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Extremal Non-Bonding Orbitals *

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Abstract

A graph G is singular of nullity η if the nullspace of its adjacency matrix $\mathbf{G}$ has dimension η. In the Hűckel model, a molecular graph of nullity η has η non-bonding orbitals (NBOs). By considering the properties of vertices playing different roles in a singular graph, we give a geometrical significance to the maximal induced subgraphs that have lower rank. We determine lower and upper sharp bounds for the order of the substructures where the spin of the NBO electrons is concentrated. In the case of degeneracy of the NBOs, lack of stability points towards a "first order"Jahn-Teller distortion, resulting in a combined effect of the NBOs.

1 Introduction

A graph G is said to be of order n if it has n vertices. For a labelling of the vertices $\{1, 2, \ldots n\}$, the adjacency matrix of a graph G, denoted by $\mathbf{A}(G)$ (or simply $\mathbf{A}$ or $\mathbf{G}$), is the $n \times n$ matrix (a_{ij}), where $a_{ij} = 1$ if $\{ij\}$ is an edge and 0 otherwise. The *spectrum* $Sp(G)$ of a graph G consists of the collection, with repetitions, of the eigenvalues of $\mathbf{A}$, which are

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the solutions of the characteristic equation $\det(\lambda\mathbf{I} - \mathbf{A}) = 0$. Since relabelling the vertex set of a graph produces similar adjacency matrices, the spectrum is an invariant of G. The multiplicity of the eigenvalue zero in $Sp(G)$ is referred to as the *nullity*[1], $\eta(G)$, of G. Note that by the Dimension Theorem, for a linear transformation $\mathbf{G}$, $\eta(\mathbf{G}) + \text{rank}(\mathbf{G}) = |G|$. The difference between the number of positive and negative eigenvalues of $\mathbf{A}$ is referred to as the *signature* of G.

A graph G on n vertices is *singular* if $\eta(G) > 0$; that is, if there exists $\mathbf{x} \neq \mathbf{0}, \mathbf{x} \in \mathbb{R}^n$, such that $\mathbf{Ax} = \mathbf{0}$. Since $\mathbf{A}$ satisfies $\mathbf{Ax} = \lambda\mathbf{x}$ for the eigenvalue $\lambda = 0$ and $\mathbf{x} \in \ker(\mathbf{A})$, we refer to $\mathbf{x}$ as a *kernel eigenvector* of G.

In Hűckel molecular orbital theory, a simplified Schrődinger equation applied to a π–conjugated molecule whose C-skeleton is the same as that of G, is $\mathbf{Ax} = \lambda\mathbf{x}$. The eigenvalues λ of $\mathbf{A}$ estimate the energies of the π-electrons in conjugated unsaturated systems, while the eigenvectors $\mathbf{x}$ of $\mathbf{A}$ model the π–molecular orbitals. The eigenvalue zero is associated with the non-bonding orbitals (NBOs) of a π–conjugated molecule represented by the kernel eigenvectors of $\mathbf{A}$.

For a graph G, $rank(\mathbf{G})$ is therefore the number of non-zero eigenvalues of the adjacency matrix. For a graph with at least one edge, the rank is bounded below by two and above by the order of the graph. These bounds were improved by a number of authors.

The results of a computer search for graphs with six non-zero eigenvalues is given in [7]. There are 1644 non-isomorphic such graphs on six to fourteen vertices. In [8], both upperbounds and lower bounds are discussed. In [14], a lower bound for the rank in terms of parameters of singular subgraphs of G is given. In [19], the rank is shown to be bounded by a function of the number of negative eigenvalues of G.

This paper is motivated by the following mathematical curiosities that have chemical implications in Molecular Orbital Theory:

1. What properties must a vertex possess within a graph so that the rank remains constant or changes by a particular number on deleting the vertex?
2. If no two columns of $\mathbf{A}$ are identical, what is the largest number of positions on which

[1]The term $corank(\mathbf{A})$ is also used for nullity($\mathbf{A}$) in the literature.

two columns coincide?

3. How does the structure of a singular graph control the rank?

We address the above questions in sections 2, 3 and 4 respectively. Known results are surveyed and we supply proofs where it is expedient for the global understanding of the concepts presented.

