

## DETERMINING SELECT EIGENVALUES BY EMBEDDING SMALLER STRUCTURES ONTO LARGER ONES

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**Abstract.** A systematic procedure for determining select eigenvalues by embedding smaller substructures onto larger ones is described. Embedding of pentadienyl is unique because the eigenvector coefficient of the central carbon vertex has exactly twice the magnitude of each end carbon vertex.

A graph  $G$  is defined in terms of a set  $V(G)$  of vertices and a set  $E(G)$  of edges consisting of unordered pairs of vertices. For a subgraph  $G'$ ,  $V(G') \subseteq V(G)$  and  $E(G') \subseteq E(G)$  where the components or fragments of a graph or subgraph are connected pieces. An embeddable graph  $G$  can be broken into fragments collectively called a spanning subgraph  $G'$  where  $V(G') = V(G)$ . The fragments will be  $K_1$  and  $F_z$  components where the latter will possess common eigenvalues. If a bipartite subgraph  $G^*$  of a graph  $G$  can be embedded (covered) by alternating  $K_1$  fragments with  $m$  identical  $F$  fragments with alternating signs, then  $F_+ \cup K_1 \cup F_- \cup K_1 \cup \dots \subset G^* \subseteq G$  and  $F_+ \cap K_1 \cap F_- \cap K_1 \cap \dots = 0$ .  $K_1$  represents a node position (vertex) which has zero coefficients in the corresponding eigenstates. Also, the sum of the associated coefficients of vertices attached to each  $K_1$  node vertex must equal zero which is fulfilled if the fragment signs alternate. Tree graphs with linear paths on  $n$  vertices (carbon vertices) without branches (i.e., having only degrees -1 and -2) are designated by  $P_n$  and cycles on  $n$  vertices by  $C_n$ . A path on one vertex ( $P_1$ ) is the complete graph  $K_1$  and a path on two vertices ( $P_2$ ) is the complete graph  $K_2$ . A fragment subgraph is a graph that can be dissected from a larger graph by removing or deleting the  $K_1$  vertices, called nodes. Embedding occurs

when a set of identical fragment subgraphs (or fragment subgraphs with common eigenvalues,  $\epsilon$ ) are obtained by dissection of a larger graph. For example, removal of the central vertex from  $P_5$  gives two  $K_2$  subgraphs, and, therefore,  $P_5$  can be embedded by  $K_2$ ; in this example the node is also a cut vertex and both  $K_2$  and  $P_5$  have  $\epsilon = \pm 1$ .

In a prior paper, the use of embedding for determining select eigenvalues as an aid in determining the total characteristic polynomial of small molecules was introduced.<sup>1</sup> The purpose of this presentation is to emphasize and illustrate the use of embedding in determining select eigenvalues principally on large molecules. The reader should review the rules for embedding given in the lead paper under subspectral components.<sup>1</sup>

#### Pentadienyl Embedding

The embedding of the symmetrical substructures of methyl radical, ethene and benzene is straightforward. However, the embedding of fragments with different kinds of vertices in polycyclic systems needs to be done so as to match up equivalent positions through each node position. This is aptly illustrated by the embedding of pentadienyl onto larger alternant molecules. Consider the examples presented in Figure 1. The three monocyclic isomers of phenylpentadienyl (1 to 3) all have the eigenvalues associated with pentadienyl. Here the 1-positions of the (+)-pentadienyl fragments can coincide with the 1-, 2-, and 3-positions of the (-)-pentadienyl fragment, but as soon as one goes to the dicyclic systems (4 and 6) the situation changes. 2-Ethenyl naphthalene (4), the analog of 1, has no eigenvalues in common with pentadienyl, whereas 1-ethenyl naphthalene (6), the analog of 2 does. If one examines the coefficients of the normalized wave function for the eigenstate of  $\epsilon = \sqrt{3}\beta$  in the pentadienyl fragment (5), one sees that the coefficient magnitude for position-3

