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Local Symmetries for Molecular Graphs

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Abstract

Local graph symmetry groups are formally defined as acting in a non-identical fashion on just a proper (local) subset of a graph's vertices, and consequent theorems are established for adjacency matrices so as to simplify eigensolutions. These groups sometimes enlarging on the usual point groups, are illustrated, with examples of the application of the theorems. Some discussion of further utility, on elaborated models & on identification of so-called "accidental" degeneracies, is indicated.

1. Introduction

The standard approach for the use of symmetry in quantum mechanical problems – say for electronic structure – is to form a basis of vectors symmetry adapted to the different irreducible representations (IRs) of the full symmetry group of operations commuting with the Hamiltonian. The generation of the IRs is typically viewed as a separate problem. This overall approach is undoubtedly a seminally important to provide exact symmetry-mediated quantum numbers, such as then relate to degeneracies and various selection rules – besides the block-diagonalization of the original Hamiltonian matrix. See, *e.g.*, Wigner[1] and numerous later books. But when it comes to dealing with graphs and their adjacency or Laplacian matrices, there often seem to be other things going on – with additional associated degeneracies, isospectralities, eigenvector localizations, and "higher" (non-geometric) symmetries. See, *e.g.*,[2,3,4,5].

Here we look at a novel approach to deal with graph symmetry, complicitly mixed up with the construction of a hierarchy of symmetries, especially starting with more "local" symmetries (of the graph automorphism group), where typically the more local symmetries are only subsymmetries. The approach has precedent in the schemes emphasized by McClelland[6], by D'Amato and Gimarc[7,8], by Davidson[9], by Tang *et al.*[10], and by Mandal[11,12].

But here we give a general theorematic formulation, with a simple illustrative application. Often the extended symmetries do not persist to the full Schrodinger equation, so are approximate, though it may be noted that in fact they extend[6] rigorously to Hubbard & Hubbard-PPP models. In an accompanying paper[13] we apply the method to the simplest (proto-typical) dendrimer, namely the degree-3 Bethe tree – and look for qualitatively distinctive features of the eigensolutions. As a further potential application dendrimers may be noted to be a class of molecules with graphs which admit a natural hierarchy of our local symmetries, and application to general dendrimers is also conceivable.

2. Theoretical Methods

2.1. General Results

Let $G\,(V,E)$ be a graph, with adjacency matrix $\mathbf{A}$, and let $\hat{\mathcal{A}} = \hat{\mathcal{A}}(G)$ be an automorphism group of G with permutations $\pi \in \mathcal{A}$ realized as matrices on V such that $\pi\mathbf{A} = \mathbf{A}\pi$. Then following the standard approach one has:

Theorem 1: Each eigenvector of $\mathbf{A}$ can be chosen to transform in accordance with an irreducible representation of a group $\mathcal{A}$ of automorphisms of G.

Letting $S \subseteq V$, we define $\mathcal{A}_S = \mathcal{A}_S(G)$ as the set of automorphisms of G which leave $\bar{S} \equiv \{i \in V \mid i \notin S\}$ fixed (*i.e.*, $\pi \in \mathcal{A}_S \Rightarrow \pi i = i, \;\; i \in \bar{S}$). Then $\mathcal{A}_S$ is said to be *S-localized*. Also a vector $\vec{v}$ is *localized on* $S \subseteq V$ if the components v_i of $\vec{v}$ are $= 0$ for $i \notin S$. Then our first local subsymmetry theorem is:

Theorem 2: Eigenvectors of $\mathbf{A}$ transforming in accordance with a non-identity irreducible representation of an *S-localized* automorphism group $\mathcal{A}_S$, are localized on *S* and are given as solutions on the restriction of G to *S*.

