match no.1 pp. 183-196 1975

GRAPHS IN QUANTUM CHEMISTRY

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The purpose of this paper is not so much to report results as to express some thoughts about possibilities for the application of graphs in quantum chemistry.

Aspects of graph theory are used extensively in HMO theory [1]. However, in HMO theory graphs may be interpreted in two different ways:

(1) as the structural graph of the conjugated system considered [2] or

(2) as a graph in which vertices correspond to the basis functions used for the construction of the HMO's ("basis graph").

1. Basis Graphs.

The concept of basis graphs may be extended to quantum chemical methods other than HMO theory. This, however, implies that a one-to-one correlation exists between the set of vertices, $U = \{..., U_r, U_s, U_t, ...\} = \{..., r, s, t, ...,\}$ and the elements of the basis vector, $\underline{\varphi} = (...\varphi_r \varphi_s \varphi_t ...) = (...r\ s\ t...)$.

$$U = \{..., r, s, t, ...\} \sim (...r\ s\ t...) = \varphi \qquad (1)$$

The basis functions are then mapped as an edgeless graph,

$$\mathcal{G}^{O} = [U, K] \quad \text{where} \quad |K| = O\ . \qquad (2)$$

The basis graph $\mathcal{G}^{\circ}$ consists of precisely as many components as basis functions. Each component is a complete graph of zero order.

In the basis $\underline{\Phi}$ an operator $\hat{\mathcal{O}}$ is represented by the integrals $\langle r|\hat{\mathcal{O}}|s\rangle$. If product functions or their linear combinations are used in the final description of the system considered, integrals of the type $\langle rs|\hat{\mathcal{O}}|tu\rangle$ also occur.

If each integral $\langle r|\hat{\mathcal{O}}|s\rangle$ between different basis functions, $r \neq s$, which does not vanish essentially creates an edge, $K_{rs} = \{r,s\}$ in $\mathcal{G}^{\circ}$, $\mathcal{G}^{\circ}$ successively alters to $\mathcal{G}$. In this operation the integrals

$\langle r|\hat{\mathcal{O}}|r\rangle$ .....may be attached directly to the vertex U_r and

$\langle r|\hat{\mathcal{O}}|s\rangle$ .....may be attached directly to the edge K_{rs}.

The values of these integrals are contributions to the weight of the vertices or edges. Unfortunately no direct attachment if the integrals of the type $\langle rs|\hat{\mathcal{O}}|tu\rangle$ is possible. However, if an expansion of the more center integrals in terms of the one and two center integrals exists such as

$$\langle rs|\hat{\mathcal{O}}|tu\rangle = \sum_{\substack{\mu,\nu \\ \{\mu,\nu\}\ \{r,s,t,u\}}} \lambda_{\mu\nu} \langle u|\hat{\mathcal{O}}|\nu\rangle \qquad (3)$$

in which $\mu=\nu$ or $\mu\neq\nu$, these difficulties are removed. The value of $\langle rs|\hat{\mathcal{O}}|tu\rangle$ is divided into contributions to the weights of the vertices and to the edges involved.

By carrying out this procedure for all the integrals produced by the operator $\hat{\mathcal{O}}$ and by summing up the different contributions to the vertex weights, W_{rr}, and the edge weights, W_{rs}, a graph $\mathcal{G}$ is obtained which has the same vertex set U as the basis graph $\mathcal{G}^{\circ}$. In general $\mathcal{G}$ will be

an irregular weighted complete graph $\mathcal{K}_n$. But if between two particular subsets of U all the integrals produced by $\hat{\mathcal{O}}$ vanish essentially[+] the resulting graph, $\mathcal{G}$, may consist of several components each of which is an irregular weighted complete graph. Any edge in $\mathcal{G}$ in which the sum of the contributions to its weight accidently equals zero should not be omitted.

