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Symmetry Properties of the Hückel Matrix

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The existence of excessively degenerate eigenvalues occuring often in the Hückel approach is discussed from the point of the topological matrix. First the full symmetry group of the Hückel problem of three typical examples is discussed and its relation to the commonly used geometrical symmetry group is established. Excessive degeneracy of eigenvalues of Hückel spectra may now be interpreted in terms of the irreducible representation of the full Hückel graph group. The results then are generalized to give more extended though no fully general conditions for excessive degeneracies in Hückel eigenvalues spectra. Furthermore conditions for removal of excessive degeneracy are discussed.

Die Eigenwerte des Hückelproblems von einfachen Systemen zeigen oft höhere Entartungen als auf Grund der geometrischen Symmetrie zu erwarten wäre. Dieses Phänomen wird vom Standpunkt der topologischen Matrix diskutiert. Zuerst wird anhand von drei Beispielen der Zusammenhang der vollen Symmetriegruppe des Hückelproblems mit der üblicherweise verwendeten geometrischen Deckgruppe hergeleitet und die damit verbundene excessive Entartung von Eigenwerten erklärt. Für das Auftreten excessiver Entartung werden sodann Bedingungen angegeben und es wird gezeigt wie diese durch Einführung von gewissen Resonanzintegralen aufgehoben werden kann. Schließlich wird kurz auf den Zusammenhang mit den Permutationsgruppen hingewiesen.

Les valeurs propres du problème de Hückel pour des systèmes simples possède souvent une dégénérescence plus élevée que celle de la géometrie. Ce phénomène sera discuté par la méthode des matrices topologique.

Au moyen d'examples pour lesquels nous comparons le groupe géométrique et le groupe global du problème de Hückel, nous expliquons la dégénérescence excessive des valeurs propres. Nous déterminons les conditions d'existence de cette dégénérescence et les moyens qui permettent de la lever. Nous indiquons ensuite brièvement le rapport avec les groupes de permutations.

1. Introduction

Eigenvalue spectra obtained by the Hückel method often exhibit higher symmetry than the geometrical symmetry group of the π-center configuration would admit. In its simplest form the Hückel approach corresponds uniquely to eigenvalue problems associated with graphs and therefore is essentially of a topological or combinatorial nature. The relation to topology has been investigated by several authors [1, 2, 3], but apparently no study has been published so far concerning the relation between the topological aspects of the Hückel problem and its frequently occuring excessive symmetry. In this paper we give a number of conditions for the occurence of excessive symmetry and the nature of this symmetry. A number of typical cases will be analyzed. However, it is felt that the general problem of the Hückel symmetry is of a rather complex nature and no attempt is made to treat it exhaustively.

2. Definitions

The set of π-centers $\Pi = \{\pi_1, \pi_2, \ldots, \pi_N\}$ and the set of edges between nearest neighbours $P = \{\chi_1, \chi_2, \ldots, \chi_M\}$ define the graph (Π, P) [4] of the system.

If the Coulomb integral H_{ii} of all π-centers and all resonance integrals H_{ik} between nearest neighbours are taken equal,

$$\begin{aligned} H_{ii} &= \alpha = -|\alpha| ; \\ H_{ik} &= \beta = -|\beta| \quad \text{if } i \text{ and } k \text{ bonded}, \\ H_{ik} &= 0 \qquad\qquad \text{if } i \text{ and } k \text{ not bonded}, \end{aligned}$$

then the Hückel eigenvalue problem may be written:

$$|\boldsymbol{H} - \lambda \boldsymbol{I}| = |\alpha \boldsymbol{I} + \beta \boldsymbol{Z} - \lambda \boldsymbol{I}| = \left| \boldsymbol{Z} - \frac{\lambda - \alpha}{\beta} \cdot \boldsymbol{I} \right| = |\boldsymbol{Z} - x\boldsymbol{I}| = 0 , \qquad \lambda = \alpha + x\beta ,$$

where $\boldsymbol{Z}$ represents the *incidence matrix* (topological matrix) of the system. In the sense of Bellman [5] $\boldsymbol{Z}$ is symmetric and nonnegative.

The set of all symmetry operators $\{g_1, g_2, \ldots, g_n\}$ which commute with the Hamilton operator H_{op} of the Hückel problem form the group $\mathscr{G} = \{g_1, g_2, \ldots, g_n\}$ of the graph. These symmetry operators map incident elements of the graph onto incident elements. Each group operator $g \in \mathscr{G}$ maps the element $\pi_i \in \Pi$ and $\chi_j \in P$ into

$$g\pi_i = \pi_{i'} \in \Pi \quad \text{and} \quad g\chi_j = \chi_{j'} \in P .$$

The sets of π-centers and edges Π and P respectively can be used as a basis to construct a representation of the group through permutation matrices $\boldsymbol{\Gamma}_\Pi(g)$ and $\boldsymbol{\Gamma}_P(g)$. They are defined by the relations

$$\begin{aligned} g\{\pi_1 \ldots \pi_N\} &= \{\pi_{1'} \ldots \pi_{N'}\} = \{\pi_1 \ldots \pi_N\} \boldsymbol{\Gamma}_\Pi(g) , \\ g\{\chi_1 \ldots \chi_M\} &= \{\chi_{1'} \ldots \chi_{M'}\} = \{\chi_1 \ldots \chi_M\} \boldsymbol{\Gamma}_P(g) . \end{aligned}$$

The following shorthand notation for the representation matrix will be often used in this paper:

$$g\{\pi_1 \ldots \pi_N\} = \{1' \ldots N'\} = \{\pi_1 \ldots \pi_N\} \boldsymbol{\Gamma}_\Pi \ (g) .$$

The representations $\boldsymbol{\Gamma}_\Pi$ and $\boldsymbol{\Gamma}_P$ are homomorphic. It follows from the definition that for all $g \in \mathscr{G}$ the relation $\Gamma_\Pi^\dagger(g)\, \boldsymbol{Z} \Gamma_\Pi(g) = \boldsymbol{Z}$ holds.

