend on the actual values of matrix elements $H_{ij} \neq 0$, the multiplicity of eigenvalue $\varepsilon = 0$ is determined only by the topology of the graph G of Hamiltonian H of Eq. (1). Thus these $\varepsilon = 0$ energy levels are stable under off diagonal and vibrational disorder if the topology and the appropriate H_{ii} diagonal elements are fixed. In this case only those $H_{ii} = 0$ diagonal elements that are important for the nonexistence of mutation graphs must be fixed.

A graph G^1 is an induced subgraph of graph G^0 if G^1 is a subgraph and it contains all the edges from G^0 which connect the vertices of G^1. If a graph of a Hamiltonian H contains the induced subgraph of Fig. 1, then the $\varepsilon = 0$ eigenvalue is at least a $(v-1)$-fold eigenvalue. We can take away at least $(v-1)$ vertices from this graph to have a mutation graph. As our present purpose is to show the existence of topologically determined eigenvalues, we shall deal with the consequences of the structure of Fig. 1. (For
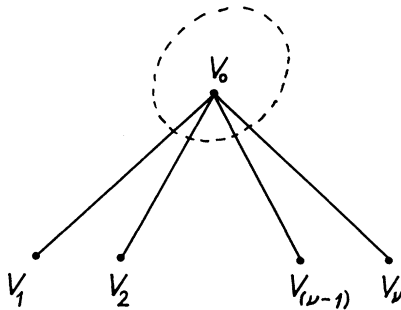
other structures not having mutation graphs see Ref. 8.) If the induced subgraph of Fig. 1 appears more than once with different v values then the multiplicity of the $\varepsilon = 0$ eigenvalue is the sum of the multiplicity of different induced subgraphs. If, for example, the graph G of a Hamiltonian has the structure of Fig. 2, then the $\varepsilon = 0$ eigenvalue is at least a $(\mu+2)$-fold eigenvalue of the Hamiltonian. That is,

$$(3-1) + (2-1)(\mu-2) + (3-1) = \mu+2 . \tag{4}$$

Let us introduce the concept of the H^S shifted Hamiltonian,

$$H^S = H - H_{kk} I , \tag{5}$$

where I is the unit operator (unit matrix) and H_{kk} is one of the diagonal elements of the Hamiltonian H. If the $\varepsilon = 0$ value is a v-fold eigenvalue of the Hamiltonian H^S then the $\varepsilon = H_{kk}$ value is also a v-fold eigenvalue of the Hamiltonian H. The multiplicity of the $\varepsilon = H_{kk}$ eigenvalue will be at least v, if we fix the $H_{ij} = 0$ nondiagonal and $H_{ii} = H_{kk}$ diagonal elements in H and change all the other matrix elements. More precisely we have to fix only those $H_{ii} = H_{kk}$ values that influence the existence or nonexistence of the mutation graphs. If Fig. 1 is the graph of the shifted Hamiltonian H^S, than we have to fix only the diagonal elements H_{ii} corresponding to vertices v_1, $v_2, \ldots, v_{v-1}, v_v$. The above defined shifting of the Hamiltonian H annihilates the loops corresponding to the value H_{ii}.

In the case of first neighbor interaction it is useful to define the cluster graph G^C. The number of vertices in G^C is equal to the number of the atoms in the cluster. The (v_i, v_j) belongs to G^C if the atoms i and j are first neighbors. There are no loops in G^C.

Let us suppose that we are using a one-orbital one-site approximation and the graph of the shifted Hamiltonian has the form of Fig. 1 or Fig. 2. In this case the multiplicity of the $\varepsilon = \varepsilon_s$ eigenvalue is at least $(v-1)$ for Fig. 1 and at least $(\mu+2)$ for Fig. 2, where $\varepsilon_s = H_{ii}$ is the site energy of the site orbitals.

If the atoms of our cluster contain s, p_x, p_y, and p_z orbitals and the cluster graph G^C is shown in Fig. 1, then the multiplicity of the $\varepsilon = \varepsilon_p$ eigenvalue is at least v, where $\varepsilon_p = H_{ii}$ is the diagonal element for the orbitals p_x, p_y, and p_z. For tight-binding parameters, see Refs. 2 and 3. In the special case of Fig. 2 the multiplicity of the $\varepsilon = \varepsilon_p$ energy level is at least $(2\mu+2)$. Namely,

$$3 + 2(\mu-2) + 3 = 2\mu+2 , \tag{6}$$

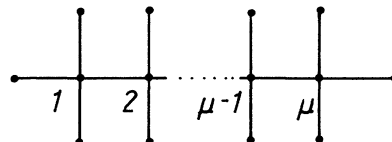when Fig. 2 is the cluster graph G^C of atoms with p orbitals.

