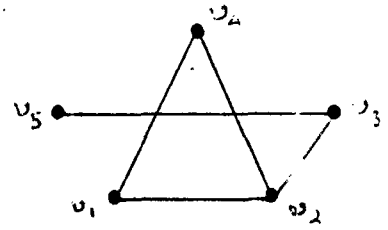
CHAPTER - 1

Definitions:

1.1 Graph : A wide variety of definitions of a graph has been found in the literature [1-3]. According to the definition given by Harary[4], a graph G consists of a finite non-empty set V = V(G) of p points together with a prescribed set X of q unordered pairs of distinct points of V. Each pair x = (u,v) of points in the set X is an edge of G, and x is said to join the vertices u and v.

For example, let us consider $V = \{v_1, v_2, v_3, v_4, v_5\}$ and $X = \{(v_1,v_2), (v_2,v_3), (v_3,v_5), (v_1,v_4), (v_2,v_4)\}$. The graph is $G_{1.1}$ shown in fig.1.1.

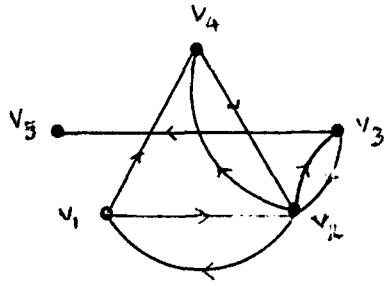


$G_{1.1}$ (Fig.1.1)

There are several other variations of a graph. The above definition of a graph does not permit a 'loop', that is, a line joining a point to itself. In a 'multigraph' no loops are allowed but more than one line can join two vertices. If both loops and multiple edges are permitted we have a pseudo-graph. A directed graph or digraph consists of a finite non-empty set V of points together with a prescribed collection X of ordered pairs of distinct points. For example,

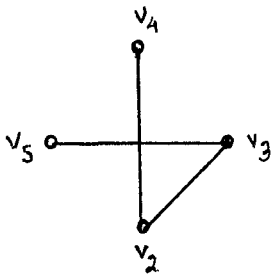
$V = \{v_1, v_2, v_3, v_4, v_5\}$ and $X = \{(v_1,v_2), (v_2,v_1), (v_2,v_3), (v_3,v_2), (v_3,v_5), (v_1,v_4), (v_2,v_4), (v_4,v_2)\}$

form a digraph (D) shown diagramatically in fig. 1.2.

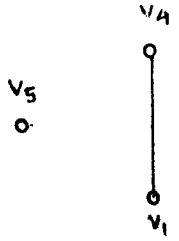


D (Fig.1.2)

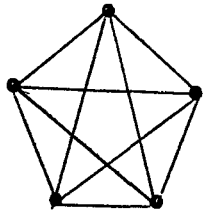
1.2. Special graphs: If some vertices of G are removed along with all edges incident to them the result is a subgraph. $G_{1.1}-v_1$, $G_{1.1}-v_2-v_3$ are two subgraphs of $G_{1.1}$ and are shown in fig.1.3. A subgraph is also obtained by deletion of some edges of G.



$G_{1.1}-v_1$ (Fig.1.3) $G_{1.1}-v_2-v_3$



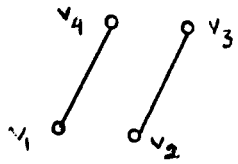
If G contains all possible edges then it is called a complete graph and is denoted by K_n. A complete graph K_5 with five vertices is shown in fig.1.4.



K_5 (Fig.1.4)

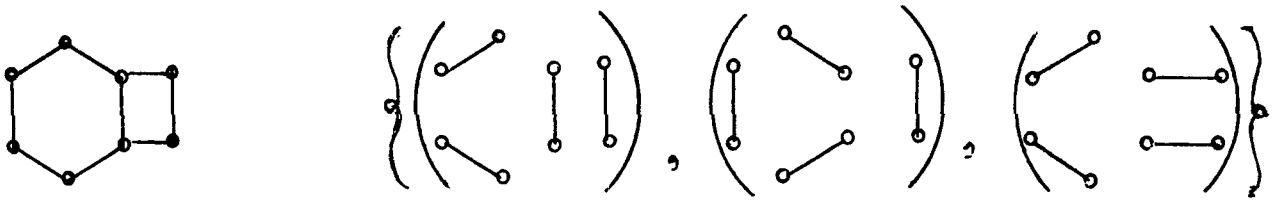
'Degree' of a vertex is the number of other vertices joined to it. A graph in which all vertices are of the same degree is called a 'regular graph'. Thus K_n is a regular graph of degree n-1 and a cycle C_n is a regular graph of degree 2.

1.3 Sachs graphs : A Sachs graph is a graph whose components are cycles and/or complete graphs with two vertices, K_2. For example $G_{1.2}$, shown in fig.1.5, is a collection of Sachs graphs with vertices contained in $G_{1.1}$.