2 Core Vertices

The graphs we consider are simple, that is they have no loops or multiple edges. For an arbitrary labelling of the vertices of a graph and a feasible kernel eigenvector $\mathbf{x} \in \mathbb{R}^n$, $\mathbf{x} \neq \mathbf{0}$, the $n \times n$ real symmetric $0-1$ adjacency matrix $\mathbf{A}$, satisfying $\mathbf{Ax} = \mathbf{0}$, defines singular graphs with $\mathbf{x}$ as a nullvector in the nullspace of $\mathbf{A}$. The non-zero restriction $\mathbf{x}_F$ of $\mathbf{x}$ defines an induced subgraph F, of the respective graph G, induced by the vertices corresponding to the non-zero entries of $\mathbf{x}$. If the vertices of F are labelled first, then $\mathbf{x} = (\mathbf{x}_F, \mathbf{0})^t$. If $\mathbf{Ax} = \mathbf{0}$ and $\mathbf{x} = \begin{pmatrix} \mathbf{x}_F \\ \mathbf{0} \end{pmatrix}$, where all the $|F|$ entries of $\mathbf{x}_F$ are non-zero, then the $|F| \times |F|$ submatrix $\mathbf{F}$ of $\mathbf{A}$, satisfies $\mathbf{F}\mathbf{x}_\mathbf{F} = \mathbf{0}$ and defines an induced subgraph F of G called a *core of* G, denoted by $(F, \mathbf{x}_F)$ or just F when the context is clear. If $\mathbf{x} = \mathbf{x}_F$, then G is said to be a *core graph*. Note that a core of G is a core graph in its own right.

The five-vertex path P_5 has nullity one, and core $\overline{K_3}$, that is the three-vertex graph with no edges. The four-cycle C_4, is itself a core graph of nullity two, since for a normal labelling round the cycle, $\mathbf{C}_4(\mathbf{x}) = \mathbf{0}$ where $\mathbf{x} = (1, 1, -1, -1)^t$. Note that C_4 has also two distinct cores, each being $\overline{K_2}$.

2.1 Deleting Core Vertices

When a vertex and the edges incident to it are deleted from a graph, the nullity, may change by at most one so that, by the Dimension Theorem, the rank may remain unchanged or decrease by at most two. These considerations are in line with *Cauchy's in-*

equalities for Hermitian matrices, also known as the Interlacing Theorem [9]. For graphs, it may be stated as follows:

Theorem 2.1 Interlacing Theorem*: Let G be an n-vertex graph and $v \in \mathcal{V}$. If the eigenvalues of G are $\lambda_1, \lambda_2, \ldots, \lambda_n$ and those of $G-v$ are $\mu_1, \mu_2, \ldots, \mu_{n-1}$, both in non-increasing order of magnitude, then $\lambda_1 \geq \mu_1 \geq \lambda_2 \geq \mu_2 \geq \ldots \geq \mu_{n-1} \geq \lambda_n$.*

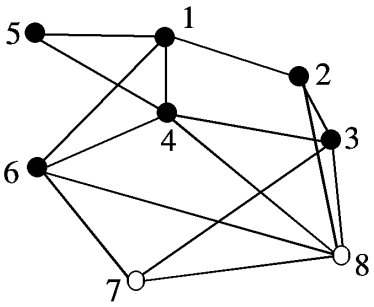

Figure 1: Singular configurations are induced subgraphs of a singular graph.

A basis B for the nullspace can be transformed into another, B', by linear combinations of the vectors of B. However, the union of the collections of the positions of the non-zero entries in the basis vectors is the same for all bases. There is therefore a bipartition of the vertices that has a direct bearing on the change in rank on deleting a vertex. If a vertex of a graph G lies on some core determined by the vectors in B, then it is said to be a *core vertex*. Vertices not lying on any core are said to be *core-forbidden*. The vertices 7 and 8 of the graph in Figure 1 are core-forbidden vertices. Thus if $\mathbf{A}$ is the adjacency matrix of a singular graph G, the partition of the vertex set $\mathcal{V}(G)$ into CV and core-forbidden vertices, $\mathcal{V}(G)\backslash\mathrm{CV}$, is independent of the basis used for the nullspace. The following result is immediate.