FIG. 1. Graph G^0 and induced subgraph G^1. The induced subgraph G^1 is described by the vertices v_0, v_1, $v_2, \ldots, v_v$ ($v > 1$) and edges (v_0, v_1), $(v_0, v_2), \ldots, (v_0, v_v)$. The graph G^0 contains the graph G^1 and other vertices and edges that are symbolized by dashed lines.

FIG. 2. A special graph structure containing μ times the subgraph of Fig. 1. The corresponding v values are $v_1 = 3$, $v_2 = \cdots = v_{(\mu-1)} = 2$, and $v_\mu = 3$.

The proof of our statements concerning the p orbitals is a little lengthy and we shall present it in another paper. In special cases, however, it can very easily be verified numerically. According to our numerical calculations there are topologically determined energy levels for d orbitals as well.

Let us now turn to the applications. The one-site one-orbital approximation is widely used in the study of localization and quantum transport.[9-16] The nondiagonal matrix elements are calculated by the formula

$$H_{ij} = -V_0 \exp(-R_{ij}/\alpha_H) , \qquad (7)$$

where $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ is the distance between the sites i and j. In such calculations the diagonal elements are kept at a constant value and the range of exponential interaction α_H is changed with fixed site positions. If α_H is sufficiently small, the large central peak of the DOS at the site energy $\varepsilon_f = H_{ii}$ can be explained by the existence of clusters that do not have mutation graphs. As the Fermi level is usually at $\varepsilon_f = H_{ii}$, the hopping conductivity[1] between the separated clusters can be regulated by the topological arrangement of the sites. Numerical calculations for amorphous carbon[17] showed that these topologically determined sites are mostly localized at the circumferences of the clusters.

Kirkpatrick and Eggarter[18] studied binary alloys $A_x B_y$ and they found a class of localization sites which are not isolated from the bulk of the material. They presented some possible configurations of atoms A which are not isolated, but still possess a localized eigenstate. These configurations can be described by the present graph theoretical methods. We mention here that some configurations of Kirkpatrick and Eggarter produce energy levels that depend on the H_{ij} off-diagonal values. In their Hamiltonian the off-diagonal disorder was not taken into account.

The induced subgraph of Fig. 1 often appears in the cluster graphs G^C of carbon and silicon clusters.[19,20] These clusters contain several electronic energy levels that are determined by the topology of atoms with s, p_x, p_y, and p_z orbitals.

Summarizing we can say that in tight-binding approximation, and if the topology is determined by the first-neighbor interaction there are stable electronic energy levels that are determined by the topology of the structure. The theory presented in this paper can be used for designing clusters with the desired electronic structures.

[1] J. M. Ziman, *Models of Disorder* (Cambridge Univ. Press, Cambridge, England, 1979).

[2] W. A. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980).

[3] D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[4] A. Graovac, I. Gutman, and N. Trinajstić, *Topological Approach to Chemistry of Conjugated Molecules* (Springer, Berlin, 1977).

[5] D. M. Cvetković, M. Doob, and H. Sachs, *Spectra of Graphs* (Deutscher Verlag, Berlin, 1980).

[6] F. Harary, *Graph Theory* (Addison-Wesley, Reading, MA, 1972).

[7] M. J. Rigby, R. B. Mallion, and A. C. Day, Chem. Phys. Lett. **51**, 178 (1977); see also **53**, 418(E) (1978).

[8] S. Kugler and I. László, Phys. Rev. B **39**, 3882 (1989).

[9] M. K. Gibbons, D. E. Logan, and P. A. Madden, Phys. Rev. B **38**, 7292 (1988).

[10] A. Blumen, J. P. Lemaistre, and I. Mathlouthi, J. Chem. Phys. **81**, 4610 (1984).

[11] A. Puri and T. Odagaki, Phys. Rev. B **29**, 1707 (1984).

[12] W. Y. Ching and D. L. Huber, Phys. Rev. B **26**, 5596 (1982).

[13] W. Y. Ching and D. L. Huber, Phys. Rev. B **25**, 1096 (1982).

[14] A. C. Fertis, A. N. Andriotis, and E. N. Economou, Phys. Rev. B **24**, 5806 (1981).

[15] B. T. Debney, J. Phys. C **10**, 4719 (1977).

[16] M. Kikuchi, J. Phys. Soc. Jpn. **37**, 904 (1974).

[17] I. Varga and J. Pipek, Phys. Rev. B **42**, 5335 (1990).

[18] S. Kirkpatrick and T. P. Eggarter, Phys. Rev. B **6**, 3598 (1972).

[19] I. László, Int. J. Quantum Chem. 2 **12**, 105 (1977).

[20] I. László, Int. J. Quantum Chem. **21**, 813 (1982).