$G_{1.2}$ (Fig.1.5)

1.4. Matchings: Two edges of a graph G are said to be independent if they are not incident to a common vertex. A K-matching of a graph is a selection of K mutually independent edges. The number of K-matchings of a graph G is denoted by $m(G,K)$. For the graph $G_{1.3}$, $m(G_{1.3},4) = 3$. These are shown in fig.1.6.



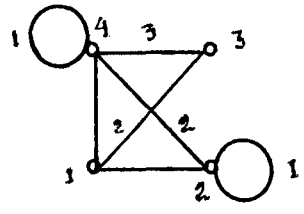
$G_{1.3}$ (Fig.1.6) 4-matchings of $G_{1.3}$

1.5. Weighted graph: Let $V=\{v_1,v_2,.....,v_n\}$ be the finite set of vertices and $W = [w_{ij}]$, i,j=1 to n be a 'weight matrix'of order n x n . Let f be a mapping which associates each element of W to an undordered pair of elements of V. Then for every $w_{ij} \in W$ there exixts a unique pair $(v_i,v_j), v_i \in V$, $v_j \in V$ such that

$$f : w_{ij} \longrightarrow (v_i,v_j)$$

then the set V together with the weight matrix W and mapping f forms a 'weighted graph'. w_{rr} and w_{ij} are called respectively the weights of the vertex v_r and the edge joining the vertices v_i and v_j. When $w_{ij} = 0$ the vertices v_i and v_j are disconnected in the weighted graph (G,W). A weighted graph carrying information of the weight matrix W is shown in fig.1.7.

$$W = \begin{bmatrix} 0 & 1 & 2 & 1 \\ 1 & 1 & 0 & 2 \\ 2 & 0 & 0 & 3 \\ 1 & 2 & 3 & 1 \end{bmatrix}$$



(G,W)

(Fig.1.7)

It is obvious that any real symmetric matrix is representable by a weighted graph.

1.6. The adjacency matrix: The information about the adjacency relation for the vertices $v_1,v_2,.....,v_n$ of a graph G can be converted into a matrix using the following natural definition.

The adjacency matrix **A** = **A**(G) of the graph G with n vertices is a square matrix of order nxn whose entry in the i-th row and j-th column is defined as

a_{ij} = 1 if the vertices v_i and v_j are connected

= 0 otherwise.

The adjacency matrix $\mathbf{A}(G_{1.1})$ of the graph $G_{1.1}$ is given below:

$$\mathbf{A}(G_{1.1}) = \begin{bmatrix} 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 1 & 0 \\ 0 & 1 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix}$$

Adjacency matrix of the weighted graph (G,W) is same as its weight matrix W with the following definition.

$$a_{ij} = w_{ij} \text{ and } a_{ii} = w_{ii}$$

where w_{ij} is the weight of the edge connecting v_i and v_j and w_{ii} is the weight of the loop at the vertex v_i.

A discussion about the use of adjacency matrices of graphs in HUckel molecular orbital(HMO) theory would be relevant at this stage. Under the HUckel approximations, the hamiltonian matrix elements of a conjugated hydrocarbon are

$$\begin{aligned} [\mathbf{H}]_{ij} = H_{ij} &= \alpha \quad \text{for } i = j \\ &= \beta \quad \text{for } i,j \text{ adjacent} \\ &= 0 \quad \text{otherwise} \end{aligned} \qquad \ldots\ldots (1.1)$$

where α is the Coulomb integral of a conjugated C atom and β is the resonance integral between two adjacent sp^2-C atoms. Let **A** be the adjacency matrix of the molecular graph whose vertices represent the conjugated C atoms and edges represent the C-C σ-bonds. If we define a new matrix **H'** as

$$\mathbf{H'} = \alpha\mathbf{I} + \beta\mathbf{A} \qquad \ldots\ldots (1.2)$$

where **I** is the identity matrix of the size of **A**, then

$$\begin{aligned} [\mathbf{H'}]_{ij} &= (\alpha\mathbf{I} + \beta\mathbf{A})_{ij} \\ &= \alpha.1 + \beta.0 \quad \text{for } i = j, \\ &= \alpha.0 + \beta.1 \quad \text{for } i,j \text{ adjacent} \\ &= \alpha.0 + \beta.0 \quad \text{otherwise} \\ &= H_{ij} \end{aligned} \qquad \ldots\ldots (1.3)$$

Thus, **H'** = **H**. Hence the hamiltonian matrix can be resolved into two components as

$$\mathbf{H} = \alpha\mathbf{I} + \beta\mathbf{A} \qquad \ldots\ldots (1.4)$$

It is at once evident that **H** commutes with **A**:

$$\mathbf{HA} - \mathbf{AH} = (\alpha\mathbf{I} + \beta\mathbf{A})\mathbf{A} - \mathbf{A}(\alpha\mathbf{I} + \beta\mathbf{A})$$
$$= \alpha\mathbf{IA} - \alpha\mathbf{AI}$$
$$= \mathbf{0} \text{ (null matrix)}$$

Thus **A** and **H** should have the same set of eigenvectors.