Proposition 2.2 *For all possible bases of the nullspace, the set* CV *of core vertices is an invariant of a graph G.*

It follows that the set of core-forbidden vertices, $\mathcal{V}(G)\backslash\mathrm{CV}$, is also an invariant of G. This concept has been used *ad hoc* in the theory of singular graphs. [1, 5, 13].

Lemma 2.3 *If H is an induced subgraph of a graph G, then $rank(H) \leq rank(G)$.*

Proof: This is true for all principal submatrices $\mathbf{H}$ of $\mathbf{G}$. Also, since on adding a vertex to a graph, the nullity increases by one, remains unchanged or decreases by one, the rank does not decrease. ■

By Lemma 2.3, the rank of a graph is an upperbound for the rank of its vertex-deleted subgraphs. The following result characterizes core vertices in a singular graph.

Proposition 2.4 *The rank of a graph remains unchanged on deleting a vertex v if and only if v is a core vertex.*

Proof: The rank of a graph remains unchanged on deleting a vertex v if and only if the number of kernel eigenvectors in the nullspace of the adjacency matrix reduces by one. We show that a necessary and sufficient condition for the rank to remain constant is that v is a core vertex.

Let G be a singular graph of nullity η, having the core vertices labelled first with the core vertex v being among the first η vertices. If $B = \{\mathbf{z}_1, \mathbf{z}_2, \ldots, \mathbf{z}_\eta\}$ is a basis for the nullspace of the adjacency matrix of G, then the $\eta \times n$ matrix $\mathbf{M}$ whose rows are the η vectors in B, has rank η. By row reduction, $\mathbf{M}$ can be reduced to the Hermite Normal form $\mathbf{M}'$, in which, to the (column) position of the first non-zero entry of each of the η row vectors, there corresponds a zero entry in all the other rows. One of these positions is that of v. Since row reduction is equivalent to taking linear combinations of the kernel eigenvectors, the rows of $\mathbf{M}'$ are a full set of η linearly independent kernel eigenvectors of G. Deleting v, affects just one of the row vectors so that the remaining $\eta - 1$ rows of $\mathbf{M}'$, restricted to $G - v$, are kernel eigenvectors of $G - v$. Moreover, there are no more kernel eigenvectors linearly independent of these $\eta - 1$ row vectors for $G - v$, as otherwise these can be extended (by adding a zero in the v position), contributing a kernel eigenvector of G linearly independent of the rows of M and the nullity of G would then be more than

η. If u is a core-forbidden vertex, deleting it leaves all η rows of $\mathbf{M}'$, restricted to $G-u$, as kernel eigenvectors of $G-u$. ■

The core vertices can also be seen in the context of graph angles [3]. They are the vertices v such that $\mathbf{P}\mathbf{e}_v = 0$, where $\mathbf{P}$ is the orthogonal projection of $\mathbb{R}^n$ (with standard orthonormal basis $\mathbf{e}_1, ..., \mathbf{e}_n$) onto the eigenspace of 0. In the chemical context, the entries of $\mathbf{x}$ determine the distribution of the electron(s) occupying the NBO: from them follow the charges on the atoms, the bond-orders and, in the case of single occupation, the net spin density at each site. For a labelling of G, a zero entry in the ith position of $\mathbf{x}$ indicates a lack of charge at the ith C-centre. The NBO-charge is distributed among the C-atoms in proportion to the square of the entries of $\mathbf{x}$. Thus the charge is concentrated in the substructure, the core with respect to $\mathbf{x}$, that corresponds to the non-zero entries of $\mathbf{x}$. The eigenvalue zero of $\mathbf{A}$, for a molecular graph G, indicates the presence of a NBO, $\mathbf{x}$, with no net stabilization or destabilization.

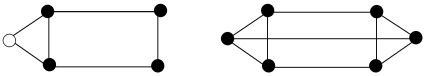

Figure 2: Adding a vertex so as to increase the nullity.

Non-adjacent vertices having the same neighbours are said to be **duplicate vertices**[2]. A trivial way of increasing the nullity is to add a duplicate vertex since this results in two equal rows of the adjacency matrix. Adding an isolated vertex to a graph also increases the nullity. Note that graph invariants such as rank and chromatic number remain constant when a duplicate or isolated vertex is added. A non-trivial way of increasing the nullity is shown in Figure 2. The nullity of the graph on five vertices is one and increases to two for the six-vertex graph. Thus both graphs shown in Figure 2 have four non-zero eigenvalues.