3. The Group of the Graph

3.1. Illustrative Examples

The following discussion considers the relation between the graph group $\mathscr{G}(g)$ and the group $\mathscr{H}(h)$ of geometrical symmetry operations which map the graph onto itself as a whole.

In order to make the definition of $\mathscr{G}(g)$ more specific we first discuss three examples of increasing complexity.

3.1.1. Isopropenyl-Phenylradical. Fig. 1 shows the Hückel graph and the incidence matrix of this π-system. The graph has the geometrical symmetry $\mathscr{C}_2$ and the following matrix representations of the symmetry operators e and c_2 may be given.

$$\boldsymbol{\Gamma}_{\Pi}(e)=\begin{pmatrix}1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1\end{pmatrix}=\{1\ 2\ 3\ 4\ 5\ 6\ 7\ 8\ 9\},\qquad \boldsymbol{\Gamma}_{\Pi}(c_2)=\begin{pmatrix}\cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ 1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1\end{pmatrix}=\{2\ 1\ 4\ 3\ 6\ 5\ 7\ 8\ 9\}.$$

These matrices leave $\boldsymbol{Z}$ obviously invariant.

This is however not the full group of the graph, since mappings k and l which are represented by

$$\boldsymbol{\Gamma}_{\Pi}(k)=\begin{pmatrix}1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1\end{pmatrix}=\{1\ 2\ 4\ 3\ 6\ 5\ 7\ 8\ 9\},\qquad \boldsymbol{\Gamma}_{\Pi}(l)=\begin{pmatrix}\cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ 1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1&\cdot\\ \cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&\cdot&1\end{pmatrix}=\{2\ 1\ 3\ 4\ 5\ 6\ 7\ 8\ 9\}$$

also commute with $\boldsymbol{Z}$.

The four representation matrices form a matrix group which is isomorphic to the group $\mathscr{C}_{2v}$. The two additional group elements k and l map the subsets $\Pi_{\rm I} = \{\pi_3\,\pi_4\,\pi_5\,\pi_6\,\pi_8\,\pi_9\}$ and $\Pi_{\rm II} = \{\pi_1\,\pi_2\,\pi_7\}$ onto themselves. They may be visualized as "internal rotation" around the 7–8 bond. Under $\mathscr{C}_2$ the reducible representation $\boldsymbol{\Gamma}_{\Pi}$ splits into $6A+3B$; under $\mathscr{C}_{2v}$ into $6A_1+B_1+2B_2$.

Since $\mathscr{C}_2$ and $\mathscr{C}_{2v}$ have only one dimensional representations, all Hückel eigenvalues are nondegenerate. The graph is of the alternant type and the Coulson-Rushbrooke pairing theorem holds. This is shown by Fig. 2a, which clearly represents these properties of the Hückel spectrum of isopropenylphenyl radicals.

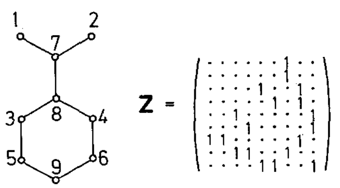


Fig. 1. Graph and incidence matrix of the isopropenyl-phenylradical

3.1.2. Consider the Graph and Incidence Matrix of Diphenyl (Fig. 3). The crystallographic point group $\mathscr{H}(h)$ is the matrix group consisting of the matrices

$$\Gamma_\Pi(e) = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{pmatrix} = \{1\,2\,3\,4\,5\,6\,7\,8\,9\,10\,11\,12\},$$

$$\Gamma_\Pi(c_2(z)) = \begin{pmatrix} \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{pmatrix} = \{3\,4\,1\,2\,7\,8\,5\,6\,9\,10\,11\,12\},$$

$$\Gamma_\Pi(c_2(y)) = \begin{pmatrix} \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \end{pmatrix} = \{4\,3\,2\,1\,8\,7\,6\,5\,10\,9\,12\,11\},$$

$$\Gamma_\Pi(c_2(x)) = \begin{pmatrix} \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \end{pmatrix} = \{2\,1\,4\,3\,6\,5\,8\,7\,10\,9\,12\,11\}.$$

The matrix group $\mathscr{H}(h)$ is therefore isomorphous to $\mathscr{D}_2$.

However, the mapping k with the representation matrix $\Gamma_\Pi(k)$ is a further symmetry element of the graph not contained in $\mathscr{H}(h)$:

$$\Gamma_\Pi(k) = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{pmatrix} = \{1\;4\;3\;2\;5\;8\;7\;6\;9\;10\;11\;12\}.$$

