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Degenerate Eigenvalues of the Hückel Matrix

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The behaviour of degenerate eigenvalues in Hückel systems is investigated under insertion of an additional bond or an additional centre. In the first case the degeneracy of any given eigenvalue is reduced by not more than two, in the second case by not more than one.

Key words: Hückel matrix, degenerate eigenvalues of ~

1. Introduction

The eigenvalues of a Hückel problem very often show a degeneracy which cannot be explained by geometrical symmetry alone. In an earlier paper [1] the relation between the full symmetry group of the Hückel problem and the generally used geometrical group has been discussed, and some conditions for the removal of the "excessive" degeneracy have been given. The connection between the Hückel problem and graph theory has been discussed by Günthard and Primas [2] and was reviewed by Gutman and Trinajstic [3] as well as Rouvray [4].

An astonishing property of many quite complicated Hückel systems is that their eigenvalue spectra contain sets of eigenvalues which are typical for small frequently encountered fragments. This suggests that during the process of constructing a complicated system some of the fragment eigenvalues will survive. In this paper we investigate the topological aspects of this behaviour and study the effects of the insertion of a bond between two fragments and of the insertion of a centre which is bonded to several fragments.

2. Graphs and Matrices

The topological aspects of a Hückel system can best be discussed in terms of the vertex adjacency matrix A of the corresponding Hückel graph. All matrix elements

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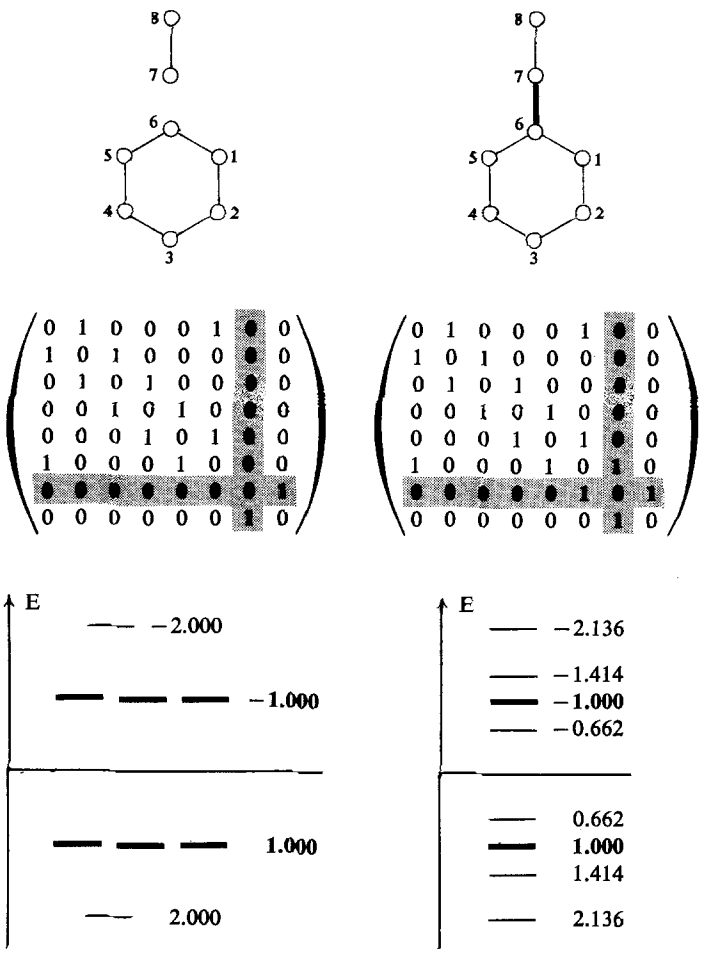

Fig. 1. The edge adjacency matrices and their eigenvalue spectra. Bonding benzene and ethylene between the positions 6 and 7 changes the adjacency matrix in a single row and column. In the bonded system one of the 3-fold degenerate eigenvalues $+1$ and -1 survives