Proof: First it may be noted that theorem 1 guarantees that the eigenvectors of $\mathbf{A}$ can be chosen to be symmetry adapted to transform as IRs of $\mathcal{A}_S$. Now any component ψ_i of such a vector $\vec{\psi}$ with $i \notin S$ is left fixed by every $\pi \in \mathcal{A}_S$, so that it must associate to the identity IR of $\mathcal{A}_S$, which by our hypothesis (that $\vec{\psi}$ transforms as a non-identity IR) is excluded from the considered eigenvectors. ■

This theorem often achieves significant results, as has sometimes been shown [7-11] for the non-identity IR when $\mathcal{A}_S$ is of order 2, say as for a reflection group. Often the restriction $G\downarrow S$ of G to $S\subseteq V$ falls into disconnected fragments. For example, the graph G of Figure **1** has a 3-cyclic automorphism subgroup $\mathcal{C}_3$ which fixes the central vertex, which in turn constitutes $\bar{S}$ for this group. Then $G\downarrow S$ consists of 3 disconnected hexagons (as in Figure **1(b)**), for which the eigenvalues of each are well-known to be -2, -1, -1, +1, +1, +2. Thus each of these 6 eigenvalues occurs twice as an eigenvalue to **A** of G - this occurrence arising in accordance with the E-representation of $\mathcal{C}_3$. (Here the E-representation is decomposable into two 1-dimensional IRs E_+ and E_- which are complex conjugates of one another, and so give degenerate results, for our real **A**.) To be more explicit about the eigen-solutions, let $\vec{\psi}^{\xi}$ be the (local) eigenvector for the 1st benzene ring, whence $C_3\vec{\psi}^{\xi}$ and $C_3^2\vec{\psi}^{\xi}$ are corresponding eigenvectors for the 2nd and 3rd benzene rings, and the consequent E-eigenvectors of G are

$$\vec{\psi}^{\xi E\pm}=\vec{\psi}^{\xi}+\varepsilon^{\pm 1}C_3\vec{\psi}^{\xi}+\varepsilon^{\pm 2}C_3^2\vec{\psi}^{\xi}$$

where $\varepsilon=e^{2\pi i/3}$ and C_3 is the permutation corresponding to a rotation by $2\pi/3$. One may note that $\mathcal{C}_3$ is far from the whole automorphism group (which is isomorphic to the semidirect product $\mathcal{C}_3[\mathscr{S}_2\times\mathscr{S}_2\times\mathscr{S}_2]$ with the different $\mathscr{S}_2$ groups flipping a single one of the benzene rings around), and even other choices could be made for $\mathcal{A}_S$ fixing larger subsets $\bar{S}$ - but our choice still serves as a useful example, though the eigenvectors of **A** associated to the identity IR is the subject of the next theorem.

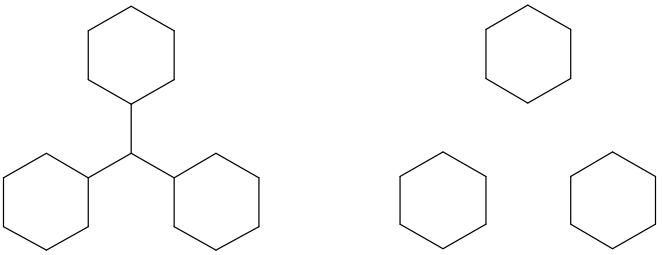

Figure 1: In (a) one example of molecular graph G manifesting a C_3-symmetry. In (b) the graph $G\downarrow S$ (when $\bar{G}$ is the central vertex of G in (a)).

The *orbits* of V under an automorphism group $\mathcal{A}$ are the different subsets $\mathcal{A}i \equiv \{\pi i : \pi \in \mathcal{A}\}$, $i \in V$. Denote the set of orbits by $V/\mathcal{A}$, and the order of a set S by $|S|$. Thus for the graph of Figure **1**, the lone central vertex is a $V/\mathcal{C}_3$-orbit, and the remaining orbits each consist of triples of vertices transformed into one another by $\pi \in \mathcal{C}_3$. We utilize some standard results[14,15] for orbits.