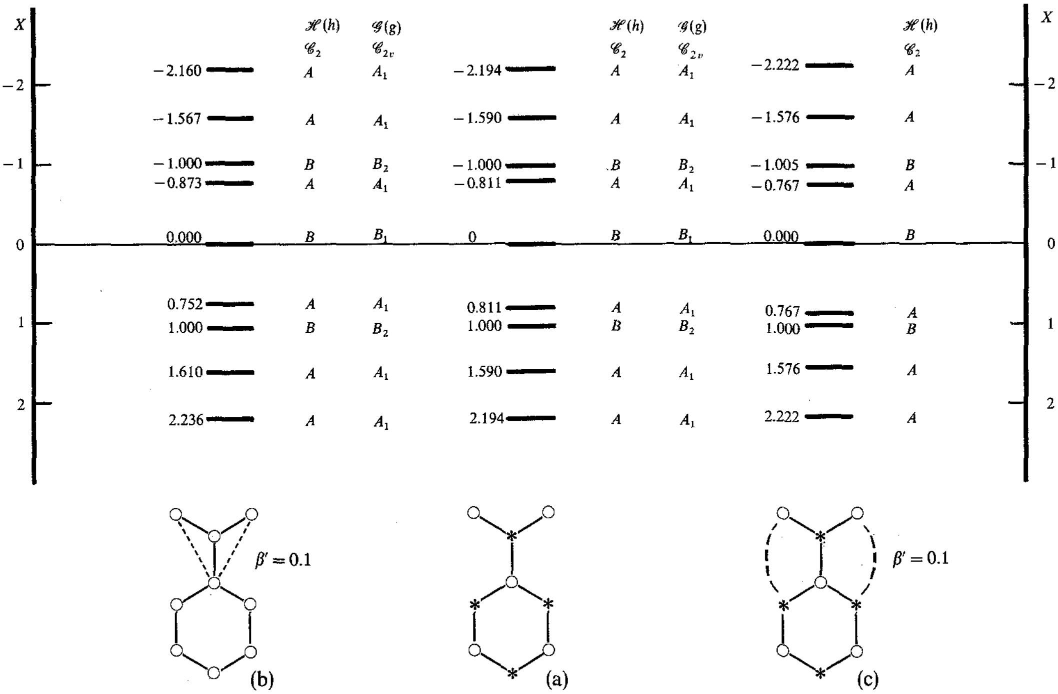


Fig. 2. Hückel-Eigenvalues of the isopropenyl-phenylradical

This new element generates together with the 4 elements of the group $\mathscr{H}(h)$ the new group $\mathscr{G}(g)$ which contains 8 elements and is isomorphic to the group $\mathscr{D}_{2d}$. The elements are collected in Table 1.

Under $\mathscr{H}(h) = \mathscr{D}_2$ and $\mathscr{G}(g) = \mathscr{D}_{2d}$ the reducible representation Γ_Π decomposes into $4A_1 + 4B_1 + 2B_2 + 2B_3$ and $4A_1 + 4B_2 + 2E$, respectively. In the latter case the spectrum has degenerate eigenvalues belonging to the representation E of degree 2 of $\mathscr{D}_{2d}$, while no such degeneracy could occur, if the graph group were $\mathscr{D}_2$. This behavior is demonstrated by the Hückel spectrum of diphenyl presented by Fig. 4a.

The topology of the group $\mathscr{G}(g) = \mathscr{D}_{2d}$ is illustrated by the diagram Fig. 5. It symbolises the group operations by lines interconnecting pairs of elements $\pi \in \Pi$ which are mapped onto each other by at least one group operation. It is obvious,

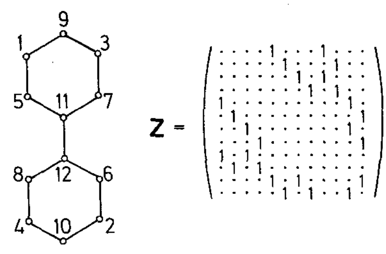


Fig. 3. Graph and incidence matrix of diphenyl

Table 1. *Representation of graph group of Diphenyl by permutation and geometrical operations*

$\mathscr{H}(h)$	$\mathscr{D}_2$	class	$\mathscr{G}(g)$	$\mathscr{D}_{2d}$	class	$\{1' \ldots 12'\}$
h_1	e	I	g_1	e	I	{1 2 3 4 5 6 7 8 9 10 11 12}
h_2	$c_2(z)$	II	g_2	c_2	II	{3 4 1 2 7 8 5 6 9 10 11 12}
h_3	$c_2(y)$	III	g_3	s_4	III	{4 3 2 1 8 7 6 5 10 9 12 11}
h_4	$c_2(x)$	IV	g_4	s_4	III	{2 1 4 3 6 5 8 7 10 9 12 11}
$\{k\}$			g_5	σ_d	IV	{1 4 3 2 5 8 7 6 9 10 11 12}
			g_6	σ_d	IV	{3 2 1 4 7 6 5 8 9 10 11 12}
			g_7	$c_{2'}$	V	{4 1 2 3 8 5 6 7 10 9 12 11}
			g_8	$c_{2'}$	V	{2 3 4 1 6 7 8 5 10 9 12 11}

