Embedding in Benzenoid Hydrocarbons

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Using the embedding scheme and a rule we proposed previously, in this work we discuss common eigenvalues and their degeneracies in benzenoid molecular graphs.

1. INTRODUCTION

The phenomenon of subspectrality, where some of the eigenvalues are common to different structures, is widespread in graph theory. A number of works have studied this by various methods.[1−19] Hall[8−10] explained the subspectrality by means of embedding a small fragment repeatedly within an alternant hydrocarbon. His embedding must satisfy the following: (i) all atoms connected directly to the fragment must be nodes; (ii) on the other side of each of these nodes will be one repetition of the fragment with opposite sign; and (iii) other branches at these nodes will also be nodes, since at all nodes the sum of nearest neighbor fragments must be zero. If all the atoms of the molecule can be included in the embedding, then the eigenvalues of the fragment become eigenvalues of the molecule. Dias[11−13] studied the Hückel spectra of conjugated molecules extensively by means of the concept of embedding and summarized the regularity for the existence of eigenvalues ± 1 in benzenoid hydrocarbons, often being accompanied by a "selective lineation". He proposed a rule as follows: "whenever a benzenoid structure can have a succession of edges bisected with a straight line drawn from one side of the molecule to other with the terminal rings being symmetrically convex relative to the line, then those rings intersected by the line can be embedded with a perpendicular succession of ethene substructures and the benzenoid structure as a whole will have at least one eigenvalue pair of plus and minus one. This straight line will be called a selective lineation". Dias also pointed out that if two or more selective lineations are present in an alternant hydrocarbon, each distinct lineation will be associated with a pair of eigenvalues $x = \pm 1$. We note that Dias has shown that alternant substructures in otherwise nonalternant systems are frequently capable of being embedded, examples of which are given in his books.[17−19] Furthermore, he has discussed this with examples of nonalternant systems which are semiembedded with the unpaired half-eigenvalue set of alternant systems. In regard to maximum degeneracy, Dias has shown this for systems in which all combinatorial embedding of a certain type overcount the degeneracy.

In continuation of their works, in our previous publication[20] we found that all embedding forms (defined as the set M) of ethene fragments in benzenoid systems can be obtained by combination of some linear independent embedding forms (defined as the subset S of the set M). The number of the elements in set S provides a lower bound of the degeneracy. Recently, we developed an embedding scheme and a rule from which eigenvalues of fullerene C_{60} and their degeneracies are derived.[21−22] Using the embedding scheme and the rule, in this work we discuss common eigenvalues of different benzenoid molecular graphs and their degeneracies. Then we propose two corollaries of the rule, which describe the node characteristics of degenerate eigenvectors and illustrate the relationship between the degeneracies of eigenvalues of a benzenoid molecular graph and its subgraphs.

2. A GENERAL EMBEDDING SCHEME

The sufficient and necessary requirement for a molecular graph sharing an eigenvalue $x = x_0$ is that its fragment eigenvector corresponding to $x = x_0$ can be embedded in the graph according to the following embedding scheme.

Embedding Scheme. A molecular graph shares a common eigenvalue x_0 with its fragments, if the corresponding eigenvectors of fragments can be embedded into the graph. The embedding must satisfy two conditions: (i) fragments are separated by nodes, and vertices which are not shared by fragments are nodes; (ii) the sum of the coefficients of the fragment eigenvector ψ'_l ($l = 1, 2, ..., m$; m is the number of embedding fragments) adjacent to each node must be zero.

The eigenvector $\Psi(x = x_0)$ of a molecular graph takes the form

$$\Psi \rightleftharpoons \sum_{l=1}^{m} \psi'_l = \sum_{l=1}^{m} k_l \psi_l \qquad (1)$$

Here ψ_l stands for an eigenvector of the lth fragment, k_l is a constant factor making condition 2 valid, the symbol "$\rightleftharpoons$" expresses the fact that the coefficient c_i of Ψ is the same as that of ψ'_l if the ith vertex is shared by lth fragmen; otherwise c_i is equal to zero (the vertex is node).

Our embedding scheme can be used in alternant and nonalternant systems. For nonalternant graphs, embeddings of subgraph eigenvectors $\psi(x_0 > 0)$ and $\psi(x_0 < 0)$ should often be dealt with separately. However, based on the pairing theorem of bipartite graphs, it is sufficient here to consider only positive eigenvalues and their corresponding eigenvectors. In the figures of this work, the ψ_l are indicated by bold lines, the coefficients of the ψ'_l are illustrated by bold dots and open circles, leaving out those of internal vertices because they are not important in our discussion on embeddings. Internal vertices are defined here as those which are joined only to vertices of the fragment.