A_{rs} between the bonded centres r and s are assigned a value of 1 and zero otherwise. In Figs. 1 and 2 we give two examples which show the changes that occur in the vertex adjacency matrix and the eigenvalue spectrum if a bond or a new bonded centre is introduced. In both cases only a single row and a single column in the vertex adjacency matrix is affected by the change and either 1 or 2 of the 3 initially degenerate eigenvalues $+1$ and -1 will survive. A very general theorem due to Ledermann [5] which connects properties of eigenvalues with a change in the corresponding matrix can be applied to the present situation: if in a Hermitian matrix the elements of r rows and their corresponding columns are modified in any way whatsoever, provided that the matrix remains Hermitian, then the number of latent roots which lie in any given interval cannot increase or decrease

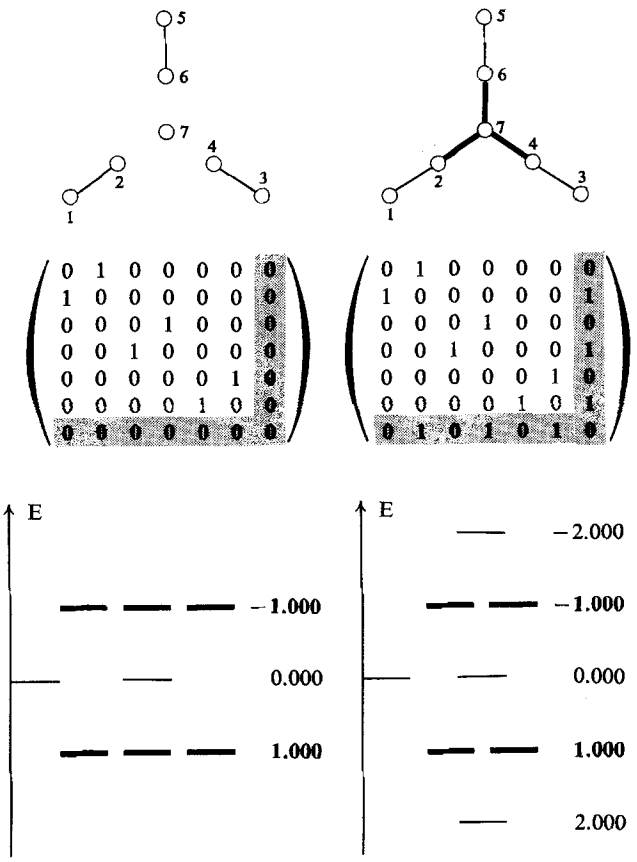

Fig. 2. The edge adjacency matrices and their eigenvalue spectra. Bonding 3 ethylenes to a centre changes the adjacency matrix in a single row and column. In the bonded system two of the 3-fold degenerate eigenvalues of $+1$ and -1 as well as the zero eigenvalue survive

by more than $2r$. If an infinitesimal interval about the degenerate eigenvalues is considered one obtains immediately: *If a bond is inserted in a Hückel graph the degeneracy on any given eigenvalue is reduced by not more than two.*

The case of insertion of a bonded centre requires a further comment. Again the degeneracy of the eigenvalues would seem to be decreased by two. The isolated vertex, however, could have been initially valued to any of the degenerate eigenvalues increasing in each case the initial degeneracy by one. If the eigenvalue belonging to the isolated vertex is not counted we have the following behaviour: *If a new vertex is bonded to a Hückel graph, the degeneracy of any given eigenvalue is reduced by not more than one.*

Two examples will be considered to illustrate these theorems. In Fig. 3 the effect of adding a twelfth centre to an 11-perimeter system is considered. Even though the twofold degeneracy of the 11-perimeter is lifted, each of the 12-centre systems will