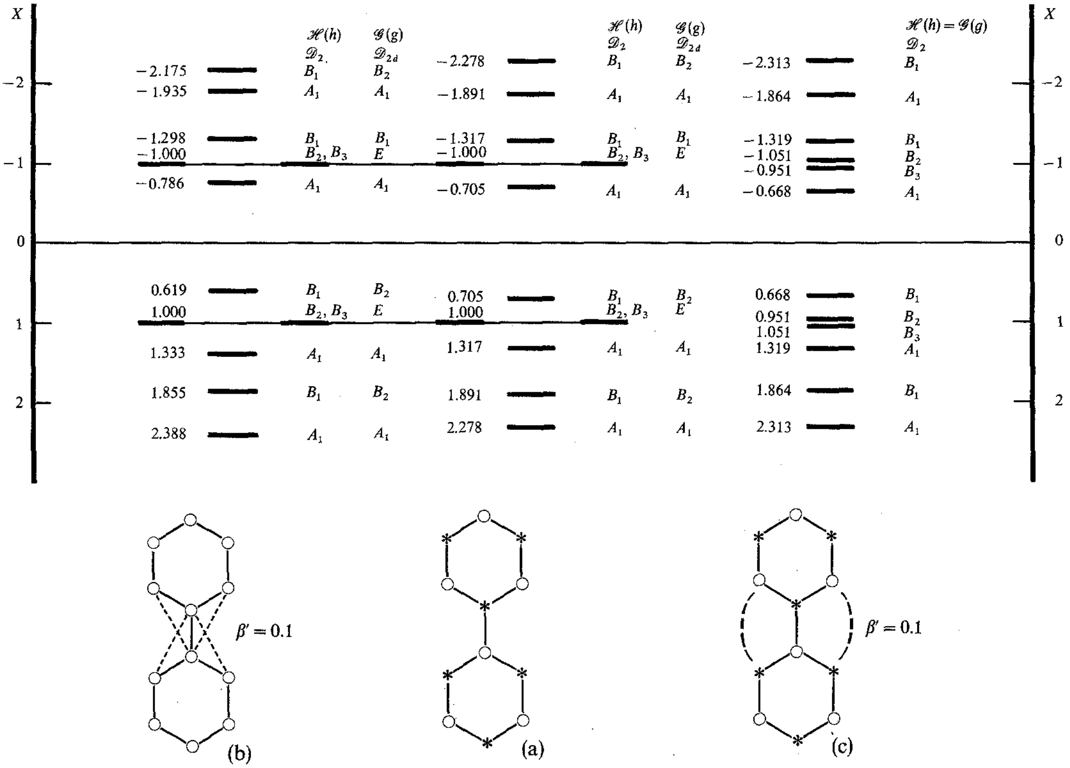


Fig. 4. Hückel-Eigenvalues of diphenyl

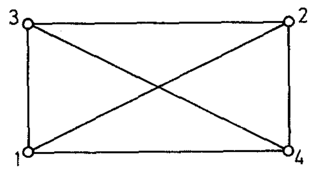


Fig. 5. Diagram of the Hückel graph group of diphenyl

Table 2. *Representation of graph group of triphenylmethyl-radical by permutations and geometrical operations*[a]

$\mathscr{H}(h)$	$\mathscr{D}_3$	class	$\mathscr{G}(g)$	$\mathscr{O}_h$	class	$\{1' \ldots 6'\}$
h_1	e	I	g_1	$e(1)$	I	{1 2 3 4 5 6}
h_2	$c_3(2)$	II	g_2	$c_3(8)$	II	{2 3 1 5 6 4}
h_3		II	g_3		II	{3 1 2 6 4 5}
h_4	$c_2'(3)$	III	g_4	$c_2(6)$	III	{4 6 5 1 3 2}
h_5		III	g_5		III	{6 5 4 3 2 1}
h_6		III	g_6		III	{5 4 6 2 1 3}
$\{k\}$			g_7	$c_2 i(3)$	IV	{4 2 3 1 5 6}
			g_8	$c_3 i(8)$	V	{5 3 1 2 6 4}
			g_{12}	$c_2 i(6)$	VI	{1 6 5 4 3 2}
			g_{13}	$c_4 i(6)$	VII	{3 5 4 6 2 1}
			g_{21}	$c_2(3)$	VIII	{4 5 3 1 2 6}
			g_{35}	$c_4(6)$	IX	{1 6 2 4 3 5}
			g_{46}	$i(1)$		{4 5 6 1 2 3}

[a] At least one element from each class is given.

that the group diagram is identical with the universal graph of 4 points. This is equivalent to the digonal scalenohedron being a typical polyhedron of the group $\mathscr{D}_{2d}$.

3.1.3. As a Third Example we Consider Graph and Incidence Matrix of the Triphenylmethyl-Radical (Fig. 6). The subset $\{\pi_1 \, \pi_2 \, \pi_3 \, \pi_4 \, \pi_5 \, \pi_6\}$ may be used as a basis for the construction of a faithful representation. By actual construction using a computer program for permutation groups the group collected in Table 2 is obtained, which shows that $\mathscr{G}(g)$ is isomorphic to $\mathscr{O}_h$. It also gives the correspondence of the permutations of $\mathscr{G}$ with the group operations of $\mathscr{O}_h$.

The HMO spectrum of triphenylmethyl radical is shown in Fig. 7. The full representation Γ_Π of the graph group $\mathscr{G}(g)$ is 19 dimensional and decomposes under $\mathscr{O}_h$ into $\Gamma_\Pi = 5A_{1g} + 4E_g + 2F_{1u}$, whereas under the geometrical group $\mathscr{D}_3$ it decomposes according to $\Gamma_\Pi = 5A_1 + 2A_2 + 6E$. As may be seen from Fig. 7a the HMO spectrum contains two fivefold degenerate eigenvalues. By inspection of the transformation properties of corresponding eigenvectors, the fivefold degeneracy may be shown to originate from an accidental degeneracy of a E_g and a F_{1u} eigenvalue.