In benzenoid systems, some fragment eigenvectors corresponding to $x_0 = \pm 1, \pm\sqrt{2}$, and their embeddings are shown in Figures 1 and 2, respectively. Graph **1** (an ethene molecular graph) in Figure 1 is the smallest fragment sharing eigenvalues ± 1. Obviously, the embeddings of the ethene

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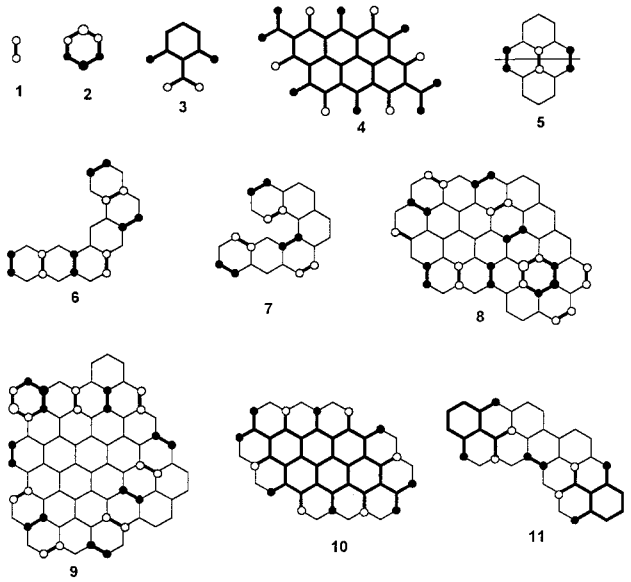


Figure 1. Some examples of subgraphs **1**−**4** sharing eigenvalues ±1 and embeddings of these fragment eigenvectors in benzenoid graphs **5**−**11**. Dias' "selective lineation" is indicated with a thin straight line.

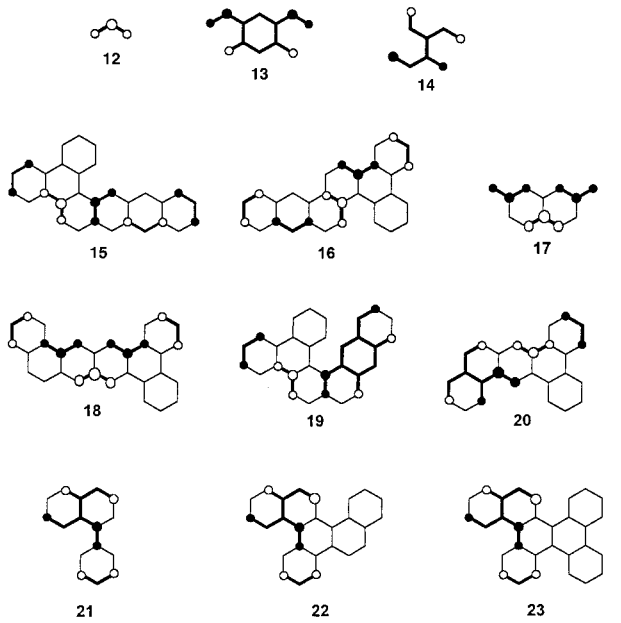
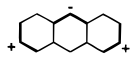


Figure 2. Illustrations of some fragments sharing eigenvalues ± $\sqrt{2}$ and embeddings of their eigenvectors in benzenoid systems.

fragment and its eigenvector are equivalent. The embeddings in graphs **5**−**7** consist of ethene fragments only. All embedding styles of an ethene fragment in a benzenoid graph were approached in our previous publication. There exists a selective lineation in graph **5**, which is readily found by inspection. The embedding styles in graphs **8**−**11** express that it is not enough to considering only embeddings of ethene fragments for determining eigenvalue $x = 1$ of a molecular graph.