Lemma 3. For $\mathcal{A}$ a group acting on a set V, the orbits ($V/\mathcal{A}$) partition V.

This is especially well-known (and easy to prove).

Lemma 4. Let $i, j \in \mathcal{A}a$, $\mathcal{A}$ an automorphism group on V, with $a \in V$. Then $|\{\pi \in \mathcal{A} : \pi i = j\}| = |\{\pi \in \mathcal{A} : \pi a = a\}|$ divides $|\mathcal{A}|$.

Proof: Evidently $\{\pi \in \mathcal{A} : \pi j = j\} \equiv \mathcal{A}_j$ is the subgroup of $\mathcal{A}$ leaving j fixed. Granted $j \in \mathcal{A}a$, there is $\sigma \in \mathcal{A}$ such that $j = \sigma a$, whence $a = \sigma^{-1} j$, and also $\{\pi \in \mathcal{A} : \pi\sigma a = \sigma a\} = \{\pi \in \mathcal{A} : \sigma^{-1}\pi\sigma a = a\}$. But defining $\pi_\sigma \equiv \sigma^{-1}\pi\sigma$, we have $\mathcal{A}_j = \{\sigma\pi_\sigma\sigma^{-1} \in \mathcal{A} : \pi_\sigma a = a\} = \sigma\mathcal{A}_a\sigma^{-1}$, so that all $\mathcal{A}_j$, $j \in \mathcal{A}a$, have the same order. Next for $j \in \mathcal{A}a = \mathcal{A}i$, there must be a $\tau \in \mathcal{A}$ such that $\tau i = j$, so that $\{\pi \in \mathcal{A} : \pi i = j\} = \{\pi \in \mathcal{A} : \pi\tau^{-1} j = j\} = \tau\{\pi_\tau \in \mathcal{A} : \pi_\tau j \in j\} = \tau\mathcal{A}_j$ is evidently a left coset of $\mathcal{A}_j$, and has the same order as $\mathcal{A}_j$, and $\mathcal{A}_a$. The number of such cosets is (of course) $|\mathcal{A}|/|\mathcal{A}_j| = |\mathcal{A}|/|\mathcal{A}_a|$, so that $|\mathcal{A}_a|$ divides $|\mathcal{A}|$. ■

Again these lemmas are standard[14,15] for the action of a group $\mathcal{A}$ on a general set V fixed by $\mathcal{A}$, independently of V being the vertex set of a graph. The orbits $V/\mathcal{A}$ may be concisely represented by a *complete set* $A \subseteq V$ *of representatives* of the orbits of $V/\mathcal{A}$, which is to say the different $a \in A$ generate each orbit exactly once: $V/\mathcal{A} = \{\mathcal{A}a \,|\, a \in A\}$ & $a \neq b \Rightarrow \mathcal{A}a \cap \mathcal{A}b = \varnothing$. Granted such an $\mathcal{A}$ as an automorphism group of $G = (V, E)$, an $\mathcal{A}$*-condensed* graph $G/\mathcal{A}$ is defined to have vertex set $V/\mathcal{A}$ and edges $\{\mathcal{A}a, \mathcal{A}b\}$ if there are $i' \in \mathcal{A}a$ and $j' \in \mathcal{A}b$ such that $\{i', j'\} \in E$. Moreover, for such an edge of $G/\mathcal{A}$, define a weight

$$w_{\mathcal{A}a,\mathcal{A}b} = |\mathcal{A}a|^{-1/2} |\{\{i, j\} \in E(G) : i \in \mathcal{A}a, j \in \mathcal{A}b\}| |\mathcal{A}b|^{-1/2}.$$

This then defines a weighted adjacency matrix $\mathbf{W}$ on $G/\mathcal{A}$, which may evidently have diagonal elements. Also note that there are different expressions for $w_{\mathcal{A}a,\mathcal{A}b}$:

Lemma 5. The edge weight $w_{\mathcal{A}a,\mathcal{A}b}$ of $G/\mathcal{A}$ with $a, b \in A$ satisfies:

$$w_{\mathcal{A}a,\mathcal{A}b} \equiv \left|\mathcal{A}a\right|^{-1/2} \left|\{\{i,j\}\in E(G): i\in \mathcal{A}a,\, j\in \mathcal{A}b\}\right| \cdot \left|\mathcal{A}b\right|^{-1/2}$$
$$= \left|\mathcal{A}a\right|^{1/2} \left|\{\{a,j\}\in E(G): j\in \mathcal{A}b\}\right| \cdot \left|\mathcal{A}b\right|^{-1/2}$$
$$= \left|\mathcal{A}a\right|^{-1/2} \cdot \left|\{\{i,b\}\in E(G): i\in \mathcal{A}a\}\right| \cdot \left|\mathcal{A}b\right|^{1/2}$$

Proof: For $i\in\mathcal{A}a$, there is $\pi\in\mathcal{A}$ with $i=\pi a$, and $\{i,j\}=\{\pi a,j\}\in E \Leftrightarrow \{a,\pi^{-1}j\}\in E$ with j and $\pi^{-1}j$ in the same orbit (say $\mathcal{A}b$). Thus the cardinality of $\{\{i,j\}\in E: j\in\mathcal{A}b\}$ & $\{\{a,j'\}\in E: j'\in\mathcal{A}b\}$ are the same, and $\{\{i,j'\}\in E: i\in\mathcal{A}a,\, j'\in\mathcal{A}b\} = \dot{\bigcup}_{i\in\mathcal{A}a}\{\{i,j\}\in E$ when $j\in\mathcal{A}b$ with each one of the components in the disjoint union of the same size. That is, $\{\{i,j\}\in E: i\in\mathcal{A}a,\, j\in\mathcal{A}b\} = \left|\mathcal{A}a\right|\cdot\left|\{\{a,j\}\in E: j\in\mathcal{A}b\}\right|$ so that the first result of the lemma is obtained. The second result follows similarly. ■

Theorem 6: Each eigenvector $\vec{\psi}$ of $\mathbf{A}$ transforming in accordance with the identity IR of $\mathcal{A}_S$, corresponds to an eigenvector $\vec{\psi}'$ with the same eigenvalue on the condensed (weighted) graph $G/\mathcal{A}_S$ such that when both $\vec{\psi}'$ and $\vec{\psi}$ are normalized, their components are related $\psi'_{\mathcal{A}_S a} = \left|\mathcal{A}_S a\right|^{1/2}\cdot\psi_a$, $a\in\mathbf{A}$.

Proof: An eigenvector $\vec{\psi}$ totally symmetric under $\mathcal{A}_S\equiv\mathcal{A}$ has $\psi_{\pi k}=\psi_k$, $\forall\pi\in\mathcal{A}$, and with λ the eigenvalue for $\vec{\psi}$ satisfies

$$\sum_b^{\in A}\sum_j^{\in\mathcal{A}b}\mathbf{A}_{ij}\psi_b = \sum_j^{\in V}\mathbf{A}_{ij}\psi_j = \lambda\psi_i = \lambda\psi_a$$

where $i\in\mathcal{A}a$. Now

$$\sum_j^{\in\mathcal{A}b}\mathbf{A}_{ij} = \sum_j^{\in\mathcal{A}b}\left|\{\{i,j\}\}\cap E\right| = \left|\{\{i,j\}\in E: j\in\mathcal{A}b\}\right| = \left|\mathcal{A}a\right|^{-1/2} w_{\mathcal{A}a,\mathcal{A}b}\left|\mathcal{A}b\right|^{1/2}$$

having used lemma 5. Thus

$$\sum_b^{\in A}\left|\mathcal{A}a\right|^{-1/2} w_{\mathcal{A}a,\mathcal{A}b}\left|\mathcal{A}b\right|^{1/2}\psi_b = \lambda\psi_a$$