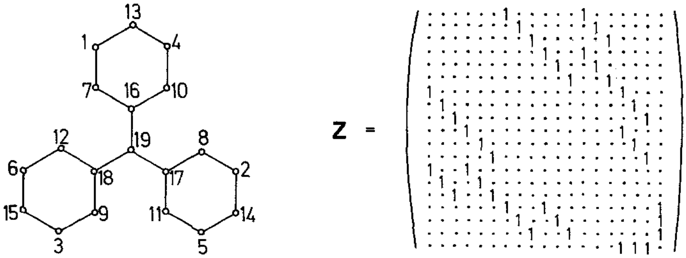


Fig. 6. Graph and incidence matrix of the triphenylmethyl-radical

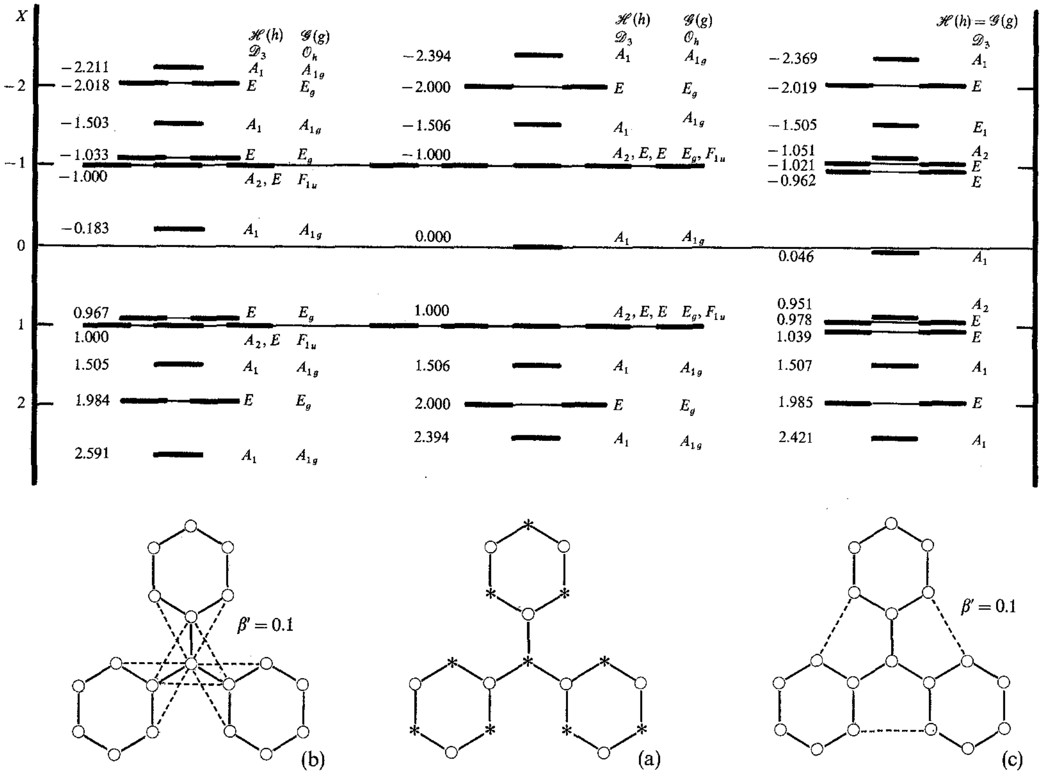


Fig. 7. Hückel-Eigenvalues of the triphenylmethyl-radical

Again consideration of the group diagram symbolizing the topology of $\mathscr{G}(g)=\mathscr{O}_h$ is instructive, c.f. Fig. 8. The group operations $g \in \mathscr{G}(g)$ mapping the six elements of the equivalent set $\{\pi_1\, \pi_2\, \pi_3\, \pi_4\, \pi_5\, \pi_6\}$ onto each other are now represented by straight lines connecting each pair which at least by one group operation is interrelated. Obviously the group diagram is the universal graph of the set $\{\pi_1 \ldots \pi_6\}$, i.e. the graph of the octahedron including all diagonals. Again the octahedron is a typical polyhedron of the group $\mathscr{O}_h$.

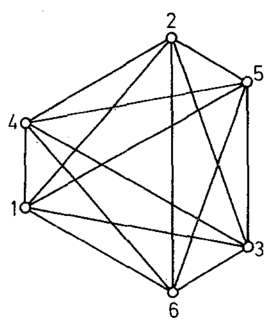


Fig. 8. Diagram of Hückel graph group of triphenylmethyl-radical

3.2. *More General Formulation of the Hückel Graph Group Problem*

The examples discussed so far have the common feature, that the set Π of the graph (Π, P) may be divided into subsets $\Pi_1\ \Pi_2 \ldots \Pi_s$, each of which may consist of equivalent subsets Π_{sk}, with the following properties:

$$\Pi = \Pi_1 \cup \Pi_2 \cup \ldots \Pi_s\,; \qquad \Pi_s \cap \Pi_{s'} = \delta_{ss'}\,\Pi_s\,; \qquad s, s' = 1, 2, \ldots,$$
$$\Pi_s = \Pi_{s1} \cup \Pi_{s2} \cup \ldots \Pi_{sk}\,; \qquad \Pi_{sk} \cap \Pi_{sk'} = \delta_{kk'}\,\Pi_{sk}\,; \qquad k, k' = 1, 2, \ldots.$$

Similarly the set P contains subsets P_s of equivalent subsets P_{sk}, which define incidence within the sets Π_{sk}. In addition P contains subsets $P_{ss'}$, which define incidence between sets Π_s and $\Pi_{s'}$ or sets $P_{sk,sk'}$, which define incidence between $\Pi_{sk}, \Pi_{sk'}$, $k \neq k'$, or both.