2. Weight Matrices.

The weights of the vertices and edges of $\mathcal{G}$ may be ordered to the weight matrix $\underline{\underline{W}}$ of $\mathcal{G}$

$$\underline{\underline{W}} = (W_{rs}) \tag{4}$$

If all the weights are real numbers[++] the weight matrix is symmetric

$$\underline{\underline{W}}^T = \underline{\underline{W}} \tag{5}$$

The weight matrix $\underline{\underline{W}}$ basically represents the quantum chemical problem set up by the operator $\hat{\mathcal{O}}$ in the basis $\underline{\varphi}$. Therefore, the eigenvalues of $\underline{\underline{W}}$ exactly equal the eigenvalue of $\hat{\mathcal{O}}$ in $\underline{\varphi}$. The weighted graph $\mathcal{G}$ represents the graph formulation of the quantum chemical problem considered; the strucutre of $\mathcal{G}$ is precisely the structure of the quantum chemical problem. This is confined by the limits set up by the necessity for an expansion like (3).

Generally the weight matrix describes a particular

[+]this might occur due to symmetry reasons.

[++]this is always the case if the operator $\hat{\mathcal{O}}$ is hermitian.

distribution of a distinct quality represented by the operator $\hat{\mathcal{O}}$ over the different vertices and edges of a graph. In this way the elements of $\underline{\underline{W}}$ are related to a particular scaling of the quality considered. The weight matrix $\underline{\underline{W}}$ corresponds to a distinct zero point and to a distinct unit of the quality which $\underline{\underline{W}}$ represents. If the unit is changed from [A] to [B] = k[A] the weight matrix also changes.

$$\begin{aligned} \underline{\underline{W}}\ [A] &\rightarrow \underline{\underline{W}}'\ [B] \\ \underline{\underline{W}}' &= \frac{1}{k}\ \underline{\underline{W}} \end{aligned} \tag{6}$$

If the zero point of the scale is transformed by a[A] the resulting weight matrix $\underline{\underline{W}}''$ is given by

$$\underline{\underline{W}}'' = \underline{\underline{W}} + a \cdot \underline{\underline{I}} \tag{7}$$

where $\underline{\underline{I}}$ is the unity matrix of the same order as $\underline{\underline{W}}$. Eq. (7) illustrates that only the diagonal elements of $\underline{\underline{W}}$ represent absolute amounts of the quality considered; the off diagonal elements represent relative amounts.

It is interesting to note that the adjacency matrix $\underline{\underline{A}}$ represents the quality of neighbourhood which can have only two values indicated by 1 (neighbourhood) and 0 (no neighbourhood).

3. Weighted Complete Graphs.

A complete graph $\mathcal{K}_n$ with n vertices is

(1) uniformily weighted if

(1.1) all vertices have the same weight, $W_{rr}=W_{ss}=\ldots=a$;

(1.2) all edges have the same weight, $W_{rs}=W_{st}=\ldots b$;

(2) regularily weighted if

(2.1) all vertices have the same weight, $W_{rr}=W_{ss}=\ldots=a$;

(2.2) not more than $(n/2)$ different edge weights exist which associate with the edges in such a way that each edge wreath can be mapped onto each other edge wreath of $\mathcal{H}_n$; or

(3) irregularily weighted in all other cases.

The weight matrix $\underline{\underline{W}}$ of a uniformily weighted complete graph $\mathcal{H}_n(a,b)$ is given by

$$\underline{\underline{W}} = a\underline{\underline{I}} + b\underline{\underline{A}} \tag{8}$$

$\underline{\underline{I}}$ is the unity matrix and $\underline{\underline{A}}$ the adjacency matrix of $\mathcal{H}_n$. Comparison of eq. (8) with eqs. (6) and (7) shows that $\underline{\underline{A}}$ leads to $\underline{\underline{W}}$ with a particular change of scaling. The characteristic polynomial corresponding to $\underline{\underline{W}}$ should be equal to that of $\underline{\underline{A}}$

$$X(\mathcal{H}_n|0,1) = (x-1)^{n-1}(x+n-1) \tag{9}$$

except for the different scaling. Thus the following is obtained

$$X(\mathcal{H}_n|a,b) = [x+a-b]^{n-1}\ [x+a+(n-1)b] \tag{10}$$

If $\{\varphi_r\}$ denotes the set of orthonormalized basis functions corresponding to the vertex set $\{r\}$ of the uniformly weighted graph $\mathcal{H}_n(a,b)$ the function correlated to the non degenerated eigenvalue $x_o = -a-(n-1)b$ is given by