Under the HÜckel approximation $S_{ij} = \delta_{ij}$, the overlap matrix is just the identity matrix I and the secular determinant for the conjugated molecule is,

$$\det(\mathbf{H} - \epsilon\mathbf{I}) = 0 \qquad \ldots\ (1.5)$$

or, $\det(\alpha\mathbf{I} + \beta\mathbf{A} - \epsilon\mathbf{I}) = 0$

or $\det\{\mathbf{A} - (\epsilon-\alpha)/\beta\ \mathbf{I}\} = 0$

If α is set to be the zero and β the unit of energy, the above equation becomes

$$\det(\mathbf{A} - \epsilon\mathbf{I}) = 0 \qquad \ldots\ (1.6)$$

Comparing (1.5) and (1.6) we find that **H** and **A** have the same set of eigenvalues.

The above correspondence between **A** and **H** can be shown to be valid for heteroconjugated systems also. In such a case the molecular graph is a specially designed weighted graph. Let us consider the i-th heteroatom in a conjugated molecule and let the j-th atom be adjacent to it. The corresponding elements of the HÜckel hamiltonian matrix are,

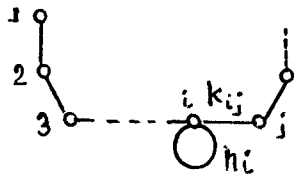
$$H_{ii} = \alpha_i = \alpha + \delta\alpha = \alpha + h_i\beta$$
$$H_{ij} = \beta_{ij} = k_{ij}\beta \quad i,j \text{ adjacent}$$
$$H_{il} = 0 \text{ for } i,l \text{ non-adjacent.}$$

Here α is the Coulomb integral for a benzene carbon atom and β is the resonance integral for a C-C bond in a benzene molecule. Let us now draw a molecular graph ($G_{1.4}$) for the system under consideration in the usual way adopted for conjugated hydrocarbons, but with the following modifications:

(a) To the vertex i is attached a loop of weight h_i and

(b) to the edge (i,j) is assigned a weight k_{ij}.

The adjacency matrix of this graph is , then ,



$G_{1.4}$

$$
\mathbf{A}=\mathbf{A}(G_{1.4})=
\begin{array}{c}
\\ 1 \\ 2 \\ 3 \\ \vdots \\ \\ i \\ j \\ \vdots
\end{array}
\begin{array}{c}
\begin{array}{cccccccccc} 1 & 2 & 3 & \ldots & \ldots & i & j & \ldots & \ldots \end{array} \\
\begin{bmatrix}
0 & 1 & 0 & \ldots & \ldots & \ldots & \ldots & \ldots & . \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & . \\
 & & & & & & & & \\
 & & & & & & & & \\
 & & & & & & & & \\
\ldots & \ldots & \ldots & \ldots & \ldots & h_i & k_{ij} & \ldots & \ldots \\
\ldots & \ldots & \ldots & \ldots & \ldots & k_{ij} & 0 & \ldots & \ldots \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots
\end{bmatrix}
\end{array}
$$

with $k_{ij} = k_{ji}$. Thus, $A_{ii} = h_i$ and $A_{ij} = k_{ij}$ and $A_{il} = 0$ if i and l are non-adjacent. Now if we construct a new matrix $\mathbf{H}'$ as

$$\mathbf{H}' = \alpha\mathbf{I} + \beta\mathbf{A}$$

then

$$H'_{ii} = \alpha.1 + \beta.h = H_{ii},$$

$$H'_{ij} = \alpha.0 + \beta k_{ij} = H_{ij} \quad i,j \text{ adjacent}$$

$$H'_{il} = \alpha.0 + \beta.0 = 0 \quad i,l \text{ non-adjacent}$$

Thus $\mathbf{H} = \mathbf{H}' = \alpha\mathbf{I} + \beta\mathbf{A}$ and with this decomposition of $\mathbf{H}$ one can, as before, show that $\mathbf{H}$ has the same set of eigenvalues and eigenvectors as that of $\mathbf{A}$.

The eigenvalue problem of the hamiltonian matrix in HMO theory thus reduces to that of the adjacency matrix of the corresponding molecular graph. The HMO theory can, therefore, be viewed as a subset of graph theory as stated by Gutman & Trinajstic[5] and McClelland[6].

References:

1. Berge, C.,'The theory of graphs and its application', London : Methuen, 1962.

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3. Gutman, I.,and Polansky, O.E.,'Mathematical concepts in organic chemistry', Berlin Heidelberg, New York: Springer, 1986.

4. Harary, F.,'Graph theory', Reading(Mass) : Addison-Wesley, 1972.

5. Gutman, I., and Trinajstić, N.,Topics curr.chem.42 (1973),49.

6. McClelland, B.J., Molecular Physics, 45 (1982),189.