Figure 2 shows that eigenvectors $\psi(x = \sqrt{2})$ of fragments (**12**−**14**) can be embedded in benzenoid molecules (**15**−**23**). Allyl is the smallest fragment having eigenvalues $x = \sqrt{2}$, whose eigenvector $\psi(x = \sqrt{2})$ can be represented with (1, $\sqrt{2}$, 1); here the normalization coefficient 1/2 is omitted. For the embedding style in graph **15** and **16**, equivalent positions on different allyl fragments always match up through each node position. In the eigenvector $\Psi(x = \sqrt{2})$ obtained in such manner, k_l within e 1 is always equal to 1. Though relative positions of the fragments in graph **17** do not match up, if $k_1 = k_3 = -1$ and $k_2 = \sqrt{2}$, requirements of the embedding scheme are still satisfied. The embeddings of **22** and **23** can be derived by connecting different branches at nodes of embedding in graph **21**. Furthermore, as pointed by Dias, the embedding retains still if a heteratom or connection of a nonalternant fragment is placed at node position.

One may find the fact easily that sometimes a molecular graph may not share each eigenvalue of the embedding fragment. For example, though an anthracene molecule graph **24** (with the spectrum: $0. \pm\sqrt{2}$) can be embedded by allyl fragments following Hall's rule, only eigenvalues



$\pm\sqrt{2}$ emerge in the spectrum of anthracene. Our embedding scheme suggests that, in general, the maximum eigenvalues of fragments, which can be embedded in an alternant graph according to Hall's rule, will exist in the graph. However, the eigenvalues of some fragment, say 1,3-butadiene (with the spectrum: $x = \pm(\sqrt{5} \pm 1)/2$), are always shared by the embedded system. The reason is explained as follows. Because the coefficients of the characteristic polynomial of a graph are integers, if the graph has the eigenvalue $x = a + b\sqrt{c}$, (a, b, and c are integers), then it shares the eigenvalue $x = a - b\sqrt{c}$. For an alternant system, according to a pair theorem, the molecule also has the eigenvalues $x = -a - b\sqrt{c}$ and $-a + b\sqrt{c}$. Thus, if 1,3-butadiene fragments can be embedded in a benzenoid molecule, all eigenvalues of this fragment will exist in the molecule.

From the fundamentals of quantum chemistry, we see that corresponding to an eigenvalue x_0 of a molecular graph, the eigenvector $\Psi(x_0)$ is nondegenerate if there exists only one embedding style (one eigenvector). If a nondegenerate eigenvector of a molecular graph has node/s, the eigenvectors can be obtained by embedding eigenvectors of fragments such as those in graphs **5**−**11** in Figure 1 and **15**−**23** in Figure 2; otherwise the eigenvector can only be embedded trivially by the corresponding eigenvector of the graph. However, section 3 will explain that for a molecular graph a degenerate eigenvector can always be obtained nontrivially by embedding of the fragment eigenvectors.

3. THE DEGENERACY OF THE EIGENVALUE $X = X_0$

A molecular graph can have one or more embedding styles belonging to the eigenvalue $x = x_0$. Suppose all embedding styles associated with x_0 constitute a set **A**; we define a subset **A***, **A***⊂**A**, the elements of **A*** satisfying the condition that at least one vertex, which is called the characteristic vertex and denoted by v_η (η is the number of elements in **A***), of each element in **A*** is not covered by another element of **A***. According to the definition of **A***, it is apparent that each element (embedding style) in **A*** cannot be obtained by combination of the others in **A***. Thence we characterize the elements in **A*** as linearly independent. Rule 1 presents

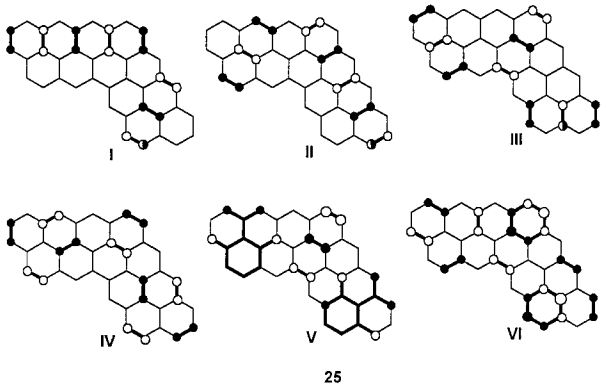


Figure 3. Six embeddings $\Psi(x = 1)$ in graph **25**.

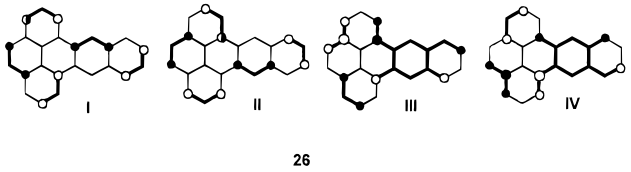


Figure 4. Four embeddings $\Psi(x = \pm\sqrt{2})$ in graph **26**.

a graph-theoretical method for determining degeneracy of a molecular graph.