$$\Psi_o(\mathcal{H}_n|a,b) = n^{-1/2} \cdot \sum_{r=1}^{n} \varphi_r \tag{11}$$

The functions correlated to the $(n-1)$ degenerated eigenvalues $x_j = -a+b$, $j = 1,2\ldots,(n-1)$ are given by

$$\Psi_j(\mathcal{K}_n\ a,b) = [2(n-j)]^{-1/2}\{(n-j)\varphi_j - \sum_{j+1}^{n}\varphi_r\};\quad 1\leq j\leq(n-1) \qquad (12)$$

If the basis functions are not orthogonal to each other functions (11) and (12) are altered only in the normalisation factors.

Condition (2.2) for regularily weighted graphs suggests several properties. Mapping of the edge wreaths onto each other indicates the congruency of all edge wreaths. Since an edge wreath of $\mathcal{K}_n$ contains $n-1$ edges which cannot be weighted by more than $n/2$ different edge weights, from the congruency it follows that: (a) at least pairs of the edges of an edge wreath have equal weights; and (b) if n is even not more than one edge of the edge wreath is singly weighted. By collecting precisely those edges which have the same weight b_ν, edge subgraphs of $\mathcal{K}_n$ are obtained which are uniformly weighted cyclic graphs $\mathcal{C}_n(b_\nu)$. An additional subgraph, consisting of $n/2$ components, each of which is the complete graph $\mathcal{K}_2(a,b_{n/2})$ appears only if n is even.

It is obvious that the weight matrix of a regularily weighted graph has the circulant form. Therefore, the characteristic polynominals are:

$$X(\mathcal{K}_{2m+1}|a,b_\nu) = \prod_{j=0}^{2m}\left[x + 2\sum_{\nu=1}^{m} b_\nu \cos\frac{2j\nu\pi}{2m+1}\right]$$

$$X(\mathcal{K}_{2m+2}\ a,b) = \prod_{j=0}^{2m+1}\left[x + 2\sum_{\nu=1}^{m} b_\nu \cos\frac{2j\nu\pi}{2m+2} + (-1)^j b_{m+1}\right] \qquad (13)$$

The relationships between a regularily weighted complete graph $\mathcal{K}_n(a,b_\nu)$ and the first $n/2$ powers of the uniformly

weighted cyclic graphs [3], $\mathcal{C}_n^{(\nu)}(a,b_\nu)$ should be noted.

4. Characteristic Polynomials of Joints of Uniformly Weighted Complete Graphs.

In general, quantum chemical applications of graph theory will lead to irregularily weighted complete graphs. However, these graphs may often contain uniformly weighted subgraphs. If the irregularily weighted complete graph $\mathcal{K}_n$ is interpreted as a joint [4] of M uniformly weighted graphs $\mathcal{K}_{m_\nu}$, general expressions for the characteristic polynomials can be obtained.

If $\mathcal{K}_n$ represents the joint

$$\mathcal{K}_n = \mathcal{K}_{m_1} \circ \mathcal{K}_{m_2} \circ \ldots \circ \mathcal{K}_{m_\nu} \circ \ldots \circ \mathcal{K}_{m_M} \tag{14}$$

then

$$n = \sum_{\nu=1}^{M} m_\nu \tag{15}$$

Furthermore if $\mathcal{K}_n$ and the $\mathcal{K}_{m_\nu}$ are defined by

$$\mathcal{K}_n = [U_n, K_n] \quad \text{and} \quad \mathcal{K}_{m_\nu} = [U_\nu, K_\nu] \tag{16}$$