Or if we abbreviate $\left|\mathcal{A}c\right|^{1/2}\psi_c \equiv \psi'_c$, we have

$$\sum_b^{\in A} w_{\mathcal{A}a,\mathcal{A}b}\psi'_b = \lambda\psi'_a \quad \text{or} \quad \mathbf{W}\vec{\psi}' = \lambda\vec{\psi}'.$$

Finally the norms are related via

$$\langle\vec{\psi}'|\vec{\psi}'\rangle = \sum_a^{\in A}\psi'_a\psi'_a = \sum_a^{\in A}\left|\mathcal{A}a\right|\cdot\psi_a\cdot\psi_a = \sum_a^{A}\sum_j^{\in\mathcal{A}a}\psi_j\psi_j\langle\vec{\psi}|\vec{\psi}\rangle$$

Thus a corresponding like-normalized vector of $\mathbf{W}$ is identified. ■

These theorems generalize those of McClelland[6], D'Amato[7,8], Davidson[9] and Tang *et al.*[10], which often dealt with the specific case of $\mathcal{A}_S$ of order 2. Davidson[9] and Tang *et al.*[10] address the cyclic case. In these works the eigenvectors are ignored, with focus on the characteristic polynomial, from which the eigenvalues are viewed to be determined.

3. Results & Discussion

3.1. Example & General Scheme

We may continue our simple example, with the $\mathcal{A}_S = \mathcal{C}_3$ case of Figure **1** to give the eigensolutions for the identity IR of $\mathcal{C}_3$. The graph $\mathbf{G}/\mathcal{C}_3$ is as in Figure **2**, where the bold face edge has a weight of $\sqrt{3}$. Notably if so wished this graph could be further solved using its $\mathcal{C}_2$ symmetry group. The application of theorem 2 gives a single edge to solve, and the application of theorem now gives $(\mathbf{G}/\mathcal{C}_3)/\mathcal{C}_2$ as in Figure **3**: a weighted path graph, with successive edges having weights, $\sqrt{3}$, $\sqrt{2}$, 1, $\sqrt{2}$.

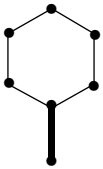

Figure 2: The condensed graph $G/\mathcal{C}_3$.

Figure 3: The doubly condensed graph $(G/\mathcal{C}_3)/\mathcal{C}_2$.

Thus for the example of Figure **1**, the utility of our theorems **2** & **6**. The overall mode of application might be made a little more explicit, with:

Corollary 7. Suppose the restriction of G to S falls into disjoint fragments such that every nonidentity $g \in \mathcal{A}_S$ moves at least one fragment into another. Then the eigenvalues associated to the non-identity IRs of $\mathcal{A}_S$ are given as the eigenvalues of the fragments which are nonequivalent under $\mathcal{A}_S$.

This and the theorem **6** suggest a systematic scheme to utilize the localized symmetries especially when a suitable sequence of them can be identified:

- Start with a maximally localized choice for $\mathcal{A}_S$, such choice if in a hierarchy likely involving sets S which are disjoint from one another.
- Use corollary **7** to find the eigenvectors associated to nonidentity IRs of these $\mathcal{A}_S$.
- Then theorem **6** is used to make a contracted graph for these $\mathcal{A}_S$.
- A new next maximally localized automorphism group is identified for this contracted graph, repeating the whole procedure (till the hierarchy is exhausted).

A general application of such procedure occurs in the next paper, concerning the prototype of a general circumstance where the present methodology is especially felicitous in this iterative form.