By Proposition 2.4 and by interlacing, the rank remains constant on deleting a core vertex, whereas it decreases if a core-forbidden vertex is deleted. Removal of a core-forbidden vertex from a n-vertex graph G of rank r, may result in a graph of rank $r-1$ and the same

[2]Two duplicate vertices are also referred to as *vertices of the same type* [12] or *twins* [8].

nullity as for G, provided no new cores are created in $G - v$. Alternatively, the removal of a core-forbidden vertex may produce a new core in $G - v$, in which case the nullity increases by one, forcing the rank to reduce by two. If the new core created happens to be $\overline{K_2}$ (the subgraph consisting of two isolated vertices), then duplicate vertices are produced in $G - v$, whose adjacency matrix would then have two identical rows. A sharp upperbound for the number of non-zero entries coinciding in two identical rows of $G - v$ is $n - 3$, as in the case of G_2 of Figure 3, when a pair of duplicate vertices a and b are adjacent to all the remaining vertices in $G - v$.

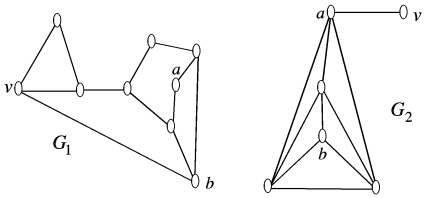

Figure 3: Non-canonical vertex-deleted subgraphs.

3 Change in Rank

In this section we answer question 2, giving a new proof by interpreting the effects on the rank when deleting vertices of different properties.

Following A. Torgašev and M. Lepović, we call graphs with no duplicate vertices, *canonical* [3] [20, 7]. Note that all four graphs shown in Figures 2 and 3 are canonical. Both $G_1 - v$ and $G_2 - v$ of Figure 3 are non-canonical. To answer question 2, therefore, the minimal number of vertices to be deleted, from a canonical graph to produce a non-canonical subgraph, needs to be determined.

There are only finitely many canonical graphs of any given rank. Kotlov and Lovász obtained Ramsey type bounds for the largest number of vertices of a canonical graph of

[3] Canonical graphs are also referred to as *reduced* graphs [4] in the literature.

a particular rank [8]. They based their arguments on the following result for which we give a new perspective based on the structure of singular graphs. Our proof of this result elucidates the possible substructures that may be present and gives a sharp upperbound for the order of the induced substructures that may be non-canonical within a graph.

Lemma 3.1 *Let G be a canonical graph without isolated vertices and of rank r. If deletion of vertices from G results in a maximal graph H of lower rank, then*
(i) no two rows (or columns) of $\mathbf{A}(G)$ coincide on more than $|H|$ positions;
(ii) H has at most two duplicate vertices (i.e. no triplets);
(iii) if H has a pair of duplicate vertices, then its rank is exactly $r-2$.

Proof: We consider graphs with core forbidden vertices first. By Proposition 2.4, for the rank to decrease on deleting a vertex, the vertex chosen for deletion must not be a core vertex. On deleting a core-forebidden vertex, either the nullity remains unchanged or it increases by one, by interlacing. In the former case, the rank decreases by one and in the latter by two.

If the rank decreases by one, then no new cores are created and therefore no two vertices become duplicate vertices. In H no two rows are identical. Thus in G no two rows coincide on $|H|$ positions or more.

If on the other hand the rank decreases by two, then the dimension of $\ker(\mathbf{A})$ increases by one and a new core is created. It could happen that two vertices which in G were not duplicates, become so in H. In such a scenario, two rows of H are identical. Thus in $\mathbf{A}(G)$, the corresponding two rows coincide on exactly $|H|$ positions. If the core created does not correspond to duplicate vertices, then rows of $\mathbf{A}(G)$ coincide on less than $|H|$ positions.