U_n represents the union of all U_ν's

$$U_n = \bigcup_{\nu=1}^{M} U_\nu \tag{17}$$

However, the union of all edge sets K_ν is only a subset of K_n. If K_v denotes the difference

$$K_v = K_n - \bigcup_{\nu=1}^{M} K_\nu \tag{18}$$

then K_v represents the union of all those edges $\{U_rU_s \mid U_r \varepsilon U_\mu,\ U_s \varepsilon U_\nu,\ \mu \neq \nu\}$ which are incident to vertices

not belonging to the same subgraph $\mathcal{K}_{m_\nu}$. If $K_{\mu\nu}$ denotes the union of all edges connecting $\mathcal{K}_{m_\mu}$ and $\mathcal{K}_{m_\nu}$

$$K_{\mu\nu} = \bigcup_{r,s} \{U_r U_s | U_r \varepsilon U_\mu, U_s \varepsilon U_\nu;\ \nu \neq \mu\} \tag{19}$$

the subset K_ν of eq. (16) is obtained by

$$K_\nu = \bigcup_{1 \leq \mu < \nu \leq M} K_{\mu\nu} \tag{20}$$

If all $\mathcal{K}_{m_\nu}$'s are uniformly weighted graphs as indicated above

$$\mathcal{K}_{m_\nu} = \mathcal{K}_{m_\nu}(a_\nu, b_\nu) \tag{21}$$

and if the weights of all edges $\{U_r U_s\} \varepsilon K_{\mu\nu}$ are the same, $W_{\mu\nu} = C_{\mu\nu}$, the characteristic polynomial

$$X(\mathcal{K}_n\ a_\nu,\ b_\nu,\ C_{\mu\nu}) = f_M(x) \cdot \prod_{\nu=1}^{M} (x + a_\nu - b_\nu)^{m_\nu - 1} \tag{22}$$

is obtained from the determinant $||x.\underline{I} + \underline{W}||$ by elementary calculation. In eq. (20) $f_M(x)$ denotes the function which might be derived by expanding the generally non symmetric determinant $||D_{\nu\mu}||$

$$\begin{aligned} f_M(x) &= ||D_{\mu\nu}|| \\ D_{\mu\nu} &= x + a_\mu + (m_\mu - 1) b_\mu \\ D_{\mu\nu} &= m_\mu c_{\mu\nu} \\ D_{\nu\mu} &= m_\nu c_{\mu\nu} \end{aligned} \tag{23}$$

It should be noted that the degenerated eigenvalues of the $\mathcal{K}_{m_\nu}$'s remain unperturbed whereas the non degenerated eigenvalues of the $\mathcal{K}_{m_\nu}$'s combine together. This behaviour is due to the automorphism group of $\mathcal{K}_n$. If Polya's conditions of

congruency [5] are interpreted such that an edge of the particular weight w may only be mapped onto an edge of the same weight w, and if all the weights a_ν, b_ν, $c_{\mu\nu}$ are mutually different, the automorphism group of $\mathcal{K}_n$ is given [6] by

$$\Gamma(\mathcal{K}_n) = \Gamma(\mathcal{K}_{m_1}) + \Gamma(\mathcal{K}_{m_2}) + \ldots + \Gamma(\mathcal{K}_{m_M}) \qquad (24)$$

Since the automorphism group of a uniformly weighted graph $\mathcal{K}_m$ is the symmetric group $\mathcal{S}_m$ it follows that

$$\Gamma(\mathcal{K}_n) = \mathcal{S}_{m_1} + \mathcal{S}_{m_2} + \ldots + \mathcal{S}_{m_\nu} + \ldots + \mathcal{S}_{m_M} \qquad (25)$$

In general it should be possible to show that only the non degenerated eigenvalues of the $\mathcal{K}_{m_\nu}$'s belong to the totally symmetric irreducible representation of $\mathcal{S}_{m_\nu}$ and $\Gamma(\mathcal{K}_n)$ but each set of the degenerated eigenvalues belongs to another irreducible representation of $\mathcal{S}_m$ and $\Gamma(\mathcal{K}_n)$. While only the functions of type (11) combine together in $f_M(x)$, all the functions of type (12) remain unchanged.

