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
$A_{rs}$ 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