The last possibility to consider is for core graphs. Each vertex is a core vertex and on deletion of a vertex, the rank does not change. However core forbidden vertices appear on deletion of one or more vertices and a maximal graph H of lower rank can be determined. Thus no two rows of $\mathbf{A}(G)$ coincide on more than $|H|$ positions as described above. ■

This proof answers the second question we posed in a manner that emphasises the internal structure of the molecule. We note that in graphs with no isolated vertices, duplicate

vertices correspond to a core-order of two, the smallest possible. Thus two is a lower bound for the order of the substructures where the spin of the NBO electrons is concentrated and it is reached by molecular graphs with duplicate vertices. Duplicate vertices were also studied in [2] where the authors viewed them as providing the threshold case in the concept of graph singularity.

4 Relating Graph Structure to the Rank

In this section we investigate problem 3. We study the nullity and the rank in parallel. We address the problem in a way that requires more details about the structure of singular graphs. Since it is the existence of the **non-zero part** $\{\mathbf{x}_F \in \mathbb{R}^{|F|}\}$ of the kernel eigenvector $\begin{pmatrix} \mathbf{x}_F \\ \mathbf{0} \end{pmatrix}$ of a graph G that determines that G has cores $\{F\}$ and therefore is singular, the substructures are determined by the non-zero part of the kernel eigenvectors of G.

4.1 Singular Configurations

It is instructive to deal first with graphs of nullity one, that is when the nullspace has only one generator (up to scalar multiples).

Lemma 4.1 *The number of vertices of a graph G of nullity one, with core $(F, \mathbf{x}_F)$, is at least $|F| + \eta(F) - 1$.*

Proof: For a graph G of nullity one, the core is uniquely determined and is an induced subgraph of G. By interlacing, at least $\eta(F) - 1$ vertices need to be added to F to produce G, in such a way that the nullity reduces by one with each vertex addition. ■

When this lower bound is reached, the singular graph G exhibits an *extremal* property[4]. It has the minimum order among singular graphs for a given core $(F, \mathbf{x}_F)$.

[4]We know of no cores that cannot be 'grown' into singular configurations.

Definition 4.2 *A graph G, $|G| \geq 3$, is a* **singular configuration**, *with core $(F, \mathbf{x}_F)$, if it is a singular graph, of nullity one, with F as an induced subgraph, having $|F|+\eta(F)-1$ vertices, satisfying $|F| \geq 2$, $\mathbf{F}\mathbf{x}_F = \mathbf{0}$ and* $\mathbf{G}\begin{pmatrix}\mathbf{x}_F\\ \mathbf{0}\end{pmatrix} = \begin{pmatrix}\mathbf{0}\\ \mathbf{0}\end{pmatrix}$.

A singular configuration is necessarily connected. Otherwise it either has two singular components and nullity more than one or else it has a non-singular component and the number of vertices of G exceeds $|F| + \eta(F) - 1$. The proof of Proposition 4.1 suggests a greedy algorithm to construct a subclass of singular configurations with a particular core.

Construction 4.3 Starting with a feasible core $(F, \mathbf{x}_F)$ and $\eta(F) > 1$, if a connected graph S of nullity one with kernel eigenvector $\begin{pmatrix}\mathbf{x}_F\\ \mathbf{0}\end{pmatrix}$ is produced by adding a minimal set $\mathcal{P}$ of independent vertices, until the nullity is reduced to one, then S is a singular configuration . Note that a vertex is accepted in $\mathcal{P}$ only if it reduces the nullity by one on adding it to the graph. The signature remains constant throughout this construction, while the rank increases by two with each vertex addition, so that $rank(S) = rank(F) + 2|\mathcal{P}|$. In general, there may be non-isomorphic singular configurations with the same $(F, \mathbf{x}_F)$, as seen for the subgraphs $G - \{7\}$ and $G - \{8\}$ of the graph in Figure 1. The set of independent vertices added to the core, to form S, is said to be the *periphery* $\mathcal{P}$ of S, with respect to $\mathbf{x}_F$. This construction produces the simplest singular configurations where there are no edges between pairs of vertices of $\mathcal{P}$. Such a singular configuration S is said to be a *minimal configuration* (MC) since not only the number of vertices but also the number of edges is as small as possible. There are $p = \begin{pmatrix}|\mathcal{P}|\\ 2\end{pmatrix}$ possible subsets of edges between pairs of distinct vertices of $\mathcal{P}$ and therefore 2^p possible singular configurations with a particular spanning minimal configuration .