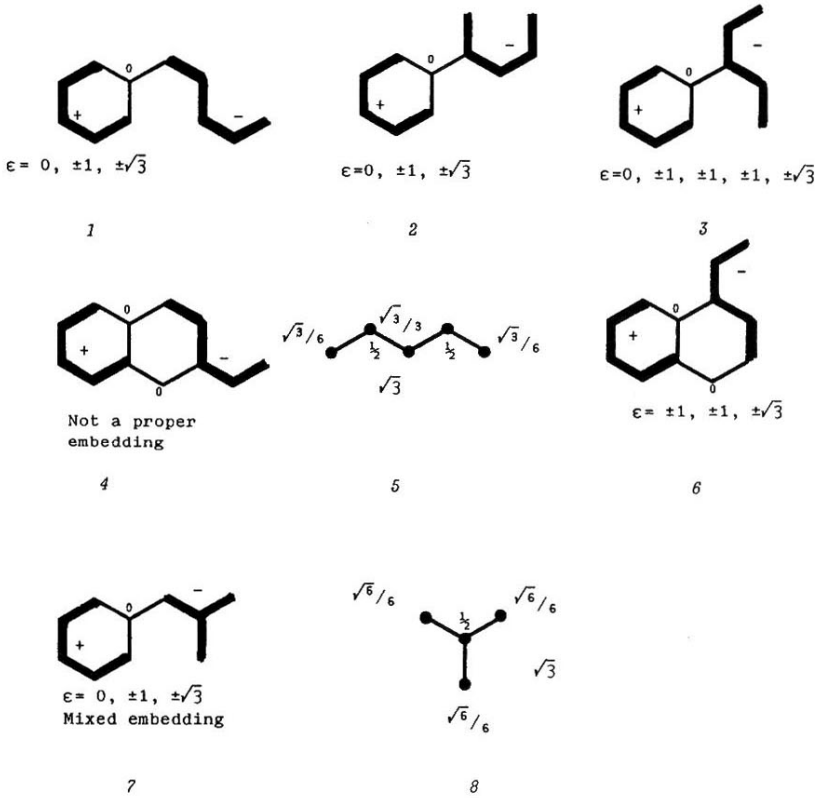


Figure 1 . Pentadienyl embedding.

is twice that of position-1. Since proper embedding requires that the sum of the coefficients of all vertices attached to every zero node position be zero, in 1 the position-1 coefficient of the (-)-fragment must be two times larger than the coefficient magnitude on position-1 of the attached (+)-fragment. This would require that the position-3 coefficient in the (-)-fragment of 4 to be four times larger than the position-1 coefficient of the (+)-fragment; thus the sum of the coefficients through the additional node in 4 can not sum to zero and is not a proper embedding. In 3 the position-3 coefficient of the (-)-fragment is twice the magnitude of the coefficient value for position-1 in the (+)-fragment. This means that the magnitude of the position-1 coefficient on the (-)-fragment of 6 matches the magnitude of the position-1 coefficient of the (+)-fragment, and therefore 6 is a proper embedding. The embedding of pentadienyl fragments in polyhexagonal systems is unique because the position-3 coefficient of this fragment is exactly twice the magnitude of the position-1 coefficients.

A single example of mixed embedding of a trimethylenemethane diradical fragment with a pentadienyl is presented by 7 in Figure 1. No examples of similar mixed embeddings in fused polyhexagonal systems were found. Figure 2 presents examples of pentadienyl embedding in an assortment of large molecules. For those molecules that were not radicals, the Kekule' numbers (K) were invariably divisible by three. Four of the five last structures in Figure 2 had two distinctly different (and mutually exclusive) embeddings of pentadienyl and are therefore doubly degenerate in these eigenvalue sets. Also, placement of polyene substituents on any primary or secondary node position in the examples given throughout this paper will not alter the embedding pattern shown.