The subdivision of the sets Π, P may be illustrated by Example 3.1.3. Here referring to Fig. 6.

$$\begin{aligned}
\Pi_1 &= \pi_{19}\,, \\
\Pi_2 &= \Pi_{21} + \Pi_{22} + \Pi_{23}\,, \\
\Pi_{21} &= \{\pi_1 \pi_4 \pi_7 \pi_{10} \pi_{13} \pi_{16}\}\,, \\
\Pi_{22} &= \{\pi_2 \pi_5 \pi_8 \pi_{11} \pi_{14} \pi_{17}\}\,, \\
\Pi_{23} &= \{\pi_3 \pi_6 \pi_9 \pi_{12} \pi_{15} \pi_{18}\}\,, \\
P_{1,2} &= \{\chi_{16,19}\ \chi_{17,19}\ \chi_{18,19}\}\,, \\
P_2 &= P_{21} + P_{22} + P_{23}\,, \\
P_{21} &= \{\chi_{1,7}\ \chi_{7,16}\ \chi_{16,10}\ \chi_{10,4}\ \chi_{4,13}\ \chi_{13,1}\}\,, \\
P_{22} &= \{\chi_{2,8}\ \chi_{8,17}\ \chi_{17,11}\ \chi_{11,5}\ \chi_{5,14}\ \chi_{14,2}\}\,, \\
P_{23} &= \{\chi_{3,9}\ \chi_{9,18}\ \chi_{18,12}\ \chi_{12,6}\ \chi_{6,15}\ \chi_{15,3}\}\,.
\end{aligned}$$

The geometrical group $\mathscr{H}(h)$ is now defined as the group of all incidence conserving mappings of (Π, P) onto itself, which *simultaneously* map all sets Π_s onto themselves. Since the sets $\Pi_{s1}\ \Pi_{s2} \ldots \Pi_{sk}$ under the operations $h \in \mathscr{H}(h)$ are mapped among themselves and never are mapped onto sets $\Pi_{s'k'}$, $s' \neq s$, the matrix group $\boldsymbol{\Gamma}_\Pi$ is a direct sum of homomorphous matrix groups. Any faithful component $\boldsymbol{\Gamma}_{\Pi_s}$ of $\boldsymbol{\Gamma}_\Pi$ associated with a particular set Π_s may be taken as the definition of the geometrical group $\mathscr{H}(h)$: for any $h \in \mathscr{H}(h)$ and $\pi_{sr} \in \Pi_s$

$$h\{\pi_{s1}\ \pi_{s2} \ldots\} = \{\pi'_{s1}\ \pi'_{s2} \ldots\} = \{\pi_{s1}\ \pi_{s2} \ldots\}\,\boldsymbol{\Gamma}_{\Pi_s}(h)\,.$$

Obviously any faithfull component $\boldsymbol{\Gamma}_{\Pi_s}$ may further be associated to a particular set of elements $\pi \in \Pi_s$ as may be seen from the three examples given above.

The occurence of excessive symmetry depends on the incidence between sets, i.e. on the nature of the sets $P_{s,s'}$ and $P_{sk,sk'}$. In the examples discussed above there is only one subset $P_{s,s'} \subset P$ which defines incidence between different subsets $\Pi_s, \Pi_{s'} \subset \Pi$. In the case of example 3.1.3 it is the subset $P_{1,2}$, which defines incidence between Π_1 and Π_2. If now further proper incidence conserving mappings of (Π, P) onto itself exist, which map exclusively elements $\pi \in \Pi_{sk}$ among themselves, they constitute a matrix group $\boldsymbol{\Gamma}_{\Pi_{sk}}$ *associated* with the set Π_{sk}[1]. $\mathscr{K}_s(k)$ is defined by the matrix group $\boldsymbol{\Gamma}_{\Pi_{sk}}$, which obviously is a direct sum of unit matrices representing the identical mappings of $\Pi_{s\bar{k}}$ onto $\Pi_{s\bar{k}}, \bar{k} \neq k$, and the incidence conserving mappings of Π_{sk} onto itself. Again any faithful component of $\bar{\boldsymbol{\Gamma}}_{\Pi_{sk}}$ may be used to

[1] It is easily seen that all equivalent sets $\Pi_{sk} \subset \Pi_s$ admit isomorphous matrix groups $\Gamma_{\Pi_{sk}}$.

define the abstract group $\mathscr{K}_s(k)$. Hence by definition for any $k \in \mathscr{K}_s(k)$

$$k\{\Pi_{s1}\,\Pi_{s2}\,\ldots\,\Pi_{s\bar{k}}\,\ldots\} = \{\Pi'_{s1}\Pi'_{s2}\,\ldots\,\Pi'_{s\bar{k}}\,\ldots\}$$

$$= \{\Pi_{s1}\,\Pi_{s2}\,\ldots\,\Pi_{s\bar{k}}\,\ldots\} \begin{Bmatrix} \mathrm{I} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \mathrm{I} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \bar{\Gamma}_{\Pi_{s\bar{k}}} & \cdot & \cdot & \cdot \end{Bmatrix}.$$

In most practical cases $\mathscr{K}_s(k)$ has order $o(\mathscr{K}_s)=2$.

If each of the sets Π_s, $\Pi_{s'}$ admits a group $\mathscr{K}_s$, $\mathscr{K}_{s'}$, then obviously for any $k \in \mathscr{K}_s$, $k \in \mathscr{K}_{s'}$, $s \neq s'$ we have

$$k \cdot k' = k' \cdot k\,.$$

This immediately follows from the structure of the matrices $\Gamma_{\Pi_{sk}}(k)$ and $\Gamma_{\Pi_{s'k}}(k')$.

In the following discussion we restrict ourselves to the case of a single $\mathscr{K}$, to which all Examples 3.1 belong. In order to construct the Hückel graph group $\mathscr{G}(g)$ we consider the complex $\mathscr{H}(h) \cdot \mathscr{K}(k)$. Since clearly the groups $\mathscr{H}(h)$, $\mathscr{K}(k)$ and $\mathscr{G}(g)$ are subgroups of the symmetric group of degree N (N equals the number of π-centers), the following three *cases may* arise [6].