In [12], a catalogue of all minimal configurations of core-order two to five is included. Note that a singular configuration and its spanning minimal configuration have a common core as an induced subgraph. Reversing the construction process, the nullity increases with each periphery vertex-deletion from S.

The following result proved in [17] , shows the significance of singular configurations, as the substructures of a singular graph. It provides a necessary condition, in terms of

admissible subgraphs, for a graph to be of a specific nullity η.

Proposition 4.4 *Let H be a singular graph of nullity η, without isolated vertices. There exist η* singular configurations *as induced subgraphs of H.*

4.2 Adding edges

We consider now the effect on the rank as a minimal configuration is converted into a singular configuration by adding edges between pairs of distinct vertices of $\mathcal{P}$. For a minimal configuration N, if the vertices of F are labelled first, followed by those of $\mathcal{P}$, then for $\mathbf{x} = \begin{pmatrix} \mathbf{x}_F \\ \mathbf{0} \end{pmatrix}$, $\mathbf{Nx} = \mathbf{0}$. Note that if edges are added joining some or all of the distinct pairs of vertices in $\mathcal{P}$, then the singular configuration , S, produced still satisfies $\mathbf{S}\begin{pmatrix} \mathbf{x}_F \\ \mathbf{0} \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ \mathbf{0} \end{pmatrix}$.

Theorem 4.5 *Adding edges between distinct vertices of the periphery of a minimal configuration leaves the rank unchanged.*

Proof: Let $(F, \mathbf{x}_F)$ be the core of the minimal configuration N. For edges to be added between vertices of the periphery, $|\mathcal{P}|$ is at least two, so that $\eta(F) \geq 3$.

Labelling the F-vertices first, we have

$$\mathbf{N} = \begin{pmatrix} \mathbf{F} & \mathbf{P} \\ \mathbf{P}^t & \mathbf{0}_{\eta(F)-1} \end{pmatrix}, \tag{1}$$

where $\mathbf{O}_{\eta(F)-1}$ is the square zero matrix of order $\eta(F) - 1$, and $\mathbf{P}$ describes the edges between the peripheral vertices and the vertices of F.

If G is obtained on adding edges, then

$$\mathbf{G} = \begin{pmatrix} \mathbf{F} & \mathbf{P} \\ \mathbf{P}^t & \mathbf{Q} \end{pmatrix}, \tag{2}$$

where $\mathbf{Q}$ is the square matrix of order $\eta(F) - 1$, which describes the edges added between pairs of vertices of the periphery in G.

Let $\stackrel{r}{=}$ denote rank equivalence. By row reduction of the top $|F|$ rows,

$$\mathbf{G} \stackrel{r}{=} \left(\begin{array}{c|c} \mathbf{R} & \mathbf{U} \\ \hline \mathbf{O}_{\eta(F)} & \begin{array}{l} 1\ ....\ \ ....\ \ ... \\ 0\ 1...\ \ ....\ \ ... \\ \ \ ...\ \ ....\ \ ... \\ 0\ 0...\ \ ....\ \ ...0\ 1 \\ 0\ 0...\ \ ....\ \ ...0\ 0 \end{array} \\ \hline \mathbf{P}^t & \mathbf{Q} \end{array}\right), \tag{3}$$

where each entry of the $\eta(F)$ rows of $\mathbf{O}_{\eta(F)}$ is zero. The matrix $\mathbf{R}$ is also zero in the case when $F = \overline{K_{\eta(N)}}$. Each entry on the main diagonal of the submatrix consisting of the $\eta(F) - 1$ rows below $\mathbf{U}$ is 1.

Now $\mathbf{Q}$ can be row reduced to zero using the $\eta(F) - 1$ non-zero rows above it. In so doing, $\mathbf{P}^t$ changes but since each row of $\mathbf{P}^t$ is linearly independent of those of $\mathbf{F}$ (or of $\mathbf{R}$) and the rows of $\mathbf{P}^t$ form a linearly independent set of vectors, it follows that no row of $\mathbf{P}^t$ can be row reduced to zero. Thus the nullity of $\mathbf{G}$ equals that of $\mathbf{N}$. ■

A minimal configuration is a singular configuration and therefore connected. In a minimal configuration N, a vertex of $\mathcal{P}$ is joined to core-vertices only and the vertex degree of $v \in \mathcal{P}$ is at least two [12]. If a vertex is deleted from a singular configuration , the nullity changes. It increases to two if v is a periphery vertex but reduces to zero if v is a core vertex [18]. An induced singular configuration in a singular graph G sharing the same core as G enables us to determine a lower bound for the rank.