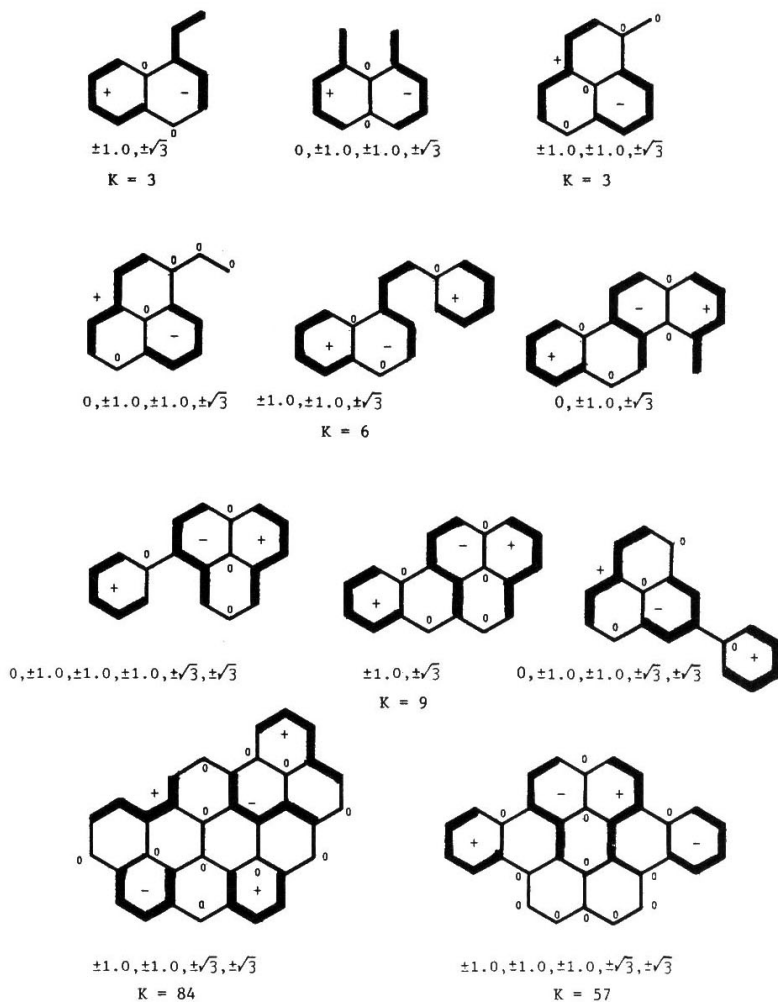
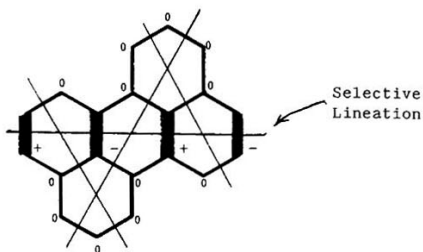


Figure 2 . Example pentadienyl embeddings.

Ethene Embedding and Selective Lineations

Whenever a benzenoid structure can have a succession of edges bisected with a straight line drawn from one side of the molecule to the other with the terminal rings being symmetrically convex relative to this line, then those rings intersected by the line can be embedded by a perpendicular succession of ethene substructures and the benzenoid structure as a whole will have at least one eigenvalue pair plus and minus one. This straight line is designed a selective lineation.<sup>2</sup> For each distinct selective lineation present in an alternant hydrocarbon there will be a corresponding eigenvalue pair of  $\epsilon = \pm 1.0\beta$ . Thus coronene and phenalenyl both have three selective lineations and are triply degenerate in  $\epsilon = \pm 1.0\beta$ , perylene has four selective lineations and is quadruply degenerate in  $\epsilon = \pm 1.0\beta$ , and biphenyl has two selective lineations and is doubly degenerate. This is illustrated below with perylene where only one set of perpendicular ethene substructures are explicitly shown. Since embedding is a sufficient but not necessary requirement for the presence of a set of eigenvalues, note that selective lineation only prescribes a minimum degeneracy.<sup>2</sup>

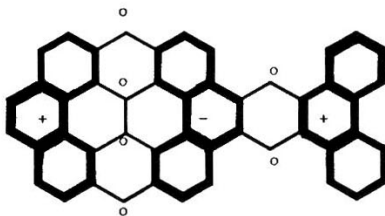


$$\epsilon = \pm 1.0, \pm 1.0, \pm 1.0, \pm 1.0 \beta$$

### Other Examples of Embedding

A general procedure for determining eigenvalues by inspection is as follows. First, determine if the molecule has a mirror-plane fragment. If it does see if the eigenvalues of the mirror-fragment can be found in standard reference sources.<sup>3-5</sup> Second, determine if the molecule has a selective lineation or is a radical(polyradical)structure. Third, successively determine if the polyene structure(and/or mirror fragment)can be embedded by ethene, allyl, 1,3-butadiene, pentadienyl, benzene, or naphthalene. To expedite this third step, note that benzene and allyl embedding requires that the number of Kekule<sup>e</sup> structures(K)associated with the benzenoid under investigation be divisible by two and pentadienyl and naphthalene embedding requires that K be divisible by three. In the fourth and final step, investigate the possibility of embedding a large molecule with a more complicated substructure. Examples of embedding on large benzenoids are presented in Figure 3.

Examples of naphthalene embedding are presented in Figure 3. Both ovalene and tetrabenzo[*a,c,h,j*]anthracene can be embedded by phenanthrene, and both these molecules have phenanthrene as a mirror plane fragment. The following benzenoid hydrocarbon has no mirror plane benzenoid fragments but can be embedded by phenanthrene as shown and, therefore, has the eigenvalues of phenanthrene in its spectrum.