Rule 1. The maximum possible number of the elements (denoted by N) in **A*** is equal to the degeneracy of eigenvalue x = x_0 (denoted by d) in the molecular graph, i.e.

$$N = d \tag{2}$$

Although for a molecular graph it may be difficult to find all elements of set **A** (all embedding styles) associated with eigenvalue $x = x_0$, subset **A*** can be detected from several simple embedding styles. For example, in graph **25** six embedding forms (**I, II, III, IV, V,** and **VI**) in Figure 3 are known from our experience. On definition of subset **A***, embedding styles Figure 3 I, II, and III can be chosen as elements of **A***. In Figure 3, the symbol '◑' stands for the characteristic vertex v_i (i = I, II, III) of an embedding style. Hence, the eigenvalues $x = 1$ of graph **27** is three-fold degenerate.

Figure 4 gives another example of Rule 1. Graph **26** has four embedding styles, subset **A*** can consist in two of them, say Figure 4 I and II. Eigenvalues $\pm\sqrt{2}$ of graph **26** are double degenerate indeed. The other eigenvalues can be achieved by combination of the two embeddings, for example

$$\Psi_{III} = \Psi_I - \sqrt{2}\Psi_{II} \tag{3}$$

$$\Psi_{IV} = \sqrt{2}\Psi_I - \Psi_{II} \tag{4}$$

4. DISCUSSION

Two useful corollaries are derived straightforwardly from Rule 1.

Corollary 1. In subset **A***, each embedding style associated with a d-fold degenerate eigenvalue $x = x_0$ has at least $d - 1$ nodes.

A complete graph with N-vertices is denoted by K_N, its each vertex has the degree $N - 1$. In a complete graph K_N ($N \geq 2$), one can detect $N - 1$ embedding styles associated with $x = -1$, which construct subset **A***. For example, each of the four embeddings of graph **29** (K_5) showed in Figure

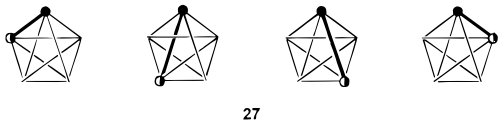


Figure 5. Four embedding styles of K_5 constructing subset **A***.

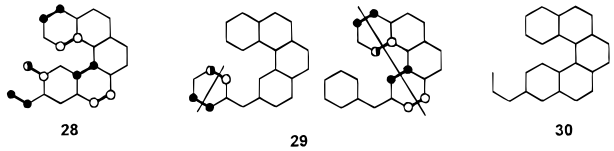
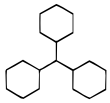


Figure 6. Independent embedding styles Ψ ($x = 1$) in graphs **28, 29,** and **30**.

5 has three nodes. Because subset **A*** consists of these embeddings, K_5 has 4-fold eigenvalue $x = -1$. In general, K_N has $(N - 1)$-fold degeneracy about eigenvalue $x = -1$. Last eigenvalue of K_N is $x = N$, the corresponding eigenvector represents total symmetry.

Corollary 2. If graph G has a d-fold degenerate eigenvalue $x = x_0$ and its subgraph G* results from deletion of one arbitrary vertex of G, then graph G* has eigenvalue $x = x_0$ with d or $(d \pm 1)$-fold degeneracy. (In ref 22, Corollary 2 was stated as that if graph G has a d-fold degenerate eigenvalue $x = x_0$ and its subgraph G* results from deletion of m arbitrary vertices of G ($m < d$), then graph G* has an eigenvalue $x = x_0$ with at least $(d - m)$-fold degeneracy.)

Corollary 2 illustrates the relationship between degeneracies of eiegnvalues of a molecular graph and its subgraph. For example, graph **7** has one nondegenerate eigenvalue $x = 1$. Graphs **28, 29,** and **30** are obtained from erasing one of different vertices of graph **7**, their degeneracies in $x = 1$ are 1, 2, 0, respectively. Independent embedding styles of



28, 29, and **30** are showed in Figure 6. For some special graphs, corollary 2 can also be used to estimate a reasonable lower bound of degeneracy in $x = x_0$. For example, deleting a center vertex of graph **31**, we obtain three benzene molecular fragments, each of them has two eigenvalues $x = 1$, and one $x = 2$. Corollary 2 shows that **31** has at least 5-fold degeneracy in $x = 1$, and 2-fold degeneracy in $x = 2$. In fact, it does.

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