3.2. Weighted Graphs

Weighted graphs as for instance arise with higher-order tight-binding models can be treated within our framework. The theorems **1** & **2** and lemmas **3**, **4**, & **6** apply as they stand, so long as the permutation matrices $\boldsymbol{\pi}$ commute with the new Hamiltonian matrix $\mathbf{W}$ even with weights. Though "full" 1-electron Hamiltonians should only preserve point-group symmetry, we emphasize that the additional symmetry such as found in our Hückel-model (example of Figure **1**), still often persists in a weighted tight-binding model extended to include next-neighbor interactions – even if a corresponding low-order non-identity overlap matrix is included. For instance, the same graphical symmetries found for the adjacency matrix associated to the graph of Figure **1**, still apply with next-neighbor interactions as in Figure **4**. In this case one has a weighted matrix $\mathbf{W} = \mathbf{A} + \beta' \mathbf{A}_2$, where β' is a parameter of magnitude <1. There is a weighted graph wG now as indicated in Figure **4**, with edges $E(wG) = E(G) \oplus wE_2(G)$, where $E_2(G) \equiv \{\{i,k\} : A_{ij} A_{jk} = 1, i \neq k\}$ is the set of next-nearest neighbors of G and the factor w indicates a weighting for $E_2(G)$ (and we have assumed that G has no triangular cycles).

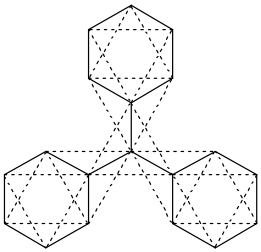

Figure 4: Graph G in addition with differently weighted next-neighbor interaction, appearing as dashed lines.

Another sort of weighted graph may be recognized[16,17] to arise[18,19,20,21] in the context of dealing with all the valence electrons of an alkane – where there is a graph node for each (sp^3) hybrid orbital of each C atom as well as a node for each 1s H-atom orbital. Here the weights arise because the internal "bonds" between different sp^3-hybrids on the same C atom have a notably lesser weight than that of the (single) bonds between atoms.

One may even entertain a non-identity overlap $\mathbf{S} = \mathbf{I} + s\mathbf{A}$, where s is an overlap parameter also with a magnitude <1. Then the eigen-problem is

$$\mathbf{W}\psi = \lambda \mathbf{S}\psi$$

Here the local symmetry operations (typically) commute with both $\mathbf{W}$ & $\mathbf{S}$, so that one may show:

Lemma 8 – The edge weight $w_{\mathcal{A}a,\mathcal{A}b}$ of $\beta' G / \mathcal{A}$ with $a,b \in A$ satisfies:

$$w_{\mathcal{A}a,\mathcal{A}b} \equiv |\mathcal{A}a|^{-1/2} \sum_{i}^{\in \mathcal{A}a} \sum_{j}^{\in \mathcal{A}b} W_{i,j} \cdot |\mathcal{A}b|^{-1/2} = |\mathcal{A}a|^{1/2} \sum_{j}^{\in \mathcal{A}b} W_{a,j} \cdot |\mathcal{A}b|^{-1/2} = |\mathcal{A}a|^{-1/2} \sum_{i}^{\in \mathcal{A}a} W_{i,b} \cdot |\mathcal{A}b|^{1/2}$$

and the edge weight of the overlap matrix $\mathbf{S}$ is

$$s_{\mathcal{A}a,\mathcal{A}b} \equiv |\mathcal{A}a|^{-1/2} \sum_{i}^{\in \mathcal{A}a} \sum_{j}^{\in \mathcal{A}b} s_{i,j} \cdot |\mathcal{A}b|^{-1/2} = \delta_{a,b} + |\mathcal{A}a|^{-1/2} \sum_{i}^{\in \mathcal{A}a} \sum_{j}^{\in \mathcal{A}b} A_{i,j} \cdot |\mathcal{A}b|^{-1/2}$$

$$= \delta_{a,b} + |\mathcal{A}a|^{-1/2} \sum_{i}^{\in \mathcal{A}a} A_{i,b} \cdot |\mathcal{A}b|^{1/2} = \delta_{a,b} + |\mathcal{A}a|^{1/2} \sum_{j}^{\in \mathcal{A}b} A_{a,j} \cdot |\mathcal{A}b|^{-1/2}$$