Proposition 4.6 *Let the connected graph Z have core $(F, \mathbf{x}_F)$ and let the singular configuration S, with a spanning minimal configuration N, be an induced subgraph of Z, having the same core $(F, \mathbf{x}_F)$. Then $rank(N) = rank(S) \leq rank(Z)$.*

Proof: If two vertices of the periphery of N are joined by an edge, $rank(S) = rank(N)$ by Theorem 4.5. The result now follows by Lemma 2.3. ■

4.3 Core Size Sequence

The number of maximal connected graphs of rank r that can be obtained is bounded above by 2^r. To investigate by how much the rank increases as a singular configuration is grown into a larger graph of nullity $\eta \geq 1$, we consider the entries of basis vectors for ker$\mathbf{A}$. Let $wt(\mathbf{x})$ denote the **weight** or number of non-zero entries of the vector $\mathbf{x}$. We adopt the convention to write a basis for the nullspace of $\mathbf{A}$ in which the kernel eigenvectors are *ordered* according to the monotonic non-decreasing *sequence* of the weights of its vectors. A maximal set of linearly independent vectors $\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_\eta$ in the nullspace of $\mathbf{A}$, with the smallest total weight $\sum_{i=1}^{\eta} wt(\mathbf{x}_i)$, are said to form a *minimal basis* B_{min} for ker($\mathbf{A}$). A result that holds for any vector space is proved in [6] and applied here to ker$\mathbf{A}$:

Proposition 4.7 *Let $B_1 = (\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_\eta)$, with weight sequence $t_1, t_2, \ldots, t_\eta$, be a minimal basis for ker$\mathbf{A}$. If $B_2 = (\mathbf{w}_1, \mathbf{w}_2, \ldots, \mathbf{w}_\eta)$ is another ordered basis for ker$\mathbf{A}$, with weight-sequence $s_1, s_2, \ldots, s_\eta$, then $\forall i, \quad t_i \leq s_i$.*

In $B_{min} = (\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_\eta)$, the smallest and largest weights $wt(\mathbf{u}_1)$ and $wt(\mathbf{u}_\eta)$ have been referred to as the graph singularity κ in [2, 11] and core-width τ in [14], respectively. The *core-order sequence* of a singular graph G is the weight-sequence of a minimal basis B_{min}, for ker$\mathbf{A}$. Proposition 4.7 establishes the well definition of the *core-order sequence* of G. The basis, B_{min}, for ker$\mathbf{A}$ determines a *fundamental system of cores* of G.

Corollary 4.8 [6] *The core-orders in a fundamental system of cores is a graph invariant.*

In the basis B_{min}, the entries in $\mathbf{x}$ are taken to be integers, with a greatest common divisor of one. In the chemical model, however, eigenvectors belonging to an energy level are taken to be of unit length and orthogonal. For a degenerate NBO in the Hűckel model, orthogonalization may force the vectors in B_{min} to be transformed to others, representing the non-bonding orbitals, which are their linear combination, involving more centres in the distribution of charge, bond-order and spin.

4.4 Computing the Rank of Graphs

If the rank of a subgraph H is known, then to determine the rank of the parent graph G, the change in rank, on adding vertices with particular neighbours until G is formed, needs to be known.

By Proposition 4.4, if the nullity of G is one, with core $(F, \mathbf{x}_F)$, then it is possible to delete a maximal subset $L \in \mathcal{V}(G) \backslash \mathcal{V}(F)$ of vertices of G such that $S = G - L$ is still of nullity one with core F. This suggests another way of constructing singular configurations. The set L of vertices is in general not unique, so that distinct singular configurations, with the same core $(F, \mathbf{x}_F)$ and order, may be found as induced subgraphs of G. For instance, in the graph G of Figure 1, L is $\{7\}$ or $\{8\}$ corresponding to distinct singular configurations $G - \{7\}$ or $G - \{8\}$ respectively. Note that $|L|$ is constant for all S and that the signature may alter as the vertices of L are deleted one by one. Moreover, for graphs of nullity one, the set L of vertices contributes $|L|$ to the rank of G.