The following <u>example</u> of an all valence electron calculation of methane CH_4 may illustrate a practical application of the previous discussion. There are 8 basis functions $\{\varphi_r \; r = 1,2,\ldots,8\}$. The first four, $\{\varphi_1, \varphi_2, \varphi_3, \varphi_4\}$, denote the 1s-AO of the H-atoms, $\{H_1, H_2, H_3, H_4\}$; the last four, $\{\varphi_5, \varphi_6, \varphi_7, \varphi_8\}$ denote the sp^3 hybrid orbitals of the C-atom which point to the H-atoms (Fig. 1). The basis graph $\mathcal{G}^o$ consists of 8 vertices: 4 are one particular type (o); and 4 are another type (●), see Fig. 2. In the corresponding

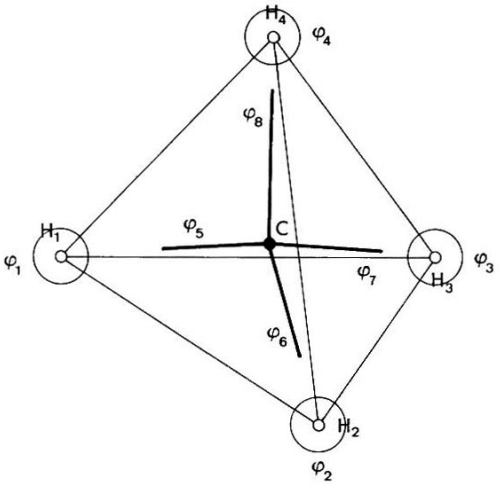

Fig. 1 Basis functions for CH_4

$\{\varphi_1, \varphi_2, \varphi_3, \varphi_4\}$ .... 1s-atomic orbitals at H

$\{\varphi_5, \varphi_6, \varphi_7, \varphi_8\}$ .... $2sp^3$-hybrid orbitals at C

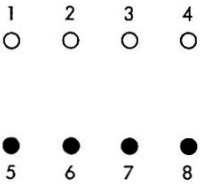

Fig. 2 Basis graph $\mathcal{G}^\circ$

o ... 1s-atomic orbitals at H

• ... $2sp^3$-hybrid orbitals at C

the vertex j corresponds to φ_j

weighted graph $\mathcal{G}$ (Fig. 3) two uniformly weighted complete graphs $\mathcal{K}_4(h,d)$ and $\mathcal{K}_4(c,e)$ are subgraphs of $\mathcal{G}$.

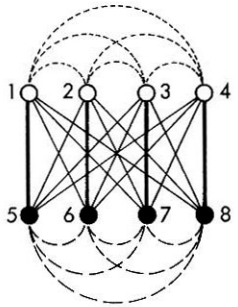

Fig. 3 Weighted graph $\mathcal{G}$

vertex weights: o...h ; ●... c

edge weights: —— a ----- d
—— b – – – e

By using the weights indicated in Fig. 3, the characteristic polynomial of $\mathcal{G}$ is expressed as

$$X(x) = \det || \underline{\underline{W}} + x.\underline{\underline{I}} || = \begin{vmatrix} y & d & d & d & a & b & b & b \\ d & y & d & d & b & a & b & b \\ d & d & y & d & b & b & a & b \\ d & d & d & y & b & b & b & a \\ a & b & b & b & z & e & e & e \\ b & a & b & b & e & z & e & e \\ b & b & a & b & e & e & z & e \\ b & b & b & a & e & e & e & z \end{vmatrix} \tag{26}$$

in which $y=x+h$ and $z=x+c$. $X(x)$ is obtained as

$$X(x)=[(x+c-e)(x+h-d)-(a-b)^2]^3[(x+c+3e)(x+h+3d)-(a+3b)^2] \tag{27}$$

This leads to an eigenvalue spectrum consisting of 2 non degenerated levels and 2 groups of threefold degenerated levels. This structure is due to automorphism group

$$\Gamma(\mathcal{G}) = \mathcal{S}_4[\mathcal{E}_2] \tag{28}$$

5. Other Applications.

The characteristic polynomial of uniformily weighted and regularily weighted graphs may be used to derive the upper and lower bounds for the eigenvalues of an irregularily weighted graph.

It has been shown [7] that the automorphism group of a graph might be of higher order than the corresponding point group. In this case, since the automorphism group consequently contains more irreducible representations than the point group a further splitting of secular determinants is sometimes allowed.

I thank Mrs. Alice Bock for the careful revision of the English text and its typing and Mrs. Ilse Schneider for the drawing of the figures.

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