The proof proceeds using the same sort of methodology as for lemma **5**. Yet further, that $\mathbf{W}$ & $\mathbf{S}$ occurring in $\mathbf{W}\psi = \lambda \mathbf{S}\psi$ commute with one another immediately implies:

Corollary 9 – The matrices $\mathbf{W}$ & $\mathbf{S}$ have simultaneous eigenvalues $\lambda(\mathbf{W})$ & $\lambda(\mathbf{S})$ which correspond to $\lambda = \lambda(\mathbf{W}) / \lambda(\mathbf{S})$ in the (generalized) eigenvalue problem $\mathbf{W}\psi = \lambda \mathbf{S}\psi$. All have common eigenvectors, with the condensation of theorem **6** applying, with the new weights given in lemma **8.**

Thence through this next-nearest neighbor approximation, much of what already has been described for the nearest-neighbor model is retained.

3.3 Excessive Eigenvalue Degeneracy

One of the on-going[2,3,4] "mysteries" of molecular graphs and their associated Hückel eigenspectrum has been their occasional seeming excessive (or accidental) degeneracies. Now in fact our theorem **2** leads to an understanding of at least some of these seeming "accidents". To understand this we consider the case when the local set $S \subset V$ and the local

automorphism group $\mathcal{A}_S$ is a proper subgroup of the full automorphism group $\mathcal{A} \equiv \mathcal{A}_V$. In this case we have eigenvectors to $\mathbf{A}$ for eigenvalue λ which are also symmetry adapted to a nonsymmetric irreducible representation α_S of $\mathcal{A}_S$ -- which is to say the eigenvectors are labelled by α_S along with the columns i of α_S, say as $\psi(\lambda, \alpha_S i)$ – and further these eigenvectors transform under group operations $G_S \in \mathcal{A}_S$ thusly

$$G_S \cdot \psi(\lambda, \alpha_S i) = \sum_j^{\alpha_S} \alpha_S(G_S)_{j,i} \cdot \psi(\lambda, \alpha_S j)$$

where $\alpha_S(G_S)_{j,i}$ is the (j,i)th element of the irreducible representation matrix $a_S(G_S)$ for the element $G_S \in \mathcal{A}_S$. These symmetry adapted vectors may be further used (e.g., following chap. 7 of Curtis & Reiner[23]) to induce a representation of the full group $\mathcal{A}$, using a set $\mathcal{C}$ of coset multipliers for distinct (left) cosets of $\mathcal{A}_S \subset \mathcal{A}$, this latter meaning that

$$\mathcal{A} = \bigoplus_C^{\in \mathcal{C}} C\mathcal{A}_S$$

where the direct sum here is just a disjoint union over the collection of distinct cosets $C\mathcal{A}_S \equiv \{CG_S : G_S \in \mathcal{A}_S\}$. Evidently for two distinct coset multipliers C_1 & C_2 it must occur that $C_1^{-1}C_2 \notin \mathcal{A}_S$, whence we see that $C_1 S$ & $C_2 S$ are distinct, and the members of

$$B_\lambda(\alpha_S \uparrow) \equiv \{C \cdot \psi(\lambda, \alpha_S i) : C \in \mathcal{C}, \text{ranging (over columns of)}\}$$

being localized on different disjoint sets (conjugate to S) must also be linearly independent. Thus $B_\lambda(\alpha_S \uparrow)$ is a basis for a representation $\alpha_S \uparrow$ of the full group $\mathcal{A}$. This is to say for an arbitrary element $G \in \mathcal{A}$, there are unique $C_1 \in \mathcal{C}$ & $G_S \in \mathcal{A}_S$ for which $G = C_1 G_S$. And similarly there must also be unique $C_{12} \in \mathcal{C}$ & $G_{S12} \in \mathcal{A}_S$ such that $C_1 G_S C_2 = C_{12} G_{S12}$, whence we have