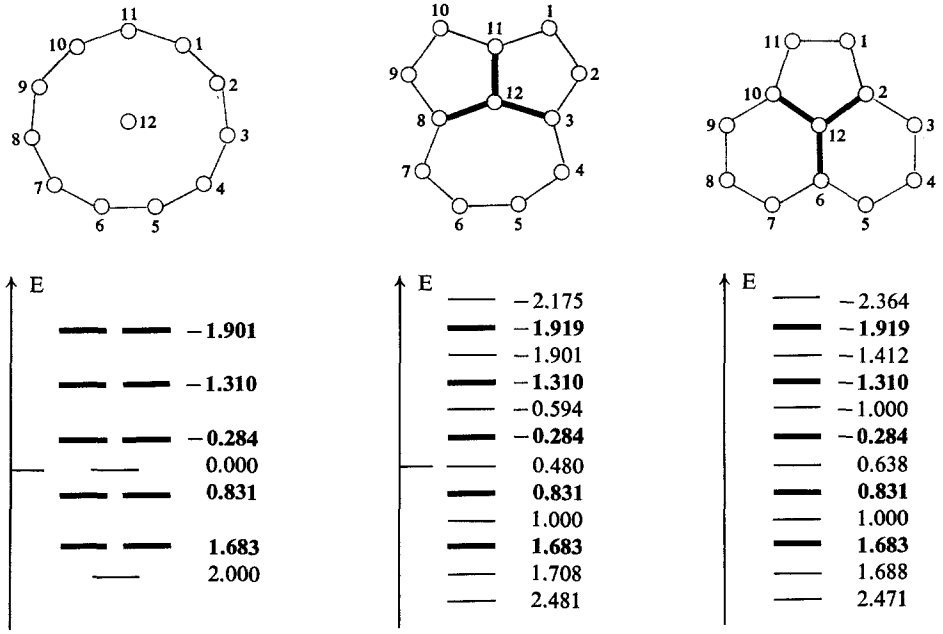

Fig. 3. The eigenvalue spectra of 11-perimeter systems. In the bonded systems five of the initially doubly degenerate eigenvalues survive

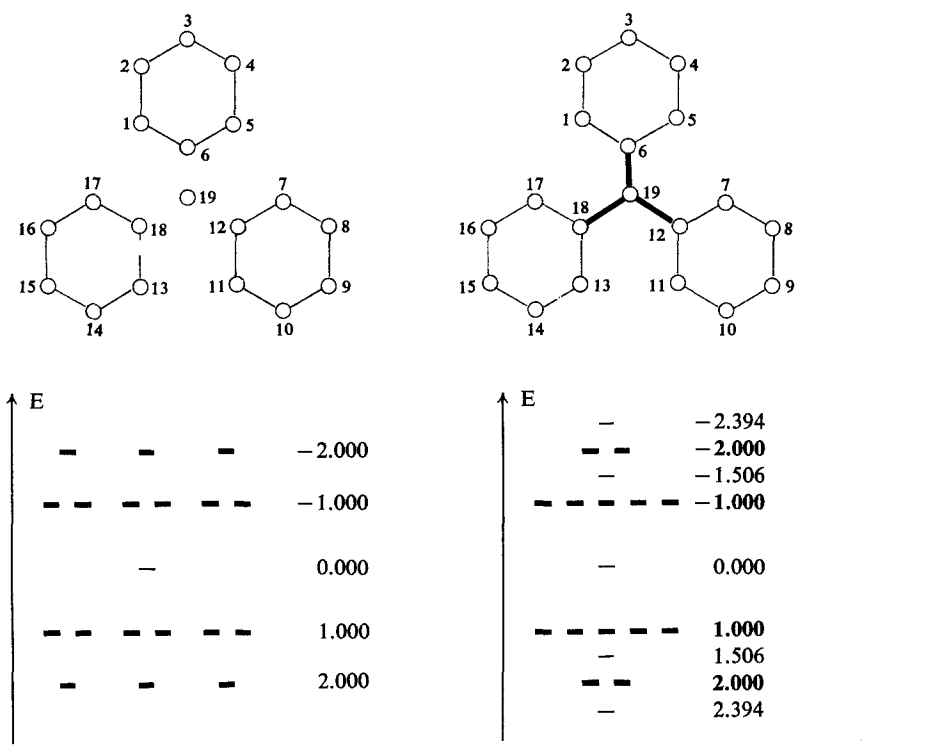

Fig. 4. The eigenvalue spectra of the triphenylmethyl radical. 14 of the 19 eigenvalues can be derived from the present theorems without any calculations

have 5 eigenvalues in common with the 11-perimeter system. In Fig. 4 the triphenylmethyl radical is shown. The theorems given allow us to immediately identify 14 of the 19 eigenvalues without any calculations. Considering in addition the five regions $-\infty \to -2$, $-2 \to -1$, $-1 \to +1$, $+1 \to +2$, $+2 \to \infty$, we can also conclude that in each region the change of the number of eigenvalues cannot be more than 1. Each of the remaining 5 eigenvalues must thus fall in one of the mentioned regions.

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