(i) If for any $h \in \mathscr{H}$, $k \in \mathscr{K}$, $h \cdot k = k \cdot h$ then the graph group $\mathscr{G}(g)$ is given by

$$\mathscr{G} = \mathscr{H} \cdot \mathscr{K}$$

and its order $o(\mathscr{G}) = o(\mathscr{H}) \cdot o(\mathscr{K})$.

Hence in this case the complete system of irreducible representations of $\mathscr{G}(g)$ is obtained from a complete system of irreducible representations of $\mathscr{H}(h)$ and the factor group

$$\mathscr{G}/\mathscr{H} = \sum_{k \in \mathscr{K}} \mathscr{H} \cdot k$$

which obviously is isomorphous to $\mathscr{K}$. If $\mathscr{K}$ is abelian the dimensions of irreducible representations of $\mathscr{G}$ are the same as for $\mathscr{H}$ and therefore the degeneracies of eigenstates under both groups are the same, i.e. no excessive degeneracies appear, if the geometrical group $\mathscr{H}$ is taken as representative for the Hückel-problem. As a typical example for this situation we refer to Example 3.1.1 studied above, where $o(\mathscr{K}) = 2$ and $\mathscr{H}$ and $\mathscr{G}$ are isomorphous to $\mathscr{C}_2$ and $\mathscr{C}_{2v}$ respectively.

(ii) If $\mathscr{H} \cdot \mathscr{K} = \mathscr{K} \cdot \mathscr{H}$, but if not all $h \in \mathscr{H}$ and $k \in \mathscr{K}$ commute, then, since $\mathscr{H} \cup \mathscr{K} = e$,

$$\mathscr{G} = \mathscr{H} \cdot \mathscr{K} = \mathscr{K} \cdot \mathscr{H}$$

and $\mathscr{G}$ is a group of order $o(\mathscr{G}) = o(\mathscr{H}) \cdot o(\mathscr{K})$. The irreducible representations of $\mathscr{G}$ cannot generally be derived from those of $\mathscr{H}$. In case where $o(\mathscr{K}) = 2$, $\mathscr{G}$ has order $2 \cdot o(\mathscr{H})$ and $\mathscr{H}$ is a normal divisor of $\mathscr{G}$ of index 2. Hence

$$\mathscr{G} = \mathscr{H} \cdot e + \mathscr{H} \cdot k\,.$$

Even in this simple case not all the irreducible representations of $\mathscr{G}$ may be obtained from those of $\mathscr{H}$ and the factor group representations. If $\mathscr{H}$ is abelian, $\mathscr{G}$ is not abelian and has irreducible representations of dimension $\geqq 2$. As a consequence under these conditions Hückel spectra will exhibit higher degeneracy than expected from the geometrical group $\mathscr{H}$. For a typical situation, where case (ii) is realized, we refer to Example 3.1.2. Here $\mathscr{H}$ and $\mathscr{G}$, respectively, were found to be isomorphous to $\mathscr{D}_2$ (abelian) and $\mathscr{D}_{2d}$ (nonabelian) and the Hückel spectrum of diphenyl exhibits excessive degeneracy.

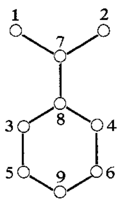
(iii) If $\mathscr{H} \cdot \mathscr{K} \neq \mathscr{K} \cdot \mathscr{H}$ then $\mathscr{H} \cdot \mathscr{K}$ is not a group and the graph group has to be constructed from the groups $\mathscr{H}$ and $\mathscr{K}$ by application of the elementary group laws. No general simple method seems to exist which would allow unique characterization of the structure of the graph group $\mathscr{G}$ without actual construction of it.

As an example representative for case (iii) we refer to the Hückel problem of triphenylmethyl radical, 3.1.3, where $\mathscr{H}$ and $\mathscr{K}$ were found to be isomorphous to $\mathscr{D}_3$ and $\mathscr{C}_2$, respectively, and $\mathscr{G}$ is isomorphous to $\mathscr{O}_h$. The construction of the graph group $\mathscr{G}$ in this case may actually be effectuated in a rather efficient way by using theorems on group decompositions modulo two subgroup [7]. We restrain to reproduce the proof here.

4. Remarks

4.1. More General Valuations of the Hückel Graph

Excessive symmetry in Hückel problems may persist, if the simple valuation $\alpha_{ii} = \alpha$, $\beta_{ik} = \beta$ is generalized to take into account more detailed models for Coulomb and resonance integrals, and if only nearest neighbor interactions are admitted. It is easily verified that the Hückel matrix of the graph Fig. 9 commutes with Γ_{Π} of



$\alpha_1 \ = \alpha_2$	$\alpha_3 \ = \alpha_4$
$\beta_{1,7} = \beta_{2,7}$	$\beta_{3,5} = \beta_{4,6}$
α_7	$\alpha_5 \ = \alpha_6$
$\beta_{7,8}$	$\beta_{5,9} = \beta_{6,9}$
α_8	α_9
$\beta_{3,8} = \beta_{4,8}$	

Fig. 9. Generalized evaluation of Hückelproblem of isopropenyl-phenylradical conserving four group symmetry $\mathscr{C}_{2v}$

Example 3.1.1, independently on the choice of the parameters α_1, $\beta_{1,7}$, α_7, $\beta_{7,8}$, α_8, $\beta_{3,8}$, α_3, $\beta_{3,5}$, α_5, $\beta_{5,9}$ and α_9. Hence its graph group is still isomorphous to $\mathscr{C}_{2v}$ and therefore the excessive symmetry of the simple valuation incidence matrix 3.1.1 persists for much more general valuations of the Hückel parameters. One may conclude, that all graph valuations consistent with the geometrical group $\mathscr{H}$ lead to the same graph group as does the simple valuation $\alpha_{ii} = \alpha$, $\beta_{ik} = \beta$ for nearest, $\beta_{ik} = 0$ for nonnearest neighbors.