$$G \cdot C_2 \psi(\lambda, \alpha_S i) = C_{12} G_{S12} \cdot \psi(\lambda, \alpha_S i) = \sum_j \alpha_S(G_{S12})_{ji} . C_{12} \psi(\lambda, \alpha_S j)$$

which verifies the claim that $B_\lambda(\alpha_S \uparrow)$ forms a basis for a representation of $\mathcal{A}$. This *induced* representation $\alpha_S \uparrow$ evidently has $(C_{12} j, C_1 i)$th matrix element

$$\alpha_S \uparrow (C_1 G_S)_{C_{12} j, C_1 i} = \alpha_S(G_{S12})_{j,i} \text{ where } C_1 G_S C_2 \in C_{12}\mathcal{A}_S \text{ & } G_{S12} \equiv C_{12}^{-1} \cdot C_1 G_S C_2$$

Now because all these group elements commute with $\mathbf{A}$, we see that

$$\mathbf{A} \cdot C_2 \psi(\lambda, \alpha_S i) = C_2 \mathbf{A} \psi(\lambda, \alpha_S i) = \lambda C_2 \psi(\lambda, \alpha_S i)$$

Overall this establishes:

Theorem 10 – The members of the basis $B_\lambda(\alpha_S\uparrow)$ for the carrier space of the representation $\alpha_S\uparrow$ induced from a nonsymmetric irreducible representation α_S of $\mathcal{A}_S \subset \mathcal{A}$ are all degenerate.

In particular, this degeneracy applies regardless of whether $\alpha_S\uparrow$ is irreducible. This then accounts for (some) "accidental" degeneracy (beyond that dictated from the size of the irreducible representations of $\mathcal{A}$). For example this extends the considerations of Wild *et al*[3] who propose using the full automorphism group $\mathcal{A}$ which occasionally is larger than the ordinary point group of the molecule (associated to the adjacency matrix **A**). Wild *et al* note the local structure of different group elements associated to our $\mathcal{A}_S \subset \mathcal{A}$, but their aim is just to use the group theory as an aid to construct irreducible representations of $\mathcal{A}$ – our construction by-passes this and identifies additional degeneracy, when $\alpha_S\uparrow$ is not irreducible. Of course, $\alpha_S\uparrow$ is sometimes irreducible, whence the symmetry adaptation to just α_S of $\mathcal{A}_S$ is sufficient[24] (& economically so) to obtain symmetry adaptation to $\mathcal{A}$.

4. Conclusion

A potentially very useful general approach to dealing with local graph symmetries has been described and briefly illustrated. A more complete illustration is described in a follow-up paper, where a virtually complete solution to "Bethe tree" graphs result upon utilization of our present approach – and indeed it seems similarly to facilitate ready solution to the general class of "dendrimer" graphs. Moreover, as noted in the discussion above, there should be applications to stellated (alkane) graphs, and even quantum-chemically weighted extended Hückel theories. Yet further the types of groups extend to selected PPP-Hubbard type models[5]. The localization of the eigenvectors is here seen to be central to our development, and have some novel implications – one such being the identification of a simple rationale for what are otherwise seen[2,3,4,5] as "accidental" degeneracies manifested by the Hückel model, as discussed in conjunction with theorem **10**. This is understandable in that each local area which are mutually transformed into one another give degeneracies based on the number of such (disjoint) localities – a number generally exceeding the dimensions of irreducible representations of the full automorphism group. Further novel implications of the locality features are pursued in our subsequent work[13,14]. In our approach associated to the local symmetries, there are localized MO eigenvectors which seem to have special chemico-physical relevance – perhaps even more-so than the conventional delocalized symmetry-

adapted eigenvectors – these localized MOs are imagined to be better adapted to deal with electron-correlation or perturbations due to substitutions (which themselves are “local”). As such the current results offer much promise.

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