Proposition 4.9 *Let G be a graph of nullity one with core $(F, \mathbf{x}_F)$ and a singular configuration $S(F, \mathbf{x}_F)$ as an induced subgraph. The rank of G is given by $rank(G) = rank(S) + |L|$.*

We shall generalize this result for any nullity in Proposition 4.11.

In the proof of Proposition 2.4, the rows of $\mathbf{M}'$ form a basis that can determine the minimum weight sequence and one of a possible number of minimal bases B_{min}. The determination of minimum rank as τ varies is regarded as an *extremal* problem [14].

A core of nullity one is a *nut graph*. For particular properties of nut graphs, see [15]. Now we present a sharp lower bound for the rank of a graph of any nullity, reached when the core is a nut graph.

Corollary 4.10 *Let the singular connected graph Z have core-width τ with corresponding core F_τ. Then $rank(Z) \geq \tau - 1$. If equality holds, then F_τ is a nut graph and Z is a core graph.*

Proof: By Lemma 2.3, the rank of a singular configuration S with core F_τ induced in Z satisfies rank$(Z) \geq |S| - 1$. Since the nullity $\eta(F_\tau)$ of the largest core in a fundamental system of cores, is at least one, rank$(Z) \geq \tau + \eta(F_\tau) - 2 \geq \tau - 1$. If equality holds, $\tau - 1 = rank(Z) \geq \tau + \eta(F_\tau) - 2$, then $\eta(F_\tau) \leq 1$. Since F_τ is singular, $\eta(F_\tau) \geq 1$, so that F_τ is a nut graph.

By Proposition 2.4, $rank(G) = rank(F_\tau)$ implies that each vertex added to F_τ to form G increases the nullity, creating a new core, so that the vertices added, are core vertices. If F_τ is a nut graph, then each vertex of G lies on a core. Thus G is a core graph. ■

For graphs of nullity at least one Proposition 4.9, can be generalized. We introduce the parameter Y that measures the contribution to the rank by the vertices not in the chosen singular configuration .

Proposition 4.11 *Let the induced subgraph $S(F, \mathbf{x}_F)$ of a connected graph Z of nullity η be a singular configuration with $\mathbf{x}_F \in B_{min}$. If a set L of vertices are added to S to obtain Z, then $rank(Z) = rank(S) + Y$, where $Y = |L| - \eta(Z) + 1$.*

Proof: Label S with the last vertex being in F and continue to add L to form Z. The first $|S| - 1$ rows of $\mathbf{A}(Z)$ are linearly independent and the rank of the first $|S|$ rows is $|S| - 1$. Each of the last $|L|$ rows either does not contribute to the rank when it creates a new core in Z or else increases the rank. In the latter case, the increase may be one or two. It is one if the adjacencies of the added vertex are compatible with the cores induced in Z and two if a core of Z is destroyed. Thus besides the first $|S| - 1$ rows, only $|L| - (\eta(Z) - 1)$ rows contribute further to the rank. ■

4.5 Chemical Implications

Duplicate vertices belong to the same orbit of the automorphism group of a graph. So they must have identical entries in each eigenvector, except in zero-eigenvalue vectors, when the sums of entries on their neighbours will be equal. For all eigenvalues, however, their charges and their bond orders to neighbours will be equal.

An n–vertex molecule with a single NBO occupied by an electron, with spin shared among all sites, is a nut graph with maximal core-width $\tau = n$. By Corollary 4.10, for degeneracy of the NBO in a core graph Z with core-width τ satisfying $rank(Z) = \tau - 1$, the Hűckel model predicts that one of the orbitals corresponds to the vertices of a nut graph in Z. Moreover if it is occupied by an electron, every centre or vertex in the graph receives its share of charge, bond-order and spin. In reality, group theory shows that Jahn-Teller distortion occurs in which any non-linear molecule in a degenerate electronic state, will distort spontaneously so as to remove the degeneracy and make a more stable system.

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