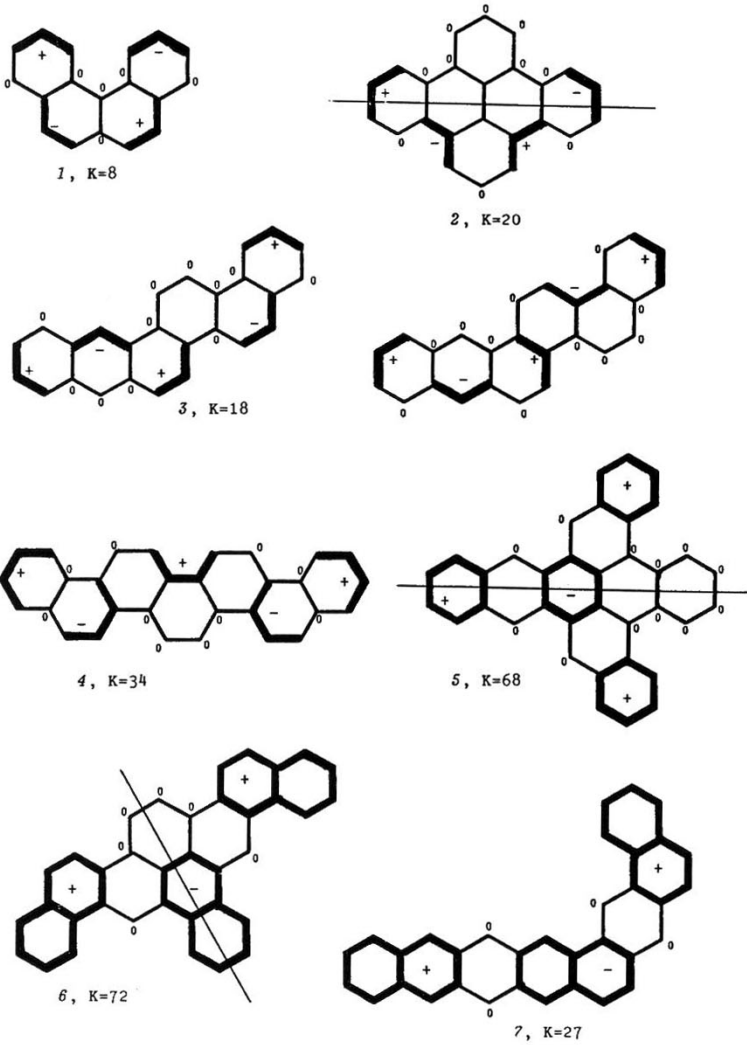


Figure 3 . Illustrative embeddings of allyl, butadiene, benzene, and naphthalene fragments on benzenoid hydrocarbons.



#### Successive Incremental Embedding on Polymer Strips

Figure 4 gives two infinitely long polymer strips. Disregarding end effects the upper nonclassical polymer strip can be embedded by pentadienyl and its increasing longer homologs shown. For this infinite number of embeddings to be valid, it must be concluded that this polymer strip has a conduction/valence band electronic structure.<sup>2</sup> Determination of the eigenvalues for the first few pentadienyl homologs allows one to qualitatively see that for this polymer there is an energy gap between 0 and  $1.0\beta$  and that continuous band exists from  $1.0\beta$  to  $>2.1\beta$ . Thus this polymer may be ferromagnetic due to the electron spins but it can not be conductive. Similarly, the classical acene polymer strip can be progressively embedded by increasingly longer acenes, and determination of all the different embedding eigenvalues up to pentacene allows one to qualitatively ascertain that no energy gap exists between the valence and conduction bands of this polymer strip. Therefore the acene polymer strip should be electrically conductive but not ferromagnetic.

#### Embedding on Nonalternant Hydrocarbons

Although embedding is strictly applicable to alternant hydrocarbons, a daughter nonalternant hydrocarbon created by adding a polyene bridging fragment to the node positions of a parent alternant hydrocarbon would still possess the same embedding pattern. Thus, fluoranthene (Figure 5) is a nonalternant hydrocarbon having eigenvalues of  $\epsilon = \pm 1.0\beta$  because ethene can be embedded on the alternant naphthalene fragment where the 1,8-node positions possess a phenylene bridge forming the pentagonal ring. Other examples are also presented in Figure 5.