4.2. Removal of Excessive Symmetry

As pointed out in 3.2 excessive symmetry occurs if the graph (Π, P) admits proper mappings of the type defining the groups $\mathscr{K}_s$. Obviously these groups reduce to identity, if P contains edges, which do not allow proper mappings within subsets Π_{sk} conserving incidence. This is equivalent to introduction of appropriate nonnearest neighbor interactions. In order to demonstrate the consequence of nonnearest neighbor interactions for symmetry we again refer to examples discussed above.

If instead of the graph shown in Fig. 2a the graph Fig. 2b is used for the Hückel problem of isopropenyl-phenylradical (Example 3.1.1), the symmetry group is still isomorphous to $\mathscr{C}_{2v}$ and the spectrum is shifted and looses the pairing symmetry, since graph 2b is of the nonalternating type. The graph group of graph Fig. 2c is isomorphous to $\mathscr{C}_2$, but the graph is alternating. Since both groups $\mathscr{C}_{2v}$ and $\mathscr{C}_2$ are abelian, the introduction of symmetry reducing nonnearest neighbor interactions cannot produce splittings of levels but only shifts.

In Example 3.1.2 the graph Fig. 4b has the same group as the graph Fig. 4a, namely $\mathscr{D}_{2d}$. Their spectra therefore exhibit the same degeneracies, but are numerically different. In particular graph Fig. 4b is nonalternating and its spectrum does not obey the Coulson-Rushbrooke pairing theorem. These properties contrast with those of the graph shown in Fig. 4c, whose nonnearest neighbor interactions are of such a nature, that its group is isomorphous to $\mathscr{D}_2$ and therefore shows no excessive symmetry in its spectrum. However the pairing property is retained.

The Example 3.1.3 is particularly instructive with respect to the relation of nearest neighbor interactions to spectral properties. Consider first graph Fig. 7b as compared to Fig. 7a. Again graph Fig. 7b has the same symmetry as 7a, namely $\mathscr{O}_h$, but it is of the nonalternating type. The spectrum of graph Fig. 7b clearly shows the violation of the pairing theorem and furthermore the removal of the accidental degeneracy of a pair of E_g and F_{1u} levels by the overnext nearest neighbor interactions occuring in graph Fig. 7b. On the other hand the nonnearest neighbor interactions introduced in graph Fig. 7c, which also is nonalternating, drastically reduce the graph symmetry to $\mathscr{D}_3$ and therefore remove both the excessively degenerated F_{1u} levels, the accidental degeneracy mentioned before as well as the pairing symmetry.

It seems to be difficult to give more general topological conditions for removal of excessive symmetry. However the examples discussed should demonstrate typical cases for the effect of nonnearest neighbor interactions on the symmetry group of the Hückel problem.

4.3. Automorphisms of the Hückel Graph Group

Since the numbering of the elements $\pi \in \Pi$ is arbitrary, any numbering may be obtained from a reference ordering by application of the operators p of the symmetric group $\mathscr{S}_N$ of order $N!$. In general $p\boldsymbol{Z} \neq \boldsymbol{Z}p$ for arbitrary $p \in \mathscr{S}_N$ (which in order to conserve incidence, has to be applied also to the elements $\chi \in P$). Since $\mathscr{G}(g)$ is a subgroup of $\mathscr{S}_N$, the transformations $p^{-1}\mathscr{G}(g)\,p$ define automorphisms of $\mathscr{G}(g)$. Among these the inner automorphisms $g^{-1}\mathscr{G}(g)\,g$ occur, for which $g\boldsymbol{Z} = \boldsymbol{Z}g$. If we now consider the decomposition

$$\mathscr{S}_N = \mathscr{G}\,e + \mathscr{G}p_2 + \cdots + \mathscr{G}p_n$$

where $n = N!/o(\mathscr{G})$, then for each element $gp_k \in \mathscr{G}p_k$, one has

$$(gp_k)^{-1}\,\boldsymbol{Z}(gp_k) = p_k^{-1}\,\boldsymbol{Z}p_k\,.$$

Hence each element $p_k \in \{e\, p_2\, p_3 \ldots p_n\}$ defines an automorphism $p_k^{-1} \mathscr{G} p_k$, for which the matrix $p_k^{-1} \boldsymbol{Z} p_k$ is an invariant under the transformations $p_k^{-1} g p_k \in p_k^{-1} \mathscr{G} p_k$.

4.4. Relations to Theory of Permutation Groups

All definitions and results discussed so far may be reformulated in terms of permutation groups [8]. No detailed discussion of this aspect of the Hückel graph problem will be made here, however a few statements may be in order. First we note that the group of the matrix $\boldsymbol{Z}$ is intransitive or transitive whether or not the set Π decomposes into equivalent sets. Each component is transitive and holomorphous to $\mathscr{G}(g)$, any faithful component may be considered to define $\mathscr{G}(g)$. Well established relations between finite abstract groups and isomorphic permutation groups may therefore be used for construction of the abstract group $\mathscr{G}(g)$ from isomorphous permutation groups. Actually the most convenient method for construction of the group is the use of a computer program for permutation groups. Such a program has been used for generation of the Hückel graph group of the examples discussed above.

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8. c.f. [7], p. 110.

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