

S U M M A R Y

The object of the present investigation is to find answers to the following questions:

1. One method of expressing eigenvector component C_{ij} as a polynomial of eigenvalue x_j has been given by Kassman. Is it possible to find other methods?
2. Is it possible to obtain the Characteristic Polynomial (CP) by using the methods of obtaining the above type of expressions?
3. Can graph-factorisation algorithm be developed on a true graph-theoretical basis (i.e., without using any element of group theory)?
4. How can a graph be converted into a weighted linear chain without affecting its eigenvalues? Can any significant eigenspectral feature of a graph be obtained after converting it into an isospectral linear chain?
5. Charge-transfer (CT) absorption bands of a series of molecular complexes of a particular π -electron acceptor with number of structurally related π -donors show systematic change. Such changes are in keeping with the highest occupied molecular orbital (HOMO) energies of the π -donors. How can the above graph factorisation method be used to interpret the observed changes in CT bands ?
6. Is it possible to locate the HOMO eigenvalue of a conjugated/ heteroconjugated system without computing the entire eigenspectrum of the molecular graph? How does the HOMO energy change with change in the heteroatom Hückel parameters h and k ?

The investigations for questions 1 to 4 have been described in section A of the thesis and those for 5 & 6 in section B. The thesis starts with an introductory chapter (Chapter-1) containing definitions of some terms that are used frequently in the subsequent chapters. A correlation between Hückel theory and graph theory for both conjugated hydrocarbons and heteroconjugated systems have also been shown in this chapter.

Chapter-2 of the thesis contains a review on the known methods of construction of characteristic polynomials (CP). Attempt has been made to clarify the mathematical basis of the methods such as Sachs theorem, Hosoya's method etc. The review covers the following:

- (1) Method utilising Sachs theorem for both weighted and unweighted graphs

- (2) Some recursion formulas.
- (3) The enumeration principle of Hosoya.
- (4) The μ -polynomial method of Gutman.
- (5) The method using Ulam subgraphs.
- (6) The matching polynomial via Fibonacci relations.
- (7) Symmetry factorisation method.
- (8) CP via symmetric function theory.
- (9) The Krylov method.
- (10) Le Verrier - Faddeev- Frame method.
- (11) CP by polynomial matrix method.
- (12) CP by pruning method, and
- (13) CP by iterative pruning method developed by Balasubramonian and Randić.

Each method is appropriately illustrated.

In chapter-3 two new graph theoretical methods have been developed for expressing eigenvector component (C_{ij}) of a graph in terms of the eigenvalue, x_j . One method utilised Ulam subgraphs and the other is based on computing cofactor A_{ij} of the (i,j) element of the adjacency matrix of the graph. The method fails to give all the eigenvectors when there is degeneracy (alternatively called 'multiplicity') in the eigenvalue spectrum of the graph. However, some significant results concerning the nature of degeneracy (e.g., two-fold or three-fold etc.) can be derived from the Ulam subgraphs method.

Chapter-4 contains a method of construction of CP based on the method of determination of cofactors by method (B) of chapter-3. A significant simplification of the method for determination of signs has been made in this chapter.

In chapter-5 an algorithm has been developed for step-wise factorisation of symmetric graphs for simultaneous determination of eigenvalues and eigenvectors. "Symmetry" here is "topological" (graph-theoretical) and not Euclidean. The method of derivation of the algorithm requires no element of group theory (like, the point group of the graph, its character table, etc.).

Chapter-6 describes a graph-theoretical algorithm for converting a weighted undirected graph into an isospectral linear chain. Graph-spectral features of some interesting graphs, such as, a complete graph, a cycle, a

tetrahedral and an octahedral graph have been shown to be clearly brought out when they are transformed into linear chains without changing the eigenvalues. Conversion of a graph into isospectral linear chain means converting the adjacency matrix of the graph into a tridiagonal form. It has been found that graphs having n -fold multiplicity in their eigenspectrum have $(n-1)$ disconnections in their corresponding isospectral linear chains. This is in keeping with an important theory of matrix algebra e.g., real symmetric matrices having n -fold multiplicities in their eigenvalues have $2(n-1)$ zero off-diagonal elements in their tridiagonal form. As G and L_n have the same set of eigenvalues, they also have the same CP. It is much easier to construct CP of L_n than that of G . Moreover, calculation of spectral moments of different orders and writing expressions for C_{ij} in terms of x_j require tracing of various paths along the edges of G . This task is forbiddingly difficult for large graphs with many fused rings; but it is much easier with a linear chain. This is also a motive for developing a graph-linearisation algorithm.

Works on application of graph-theoretic techniques in (i) explaining trends in charge-transfer bands of molecular complexes and (ii) obtaining HOMO/LUMO energy of some organic π -electron donor/acceptor molecules using Budan-Fourrier theorem have been described in chapter-7 & 8 which form section B of the thesis.

In chapter-7, the charge-transfer spectra of some molecular complexes formed between the following donor-acceptor pairs have been studied :

Donor	Acceptor
i) A series of polymethylbenzenes	Iodine monochloride (ICl)
ii) A series of <i>t</i> -butyl substituted furans	Tetracyanoethylene (TCNE)
iii) A series of <i>t</i> -butyl substituted thiophenes	TCNE

It is observed experimentally that the charge-transfer absorption maxima ($h\nu_{CT}$) of complexes of some particular acceptor with the above mentioned series of donors change regularly as the number and/or position of alkyl substituent(s) change progressively in the benzene, furan and thiophene rings. The aim of the study is to explain such changes in $h\nu_{CT}$ with the help of Coulson-Longuet-Higgins perturbation technique within HMO formalism and to obtain inductive effect PMO parameter of *t*-butyl group and hyperconjugative effect PMO parameter of methyl group from such interpretations. When the Hückel hamiltonian matrix of such a molecule is represented by a graph the parameters h and k

appear as weights of the corresponding vertices and edges. The eigenvalues and eigenvectors of the π -type systems, viz. benzene, thiophene and furan have been developed by graph-theoretic techniques developed in section A.

Chapter-8 contains application of Budan-fourrier theorem for analysis of polynomials of some π -systems. By studying the signs of the terms in the CPs and their derivatives of the molecular graph, energy level patterns and the upper and lower bounds to the smallest and largest positive eigenvalues have been determined for aniline- and p-phenylenediamine-like systems. The dependence of the HMO energies of the highest occupied molecular orbitals on the heteroatom Hückel parameters represented by h and k, has been ascertained. The results are in agreement with the trends in the actually computed energy values compiled by Coulson and Streitwieser. The derived modes of dependence of the HMO energy on h and k correctly predict the trends in electron donor properties of the systems under study with variation in electronegativities of the heteroatoms.