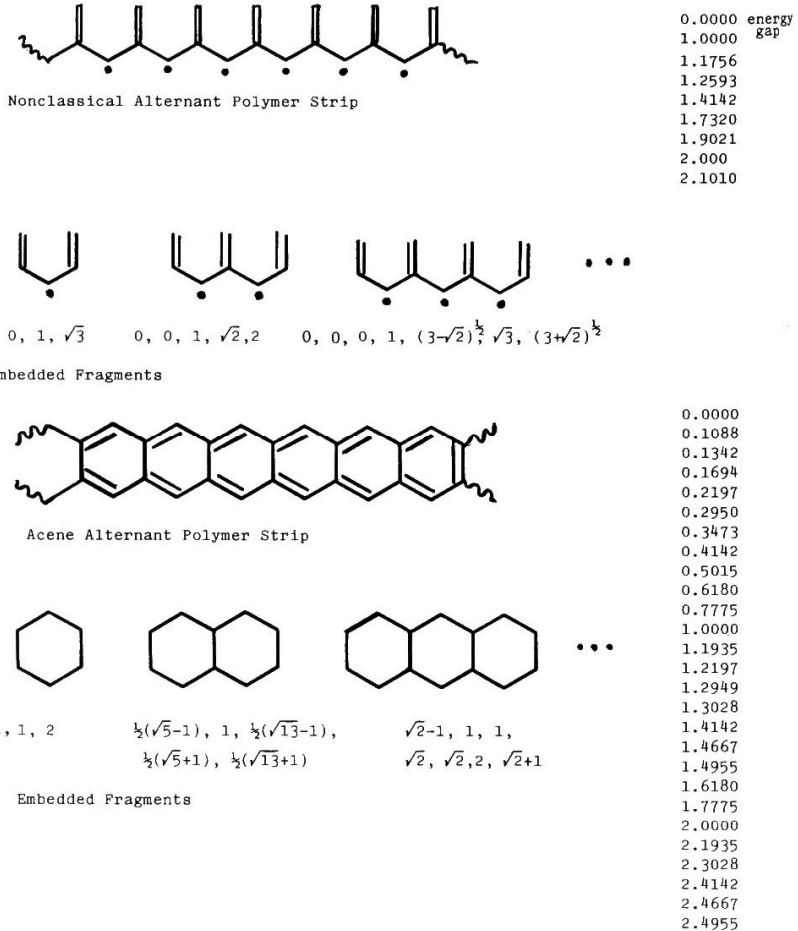


Figure 4. Repetitive embedding in infinitely long polymer strips.

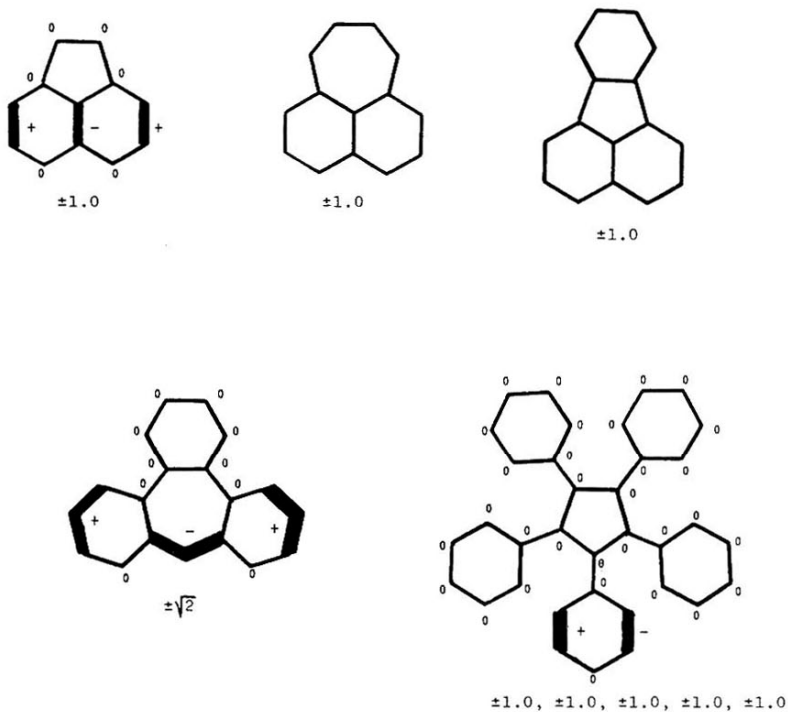


Figure 5. Examples of embeddable alternant hydrocarbon fragments with nonalternant hydrocarbon attachments on node positions of the former.

### Summary

Every molecule can be embedded by itself. Molecules with a mirror plane bisecting only vertices can be embedded by the mirror fragment where the bisected vertices become nodes. Alternant hydrocarbon molecules can be frequently embedded by smaller fragments. Nonalternant hydrocarbon molecules can sometimes be embedded in the alternant hydrocarbon fragment if it is linked through node positions to the nonalternant portion. Placement of heteroatoms or polyene substituents at node positions does not change the embedding of a molecular graph. The process of embedding is equally applicable to both the HMO and the extended HMO methods.

### References

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